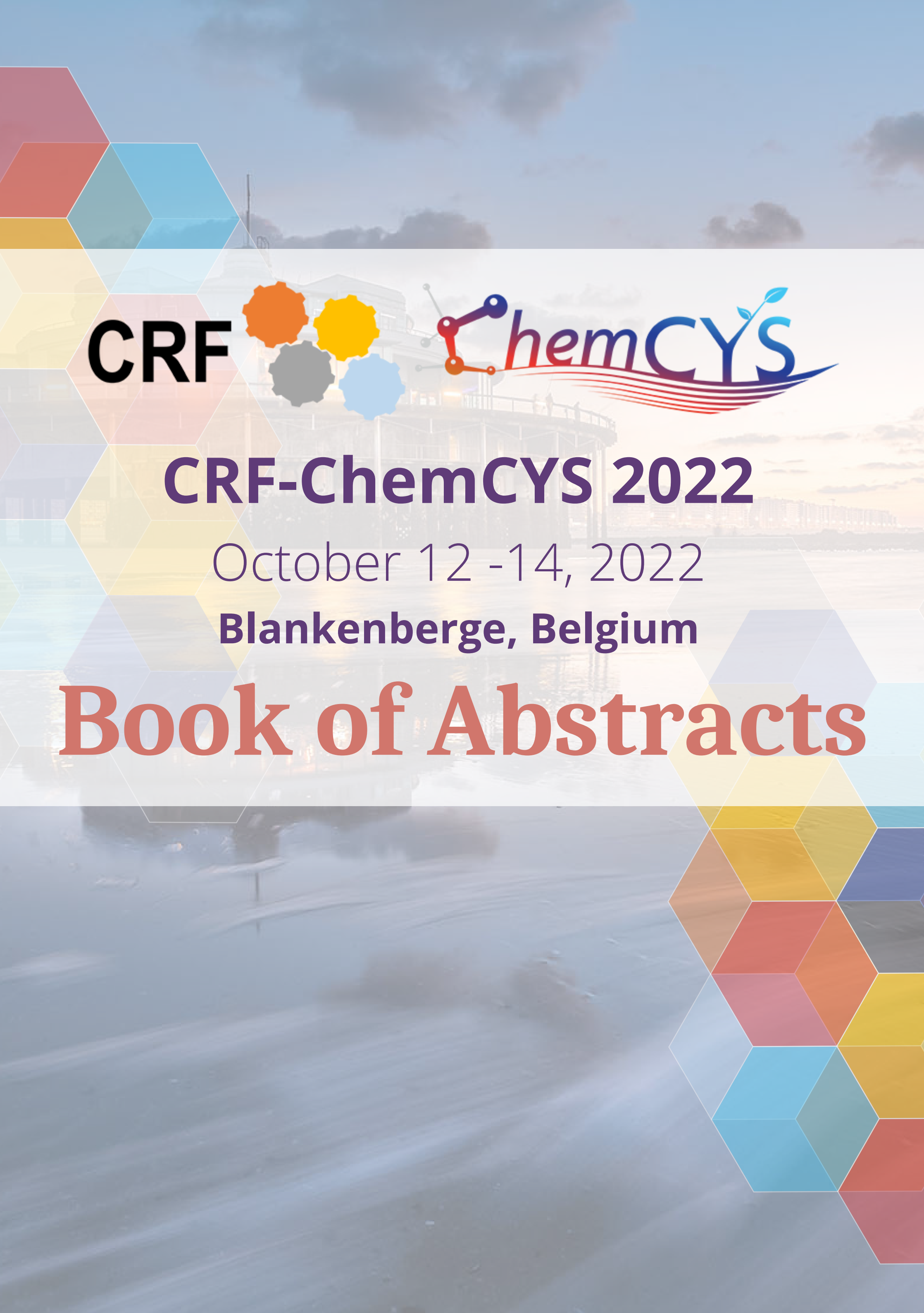

CRF-ChemCYS 2022

October 12 -14, 2022

Blankenberge, Belgium

Book of Abstracts

Programme CRF-ChemCYS symposium

October 12-14, 2022

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Chemical Research in Flanders

ChemCYS

An initiative of Flemish Universities & KVCV

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Welcome to the ‘CRF-ChemCYS 2022’ Symposium!

This CRF-ChemCYS 2022 symposium is a joint initiative of the FWO Scientific Research Communities ”Sustainable chemical processes for synthesis of fine chemicals” and “Catalysis research: from individual active sites to reactors”, together with the youth division of the Royal Flemish Chemical Society (KVCV). With over 400 participants, this edition is a big success and will be a real showcase for the excellent research in Flanders, as well as abroad. It succeeds in gathering the chemical research community of Flanders (especially young scientists) working towards innovation, based on fundamental research. It stimulates the creation of new chemical knowledge and chemical products, processes, methods, systems, but above all networks. CRF-ChemCYS 2022 will offer a forum to participants from academia, industry and professional organisations to exchange ideas and identify new research opportunities.

Chemical research at universities, research institutes and industry in Flanders is extremely diverse, which offers great opportunities and a good basis for nurturing new initiatives and new start-ups. In order to cover chemical research in the broadest sense and foster interdisciplinary interaction, the CRF-ChemCYS 2022 symposium is organised around six topics which are considered to play a key role in sustainable development:

- Functional Materials
- Chemistry meets Biology
- Chemical Synthesis and Methodologies
- Energy and Environment
- Chemical Processes and Reactor Technologies
- Renewables and Sustainability

The main goal of this initiative is to stimulate the interaction between disciplines, between academic research and industry, and to initiate new interdisciplinary research.

The program is a mix of invited lectures by influential international scientists, leading researchers in Flanders and researchers at different stages of their scientific career.

With 3 plenary lectures, 9 keynote lectures, 108 oral presentations and 146 posters, as well as a social program (featuring Totally Soul during an after-dinner get together (party?), KaféCV and soft skill seminars), CRF-ChemCYS 2022 offers plenty of opportunities for meeting people, networking and developing new collaborations.

We thank all our sponsors for their generous support to this conference. Thanks to their effort we were able to offer low registration fees including all meals and conference dinners.

We wish you a successful and enjoyable CRF-ChemCYS 2022 and we invite you to provide us with feedback and suggestions.

The organising committee

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KaféCV

Since its conception, KaféCV has grown to be an established value during ChemCYS and we are happy to proceed with this during CRF-ChemCYS 2022. The KaféCV networking event can be considered an unconventional "job fair" which allows the visitors to interact with more than 25 representatives from the chemical and pharmaceutical industries and research institutions. They will share their personal professional experience while giving you the opportunity to enjoy some drinks. If you have ever wondered what life would be like after graduation, you might get a glimpse behind the scenes of various jobs in chemistry and/or pharmaceutical sciences. The speakers will gladly tell you all about their daily job content, career, responsibilities, etc. Additionally, the represented companies and institutions can seize this opportunity to promote themselves towards potential employees.

The curricula vitae of the invited speakers were provided to you in a separate booklet. We advise you to interact with as many speakers as possible and thus to move on regularly. This ensures that all visitors will have the chance to meet all speakers.

Soft Skill Seminars

Marieke Impens - *The Human Link*

Stress-les(s): coping with stress in an academic environment

The context of the university is challenging...and certainly not just intellectually. These sessions will help you stay (or get back) mentally energized. You will gain a lot of scientific insights and hands-on tools that will help you get a better grip on the chaos that stress sometimes causes. Stressors will inevitably be part of your job from time to time and being nervous is sometimes part of it. But with the tools you get, this does not necessarily have to evolve into a loss of job satisfaction. Care for yourself and care for colleagues is the central topic of this stress-less(on).

Heleen Vander Beken - *Scimingo*

Time to reach out! A crash course on scientific communication

As a researcher, you might not be used to reaching out to the broad audience. But why wouldn't you take the opportunity to share your work, inform the audience and discover new opportunities for your research? In this seminar, you will be inspired by examples of effective science communication, but you will also get a hands-on crash course about how to start reaching out yourself!

Plenary lecture 1 – abstract

Chemical Information: building bridges for chemistry

Jonathan Goodman

University of Cambridge

Molecules are a fundamental unit of information. Knowledge of molecular structure enables diverse scientists to communicate chemistry precisely. If we want to understand how molecules interact with their environment, we first need to be able to determine and communicate molecular structure. Our DP5 approach, which builds on the popular DP4 algorithm, helps to determine what information we can infer from NMR spectra and contributes to the determination of structure. The InChI, IUPAC's chemical identifier, is a canonical label for molecules: any two scientists working anywhere in the world on the same molecule should use the same InChI whether or not they are in touch with each other. Our contributions to the development of these tools help build up databases of reliable chemistry which enable us to discover and to understand molecular reactivity and molecular activity. This will help to build bridges within the chemical sciences and to other disciplines.

Plenary lecture 2 – abstract

Water in coherent light

Gerhard Grübel

European XFEL, Holzkoppel 4, 22869 Schenefeld, Germany & University of Hamburg, Notkestrasse 85, 22607 Hamburg, Germany

Water is undoubtedly the most important liquid on earth and plays an important role throughout various scientific disciplines ranging from physics and chemistry to biology and geoscience. It is well known that water shows many anomalous properties, such as density maxima and diverging thermodynamic properties under supercooled conditions. Despite its importance, most of those anomalies are not understood. It is however believed that their origin lies in the complex hydrogen bonding network of water.

We will show how coherent X-rays from modern accelerator based light sources can contribute to a deeper understanding of the structure and dynamics of water and how key experts from different areas of water-related sciences work together within the Hamburg "Centre for Molecular Water Science" (CMWS) (www.cmws-hamburg.de).

Plenary lecture 3 – abstract

The new chemist

Prof. Javier Garcia Martinez

IUPAC President, igarcia-martinez@iupac.org

There is a widening gap between chemistry that is possible and chemistry that is taught. [1] During my presentation, I will describe some key advances in chemistry that are radically changing the way in which chemistry is conducted in research labs and industries around the world and I will also discuss some of the initiatives we are developing at IUPAC to rethink chemistry education. In particular, System Thinking represents a great opportunity to transcend structure and reactivity and connect the molecular world with the world's needs. [2,3] I will also comment on how role models and mentors can help us identify and achieve personal and professional goals. [4]

We at IUPAC are developing a number of initiatives to empower and support young chemists, particularly the actions that we are collaborating on with the International Younger Chemists Network. [5] During my talk, I will describe some of them and the ways in which early career chemists from all over the world can get involved in the activities and structure of IUPAC. There are many opportunities now to engage with IUPAC as we are organizing a number of activities for the International Year of Basic Science for Sustainable Development [6] to foster the role of chemistry in building a more sustainable future, including the Global Conversation on Sustainability. [7]

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Guest editorial

The new chemist

This is a guest editorial by **Javier García Martínez,** *professor of inorganic chemistry at the University of Alicante and cofounder of Rive Technology.*

In 2012, George Dahl was a Ph.D. student at the University of Toronto. That year, he led the group that won the Merck Drug Discovery Competition. Remarkably, nobody in the group knew anything about chemistry or biology; they simply programmed their computers to recognize properties that scientists were not able to predict. More recently, professor Leroy Cronin at the University of Glasgow compared the ability of researchers in his laboratory with that of robots to discover and crystallize new polyoxometalates. His conclusions are disturbing: Machines outperform scientists both in their predictions and their ability to explore the crystallization space. So what role might chemists play in a future when machines outperform us in the ability to design and carry out experiments? Scientists' creativity, critical thinking, and leadership skills will be increasingly important in highly automated labs and chemical factories. The best human qualities and the most advanced artificial intelligence are the basis of a new chemistry that cannot be predicted by merely extrapolating what we know today. However, for this opportunity to be fully realized, chemists should be able to talk to machines. Unfortunately, few chemists can actually code, let alone program a robot or write an algorithm to design and run a better set of experiments. Robotics or AI are rarely part of the chemistry curriculum, even at graduate school. This is especially worrisome considering that a recent report by Dell Technologies estimates that 85% of the jobs that will exist in 2030—when our current students will be in their early 30s—have not been invented yet but will definitely require those skills.

The chemical industry will be profoundly transformed by the convergence of technologies that defines the fourth industrial revolution. According to the World Economic Forum, the digitalization of the chemical industry will create revenues in the $310 billion to $550 billion range, reduce CO$_2$ emissions by 60 million to 100 million metric tons, and avoid 2,000 to 3,000 injuries over the next decade. This will require profound adaptations—and on a very short notice—in the workforce, leadership, and organization of a $5 trillion industry.

AI will help chemists make sense of the huge amount of data that we generate. Novel data visualization and digital learning tools will provide us with unprecedented capabilities and help us gain new and sounder insights by analyzing our experiments and available data. However, making new discoveries is only one step in the process of solving the problems we are facing today. For those innovations to have real impact, they must become commercial realities; and that happens only if there are chemists willing to take risks, create new companies, and lead the industry to a new era of exciting opportunities.

Despite our technological might, the global challenges are becoming more acute, urgent, and interconnected. We desperately need leaders who have vision, deep knowledge, and the ability to connect complex data, new information, and apparently unrelated ideas. It's also critical they have empathy, great communication skills, and the ability to lead and inspire others. Now more than ever, scientists must assume their roles as opinion leaders and as role models for young people. If we want our opinions to be heard, we must participate in the key debates of our time; if we do not, others will talk about science in our place. Studying reality is important, but if we want to change it, we must get involved and inspire young people to become leaders who will make the solutions we propose a reality.

George Dahl is now a research scientist at Google. Many like him—innovating in other areas of science—will help us make new discoveries in the chemical sciences by broadening the range of tools and views available to us. But chemists will still have a major role to play: Just like finding the most active molecule for an intended target is far from having a cure for a particular illness, chemists will have to lead beyond basic discovery and invention and into building a better and more sustainable future. Are you ready for the challenge?

Keynote lecture 1 – abstract

Tailored molecular design of organic chromophores – from thermally activated delayed fluorescence to dual-functioning photosensitizers

Wouter Maes

Hasselt University, Institute for Materials Research (IMO-IMOMEC) and IMOMEC Division, IMEC,
Wetenschapspark 1, 3590 Diepenbeek

Over the last two decades, electroluminescence from organic chromophores has evolved into a flourishing industry. Fundamental materials and device research efforts have been key to this commercial success. The optoelectronic properties of organic semiconductors match very well to the requirements of light emission in the visible range. However, developing materials affording efficient near-infrared (NIR) emission is considerably less straightforward, in particular when aiming to avoid the use of (toxic) heavy metals to achieve triplet leveraging. At UHasselt, the fundamental challenge to achieve efficient NIR emission from all-organic π-conjugated molecules is tackled by the judicious – computationally guided – design and synthesis of original donor-acceptor chromophores affording strong photo- and electroluminescence through either classical fluorescence, thermally activated delayed fluorescence (TADF), or a combination of both. We acknowledge the importance of careful structural and photophysical characterization – in collaboration with external experts – and have the possibility to test the final materials in state-of-the-art organic light-emitting diodes (OLEDs) to afford detailed structure-property relations.

When aiming at NIR emission and triplet manipulation in all-organic chromophores, one inherently approaches the ideal characteristics of dual-functioning organic photosensitizers for photodynamic therapy. In recent years, we have developed a number of rationally designed dyes active in the phototherapeutic window and showing balanced brightness and phototoxic power.

In this contribution, an overview will be given of our most recent results in both research domains.

Keynote lecture 2 – abstract

Ultrasonic microreactors for chemical manufacturing

Simon Kuhn

Department of Chemical Engineering, KU Leuven, Belgium

Small scale flow reactors have great advantages over conventional reactors, such as well-controlled flow patterns and increased surface-to-volume ratios, resulting in enhanced heat and mass transfer rates. Coupled with other benefits such as inherent safety allowing to perform reactions at elevated temperatures, pressures, or using highly reactive intermediates, they have become an attractive choice for the continuous manufacturing of chemicals and pharmaceuticals. However, these applications are still hindered by two important obstacles namely, weak convective mixing and issues regarding solids handling.

Integrating ultrasound with small scale flow reactors has proven to be one of the more promising methods to address clogging and mixing issues. We will showcase the synergistic effect of ultrasound for electro- and photochemical processes.

Firstly, we will present the design of an electrochemical reactor with integrated ultrasound actuators. The acoustic irradiation will result in increased species transport between the electrodes via acoustic streaming. As a proof-of-principle, this reactor is applied to achieve controlled electrolyte-free atom transfer radical polymerization of methyl acrylate.

Secondly, we show that a liquid slug in gas–liquid segmented flow in microchannels can act as an acoustic resonator to disperse large amounts of small liquid droplets into the gas phase (atomization). The observed atomization increases the interfacial area between the two phases considerably, which can be utilized for processes limited by gas–liquid mass transfer and/or phase distribution within microchannels. We apply this principle to a two-phase photochemical reaction to highlight the increase in conversion.

In conclusion, operating ultrasound reactors in resonance modes allows further intensification of chemical synthesis.

Keynote lecture 3 – abstract

Synthetic biology as a driving force for biobased production of chemicals using microbial cell factories

Evelien Peeters

Vrije Universiteit Brussel

Driven by the urgent societal need to mitigate climate change and environmental pollution, we are witnessing an industrial transition from petrochemical production schemes to more sustainable biobased production by making use of microbial fermentation processes. The use of renewable biomass feedstocks and production of fully biodegradable products with minimal environmental impact offers viable and future-proof alternatives for a classical linear economic concept. However, although the use of whole-cell biocatalysts has been established a long time ago and a huge diversity of feedstocks and products have been demonstrated on a small scale, the processes that have matured to industrial-scale implementation are still limited. A large bottleneck is caused by limitations in cost efficiency of the biobased processes, for example because of low productivities or yields upon using native microbial populations. In the last two decades, comprehensive system-level understanding of microbial cells and technological developments such as large-scale DNA synthesis have spurred the emergence of synthetic biology as a new interdisciplinary research field. Synthetic biology implies an advanced bottom-up engineering of biological systems for novel functionalities. Soon after the inception of this new research field, its application was quickly oriented towards the improvement of productivities in microbial production processes. In this keynote lecture, I will explain how synthetic biology has become a driving force for the development of more performant cell factories, for example by performing combinatorial engineering of production pathways or by introducing dynamic pathway regulation using biosensor elements. This will be illustrated with examples from ongoing research, such as the engineering of cell factories for production of long-chain fatty acids or for bioplastic production with a customized monomeric composition. Finally, I will share some views on internationally established roadmaps of future developments in synthetic biology for industrial biotechnology.

Keynote lecture 4 – abstract

Cyclodextrin metal-organic frameworks: from sugars to nanomaterials for biological applications

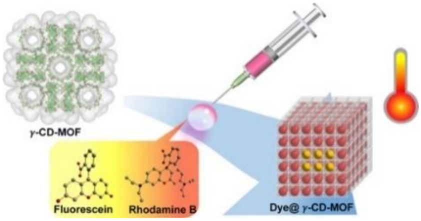
Kristof Van Hecke

XStruct group, Department of Chemistry, Ghent University, Krijgslaan 281-S3, B-9000 Ghent, Belgium

Cyclodextrins (CDs) form a family of naturally abundant, cyclic oligosaccharides, consisting of cone-shaped molecules, with a hydrophobic internal a hydrophilic external surface. Through the coordination of CDs with alkali metal ions (Na+, Rb+, Cs+, K+,…) biocompatible, porous metal-organic frameworks (CD-MOFs) can be obtained.[1] These CD-MOFs are attractive materials for practical applications as they can be considered as biocompatible, biodegradable, inexpensive MOF alternatives.

We first designed macro- and nanosized core, as well as core-shell, γ-cyclodextrin MOFs (γ-CD-MOFs) and used them as platforms for the encapsulation of dye molecules (rhodamine B, fluorescein) to develop the first CD-MOF-based ratiometric optical thermometers. Temperature measurements are critical in biomedical applications, because conditions involving inflammation or cancer are accompanied by hyperlocal temperature changes in the affected tissues.[2]

Second, we incorporated silver and gold nanoparticles (AgNPs, AuNPs) in γ-CD-MOFs. Both AgNPs and AuNPs are plasmonic, which means they could be exploited to concentrate light at a certain wavelength, providing local heating and, thus, be employed for photothermal therapy and can play a beneficial role when it comes to CD-MOFs used as drug delivery systems.



This is the first work where CD-MOFs are proposed for the development of luminescent thermometric materials, and in combination with plasmonic AuNPs and AgNPs. By employing this approach, various dyes can be combined, which opens new possibilities toward the future development of a wide range of biological (plasmonic) nanothermometers.

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Keynote lecture 5 – abstract

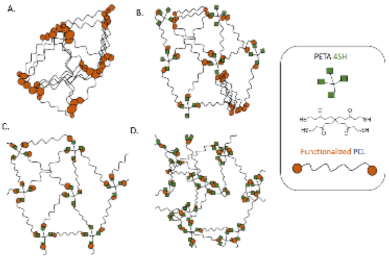
Photo-crosslinkable polymer platform: from bioinks to shape memory polymers

Sandra Van Vlierberghe

Ghent University, Ghent Belgium & Vrije Universiteit Brussel, Brussels, Belgium

Biofabrication is a specific area within the field of tissue engineering which takes advantage of rapid manufacturing (RM) techniques to generate 3D structures which mimic the natural extracellular matrix (ECM). A popular material in this respect is gelatin, as it is a cost-effective collagen derivative, which is the major constituent of the natural ECM. The material is characterized by an upper critical solution temperature making the material soluble at physiological conditions. To tackle this problem, the present work focusses on different gelatin functionalization strategies which enable covalent stabilization of 3D gelatin structures [1-4]. In a second part, synthetic acrylate-endcapped, urethane-based precursors (AUP) based on polyesters, will be discussed with exceptional crosslinking behaviour and CAD-CAM mimicry compared to conventional materials [5,6]. Within this synthetic material class, also insight will be provided on the shape memory properties of polyester-based AUPs [7]. Both chain growth and step growth polymerization mechanisms (see figure) along with their mechanical properties and processability potential will be addressed [5,6].

Several polymer processing techniques will be covered including conventional 3D printing using the Bioscaffolder 3.1, Digital Light Projection (DLP) [6] and two-photon polymerization [2, 3, 5]. A number of biomedical applications will be tackled including adipose tissue engineering, vascularization [2], ocular applications, etc. In a final part, attention will be paid to the valorization of our biomaterial platform technology through the launch of our spin-off company BIO INX. The results show that chemistry is a valuable tool to tailor the properties of (bio)polymers towards light-based processing while preserving the material biocompatibility.



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[7] Delaey J, et al. PCT/EP2021/062055, 2021.

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OUR
PURPOSE
To enhance the quality
of life in a material way —
today and for future
generations
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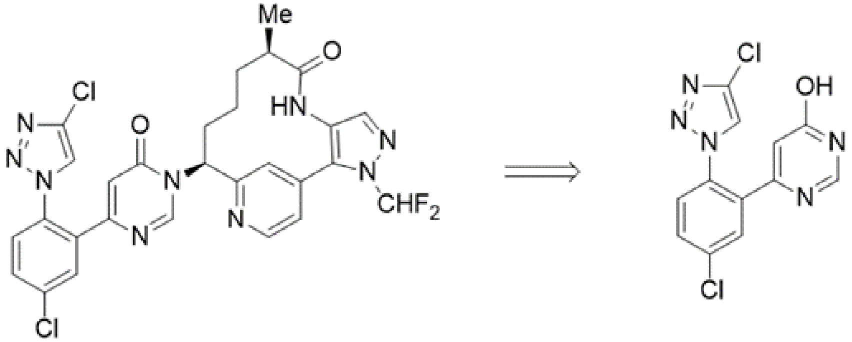
Keynote lecture 6 – abstract

Chemical process development of the Milvexian side chain

Ilse Vogels

Chemical Process Research & Development, Janssen Pharmaceutica, Turnhoutseweg 30, 2340 Beerse (Belgium), ivogels@its.jnj.com

Beyond the challenge of inventing any new medicine, Process Chemists are tasked with designing the best chemical process for every product in the pipeline. Chemistry alone can make all the difference between an unviable product and a drug that is affordable and accessible to every patient that needs it. In many cases, a completely redesigned novel synthetic route is needed to meet this objective. Chemists at Janssen working on the development of the novel antithrombotic agent Milvexian [1] optimized a 4-step process to the side chain intermediate 1 to leverage the initial supplies needed for Milvexian clinical studies. Next, new chemistry was developed to design a shorter and more sustainable route.



Milvexian **1**

[1] A. K. Dilger et al. J. Med. Chem. 2022, 65, 3, 1770–1785

Keynote lecture 7 – abstract

How can techno-economic and techno-sustainability assessment contribute to chemical research

Steven Van Passel

University of Antwerp

A techno-economic assessment (TEA) combines process modeling and engineering design with an economic evaluation at early stages of technology development. From 2010, a large increase in the number of techno-economic assessments (or analyses or evaluations) is observed. This indicates the interest to include an economic evaluation during the development of alternative energy fuels and environmental technologies, tackling the need for green, clean technology including the development of green chemistry and technological options to mitigate greenhouse gas emissions. This presentation explains what a TEA is and what type of questions can be answered by a TEA. Advantages will be listed together with some well-known pitfalls. In addition to these strengths and weaknesses, opportunities and threats for TEA are explained using chemical TEA-examples such as (i) lignin-first biorefinery with a reductive catalytic fractionation process; (ii) pyrolysis of mixed plastic waste and (iii) microalgae biorefineries.

Keynote lecture 8 – abstract

Impact chemicals strategy for sustainability on chemical research and development

Kristel Bernaerts[1] & Tine Cattoor[2]

[1]KU Leuven, [2]essenscia

With the launch of the Chemicals strategy for Sustainability in October 2020 [1], the European Commission set the target high for the chemicals policy for the coming years to contribute to a zero pollution ambition [2] - a key deliverable of the European Green Deal. Not only a review of the current chemicals and product policy framework and the introduction of new regulatory mesures to identify and phase out the most hazardous chemicals can be expected. Developing a new Safe and Sustainable by Design concept [3] intends to boost innovation in the chemical sector towards more safe (id less hazardous) and more sustainable chemicals and processes, throughout their life cycle.

This keynote will give you a state of play of the implementation of the Chemicals Strategy for sustainability and recommendations to take into consideration in future research and development.

[1] Chemicals strategy (europa.eu)

[2] Zero pollution action plan (europa.eu)

[3] JRC Publications Repository - Safe and Sustainable by Design chemicals and materials Review of safety and sustainability dimensions, aspects, methods, indicators, and tools (europa.eu)

Keynote lecture 9 – abstract

Towards a climate-neutral chemical industry in Europe: governance & policy

Sebastian Oberthur

Vrije Universiteit Brussel, Belgium

In order to prevent the worst impacts of climate change and limit the increase of global average temperatures to 1.5/2°C, the European chemical industry needs to drastically reduce greenhouse gas emissions by 2030 and become fully climate neutral by 2050, at the very latest. This requires (1) the phase out and substitution of fossil fuels as inputs and in processes, and (2) a radical increase in material efficiency and circularity through recycling, product design/standards and product substitution where more sustainable alternatives exist.

To achieve and facilitate the necessary transformation of the chemical industry, a mix of policy instruments needs to be deployed. This policy mix must be multifaceted to effectively address the diverse key drivers and barriers of the climate transition in the chemical industry. It requires a mix of economic incentives (carbon pricing and subsidies/funding), regulatory standards (product standards, recycling obligations, use restrictions, etc.) and informational instruments (labelling, certification, etc.). Given strong transnational interdependencies and competition, international cooperation also is a key ingredient of the mix.

The European Union has developed a varied policy framework that includes many of the elements required, but also needs to be further developed. Operating in tandem with various member-state policies, key elements of the existing EU framework include the EU Emissions Trading System (ETS), support for R&D (Horizon Europe, SET Plan, etc.), various investment funds/schemes (Innovation Fund, InvestEU, NextGeneration EU, etc.). In addition, the international policy dimension of the decarbonisation of energy intensive industries is being developed (EU Carbon Border Adjustment Mechanism, Climate Club under the G7). In addition, the development of further informational and regulatory elements will be required to enhance circularity and material efficiency as well as to address strong inter-sectoral interactions (e.g. supply of electricity and hydrogen). Chemical industry expertise will be indispensable for building and enhancing an effective policy framework.

Conference timetable

		Chair
FM	Functional Materials	Prof. Danny Vanpoucke
CB	Chemistry meets Biology	Prof. Ana Cunha
CS&M	Chemical Synthesis & Methodologies	Prof. Dirk Vanderzande
E&E	Energy & Environment	Prof. Elke Debroye
CP&RT	Chemical Processes & Reactor Technologies	Prof. Evelien Baeten
R&S	Renewables & Sustainability	Prof. Thomas Heugebaert

9:00		Registration & Pick-up Room keys	Entrance Hall
10:30		**Welcome & opening**	Auditorium
10:50		**What is chemistry Europe?** Shaun Scally – *Wiley*	Auditorium
11:05	P1	**Chemical information: building bridges for chemistry** Jonathan Goodman – *University of Cambridge*	Auditorium
11:55	K1	**Tailored molecular design of organic chromophores – from thermally activated delayed fluorescence to dual-functioning photosensitizers** Wouter Maes – *UHasselt*	Auditorium
12:30	K2	**Ultrasonic microreactors for chemical manufacturing**	Auditorium

		Simon Kuhn – *KU Leuven*				
13:10		Lunch & Pick-up Room keys			Foyer	
	Auditorium: **FM**		Room 2, 3 & 4: **CB**		Room 5: **CS&M**	
14:30	FM-O1	**Hydrotalcites as effective and selective catalysts for the condensation of small sugars towards the synthesis of polyol-based flame retardants** Fatima Rammal *KU Leuven*	CB-O1	**Chemical evolution driven by self-assembly** Omer Markovitch *University of Groningen*	CS&M-O1	**9-Boratriptycenes: a Lewis superacids story** Arnaud Osi *University of Namur*
14:50	FM-O2	**Phenylpyridine and bipyridine based covalent organic frameworks as metal free photocatalysts for the visible light aerobic oxidation/Povarov cyclization** Maarten Debruyne *Ghent University*	CB-O2	**Development of a high-bioanalytical platform for metabolomics** Katyeny Manuela da Silva *University of Antwerp*	CS&M-O2	**Dearomative cyclopentannulation of indoles and benzofurans** Bram Ryckaert *Ghent University*
15:10	FM-O3	**Synthesis, characterization and biological features of saponin based nanoparticles**	CB-O3	**Towards the one-pot upgrading of glucose to HMF through hybrid chemo-enzymatic catalysis**	CS&M-O3	**9-phosphatriptycenes as Lewis bases for the frustrated Lewis pair-catalyzed hydrogenation**

		Cansel Askim Tiryaki *Ege University*		Marty Kinnaer *UC Louvain*		**of unactivated olefins: a DFT and experimental study** Damien Mahaut *University of Namur*
15:30	FM-O4	**Towards stable hybrid perovskites for optoelectronics: designing large organic cations** Wouter Van Gompel *UHasselt*	CB-O4	**Ultralarge virtual screening identifies SARS-CoV-2 main protease inhibitors with broad-spectrum activity against coronaviruses** Andreas Luttens *Uppsala University*	CS&M-O4	**Selective iminitation of 3-oxo-β-lactams – new route towards 3-amino-β-lactams** Sari Deketelaere *Ghent University*
	Room 6: **E&E**		Room 13: **CP&RT**		Room 14: **R&S**	
14:30	E&E-O1	**Industrial decarbonization for the energy transition** Talieh Rajabloo *UHasselt*	CP&RT-O1	**Demystifying the thermodynamics of furfural derivatives aiming at improved separation process design** Ilah Joos *Ghent University*	R&S-O1	**Heat triggered debondable adhesives** Tim Maiheu *Ghent University*
14:50	E&E-O2	**Integrated direct air capture and**	CP&RT-O2	**Numerical analysis to reduce axial dispersion with active lateral flow**	R&S-O2	**Mechanosynthesis of N-heterocyclic carbene complexes**

		electrochemical CO2 conversion Oriol Gutierrez *VITO*		Pierre Gelin *Vrije Universiteit Brussel*		Gianmarco Pisano *Ghent University*
15:10	E&E-O3	**Plasma catalysis for CO2 hydrogenation: unlocking new pathways toward CH3OH** Roel Michiels *University of Antwerp*	CP&RT-O3	**Synthesis of heterogeneous metal oxides catalysts by humid air plasma glidarc: study of the effect of the post-discharge** Fanny Hanon *UC Louvain*	R&S-O3	**Microkinetic analysis of ethylene hydroformylation on a heterogeneous Rh-modified MOF catalyst** Sébastien Siradze *Ghent University*
15:30	E&E-O4	**Understanding the mechanism of CO2 methanation over MgO-Ni/SiO2** Yufei Xie *Ghent University*	CP&RT-O4	**Experimental assessment of the ethyl acetate synthesis kinetics by direct addition of ethylene to acetic acid on a silicotungstic acid catalyst** Bram Van Wettere *Ghent University*	R&S-O4	**Lewis acid catalyzed synthesis of methionine hydroxy analogues from tetroses** Sergio Calderon-Ardilla *KU Leuven*
15:50		Poster Session 1 & Coffee Break			Cafetaria	
17:00	K3	**Synthetic biology as driving force for biobased production of chemicals using microbial cell factories** Eveline Peeters – *Vrije Universiteit Brussel*			Auditorium	

17:35	K4	**Cyclodextrin metal-organic frameworks: from sugars to nanomaterials for biological applications** Kristof Van Hecke – *Ghent University*	Auditorium
18:10		Pick-up Room keys	Entrance Hall
19:00		Dinner	Restaurant
20:30		KaféCV	Cafetaria

7:30-9:00		Breakfast			Restaurant	
9:00	P2	**Water in coherent light** Gerhard Grübel – *University of Hamburg*			Auditorium	
9:50	K5	**Photo-crosslinkable polymer platform: from bioinks to shape memory polymers** Sandra Van Vlierberghe – *Ghent University*			Auditorium	
10:25		Coffee break			Foyer	
10:55	K6	**Chemical process development of the Milvexian side chain** Ilse Vogels – *Janssen Pharmaceutica NV*			Auditorium	
	Auditorium: **FM**		Room 2, 3 & 4: **CB**		Room 5: **CS&M**	
11:30	FM-O5	**Methacrylate-endcapped urethane-based polyesters – influence of backbone and spacer on thermal properties and crosslinking** Jasper Delaey *Ghent University*	CB-O5	**Biodegradation of maleic anhydride-grafted polycaprolactone (PCL-g-MA) with lipase** Kotchaporn Thangunpai *University of Tsukuba*	CS&M-O5	**Development of bulk-like CdS and CdSe quantum dots for optical gain** Margarita Samoli *Ghent University*
11:50	FM-O6	**Crosslinked polyaspartic acid hydrogels as biobased and biodegradable**	CB-O6	**Reactivity of peroxidases and chlorite dismutases with chlorite and hypochlorite: a**	CS&M-O6	**Design, synthesis and characterisation of novel donor-acceptor combinations affording**

		alternative for polyacrylic acid Lauren De Grave *Ghent University*		**spectroscopic investigation of short-lived intermediates trapped by fast freeze-quenching** Ilenia Serra *University of Antwerp*		**low voltage losses in indoor organic photovoltaics** Dries Theunissen *UHasselt*
12:10	FM-O7	**UV -assisted cryogelation of poly(2-oxazoline)s towards supermacroporous hydrogels** Tomas Sedlacik *Ghent University*	CB-O7	**An unbiased approach to exploring biomolecular reactions with hybrid QM/MM** Neil McFarlane *KU Leuven*	CS&M-O7	**Electron microscopic approaches in identifying, understanding & design of catalysts** Sreeprasanth Sree Pulinthanathu *KU Leuven*
	Room 6: **E&E**		Room 13: **CP&RT**		Room 14: **R&**	
11:30	E&E-O5	**Green ammonia synthesis process with Plasma-driven Nitrogen Oxidation and Catalytic Reduction of Adsorbed NOx (PNOCRA process)** Lander Hollevoet *KU Leuven*	CP&RT-O5	**Characterization of an acoustic streaming microreactor: uncovering the effect of acoustic streaming on crystallization** Cedric Devos *KU Leuven*	R&S-O5	**Recyclable polyurethane elastomers via dynamic covalent chemistries** Hiba Kassem *Ghent University*

11:50	E&E-O6	**Exploring the reactivity of a Solid Micellar Catalyst (SOMIC) for low-temperature methanol synthesis** Catarina Martins de Brito Mendes *Ghent University*	CP&RT-O6	**Photometric determination of trace amounts of Al in cc. NaCl solutions used by the chlor-alkali industry - coagulation and sedimentation studies** Benjamin Csorba *Budapet University*	R&S-O6	**Catalytic pyrolysis of a polyethylene melt with high selectivity to light olefins and low coke formation** Brent Smeyers *KU Leuven*
12:10	E&E-O7	**Sustainable hydrogen from free sunlight and seawater using stabilized plasmonic modified TiO2** Fons Dingenen *University of Antwerp*	CP&RT-O7	**Characterization of flows in microchannels with scanning 3D µPIV** Quentin Galand *Vrije Universiteit Brussel*	R&S-O7	**Sustainable synthesis of aromatic building blocks via the upcycling of polystyrene based plastic waste** Yuman Qin *University of Antwerp*
12:30		Lunch			Foyer	
	Auditorium: **FM**		Room 2, 3 & 4: **CB**		Room 5: **CS&M**	
13:50	FM-O8	**Developing design rules for room temperature phosphorescence in solution from purely organic molecules**	CB-O8	**NMR-based metabolomics reveals a metabolic shift after surgical resection of non-small cell lung cancer**	CS&M-O8	**NHC complexes in flow (NHC = N-heterocyclic carbene)**

		Simon Paredis *UHasselt*		Elien Derveaux *UHasselt*		Andreas Simoens *Ghent University*
14:10	FM-O9	**Self-assembly behavior of molecules under confinement conditions** Lihua Yu *KU Leuven*	CB-O9	**Hyphenation of temperature-responsive chromatography and ultrafast chiral chromatography as a generic comprehensive two-dimensional method for the analysis of chiral pharmaceuticals** Turaj Rahmani *Ghent University*	CS&M-O9	**Group IV Metal oxo cluster based catalysts for the direct formation of amide bonds** Francisco de Azambuja *KU Leuven*
14:30	FM-O10	**3D printing, where hydrogels and tissue engineering meet** Martina Meazzo *Ghent University*	CB-O10	**Novel microfluidics approaches for selection and enhancement of sperm motility for improved fertilization** Vyacheslav Misko *Vrije Universiteit Brussel*	CS&M-O10	**Development of a combined methodology towards mechanistic investigation of rare metal-free, light activated catalysts** Andrea Guidetti *University of Antwerp*
14:50	FM-O11	**Isomeric modulation of thermally activated delayed fluorescence**	CB-O11	**Development of fluorescent ligands for voltage-gated ion channels**	CS&M-O11	**Synthesis of bridged bicyclic nitrogen scaffolds via orthogonal tandem catalysis**

		properties in deep-red/near-infrared emitters Sonny Brebels *UHasselt*		Carlotta Borgarelli *KU Leuven*		Marjo Waeterschoot *University of Antwerp*
	Room 6: **E&E**		Room 13: **CP&RT**		Room 14: **R&S**	
13:50	E&E-O8	**Techno-economic model for the application potential of hydrogen storage technologies** Lucas Hanssens *KU Leuven*	CP&RT-O8	**Exploration of catalytic pyrolysis with active learning** Yannick Ureel *Ghent University*	R&S-O8	**A green analytical method to characterize unsaturated hydrocarbons in waste polyolefin pyrolysis oil using FT-IR** Trang Thi Bui *University of Antwerp*
14:10	E&E-O9	**Catch the heat!** Ionut Tranca *Vrije Universiteit Brussel*	CP&RT-O9	**Electrochemical conversion of CO2 to formic acid at elevated temperatures** Alana Rossen *University of Antwerp*	R&S-O9	**Use of FTIR microspectroscopy to assess the extraction viability of food waste** Paula Varas Perez *UHasselt*
14:30	E&E-O10	**Innovative battery materials: it's all about chemistry!** Dries De Sloovere *UHasselt*	CP&RT-O10	**Enabling flow synthesis of zeolites** Dries Vandenabeele *KU Leuven*	R&S-O10	**3D investigation of nanoparticle assemblies by electron tomography** Safiyye Kavak *University of Antwerp*

14:50	E&E-O11	**Technical and economical aspects of advanced biofuel production and separation** Keikhosro Karimi *Vrije Universiteit Brussel*	CP&RT-O11	**Microfluidic magnetic platform for repetitive coating of particles** Amaury de Hemptinne *Vrije universiteit Brussel*	R&S-O11	**Fresh water production from atmospheric air: technology and innovation outlook** Robin Peeters *KU Leuven*
15:10		Poster session 2 & Coffee break			Cafetaria	
	Auditorium: **FM**		Room 2, 3 & 4: **CB**		Room 5: **CS&M**	
16:20	FM-O12	**Turning 3D-COFs into luminescent ratiometric thermometers** Laurens Bourda *Ghent University*	CB-O12	**Immobilizing neuroglobin in mesoporous materials – monitoring protein structure and dynamics with spin-label electron paramagnetic resonance** Lore Van Den Bergh *University of Antwerp*	CS&M-O12	**Synthesis and structural characterization of phosphate-based geopolymers** Marko Rukavina *University of zagreb*
16:40	FM-O13	**Controlled self-assembly of molecular motors and switches at the solution/solid interface: towards light induced coherent rotary motion** Robby Reynaerts *KU Leuven*	CB-O13	**Effect of membrane curvature and lipid composition on membrane permeability in liposomal drug delivery** Samaneh Davoudi *Ghent University*	CS&M-O13	**Construction of M-C and M-N bonds: "golden" synthons, materials, pre-catalysts and mechanistic probes** Nikolaos Tzouras *Ghent University*

	Room 6: **E&E**		Room 13: **CP&RT**		Room 14: **R&S**	
16:20	E&E-O12	**Characterization of degradation products from advanced oxidation processes using temperature responsive comprehensive LCxLC-HRMS** Elena Bandini *Ghent University*	CP&RT-O12	**On the relevance of molecular machine learning in industrial chemistry** Maarten Dobbelaere *Ghent University*	R&S-O12	**An experimental study on the optimization of process parameters for super-dry reforming of methane** Michiel Van Cauwelaert *Ghent University*
16:40	E&E-O13	**Identification of synthetic antioxidants in consumer products through LC-QTOF-MS** Maarten Roggeman *University of Antwerp*	CP&RT-O13	**CFD – study for enhanced degassing of a dehydrogenation reactor for liquid organic hydrogen carriers** Laurens Van Hoecke *University of Antwerp*	R&S-O13	**Acidity and metal ratio effects on the low temperature hydrodeoxygenation of anisole over NiCu on SiO2 and γ-Al2O3** Tom Vandevyvere *Ghent University*
17:00	K7	**How can techno-economic and techno-sustainability assessment contribute to chemical research?** Steven Van Passel – *University of Antwerp*			Auditorium	
17:35	K8	**Impact chemicals strategy for sustainability on chemical research and development** Kristel Bernaerts – *KU Leuven* & Tine Cattoor – *essencia*			Auditorium	

Thursday October 13, 2022

18:10	Group picture	In front of venue
19:30	Aperitif	Cafetaria
20:30	Dinner	Restaurant
22:00-3:00	Live performance by Totally Soul	Cafetaria

8:00- 9:30		Breakfast			Restaurant	
9:30	K9	**Towards a climate neutral chemical industry in Europe: governance & policy** Sebastian Oberthur – *Vrije Universiteit Brussel*			Auditorium	
	Auditorium: **FM**		Room 2, 3 & 4: **CB**		Room 5: **CS&M**	
10:05	FM-O14	**Light-stabilized dynamic materials: tuning the dynamic character** Alyssa Ghielmetti *Ghent University*	CB-O14	**The notorious Z.B.G.: synthesis and biological evaluation of potent HDAC6 selective inhibitors with a non-hydroxamic acid zinc binding group to overcome therapeutic limitations** Silke Geurs *Ghent University*	CS&M-O14	**Selective nickel-catalyzed hydrodeacetoxylation of aryl acetates** Gilles De Smet *University of Antwerp*
10:25	FM-O15	**Bio-inspired mineralization of CO2 to functional CaCO3: effect of different CO2 absorption promotor and crystal growth modifier**	CB-O15	**Solid-phase peptide synthesis, folding and biological characterization of carboxyterminally truncated human CXC chemokine ligand 10 CXCL10(1-73)**	CS&M-O15	**Transformations of phosphonochloridates to phosphonates and phosphonamidates under mild coupling conditions**

		Dharmjeet Madhav *KU Leuven*		Luna Dillemans *KU Leuven*		Simon Backx *Ghent University*
	Room 6: **E&E**		Room 13: **CP&RT**		Room 14: **R&S**	
10:05	E&E-O14	**Lignin-supported heterogeneous photocatalyst for the direct generation of H2O2 from seawater** Peng Ren *University of Antwerp*	CP&RT-O14	**Enhancing CO2 conversion by plasma reactor in series** Rani Vertongen *University of Antwerp*	R&S-O14	**Let the sun do your chores!** Hannelore Peeters *University of Antwerp*
10:25	E&E-O15	**Template synthesis of fibrous catalysts for environmental application** Maximiliano Rodriguez *UC Louvain*	CP&RT-O15	**Ray tracing-assisted optimization of light absorption in gas-liquid flow photosensitized oxidations** Anca Roibu *KU Leuven*	R&S-O15	**Improved induction adsorptive CO2 capture process** Mohsen Gholami *Vrije Universiteit Brussel*
10:45		Coffee Break			Foyer	
	Auditorium: **FM**		Room 2, 3 & 4: **CB**		Room 5: **CS&M**	
11:15	FM-O16	**Fine-tuning the endcap chemistry of acrylated poly(ethylene glycol)-based hydrogels for the treatment of burn wounds**	CB-O16	**Photo-alkylation of DNA secondary structures, exploiting photosensitizer and ligand co-localization: from structure-selectivity**	CS&M-O16	**Defective UiO-66 metal-organic frameworks as aldol reaction catalysts: Impact of surface defects on activity and selectivity**

		Manon Minsart *Ghent University*		**towards sequence-specificity** Enrico Cadoni *Ghent University*		Noor Aljammal *Ghent University*
11:35	FM-O17	**Rhodium anchored onto a covalent triazine framework as heterogeneous catalyst for transfer hydrogenation of N-heterocycles in water** Jonas Everaert *Ghent University*	CB-O17	**Chromium toxicity: the role of analytical chemistry in exposure to chromium** Jelle Verdonck *KU Leuven*	CS&M-O17	**Aluminium and acid site diversity during zeolite crystallization and thermal activation** Julien Devos *KU Leuven*
11:55	FM-O18	**Unravelling the performance of Pt-Ni ORR electrocatalysts by combining electrochemical with advanced TEM studies** Sven Arnouts *University of Antwerp*	CB-O18	**A simple model for the Pauli repulsion with utility in QM, MM and chemical education** Jordy Peeters *Vrije Universiteit Brussel*	CS&M-O18	**Catalyst-free solution polymerization of poly(alkylene terephthalate)s: towards high molar masses and molar mass control** Lenny Van Daele *Ghent University*
	Room 6: **E&E**		Room 13: **CP&RT**		Room 14: **R&S**	
11:15	E&E-O16	**Modeling realistic catalyst nanoparticles for Fischer-Tropsch synthesis using**	CP&RT-O16	**Innovative Au-Sn-SiO2 bifunctional material for**	R&S-O16	**Screening of biomass residue streams for their applicability as feedstocks**

		machine learning potentials Konstantijn Rommens *Ghent University*		**the upgrading of glycerol to methyl lactate** Margot Van der Verren *UC Louvain*		**for activated carbon production and their compliance as electrode material** Willem Vercruysse *UHasselt*
11:35	E&E-O17	**Effect of pH cycling and background ions on the formation of stable magnesium carbonate at low temperature** Veerle Vandeginste *KU Leuven*	CP&RT-O17	**Catalytic dehydration of 1,3-Butanediol into 1,3-Butadiene** Ghinwa Fayad *KU Leuven*	R&S-O17	**Sodium aluminate-based materials as promising catalysts for biodiesel production** Giovanni Pampararo *UC Louvain*
11:55	E&E-O18	**Unravelling the mysteries of arsenic in the Zenne river (Belgium): sources, distribution, geochemistry, and bioavailability** Vendula Smolikova *Vrije Universiteit Brussel*	CP&RT-O18	**Perspectives of continuous heterogeneously catalyzed hydroformylation of large olefins** Maria Manzano Herrero *Ghent University*	R&S-O18	**NMRCoRe@CMWS as a node of convergence in molecular water science in Flanders** Eric Breynaert *KU Leuven*
12:15-13:30		Lunch			Restaurant	
13:30	P3	**The new chemist** Javier Garcia Martinez – *IUPAC President*			Auditorium	

14:30	**The Human Link** Stress-les(s): coping with stress in an academic environment *ROOM 5*	**Scimingo** Time to reach out! A crash course on scientific communication *ROOM 2, 3 & 4*
15:40	Start Closing Ceremony	Auditorium
15:50	Chemistry Europe Fellows Award Tatjana Parac-Vogt *KU Leuven*	Auditorium
15:55	Incentive Awards C.G.B.-C.B.B. Roy Lavendomme – *Ghent University* & Ruben Van Lommel – *KU Leuven/ Vrije Universiteit Brussel*	Auditorium
16:10	Poster and Oral Contribution Awards	Auditorium
16:45	Final Word	Auditorium
16:50	End of CRF-ChemCYS symposium 2022	Auditorium

FM-O1

Hydrotalcites as effective and selective catalysts for the condensation of small sugars towards the synthesis of polyol-based flame retardants

Rammal Fatima[1], *Khalil Ibrahim*[1], *Lorenz Ward*[1], *Scodeller Ivan*[1], *Van Vaerenbergh Beau*[2], *De Schrijver Bert*[2], *Makshina Ekaterina*[1], *Sels Bert*[1]

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[2] *Oleon, Belgium*

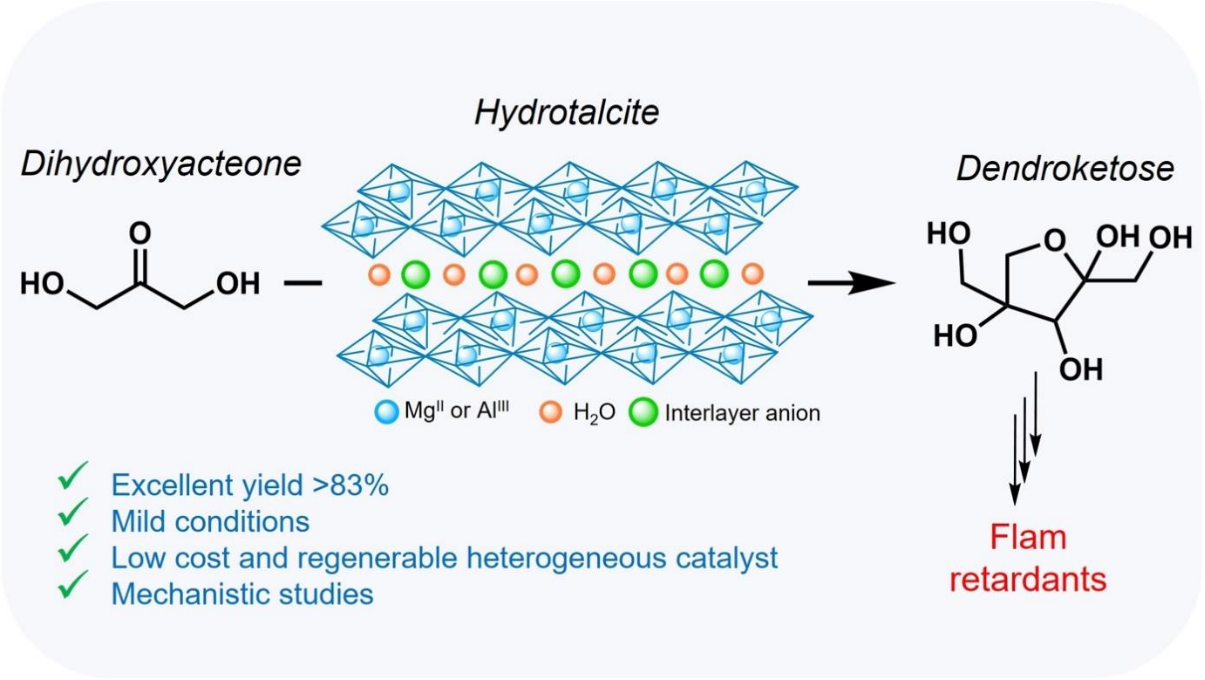
Keywords: Hydrotalcire; Layered materials; Dihydroxyacetone; Dendroketose; Flame-retardants

Aside from their use as precursors in a variety of chemical materials ranging from surfactants and plasticizers to polymer crosslinkers, branched polyols have gained additional interest due to their ability to be converted by esterification into lubricants and moisturizers or, more importantly, into green flame retardants by phosphorylation reaction as a direct replacement for bromine and chlorine-containing alternatives.

Therefore, the development of an efficient and sustainable approach for the synthesis of branched polyols is of great interest. Thus, the objective of this work is to realize the condensation of dihydroxyacetone into branched sugars (dendroketose) by means of a stable and robust heterogeneous catalysis in order to obtain the corresponding branched polyols via hydrogenation. In terms of heterogeneous basic catalysts, hydrotalcite is one of the most important candidates to realize the base-catalyzed condensation of dihydroxyacetone. This is due to their interesting structural properties, their ease of synthesis, and the various active sites that lead to a selective aldolization.

Our approach consists in studying the activity of hydrotalcite in condensation chemistry as a function of its composition, layered structure, and porous characteristics. These different parameters define the strength, nature, and accessibility of the different active basic sites which have been investigated by means of FT-IR spectroscopy, nitrogen physisorption, and XRD measurements. Interestingly, additional optimization studies were conducted in order to improve the stability of the catalyst and subsequently promote a successful hydrogenation process.

Thus, the gain in mechanistic insights allowed the selection of an adapted pretreatment process that improves the properties and stability of hydrotalcites as heterogeneous catalysts, which was successfully applied for the formation of branched sugars under mild conditions and suitable for late-stage functionalization. The catalyst characterization, as well as mechanistic studies, will be discussed in this presentation.



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FM-O2

Phenylpyridine and bipyridine based covalent organic frameworks as metal free photocatalysts for the visible light aerobic oxidation/Povarov cyclization

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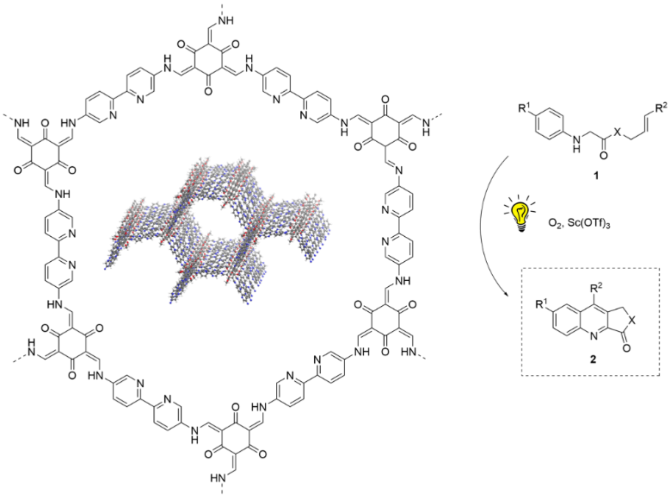
Keywords: Covalent organic frameworks; photocatalysis; heterogeneous catalysis; Povarov cyclization

Covalent organic frameworks (COFs) are crystalline, porous polymers constructed completely from organic building blocks. They possess high surface areas, can be tailor made towards specific applications, can be very chemically stable and are insoluble, making them ideal for use as heterogeneous catalysts. Applying COFs as metal free heterogeneous photocatalysts forms a convenient alternative for the commonly used iridium and ruthenium metal complexes that are expensive, toxic and difficult to separate and recycle.

In this work stable bipyridine or phenylpyridine based COFs were synthesized and applied towards the one-pot aerobic oxidation/Povarov cyclization, a mild and efficient way to synthesize quinolines. Sc(OTf)3 proved to be the most effective Lewis acid co-catalyst for this transformation and a wide range of quinoline-fused lactones/lactams (2) were synthesized from substrates (1) proving the value of these COFs as heterogeneous photocatalysts for complex organic transformations.



FM-O3

Synthesis, Characterization and Biological Features of Saponin Based Nanoparticles

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Keywords: Saponin ; Chitosan ; Nanoparticle ; Drug release

Saponins are glycosides, usually with a triterpenic or steroidal aglycone, which have surfactant property due to their distinctive structure. In addition to this, saponins attract attention because they form complexes with cholesterol and have antifungal and antibiotic activities. Thus, in this study, we investigated the Cephalaria plant species which are very rich in saponins. Cephalaria saponins have valuable biological activities, and for this reason they have an important place for drug release and disease treatment1,2. Drug release has emerged as one of the most important treatment techniques in the treatment of various diseases such as cancers, vascular diseases and virus infections3.

According to the literature research, it has been determined that there are limited studies about the release of saponin-loaded chitosan nanoparticles. In this circumstances , our first aim was to obtain the targeted saponins from Cephalaria species by different extraction, isolation and purification processes and find their structures with advanced spectroscopic methods. The saponin riched n-butanol extract was prepared from Cephalaria species and then further chromatographic methods such as VLC, MPLC, CC, PTLC, TLC were examined on this extract. For structural determination studies the advance NMR techniques (1D,2D NMR) and HRESI-MS method were used. The saponin-loaded chitosan nanoparticles (SPCSNP) were synthesized by ionic gelation technique and characterized by FTIR, SEM and DSC. The encapsulation efficiency (EE) and in vitro release profile in pH=7,4 phosphate buffer at 37 °C were determined by using UV at 450 nm. The encapsulation efficiency and particle size of SPCSNP were found 68% ± 2.52 and 90 ± 8.41 nm, respectively.

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FM-O4

Towards stable hybrid perovskites for optoelectronics: designing large organic cations

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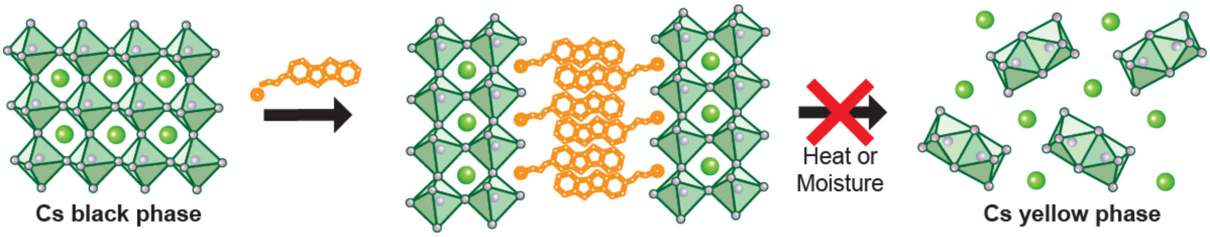
Keywords: Hybrid perovskites; optoelectronics; organic cations

Hybrid organic-inorganic perovskites have received tremendous research attention over the past decade for use in optoelectronic applications such as solar cells, LEDs and photodetectors. They combine excellent optoelectronic properties, tunable absorption and emission ranges, and solution processability. However, their commercialization is currently hindered by their limited intrinsic stability. A prime route to obtain more stable perovskite materials is the addition of a large organic ammonium cation to form quasi-2D perovskites.[1-2]

We employ a tailored polyheterocyclic aromatic ammonium cation either as an additive in the precursor solution to obtain a quasi-2D perovskite for use in photodetectors, or as an interlayer in solar cells.

The tailored organic cation was added to a CsPbI3 precursor solution to obtain a <n> = 2 quasi-2D perovskite film. We compared the stability and performance of this film to that of a state-of-the-art (BA)2CsPb2I7 (<n> = 2) film. While the (BA)2CsPb2I7 film starts to degrade at 130 °C, the thermal stability of the film containing the large polyheterocyclic aromatic ammonium cation is significantly enhanced to 230 °C. Furthermore, while the (BA)2CsPb2I7 film degrades into (BA)2PbI4 and other compounds after 1 day of storage in air at 77% relative humidity, the film containing our tailored cation shows excellent resistance against humidity, with no apparent degradation after five months. We fabricated planar photodetectors using both films. The specific detectivity of the photodetectors with films containing our tailored cation is similar in magnitude compared to those containing the state-of-the-art (BA)2CsPb2I7 films.

The same organic cation was also used as an interlayer in a solar cell between a NiOx hole-transporting layer, and a 3D perovskite leading to an enhanced lifetime of photo-generated charge-carriers based on TRPL measurements. Furthermore, an improvement of ~ 40 mV in VOC is achieved in solar cells. The moisture stability of the solar cells was enhanced with the presence of the interlayer.



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FM-O5

Methacrylate-endcapped urethane-based polyesters – influence of backbone and spacer on thermal properties and crosslinking

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Keywords: methacrylates; AUP; photo-polymerisation

Acrylate-endcapped urethane-based precursors are an interesting type of polymers resulting from the reaction of a diisocyanate with a backbone and an acrylate-endcapped spacer .1,2,3 These materials show interesting solid state crosslinking behavior where crosslinking in solid state proceeds faster and more efficient than in molten state or in solution.1 This behavior is attributed to a preorganization induced by the crystallization of the backbone, resulting in a phase separation which allows for the creation of a mobile acrylate-rich phase.2

In this work, methacrylated variants of these polymers were synthesized constituting different polyester backbones (poly-ε-caprolactone (PCL), poly-L-lactide (PLLA) and amorphous poly-D,L-lactide (PDLLA)).3 Moreover, each backbone was connected with methacrylate endcaps either directly or through the use of a spacer to evaluate the influence of a spacer on the thermal properties of the polymer as well as on the crosslinking behavior. While previous research has mostly focused on acrylate-endcapped PCL while this research also includes PLA in both crystalline and amorphous form and is the first to report the influence of the spacer in this type of material for amorphous polymers

Endcaps were synthesized by reacting 1.2 equivalents of poly(ethylene glycol) monomethacrylate (Mn = 500 g/mol) or hydroxyethyl methacrylate dissolved in dry THF (1:1 m/V) overnight with isophorone diisocyanate (IPDI), in the presence of stannous octoate (SnOct2, 500 ppm) as catalyst and triphenyl phosphite (500 ppm) and phenothiazine (500 ppm) as stabilizers, at 65°C under argon atmosphere.

PLLA and PDLLA (Mn = 8000 g/mol) were synthesized by reacting L-lactide or D,L-lactide (20 g, 138.7 mmol) respectively with ethylene glycol (0.16 g, 2.5 mmol) as initiator, catalyzed by SnOct2 (1.02 g, 2.5 mmol). The resulting polymer was precipitated in cold hexane. PCL (Mn = 2000 g/mol, Sigma Aldrich) was used as received. Backbone batches were subdivided in two and each half was reacted with a different endcap. Therefore, the backbones were dissolved in dry THF (1:4 m/V) at 40°C, followed by a dropwise addition of the endcap in THF (1.2 eq, 1:1 V/V) at 75°C. Reactions were ran overnight and the final polymer was obtained by precipitating in a 10x excess of cold hexane. Backbones were analyzed using 1H-NMR spectroscopy to obtain the Mn. The synthesized methacrylate-endcapped urethane polymers (MUP) were characterized using 1H-NMR spectroscopy to assess the methacrylate content and the degree of substitution. Thermogravimetric analysis (TGA) was performed to obtain the degradation temperature (Td). Differential scanning calorimetry (DSC) was performed on uncrosslinked and crosslinked samples to obtain glass transition (Tg) and crystallization temperatures (Tc). Differential photo-calorimetry (DPC) was performed to analyze photo-induced crosslinking kinetics (in the presence of Irgacure 2959, 2 mol%) and the degree of conversion. HR-MAS NMR spectroscopy was performed to analyze the crosslinking efficiency.

The results indicated that depending on the backbone chemistry, the presence of a spacer between backbone and methacrylate endcap can have a significant influence. As expected, the presence of a spacer resulted in a decreased Tg along with a broader Tg region . This effect can be attributed to the spacer acting as an internal plasticizer, mainly acting on the outer regions of the backbone, resulting in the broadening and overall drop of the Tg region. When considering the Td, the presence of a spacer had a negligible influence on the semi-crystalline polymers while the Td increased for amorphous PDLLA when a spacer was present.

Additionally, the presence of a spacer accelerated methacrylate reaction and resulted in increased conversions for semi-crystalline polymers when crosslinked above the Tg. However, when cooled below their Tg, the conversion of methacrylates approached 0%, indicating that these systems exhibited insufficient mobility. For amorphous polymers on the other hand, the presence of a spacer always decreased conversion irrespective of the given temperature. However, when a spacer was present, decreasing the temperature below the Tg of the material only resulted in a minor drop of conversion while materials without a spacer or semi-crystalline materials with and without a spacer showed no conversion below their Tg. This indicates that the presence of a spacer is desirable in semi-crystalline materials at temperatures higher than their Tg or amorphous materials when solid state crosslinking is desired. On the other hand, the absence of a spacer is desirable when reacting in melt or flow.

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FM-O6

Crosslinked polyaspartic acid hydrogels as biobased and biodegradable alternative for polyacrylic acid

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Keywords: /

Microplastics are nowadays ubiquitous and form a growing problem for the environment. These plastics can unintentionally enter our food chain via marine animals and plankton, causing harmful effects on human health [1]. Therefore, this project aims to contribute to the reduction of microplastics' pollution through the development of a biobased and biodegradable alternative for the water-soluble polymer polyacrylic acid, which is widespread in a variety of applications including disposable diapers, cosmetics, pharmaceuticals, paints, etc. We have developed several derivatives of (photo-)crosslinkable polyaspartic acid, which has similar properties compared to polyacrylic acid, but with the advantage that it is both biobased and biodegradable. These derivatives are evaluated in a range of applications, going from 3D-printing for biomedical purposes over cosmetic applications to the development of superabsorbent polymers.

Both methacrylate (AEMA) and norbornene (NB) moieties have been incorporated in polyaspartic acid (polyASP) by functionalization of the polyaspartic acid precursor polysuccinimide (PSI) with the corresponding primary amine, followed by alkaline hydrolysis to induce ring-opening of the remaining succinimide units. We successfully synthesized a range of norbornene-modified (polyASP-NB) and methacrylate-modified polyaspartic acids (polyASP-AEMA) with substitution degrees (DS) between 10 – 69 % and 10 – 23 % respectively. These can form networks via photo-induced crosslinking in the presence of a suitable photo-initiator (and a thiolated crosslinker in case of norbornene), which was proven via in situ photo-rheology measurements. Hydrogel networks were realized from polyASP derivatives with low DS (10 – 25 %) by casting a solution of 20 or 30 w/v% polyASP derivative with 2 mol% Li-TPO-L photo-initiator and 0.5 equivalents dithiothreitol (DTT) in case of polyASP-NB, between two glass plates followed by UV-A irradiation (315 – 400 nm) for 30 minutes. The swelling ratio and gel fraction (GF) of the hydrogels were determined by means of equilibrium swelling in double distilled water. For a solution of 30 w/v% polyASP-NB (DS 15 %), in situ photo-rheology measurements showed a storage modulus (G') of 15 kPa. The hydrogel had a GF of 75.9 ± 2.8 % and a swelling capacity of 44.9 ± 1.0 g/g. A solution of 20 w/v% polyASP-NB (DS 15 %) on the other hand formed a less stiff hydrogel with a G' of 5 kPa, a GF of 67.4 ± 1.4 % and a swelling capacity of 128.8 ± 8.7 g/g, hence it can be classified as a superabsorbent polymer (SAP). Therefore, this hydrogel was lyophilized and grinded to powder, which was incorporated in mortar as an additive to enhance self-sealing and self-healing of cracks. The influence of the polyASP-NB SAP on the mechanical properties was studied by means of three-point bending tests, compressive strength tests and air void analysis. Sealing and healing properties of the SAP were studied exploiting water permeability tests before and after healing cycles. The SAP proved to be very efficient for sealing of cracks, shown by a reduction of the water permeability with 50 to 54 %. The effect on the healing of the mortar was however limited. Furthermore, due to the higher mechanical stiffness and lower swelling ratio, polyASP-AEMA with DS 10% (for 30 w/v% G' = 100 kPa, GF = 98.1 ± 2.0 %, swelling ratio = 8.9 ± 0.8 g/g) was used to develop resin formulations for DLP 3D-printing. A range of formulations with varying polyASP-AEMA concentration, type and concentration of photo-initiator and photo-absorber were screened to assess their processability. The most promising formulations will serve as a basis to further optimize the printing parameters and composition to eventually print structures for biomedical applications. Biodegradability studies of the developed materials are ongoing and all materials serving biomedical applications will be evaluated for their biocompatibility.

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FM-O7
UV -assisted cryogelation of poly(2-oxazoline)s towards supermacroporous hydrogels

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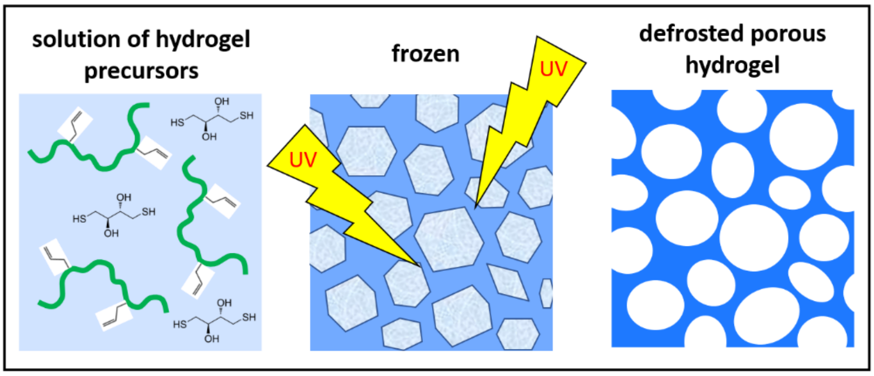
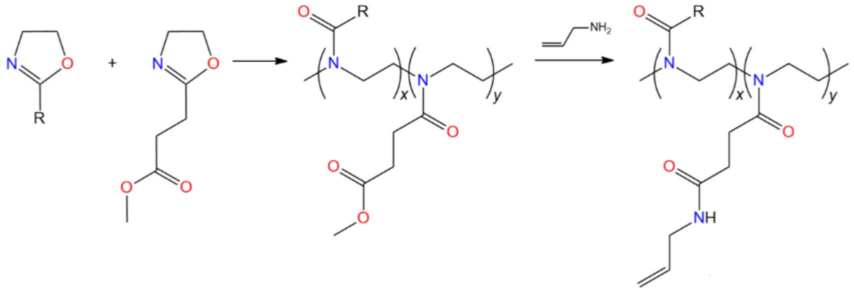
Keywords: porous hydrogels; poly(2-oxazoline)s; cryogelation

Porous hydrogels are highly desired materials in many biotechnological and medical applications. However, preparing hydrogels with an interconnective pore structure and a suitable mechanical strength can be challenging. One of the successful methods is based on gelation in a frozen state, resulting in sponge-like hydrogels with an interesting mechanical behavior despite of high pore volume and water content.[1] These materials, cryogels, can be compressed to high level without any structural damage, while water present in pores drains out. After deformation, cryogels quickly retain their original shape as the water is drawn back into the porous structure due to capillary forces.

Specific application demands constantly drive searching for new polymers suitable for cryogelation. Among others, poly(2-oxazoline)s appears as promising building block for cryogels. Not only they are biocompatible but they can be synthesized in very controlled manned to tailor their properties and properties of resulting hydrogels to meet specific application demands. Recently, our group reported the development of porous poly(2-oxazoline)s through high-internal phase emulsion polymerization for water purification and quantification of phenolic compounds.[2]

The presented study has focused on the development of supermacroporous hydrogels based on poly(2-oxazoline)s through UV-assisted cryogelation. Photocurable poly(2-oxazoline)s were obtained by cationic ring opening polymerization of 2-alkyl-2-oxazolines with methyl 3-(2-oxazoline-2-yl)-propanoate followed by amidation of methylesters with allylamine. The resulting poly(2-oxazoline)s with allyl side chains were crosslinked using thiol-ene “click” chemistry upon UV-irradiation, resulting in fast gelation. The prepared cryogels were characterized in terms of water uptake capacity and mechanical properties to evaluate their application potential. Poly(2-oxazoline)s thus become one of few examples of cryogels made through UV-assisted crosslinking. Poly(2-oxazoline) cryogels could be used in water purification or serve as porous scaffolds in biomedical applications and offers a new platform for the development of functional soft porous materials.





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FM-O8

Developing design rules for room temperature phosphorescence in solution from purely organic molecules

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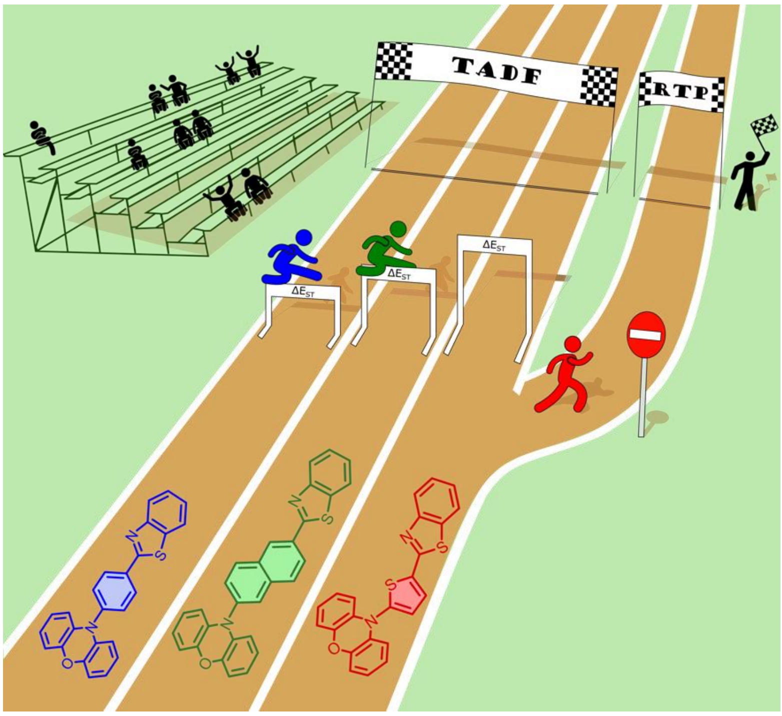
Keywords: donor-acceptor fluorophores; room temperature phosphorescence; singlet oxygen; thermally activated delayed fluorescence; time-resolved spectroscopy

Organic molecules showing room temperature phosphorescence (RTP) are gaining increasing attention due to their long-lived triplet excitons and large Stokes shifts. Moreover, from a fundamental point of view, phosphorescence is a highly interesting process because of its spin-forbidden nature. Until recently, the development of phosphorescent materials was generally achieved by introducing heavy metals to achieve large spin-orbit coupling (SOC) values and thereby allow mixing between excited singlet and triplet states, facilitating intersystem crossing (ISC). However, this development is slowed down nowadays due to the toxic nature and fast depletion of the required heavy metals. In recent years, more efforts have been devoted to metal-free organic phosphorescent molecules. The design of purely organic RTP emitters is challenging because of the significant decrease in SOC, which affects the efficiency of the ISC process. Researchers have already developed some design strategies to enhance SOC and thereby facilitate ISC in metal-free organic molecules, such as introducing carbonyl groups, halogen atoms, and heteroatoms. After enabling triplet exciton formation via ISC, upconversion mechanisms such as triplet-triplet annihilation (TTA) or thermally activated delayed fluorescence (TADF), which are generally faster than the spin-forbidden phosphorescence, should also be avoided. This can be done by clever molecular design. Even more critical for the appearance of phosphorescence is the suppression of fast non-radiative relaxation from the excited triplet state to the ground state, caused by collisions and/or triplet quenching. This can be realized by molecular packing, i.e. doping the emitter in a host material, crystallization, or the introduction of organic frameworks. A more interesting question is, however, whether it is possible to develop a set of rules to design organic molecules showing efficient RTP in solution. This is challenging due to the increasing rotational degrees of freedom in solution as compared to a solid-state environment. This presentation will focus on the development of such design rules by altering the structural features of a specific donor-π-acceptor structure based on typical TADF donors, different π-bridges, and benzothiazole acceptor units.



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FM-O9
Self-assembly behavior of molecules under confinement conditions

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Keywords: molecular self-assembly; confinement conditions; HOPG

In this presentation I will mainly focus on the self-assembly behavior of molecules under lateral confinement conditions on chemically modified highly oriented pyrolytic graphite (HOPG). Molecular self-assembly at solid surfaces is a rather complicated process involving different types of dynamics including adsorption and desorption.1 Fundamental understanding is crucial to design the molecular structure and regulate the formation of self-assembled molecular networks (SAMNs).2,3 Several groups have investigated the nucleation-growth process of SAMNs at step edges or under confinement conditions.4,5

Here, I will introduce two types of molecule-based confinement conditions, that require the chemical modification of the HOPG substrate. The first type ("random confinement space") is created by the spatially-random covalent attachment of aryl groups on HOPG. The second type ("nanocorrals or nanocontainers") is the result of a nanolithography process, where pristine HOPG areas are formed by the local removal of the covalently attached aryl groups using the tip of a scanning tunneling microscope. Several chemical systems are investigated.

Upon dropcasting a quinonoid zwitterion derivative (QZ-C16) on top of the "random confinement space", well-ordered domains could still be observed at and even below the threshold concentration, i.e. the concentration below which no self-assembly is observed on pristine graphite . The number and size of well-ordered QZ-C16 SAMNs at the liquid/solid interface is strongly affected by the random confinement space. The distinct self-assembly behavior on the modified surfaces provides an additional mechanistic understanding of molecular assembly at early stages. When the self-assembly of long alkanes is investigated in the nanocontainers, certain orientations of molecular domains are preferred, i.e. along the slow scanning axis to form the nanocorrals. As the alkyl chain length decreases though, this alignment effect becomes weaker.

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FM-O10
3D printing, where hydrogels and tissue engineering meet

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Keywords: Hydrogel; 3D printing; tissue engineering

Tissue engineering (TE) aims to replace and repair damaged tissues. Incorporating the three main TE triad elements (cells, biological factors and scaffolds) needs a good scaffolding technique. Additive manufacturing (AM) techniques are the most common ones.

As any polymer processing technique, AM requires materials that are compatible with the processing technique of choice1. Hydrogels have been used as one of the most common materials constituting TE scaffolds over the past two decades due to their ability to maintain a distinct 3D structure, to be printed in different ways, to provide mechanical support for the cells in the engineered tissues, and to simulate the native extracellular matrix.

Starting from a patented polymer family (structure cannot be disclosed), 3D scaffolds were developed using different printing techniques.

The first technology was extrusion-based 3D printing. The parameters that were varied include: the printing temperature (from 50-60°C), the printing speed (50-400 mm/min), the printing pattern (0°/90°, 0°/45°, …) and the photoinitiator (PI) concentration (1-4 mol%).

The second technology was digital light processing (DLP). The required liquid polymer phase was prepared using different hydrogel building block concentrations (ranging from 30–90 % w/v), varying PI concentrations (from 5-20 mol%) and a photoblocker concentration of 1 mol%. The printing parameters varied include: the UV-exposure time (from 3-10 s) and the intensity of the UV-lamps (from 10-30 mW/cm2).

The third technology investigated was indirect rapid prototyping. To obtain a hydrogel scaffold, a sacrificial PLA mould (pore size 400 µm, strut size 250 µm) was printed using a FDM printer (Ultimaker 3) at a printing temperature and speed of 200°C and 20 mm/s respectively. Subsequently the scaffolds were filled with hydrogel precursors. Finally, the PLA mould was dissolved in chloroform.

Before being mechanically tested, using destructive and non-destructive testing (NDT), the efficiency of the UV-cross-linking process of the scaffolds was verified through sol-gel testing. Minimal gel-values of 80-90% are targeted as go/no go criterion for further testing.

Using our newly developed polymer family, reproducible scaffolds were obtained using different technologies. All scaffolds reveal gel fractions exceeding 90%.

In a first part of the mechanical testing, the 3D printed scaffolds (pore size 250 µm, strut size 380-480 µm) were subjected to mono-axial compression using Dynamic Modulus Analysis – DMA as NDT and to DT. The studies showed that the material revealed mechanical properties relevant for various TE applications (i.e. in the range of 0.2-30 MPa depending on the printing composition, the scaffold design and the hydrogel building block concentration).

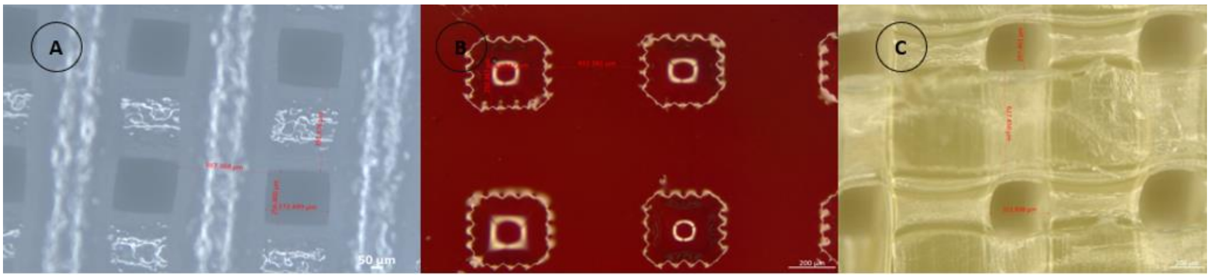
As the applied extrusion-based technology permitted to vary and investigate different pattern orientations, the results from the (N)DT were used to optimize the 3D printing parameters. The DMA results revealed the complex modulus of the 0°/45°/90°/135° printing pattern to be superior to the other two patterns most likely due to its more isotropic structure (i.e. 8.22 ± 0.2 MPa compared to respectively 5.99 ± 0.3 MPa for 0°/45° and 5.66 ± 0.2 MPa for 0°/90°).

The results obtained from destructive compression static tests were aligned with the DMA results.

DLP printed scaffolds (pore size 250 µm and strut size 400-450 µm) were subjected to DT technique and showed comparable results with scaffolds obtained through the extrusion-based technology.

For the scaffolds obtained by indirect printing, the first goal was to create a negative mould with minimal material waste. For these scaffolds, (N)DT analysis will be performed in the upcoming months and presented during the meeting. Microscopic analysis of the obtained hydrogel scaffolds (pore size 200 µm, strut size 600 µm) already revealed a comparable structure to the scaffolds obtained through extrusion-based printing and DLP.

Our data indicate that applying various printing techniques enable us to develop scaffolds, revealing comparable mechanical properties. This indicates the great versatility of the material under study.



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FM-O11

Isomeric modulation of thermally activated delayed fluorescence properties in deep-red/near-infrared emitters

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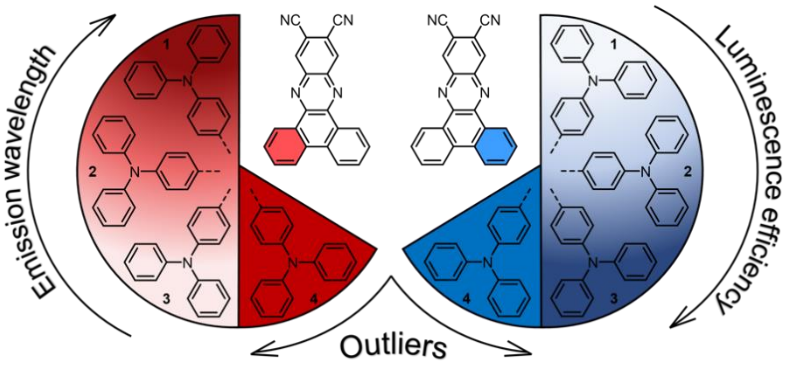
Keywords: near-infrared fluorescence;thermally activated delayed fluorescence;organic light-emitting diodes

The requirements of applications with emission in the visible range (e.g. lighting, displays) are well tuned to the opto-electronic properties of typical organic semiconductors.(1) Developing materials suited for efficient near-infrared (NIR) emission – desirable to enable new classes of applications spanning from through-space communication and biomedical therapies to sensors and more general security applications – is considerably less straightforward, however. The challenge to achieve efficient NIR emission from all-organic π-conjugated systems can be tackled by the computationally guided design and synthesis of donor-acceptor type chromophores affording high photo- and electroluminescence quantum yields through either classical fluorescence or by leveraging triplets in materials optimized for thermally activated delayed fluorescence (TADF). While the mechanism of TADF allows an increase of the theoretical internal quantum efficiency to 100 % (as opposed to the 25 % in classical fluorescence), it proves to be much harder to harmonize with the general design of NIR emitters.(2-4) One under-explored strategy to potentially improve the overall (TADF) emission properties entails the design and comparison of regioisomers, i.e. systems with altered donor-acceptor configurations, created by changing the location of the attachment point on the acceptor moiety. In the presented work, utilizing dibenzo[a,c]phenazine-dicarbonitrile (DBPz-CN) as a well-performing and often-used acceptor template in the design of red/NIR-emitters, four isomers were designed, computationally simulated, synthesized and fully characterized.(5-9) Functionalized triphenylamine (TPA) was used as a typical, commercially available donor moiety. TPA is a strong donor that generally increases the oscillator strength and solubility of the chromophore, while still often allowing the singlet-triplet splitting energy to be adequately reduced. Density functional theory (DFT) was used for computational calculations to compare relative differences in dihedral angle, oscillator strength and relevant energy levels, and to correlate these to changes in the structure and electron density. Lastly, time-resolved emission spectroscopy (TRES) was utilized to probe the time-dependent emission of the different isomer systems in (doped) films in order to derive the important TADF properties. Via 'isomeric modulation', we are thus able to analyse the effect of geometry, orientation and electronic interaction on the underlying emission characteristics of such donor-acceptor systems.



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FM-O12
Turning 3D-COFs into luminescent ratiometric thermometers

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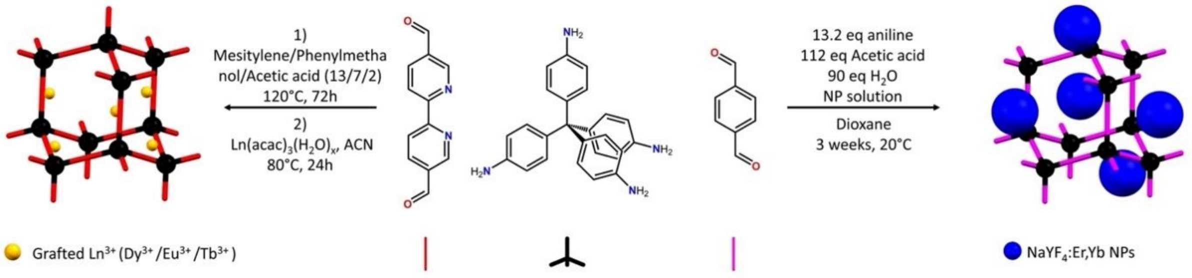
Keywords: Covalent Organic Frameworks; Lanthanide; Temperature sensors

Covalent Organic Frameworks (COFs)[1] can be obtained as highly stable and crystalline permanently porous materials.[2] Until now, most of the COF research has been focused on two dimensional (2D) COFs, as those are easier to obtain in crystalline form. However, due to the shift from weak interlayer interactions to fully covalent bonded materials, three dimensional (3D) COFs are highly interesting.[2] Moreover, the structural diversity of 3D COFs is far higher, even enlarging the designability of these materials.

2D COFs have already been studied to accommodate trivalent lanthanide ions (Ln3+), as well as Ln3+ complexes and have been used as temperature sensors.[3, 4] Most often, this is achieved by grafting of Ln(acac)3 complexes to the COF/MOF material.[3] Additionally, lanthanide-doped upconversion nanoparticles (UCNPs) have recently been impregnated in MOFs to measure temperature in-situ during a MOF-catalyzed reaction.[4]

However, the combination of 3D COFs and lanthanides have scarcely been explored. Up to date, there is only one report of a 3D COF grafted with a Eu3+ complex for use as chemosensor.[5] Additionally, to the best of our knowledge, no works have been reported on the use of 3D COFs as thermometers or the combination of COFs with lanthanide nanoparticles (NPs).

In this work, we developed hybrid Ln@3DCOF materials, suitable for temperature sensing applications. To achieve this, two distinct routes were followed. A bipyridine 3D COF (Bipy COF) was grafted with different ratios of Ln3+ complexes and a non-functionalized COF (COF-300) was grown as a nanocomposite with NaYF4:Er3+,Yb3+ NPs grown in situ in the COF matrix. Both types of materials showed good luminescent properties and potential as ratiometric thermometers.



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FM-O13

Controlled self-assembly of molecular motors and switches at the solution/solid interface: Towards light induced coherent rotary motion

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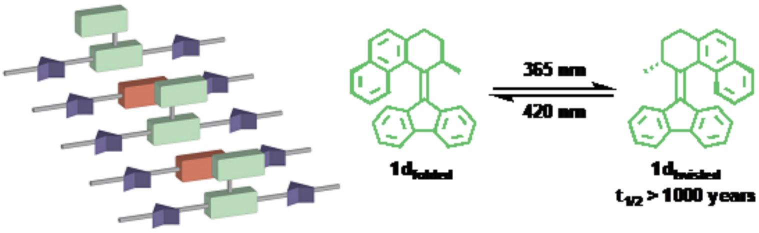
Keywords: Supramolecular self-assembly;2D molecular networks; Molecular motors; STM

Molecular machines are ubiquitous in biology. They often exhibit a unique ability to respond and adapt to external stimuli. Such stimulus responsive motion of the biological motors and switches is central to their function. Biological molecular motors based on proteins such as myosins and kinesin consume the energy produced by hydrolysis of ATP and use it to produce motion at the nanometer scale effectively carrying out mechanical work. Taking inspiration from Mother Nature, chemists have designed and synthesized synthetic molecular motors, which can undergo continuous directional motion in response to a stimulus. Different molecular designs have been proposed, synthesized and demonstrated to undergo controlled motion under the influence of external triggers such as chemical energy, electric field, heat and light irradiation. The use of light as a trigger is particularly attractive because it can be delivered with high spatial and temporal precision, and no chemical waste is produced in the system. Furthermore, assembling such molecular motors and switches on solid surface imparts a high degree of coherence in their orientation and packing leading to well-defined self-assembled molecular networks where the stimulus induced motion of such motors and switches can be studied using state-of-the-art nanoscale imaging techniques such as scanning tunnelling microscopy (STM), which provide resolution at the sub-nanometer scale. In this contribution I will discuss different strategies to immobilize molecular motors and switches on a solid surface via controlled self-assembly. I will also introduce molecular design aspects taken into consideration for the synthesis of these systems and discuss our ongoing attempts to characterize the light-induced single molecule rotary motion in-situ at the solution-solid interface.



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FM-O14
Light-Stabilized Dynamic Materials: Tuning the Dynamic Character

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Keywords: Photochemistry; Dynamic Materials; Diels-Alder reactions; Gels

Light-responsive dynamic chemistry is of great interest for applications in polymer science.1–3 In this context, light-stabilized dynamic materials have been developed recently.4 These polymers form and remain a cross-linked gel under green light irradiation, whereas in the dark a spontaneous dissociation of the cross-links occurs and hence the materials liquify. The exploited mechanism is based on a green (λ = 515 – 525 nm) light-driven reversible Diels-Alder cycloaddition between a triazolinedione and naphthalene moiety and a thermal cyclo-reversion, which is sufficiently fast at room temperature. This particular behaviour allows the material properties (e.g., stiffness) to be switched solely by using a green light source and thus the need for more intrusive triggers (e.g., UV-light, heat) is by-passed to obtain covalent bond formation and dissociation. The present light-stabilized dynamic materials chemistry has been successfully incorporated into a few polymer applications mainly on the basis of poly(methyl methacrylate).5,6 The dynamics of the covalent bond is currently limited by the substitution of the naphthalene moiety used to modify the polymer. To fully exploit the light-stabilized dynamic chemistry for polymer applications where a temporarily light-stabilized cross-linking adds value, it is necessary to tune the dissociation dynamics and expand the concept to various polymer backbones. We investigated the influence of molecular design on the dynamics of the light-stabilized chemistry and how it can be exploited to provide a set of molecules offering materials with slower and faster dissociation which is currently being submitted. Towards this end, we isolated a regio-selective naphthalene moiety, offering high temporal precision, and implemented it in polymer backbones such as poly(N-isopropyl acrylamide), thus offering light-stabilized dynamic materials a path into new challenging and unprecedented polymer applications. In addition, we investigated the influence of molecular and polymeric parameters to obtain high precision over light-stabilized dynamic gel properties.

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FM-O15

Bio-inspired mineralization of CO2 to functional CaCO3: effect of different CO2 absorption promotor and crystal growth modifier

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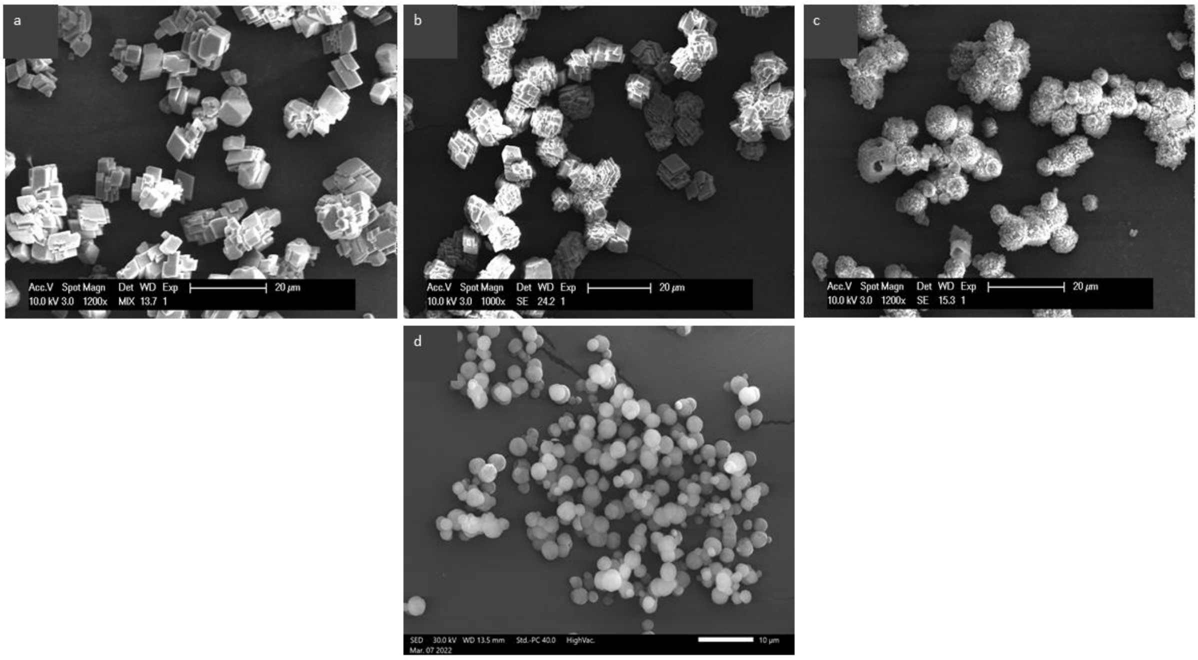
Keywords: Functional carbonates; CO2 utilization; biomineralization; crystallization; green chemistry

Atmospheric CO2 concentration has reached up to 420 parts per million in 2021 (April); this is ca. 50% greater than that in the preindustrial era [1]. The increased concentration of atmospheric CO2, along with other greenhouse gases, has caused approximately 1 °C global warming, and it is likely to reach 1.5 °C between 2030 and 2052 if it continues to increase at the current rate [2]. CO2 mineralization which involves the reaction of CO2 with alkaline earth metal cations, mainly Mg2+ and Ca2+, to form carbonates minerals, is a promising technique that could be crucial for combating global warming via CO2 utilization and long term storage [3].

In this study, we produce several synthetic structures of CaCO3 through simultaneous CO2 capture and mineralization using surfactant and water-soluble polymer as crystal growth modifiers. The controlled crystallization of carbonate is inspired by the natural formation of nacre, which consists of 95% CaCO3 and 5% biopolymers, and is produced naturally via biomineralization. We investigated the effect of different CO2 absorption promotors (organic and inorganic) and crystal growth modifiers on CaCO3 shape, size, and polymorphs with the focus on developing an environmentally friendly and highly efficient method for functional CaCO3 synthesis via CO2 utilization. At the optimized conditions, we achieved 90% Ca2+ ions conversion to CaCO3 within 5 minutes of CO2 bubbling at 0.5 liters per minute. The proposed method is green, efficient, and could be used for industrial Ca/CO2 rich waste valorization. The produced functional CaCO3 (figure attached) could have potential applications as adsorbents, drug delivery agents, biomedical materials, and functional fillers in polymeric composites.



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FM-O16
Fine-tuning the endcap chemistry of acrylated poly(ethylene glycol)-based hydrogels for the treatment of burn wounds

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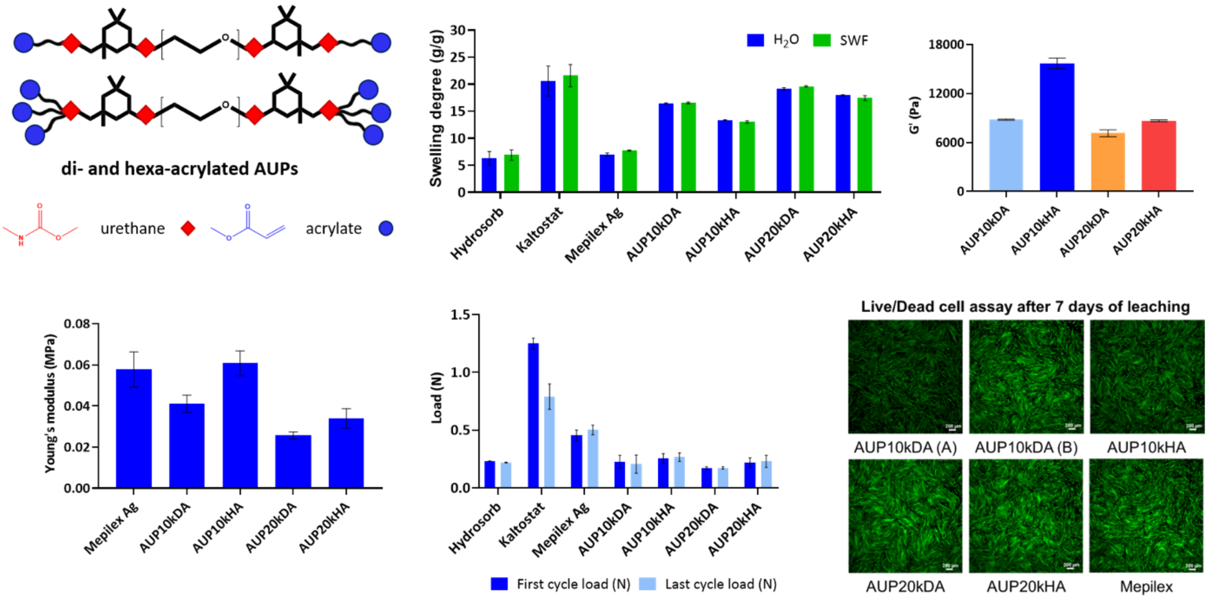
Keywords: hydrogels; burn wounds; exudate; biocompatibility

Burn wounds remain a global medical concern [1]. To date, a wide range of wound dressings is commercially available with hydrogel-based dressings being the most relevant for exuding wounds as they can both absorb and donate moisture, thus ensuring a desirable moisture control of the wound healing environment. Hydrogels are constituted of natural or synthetic polymers, with the latter being more easily tunable towards desirable properties and being less subject to batch-to-batch variability [2]. Unfortunately, commercial hydrogel wound dressings often suffer from inferior mechanical strength and/or require the use of a secondary dressing. The current research focuses on the development of hydrogel-based wound dressings combining mechanical strength with high exudate absorption capacities using acrylate-endcapped urethane-based precursors (AUPs) [3]. AUPs with varying poly(ethylene glycol) backbone molar masses (10 and 20 kg/mol) and endcap chemistry were successfully synthesized as indicated by 1H NMR spectroscopy, yielding di- and hexa-acrylated polymers (DA and HA, respectively). The materials were subsequently processed into UV-cured hydrogel sheets and were benchmarked against several commercial wound dressings (i.e. Hydrosorb, Kaltostat and Mepilex Ag). High gel fractions (> 90 %) were observed for all materials together with nearly complete acrylate conversion (> 98 %) resulting from high resolution magic angle spinning (HR-MAS) NMR spectroscopy, indicating highly efficient crosslinking independent of the backbone molar mass or endcap agent. The AUP materials exhibited significantly ($p < 0.05$) higher swelling degrees compared to the commercial dressings in ultrapure water, phosphate buffered saline (PBS) and simulated wound fluid (SWF) (ranging between 12.7 and 19.6 g/g). Higher swelling degrees in water, PBS and SWF could be realized by increasing the backbone molar mass or by decreasing the amount of acrylate functionalities from six to two. The tunability of the wound dressing properties was also evidenced by tensile tests (Young's moduli of 26 – 61 kPa, swollen state), rheology (storage moduli of 7100 – 15700 Pa, swollen state) and fatigue testing. The Young's modulus of AUP10kHA was comparable to Mepilex Ag, while the swelling degree of Mepilex Ag was significantly lower. The elasticity of the synthesized materials led to an increased resistance against fatigue, as no differences in first and last load were observed between cycles. The di- and hexa-acrylated AUPs showed excellent in vitro biocompatibility in the presence of human foreskin fibroblasts (HFF), as evidenced by indirect 3-(4,5-dimethylthiazol-2-yl)-5-(3-carboxymethoxyphenyl)-2-(4-sulfophenyl)-2H-tetrazolium (MTS) assays and live/dead cell assays. It can be concluded that the AUPs are very promising to serve wound healing applications and are able to compete with several commercial wound dressings.



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FM-O17

Rhodium anchored onto a covalent triazine framework as heterogeneous catalyst for transfer hydrogenation of N-heterocycles in water

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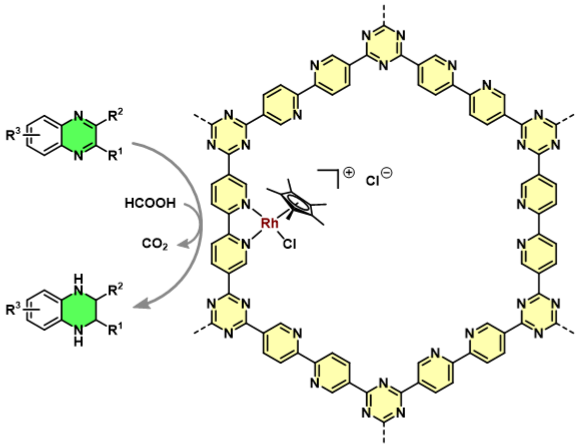
Keywords: Covalent triazine frameworks; transfer hydrogenation; heterogeneous catalysis; tetrahydroquinoxalines;

Covalent triazines frameworks (CTFs) are organic, nanoporous polymers that recently emerged as highly effective materials in catalytic applications. Their extensive tailorability, high surface areas and chemical robustness make them the ideal candidates as metal support in the development of recyclable catalysts. In this work, a bipyridine-based CTF was synthesized and decorated with a Rh(III) complex. The heterogeneous Rh@bpyCTF catalyst was then applied in the transfer hydrogenation reaction, a convenient and mild alternative to the direct hydrogenation. A broad set of quinoxalines and various other N-heterocycles were efficiently converted by the heterogeneous catalyst, using formic acid as the hydrogen donor and water as the solvent. The reduction in aqueous medium was shown to be highly pH-dependent, with the highest conversion rate at slightly acidic pH. The catalytic performance of the Rh@bpyCTF was both evaluated in a batch and in a continuous-flow setup.



FM-O18

Unravelling the performance of Pt-Ni ORR electrocatalysts by combining electrochemical with advanced TEM studies

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Keywords: Electrochemistry; advanced TEM; Ligands; Electrocatalysis; Pt-Ni

Over the last years there is an increasing demand for the improvement of the activity, selectivity and stability of catalytic nanoparticles (NPs) used in industrially important chemical reactions, including the oxygen reduction reaction (ORR) for fuel cell applications and the electrochemical CO2 reduction reaction (eCO2RR) in the battle against global warming. While the ORR suffers from sluggish kinetics, the eCO2RR is experiencing problems regarding product selectivity and the competing hydrogen evolution reaction (HER). In order to mitigate these shortcomings, extensive research has been conducted by the electrochemical community towards the improvement of the activity, stability and selectivity of the used electrocatalysts.[1] A selected way to achieve these goals is the use of heterometallic NPs, combining the individual properties of different metals in one particle. Indeed, it has been shown that alloyed nanoparticles exhibit better catalytic performance for the ORR compared to standard Pt catalysts.[2,3] However, the chemical composition is not the only parameter influencing the performance of a catalyst material. Apart from the actual nature of the catalyst itself, the presence of surface ligands on catalyst surfaces can have a direct effect on the catalytic performance. As such, ligand removal can prove to be an essential step during the synthesis procedure of electrocatalytic nanoparticles. In this work, Pt-Ni NPs are synthesized via thermal deconvolution and subsequent reduction of the metal precursors using methods adapted from literature.[2,4] Ligand removal was performed via different techniques (acid, thermal, centrifugation) in order to investigate the effectiveness of the diverse procedures. The composition of the resulting nanoparticles was probed using ICP-MS. Further characterization of the structure and composition in 2- and 3-dimensions was performed using high resolution high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) imaging and energy dispersive X-ray spectroscopy (EDS). In addition, Exit Wave Reconstruction (EWR), a technique where a focal series of TEM images is exploited to retrieve phase information, was utilized, which allowed the visualization of nanoparticles and their surrounding ligands simultaneously at the atomic scale. [5,6] These investigations were combined with electrochemical characterization using cyclic voltammetry (CV) and linear sweep voltammetry (LSV) on activated Pt-Ni particles. This way, we could correlate the presence of surface ligands to the catalytic activity. Furthermore, through long-term studies, we were able to probe the effect of surface ligands on nanoparticle stability. The combined knowledge from this research will in turn lead to the design and synthesis of improved catalytic materials.

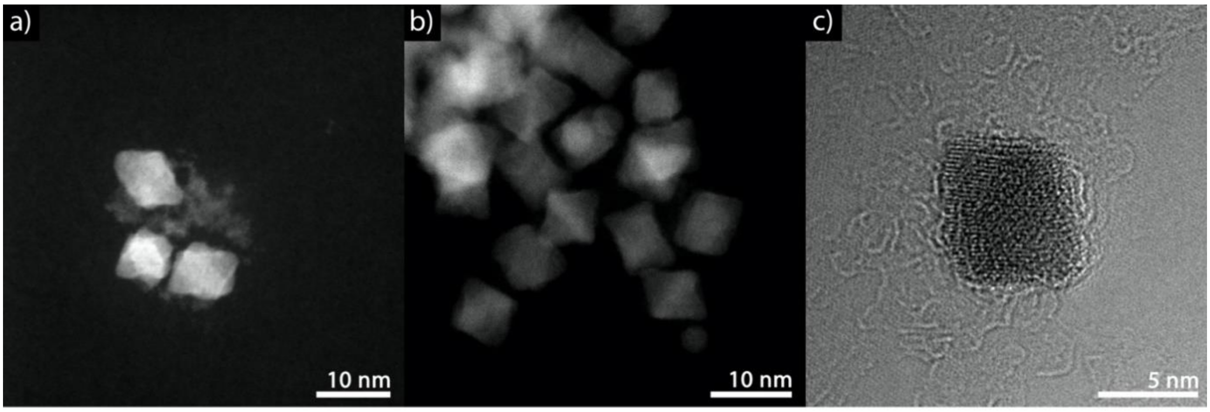

Figure 1: a) HAADF-STEM image of octahedral Pt-Ni NPs before ligand removal, b) HAADF-STEM image of octahedral Pt-Ni NPs after ligand removal, c) high resolution TEM image of an octahedral Pt-Ni NP surrounded by ligands.

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Chemistry meets Biology (CB)

CB-O1

Chemical Evolution Driven by Self-assembly

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Keywords: Supramolecular; Macromolecular; Evolution; Systems Chemistry; Replication; Fidelity; Origin of Life

Self-replicating systems are likely to have played a central role in the origin of life. One such class of systems relies heavily on self-assembly as part of their dynamics and replication [1,2]. While there have been reports of such chemical systems giving rise to self-replication, their potential for Darwinian evolution remains open. We recently started focusing on replication fidelity (the degree of replication exactness) in one such chemical system, where self-replication is driven by self-assembly [3], as the first step towards deciphering its capacity for Darwinian evolution. Interestingly, this fidelity was found to be comparable to that to that of RNA-catalyzed RNA elongation [4]. The latter suggests that the information encoded in the chemical system can be faithfully transmitted and therefore has the potential to evolve by selection. The latter raises the question: if life started in the chemical domain and if indeed synthetic chemical systems can exhibit relatively similar fidelity to that of simple biological systems, then can a new form of life be built with a chemistry that is different from current biochemistry?

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CB-O2
Development of a high-bioanalytical platform for metabolomics

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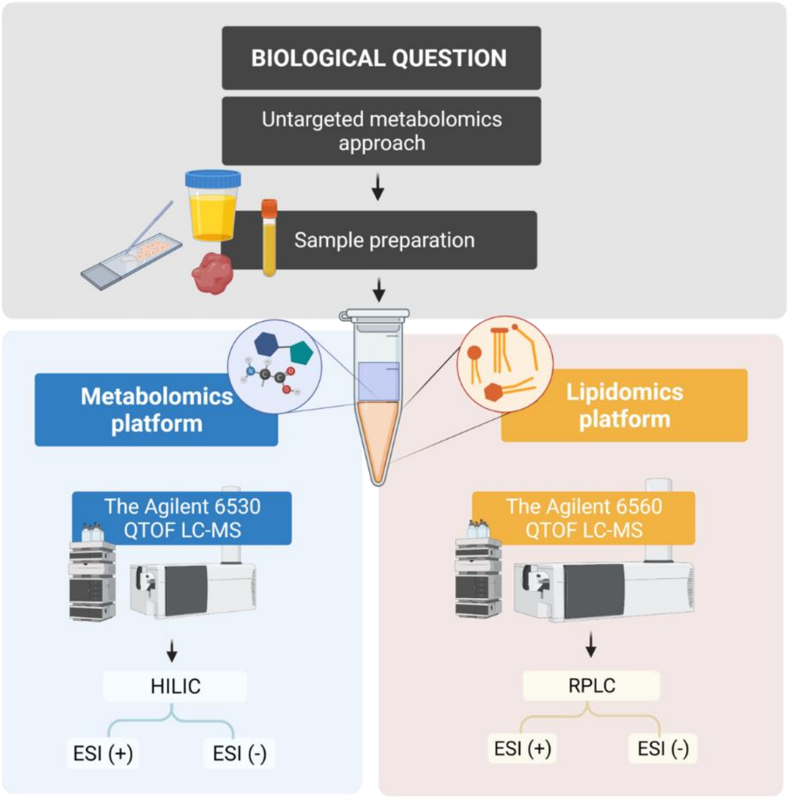
Keywords: analytical chemistry; mass spectrometry; liquid chromatography; ion mobility

Metabolomics is the study of small endogenous molecules (<1700 Da) in biological samples (cell extracts, tissues, plasma, urine) or organisms to find key metabolites in various biological processes. In practice, data acquired by advanced analytical techniques (i.e., mass spectrometry) are processed and analyzed by statistical methods to reveal changes in metabolic patterns that can be associate with the subject's metabolic condition affected by genotype, physiology, environment, lifestyle, and/or diet. Liquid chromatography-mass spectrometry (LC-MS) is currently the most used analytical technique in untargeted metabolomics applications, as it allows the detection of hundreds of polar metabolites and lipids [1]. However, the same method cannot cover the metabolome and lipidome (e.g., the LogP for citric acid -1.64, while the predicted (XLogP) for LPC(18:0) and TG(48:0) are 6.6 and 22.1, respectively). Therefore, two workflows were optimized to increase this coverage: 1. Polar Metabolites: Optimization of different LC stationary phases, mobile phase composition, instrumental parameters. The optimized methods were applied to analyze different biological matrices (urine, plasma, and liver cell extracts) [2]. 2. Lipidomics: Lipids are highly diverse compounds, for instance, lipids with the same fatty acyl chain length and level of saturation can have different structural isomers that might still co-elute and can often not be distinguished LCMS. Therefore, an additional technique, ion mobility (IM), was used in addition to LC-MS analysis [3]. The optimized LC-IM-MS method included the calculation of compound-dependent collision cross section (CCS) values with <3% error compared with predicted values and successfully applied for high confidence lipid annotation in biological samples.



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CB-O3

Towards the one-pot upgrading of glucose to HMF through hybrid chemo-enzymatic catalysis

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Keywords: chemo-enzymatic; catalysis; biomass

In a world where the demand for specialty chemicals is ever increasing, the need for a renewable alternative to their typical fossil source is inevitable. One of green chemistry's most promising tools is given to us by nature: enzymes. Their ability to catalyze chemical reactions with very high selectivity and specificity makes them extremely powerful when it comes to create high value-added chemicals.[1] Unfortunately, the intrinsic nature of enzymes also makes them hard to stabilize, recover and ultimately reuse. In this regard, efforts are made to immobilize enzymes on a solid carrier and turn them into a heterogeneous (bio)catalyst.

Thus, new class of catalysts is emerging: Hybrid Chemo-Enzymatic Heterogeneous Catalysts (HCEHC).[2] HCEHC are multifunctional catalysts combining the action of the enzyme and of the solid; in this class of catalysts, the support is more than an inert solid; it is catalytically active, working in concert with the enzyme. This allows for one-pot cascade reactions (even with unstable chemical intermediates) while benefiting from both the advantages of the enzymes and the robustness of heterogeneous catalysts.[3]

Here, we will develop new hybrid chemoenzymatic heterogeneous catalysts dedicated to the direct production 5-HMF from glucose. In continuity with the concept previously developed in our group,[4] this catalyst would be made of aggregated Glucose Isomerase encapsulated in hollow spheres of H-ZSM-5, a material displaying high Bronsted acidity and reportedly catalyzing the dehydration of fructose in aqueous or biphasic media. [5]

In this cascade of reactions, the first step is thermodynamically limited to a maximum conversion of <60%. The one-pot cascade reaction would then have the added benefit of negating this equilibrium via the dehydration of fructose produced in the medium.

Before performing the cascade reaction, both steps must be optimized. So far, optimal conditions have been found for the isomerization of glucose to fructose by Glucose Isomerase from S. rubiginosus. The enzyme has also shown to be stable and active at up to 80°C in water. More work is being carried out to synthesize a dehydration catalyst able to operate under these mild conditions. To better discriminate the capabilities of different materials, catalytic tests are currently performed in a water/organic biphasic medium at 120°C, which are more favorable conditions for the dehydration step.

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CB-O4

Ultralarge Virtual Screening Identifies SARS-CoV-2 Main Protease Inhibitors with Broad-Spectrum Activity against Coronaviruses

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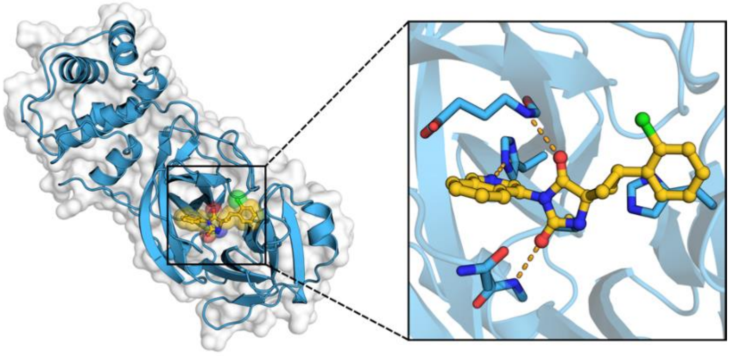
Keywords: Viruses; Molecular docking; COVID-19; Protein crystallography; inhibitors

The severe acute respiratory syndrome coronavirus 2 (SARS-CoV-2) has caused the greatest health crisis of this generation and already led to >5 million deaths worldwide. Analogous to common cold viruses, SARS-CoV-2 is expected to continue to circulate and pose a significant threat to our society. Despite promising vaccination and booster programs against COVID-19, antiviral drugs will likely be crucial to control the future outbreaks of coronaviruses. Among the proteins encoded by the SARS-CoV-2 genome, the main protease (Mpro) has emerged as a promising target. Inhibition of Mpro blocks the processing of polyproteins produced by translation of the viral RNA, which is an essential step in SARS-CoV-2 replication. The determination of high-resolution crystal structures of SARS-CoV-2 proteins has enabled virtual screening campaigns to identify hits that can be developed into antiviral drugs. Structure-based docking algorithms can sample and score binding poses in seconds, making it possible to evaluate large libraries and this approach is not restricted to compounds that are physically available. The size of libraries with commercially available compounds is growing rapidly and >20 billion make-on-demand molecules are currently available from chemical suppliers. These libraries provide opportunities to identify potential therapeutic agents that can readily be synthesized and tested for activity, but require development of effective strategies for navigation in this enormous chemical space. We present two different strategies to search for Mpro inhibitors in ultra-large chemical libraries using structure-based docking. Synergy between molecular modeling, protein crystallography, and organic synthesis led to a novel broad-spectrum inhibitor of coronaviruses.



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CB-O5
Biodegradation of Maleic Anhydride-Grafted Polycaprolactone (PCL-g-MA) with Lipase

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Keywords: Biodegradation Materials; Lipase; Grafted Polycaprolactone; Maleic Anhydride

Plastics are one of the most widely used materials because of their low-cost and simple production. However, plastic production and plastic wastes cause a huge impact on the environment and biology. One of the solutions is to develop degradable polyesters that can be easily degraded in the natural environment. Polycaprolactone (PCL) is one of the aliphatic degradable synthetic polyesters usually used owing to high resistance to water, oil, and solvent and microbial attack. Biodegradation of PCL commonly progresses by microorganisms, or more accurately, enzymes they produce. Because PCL normally has a semi-crystalline structure in the environmental condition, it takes 2-3 years to completely degrade in natural conditions. Lipase is a common enzyme that hydrolyzes ester groups. There are many factors for studying the degradation reaction such as crystalline morphology, molecular weight, and so on [1]. The idea of grafting PCL is one of the methods for improving the hydrophilic property and increasing the amorphous region ratio. Maleic Anhydride (MA) is commonly used to synthesize for modifying PCL. When MA is added to the PCL structure, the molecular weight of PCL decreased, indicating the MA addition concurrently scissors PCL chains during the reaction [2]. In this study, we studied the degradation factors in comparison between pure PCL and modified PCL-g-MA. The enzymatic degradation was studied and modified based on previous studies [3]. A total of 10 mg of PCL and PCL-g-MA films were each placed into a 15ml-centrifuge tube containing a 0.025 M phosphate buffer solution at pH7. Each 10 mg sodium azide was added to the tubes to inhibit the enzymatic reaction. A total of 10 mg Lipase PS was added to the enzyme group. The experiments were designed to study the factor with and without Lipase PS (Enzyme and Control group). All of the experiments were carried out and incubated at 37 °C in a water bath. The medium solutions were replaced every 24 h for simulating the environmental condition. The films were picked up periodically, washed with distilled water, and dried until constant weight. The films before and after degradation were characterized by scanning electron microscopy for observation and differential scanning calorimetry for measuring and calculating the crystallinity.

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CB-O6

Reactivity of peroxidases and chlorite dismutases with chlorite and hypochlorite: a spectroscopic investigation of short-lived intermediates trapped by fast freeze-quenching

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Keywords: chlorite dismutases; peroxidases; EPR spectroscopy; fast freeze-quench

Chlorite (ClO2-) and hypochlorite (ClO-) are strong oxidants commonly employed as bleaching agents or disinfectants, however, concerns have been raised around their presence in the environment as pollutants. Chlorite dismutases (Clds) are heme b-containing oxidoreductases which possess the unique ability to decompose ClO2- into harmless Cl- and O2. Investigations into the underlying reaction mechanism thus open ways for potential biotechnological and bioremediation applications [1]. Horseradish peroxidase (HRP), a model enzyme for heme peroxidases, is also known to react with both chlorite and hypochlorite [2]. During the reaction of Clds and HRP with ClO2- and ClO- short-lived intermediates involving transient radicals are formed, making these systems suitable to be studied by electron paramagnetic resonance (EPR) spectroscopy. Given the short time scales of these reactions, a fast freeze-quenching device is needed to trap the transient radical species and collect the frozen sample directly into the EPR tube. In this work we present a comparative EPR investigation of the intermediate states formed during the reaction of HRP, Cld and dye-decolorizing (Dyp) peroxidase with either chlorite or hypochlorite, to identify common and distinct mechanistic features of these closely related enzymatic systems. The results are discussed in the context of the similarities in the active sites of the selected enzymes and the known key residues for their catalytic activities. In addition to that, we present our recent findings [3] on the different binding modes of the substrate-analogue nitrite by chlorite dismutases and we discuss them with regard to the role of the conserved distal arginine which is proposed to be involved in the catalytic mechanism of these enzymes. This work received funding from the European Union’s Horizon 2020 research and innovation program (Marie Skłodowska-Curie Grant Agreement n° 813209) and it was supported by the Austrian Science Funds (FWF-project P30979) and the doctoral program BioToP – Biomolecular Technology of proteins (FWF W1224).

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CB-O7
An unbiased approach to exploring biomolecular reactions with hybrid QM/MM

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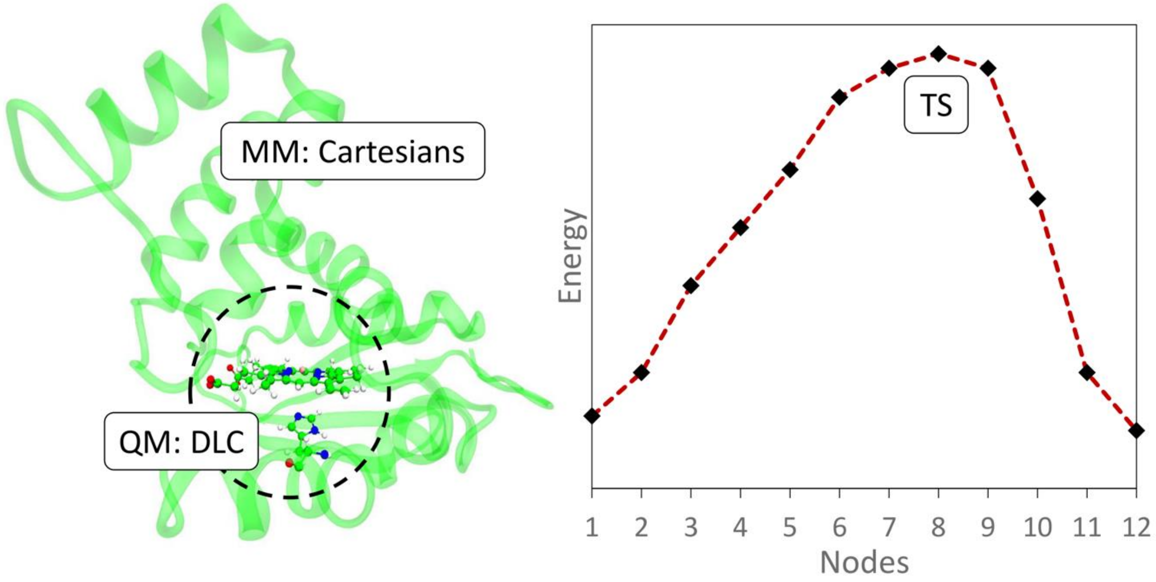
Keywords: Computational Chemistry; QM/MM; Biochemistry; Enzymes; Transition State

The location, conformation, and relative energy of transition states is crucial for the understanding of enzymatic reactions. Due to the short-lived nature of these intermediates, they are typically challenging to characterise experimentally and as such, are often evaluated using computational methodology. We use combined ab initio quantum mechanical and classical molecular mechanical (QM/MM) methods, where the active site and protein environment are both considered.[1–3] However, due to the considerable number of degrees of freedom in these systems, locating transition states with QM/MM is seldom trivial. Double-ended methods such as the nudged elastic band method are often used, but these require a coupled pair of reactant and product state structures to be available, which is not always the case.[4] Alternatively, single-ended reaction coordinate interpolation techniques such as adiabatic mapping can be used, however these tend to suffer extensively from wandering into neighbouring reaction pathways.[5] There is one branch of reaction path exploration with both double- and single-ended variants: the growing string method (GSM).[6–8] We propose the first, to the best of our knowledge, implementation of the single-ended GSM within the QM/MM framework specifically designed for locating biomolecular transition states. Only an initial structure and driving reaction coordinate is required, giving a largely unbiased method to explore the potential energy surface. Moreover, the wandering problems found in single-ended techniques are mitigated due to the two-stage (growth and optimisation) methodology behind the growing string method, where constraints are first defined by the initial input and then dynamically. This dynamic definition of reaction constraints means the system is not limited by the initial driving reaction coordinate, thereby decreasing the tendency to jump into neighbouring reaction pathways. To allow for reaction constrains which are a combination of many internal coordinates, we use delocalised internal coordinates for the QM region. To minimise computational expense, the MM region is described by the usual cartesian coordinates, giving a hybrid coordinate scheme. [9]



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CB-O8
NMR-based metabolomics reveals a metabolic shift after surgical resection of non-small cell lung cancer

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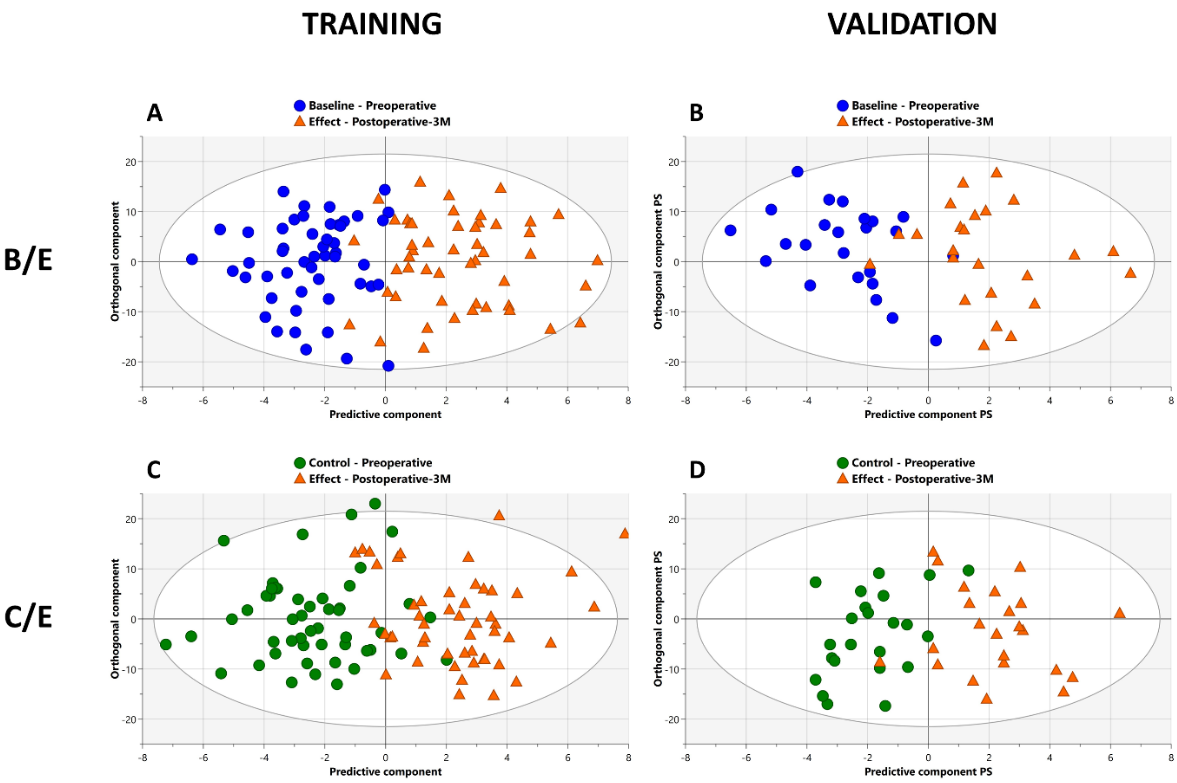
Keywords: NMR spectroscopy; NMR-based metabolomics; Non-small cell lung cancer; Early cancer detection; Multivariate discriminant analysis

Background: Lung cancer can be detected by measuring the patient's plasma metabolite profile using nuclear magnetic resonance (NMR) spectroscopy. This NMR-based plasma metabolite profile is patient-specific and represents a snapshot of the patient's metabolite concentrations. The onset of non-small cell lung cancer (NSCLC) causes a change in the patient's metabolite profile. However, the level of metabolic changes after complete surgical tumor removal is currently unknown. Patients and methods: Fasted pre- and postoperative plasma samples of 74 patients diagnosed with resectable stage I-IIIA NSCLC are analyzed using an innovative semi-targeted and quantitative 1H-NMR spectroscopy approach. This novel development includes the introduction of maleic acid as a reliable internal standard when used in combination with 4 mM trimethylsilyl-2,2,3,3-tetradeuteropropionic acid (TSP) as a protein-binding competitor. This methodology allows the absolute quantification of 62 plasma metabolites. Two preoperative and one postoperative plasma metabolite profile at three months after surgical resection are obtained for each patient (n = 222). Two types of supervised multivariate discriminant analyses are used to train classifiers presenting a strong differentiation between the pre- and postoperative plasma metabolite profiles. Validation of these trained classification models was obtained by using an independent dataset. Results: A trained multivariate discriminant classification model shows a strong differentiation between the pre-and postoperative NSCLC profiles with a specificity of 96% and a sensitivity of 92% (Fig. A). Validation of this model results in an excellent predictive accuracy of 90% (Fig. B). Validation of a second model, trained by means of the second preoperative control sample dataset (Fig. C), confirms the separation of the pre-and postoperative profiles with a predictive accuracy of 93% (Fig. D). Conclusion: For the first time, these results show that surgical removal of NSCLC generates a detectable and significant metabolic shift in blood plasma. The observed metabolic shift indicates that the NSCLC metabolite profile is determined by the tumor's presence rather than donor-specific features. Furthermore, the ability to detect the metabolic difference before and after surgical tumor resection strongly supports the prospect that NMR-generated metabolite profiles via blood samples can allow early detection of NSCLC recurrence.



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CB-O9

Hyphenation of temperature-responsive chromatography and ultrafast chiral chromatography as a generic comprehensive two-dimensional method for the analysis of chiral pharmaceuticals

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Keywords: /

Chirality is a prevalent property found in nature, caused by the presence of a (carbon) chiral center in a molecule. Many molecules with different chirality greatly vary in their chemical properties, therefore the ability for separation and detection of these molecules is of utmost importance in the biomedical and pharmaceutical industries. [1]

However, obtaining effective separation of chiral analytes in complex (biological or synthetic) samples requires high resolving power. Which can be theoretically achieved by Comprehensive two-dimensional liquid chromatography (LC x LC), as this technique would allow for a large increase in peak capacity per unit of time. However finding appropriate solvents for the second dimension might be difficult. The slow speed of chiral separations, on the other hand, has hampered the use of chiral stationary phases as the second dimension in 2D-LC. [2-4]

In this study, the enantioselective separation of a wide range of medicinal substances (log p: 0.9-4.1) is evaluated using a combination of temperature-responsive and reversed-phase chiral liquid chromatography. Temperature-responsive liquid chromatography (TRLC) in the first dimension enables analysis in purely aqueous conditions, allowing for complete (and more general) focusing of organic solutes prior to second-dimension separation. [2] By combining this with small particle (sub-2 micron) based chiral stationary phases as the second dimension in TRLCxChiral-RPLC, a chiral screening platform may be built, which in principle has a lot of potential for tackling chiral screening challenges. [4]

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CB-O10

Novel Microfluidics Approaches for Selection and Enhancement of Sperm Motility for Improved Fertilization

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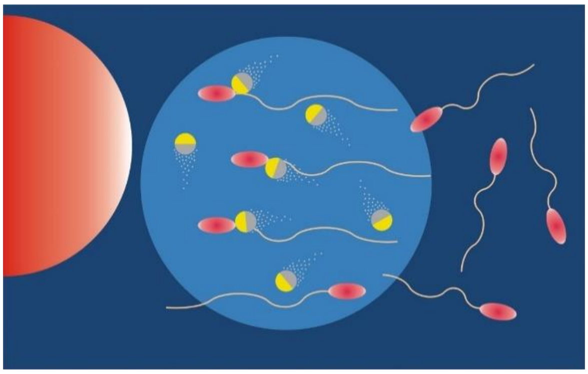
Keywords: Sperm selection; Motility enhancement; Motility transfer; Janus particles; Active matter

Motility of sperm refers to its ability to swim in a forward direction. Normal sperm motility plays a crucial role in men's reproductive health since the sperm have to be able to reach the egg in the uterus in order to fertilize it. Low sperm motility occurs as a consequence of various medical conditions and could lead to issues with fertilization. Assisted reproduction technologies include conventional sperm preparation techniques and advanced selection procedures that partially mimic female selection mechanisms. Generally, there are two approaches of selecting best sperms for fertilization. First approach is based on selecting sperms with the highest motility, their separation and delivery to the oocyte. Second approach implies enhancement of sperm motility when even the high motility sperms are not motile enough for fertilization. It was shown that adding species of higher motility to species of lower motility could result in the “motility transfer” [1]. The effect was demonstrated in a binary system of artificial microswimmers: Janus particles whose motility is caused by the catalytic chemical reactions at the surface (e.g., silica microparticles half-covered by gold or platinum, or bio-compatible high-motility Ag/AgCl Janus particles[2]). The motility enhancement was shown for particles with weak inertia, by studying their velocity distributions, and for overdamped particles, by comparing their effusion rates. The numerical analysis [1] proves that in dense binary mixtures, the width of the velocity distribution of the less active particles linearly grows with the fraction of more active particles. The number of particles moving with larger velocity is considerably enhanced. The motility transfer from the more active to the less active subsystem can raise the effusion rate of the latter by 2 to 7 times. The proposed technique can be implemented in various biological and medical systems. In case of weakly motile sperm cells, this technique has advantages over other similar proposals (e.g., self-propelled metallic rotors trapping sperms), whereby it is substantially less damaging, and it does not require the fast guest swimmers to localize and trap individual sperms. We will also discuss our recent experimental advances in motility sperm selection techniques (with living samples) using a microfluidic setup.



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CB-O11
Development of fluorescent ligands for Voltage-Gated Ion Channels

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Keywords: Fluorescent ligands; Voltage-gated ion channels

In recent decades, the number of fluorescent ligands targeting transmembrane proteins, particularly G-protein coupled receptors, has increased in tandem with high-precision optical techniques. Nevertheless, the development of fluorescent ligands for Voltage-Gated Ion Channels (VGICs), including L-type calcium channels (LTCCs), is still in its infancy, despite their prominent role in both healthy and diseased tissues [1]. For instance, changes in the expression and functional modifications of LTCCs are linked to severe cardiopathologies and neurological diseases [2].

In this presentation, the focus is both on tool development and tool application. First, we report the synthesis of a library of novel fluorescent ligands (Figure 1) aimed to investigate LTCCs in vitro and, in the future, in vivo. The design of the library was based on the coupling of the scaffold of well-known LTCC ligands, namely 1,4-dihdropyridines, to near-infrared emitting fluorophores. Thus, different racemic or homochiral 1,4-dihydropyridine scaffolds were coupled to the fluorophores via linkers which differed in length and nature (alkyl- or PEG-based linkers).

Then, the focus shifts towards the assessment of binding and the selection of the best candidate of the library for fluorescence imaging applications via live-cell calcium imaging and patch-clamp experiments. Finally, we introduce the application in fluorescence microscopy on transiently transfected HeLa cells.

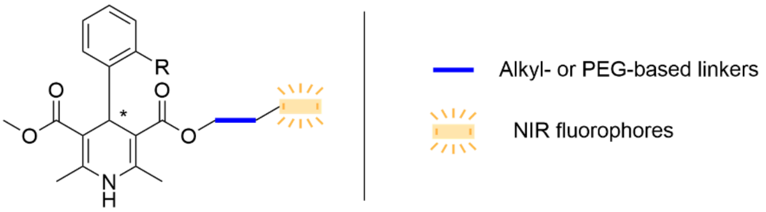

Figure 1 General structure of the library of fluorescent ligands targeting LTCC

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CB-O12

Immobilizing neuroglobin in mesoporous materials – monitoring protein structure and dynamics with spin-label electron paramagnetic resonance

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Keywords: biosensing; neuroglobin; spin-label; EPR; incorporation; porous material

The developement of biosensing instruments is a booming field of research. Often, these biosensors require the immobilisation of proteins in or upon synthetic matrices, such as metal oxides. Porous materials show a lot of promise due to their high surface area, which may facilicate a high loading of proteins and thus a high amount of active sites as well as sufficient accessibility of the active center.

However, the incorporation of proteins into such porous materials has proven to be non-trivial. The incorporation procedure as well as the characteristics of the support may accelerate protein degradation. In order to warrant a high loading of correctly folded proteins, the characteristics of the porous materials should comply to many demands, requiring controlled pore size and surface properties. Also experimental conditions, like pH and ionic strength, may limit the preperation of protein-loaded materials [1,2]. In this work, we focus on the incorporation of human neuroglobin (NGB) in mesoporous silica and titania. NGB is an iron-containing heme protein with interesting redox properties. Electron paramagnetic resonance (EPR) of the ferric form of the protein allows determining the changes in the electronic structure of the active heme site upon protein incorporation. Furthermore, site-directed spin labeling of the protein with a single nitroxide tag allows determining changes in protein dynamics and polarity of the local environment upon incorporation in the matrix using spin-label EPR. Moreover, pulsed EPR experiments on doubly-labeled proteins reveal support-induced changes in the tertiary structure of the protein. All observed structural and dynamical changes will be correlated to the characteristics of the support materials.

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CB-O13

Effect of membrane curvature and lipid composition on membrane permeability in liposomal drug delivery

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Keywords: molecular modeling; molecular dynamics simulations; liposomes; phospholipid membranes; kinetics; fatty acids

Liposomes are spherically shaped phospholipid bilayers which may be used to deliver drugs to the specific sites by encapsulating them in the hydrophilic core or the lipophilic bilayer part. However, this delivery may not be efficient because of untimely drug release. Therefore, the permeation rate through the liposomal membrane is a crucial parameter in drug design. This work investigates how two liposome parameters, i.e. the curvature and the lipid composition, affect the permeability. For this, flat bilayers and three liposomes with different diameters (11 nm, 21 nm, and 27 nm) are simulated with coarse-grained molecular dynamics. The 23 simulated systems have varying lipid composition of dipalmitoylphosphatidylcholine (DPPC), cholesterol, and fatty acids. The water permeability is determined using the counting crossings method [1]. Moreover, two types of permeants with different free energy profile across the membrane, i.e. well and barrier, are added to the simulation to investigate the effect of the permeant's solubility in the membrane [2]. New definitions for entrance, escape and liposome permeability are introduced to allow for comparison with flat bilayers. It is observed that the curvature increases the entrance permeability of the permeants, permeating from the outer space of the liposome to the inner space of the liposome. The concentration of cholesterol and fatty acids does affect the permeability, which is in accordance with the observed changes in the free energy profiles and area per lipid. As the curvature effect is smaller than the concentration effect in the simulations, the focus should lie on lipid composition when timely drug release is aimed for.

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CB-O14

The Notorious Z.B.G.: Synthesis and Biological Evaluation of Potent HDAC6 Selective Inhibitors with a Non-Hydroxamic Acid Zinc Binding Group to Overcome Therapeutic Limitations.

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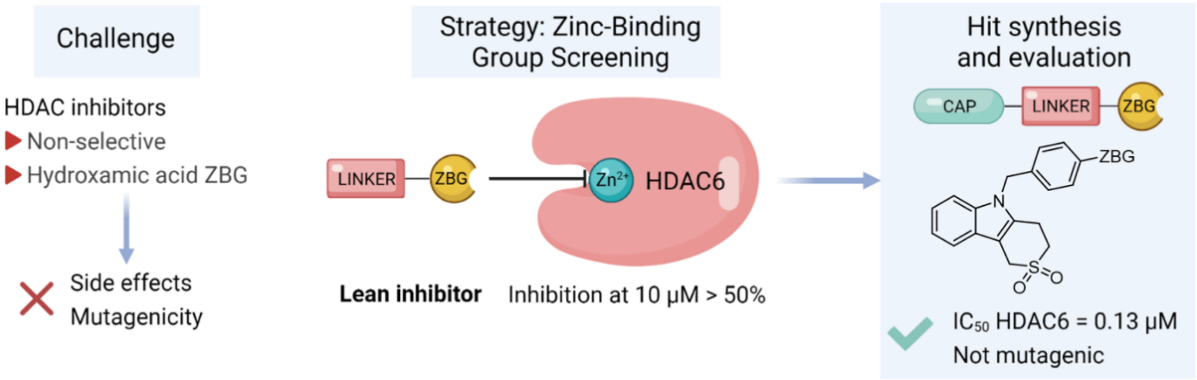
Keywords: HDAC6; zinc-binding group; HDAC6 inhibitors; lean inhibitor

Histone deacetylase 6 (HDAC6) is a crucial regulator in various cancer types and several non-oncological conditions such as inflammation and neurodegenerative disorders. Currently, hydroxamic acid-based HDAC inhibitors are used in oncology, but their application in other therapeutic areas is hampered because of their non-selective mode of action and the potential mutagenicity associated with the hydroxamic acid zinc-binding group. To enable HDAC inhibition as a therapeutic strategy beyond oncology, we searched for a potent zinc-binding group able to replace the contested hydroxamic acid by employing a lean inhibitor strategy. The resulting, more desirable metal chelator was incorporated in a set of HDAC6-selective inhibitors. Biological evaluation of these new compounds showed an IC50 in the nanomolar range, dose-dependent HDAC6 inhibition in MM1.S cells and improved genotoxicity results, rendering these new antagonists potential hits for the non-oncologic therapeutic application of HDAC inhibitors, such as in a neurological disease context.



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CB-O15

Solid-phase peptide synthesis, folding and biological characterization of carboxyterminally truncated human CXC chemokine ligand 10 CXCL10(1-73)

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Keywords: solid-phase peptide synthesis; chemokines; posttranslational modifications

The chemokine superfamily encompasses a group of structurally related chemotactic cytokines with low molecular mass (± 8-12 kDa) that contain two conserved cysteines forming disulfide bridges [1–3]. Chemokines orchestrate directional leukocyte trafficking during inflammation and homeostasis. In particular, interferon-γ inducible protein of 10 kDa (IP-10/CXCL10) is a dual-function CXC chemokine that coordinates chemotaxis of activated T cells and NK cells via interaction with its G protein-coupled receptor (GPCR), CXC chemokine receptor 3 (CXCR3) [4–6]. As a consequence of posttranslational modifications, human CXCL10 exhibits a high degree of natural structural and functional heterogeneity, whereby dipeptidylpeptidase IV (DPPIV/CD26)-processed N-terminally truncated CXCL10(3-77) functions as a chemotaxis antagonist [7]. However, the biological effect of natural processing of CXCL10 at the C-terminus has remained partially elusive. C terminally truncated CXCL10 proteoform CXCL10(1-73) has been identified in cell culture supernatant of IFN-γ-stimulated keratinocytes and fibroblasts [8–10]. Despite the postulated involvement of the C terminal amino acids in angiostatic and anti-parasitic actions of human CXCL10 [11,12], conclusive research on CXCL10(1-73) has remained particularly scarce. As such, to further explore the functioning of CXCL10(1-73), we endeavored to produce this protein by solid-phase peptide synthesis (SPPS). However, this technique remains challenging for proteins with a pronounced hydrophobic nature [13,14]. Hydrophobic proteins tend to form inter- and intra-molecular β-sheet interactions, resulting in on-resin aggregation during peptide synthesis and consequently synthesis failure. Given the relatively high proportion of amino acids with hydrophobic side chains in human CXCL10 (± 48%), CXCL10 presumably falls under this denominator. Hence, we optimized Fmoc-based SPPS of C-terminally truncated human CXCL10(1-73) and herein propose a strategy for synthesis of CXCL10 proteoforms (Figure 1). The synthesis yield was markedly improved by the concomitant utilization of a hydrophilic H-Ser(OtBu)-HMPB NovaPEG resin, four pseudoprolines and a Fmoc-L-Ile-L-Pro dipeptide. Based on algorithm-predicted [15] and experimentally-determined difficult protein regions, these specific pseudoprolines and an Fmoc-L-Ile-L-Pro dipeptide were selectively incorporated at key positions in the peptide backbone of CXCL10. Subsequently, disulfide bridge formation was obtained by incubating crude linear proteins with a basic mixture —containing 1.0 M guanidine hydrochloride and 0.1 M Tris at pH 8.5—under continuous stirring in air for 24.0 h [16]. Furthermore, we uncovered that synthetic CXCL10(1-73) has diminished in vitro affinity for glycosaminoglycans (GAGs) and an attenuated capacity to induce calcium signaling and phosphorylation of extracellular signal-regulated kinase-1/2 (ERK1/2) and protein kinase B/Akt in CXCR3A-transfected Chinese Hamster Ovary (CHO) cells compared to intact CXCL10(1-77). Consequently, these findings provide a significant step forward in our understanding of the structural and functional heterogeneity of CXCL10 proteoforms, a notion that is particularly relevant in enzyme-enriched inflammatory niches in pathological settings. These data may pave the way towards improved comprehension of the in vivo functioning and multi-layered role of natural CXCL10 proteoforms in the myriad of afflicting conditions in which this chemokine has been implicated, e.g. rheumatoid arthritis and viral infection [17–21].

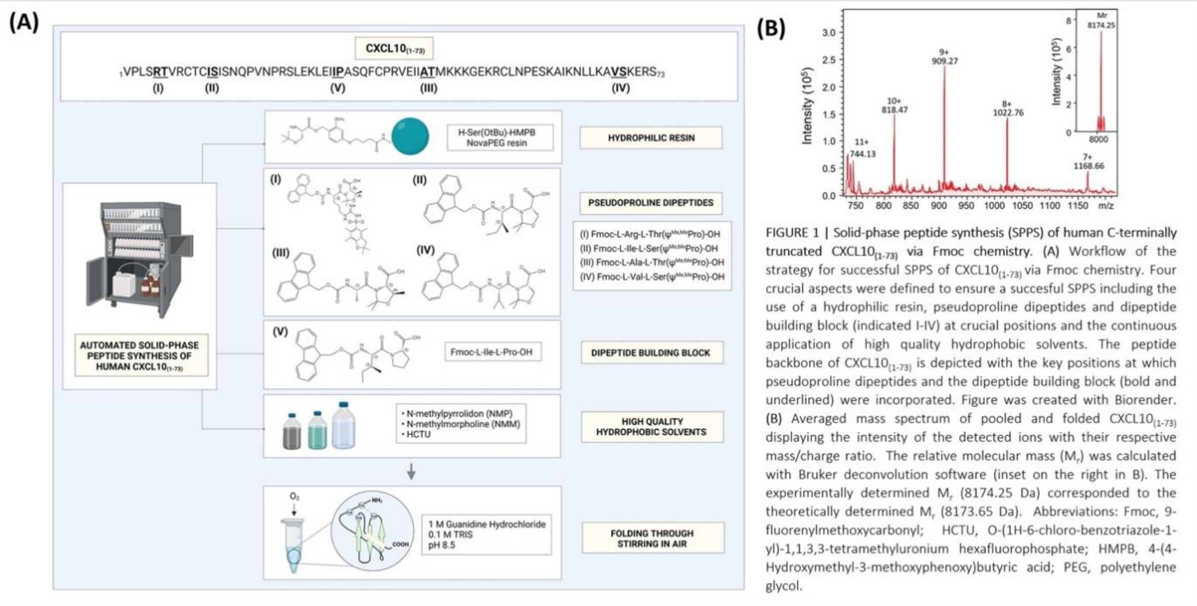

FIGURE 1 | Solid-phase peptide synthesis (SPPS) of human C-terminally truncated CXCL10$_{(1-73)}$ via Fmoc chemistry. (A) Workflow of the strategy for successful SPPS of CXCL10$_{(1-73)}$ via Fmoc chemistry. Four crucial aspects were defined to ensure a succesful SPPS including the use of a hydrophilic resin, pseudoproline dipeptides and dipeptide building block (indicated I-IV) at crucial positions and the continuous application of high quality hydrophobic solvents. The peptide backbone of CXCL10$_{(1-73)}$ is depicted with the key positions at which pseudoproline dipeptides and the dipeptide building block (bold and underlined) were incorporated. Figure was created with Biorender. (B) Averaged mass spectrum of pooled and folded CXCL10$_{(1-73)}$ displaying the intensity of the detected ions with their respective mass/charge ratio. The relative molecular mass (M$_r$) was calculated with Bruker deconvolution software (inset on the right in B). The experimentally determined M$_r$ (8174.25 Da) corresponded to the theoretically determined M$_r$ (8173.65 Da). Abbreviations: Fmoc, 9-fluorenylmethoxycarbonyl; HCTU, O-(1H-6-chloro-benzotriazole-1-yl)-1,1,3,3-tetramethyluronium hexafluorophosphate; HMPB, 4-(4-Hydroxymethyl-3-methoxyphenoxy)butyric acid; PEG, polyethylene glycol.

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CB-O16

Photo-alkylation of DNA secondary structures, exploiting photosensitizer and ligand co-localization: from structure-selectivity towards sequence-specificity

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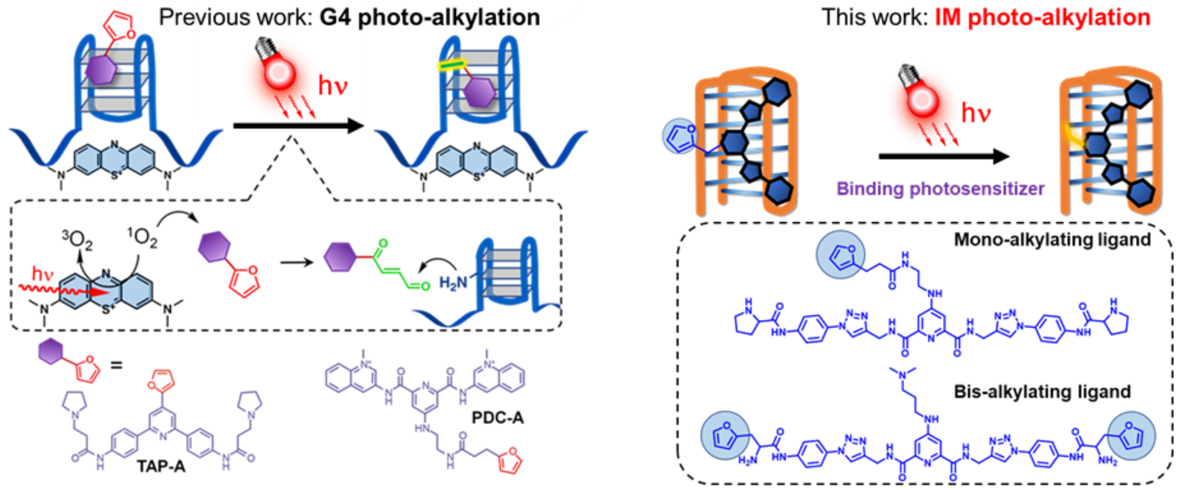
Keywords: DNA; G-quadruplex; I-motif; secondary structures; proto-oncogene; telomeric DNA; photo-alkylation

G-Quadruplex (G4) nucleic acid structures has been extensively studied and characterized in all their aspect, and their clinical relevance has been consolidated over the past decades. As a result, several libraries of small molecule ligands have been synthesized over the past decades, and highly specific G4-targeting methodologies, featuring the use of oligonucleotides and their analogues, are today available [1,2]. On the other hand, their C-rich counterpart, the I-Motifs (IMs) were put on the back burner due to the conditions in which these structures were first observed, and for a long time considered just as a mere bench phenomenon [3]. In our group, we proposed a bimolecular approach for G4-alkylation, using a pro-reactive furan-containing ligand, activated by red-light irradiation of a proximate binding photosensitizer. G4-alkylation can be achieved in a high yield at low ligand excess. HPLC and modelling studies allowed identifying potential residues involved in the reaction [4]. This methodology allowed us to tailor the activation of the pro-reactive alkylating moiety, achieving structural selectivity of G4 over other DNA secondary structures. Now, we aimed at expanding this methodology, extending the targeting towards IM-DNA structures [5]. By incorporating a furan moiety into ligands able to discriminate among dsDNA and G4-DNA structures, and by using an IM-binding photosensitizer, we showed the possibility to translate the methodology for selectively targeting these secondary DNA structures, and ultimately obtaining their sequence-specific targeting. If successful, this methodology could configure as a novel chemical tool for understanding the effect of targeting a specific structures over the thousands present in the entire genome.



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CB-O17
Chromium Toxicity: The role of Analytical Chemistry in Exposure to Chromium

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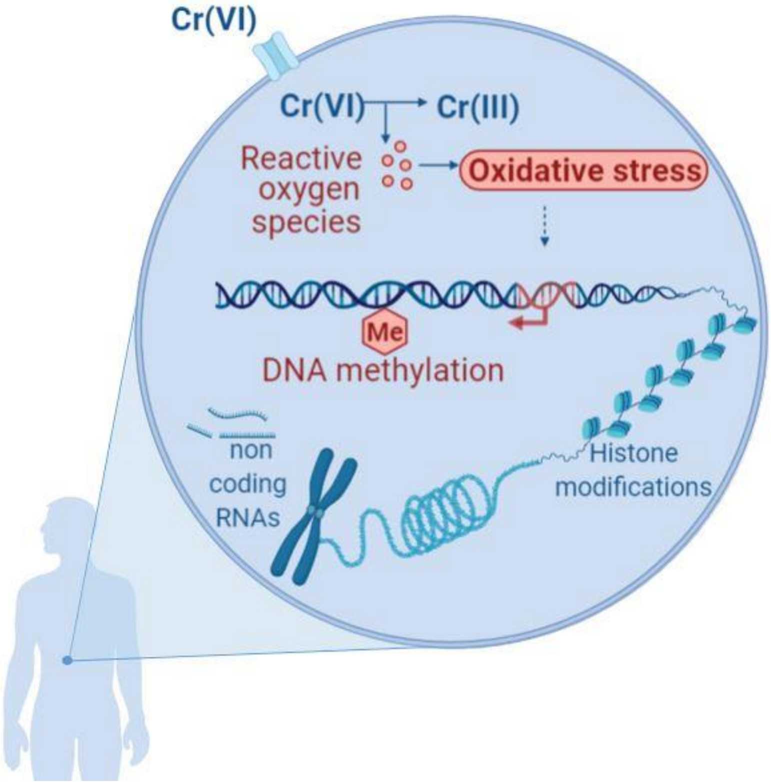
Keywords: Hexavalent chromium; toxicity; speciation; method development

Chromium (Cr) is a transition element that exists in oxidation states ranging from -2 to +6. The common stable ones in the environment are trivalent Cr(III) and hexavalent Cr(VI) chromium. Cr(III) is an important micronutrient for the human body, while Cr(VI) is highly toxic and carcinogenic. The chemistry of Cr plays a major role in its cellular entry and toxic effects. Cr(VI) in the environment mainly exists as the chromate oxyanion (CrO4). Structurally, CrO4 is very similar to the sulfate oxyanion (SO4). Therefore, CrO4 utilizes general sulfate transporters on the cell surface to enter the cell. Once inside the cell, Cr(VI) is rapidly reduced to Cr(III). This reduction process can generate free radical species which produce high levels of oxidative stress, causing damage to cellular components. Due to the differences in toxicity between Cr(VI) and Cr(III) compounds, speciation of Cr is very important. Therefore, an improved sensitive and robust method for the simultaneous determination of Cr(III) and Cr(VI) in water samples has been developed. The method uses a hyphenated micro liquid chromatography (µLC) system coupled to inductively coupled plasma mass spectrometry (ICP-MS). Cr(III) and Cr(VI) were separated with different retention times at 170 and 230 sec, respectively. This method has been applied to biological samples collected within an occupational biomonitoring study, namely the HBM4EU chromates study. This European chromates study investigated, among other things, the effect of Cr(VI) exposure on oxidative stress, global DNA methylation, global DNA hydroxymethylation and gene-specific DNA methylation in blood. The study population consists of Cr-platers, surface treatment workers and welders. Post-shift urine samples and blood samples were collected at the end of the working week. Metal concentrations were measured with ICP-MS. In addition to analysis of Cr, analysis of per- and polyfluoroalkyl substances (PFASs) were performed in plasma of Cr-platers. Analysis of methylation, hydroxymethylation and oxidative stress levels were done using LC-MS/MS. Furthermore, analysis of gene-specific DNA methylation were done using pyrosequencing. The highest Cr(VI) exposure levels were observed for Cr-platers. Furthermore, these platers were exposed to elevated levels of PFASs. Regarding epigenetic alterations, global DNA hypomethylation was observed. Furthermore, increased levels of oxidative stress was observed. These results suggest that DNA methylation may be influenced by oxidative stress.



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CB-O18
A simple model for the Pauli Repulsion with utility in QM, MM and Chemical Education

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Keywords: Pauli repulsion; molecular mechanics; quantum mechanics; chemical education

The volume and low compressibility of condensed matter can essentially be attributed to the Pauli repulsion. For the purpose of calculating this repulsive force in the context of computational chemistry, we present a simple empirical potential energy term. Conceptually, this work is based on a model in which the positively charged nucleus of each atom is embedded in a spherically symmetric negatively charge density, the center of which is displaced in response to the proximity of a non-covalently interacting atom. In practice, the model is further simplified by representing the aforementioned negative charge density as a point charge in a fashion similar to the classical Drude oscillator. This mobile point charge is also taken as the origin of the dispersion interaction, which is represented as a simple R-6 term. The resulting potential energy formula is shown to be capable of producing energy profiles that are in excellent agreement with high-level QM results on simple model systems. The present work has potential applications in post-HF and post-DFT dispersion corrections as well as in conceptually explaining the Pauli repulsion in basic chemical eduction.

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Chemical Synthesis & Methodologies (CS&M)

CS&M-O1
9-Boratriptycenes: A Lewis Superacids Story

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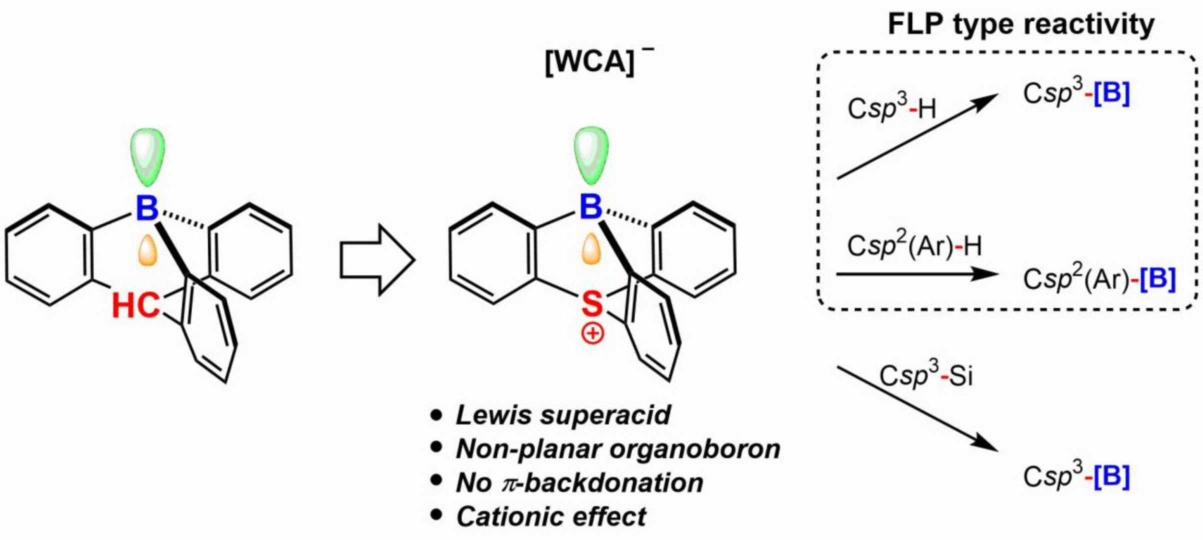
Keywords: Lewis Superacids; Pyramidal Boron; Main Group; C-H activation

Although their popularization was spurred by the discovery of frustrated Lewis pairs (FLPs) in 2006,[1] trivalent boron species are recognized since decades as prototypical Lewis acids and have found, to date, numerous applications far outside this topic.[2] It is only recently that highly electron-deficient pyramidal boranes were predicted to enable the activation of small molecules and the formation of donor-acceptor complexes of noble gases.[3]

Three years ago, the first non-planar triarylborane derived from triptycene was reported as a Lewis adduct with weakly coordinating anion (WCA) and displayed a Lewis acidity exceeding by far all known triarylboranes.[4] Thereafter, the parent 9-boratriptycene was synthesized in turn and the factors governing the exceptional Lewis acidity of these species were rationalized.[5]

Very recently, the design and synthesis of a third member of the 9-boratriptycene family was achieved based on three guidelines: (i) the orthogonal arrangement between the triptycene aryl rings π-orbitals and the boron pz empty orbital to prevent π-backdonation at boron; (ii) the high pre-pyramidalization of the boron atom to minimize the structural reorganization energy and (iii) the strong withdrawing ability of the sulfonium linker to provide high Lewis acidity at boron and preventing fast protodeboronation.[6]

In this presentation, I will tell you the story of the 9-boratriptycene derivatives and discuss about their newly explored and highly promising reactivity and applications in chemical synthesis.



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CS&M-O2
Dearomative Cyclopentannulation of Indoles and Benzofurans

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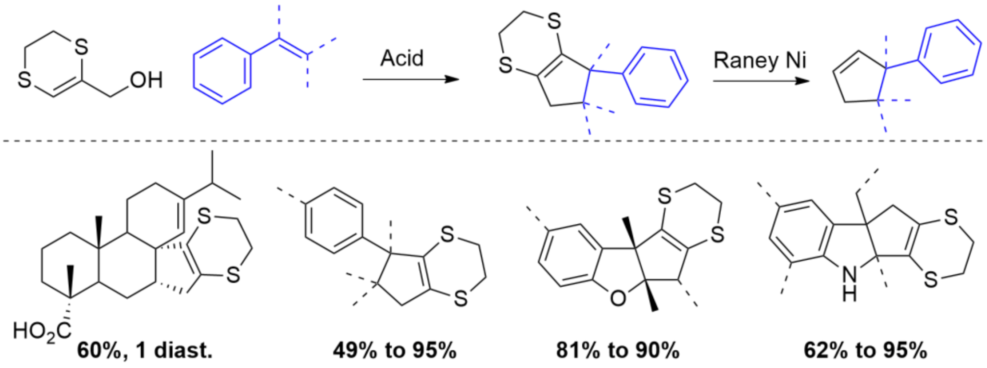
Keywords: (3+2); cationic cycloaddition; heterocycles; cyclopentane; benzofuran; indole

There is a constant call for simplification in the way molecules are synthesized. This demand becomes problematic looking at some biological interesting compounds which often have a complex carbon skeleton, more sp3 character, and a high number of chirality. Privileged scaffold of biological active compounds are excellent anchor points for drug discovery, establishing the need for synthetic methods that rapidly assemble sp3-rich carbocyclic scaffolds.

Our lab developed a (4+3) and (3+2) cycloaddition capable of synthesizing complex carbocyclic structures. Multiple success were obtained using furfuryl alcohols [1,2] and in 2016 using a dihydro-dithiin alcohol [3]. As such aiding in the simplification process of natural product synthesis.

Further research focuses on expanding the scope of this cationic (3+2) cycloaddition to explore rapid routes to common natural product frameworks. An advantage of using the dihydro-dithiin, is the ease in which the cycloadduct can be diversified towards highly functionalized cyclopentanoid compounds.



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CS&M-O3
9-phosphatriptycenes as Lewis bases for the frustrated Lewis pair-catalyzed hydrogenation of unactivated olefins: a DFT and experimental study

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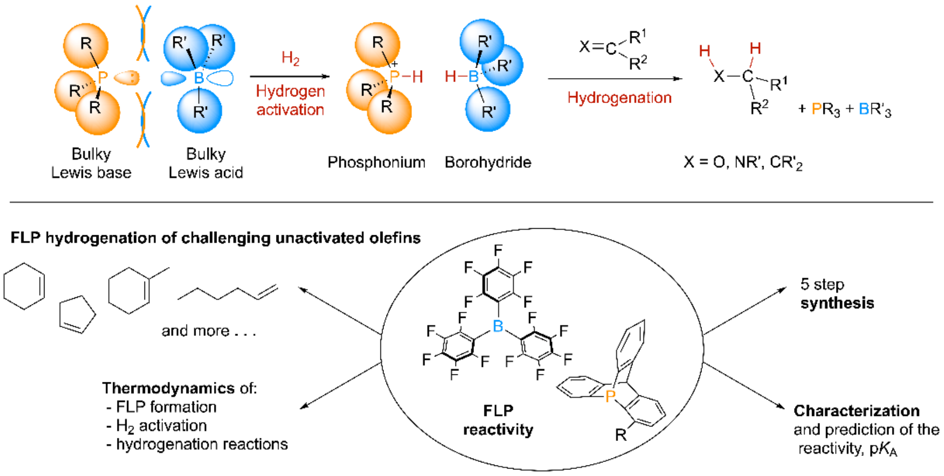
Keywords: catalysis; 9-phosphatriptycenes; frustrated Lewis pairs; hydrogenation; unactivated alkenes; density functional theory

Frustrated Lewis Pairs (FLPs) consist in sterically hindered Lewis acids and bases that cannot form Lewis adducts because of steric repulsions. These bifunctional systems, usually consisting of a strong borane and a phosphine or amine, have been extensively used as transition metal-free catalysts for hydrogenation reactions and small molecules activation (CO2, NO2, …).[1]
Over the years, this cooperativity between of boron Lewis acids and P- N- or O-Lewis bases allowed the hydrogenation of a wide variety of unsaturated substrates. Olefins stand at the edge of this latter category however since it remains a challenge in FLP chemistry and the metal-free reduction of unactivated alkenes was only seldom reported in the literature.[2] Due to their cage-shaped structure, 9-phosphatriptycene derivatives constitute promising Lewis bases to tackle such lasting challenges in FLP chemistry. The enhanced pyramidalization of their phosphorus center results in a significant weakening of its Lewis basicity and the strategic addition of ortho-substituents increases their steric bulk compared to related triarylphosphines.[3]
Herein is reported our experimental and computational investigations on the reactivity of Lewis pairs consisting in tris(pentafluorophenyl)borane and 9-phosphatriptycene derivatives. The synthetic strategy of the latter is based on the cyclization of functionalized triarylmethane precursors. By adapting the starting materials, new substituted 9-phosphatriptycenes can be obtained.[4] They are now exploited as catalysts for the hydrogenation of challenging substrates in FLP chemistry.[5] In parallel to experimental work, the structural and electronic parameters, the pKa of these compounds as well as their thermodynamics in H2 activation and hydrogenation reactions are investigated by density functional theory calculations.[6]



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CS&M-O4
Selective iminitation of 3-oxo-β-lactams – new route towards 3-amino-β-lactams

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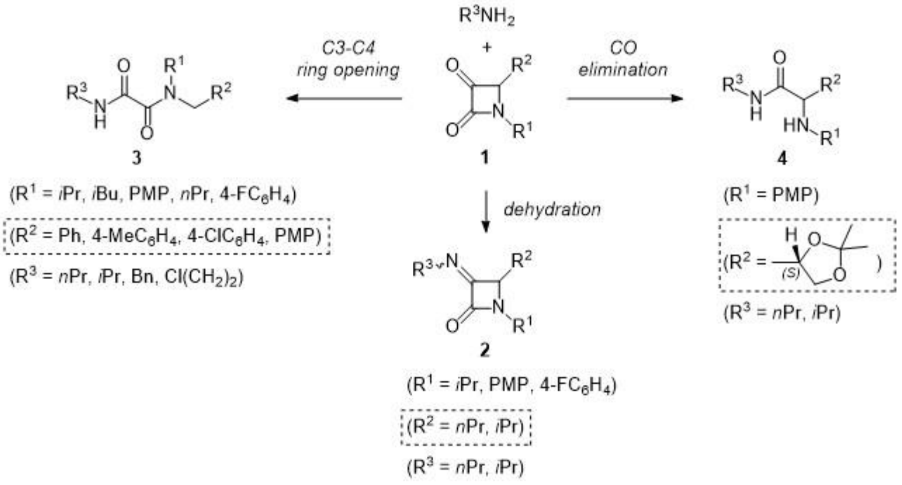
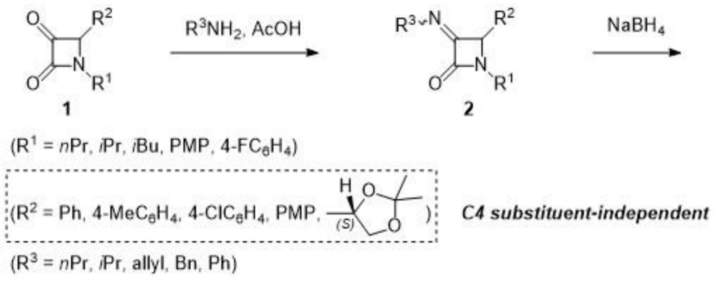
Keywords: /

β-Lactams have been recognized as versatile building blocks for the preparation of a wide variety of nitrogen-containing acyclic and heterocyclic compounds. In previous work in our group, the reactivity of 3-oxo-β-lactams 1 with respect to primary amines was investigated in-depth in an attempt to synthesize the corresponding 3-imino-β-lactams.[1] Depending on the specific azetidin-2-one C4 substituent, this reaction was shown to produce 3-imino-β-lactams 2 (through dehydration), ethanediamides 3 (through an unprecedented C3-C4 ring opening), or α-aminoamides 4 (through CO elimination).

In continuation of our interest in 3-imino-β-lactams as valuable building blocks, a selective, C4 substituent-independent protocol was developed to transform 3-oxo-β-lactams 1 into 3-imino-β-lactams 2, avoiding the undesired β-lactam ring opening. In addition, these 3-imino-β-lactams were used as precursors for the synthesis of the corresponding 3-amino-β-lactams.





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CS&M-O5
Development of Bulk-Like CdS and CdSe Quantum Dots for Optical Gain

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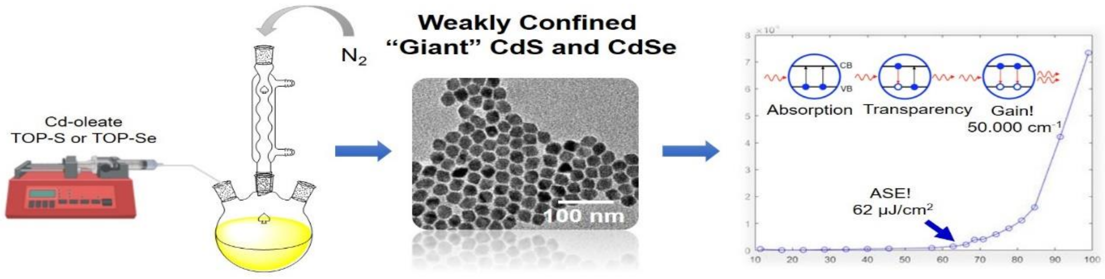
Keywords: /

Nanocolloidal semiconductors have been thoroughly investigated for their light emission applications, such as LEDs and lasers. So far, Cd-based binary quantum dots have successfully demonstrated light amplification and lasing in the red spectral region [1-3]. However, there has been interest lately to move towards studying new colloidal materials for green and near infrared stimulated emission.

Here we report the synthesis of weakly confined “giant” CdS and CdSe quantum dots using a continuous injection approach. With this protocol, we are able to grow large, defect-free wurtzite cores in a reliable manner that does not require initial seeds. Instead, nucleation and growth continuously take place via slow injection of the precursors in the reaction medium over the course of 2-3h. By controlling the volume addition of the precursors in this manner, we obtain a relatively low size dispersion by suppressing homogeneous nucleation processes and promoting seeded growth [4-6]. The reported 8-12 nm core sizes show a PLQY of 1-5 % that increases to 10-15 % with a few monolayer surface passivation of ZnS and CdS, respectively. Remarkably though, despite the low quantum yield these materials display superior gain amplitude (~50000/cm) and gain lifetime (~3 ns) to already established gain materials in the same spectral region, while simultaneously showing similar gain thresholds. Indeed, early ASE experiments on the “giant” CdS/ZnS system displayed stimulated emission with a 62μJ/cm2 threshold, which highlights this material’s promise to be used in green lasing applications.



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CS&M-O6
Design, synthesis and characterisation of novel donor-acceptor combinations affording low voltage losses in indoor organic photovoltaics

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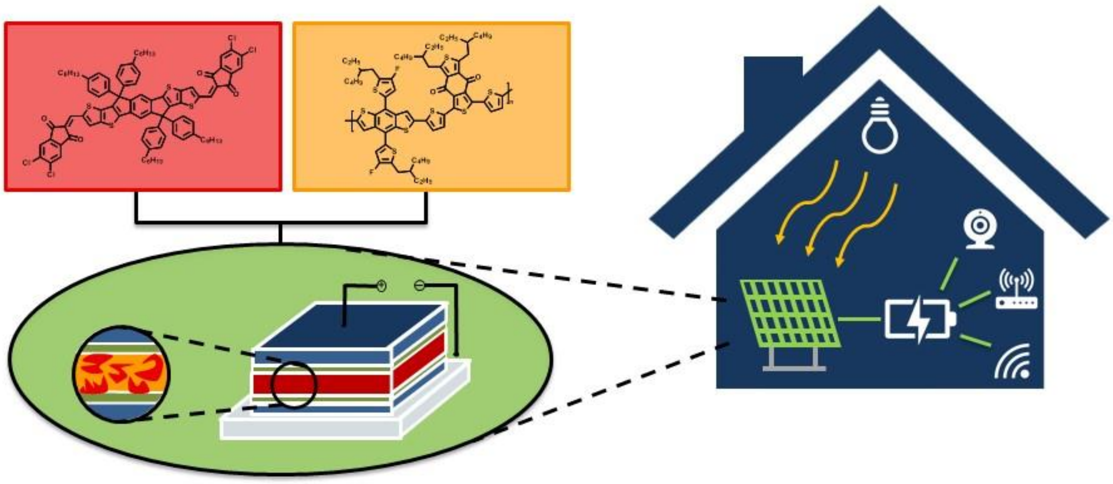
Keywords: Organic solar cells; indoor photovoltaics; medium-gap absorbers; material development

The rapid digitalisation of our society generates large networks of connected devices collecting enormous amounts of data used to monitor and further optimize numerous aspects of our daily life and society. As the power required to operate these devices continues to decrease and a significant portion of these devices will be located inside e.g. hospitals, stores, airports, offices, and factories, indoor light sources are considered a valuable asset in providing energy for these small-scale and low-power-consumption electronics. Therefore, indoor light harvesting technologies are closely monitored by the electronics industry, as it reveals a huge market to be discovered.[1] In the past decades, the global transition towards renewable and sustainable energy production stimulated the development of solar light harvesting photovoltaics and brought forward the predominant silicon based solar panels as found on most rooftops. However, under indoor or ambient lighting, the silicon solar cell dominance fades away in favour of other photovoltaic technologies, in particular organic photovoltaics (OPVs) due to their superior properties under indoor lighting conditions.[2] The highly tunable optical absorption of organic semiconductors enables the development of light harvesting donor (D) - acceptor (A) blends that closely match with the targeted narrow emission spectra of indoor lighting. The large absorption coefficients, small leakage currents under dimming light conditions and the modest independence on the lights' angle of incidence push OPV forwards as a highly suitable technology to drive low-power-consuming off-grid indoor electronics. However, OPV device efficiencies are currently constraint by open-circuit voltage losses and insufficient understanding of the mechanisms causing these losses.[3] Unfortunately, indoor conditions also result in an additional voltage loss, further lowering the device performance. Nevertheless, recent insights in the recombination phenomena occurring under indoor lighting and voltage losses in OPVs were gained and assisted in the proposal of potential solutions.[3,4] Taking into account these important insights for the development of new low-voltage-loss indoor D-A combinations, this presentation focusses on the design, synthesis and characterisation of some novel D and A organic semiconductors for indoor OPVs.



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CS&M-O7

Electron microscopic approaches in identifying, understanding & design of catalysts

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Keywords: Electron microscopy; Zeolites; catalysts

Catalysts are key materials which are already helping the industrial world in moving towards efficient sustainable solutions. Routine involvement of High Resolution Electron Microscopy in multi-disciplinary approach of design, synthesis and physicochemical characterization zeolites will be discussed taking an example of its role in identifying a novel zeolite, namely COK-24 [1]. A new zeolite, COK-24 which is an intergrowth of Erionite (ERI), and Chabazite (CHA) was successfully synthesized for the first time. The existence of an intergrowth was confirmed using XRD combined with advanced electron microscopy. The state of the art HR Microscopy equipped with high-end detectors combined with advanced image acquisition modes allows making images of improved resolution of catalytic materials (non-conducting) without any sample manipulation. Understanding the different stages of catalyst preparation and catalyst life also will be addressed taking few examples of Bifunctional catalysts [2].

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CS&M-O8
NHC Complexes in Flow (NHC = N-heterocyclic carbene)

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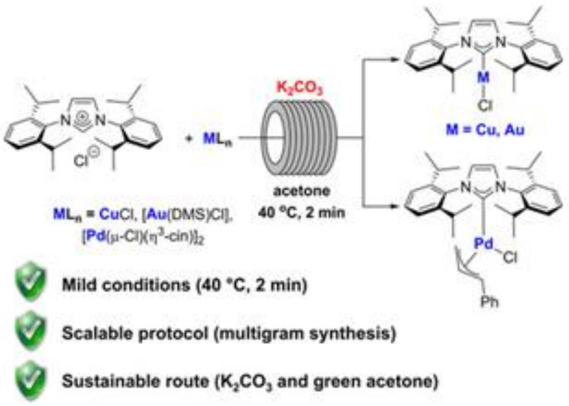
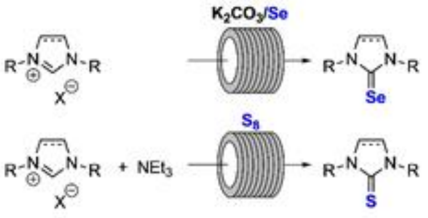
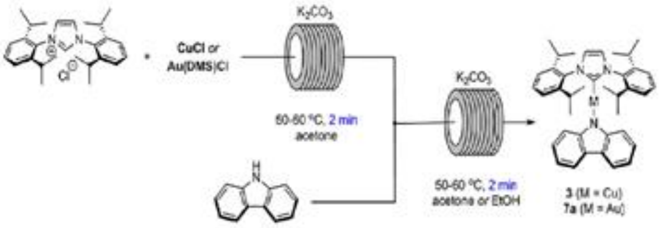
Keywords: Continuous flow synthesis; green solvents; metal complexes; N-heterocyclic carbenes

N-Heterocyclic carbenes (NHCs) have proven themselves to be a popular and versatile ligand family for the synthesis of organometallic compounds. With interesting use cases in catalysis, medicinal chemistry and material sciences, the widespread use of this novel class of ligands has been a driving force for the development of a sustainable, efficient, and user-friendly route towards their synthesis. So far, the most commonly used synthetic strategy leading to NHC complexes, has involved the generation of free NHC by deprotonation of the corresponding azolium salt with a strong base (e.g.NaH, KOtBu) and subsequent coordination to a metal or chalcogen. However, this approach presents several drawbacks such as the need for strictly anhydrous conditions and incompatibility with the use of metal precursors which are sensitive to strong bases. Alternatively, the use of weak bases and mild conditions is currently the most sustainable and attractive synthetic approach for the preparation of Late-Transition Metal-NHC complexes. In our recent pieces of work, we have translated the latter method to a continuous flow system. This technology provides superior mass and heat transfer rates and allows for the use of small volumes of reagents and in turn enables easy and safe handling of hazardous reagents. Using this setup, complete conversion of cuprate, aurate or palladate species was achieved, yielding the targeted Cu(I), Au(I) and Pd(II)-NHC complexes in excellent yield, without the need for further purification. The scalability of the process was exemplified in the multigram-scale synthesis of [Cu(IPr)Cl]. Additionally, this simplistic reactor design also proved capable of synthesizing Sulfur- and Selenium-NHC Compounds in similarly mild conditions, as well as the further arylation of the metal centre in a telescoped setup. All reactions examined proceed under extremely mild conditions and make use of technical grade acetone as solvent.







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CS&M-O9

Group IV Metal Oxo Cluster Based Catalysts for the Direct Formation of Amide Bonds

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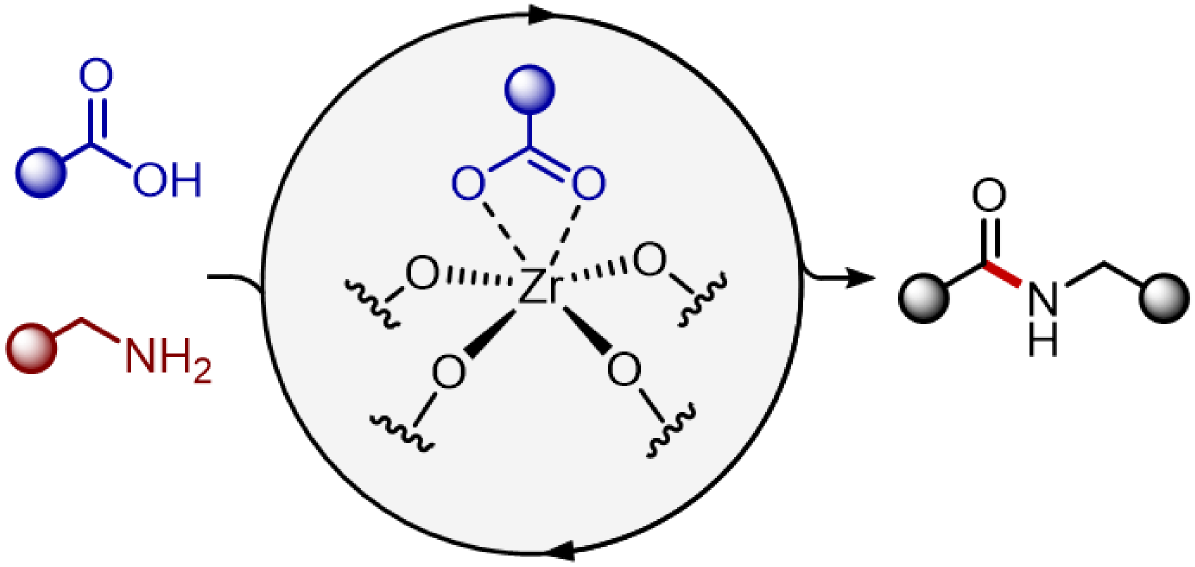
Keywords: metal-organic frameworks; clusters; polyoxometalates; amides; peptides; synthesis

The discovery and development of metal oxo cluster based catalysts for the atom-economic and water-tolerant amide bond formation directly from non-activated carboxylic acids and amines will be presented in this work. Amide bonds are pivotal structural motifs across all fields of chemistry, from biochemistry to medicinal chemistry and materials. Despite long established, current methods for the synthesis of amides still challenge modern standards of reaction efficiency, and better catalytic routes are highly desired. On the other hand, group IV metal oxo clusters have been recently discovered to streamline amide bond formation under mild conditions, largely increasing the sustainability of these reactions and breaking new ground for inorganic, organic and materials chemists to innovate in chemistry and related areas. Remarkably, these catalysts do not require anhydrous or inert atmosphere conditions, and can be even recycled without loss in reactivity. Key control experiments highlight an unusually high tolerance of the new catalysts to water in the reaction (molar excesses up to 2800), which is rather distinct from previously reported catalysts. Finally, their synthetic utility towards amides bearing a range of functional groups and heterocycles useful for medicinal, agrochemical and material chemists is demonstrated, showcasing metal oxo clusters as viable alternatives to develop robust catalysts and greener synthetic methodologies.



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CS&M-O10
Development of a combined methodology towards mechanistic investigation of rare metal-free, light activated catalysts

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[2] *Cardiff University, United Kingdom*

Keywords: Photocatalysis; EPR; Mechanistic Investigation; Copper

Photocatalysis has been an important research field in the last 40 years and has become increasingly more common as an easy way to obtain unusual reactivity and greener synthetic pathways. While compounds of rare transition metals such as ruthenium and iridium are commonly employed,[1] in recent years the interest has started to shift towards different photocatalysts, such as compounds containing more easily available transition metals like copper, which not only allow for more economically affordable catalysts but also open up reactions and selectivity that were previously inaccessible or unexplored.[2,3] In the frame of the European Programme MSCA-Horizon 2020 "Paramagnetic Species in Catalysis Research (PARACAT)" we are working to shed light on synthetic pathways that employ these alternatives.[4] In this talk we will present the insight we were able to obtain for a photocatalytic process employing commercially available photosensitizers. Our aim is to obtain important mechanistic insights through Stern-Volmer fluorescence quenching studies and EPR experiments, in order to optimize the reaction protocol and allow in the future for a rational approach to the development of similar syntheses. EPR and other spectroscopic results, as well as DFT simulations will be presented and related to different mechanistic proposals.

We gratefully acknowledge funding from Marie Skłodowska-Curie Joint Doctorate grant agreement No 813209.

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CS&M-O11
Synthesis of bridged bicyclic nitrogen scaffolds via orthogonal tandem catalysis

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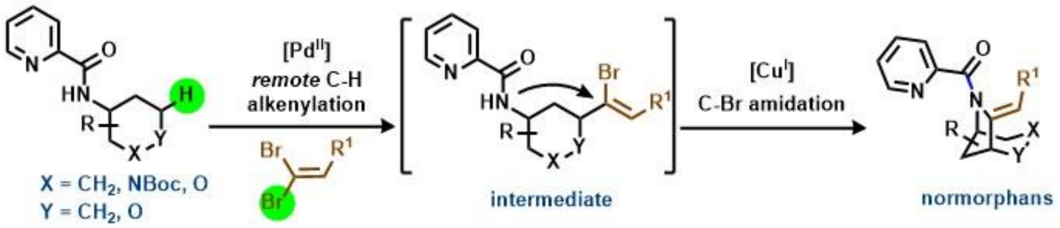
Keywords: alkenylation; bridged bicyclic nitrogen scaffolds; normorphan; remote functionalization; tandemcatalysis

Conformational restriction by joining two rings is an effective tool to modify pharmacological characteristics of drug candidates and is a key, yet underrated, strategy in medicinal chemistry.[1] The fixation of functional groups in a biologically active conformation can provide more efficient and selective ligands for various targets, often also featuring improved ADME parameters (lipophilicity, solubility, metabolic stability) in comparison to the non-restricted scaffolds. Bridged bicyclic nitrogen scaffolds are conformationally restricted analogues of saturated aminocarbo- and aminoazacycles ubiquitous structural motifs in natural products and active pharmaceutical ingredients (APIs). Moreover, complexity (as measured by fraction sp3) and the presence of chiral centers correlates with success as compounds transition from discovery, through clinical testing, to drugs. Considering these factors, bridged bicyclic nitrogen scaffolds have a huge potential in drug discovery.

Among these bridged bicyclic nitrogen scaffolds, the normorphan skeleton is especially attractive due to its rigidity, 3-dimensionality, high sp3 carbons fraction, and low molecular weight. Moreover, it forms the backbone of several natural products.[2] While a number of synthetic strategies have been developed in the past decades to access the normorphan scaffold, the routes to 7-alkylidenenormorphans in which the exocyclic enamine provides ample possibilities for post functionalization are still limited.[2] Our group developed an unprecedented site- and diastereoselective orthogonal tandem catalyzed reaction from readily accessible reactants towards 7-alkylidenenormorphans and related heterocyclic systems (oxa and aza analogues).[2]



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CS&M-O12
Synthesis and structural characterization of phosphate-based geopolymers

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Keywords: geopolymers; silico-aluminophosphate; metakaolin; phosphoric acid

Geopolymers or inorganic polymers, initially reported by Davidovits, are generally synthesized by exposing aluminosilicate precursor powders to alkaline silicate solution or phosphoric acid solution under ambient or slightly increased temperature. Despite phosphorus geopolymers have been known for almost as long as alkaline geopolymers and despite the properties of phosphate geopolymers such as better acid-resistant, thermal and dielectric behaviour surpass the properties of their alkaline analogues, phosphate geopolymers still have not matched scientific attention and industrial application comparable to their alkaline analogues. One of the reasons is certainly the use of more expensive phosphoric acid compared to alkaline sodium silicate solution. Here we conducted a synthesis and structural characterization (XRD, ATR-FTIR, TG/DTG/DTA) of phosphorus geopolymer derived from metakaolin and phosphoric acid solution, with the aim of high-tech application of phosphorus geopolymers in electronic devices. According to the available literature, the main parameter in reaction for phosphate-based geopolymers is the Al:P atomic ratio with optimal value of 1. Therefore, in this work, atomic ratio Al:P is set to approximately 1 and the water-to-binder ratio, as a measure of workability of geopolymer paste, is set to 0.5.

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CS&M-O13

Construction of M-C and M-N bonds: "Golden" synthons, materials, pre-catalysts and mechanistic probes

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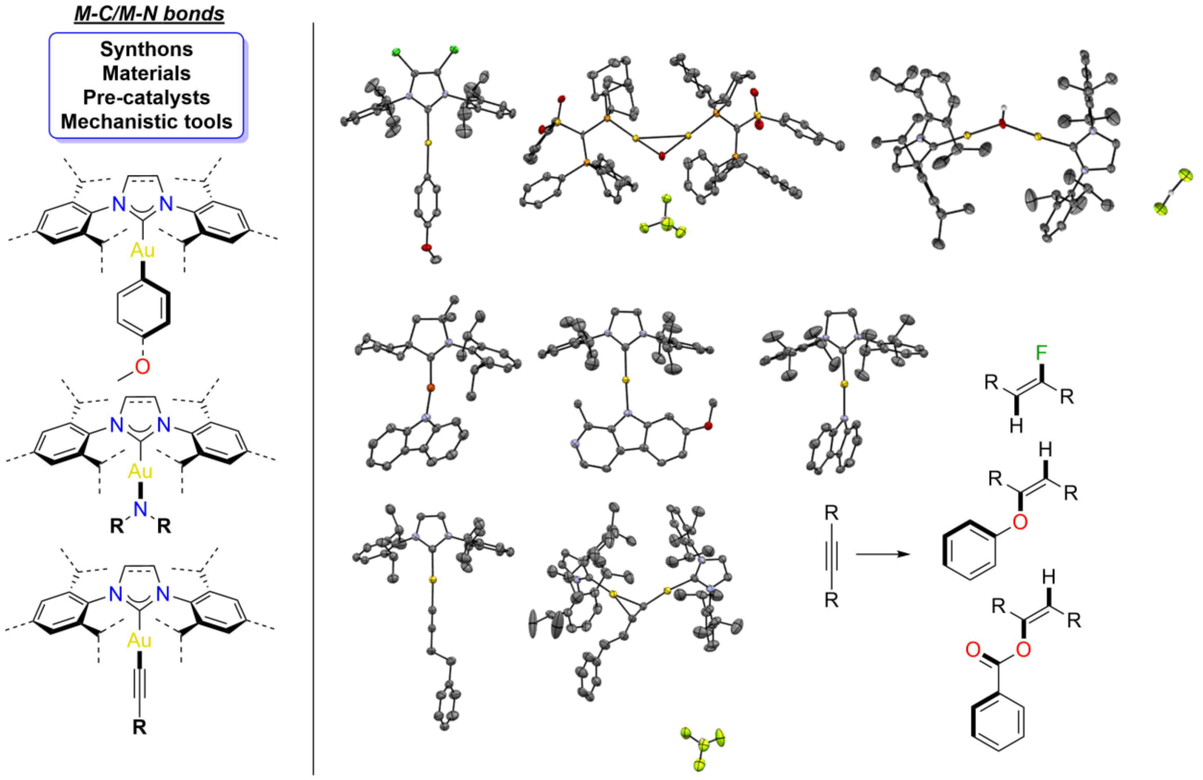
[2] *National and Kapodistrian University of Athens, Greece*

Keywords: N-heterocyclic carbenes; coinage metals; catalysis; synthetic methods; mechanistic studies

The gold-carbon bond has fundamental importance in the chemistry of gold and has been recognized as the origin of gold catalysis. The generation of such bonds is a topic of intense research to this day, owing to their relevance in catalysis, materials chemistry, and medicinal chemistry. The traditional organometallic techniques that have been utilized to construct gold-hydrocarbyl species have now been superseded by more sustainable methodologies, circumventing the need for inert conditions and toxic solvents. Moreover, the significance of complexes bearing such bonds (i.e. Au-Aryl and Au-alkynyl complexes) is now even broader, since their scope and uses have expanded to include organometallic synthesis and mechanistic studies. The same applies for complexes of the coinage metals bearing M-N bonds, and specifically those based on N-heterocyclic carbene (NHC) ligands; often called Carbene-Metal-Amide (CMA) complexes, even though the latter have emerged only recently. Herein, we will examine the latest methods for the synthesis of Au-Aryl, Au-alkynyl and CMA complexes of the coinage metals (Au, Ag, Cu) as well as the applications of these compounds as organometallic synthons, pre-catalysts in organic transformations, biorelevant or photonic materials and finally as tools to investigate catalytic transformations. More specifically, we will examine NHC-based complexes, their use in dual gold catalysis and cases where hydrogen bonding can be used to enable or affect gold catalysis, such as in the hydrofluorination of alkynes.



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CS&M-O14
Selective Nickel-Catalyzed Hydrodeacetoxylation of Aryl Acetates

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Keywords: C-O bond activation; hydrodeacetoxylation; nickel catalysis; renewable resources

The development of effective processes to transform non edible biomass into base chemicals and fuels is one of the key societal challenges to achieve a low carbon society. Lignocellulose is an ideal renewable carbon source given its abundance on earth. While the carbohydrate fraction (cellulose and hemicellulose) is commonly used to produce paper and biofuels, the lignin part is under-utilized and mostly still burned to produce energy.[1] Depolymerisation of lignin delivers polyoxygenated aromatic compounds (guaiacols and syringols) which could potentially serve as future bio-based platform chemicals to access industrially important aromatics.[2] However, replacement of low oxygen content arenes obtained by traditional petroleum refinery requires selective hydrodeoxygenation methods of these bio-based platform chemicals which proved not self-evident.[3] While selective hydrodemethoxylation can be achieved,[4] direct removal of the OH group in presence of a OMe group is not known. A broadly applicable process allowing for selective hydrodeoxygenation of challenging guaiacols and syringols has been developed. It involves activation of these oxygen-rich arenes with cheap acetic anhydride followed by nickel-catalyzed hydrodeacetoxylation of the guaiacyl and syringyl acetates.[5] The acetate is a challenging leaving group given the long standing problem of chemoselectivity for Ar-OAc versus ArO-Ac bond cleavage. The selective cleavage under our reaction conditions has been rationalized based on mechanistic experiments and DFT calculations.

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CS&M-O15
Transformations of phosphonochloridates to phosphonates and phosphonamidates under mild coupling conditions

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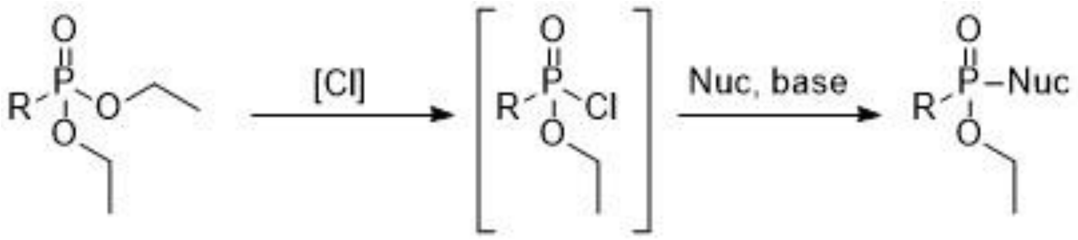
Keywords: organophosphorus chemistry; amide coupling; phosphonamidates

Organophosphorus compounds have been widely investigated for use as pharmaceuticals, flame retardants, lubricants or pesticides. Phosphonamidates in particular have recently received significant attention due to their use in antiviral drugs such as tenofovir alafenamide. However, the synthesis of phosphonamidates is by no means straightforward with multiple steps, low temperatures and dry conditions being typically required.

In this work, we present a mild coupling method to readily access a variety of organophosphorus compounds, starting from phosphonates. According to this protocol, phosphonates are first chlorinated under mild conditions, to yield the corresponding phosphonochloridates, without side products. Subsequently, these building blocks can be coupled to the desired nucleophilic partners at room temperature in the presence of bases. The scope of different phosphonester groups and alkyl groups is also studied. These relatively straightforward and mild conditions could enable efficient, sustainable synthesis of a wide range of novel end products with their applications as e.g. pharmaceuticals or agrochemicals.



CS&M-O16

Defective UiO-66 metal-organic frameworks as aldol reaction catalysts: Impact of surface defects on activity and selectivity

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Keywords: MOFs; aldol condensation; defect engineering

Aldol reactions are among the most important C−C coupling reactions in chemistry and biology. It is a well-known reaction in the fine chemical and pharmaceutical industries. Moreover, a bright future has been forecasted for this reaction in the transition from a fossil resources based society to a more sustainable one [1]. As a result, it has recently been an upsurge of interest. Great success has been achieved by a variety of basic homogenous catalysts such as KOH, Ca(OH)2 and NaOH. However, several difficulties and dangers are still associated with such catalysts due to the environmental risk and challenges in separation from the final product.

Moreover, this reaction has severe limitations due to the difficulties controlling the undesired mixture of products. For example, the base catalysts used for the initial ketone deprotonation are often also active in undesired consecutive/parallel reactions. Therefore, the potential role of acid-catalyzed aldol condensation reactions has been investigated over several catalysts.

Unlike several basic catalysts, acid catalysts, especially solid ones, seem to catalyze aldol condensation reactions selectively, avoiding undesired polymeric compounds' formation [1]. Therefore, in the present work, it seemed of interest to examine acid-catalyzed aldol reaction in more detail over UiO-66. The catalytic performance of this MOF is typically benchmarked with other base or acid solid catalysts, particularly considering Zr-based materials such as Zr-SBA-15; and Zr-Beta. Furthermore, this MOF is considered one of the milestones in the field of catalysts due to its thermal, chemical, and mechanical stability [2,3]. UiO-66 is built of hexanuclear secondary building unit (SBUs) [Zr6O4(OH)4] clusters with 12 BDC (BDC = 1,4-benzene dicarboxylate) organic linkers [2]. The chosen benchmark reaction is the aldol reaction of acetone with 4-nitrobenzaldehyde resulting in 4-hydroxy-4-(4-nitrophenyl)butan-2-one as aldol product and 4-(4-nitrophenyl)-3-buten-2-one as condensation product. In addition, we have selected a series of defective UiO-66 as a catalyst in which there is only one structural difference to gain additional information concerning the relationship between defect density and activity of the catalyst.

The defective UiO-66 has proved beneficial for aldol condensation, performing better than defect-free UiO-66. Among the proposed UiO-66, UiO-66 9/12 achieved 81% conversion and 78% aldol selectivity via solvent-free experiment at 55 °C. This is due to the increased defects, and hence the accessibility and interactions of the reactants to the active sites were enhanced. Further testing of these catalysts in a continuous-flow reactor is in progress, and it is expected to yield more information about the catalyst.

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CS&M-O17
Aluminium and Acid Site Diversity during Zeolite Crystallization and Thermal Activation

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Keywords: zeolites; synthesis; mobility; crystallization; calcination; Al distribution; acidity

A vast body of literature focuses on Al and acid site behavior in catalysis upon post-synthetic treatments. In contrast, little is known on the synthetic origin of acid sites and their distribution at the sub-nanoscale. Moreover, their behavior upon calcination is often left unconsidered. This work demonstrates bottom-up rational selection criteria for synthesis of SSZ-13 (CHA) and ZSM-5 (MFI) with tuned Al and acid site distributions. It is demonstrated that Al and acid siting are mobile through prolonged synthesis duration and during thermal activation.

Zeolites have a broad range of applications in catalysis thanks to its flexible and adaptable nature, enabling a large range of synthetic and post-synthetic modifications. Many recent findings suggest that zeolite catalysis is influenced by synergistic effects (BAS-BAS or BAS-LAS) derived from acid site proximity in particular, or Al distribution, in general. [1] Numerous studies have focussed on adequate post-synthetic treatments, such as steaming or chemical leaching strategies. [2] On the other hand, delicate engineering of zeolite crystallization (synthesis) is possible with control over lattice dimensions, crystal morphology and charge deficit. Hence, synthesis is an important consideration to take into account when deliberately making application-oriented materials with tuned Al and acid site proximity.

In our work, five crystallization systems are studied yielding ZSM-5 (MFI) and SSZ-13 (CHA). They are either made via interzeolite conversion (IZC, from FAU) or using conventional synthesis routes. [3,4] Synthesis evolution is tracked for stoichiometrically identical synthesis systems, obliviate the used SDA ($1Si:0.025Al:0.35SDA^+:0.35OH^-:\sim15H_2O$). This data demonstrates the variable tendencies to assemble Al within the forming OSDA-zeolite composites.[4] Overall, aluminum was identified as key component during all aspects of synthesis: (FAU) dissolution, nucleation, assembly and maturation. The latter will be further generalized in the talk, through an in-depth comparison with literature syntheses (published).[5]

Using an established quantification method for Al proximity based on exchange with aqueous cobalt and denoted as DCC (divalent cation capacity), a variety of synthesis parameters were examined. Single-parameter variations applied during synthesis of siliceous SSZ-13 showed that both kinetic and thermodynamic components (OH content, sodium content, …) influenced Al distribution outcome.[3] Most significantly, it was found that the internal arrangement of Al in pure SSZ-13 crystals still evolves with synthesis time. Hence, Al (or T-atoms in general) are mobile to some extent after completion of crystallization. The extent of synthesis evolution varies dependent on the synthesis system (OSDA-zeolite) composition, which was previously unreported in literature. Our work adds novel insights on the synthesis processes that regulate the final acid site distributions within zeolites by taking into account the mobility of ionic charge (Al, Na, OSDA, …) and putting them in relation with the specific structural features of the frameworks.

Furthermore, Al distributions are also found to change with the calcination temperature based on Co-exchange (DCC analysis). For the latter, we engineered a low-temperature ozone activation (calcination) process for zeolites [6] enabling us to even further stretch the DCC-range on a rational basis. In parallel to Al mobility upon prolonged hydrothermal synthesis (160ºC in alkaline water), elevated calcination temperature also seem to affect the internal Al distributions.The earlier unconsidered effect of synthesis temperature may not only help to explain contrasting results found in literature, but it may also significantly enlarge the toolbox for bottom-up rational engineering of future catalysts, for example for metal intertion and metal healing applications.

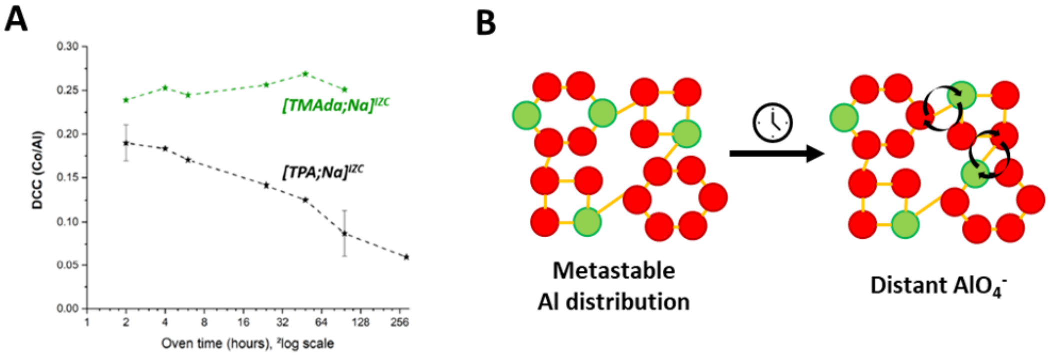

Figure 1: Evolution of Al distribution during prolonged hydrothermal synthesis: A) Divalent cation capacity (DCC, Co-exchange) for synthesis evolution for two different as-made OSDA-zeolite composites ([TPA;Na]^{IZC} & [TMAda;Na]^{IZC}).
B) Cartoon of proposed Al mobility occurring upon prolonged hydrothermal synthesis, hence after the initial crystal assembly.

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CS&M-O18

Catalyst-free solution polymerization of poly(alkylene terephthalate)s: towards high molar masses and molar mass control

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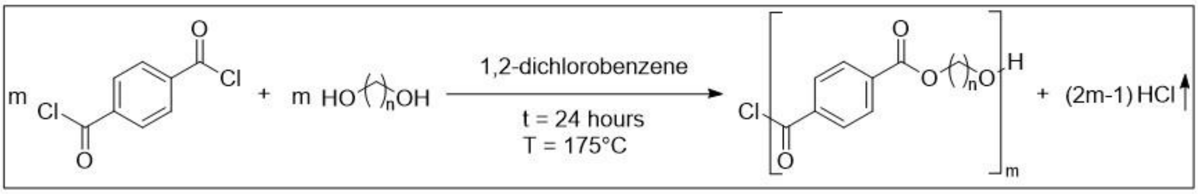
Keywords: Poly(alkylene terephthalate); polymer synthesis; molar mass; thermal characterization

Poly(ethylene terephthalate) (PET) is an established polymer serving various applications, including packaging, textile and biomedical applications. This polyester is part of the polymer family of poly(alkylene terephthalate)s (PATs). The synthesis of this polymer class typically involves a polycondensation reaction during which terephthalic acid or dimethyl terephthalate is reacted with a linear diol (e.g. ethylene glycol in the case of PET) in the presence of a catalyst. Another synthesis approach employs a ring-opening polymerization of cyclic monomers. However, both synthesis methods are associated with certain disadvantages, such as harsh reaction conditions, the requirement of a catalyst and/or limited commercial availability of the monomer.[1] Furthermore, reports about PATs with high molar masses (>100 kg/mol) are scarce and control over the polymer molar mass range is very challenging. Recently, we reported on a new synthesis enabling the synthesis of PATs using a single-step solution polymerization under milder reaction conditions in the absence of a catalyst. While this method has certain key advantages, the obtained molar mass remained limited to around 20 kg/mol.[2]

In the present research, we elaborated on our previously described synthesis route in order to obtain polymers with high molar masses and to gain control over the molar mass range. To this end, we synthesized a homologous series of PATs with various alkyl chain lengths (n = 5-12) at different comonomer ratios (i.e. ndiol/nTCL). At ratios 1.10, 1.01 and 1.00, we obtained an average DP (obtained via gel permeation chromatography) of 21 ± 2, 119 ± 24 and 153 ± 22, respectively, leading to weight-average molar masses (Mw) between 8.1 and 76.7 kg/mol. By using different comonomer ratios, we successfully obtained significantly different molar masses in a reproducible way, enabling straightforward control over the molar mass range. To obtain polymers with even higher molar masses, we further fine-tuned the comonomer ratio for PAT(n = 10). This resulted in polymers with a DP up to 616 and a Mw up to 298 kg/mol, which is among the highest values reported to date in literature.

Thermal characterization of the obtained polymers was performed using thermogravimetric analysis and differential scanning calorimetry (DSC). Degradation temperatures exceeding 300°C were observed as well as glass transition temperatures (Tg) ranging between -5.2°C and 16.0°C and melting temperatures (Tm) from 91.0°C to 148.5°C, depending on the number of methylene groups. In general, both the Tg and the Tm increase with lower number of methylene groups and an increasing molar mass. Finally, using modulated DSC, we were able to provide further evidence for the melt recrystallization phenomenon of PATs.



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Energy & Environment (E&E)

E&E-O1

Industrial decarbonization for the energy transition

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Keywords: Carbon mitigation; Energy intensive industries; Chemical and petrochemical processes; Energy transition

A considerable part of the fossil CO2 emissions comes from the industrial sector with a share of 23%, in which the energy-intensive industries, namely metal production, cement, chemicals, and manufacturing play important roles in the emission severity. Overall, the industrial sector is the second carbon emitter after energy production. Transportation and buildings are the other following sectors regarding the emission share. The main objectives of this work are the role of energy-intensive industries in energy transitions, decarbonization of petro-/chemical sectors, and introducing disruptive technologies for some petro-/chemical sectors. The primary research results of our current study revealed that although all of the innovative technologies are not available at an industrial scale or are not economically viable yet, they will play a crucial role in the energy transition in the upcoming decades.

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E&E-O2

Integrated Direct Air Capture and Electrochemical CO2 Conversion

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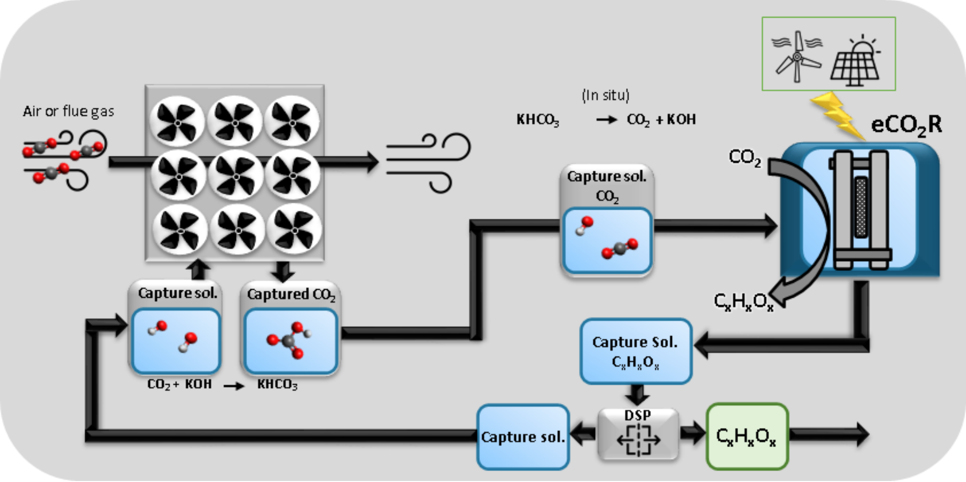
Keywords: Carbon Capture & Utilization; Electrochemical CO2 Reduction; Direct Air Capture; Bicarbonate Reduction; Zero-gap electrolyzer

Integrating the alkaline capture of CO2 from the air and the electrochemical conversion of the (bi)carbonate solution obtained in one and a single system is among the most promising strategies in the field of Carbon Capture & Utilization (CCU) technologies.[1] However, converting CO2 from bicarbonate remained a challenge for years due to the low Faradaic Efficiency (FE) and partial Current Density (CD) towards carbon products during the electrolysis of bicarbonate solutions. Recently, thanks to the advances in reactor design and in the understanding of the mechanism of bicarbonate electrolysis, promising results (FE >60% at CD >50 mA cm-2)[2] provided us with the knowhow to scale up the technology towards a proof-of-concept experimental setup where, for the first time reported, the CO2 is captured from the air in the form of a (bi)carbonate solution thought Direct Air Capture and then converted to formate and CO in a zero-gap flow electrolyzer. The results presented provide a new benchmark in the field of CCU involving the electrochemical conversion of CO2, since integrating the capture and the conversion steps is crucial for the implementation of the technology and therefore, propose a feasible procedure to reduce the global CO2 emissions.



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E&E-O3

Plasma Catalysis for CO2 Hydrogenation: Unlocking New Pathways toward CH3OH

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Keywords: Plasma; Catalysis; Plasma Catalysis; CO2 conversion; Methanol

Due to climate change there is growing interest into various strategies to convert carbon dioxide (CO2) into high-value chemicals. This is challenging as CO2 is a very unreactive molecule. An interesting route for CO2 conversion is hydrogenation to methanol (CH3OH). This route is interesting because H2 is very reactive, thus compensating for the thermodynamic stability of CO2, and because CH3OH can be used both as a fuel and a building block in the chemical industry. A possible way to enable the kinetically limited conversion of CO2 to CH3OH at ambient conditions is the combination of catalysis with a non-thermal plasma. The plasma can be used to break down the reactants into more reactive species that can then selectively recombine on the catalyst surface.1,2,3

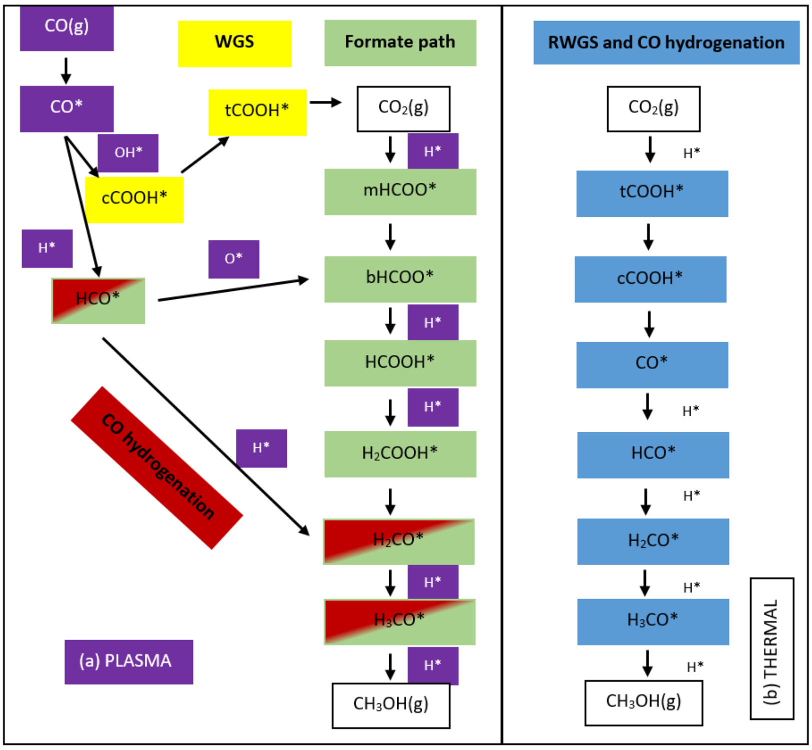
Several experimental works4,5 have been dedicated to the plasma-catalytic conversion of CO2 to CH3OH. In spite of this growing interest in plasma-catalytic CO2 hydrogenation, the underlying reaction mechanisms are still unclear. Therefore, computational modeling to study the underlying mechanisms is crucial for further optimization of the plasma-catalytic CO2 hydrogenation and for further advancement in the field of plasma catalysis in general.6

We developed a microkinetic model7 to reveal the effects of plasma-generated radicals, intermediates, and vibrationally excited species on the catalytic hydrogenation of CO2 to CH3OH on a Cu(111) surface. As a benchmark, we first present the mechanisms of thermal catalytic CH3OH formation. Our model predicts that the reverse water-gas shift reaction followed by CO hydrogenation, together with the formate path, mainly contribute to CH3OH formation in thermal catalysis.

Adding plasma-generated radicals and intermediates results in a higher CH3OH turnover frequency (TOF), showing the potential of plasma-catalytic CO2 hydrogenation into CH3OH, in accordance with the literature. In addition, CO2 vibrational excitation could further increase the CH3OH TOF, but the effect is limited due to relatively low vibrational temperatures under typical plasma catalysis conditions. The predicted increase in CH3OH formation by plasma catalysis is mainly attributed to the increased importance of the formate path. In addition, the conversion of plasma-generated CO to HCO* and subsequent HCOO* or H2CO* formation contribute to CH3OH formation. Both pathways bypass the HCOO* formation from CO2, which is the main bottleneck in the process. The most important pathways are depicted in the figure.

Hence, our model points toward the important role of CO, but also O, OH, and H radicals, as they influence the reactions that consume CO2 and CO. In addition, our model reveals that the H pressure should not be smaller than the O pressure in the plasma as this would cause O* poisoning, which would result in very small product TOFs. Thus, plasma conditions should be targeted with a high CO and H content as this is favorable for CH3OH formation, while the O content should be minimized.

In addition to the results of this model, summarized above, results of an updated version of the model, currently under development, will be presented. This model will be based on a more extensive (and at a higher level of theory) DFT data set that we have calculated ourselves. Hence, the new model will be more complete and thermodynamically consistent.



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E&E-O4

Understanding the mechanism of CO2 methanation over MgO-Ni/SiO2

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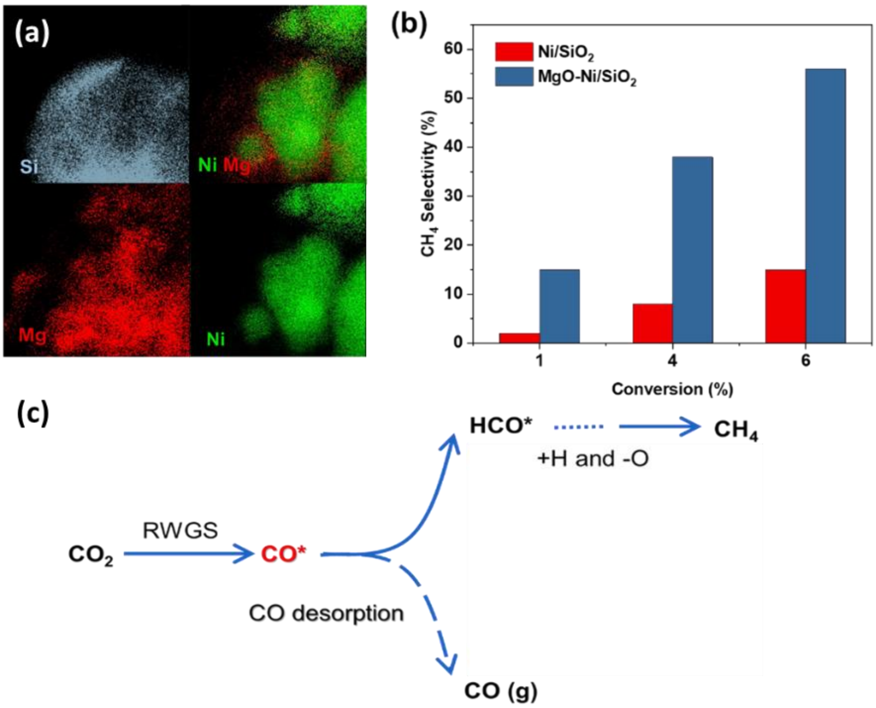
Keywords: /

Greenhouse gases produced from fossil fuel burning is the primary reason for the rising global temperature. In this respect, CO2 methanation using renewable hydrogen is particularly interesting as a carbon-neutral process because CH4 is produced from CO2, other than untapped crude oil. As catalyst, transition metal Ni with moderate performance but lower price than noble metals is a viable option. Considerable research efforts have been made in order to promote its catalytic performance and understand the reaction pathway over Ni-based catalysts. However, the mechanism is still debated due to its complexity and the unclear catalyst structure. Herein, the structure of MgO-Ni/SiO2 is unambiguously resolved and a reaction mechanism for CO2 methanation over MgO-Ni/SiO2 is proposed.

A series of MgO-Ni/SiO2 catalysts with varying MgO were prepared by sequential incipient-wetness impregnation. For a MgO loading going from 0 to 3 wt.%, the Ni metallic surface area decreases by half, indicating that MgO covered part of the metallic Ni, which is further evidenced by high-resolution STEM-EDX, see Figure 1(a). In situ QXAS during H2-TPR showed that NiO in the as-prepared samples could be completely reduced into metallic Ni.

Catalytic performance tests show that MgO addition dramatically increases the CH4 selectivity at the same CO2 conversion (Figure 1(b)). As MgO itself is hardly active, the selectivity increase must be ascribed to interaction of Ni and MgO. The formation of CH4 from CO2 might follow two pathways, direct or indirect with CO* as key intermediate. Kinetic and in situ DRIFTS tests point towards the indirect route. Moreover, transient in situ DRIFTS prove that the transformation CO → HCO* → CH4 is faster on the MgO-added sample.

This work successfully constructed a methanation catalyst, where MgO in part covers metallic Ni. The mechanism of the CO2 methanation process over MgO-Ni/SiO2 was detailed (Figure 1(c)), as well as the significance of the MgO/Ni interface, the actual active phase for CH4 formation.


(a)
Si
Ni Mg
Mg
Ni
(b)
🟥 Ni/SiO$_2$
🟦 MgO-Ni/SiO$_2$
CH$_4$ Selectivity (%)
0
10
20
30
40
50
60
1
4
6
Conversion (%)
(c)
CO$_2$
RWGS
CO*
HCO*
+H and -O
CH$_4$
CO desorption
CO (g)

E&E-O5

Green Ammonia Synthesis Process with Plasma-driven Nitrogen Oxidation and Catalytic Reduction of Adsorbed NOx (PNOCRA process)

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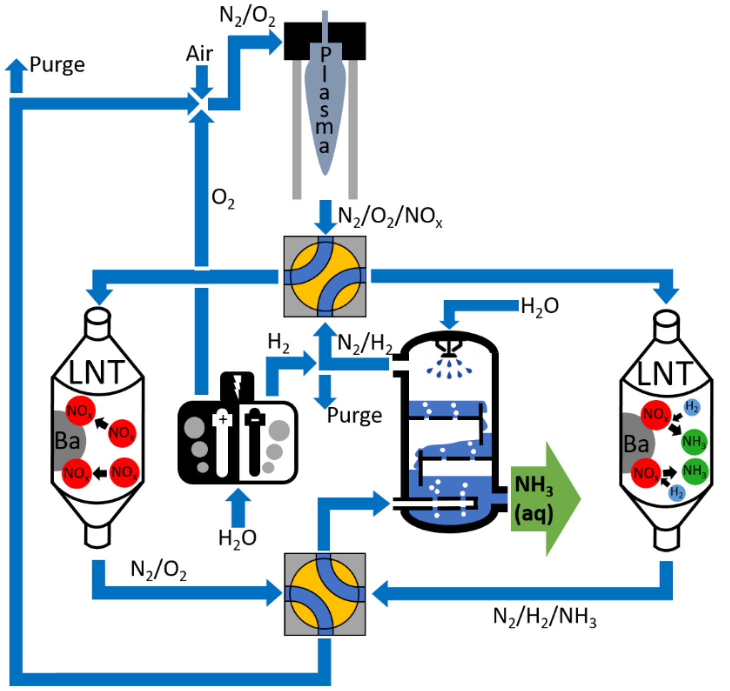
Keywords: Green Ammonia; Lean NOx Trap; Plasma Chemistry

Ammonia is an industrial large volume chemical. It is used in fertilizers and many chemical products and materials, and attracts interest as a green hydrogen carrier. The industrial production of ammonia is currently dominated by the Haber-Bosch process, which is operated only on a very large scale and typically departs from natural gas or coal. Unfortunately, the use of fossil fuels has a negative impact on global warming. Today, the Haber-Bosch process is responsible for about 1-2 % of the global CO2 emissions.

The shift from fossil to renewable energy sources has the potential to disrupt the fertilizer market and make room for alternative distributed ammonia production processes, which can be complementary with large electrified Haber-Bosch installations. The PNOCRA process (Plasma Nitrogen Oxidation and Catalytic Reduction to Ammonia) is such an alternative approach, based on the combination of Lean NOx Traps and plasma technology.

Lean NOx traps are established technology for exhaust gas treatment in the automotive industry. There, they eliminate NOx molecules from combustion engine running in oxygen rich conditions through adsorption. Periodically, the engine is run in fuel rich conditions for a short time to produce gaseous reductants, which reduce trapped NOx selectively to N2. We altered the Lean NOx trap catalyst to favor production of NH3 over N2. In the PNOCRA process, NOx is not produced in a combustion engine, but generated by a plasma process fed with ambient air.

The PNOCRA process is a new, energy-efficient route of plasma-driven green NH3 synthesis in a two-phase cycle. It produces ammonia from water, air and renewable electricity, without intrinsic CO2 footprint. The energy performance of PNOCRA is significantly better than for direct plasma-based NH3 production from N2 and H2. The new process runs at ambient pressure, which makes it especially attractive for small and medium-scale decentralized ammonia synthesis.



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E&E-O6

Exploring the reactivity of a Solid Micellar Catalyst (SOMIC) for low-temperature methanol synthesis

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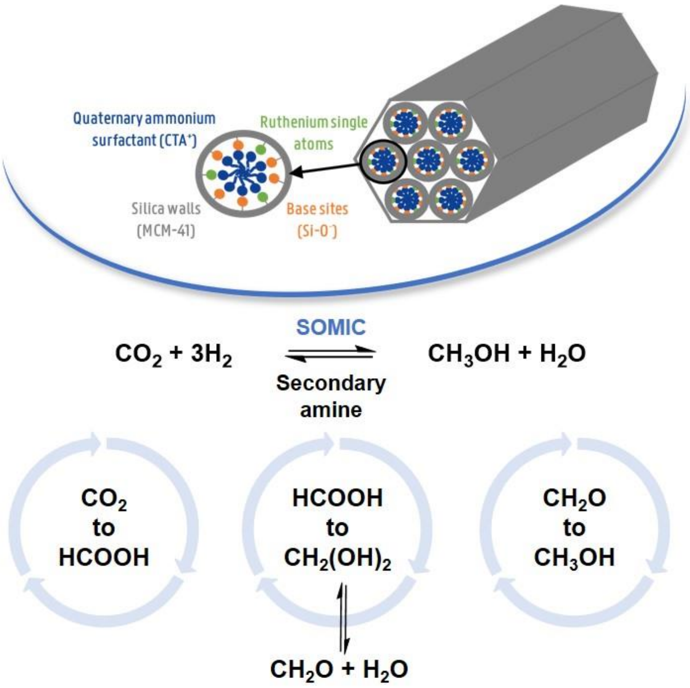
Keywords: CO2 hydrogenation; Low-temperature methanol synthesis; Single-atom catalysts

The global methanol (MeOH) market size was estimated at 98 million tons in 2021 and is expected to reach 500 million tons by 2050, based on its growing use both as a chemical feedstock, and as an alternative to crude-oil-based fuels due to its potential for energy storage and transport. Traditionally, MeOH synthesis is performed at moderate temperatures and high pressures by the use of syngas derived from fossil resources. A promising alternative is its low-temperature direct synthesis from CO2, but this route is currently hindered by the poor catalytic performance of state-of-the-art (SoA) catalysts under mild conditions. Solid micellar catalysts (SOMIC) are a new class of heterogeneous materials that consists of isolated active sites incorporated in the walls of a mesoporous matrix stabilized by surfactant molecules. The first SOMIC material, Ru(III)@MCM-4, consists of Ru(III) sites incorporated in the walls of MCM-41and stabilized by CTA+ surfactant molecules in the pores. Ru(III)@MCM-41 showed an outstanding catalytic activity for the hydrogenation of CO2 to formate in the presence of a tertiary ethyl amine (TEA) at 90°C[1], and in the selective carbonyl hydrogenation in aqueous biomass-derived feedstock at 70°C[2].

In this work, the conceptual and chemical similarity between the Ru(III) single-site catalyst and SoA Ru-based homogenous catalysts, inspired us to direct low-temperature CO2 hydrogenation over Ru(III)@MCM-41 towards methanol by the addition of a secondary amine. The SOMIC catalyst showed to efficiently hydrogenate CO2 to methanol between 60 and 90°C and at 40 bar, achieving a methanol concentration of 3.4 M. It was found that the pKa of the secondary amine plays an important role in the reaction. DFT calculations and mechanistic experiments suggest that hydrogenation proceeds stepwise via formic acid, methanediol and formaldehyde intermediates.



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E&E-O7
Sustainable Hydrogen from free sunlight and seawater using stabilized plasmonic modified TiO2

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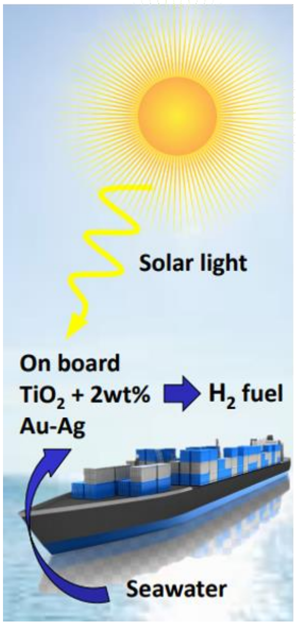
Keywords: Hydrogen; seawater; sunlight; photocatalysis; surface plasmon resonance; TiO2

In times of unstable natural gas supplies and energy costs, the world is eagerly looking for sustainable alternatives. By using photocatalysis, green H2 may be produced using free sunlight and seawater in a decentralized way [1]. However, the benchmark photocatalyst, TiO2, is only activated upon excitation by ultraviolet light (<5% of solar light), due to its large bandgap (~3.2 eV). To broaden its activity window, the concept of a plasmonic 'rainbow' photocatalyst [2] was explored, consisting of TiO2 modified with bimetallic gold-silver plasmonic composites. This photocatalyst benefits from a broadband light response, displaying an effective solar activity enhancement under AM (Air Mass) 1.5G simulated solar light. The remaining drawback of these plasmonic metals is their tendency to oxidize or destabilize, especially in harsh environments such as seawater. To ensure their stability, a Layer-by-Layer (LbL) stabilization method [3] was successfully applied. Here, a protective polymer shell is constructed with nanometer thickness control by alternatingly applying positively and negatively charged polyelectrolytes. The stabilized species showed no significant activity loss towards hydrogen gas evolution from simulated seawater, while the activity of the non-stabilized plasmonic photocatalyst fell back to the level of pristine TiO2 . Additional stress experiments (e.g. hot air treatment), high resolution high-angle annular dark-field and energy dispersive X-ray spectroscopy confirmed the protective nature of the shell, even after 10 months of ageing [4].



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E&E-O8

Techno-economic model for the application potential of hydrogen storage technologies

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Keywords: Hydrogen; energy storage; techno-economic analysis; modelling

In the last decades it has become clear that the explosive industrialisation since the Industrial Revolution has not only brought massive welfare to developed countries, but also lasting climate change, jeopardizing the sustained presence of human life in many parts of the world. To avoid climate change escalation, many countries have pledged to become carbon neutral by 2050 [1]. In order to achieve this goal, large-scale electrification, powered by carbon-neutral electricity, is necessary. Because of the current gas crisis, this electrification process is accelerated considerably. To lower their exposure to increasingly volatile gas and electricity markets, many residential owners are installing photovoltaic (PV) panels. Parallel to the attention for PV, the interest for residential heating via heat pumps is increasing [2]. Heat pumps are an essential part of the Flemish strategy for decarbonization of heating applications [3]. By combining PV and heat pumps, one can, in theory, generate enough electricity to cover the year-round need for electricity. However, in regions with cold winters, like Belgium, the combination of PV and electrical heating introduces a large seasonal energy mismatch. PV generation is most efficient in summer, while electricity is needed for heating during the winter. Figure 1 illustrates said energy mismatch for a 4-person household.

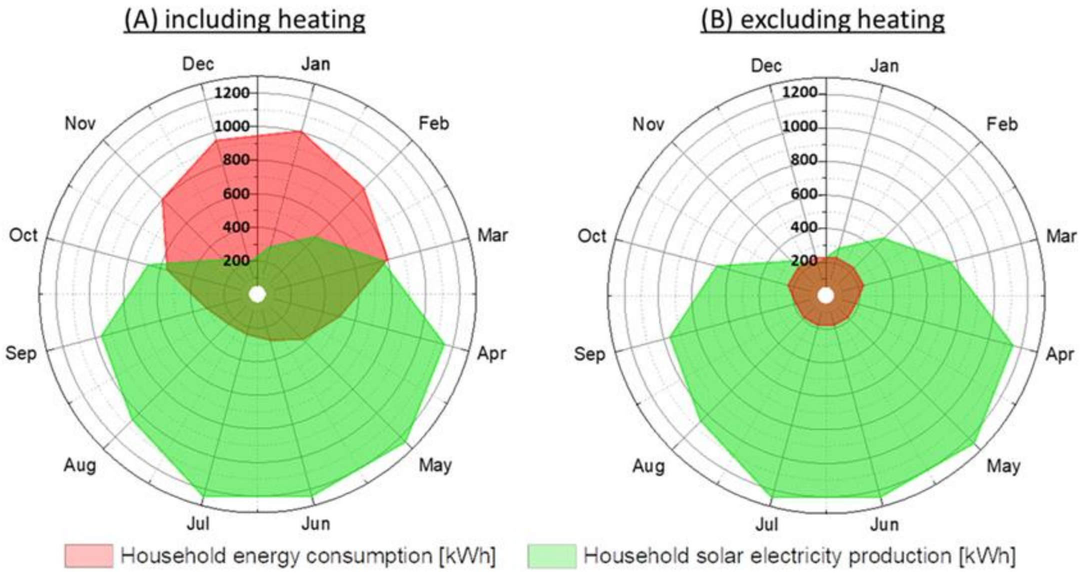

Figure 1: Seasonal energy mismatch between PV energy generation and energy consumption in a 4-person household.

Summed over many households, this kind of energy mismatch can have a large impact on grid integrity and local energy supply. Local grids are not adapted to such situations and can get congested during summer or face the risk of blackouts during winter. Seasonal storage of surplus energy in summer, to be used in winter, can resolve these issues and provide an off-grid solution to the consumer. Hydrogen is a particularly interesting energy vector for longer term energy storage, as storage capacity and power generation are decoupled, but safe storage hydrogen in a residential context remains problematic with current storage technologies.

To tackle the challenges in the developing hydrogen storage sector, we are developing a safe, new hydrogen storage technology. The goal is to store hydrogen in a pseudo-solid form in hydrogen clathrate hydrates (HCH). Clathrate hydrates are ordered water structures that can encapsulate guest molecules in cavities at high storage densities. Synthesis of HCH in bulk typically requires thousands of bars at sub-zero temperatures [5]. At COK-KAT, we are pioneering the research into the application of porous materials as 'catalyst' to alleviate pressure and temperature requirements for HCH formation.

In this work, HCH technology is applied to provide seasonal storage in a case study concerning an off-grid house. Via techno-economic evaluation in a range of macro-economic situations, the costs of this solution are compared to comparable grid electricity costs over the lifetime of the installation. The techno-economic yielded profitable results for the off-grid solution in 75% of the investigated scenarios at current behind-the-meter electricity prices.

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E&E-O9
Catch the Heat!

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Keywords: Heat storage; Heat battery; Thermochemical heat storage

Large-scale sustainable energy requires inexpensive storage technologies bridging the gap between production and consumption of energy. Thermochemical energy storage, i.e. storage of thermal energy by means of sorption/desorption of gases in bulk and porous media, is a promising technology due to high energy storage density and low cost on large scales. Within our work we explored a broad number of simple and complex metal oxide systems, as well as salt hydrates, in order to identify materials that are able to sorb water at $T < 600C$. By using a combination between DFT, advance chemical bonding descriptors and machine learning we identify descriptors that are able to predict relevant thermodynamic properties for the two classes of materials considered (metal oxides, salt hydrates).

Having as starting point the computational results obtained, we initiate the first open comprehensive database of thermochemical materials, providing a toolkit to assist researchers and engineers in materials discovery and creation of new energy storage devices. We seek thus to build an open bridge between material scientists, engineers and policymakers in the field of thermal energy storage, in order to share data and tackle collaboratively society challenges.

E&E-O10

Innovative battery materials: it's all about chemistry!

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Keywords: battery; inorganic chemistry; synthesis

Batteries are ubiquitous in our society and can be used in many applications, such as electric vehicles and stationary energy storage. Further progress in the development of batteries relies on the synergy between concepts from chemistry, physics and engineering. Creative chemical synthesis processes for the electrodes and electrolyte are a key factor in improving the functionality of battery technologies and pave the way toward a more sustainable future. This presentation will showcase a number of selected examples, where chemical approaches were used to improve the electrochemical performance and/or sustainability of current and upcoming battery chemistries.

Although commonly used in lithium-ion batteries (LIBs), the mining, refining, and processing of cobalt causes a range of detrimental societal and environmental impacts. Therefore, extensive research was performed within the Horizon 2020 COBRA project to produce a positive electrode material for LIBs that does not contain any cobalt but still reaches a high energy/power density and cycle life at a competitive cost. In a different research path, core particles of positive electrode materials were coated with a shell of a material with high conductivity, thereby enhancing their energy and power density. The synthesis of core-shell particles can also enable an improved battery cycle life.1,2 Creative chemical approaches were also used to synthesize durable negative electrode materials for sodium-ion batteries (SIBs), making use of a carbothermal reduction reaction to form a phase which can otherwise only be formed in a cumbersome synthesis method.3

The electrolyte component of batteries should have a high conductivity for ions. Conventional electrolytes are highly flammable, limiting the safety of battery operation. To improve the safety, a nonflammable class of liquid electrolyte was developed for SIBs. The combination of experimental and computational studies allowed the optimization of the coordination structure of deep eutectic solvents (DESs) as viable electrolyte alternatives. They can offer a more durable electrochemical performance compared to conventional electrolytes.4 The development of solid electrolytes for battery applications may enable the safe use of metallic anodes, thereby offering the possibility to drastically improve the energy density. Therefore, DESs were incorporated into inorganic and polymeric backbone structures, compatible with high-energy density electrode materials. This new class of solid electrolyte for battery applications was termed eutectogel and consists of inexpensive and mechanically optimized electrolytes for next-generation solid-state batteries.5,6

This work was supported by Horizon 2020 LCBAT-5 COBRA project 875568 and by Research Foundation Flanders in several projects and mandates. Furthermore, the work received the support of the European Union, the European Regional Development Fund ERDF, Flanders Innovation & Entrepreneurship and the Province of Limburg (project 936).

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E&E-O11

Technical and Economical Aspects of Advanced Biofuel Production and Separation

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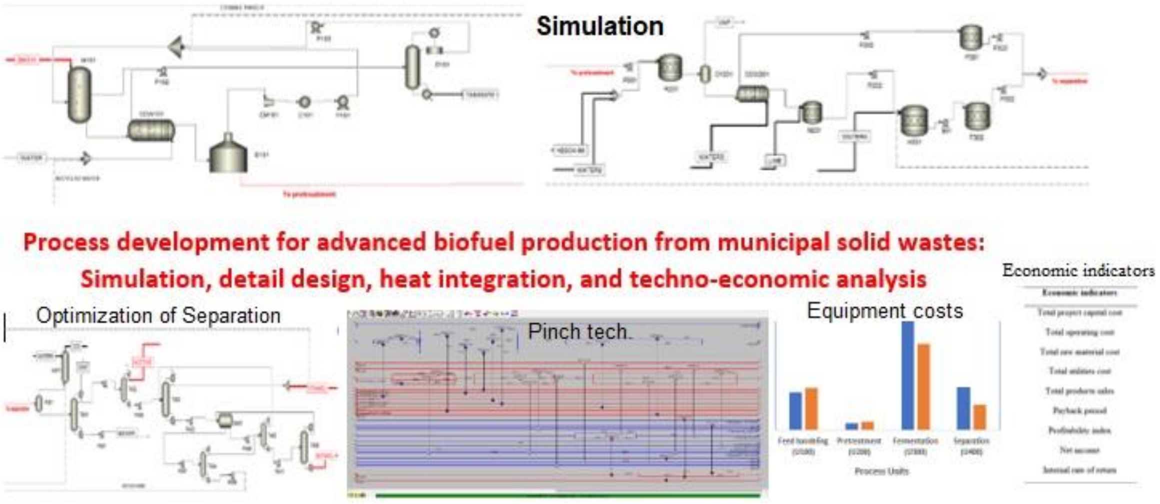
Keywords: Municipal Solid Waste; Renewable Energy Recovery; Biobutanol; Advanced Separation; Techno-economical Analysis

Biobutanol is a drop-in advanced biofuel with several advantages compared with other fuels and biofuels, e.g., bioethanol. Butanol can be produced from different resources like municipal solid waste through acetone, butanol, and ethanol fermentation. However, this process is highly complicated and includes different units, including feed treatment and detoxification, lignocelluloses pretreatment, fermentation, and products separation and purification. In this study, all the processes were simulated, designed, and optimized and the whole process was economically evaluated using Aspen Plus, Aspen Economic Analyzer, and Aspen Energy Analysis. One of the most important challenges with conventional units is the highly energy demanding separation, which is due to the low concentration of products. We tried to reduce the energy consumption of the process by using Pinch technology. The results indicated that heat integration could significantly reduce the utility consumption and improve the economy of the process; however, the process is still not economically feasible. We also implemented a novel adsorptive separation system to reduce the capital cost of the process and improve the economy of the process. The results indicated that the advanced separation systems can significantly improve the economy of the process.



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E&E-O12

Characterization of degradation products from Advanced Oxidation Processes using Temperature Responsive Comprehensive LCxLC-HRMS

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Keywords: /

Contaminants of Emerging Concern (CECs) are an expanding category of molecules identified in water, air and soil that comes from both domestic and industrial activities. CECs have high resistance to current water degradation technologies, they are persistent, and they induce toxic effects in aquatic and terrestrial ecosystems. Novel technologies that provide a promising alternative to current physico-chemical and biological processes are Advanced Oxidation Processes (AOPs). AOPs are aqueous phase oxidation processes based on the formation of species with high oxidation potential, like the hydroxyl radical (·OH), that interact with the contaminants to lead to less toxic compounds, more susceptible to bioremediation and easier to mineralize into CO2 and H2O. To assess the efficiency of AOPs is fundamental to identify the intermediates, establish the toxicity and quantify the contaminants removal as well as the degradation products formation. Powerful and sensitive analytical techniques are essential for this purpose.

Comprehensive 2D-LC (LCxLC) is a well-established separation technique for complex samples analysis, mainly thanks to its high peak capacity. Nevertheless, there are some drawbacks in LCxLC. The analysis time may be long, the system configuration is complex, the modulation introduces dilution between the first dimension (1D) and the second dimension (2D) and the second dimension high flow rate (up to 5 mL/min to have a fast cycle time necessary for the 2D separation) it is not compatible with the mass spectrometer. To overcome these problems, in this work, we use Temperature Responsive Liquid Chromatography in the 1D with Reversed-Phase LC in the 2D (TRLCxRPLC). The purely aqueous separation method for the 1D TRLC column allows for complete refocusing in the second dimension and it shows orthogonality with RPLC. To improve sensitivity, a second dimension column with a small diameter (1 mm) is selected. This allows direct connection to the MS thanks to the use of a lower flow rate. The method is demonstrated with carbamazepine as an example compound. Carbamazepine (CBZ, 5-H-dibenze[b,f]azepine-5-carboxamide) is a pharmaceutical used as an antiepileptic, one of the most detected in WWTP (Waste Water Treatment Plants) effluents, surface water and drinking water because it is refractory to biological treatment, and many conventional processes are inefficient for its removal.

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E&E-O13

Identification of synthetic antioxidants in consumer products through LC-QTOF-MS

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Keywords: Synthetic antioxidants; Food contact materials; High-resolution mass spectrometry; Chemicals of emerging concern

Synthetic antioxidants (AOX) are a group of chemicals, ubiquitous in our life with limited information on human exposure and toxicity, making them contaminants of emerging concern. AOX are additives added to e.g. plastics, personal care products, adhesives and paints. As they are not chemically bound to the matrix, they may migrate into the environment, becoming readily available for human exposure. To investigate human exposure, it is necessary to identify the AOX present in the (indoor) environment. However, AOX are not stable as their primary function is to protect the products against ageing by undergoing oxidation themselves. For this reason, the identification of AOX should be performed at the source of the exposure, the consumer products.

The present study aimed to identify two major groups of AOX, the high molecular weight synthetic phenolic antioxidants (HMW-SPA) and the organophosphite antioxidants (OPAs). Different groups of consumer products with a focus on the highest potential contribution to children's exposure deriving from the indoor environment were studied. Rubber and plastic toys have been analysed as a potential exposure pathway due to the mouthing behaviour of children. In addition, more than 40 food contact materials (FCM) were selected because AOXs may leach into food. AOX have been identified in several plastic polymers, among them recycled plastics and biopolymers, such as polylactic acid (PLA) and thermoplastic starch (TPS).

Sample preparation was performed by grinding the plastic samples to increase the extraction surface, followed by ultrasonication in acetonitrile and vortexing. Further analysis was performed by liquid chromatography coupled with high-resolution mass spectrometry (LC-HRMS). By employing suspect screening, consumer products were screened for 90 AOX, resulting in a comprehensive study on consumer products. To ensure correct identification, data analysis included fold change analysis ($FC<5$) to exclude blank contaminated features. In addition, MS/MS spectra were matched with in house libraries, Open Access databases (MassBank, MZCloud) and with spectra predicted for plausible candidates (by ACD/MS Fragmenter). This allowed for the best confidence level as proposed by Schymanski et al. [1].

In conclusion, this study gives a first overview of the synthetic antioxidants present on the Belgian market. These crucial findings fill the knowledge gap and allow for accurate future assessment of human exposure pathways.

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E&E-O14

Lignin-Supported Heterogeneous Photocatalyst for the Direct Generation of H2O2 from Seawater

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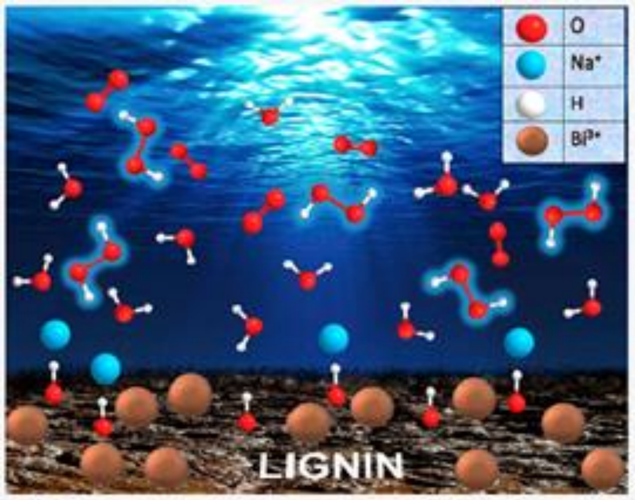
Keywords: Lignin; Hydrogen peroxide; Seawater; BiOBr photocatalyst

The development of smart and sustainable photocatalysts is in high priority for the synthesis of H2O2 because the global demand for H2O2 is sharply rising[1]. Traditional synthesis of H2O2 via the anthraquinone method is associated with the generation of substantial chemical waste as well as the requirement of a high energy input[2]. In this respect, artificial photosynthesis of H2O2 from H2O and O2, as a sustainable method, has aroused widespread interest[3]. Considering seawater accounts for 97% of the water in our planet, it is highly desired to utilize the most earth-abundant seawater instead of precious pure water for the practical production of H2O2. However, most of the existing photocatalysts suffer from serious salt-deactivated effects (salts containing in the sea water) with huge consumption of photogenerated charges, which severely limit their application in seawater[4]. Considering this, we have developed a sustainable heterogeneous photocatalyst, derived from lignin, which showed an excellent reactivity toward generating H2O2 directly from seawater under air[5]. In fact, in the presence of this catalyst, we have been able to achieve 4085 µM of H2O2. Expediently, the catalyst has shown longer durability and can be recycled more than five times to generate H2O2 from seawater. The critical advancement of this report is the demonstration of lignin as a magnifier of the photocatalytic activity for H2O2 production from seawater. Finally, full characterizations of this smart photocatalyst and a detailed mechanism have been proposed based on the experimental evidence and multiscale/level calculations. This work opens a route to provide efficient and practical catalysts for photoproduction of H2O2 in real seawater.



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E&E-O15
Template synthesis of fibrous catalysts for environmental application

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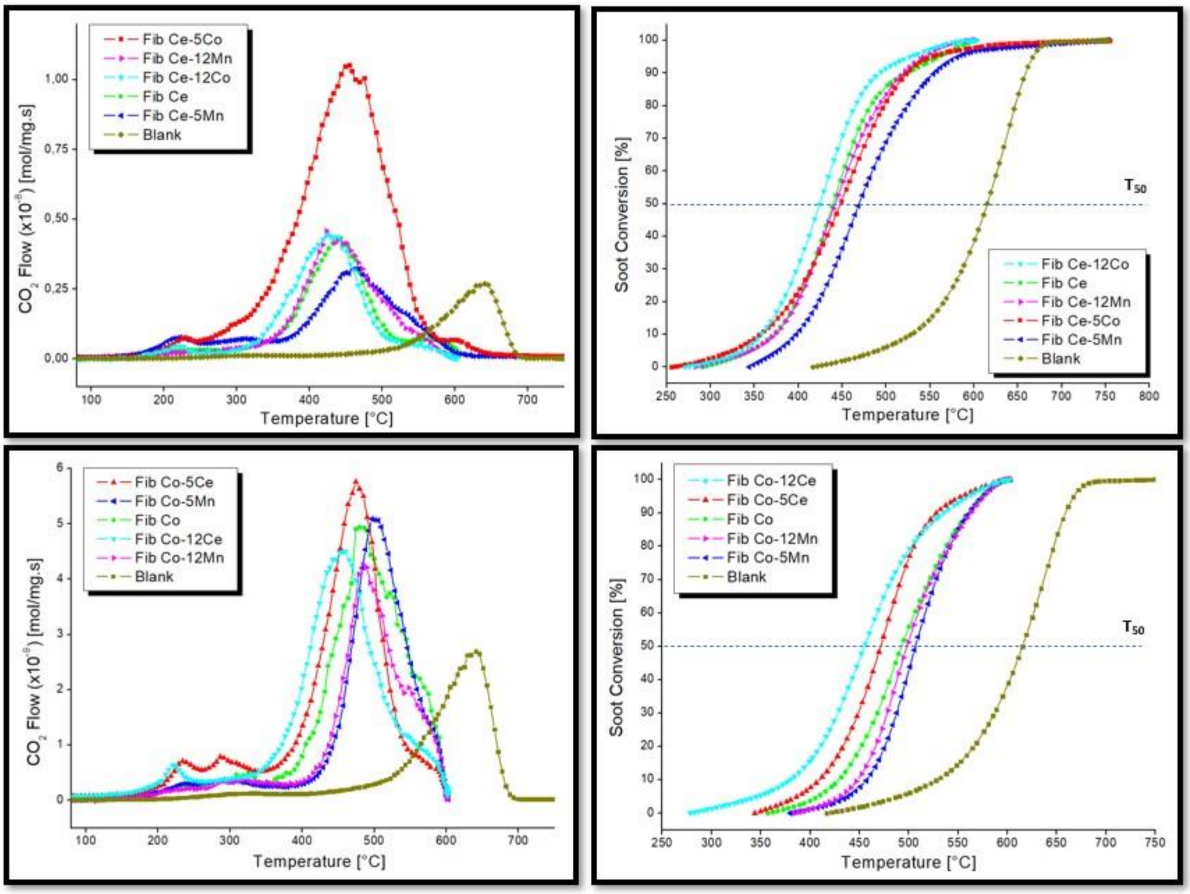
Keywords: Template; fibers; environment; pollutants; oxidation; soot; VOCs.

The world is facing a unique challenge regarding climate change: the search for cleaner technologies and, in the meantime, more efficient mitigation of environmental pollutants. Particulate matter (PM) and volatile organic compounds (VOCs) fall in this category, and they pose a serious threat for living beings and global warming [1]. Soot is mostly emitted from diesel engine exhaust gases and was chosen as a representative PM for this study [2]. On the other hand, benzene was selected, as an aromatic type of VOC. The aim of this work is to create fibrous catalysts that can abate both pollutants mentioned.

One topic that has been of relevance in recent years is the use of biotemplates as a starting point for the synthesis of heterogeneous catalysts [3]. Mother nature provides us with very sophisticated morphologies that can be retained when the template is removed [4]. This biomorphic method does not require endless steps of preparation nor solvents, it is economical, environmentally friendly and waste free.

Cotton was utilised as biotemplate to create micro-sized catalytic fibers. First, pure CeO2 and Co3O4 fibers were synthesized, followed by wet impregnation of active elements (Mn, Co, Ce) in different quantities. The catalysts were tested in the reactions of soot combustion (TPO) and benzene total oxidation. The best activity for the former reaction was obtained for ceria fibers with 12 % wt. of Co. On the other hand, for the second reaction, ceria fibers with 12 % wt. of Mn were the most active.

Characterization techniques such as ICP, XRD, ATR, BET, LRS and SEM, were employed to correlate physico-chemical properties with catalytic activity.



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E&E-O16
Modeling Realistic Catalyst Nanoparticles for Fischer-Tropsch Synthesis using Machine Learning Potentials

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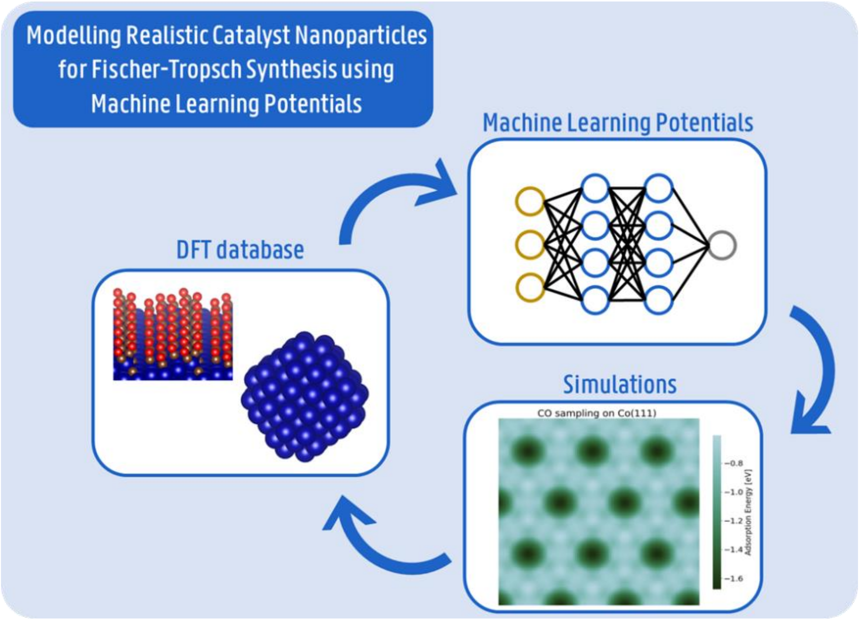
Keywords: Machine learning potential; Cobalt; Fischer-Tropsch; DFT

Catalyst nanoparticles react dynamically to the reaction environment and active sites often only form under reaction conditions. Efforts to understand and quantify this dynamic behavior are emerging both experimentally and computationally. Cobalt nanoparticles are an interesting model system for this dynamic behavior. Cobalt is the preferred catalyst for Fischer-Tropsch synthesis, the largest-scale catalytic process. Yet, the structure of the nanoparticles and, related, the nature of the active sites and the reaction mechanism remain poorly understood. Surface science experiments and Density Functional Theory (DFT) calculations suggest that the Co(0001) surface reconstructs under reaction conditions, while operando TEM images of the working catalyst and Wulff particle structures based on DFT calculations show limited changes1, 2. DFT-based calculations of clean nanoparticles suggest the presence of edges and corners, while the effect of CO on this structure has not been studied3, 4. Modeling the structure of realistic (~6 nm) CO-covered cobalt nanoparticles requires ~10000 atoms and is beyond DFT. To describe such large systems, we have developed Machine Learning Potentials (MLP) for the Co/CO system.

The Co/CO MLPs are based on artificial neural networks, where it is assumed that there exists a unique functional relationship between the atomic coordination and the potential energy5. The current generation of MLPs employs a neural network for each atom, which makes it possible to use a varying number of atoms. This new way of modeling makes it possible to scan the complete potential energy surfaces in just a few minutes, much faster than with DFT.

To train this neural network, a large database is needed. By employing Bayesian optimization routines and automated sampling of catalyst particles and surfaces, the database of the neural network potential is constructed6. Molecular dynamics simulations of different sized particles and surfaces are used to iteratively refine the machine learning potential in an active learning scheme. The simulations based on the Co/CO MLP describe the dynamic CO adlayer on industrially relevant cobalt catalyst nanoparticles, while maintaining the accuracy of DFT.



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E&E-O17

Effect of pH cycling and background ions on the formation of stable magnesium carbonate at low temperature

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Keywords: Carbonate; CO2 utilization; crystallization; magnesite; mineralization

Global warming is currently one of the biggest challenges the world is facing, with significant impacts on global surface temperature, sea level, flooding, spreading of diseases, ecology, fauna, and extreme weather events. During the transition towards an energy world dominated by renewable resources, an efficient strategy to mitigate this climate change is the capture, utilization and storage of carbon dioxide, the main greenhouse gas. One of the CO2 utilization methods is mineralization, which can be similar to long-term geological CO2 storage in underground formations. The mineralization of CO2 results in the formation of carbonate minerals, and its type depends on the availability of cations incorporated in the precipitated minerals. Calcite, a common calcium carbonate mineral, is easily formed at ambient conditions. However, this mineral dissolves easily in weak acid, for example in acidic rain water. Therefore, to achieve long term CO2 storage at ambient conditions, it is favourable to form minerals which are more resistant to acidic rain water. Magnesite is a stable magnesium carbonate, and would offer an excellent solution for long term carbon storage. Nevertheless, the reaction products of solutions with magnesium and carbonate ions at ambient conditions are generally metastable hydrated magnesium carbonates, such as hydromagnesite, dypingite, lansfordite and nesquehonite.

Here, we have investigated the effect of pH cycling and of background ions on the rate of stable magnesium carbonate (magnesite) formation. We hypothesize that pH cycling can help dissolve repeatedly the metastable magnesium carbonate minerals during the acid or dissolution phase, and promote the formation of the more stable magnesium carbonate minerals during the base or precipitation phase of the cycles. Our results show that we obtain significant magnesite formation after about 4 weeks of daily pH cycles in saline oversaturated fluids at 43 °C. We added ZnCl2 as background ions in a series of experiments, which acts as a Lewis acid, and resulted in a lower pH value for the acidic phase (5.7-6.1) in comparison to the experiments without ZnCl2 (6.5-7.0), whereas the base phase had a similar pH in the two series of experiments (7.9-8.3). The experiments with the lower pH acid phase resulted in 97% magnesite in the reaction product in the base phase at the end of the experiments after 36 daily cycles, whereas the reaction product of the other experiments contained besides magnesite also large amounts of hydromagnesite and aragonite.

E&E-O18

Unravelling the mysteries of arsenic in the Zenne River (Belgium): sources, distribution, geochemistry, and bioavailability

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Keywords: Arsenic; Water; Sediment; Diffusive Gradients in Thin films

The Zenne River is a small urban river that originates in the Walloon part of Belgium and crosses the densely populated city of Brussels and the industrial area downstream of Brussels. Although the river may seem average in terms of its length (105 km) and basin coverage (1160 km2), it represents a unique ecosystem which attracts attention in terms of its environmental status. Before 2000, most of the sewage generated by the population in the basin was discharged into the river without any treatment. Although the water quality of the Zenne has significantly improved in the last decades due to large investments in sewage water treatment, arsenic (As) concentrations remained unchanged and peaking concentrations were repeatedly reported by researchers in the past. However, no source of As pollution was ever found and thus the elevated concentrations of this toxic metalloid in the river remained an unsolved mystery.

For this reason, we aimed to: (i) assess the longitudinal profile of dissolved and particulate As distribution in river water; (ii) evaluate temporal changes of As in the tidal section of the river; (iii) assess As potential bioavailability using the Diffusive Gradients in Thin films (DGT) technique; (iv) investigate the geochemical behaviour of As in sediments; (v) identify the potential sources of As pollution.

To put the puzzle pieces together, we evaluated the results from various monitoring campaigns between 2010 and 2021 where the active and passive sampling of water and sediments was combined. Moreover, to assess the historical trends of water quality regarding As concentrations, and emission inventories, the data from Flemish Environmental Agency (Vlaamse Milieu Maatschappij – VMM) were evaluated.

Our study shows that the concentrations of As in water and sediments sharply increase in the downstream part of the Zenne River and reveals the pattern of large temporal variability caused by the tidal influence. The geochemistry of As in sediments is governed by reductive mobilization of Mn end Fe oxyhydroxides but only a small portion (7–34%) of dissolved As present in sediments porewater is labile as determined by the DGT technique. The calculated benthic flux accounts for less than 1% of the input to the river. However, we were able to identify the point source of As that is located in a surprisingly small tributary of the Zenne. The individual clues that led to this discovery will be presented at the conference.

Chemical Processes & Reactor Technologies (CP&RT)

CP&RT-O1

Demystifying the thermodynamics of furfural derivatives aiming at improved separation process design

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Keywords: /

Biorefineries in which inedible feedstock biomass is converted into platform molecules, will play an essential role in the transition from a fossil based towards a circular economy. Lignocellulosic biomass is the cheapest inedible biomass source. Moreover, it is highly abundantly available, as a result, it has been identified as the most scalable and economically viable bio-source.[1] Lignocellulose is composed of three major biopolymers, i.e., cellulose, hemicellulose and lignin. After separation of the three biopolymer fractions, lignocellulose can be converted in a large variety of chemical building blocks or platform molecules, by means of depolymerizations and subsequent chemical transformations. However, before these platform molecules can be further processed into the desired products, such as polymers or pharmaceuticals, the components present within the reactor effluent need to be separated from each other. For the design of such separation processes, adequate predictions of the phase equilibria, i.e., vapour-liquid (VLE) and liquid-liquid equilibria (LLE), of the involved bio-molecules are required. To describe these equilibria several thermodynamic models, e.g., activity coefficient models, such as Wilson,[2] or the non-random two-liquid model (NRTL),[3] and equations of state such Hayden O'Connell (HOC),[4] have been developed. These models make use of binary interaction parameters, which need to be determined from experimental phase equilibria data. This means that mixtures containing components whose phase equilibria have not yet been experimentally investigated, cannot be described using these methods. Group contribution methods can provide a solution for this, as they allow to predict the binary interactions based on the functional groups present in the different components. However, as these methods were originally designed for molecules derived from the petrochemical industry, the thermodynamic properties of bio-molecules, which are often comprised of multiple heteroatoms and/or functional groups in contrast to petrochemicals, are typically not well-described by these methods.[5]

Therefor first principle methods, such as COSMO-RS (conductor like screening model for real solvents),6 are widely regarded,[7,8] since they allow the prediction of chemical potentials of compounds in a mixture independent of experimental data, or without assuming group additivity. The goal of this work is to verify if COSMO-RS to well describe the VLE's for a mixture of industrially relevant furfural derivatives.

Method

The following compounds have been investigated within this work: furfuryl alcohol (FA), 2-methylfuran (MF), tetrahydrofurfuryl alcohol (THFA), cyclopentanone (CP), 1,4-pentanediol (14PD), THF, γ-valerolactone (GVL) and furfural itself. In this work a selection of 10 binary mixtures is analysed experimentally. In order to be representative, in this selection all functional groups present in the entire product pool are accounted for. The isobaric VLE's of the 10 considered binary mixtures are measured using a Pilodist VLE 110, either at atmospheric pressure or at 100 mbar. Samples of the liquid and condensed vapor phase were analyzed with density measurements on the Anton Paar DMA 4500 density meter or GC-FID measurements on the Shimadzu GC2010-pro. The thermodynamic consistency of the experimentally acquired VLE data were assessed using the Redlich-Kister test [9] and the Fredenslund test.[10]

On the other hand VLE simulations were performed using COSMO-RS. This was done in COSMOtherm X, based upon the σ-profiles of the components calculated with Gaussian 16. Finally, the results of the experimental and simulated VLE’s were compared by means of the mean percentage deviation (MPD) of the temperature and the liquid and vapour mole fractions, for given mole fractions and temperatures respectively.

Results and discussion

A set of 10 experimental binary VLE’s was acquired and proven to be thermodynamically consistent according to the consistency tests that were performed. Given these verified data, the COSMO-RS data for these mixture could be assessed. In Figure 1 the comparison of some of the simulated and experimental VLE’s is visualized. It is clear that the simulated and experimental data correspond well, they show the same trends, the konodes are of the same order of magnitude, no false azeotropes are predicted, etc. A more detailed investigation shows that for FA/CP, CP/THF and GVL/THFA a shift of the data is present, it is however impossible to unambiously assign this shift to a deviation in temperature or of the mole fractions. Meanwhile, for GVL/MF, the konodes of COSMO-RS are smaller than the experimental ones, indicating that COSMO-RS accounts for slightly more adhesion than was observed in the experiment. In order to ascertain that the observed deviations are not abnormal errors, but merely usual divergences, it is important to analyse the results numerically as well. Here, the MPD’s confirm that the simulated data agree well with the experimental data, as all appeared to be under the premised 5% limit. Therefore the model is considered reliable and accurate in predicting the VLE’s of the considered compounds.

Conclusion

The MPD calculations show that COSMO-RS is able to predict the VLE’s of the considered group of furanics very well. Hence, in future work, these COSMO-RS predictions can be used to obtain more accurately designed separation processes for these bio-based compounds.

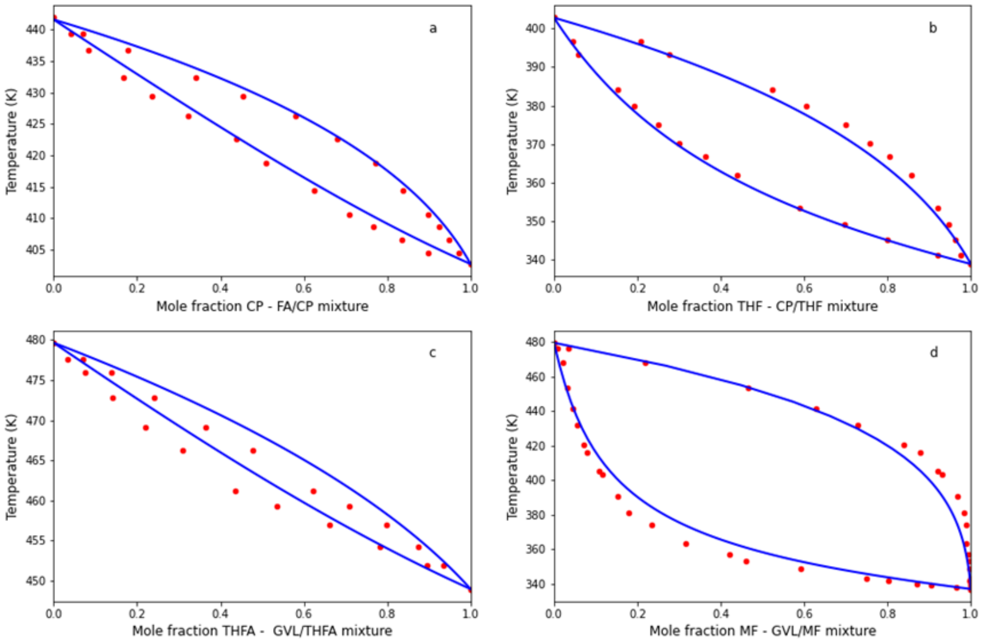

Figure 1. Comparison of the COSMO-RS results (blue) with the experimental VLE's (red), at 1013 mbar.

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CP&RT-O2
Numerical analysis to reduce axial dispersion with active lateral flow

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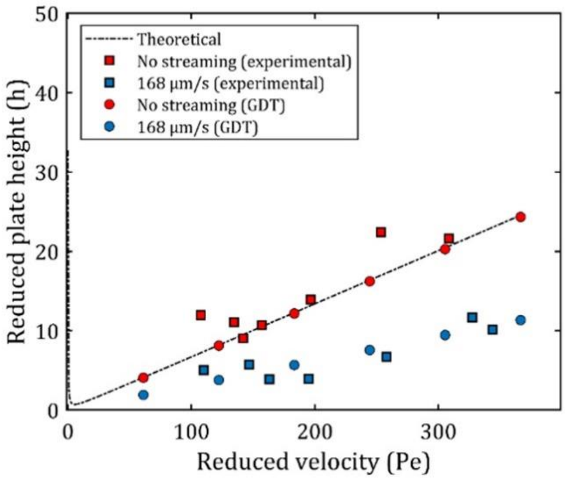
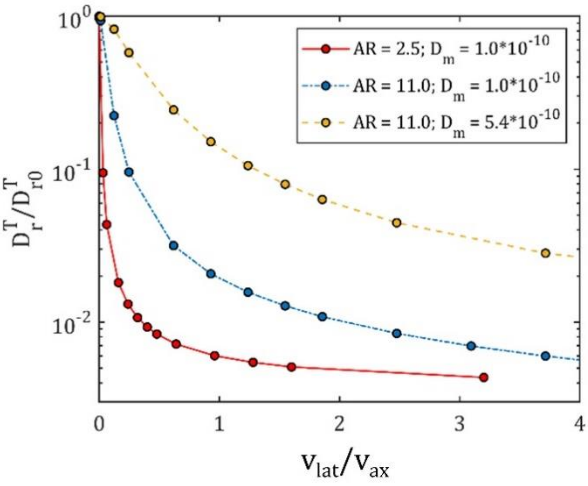
Keywords: Axial dispersion; CFD; General dispersion theory

Recently our group has introduced several methods to generate lateral fluid flow in micron-sized channels. It has been shown that this lateral flow can elegantly be used to reduce axial dispersion in analytical separations or continuous flow reactors [1,2]. To steer future developments, further investigation of channel geometry, diffusion coefficients, axial and lateral flows on dispersion is needed. In this work, a two dimensional numerical framework, based on the general dispersion theory (GDT) is presented, allowing to evaluate the effect of lateral vortices on axial dispersion.

The proposed GDT model was validated by a comparison with experimental observations, showing a good agreement (Sres = 3.88) (Figure 1, left). The model was further used to evaluate the effect of channel geometry, diffusion coefficients and lateral flow. Figure 1(right) presents the ratio of dispersion coefficients with and without lateral vortices in function the ratio of velocities for rectangular microchannels of uniform width (375 µm) and several combinations of depth to width aspect ratio AR, and solute diffusion coefficients Dm. We see that increasing either AR or Dm results in a less significant relative reduction of the dispersion coefficient. These trends reflect the fact that the secondary flow only influences the convective 'Taylor' part of axial dispersion.

These results conclude that introducing organized lateral vortices have great potential to reduce axial dispersion either in analytical separations or continuous flow reactors. This can be used to generate a more uniform residence time distribution and thus higher separation efficiencies, yields and product quality.





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CP&RT-O3
Synthesis of heterogeneous metal oxides catalysts by humid air plasma glidarc: study of the effect of the post-discharge

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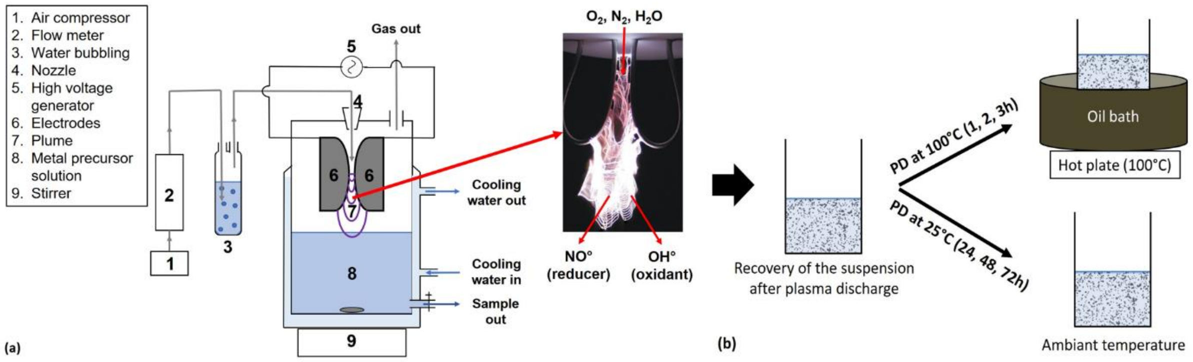
Keywords: plasma; glidarc; catalysts; oxides; post-discharge; catalysts synthesis; oxidation

In the permanent objective of obtaining greener and cheaper catalysts, plasma glidarc appears to be a promising new method of synthesis. The glidarc reactor is a system operating at atmospheric pressure and quasi-ambient temperature (Figure 1). The radicals (OH°, NO°) generated by the discharge can induce the precipitation of the corresponding metal (hydr)oxides of the precursor solutions exposed to the plasma. This method has already proved efficient for the synthesis of oxide catalysts (TiO2, SnO2, MnO2, FeOx). [1,2] For some of them (MnOx and FeOx), the effect of a post-discharge (PD) during the synthesis of these solids has been studied (Figure 1). It was observed that this step can induce new properties to the solid (metal oxide phase transformation, higher specific surface area, better catalytic activity, …). Knowing this, the aim of the research presented here is to understand the mechanism underlying the PD step, improve the understanding of plasma glidarc synthesis and optimize the method. We will demonstrate that this innovative method allows the synthesis of oxide catalysts (SnO2, MnO2, FeOx) with interesting properties that can be useful for oxidation catalysis reactions such as the degradation of polluting compounds (total oxidation of benzene).

We first explored the effect of the PD on solids undergoing this treatment. Overall, PD contributes to increase the activity of the catalysts by increasing their specific surface area and/or by decreasing the amount of "contaminating" phases, such as metal sulfate, in favor of only the metal oxide phase of catalytic interest.

Even if we know that the PD has an impact on solids synthesized by plasma glidarc, we still do not know how it operates. In the literature, different explanations are proposed such as the impact of the species created during this step (H2O2, HNO3, HNO2). [3] By UV-visible spectroscopy, HNO3 and HNO2 are indeed observed but not H2O2. However, even if HNO3 and HNO2 are effectively formed during the PD, there was still a doubt whether they had an impact on how the solid is modified. To find this out, we tried to recreate this PD step but without any of these species present (by recovering the precipitate obtained after the plasma discharge and put it into fresh water before the PD). Whatever these species are present (or not) in the medium during the PD, we still got the same type of solid. This means that the PD has purely a thermal effect and the species created do actually not have any effect on the modifications of the solid.

With this knowledge, we then suggested an optimization of the plasma precipitation procedure. Whereas classically, a precursor solution is cooled when it is exposed to the plasma discharge (Figure 1), we recreated the thermal effect of the PD by not cooling the precursor solution during the plasma exposure. Although the temperature in these conditions never exceeded 60°C, we obtained solids similar to those undergoing a PD with sometimes even better catalytic activity. This suggests that it is possible to recreate the PD effect in another way, which makes the method easier and faster.



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CP&RT-O4

Experimental assessment of the ethyl acetate synthesis kinetics by direct addition of ethylene to acetic acid on a silicotungstic acid catalyst

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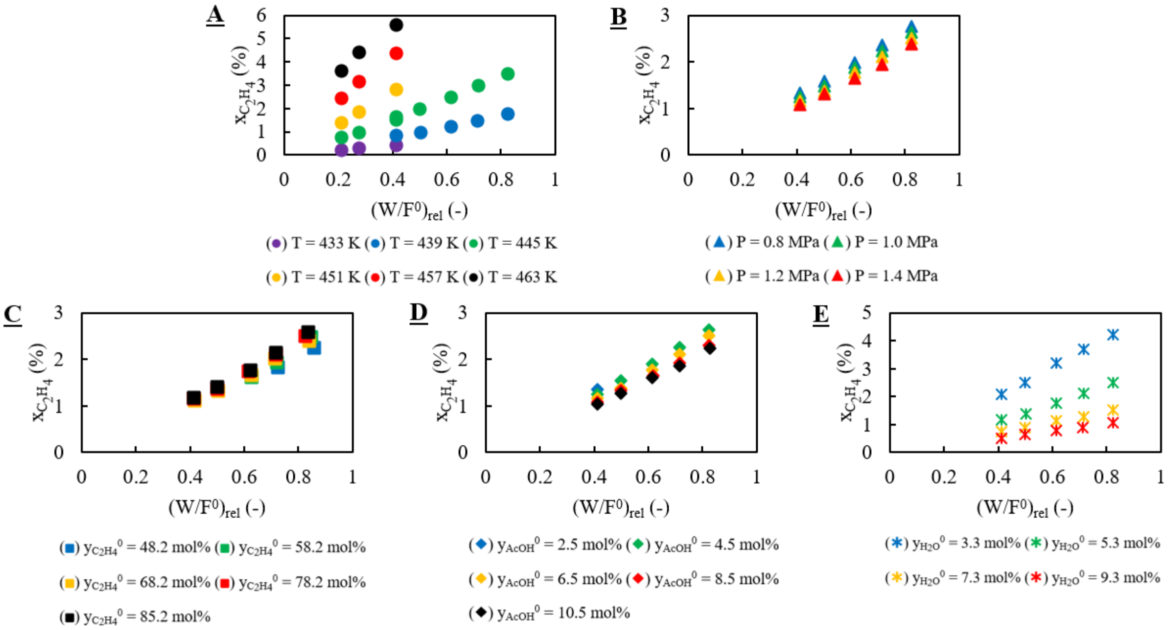
Keywords: ethyl acetate; direct addition; operating conditions; conversion; selectivity

Ethyl acetate is an important organic chemical used in glues, surface coatings, thinners, paints, inks, nail polisher removal products and as solvent in physical and chemical processes. Ethyl acetate is mainly synthesized by the esterification between ethanol and acetic acid , the Tishchenko reaction of acetaldehyde and the direct addition of ethylene to acetic acid. The direct addition is catalyzed by a solid acid such as silicotungstic acid and is commercialized by BP Chemicals and Showa Denko since the ‘90s. Due to the acidic nature of the catalyst and presence of water in the acetic acid feedstock, several byproducts, mainly ethanol and diethyl ether , but also other esters, alcohols, ethers as well aldehydes, ketones and hydrocarbons are produced.

The present work focusses on a detailed experimental investigation of the direct addition pathway towards ethyl acetate in a plug flow reactor. The effects of the operating conditions such as space time, temperature, pressure and reactant (ethylene, acetic acid and water) concentrations, on conversions and selectivities to the main products (ethyl acetate, ethanol and diethyl ether) are assessed. Experiments involving the most important reaction products in the feed were performed as well to mimic the effect of process recycles on the kinetics. The observed ethylene and acetic acid conversions varied between 0.2 to 5.5 % and 5.6 to 51.5 % respectively, while the selectivities to ethyl acetate, ethanol and diethyl ether ranged from 38.1 to 95.2 mol%, from 2.7 to 30.0 mol% and from 0.3 to 59.2 mol% respectively.

It was found that an increase in space time and temperature enhances conversions, whereas conversions decrease with pressure. A high ethylene concentration in the feed is advantageous to establish higher ethylene and acetic acid conversions, whereas a higher acetic acid and water feed concentration results in lower conversions. Co-feeding ethanol and diethyl ether results in a lower ethylene conversion, while enhancing the acetic acid conversion, whereas cofeeding ethyl acetate reduces both conversions. Selectivities are predominantly affected by conversion, resulting in a maximum selectivity to ethyl acetate at 0.5 to 1.5 % ethylene conversion, while the opposite trend was observed for the ethanol selectivity where the selectivity to diethyl ether increases monotonously with conversion. The selectivity to ethyl acetate is not affected by temperature, pressure and ethylene feed fraction, while the selectivity increases with acetic acid concentration in the feed, but decreases with water feed concentrations and when co-feeding products.

The experimental data showed that the temperature and ethylene feed concentrations can be increased to reach higher conversions without reducing the ethyl acetate selectivity. Moreover, it is beneficial to operate the ethyl acetate synthesis process at low pressure and minimize the water concentration in the feed to enhance conversions and selectivity to ethyl acetate, whereas the optimal acetic acid feed concentration is a trade-off between high conversions or a high ethyl acetate selectivity. The data and acquired insights on the reaction kinetics are essential for the construction of a kinetic model that can serve for the optimization of the operating conditions of ethyl acetate synthesis plants, that apply the ethylene-acetic acid direct addition technology on a silicotungstic acid catalyst, to reduce costs, waste and minimize impact on environment and climate.



Effect of (**A**) T, (**B**) P, (**C**) $y_{C_2H_4}^0$, (**D**) y_{AcOH}^0, (**E**) $y_{H_2O}^0$ and space time on $x_{C_2H_4}$. The reference conditions are T = 442 K, P = 1.2 MPa and C_2H_4:AcOH:H_2O:N_2 inlet molar flow ratio equal to 78.2:6.5:5.3:10.0.

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CP&RT-O5

Characterization of an acoustic streaming microreactor: uncovering the effect of acoustic streaming on crystallization

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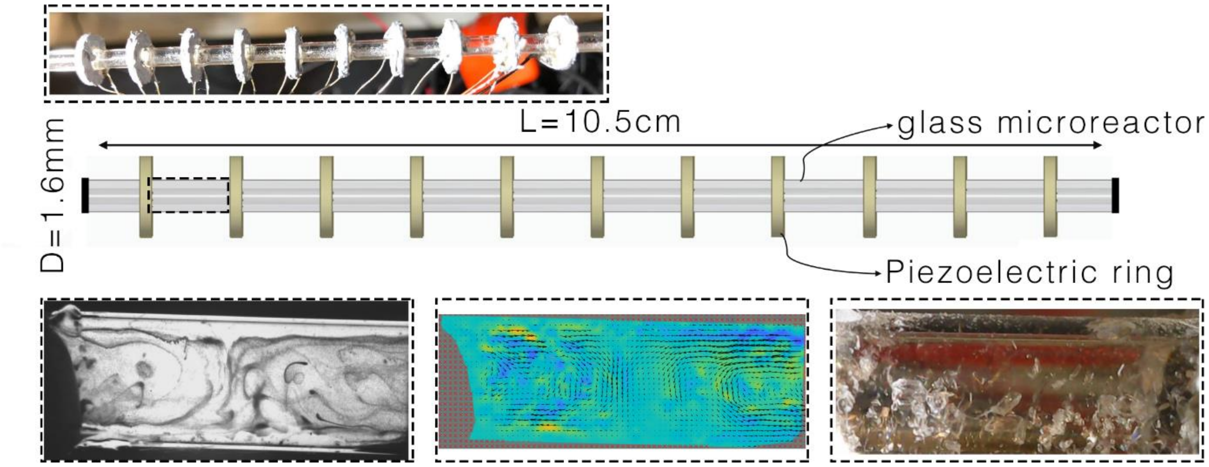
Keywords: acoustic; streaming; microreactor; crystallization; ultrasound

Microreactors are miniaturized plug flow reactors that offer several advantages compared to traditional large-scale equipment due to their small characteristic dimension and large surface-to-volume ratios. The major disadvantages of microreactors are that they are prone to clogging and have poor convective mixing. By generating streaming flows inside a reactor, some of the challenges that are associated with low Reynolds number flows can be alleviated [1]. Acoustic streaming is an example of such streaming. Acoustic streaming is caused by the viscous attenuation of an acoustic wave [1]. In microchannels acoustic streaming causes rotating vortices [1], which significantly enhances mass transfer. In this research an acoustic streaming microreactor is developed and characterized. This reactor is then used to improve and control the crystallization of an active pharmaceutical ingredient.

The microreactor is operated in batch mode, to isolate the effect of acoustic streaming from the flow effects. The microdevice presented here is based on an electrochemical microreactor with tube-in-tube design by Fransen et al. [2] and consists of a glass tube (volume=221µL) fitted with 11 piezoelectric rings, which excite a standing ultrasonic wave parallel to the surface of the reactor. The reactor can be operated at several resonance frequencies (642, 1410, and 2353kHz) and powers (1-5W). To assess the vortex formation a solution of inert polystyrene particles (2.5-2.9µm) and water (0.07 w%v) is injected into the sonicated microreactor. The particle movement is recorded using a high-speed camera and the footage is analyzed using PIVlab (MATLAB) to extract the velocity and shear field inside the microchannel. In addition, the temperature as a result of sonication is measured using an IR-camera. To determine the cavitation activity, or lack thereof, the concentration of OH-radicals present in the system is measured by terephthalic acid (TA) dosimetry [3].

The effect of low frequency ultrasound, which causes cavitation, on crystallization is well-studied [4]. In contrast, the effect of acoustic streaming on crystallization has not been extensively researched. We study the effect of acoustic streaming on nucleation for paracetamol in water crystallization. The induction time, the time until the detection of the first crystal, is measured using microscopy images. This work will contribute to the development of ultrasonic microreactors and the understanding of nucleation of small organic molecules.



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CP&RT-O6

Photometric determination of trace amounts of Al in cc. NaCl solutions used by the chlor-alkali industry - Coagulation and sedimentation studies

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Keywords: Measurement of aluminum ion; micro impurities; spectrophotometry; eriochrome cyanine R; membrane cell electrolysis

The previously widespread mercury cell technology in chlorine production has now been replaced by more environmentally friendly membrane cell electrolysis which is a BAT technology. However, this requires a much cleaner brine containing contaminants (Al, Ca, Mg, etc.) in the order of ppb at most. For this reason, it's very important to detect trace amounts of aluminum in concentrated saline media in the simplest and fastest way. Our developed analytical method provides an opportunity for this.

During the analytical procedure, a coloured complex ion is formed from the dissolved aluminum content of the sample using eriochrome cyanine R (ECR) ligand in buffered pH medium. The sensitivity of the measurement is increased by adding quaternary ammonium salt (cetyltrimethylammonium bromide). The effect of rock salt interference was eliminated by proper calibration. In our work we examined the dependence of the absorbance signal on temperature, pH, time elapsed after the addition of reactants, the order of addition of reactants, the salinity of the medium, furthermore, we examined which wavelength-absorbance values give the highest sensitivity and the best fit (highest R-square value) in case of linear calibration.

Based on our studies, it can be clearly stated that increasing the salinity of the medium significantly improves the sensitivity of the measurement. In our experience, the measurement is the most sensitive at pH 6-6.5, but the formation of the maximum analytical signal is significantly faster at pH 5. The effect of temperature on the measured absorbance is small in all cases. The dosing sequence of the substances has no effect.

Using our developed measurement method, we performed experiments to reduce the aluminum content of concentrated brine used in chlorine production. Based on these preliminary experiments, which will be presented in the Conference, the analytical method we have developed is suitable for the study of the reduction of the aluminum content and the factors influencing it. The results may contribute to improving the performance of membrane cell rock salt electrolysis in the future.

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CP&RT-O7

Characterization of flows in microchannels with scanning 3D µPIV

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Keywords: 3D Particle Image Velocimetry; Fluorescence Microscopy

Particle Image Velocimetry (PIV) is a well-known method for the experimental determination of fluid velocity fields [1]. It involves tracking particle distribution over time, thereby reconstructing the local velocity fields. Classical PIV is an in-plane measurement technique and allows the reconstruction of 2-dimensional velocity fields. Different techniques have been developed to reconstruct 3-dimensional flows in microfluidic devices. Traditional confocal microscopy [2] techniques have been adapted to rapidly change the focal plane [3, 4]. Such techniques, however, only gives 2-dimensional velocity components in a 3-dimensional volume [5]. Stereoscopic µPIV is difficult to implement and only applies to limited depth of focus (DoF) [5]. More recently, the implementation of computing algorithms allowed the development of defocusing µPIV [5] and General Defocusing Particle Tracking (GDPT) [6]. These techniques allowed increasing the spatial resolution but only apply to monodisperse particles and are accurate for particles larger than 0.5 µm over a depth of focus of the order of 100 to 200µm.

We developed a novel method to determine 3D flow profiles. Our method is based on continuously shaking the microfluidic substrate in and out of the focal plane of a fixed optical system and allows the observation over a 1 mm DoF. The proposed setup is compact and easy to use. Moreover, its use is not limited to the determination of liquid flow, it can also be used for optical imaging of e.g. cells and objects.Our set up was designed for the characterization of flows in microfluidic devices by detecting fluorescent particles. An excitation continuous blue laser beam is shaped and diffused to the VOI. The fluorescence from the particles comes back through a 100x magnification objective and is imaged by a high speed camera. The position of the sample is periodically varied by a mechanical shaker perpendicular to the optical axis, effectively displacing the focal plane and scanning the entire VOI. Its position is monitored by a capacitive sensor. Sensor data are correlated to the recorded images, allowing for accurate depth determination. A typical scanning frequency is of the order of 10 to 20 Hz, the sample position is measured with an accuracy better than 1 µm and the image acquisition frequency is 1kHz. All subsystems of the set up are operated by custom software and synchronized by a custom DAC system with temporal resolution below 2 10-5 s.

In the present contribution, we characterize the performance of the technique and we apply the methods for the 3D characterization of flows in microfluidic devices, including the investigation of acoustic flows and tracking of particles with different sizes in separation applications. Flows in a etched silicon microchannel were visualized by the addition of fluorescent tracer particles of size between 0.5 and 5 µm in water. A ceramic piezoactuator was placed at the back of the chip and used to generate an acoustic field and the technique was used to reconstruct 3D trajectories of particles within vortices. In order to obtain stables vortices in the channel, an electrical function generator is used to apply a sinusoidal voltage to the piezoelement at a frequency of 2 MHz. An active PID temperature control system was implemented and allowed maintaining a constant temperature within the samples throughout the experiments. Images of the particles were recorded during tens of seconds at 1kHz.The principle of the particle detection and positioning method is based on the analysis of the characteristics of the observed optical patterns as a function of the distance of the particles to the focal plane [6] and requires the comparison of the experimental images with calibration images.The calibration images consist of videos of stationary particles. The videos were scanned for in-focus particles using filtered thresholding, serving as anchor points. We developed an analytical parametric model of the optical pattern of the defocused particles and we obtained robust image calibration stacks, quantizing the axial dimensions and returning representative templates for local depth levels.

In flow experiments, the data processing scheme includes a sequence of algorithms. First, the video frames are pre-processed to eliminate various sources of noise. For each frame, we apply a weighted normalized autocorrelation function for every template image, using GPU acceleration. Similar detections emanating from the same particle are grouped together using morphological operators before thresholding. The centroids of the detections, the template index and the current shaker position are combined in a table of particle position detections for each frame. This cloud of 3D positions is subsequentially converted to particle trajectories through a greedy matching algorithm, i.e., pairing detections with path segments with minimal length, provided their mutual distance is below some threshold. Occasional spurious detections are detected and discarded and we now obtain short path segments across the whole video. Due to the scanning methodology, the obtained trajectories display periodic gaps, since particles will always be too out-of-focus to be detectable in some frames of the shaking cycle when the scanning depth is large. This can be addressed by joining together matching path segments into the final uninterrupted trajectories using curve fitting and interpolation. Each trajectory includes several thousand points and allows describing the flows in the liquid with very high accuracy. A statistical analysis of the dispersion of the particles positions around the reconstructed trajectories allows estimating the precision of the 3D tracking. The obtained precision of the positioning of each particle at each time is better than 1 µm in the image plane and of the order of 2 µm in the third dimension.

Our scanning µPIV technique allows the characterization of 3D flows in microreactor over a typical depth of focus of 1mm. The performances of our technique have been carefully studied and we obtained spatial resolution of the order of 1 to 2 µm. This new technology opens the door to the experimental investigation of flows in microfluidic devices with acoustic or other organized flows, targeting separator or reactor applications.

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CP&RT-O8
Exploration of Catalytic Pyrolysis with Active Learning

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Keywords: Active Learning; Design of Experiments; Chemical Recycling; Plastic Waste

Experiments are at the basis of scientific research. This is also true for chemical engineering, whether it is for the investigation of process conditions, catalysts or reactors, experiments are required for a thorough scientific understanding. These experiments are often expensive, time-consuming and labor-intensive. Furthermore with the rise of machine learning in chemical engineering accurate experimental data is becoming even more important. Design of experiments (DoE) aims to increase the efficiency of scientific research by extracting maximal information from a minimum of experiments. The combination of DoE with machine learning leads to the field of active learning, which results in a more flexible, multidimensional selection of experiments than regular DoE techniques. Active learning can be employed for the modelling of reactions with well-selected experiments, nevertheless its use is not widespread in chemical engineering [1]. To the best of our knowledge, active learning has not yet been applied in reaction modelling as current methods still require an excessive amount of data for the selection of experiments.

In this work a novel data-scarce active learning methodology for the optimal selection of experiments is proposed. This method combines Gaussian processes and clustering techniques for a flexible determination of the required experiments. In contrast to common active learning strategies, this efficient, data-scarce active learning approach already shows it benefits for a small number (10-20) of experiments. This is a significant advantage of this methodology over other active learning approaches as it enables active learning for a real experimental campaign, where only a limited amount of experiments can be executed. The algorithm is validated on a real experimental campaign to study the effect of temperature, contact time, and catalyst on the catalytic pyrolysis of plastic waste. To proof the benefits of active learning, a widely applied regular DoE technique (full-factor design) is compared to our data-scarce active learning approach.

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CP&RT-O9
Electrochemical conversion of CO2 to formic acid at elevated temperatures

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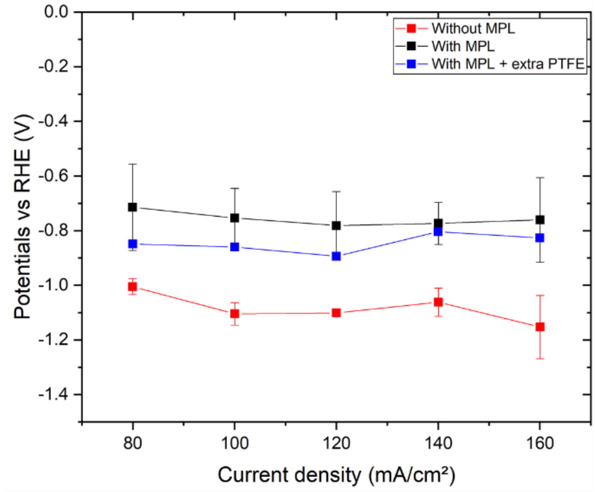
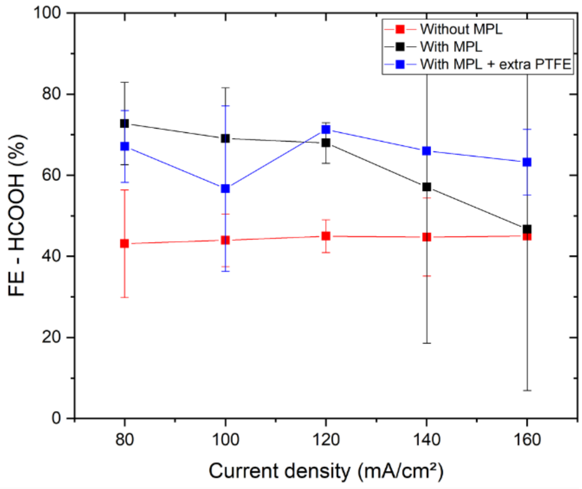
Keywords: Electroreduction; Elevated temperature; CO2; GDE; Electrocatalysis; Heterogeneous catalysis; Paired electrosynthesis

Increased levels of CO2 in the earth's atmosphere are believed to be a main cause of global warming [1]. The electrochemical reduction of CO2 into various chemicals offers a great ecological solution since it can close the carbon cycle by utilizing renewable energy, resulting in a sustainable carbon recycling system, lowering anthropogenic CO2 emissions [2]. Consequently, it has gathered significant scientific interest over the past decade. However, to make significant progress towards making the process industrially feasible, it would be beneficial to replace the typical anodic oxygen evolution reaction at the counter electrode with an economically more interesting one, like alkane dehydrogenation in order to lower cell potential and increase energy efficiency. This, however, requires the cathodic CO2 reduction to operate efficiently at elevated temperatures (up to 100°C) [3]. Unfortunately, little is known on the impact of elevated temperatures on the overall performance of CO2 electrolysers, its components, and electrocatalysts.

In this research, we investigate the effect of increasing the temperature on CO2 electrolyzers to enable selective and stable electroreduction of CO2 to formic acid. To achieve our target, we modified a CO2 electrolyzer such that it can operate at temperatures up to 85°C by placing it in a furnace. Through our research, we learned that heating the system changes several properties. For example, the hydrophobicity of the gas diffusion electrode (GDE) decreases, as does the surface tension of the aqueous electrolyte solution. Therefore, we investigated the effect of the microporous layer (MPL), treated with 5 wt% of PTFE, influencing the position of the three-phase boundary, directly affecting the CO2 electroreduction and flooding. We concluded that an MPL is indeed necessary for optimal reaction conditions, since it positively affects the potential and faradaic efficiency towards HCOOH, resulting from better pore wetting along with increased conductivity. In contrast, if too much PTFE is added onto the MPL, the reaction is negatively affected.

The next step was to investigate and compare other commercially available gas diffusion layers, that are primarily used in high-temperature proton exchange fuel cells, as we clearly see that the GDL itself affects CO2 reduction performance.





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CP&RT-O10
Enabling Flow synthesis of zeolites

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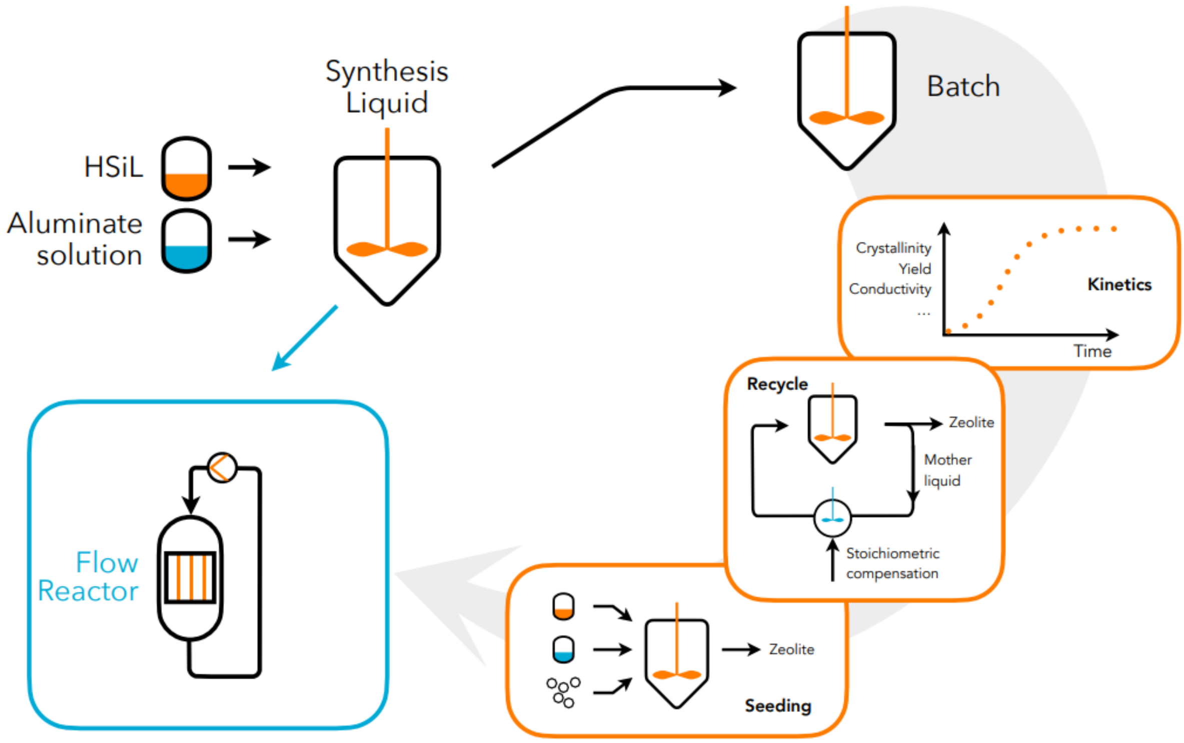
Keywords: Zeolite; Flow synthesis; HSiL

Zeolites are renowned for their versatile use in various industries with implementations ranging from bulk to very specific, niche applications. Despite their high societal value and extensive research, their synthesis, which is conventionally based on the hydrothermal treatment of aluminosilicate gels, still harbors hard-to-solve questions. The inherent heterogeneity of these media limits experimental accessibility and hinders molecular scale investigations. One way to access this information is the use of Hydrated silicate ionic Liquids (HSiLs) [1].

The development of Hydrated Silicate ionic Liquids (HSiL) synthesis strategies has been responsible for major improvements in our fundamental understanding of zeolite growth. Especially the role of water and inorganic cations is now perceived in a new way [1,2]. HSiLs are equilibrated, monophasic liquids and are therefore an ideal system to study zeolite formation. On top of that, they have surprisingly low vapor pressures, fast synthesis kinetics and moderate viscosities, making them attractive for synthesis in flowing (continuous) systems. Currently, industrial zeolite production is mainly based on a batch or semi-continuous process [3]. The transition to a continuous operation could bring opportunities for higher productivities and improved quality control by elimination of batch-to-batch variations [3,4]. Previous attempts to implement continuous zeolite synthesis were often hindered by practical limitations of gel-based syntheses. Creative solutions to solve these issues pose difficulties for further upscaling but show that a working principle is greatly demanded. Difficulties related to gels can be circumvented via the HSiL synthesis route, making this also the preferred route for zeolite synthesis in continuous flow systems.

In this work, we demonstrate that continuous flow synthesis is feasible for HSiL-based systems, and we propose a setup for further research. In this context, we investigate the recyclability of the unreacted mother liquor (which is above 95%) to minimize waste streams without sacrificing chemical control and product quality. The potential of seeding HSiL-based zeolite synthesis is considered as well as additional means for accurate control of the physicochemical state of the synthesis liquid and the crystallizing product.



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CP&RT-O11
Microfluidic magnetic platform for repetitive coating of particles

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Keywords: Superparamagnetic microparticles; Layer-by-Layer; particles migration

In this work, we use a magnetic field to control and coat magnetic microparticles (MPs) in a microfluidic platform. An interesting method for advanced particle manufacturing is the layer-by layer technique (LbL), which is based on successive dipping and rinsing to coat consecutive layers of polyelectrolytes (PE). In this work, we use the advantages of microfluidics, magnetism and LbL to produce nanostructured MPs in a continuous regime [1]. Nanolayered materials are rapidly emerging for their multiple applications including separation with a catch and release mechanism or detection with electronic sensing systems. By personalizing the coating, with biomarkers or functionalized chemicals for example, this microfluidic platform targets a large range of applications.

We produced a microfluidic chip with three parallel channels that are interconnected by bridges (Fig. 1). The MPs were injected in the central channel, while the side channels contain two oppositely charged PE solutions (polyacrylic acid (PAA) and polyethyleneimine (PEI), both at 0.033% (w/w) in ethanol). The central channel contains the washing solution (ethanol). Using external magnets, MPs can be forced to follow a zigzag pattern in our chip and switch from channel to channel through the bridges. A layer is adsorbed on the particles during each passage in the solutions. We aim to produce particles with four layers, two of each reactant. Two structures placed against each side of the microfluidic chip fix the magnet positions.

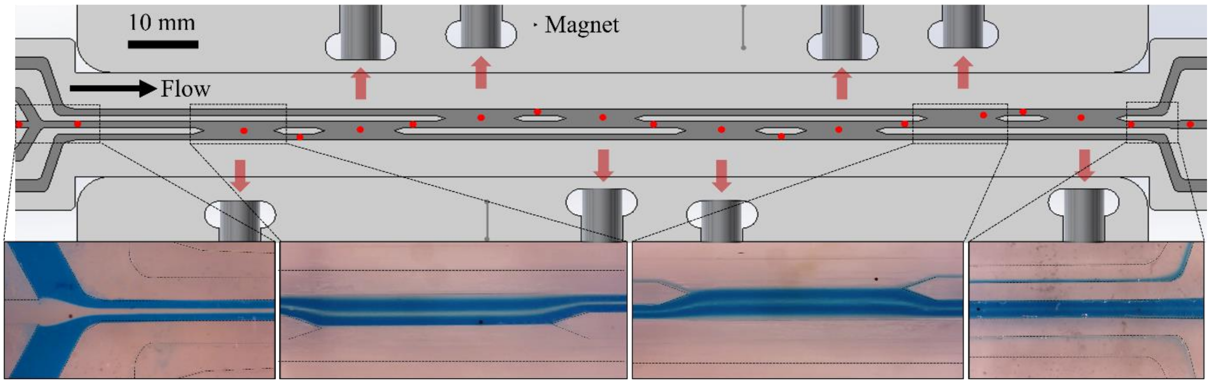
The channels have a cross section of 0.5x0.5 mm and a length of 80 mm. There are milled in cycloolefin copolymer and a cover plate was chemically bonded to close the system. The flow rates of the liquids are controlled by Fluigent pressure pumps. The magnets used are Neodym N45 Nickel. The MPs are composed of superparamagnetic nanoparticles fixed in a matrix of polymethylmethacrylate (89µm diameter, suspended in ethanol). They present an amine function at the surface that can react with PAA. In order to visualize the different layers, the PEI was labelled with a fluorescent dye (Rhodamine).

First, the microfluidic device has been evaluated using hydraulic theory and numerical simulation with Comsol Multiphysics. The design was optimized to balance the pressure between the channels and avoid liquid exchange through the interconnections. The final simulation showed a laminar regime, with no mixing between the liquids. Optimized and non-optimized designs were experimentally tested to confirm full control of the flows. Channels are separated by walls to keep diffusion between solutions to a minimum, allowing to increase the number of chip units in series in order to further increase the number of layers.

In a second step, control of particles trajectory in the chip was improved. The liquid flow rate, magnet dimension and position were varied. We tracked the motion of the particle, in axial direction carried by the liquid and deflected by the magnets in a perpendicular direction to the flow. Particles are forces to follow a desired trajectory and are successively immersed in the washing and reacting solutions: Ethanol - PAA - Ethanol - PEI - Ethanol - PAA - Ethanol - PEI - Ethanol. When the particles are coated with PAA then PEI, they become fluorescent. The more layers of PEI the particles have, the more fluorescent they become. Fluorescence of the particles was quantified to characterize the coating of the successive layers.

We developed a microfluidic platform able to coat four layers at the surface of particles. We were able to control particle trajectories in chip with well-placed magnets. We showed that with our system, we can efficiently coat magnetic microparticles with at least four layers on chip. Quantitative visualization of the particle coating was done using fluorescence.

We next aim to further increase the number of cycles in order to increase the number of layers and bring interesting properties to particles. Increasing the number of parallel channels also opens the possibility to coat the particles with more than two different reactants.



Flow focusing

Bridge 1

Bridge 7

Outlet

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CP&RT-O12

On the Relevance of Molecular Machine Learning in Industrial Chemistry

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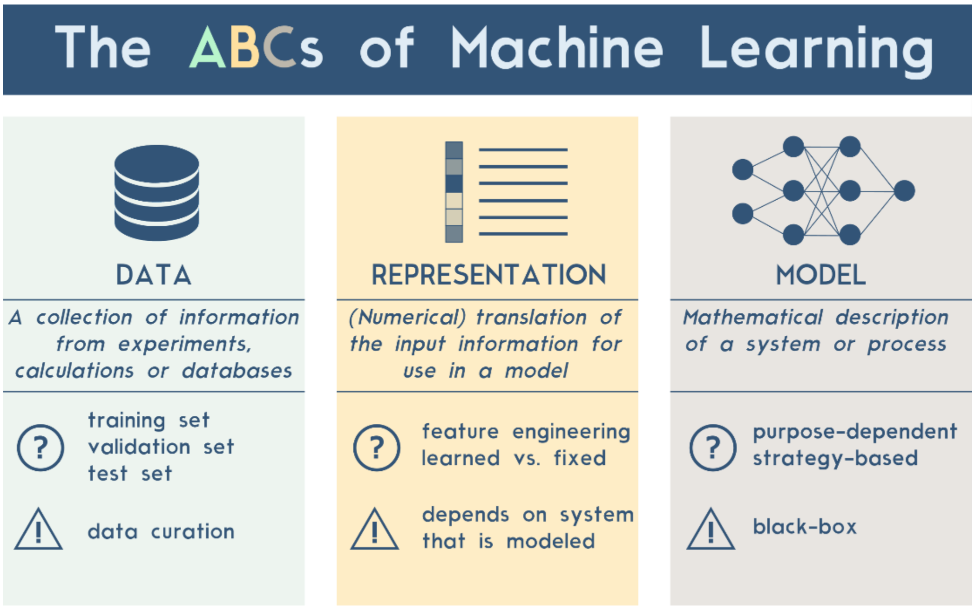
Keywords: machine learning; industrial chemistry; property prediction; qspr; artificial intelligence

In recent years, machine learning for property prediction again gained the interest of chemists and chemical engineers [1]. Again, because a first wave of machine learning interest was witnessed in the 1990s. Back then, computational resources and data availability were a limiting factor. Today, scientists and engineers possess large amounts of data and have access to powerful computers but still, machine learning is not the main tool for property calculations.

In the present contribution, Gaussian Learned Histograms of Distances, Angles, and Dihedrals (GauL-HDAD) [2], an open-source molecular machine learning software tool, is used to address the challenges of machine learning for property prediction. This model is successfully applied to molecules [2], mixtures [3], and chemical reactions to predict a wide range of physical properties using publicly available datasets. We will exemplify that there are three crucial pillars for successfully applying molecular machine learning with industrial significance (Figure 1). The first pillar addresses the correct choice of training data. The second pillar is the representation of the chemical data, which is used as input for a machine learning algorithm. The algorithm, or model, is the third crucial pillar. The correct use of data, data representations, and models makes machine learning a trustworthy element in the modeling toolbox of chemists and chemical engineers, with the potential to speed up industrial discoveries.



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CP&RT-O13

CFD – Study for Enhanced Degassing of a Dehydrogenation Reactor for Liquid Organic Hydrogen Carriers

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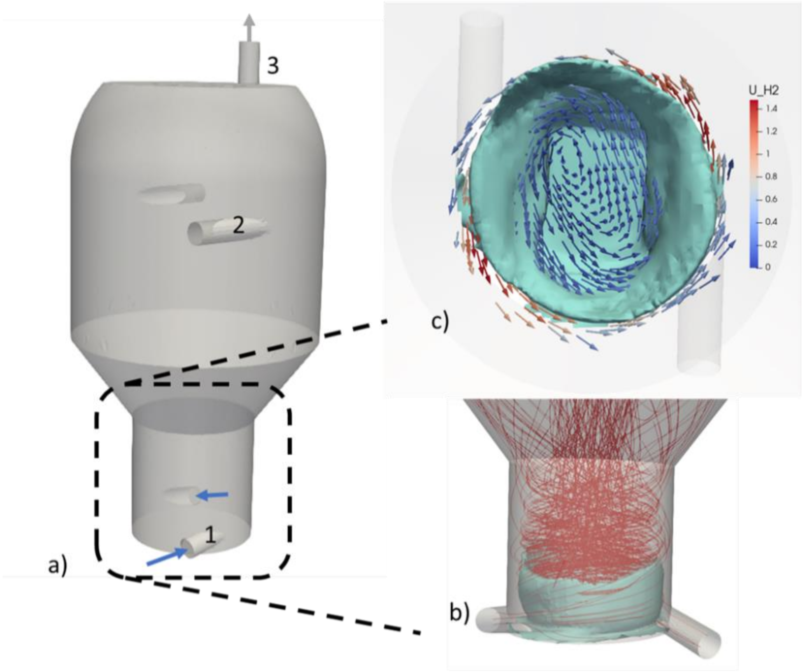
Keywords: Hydrogen Storage; Computational Fluid Dynamics; Reactor Engineering

Liquid Organic Hydrogen Carriers (LOHC) are a promising alternative for hydrogen storage for large scale applications. However, one of the key challenges holding back on the system is the efficiency of the dehydrogenation reaction. [1] This system consist of a liquid with chemically bound hydrogen, and it dehydrogenates to form gaseous hydrogen and an uncharged liquid carrier, which can be recycled. The dehydrogenation reaction is heterogenous reaction catalysed by sulfurized Pt – Al2O3 catalysts.[2] The efficiency of the reaction is controlled by the formation of hydrogen bubbles around the catalyst particles, which block catalytic sites for the hydrogen loaded liquid carrier.[3] In our research we propose a reactor system based on centrifugal motion of the liquid, this increases the shear stress induced by the liquid and causes an annulus-type profile of the gas distribution. The liquid velocity is greatly increased in the centrifugal reactor (> 2.5m/s), compared to a fixed bed reactor. However due to the high number of rotations the liquid makes, the contact time between catalyst and charged carrier is still high. This is also demonstrated by the high residence time of the reactor system. The residence time in our proposed reactors was 19s which holds up nicely to the residence time of an equivalent packed bed reactor (25s).



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CP&RT-O14
Enhancing CO2 conversion by plasma reactor in series

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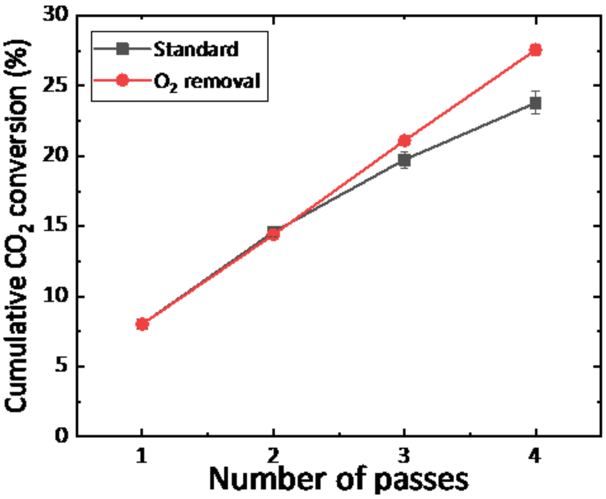
Keywords: plasma; CO2; reactor in series; O2 removal

Plasma technology is one promising approach for carbon capture and utilization (CCU). However, the conversion is often limited due to a suboptimal residence time in the plasma or recombination of the reaction products at atmospheric pressure. Both of these issues can be addressed in process design.

In this work, we designed a basic procedure to study a plasma reactor (i.e. the so-called atmospheric pressure glow discharge; APGD) in series as a first approximation of a recycle flow. With 8-10 passes through the reactor, the conversion can reach values 3.4 times higher than the single pass, and reaches a plateau due to the competition between splitting and recombination reactions.

Additionally, we explored the reactivity of O2 molecules. O atoms can either enhance the CO2 conversion (O + CO2 → CO + O2) or O2 molecules can recombine with CO, producing again CO2, by the opposite reaction (Berthelot et al., 2017). In our conditions, adding molecular oxygen to the mixture has a detrimental effect on the CO2 conversion. Removing the O2 in between each pass instead improves the conversion, as it prevents recombination reactions. This works reveals interesting opportunities for the industrialisation of plasma processes.

We acknowledge financial support from the Fund for Scientific Research (FWO) Flanders (Grant ID 110221N), the Flemish Agency for Innovation and Entrepreneurship (VLAIO) (Grant ID HBC.2021.0251), and the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation programme (grant agreement No 810182 - SCOPE ERC Synergy project).



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CP&RT-O15

Ray tracing-assisted optimization of light absorption in gas-liquid flow photosensitized oxidations

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[2] *University of Brasov, Romania*

Keywords: singlet oxygen; two-phase flow; microreactor; ray tracing; photon absorption model

The singlet oxygen produced by photosensitization has applications in synthesis of fine chemicals, wastewater treatment and photodynamic therapy.[1] Microreactor technology has shown a superior performance in gas-liquid photooxidations compared to conventional batch reactors. [2] The light absorption is the driving force of the photooxidation reaction and is determined by the operating conditions of which optimization was performed in various gas-liquid flows such as Taylor [3], annular [4] and bubbly flow [5] through extensive experimental studies. Modelling represents a faster and cost efficient approach, therefore this study aims to use ray tracing for prediction and optimization of light absorption in gas-liquid photooxidation reactions in a microreactor. Firstly, a three-dimensional ray tracing model was developed and validated by experimental singlet oxygen oxidation of 9,10-dimethylanthracene (DMA) photosensitized by Rose Bengal. Secondly, the model was employed for comparing Taylor, annular, and two bubbly gas-liquid flows in terms of volumetric absorbed photon flux relative to single-phase flow, Relative Iabs /Vliq. For each pattern, the film thickness was varied between 5 µm and 130 µm as illustrated in Figure 1. We found that bubbly flow is beneficial at low attenuation coefficients (i.e. product between photosensitizer concentration and molar absorption coefficient) and is characterized by optimal film thicknesses below 28 µm. By analyzing the photon transport, we learned that the light scattering has a significant positive effect only in the bubbly flow with very closed bubbles (“caps” bubbly flow). Taylor flow is clearly superior to bubbly flow above 51 cm-1 and is characterized by an optimal film thickness between 15 µm and 55 µm. The annular flow showed the highest Relative Iabs/Vliq as the entire liquid phase is located near the channel wall. However, the annular flow requires a film thickness of around 80 µm for an efficient light utilization. This is the first systematic comparison between different flow patterns in terms of light absorption and we learned that a single optimal flow pattern does not exist. Consequently, we envision that the future advanced photoreactors are assisted by modelling tools and have the ability to switch between flow patterns to accommodate the optimal gas-liquid distribution for each given attenuation coefficient which is imposed by the chemical system.

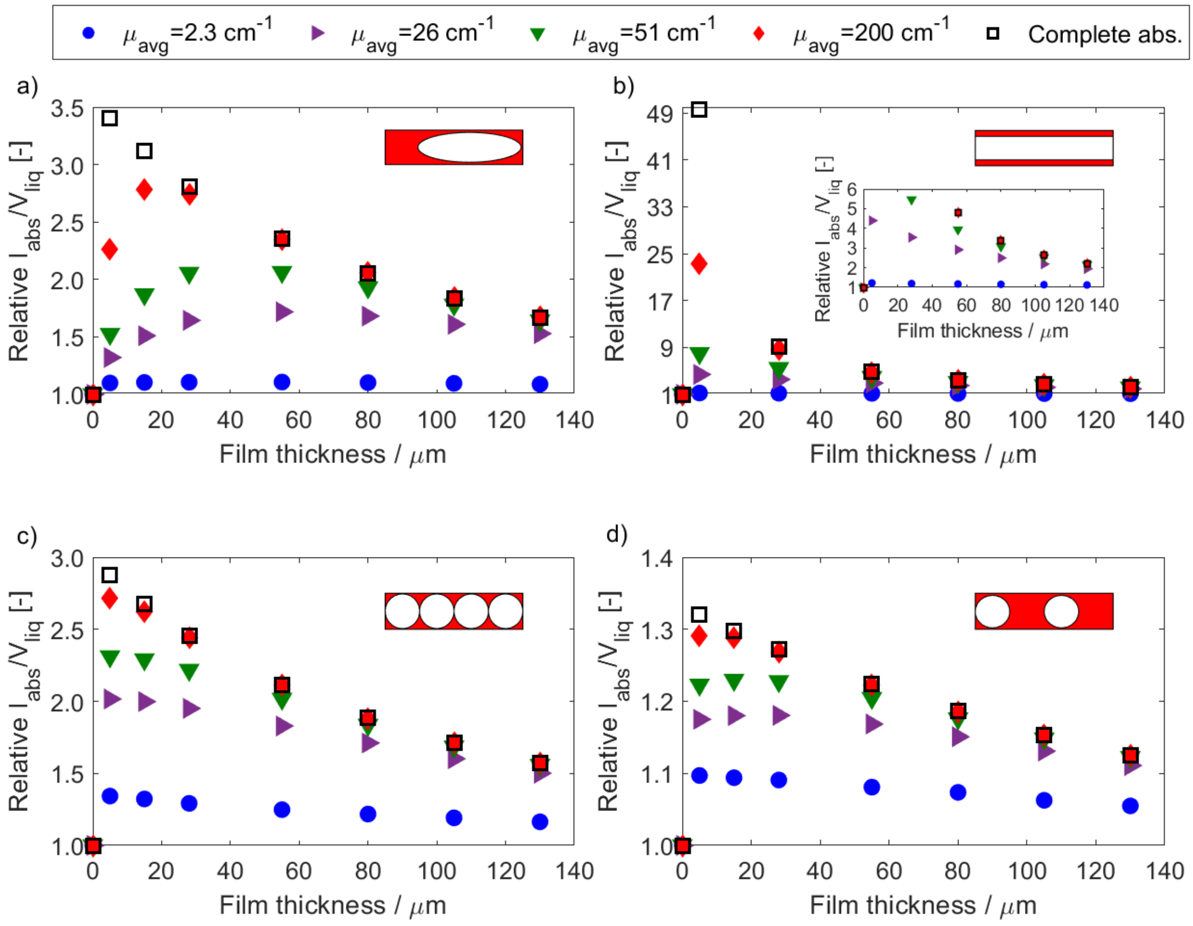

Figure 1. Relative Iabs/Vliq in function of film thickness at different attenuation coefficients for a) Taylor flow, b) annular flow, c) "caps" bubbly flow, and d) bubbly flow. Conditions: one sided LEDs-based irradiation, reactor channel diameter = 1 mm.

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CP&RT-O16

Innovative Au-Sn-SiO2 bifunctional material for the upgrading of glycerol to methyl lactate

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Keywords: Glycerol upgrading; Aerosol process; Bifunctional materials

The interest of the scientific community has recently moved toward the development of efficient catalytic process for biomass valorization as it represents a promising alternative to the existing petro-based technologies. Glycerol, the main by-product of biodiesel production, can be upgraded to methyl lactate (ML), a key platform molecule for different industrial applications (green solvent for nitrocellulose synthesis, raw materials for cosmetics and healthcare formulations). The reaction is known to proceed via the oxidation of glycerol to dihydroxyacetone (DHA), followed by the rearrangement with methanol to yield the targeted lactate. [1] Gold nanoparticles with diameters below 5 nm show high catalytic activity in glycerol oxidation and tin-based catalysts show the appropriate Lewis activity to convert DHA to ML (Fig 1 a). [2-3] It is appealing to combine both catalytic species to perform the cascade reaction directly from glycerol to ML, using a single solid catalyst.

In this work, we propose a novel one-pot strategy for the preparation of a new type of bifunctional heterogeneous catalysts. This new material is synthesized leveraging on the aerosol-assisted sol-gel process and consists of Au nanoparticles embedded in a mesoporous Sn-Si mixed oxide.

The obtained bifunctional catalyst, AuSnSiO2, displayed excellent textural properties (SSA = 440 m².g-1, Vp = 0.11 cm³.g-1, Dp = 5 nm) and the two metals were successfully and homogeneously incorporated in the material (Fig. 1 b). The formation of gold nanoparticles via the one-pot strategy was first investigated and optimized without the presence of Sn (AuSiO2) to obtain gold nanoparticles with a diameter of 3.1 nm active in the oxidation of glycerol to DHA (XGly = 59%, YDHA = 18%). The poor yield observed was caused by the overoxidation of DHA on highly active gold nanoparticles. When mechanically mixing this catalyst with a SnSiO2 catalyst to perform the cascade reaction to ML, no significant improvements of the catalytic performance were observed (XGly = 71%, YML = 19%). Working with the bifunctional catalyst, on the other hand, enhanced the methyl lactate yield. While the gold nanoparticles size in AuSnSiO2 remained small (3.4 nm), the further rapid transformation of DHA to ML on the nearby Sn sites resulted in a significant boost in selectivity to ML (overall yield up to 31% with a glycerol conversion of 61%). These results highlight the interest of bringing together in one unique material two catalytic species to run efficiently a cascade reaction. Indeed, the proximity between the two active sites is the key to enhance the selectivity toward methyl lactate during the cascade reaction. [4]

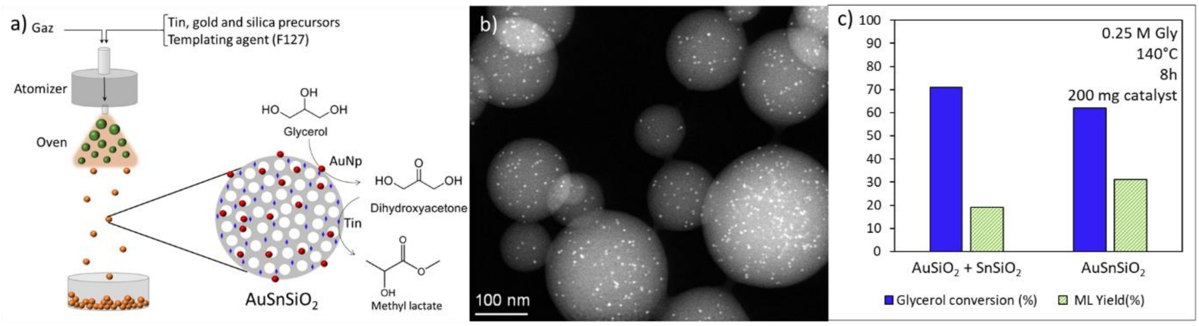

Figure 1: a) Typical procedure for the preparation of the bifunctional catalyst with the cascade reaction on the material bearing both catalytic site; b) STEM-HAADF image of AuSnSiO$_2$ highlighting the gold nanoparticles; c) Catalytic performance in the conversion of glycerol to ML of AuSnSiO$_2$ and the mechanical mixture of Au and Sn catalysts

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CP&RT-O17
Catalytic dehydration of 1,3-Butanediol into 1,3-Butadiene

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Keywords: /

1,3-Butadiene (BD) the most basic and important conjugated diene is a key derivative of the petrochemical industry and an intermediate of many industrial products [1]. It is widely used as a raw material for the manufacture of a diversity of synthetic rubbers, elastomers and polymeric resins [2]. BD is mainly produced as a by-product of the steam cracking process for ethylene and propylene production or from oxidative dehydrogenation of n-butane and n-butene [3]. However, the depletion of these non-renewable feedstocks, closely related to the rapid growth in world population, increases the demand towards BD production from a greener and more sustainable routes using biomass-derived renewable materials [4]. Butanediol isomers (i.e. 1,3-, 1,4- and 2,3-BDOs) are produced in high yields from the biomass fermentation process, therefore, the acid-catalyzed dehydration of such C4 alcohols can be regarded as an alternative potential route towards BD [2].

Our work aims to stably produce BD with a very high yield from the catalytic dehydration of 1,3-BDO in the gaseous phase. To realize this goal, the catalytic behavior of several acidic commercial zeolites with different topologies were tested at 300 °C under atmospheric pressure in a fixed-bed flow reactor. Results revealed that the framework structure of zeolites plays a crucial role in governing butadiene selectivity. In addition to topology, active site accessibility, acid strength and acid site density can have a prominent impact on conversion rate, selectivity as well as stability in such dehydration reactions. While better sites accessibility may lead to shorter diffusion paths in the catalyst particle and lower cokes formation, hence, higher conversion and higher butadiene selectivity may be achieved; weak acid sites might decrease propylene formation by hindering carbon-carbon catalytic cracking as well as formation of undesirable side products (e.g. oligomerization of butadiene). To tackle these properties, new dehydration catalysts such as mesoporous, nanosized, layered as well as Boron-incorporated zeolites were synthesized by several groups and their catalytic activity were studied. Consequently, taking into consideration all these crucial properties, there is a potential of surpassing 80% in butadiene yield from the direct dehydration of 1,3-BDO.

Acknowledgments: Moonshot project, CSCE-KU Leuven, UGent-INCAT

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CP&RT-O18
Perspectives of continuous heterogeneously catalyzed hydroformylation of large olefins

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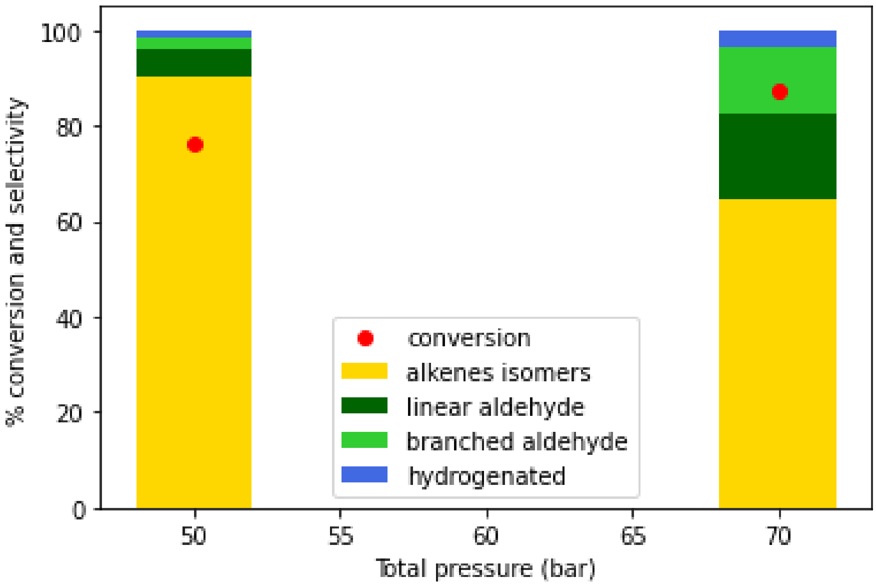
Keywords: Heterogeneous catalyst; hydroformylation; rhodium catalyst

Hydroformylation reaction, often referred to as the oxo-synthesis process, has been performed over the years for the production of aldehydes and alcohols. As it is similar to Fisher-Tropsch synthesis, it can also be catalyzed using a transition metal. Industrially, this process is carried out homogeneously using rhodium or cobalt complexes with ligands to enhance the selectivity towards the desired product. Rhodium presents higher activities than cobalt, being able to operate at milder conditions, however, it is also a much more expensive material [1]. Therefore, rhodium is preferred for light olefins where the metal losses caused by the downstream separation processes are lower. Whereas for long-chain olefins just cobalt is used. One of the main disadvantages of heterogeneous catalysts is the low selectivity (<30% at olefins conversion amounting to less than 20 %) compared to their homogeneous counterparts(up to 99% selectivity at full conversion)[2,3]. Hydrogenation side reaction can occur over the heterogeneous catalyst at moderate to high temperatures, the lower the temperature, the lower the selectivity towards the hydrogenated compound. Given the value of the double bond, not in the least in view of further chemical functionalization, hydrogenation must be avoided to enable a heterogeneously catalyzed hydroformylation competitive with the current homogeneous one. This work is focused on the analysis of long-chain olefins such as 1-decene or 1-tetradecene over rhodium nanoparticles supported on alumina. These represent different pyrolysis oil cuts.

Rhodium, as the most active noble metal for hydroformylation, can operate at temperatures below 200oC, where hydrogenation can be avoided to the maximum possible extent. This experimental research used heterogeneous rhodium catalyst packed in a hight-throughput kinetic reactor set-up, the liquid feed consisted of the targeted olefin in a paraffin mixture as a solvent, while the gas feed is an equimolar mixture of syngas.

The preliminary results for 1-tetradecene hydroformylation were promising. As can be seen from Figure 1, a 1-tetradecene conversion of around 80% is achieved, increasing with total pressure. Selectivities towards the linear aldehydes of 20% and towards the branched aldehydes of 15% are obtained. A higher total pressure results in a higher concentration of syngas in the liquid phase, where the reaction is presumed to happen, therefore hydroformylation and hydrogenation are enhanced. The rest of the product spectrum mainly consists of olefins isomers that can be subsequently functionalized rather than the hydrogenated products which have less value in the market.

Future work will be focused on the study of the reaction behaviour by varying operation conditions and monitoring the results. Hydroformylation of large olefins is possible using heterogeneous catalysts, more extensive investigation is needed to understand the reaction mechanism and the possible feasibility of the process in the actual industrial landscape.



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R&S-O1

Heat triggered debondable adhesives

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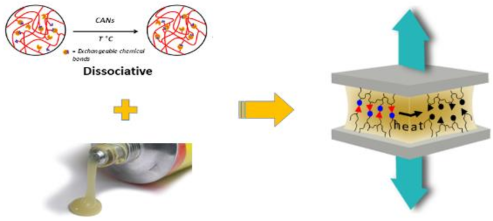
Keywords: debondable adhesives ; covalent adaptable networks

Adhesives are omnipresent in a myriad of materials and continue to impact our daily lives, as recognised by the continuous global growth of the adhesive market. Yet, challenging times lie ahead. Indeed, the design of adhesives with switchable properties that allow for the formation of reversibly bonded joints is highly desired as it brings the attractive feature of facilitating the disassembly of components, their structural repair, removal and aid their recycling.(1,2)

The goal of this work is to transform commercially available adhesive matrices into on-demand debondable adhesives by means of turning them into covalent adaptable networks. This is done by incorporation of dynamic crosslinks based on dissociative chemistries.(3,4) The decrosslinking initiated by heating the adhesives allows easy disassembly of the adhered substrates.



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R&S-O2
Mechanosynthesis of N-Heterocyclic Carbene Complexes

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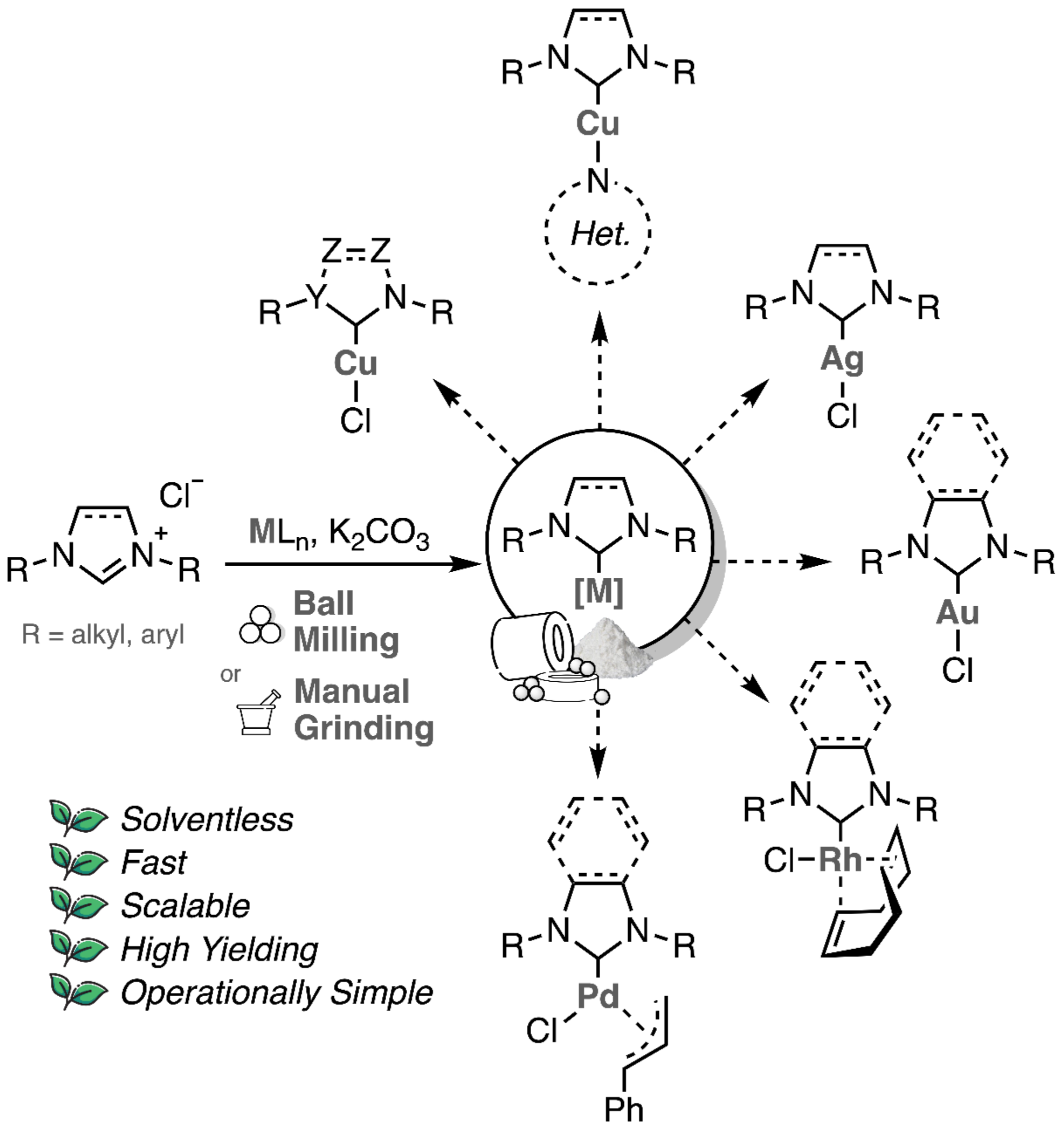
Keywords: mechanochemistry; N-heterocyclic carbene; solvent-free reaction; sustainable synthesis

The need for safer, cleaner, and most sustainable synthetic transformations has led, during the last decade, to the rapid expansion of methodologies that implement the use of mechanical energy as a mean to initiate and sustain chemical transformations. Such methodologies (mechanosynthesis) provide a solvent free (or solvent-minimized) environment in order to perform synthesis, which, from a Renewables & Sustainability perspective, is highly desirable, as in many cases, solvent use is what contributes most in defining environmental performance of any fine-chemical/pharmaceutical synthetic process.[1] Despite the considerable progress of the field in the synthesis of small organic, main group, and supramolecular molecules, very little focus has been placed on the access of organo-transition-metal complexes, a class of compounds of great interest in catalysis.

We will present our latest findings in the field, namely a general, operationally simple, and scalable mechanosynthetic approach to access transition metal N-heterocyclic carbene complexes.[2-4]



Scheme 1. Mechanosynthesis of Transition Metal-NHC Complexes.

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R&S-O3

Microkinetic analysis of ethylene hydroformylation on a heterogeneous Rh-modified MOF catalyst

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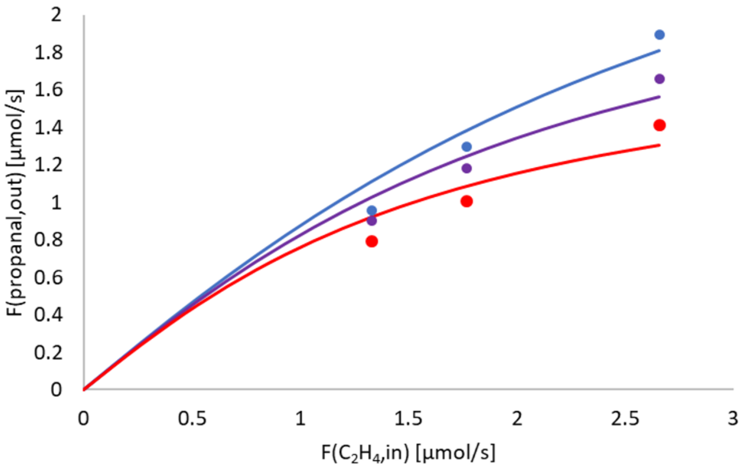
Keywords: kinetic model; ethylene; propanal; hydroformylation; heterogeneous catalysis

As a generally homogeneously catalyzed process, hydroformylation still faces issues regarding catalyst separation and recycling. However, the development of heterogeneous catalysts with the same activity and aldehyde selectivity as the widely-used ligand-modified Rh or Co catalysts remains a challenge. One approach currently gaining attention is the heterogenization of the homogeneous catalyst through immobilization on a solid material, such as a MOF. We have previously developed a microkinetic model for the hydroformylation of ethylene on a homogeneous PPh3-modified Rh catalyst [1], based on Wilkinson's dissociative mechanism. The aim is now to verify whether the reaction mechanism on a heterogenized catalyst is similar as on a homogeneous catalyst, through the development of a microkinetic model for the heterogenized catalyst.

An experimental investigation of ethylene hydroformylation on a Rh-functionalized MOF catalyst is conducted in a fixed-bed reactor in order to investigate the effects of the reaction conditions (T = 100-120 °C, p(tot) = 10-20 bar, F(C2H4) = 2.5-7.5 µmol/s, n(CO)/n(C2H4) = 1-2, n(H2)/n(C2H4) = 1-2) on the ethylene conversion and the propanal selectivity. The catalyst was synthesized starting from NU-1000 [2], a mesoporous MOF, which is first functionalized using 4-(diphenylphosphino)benzoic acid. This group then allows the homogeneous catalyst Rh(CO)H(PPh3)3 to lose one of its PPh3 ligands and get immobilized on the MOF. Propanal and ethane were observed as products, along with trace amounts of propanol.

To model the reactor, an ideal steady-state plug flow reactor is considered. For each gas phase component and intermediate, a mass balance equation is solved. The production and consumption of the components are modeled using Wilkinson's dissociative mechanism, as the catalyst is structurally very similar to the homogeneous ligand-modified Rh catalysts. The model has 10 parameters, comprising activation energies and reaction enthalpies of the considered elementary steps, which are estimated through regression to experimental data. The parameter values obtained for the homogeneous process [1] were used as initial guesses and the difference in their values can be considered to be a result of the reaction taking place in the gas phase, as opposed to in a solvent, as in the homogeneous case. The simulation results are shown in Figure 1, which exhibit a realistic trend for the outlet flow rate of propanal as a function of the inlet flow rate of ethylene. The model is able to capture the negative effect of the temperature on the conversion to propanal.



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R&S-O4

Lewis acid catalyzed synthesis of methionine hydroxy analogues from tetroses

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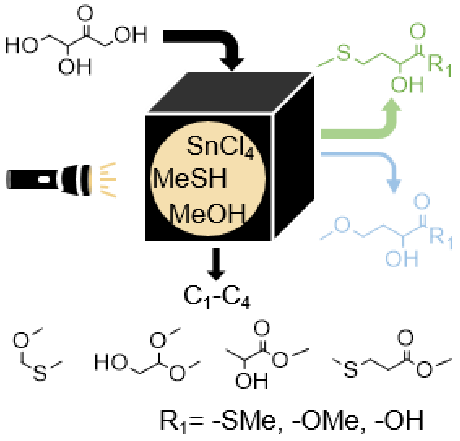
Keywords: carbohydrates, Lewis acids, methionine hydroxy analogues

The synthesis of methionine hydroxy analogues (MHAs) is of paramount importance to achieve the zero hunger and the responsible consumption and production SDGs of the UN, since these compounds are used to supplement animal feed to achieve optimal development and protein yields in livestock for human consumption [1] while minimizing livestock waste [2]. In 2018, the industrial production of methionine and its analogues was close to 1.7 million metric tons, where around 95% correspond to DL-Met and MHAs [3] obtained by chemical synthesis [4]. However, the chemical synthesis of these compounds relies heavily on non-renewable feedstock from the oil industry, such as propylene or acrolein [5], making these processes unsustainable.

We report here our results of the one pot conversion of tetroses to MHAs in the presence of MeSH, MeOH and SnCl4·5H2O. Our results show that both an adequate balance between MeSH and MeOH and the addition of small amounts of water increased the selectivity towards MHAs. The fundamental understanding of these results along with ex situ NMR studies of the reaction and compound isolation and characterization allowed to establish the main reaction pathways that govern this Lewis acid mediated transformation. The findings of this study can unlock the sustainable synthesis of MHAs from renewable feedstock like tetroses (which in turn can be obtained from abundant carbohydrates such as glucose).



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R&S-O5
Recyclable Polyurethane elastomers via dynamic covalent chemistries

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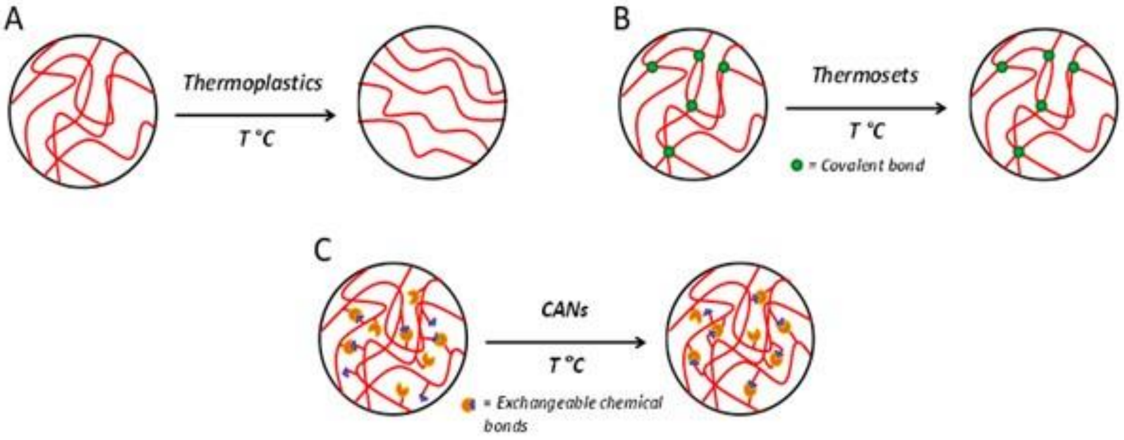
Keywords: /

Besides their outstanding mechanical, durability and insulation properties, polyurethane (PU) thermosets are resilient in diverse environments[1], [2]. Owing to these features, PUs are currently versatile materials used in a broad range of applications such as coatings, automotive, foams…[3]. However, the simultaneous high production and consumption of PUs generates a significant volume of accumulated waste that ends up either being landfilled or grinded and incinerated, by that representing a classical linear economy[4].

A much more promising approach would be to create inherent recyclable PU-thermosets by introducing dynamic covalent bonds in their polymer architecture. Various dynamic chemistries have been developed in recent years and depending on their nature, the dynamic bond exchange is usually triggered by an external stimulus such as heat or light[5], [6]. Those so-called covalent adaptable networks (CANs) hold good mechanical properties, yet at the same time they possess a decent level of malleability when exposed to stimuli. This feature allows their reprocessability and recyclability, therefore obtaining a balance between thermoset and thermoplastic properties[1].

The aim of this work is to introduce dynamic covalent chemistries in industrial relevant PU thermoset materials, allowing these materials to be recycled and reshaped. Additionally, this study will show how PU thermosets can be transformed from materials generating large volumes of wastes, into sustainable materials that can be recycled and transformed into valuable products at their "end-life".

Fig 1: Schematic illustration of the behavior of A) thermoplastics, B) thermosets and C) CANs upon heating.



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R&S-O6

Catalytic pyrolysis of a polyethylene melt with high selectivity to light olefins and low coke formation

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Keywords: Catalytic pyrolysis; Heterogeneous catalysis; Polyethylene; Light olefins; TGA

How many people are familiar with plastics as an indispensable tool in daily life? The answer to this question seems obvious. But are all these people also informed about the plastic lifecycle once it ends up as waste? Probably not. Stating that 29 million tons of plastic post-consumer waste was collected in 2020, it is clear that this part of the plastic lifecycle forms an interesting business as well. Among different plastics, polyethylene is a polymer that is mostly used for single-use packaging applications. Due to its linear hydrocarbon structure, and the high waste generation numbers, it forms a valuable feedstock for the chemical industry. Whereas common plastic waste management strategies such as mechanical recycling and incineration show limitations, chemical recycling shows high potential to close the plastic loop and complement the chemical industry with high value chemicals. Within this field, catalytic pyrolysis will be investigated as a chemical recycling strategy, using heterogeneous catalysts such as silica-alumina and zeolites. In order to obtain the optimal catalyst for this purpose, a comprehensive research methodology is developed in which catalyst testing, evaluation and optimization are intended. Starting with an explorative catalyst screening using TGA, main parameters such as catalyst activity and coke formation are evaluated. This screening is complemented with product selectivity studies by means of micropyrolysis coupled to GCxGC-FID and MS. Further research stages include catalyst testing in a semi-batch reactor, and a conical spouted bed reactor as a prototype for a more industrially feasible reactor choice. Depending on the selected catalyst and information from the initial selectivity screening, targeted end products might include light olefins or naphtha (as feedstock for existing steam cracking units). In the end, these products can be used as building blocks for new virgin polymers, realizing a full closure of the plastic lifecycle.

R&S-O7

Sustainable Synthesis of Aromatic Building Blocks via the Upcycling of Polystyrene Based Plastic Waste

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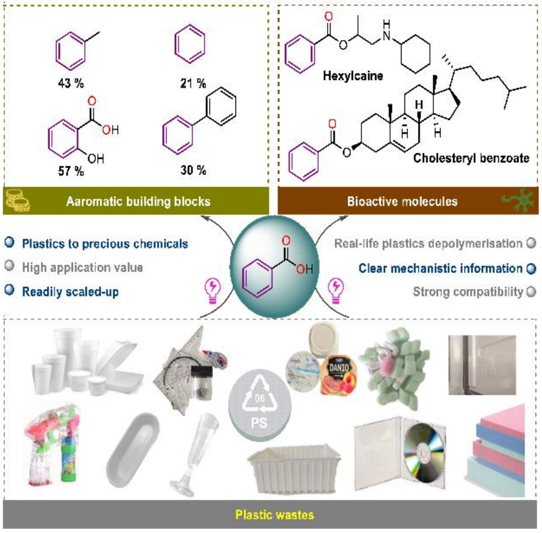
Keywords: Real-life plastic waste, metal-free, photo induced, aromatic compounds

The global market size for aromatic compounds is expected to reach $236 Billion by 2025 at a compound annual growth report (CAGR) of 7.6%. The current synthesis of the aromatics is mainly dependent on petroleum and coal-based feedstock [1]. However, these non-renewable resources will be exhausted in the near future, for example, global coal can only be used for 200 years, natural gas for around 60 years, and the worst thing is that oil has only 40 years to be exhausted! On the other hand, more than 370 million tons of plastics have been manufactured in 2021 and are estimated to exceed 500 million tons in 2050. Plastic waste has triggered a serious environmental and ecological crisis due to inadequate management and huge accumulation in landfills and oceans [2]. There if aromatic compounds can be synthesized directly from plastics, the strategy not only provides a sustainable synthetic route for the aromatic building blocks but also alleviate the plastic pollution in our society.

Based on this, we have designed a unique strategy that selectively photoconverts polystyerene-based wastes into a valuable commodity chemical – namely benzoic acid by using metal-free photocatalysts and later, this high-performance protocol degraded a series of post-consumer plastic wastes [3]. Significantly, the benzoic acid was in situ transformed into various aromatic building blocks such as toluene, benzene, salicylic acids, and so on. Furthermore, this conversion was readily scaled up into g-scale. Moreover, a possible mechanism with the aid of EPR, GC, and DFT calculations has been also proposed. We anticipate that these advances will provide an alternative solution to both dilemmas that synthesize aromatics and mitigate the severe environmental problems associated with the plastic waste.



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R&S-O8

A green analytical method to characterize unsaturated hydrocarbons in waste polyolefin pyrolysis oil using FT-IR

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Keywords: waste plastic, polyolefin, pyrolysis oil, unsaturated hydrocarbons, FT-IR

Polyolefin makes up approximately 50% of plastics consumed in Western Europe [1]. Chemical recycling is one of the preferred methods to recycle waste plastics by cracking them into basic chemical substances which can be reused in the petrochemical industry[2]. Characterizing alkenes in waste polyolefin pyrolysis oil is the key to chemical recycling, especially in the pyrolysis processes. In this way, deciding the chemical route and amount of reagents for the next process steps can be estimated correctly and easily. However, characterization is not easy because of the presence of a wide variety of different molecules and functionalities after cracking long chain hydrocarbons during the pyrolysis process of waste plastic, especially in PE (or PP) with no other functional groups, unlike other polymers (PS or PET). Moreover, feedstock for pyrolysis can come from LLDPE, LDPE, HDPE, PP, or even a mixture of them, which can lead to a big challenge to characterize each type of alkene in waste polyolefin pyrolysis oil.

Therefore, in this study, we propose a simple analysis method only using FT-IR to determine the kind and quantity of double bonds in pyrolysis oils. By studying characteristic absorption peaks of unsaturated hydrocarbons in the fingerprint region on IR spectrum between known and unknown samples, together with the estimated carbon number and molecular weight of those materials through the mass of methylene group (CH2), one main equation is proposed (EQ1', figure 1). Where the detection of double bonds per carbon has been studied by FT-IR on standard monosubstituted and 1,1 disubstituted alkenes, which are the two main alkenes in waste PE and PP pyrolysis oil. Our equation can give directly an amount of alkenes of an unknown sample under the form of "mole of double bonds per gram of sample".

After investigating and fitting calibration equations of DB/C measurement to equation EQ1', three practical methods for the different cases of olefin pyrolysis oil are developed. Afterward, our new method was applied to detect the mole of double bonds per kilogram of the standard mixtures and waste PE&PP pyrolysis oil to check the efficiency of this method. NMR was also used to confirm the accuracy. Overall, obtained results show that our method worked sufficiently well with RSD below 10% in the carbon range from C10 to C20.

This work was supported by the VLAIO Catalisti-ICON project P2PC (Plastics To Pre-cious Chemicals; project HBC.2019.0003)

$$\frac{Mole\ of\ double\ bond}{Mass\ of\ sample} = \underbrace{\left(\frac{Double\ bond}{Carbon}\right) * \frac{Number\ of\ Carbon\ in\ sample\ (\Sigma Cn)}{Molecular\ weight\ of\ sample}}_{\text{EQ 1}} = \underbrace{\left(\frac{Double\ bond}{Carbon}\right) * (\frac{1}{CH_2})}_{\text{EQ 1'}}$$

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R&S-O9

Use of FTIR microspectroscopy to assess the extraction viability of food waste

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Keywords: FTIR-microspectroscopy; food waste; imaging

The food industry generates large volumes of waste usually disposed of [1]. The use of side streams to manufacture energy, chemicals, or other valuable products is one of the pillars of circular bioeconomy and a marketable solution for waste management [2], [3]. Due to its heterogeneous and rich composition, food waste has significant economic potential, but the viability of the extraction processes is limited by the variability of the sample [4]. Developing screening tools to visualize biomass variation at different extraction stages could provide valuable information to optimize the process.

Modern devices based on hyperspectral imaging can simultaneously acquire information on the composition and spatial distribution [5]. Over the past years, some works have shown the potential of hyperspectral imaging on plant research [6]–[9]. Most of them focused on chemical changes affecting the quality of the fruits and vegetables consumed, but its applicability in food waste exploitation hasn't been widely explored.

The present research aims to inquire into the use of FTIR microspectroscopy to determine the main composition and spatial distribution of plant-based industrial residues. In the first step, spectral and spatial information of different plant waste samples was collected. After the reference material was subjected to various extraction techniques, spectral changes were examined. Our results show the potential of FTIR imaging as a screening tool to assess the viability of food waste as feedstock for extraction processes. Overall, the outcomes suggest that FTIR imaging can provide valuable information for the improvement of biorefinery processes.

This study is funded by Flanders' Food and VLAIO in the framework of the EffSep project (Grant number HBC.2019.0012)

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R&S-O10

3D Investigation of Nanoparticle Assemblies by Electron Tomography

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Keywords: nanoparticle assembly ; transmission electron microscopy ; electron tomography

Nanoparticle assemblies are great of interest in various fields due to their tunable structure and properties.[1-4] By changing the number of particles, and/or the interparticle distances, it might even become possible to reach specifically desired structures and properties for targeted usage.[5] Hereby, it is very important to investigate the structure-property relationship of the nanoparticle assemblies. In order to extract quantitative information on the 3D structure, an accurate characterization at the nanometer level is required. Transmission electron microscopy (TEM) is a useful technique to study nanomaterials. However, since conventional TEM is limited to 2D projections, it is important to perform electron tomography experiments to obtain reliable information for 3D structures. An important step to extract quantitative 3D information is the segmentation of the 3D data set. In this study, we compared three different segmentation methods to determine the number and diameter of nanoparticles in an assembly as well as the interparticle distances. In additional to manual segmentation, we applied advanced segmentation methods based on a watershed function, and a spherical Hough function.

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R&S-O11

Fresh water production from atmospheric air: Technology and innovation outlook

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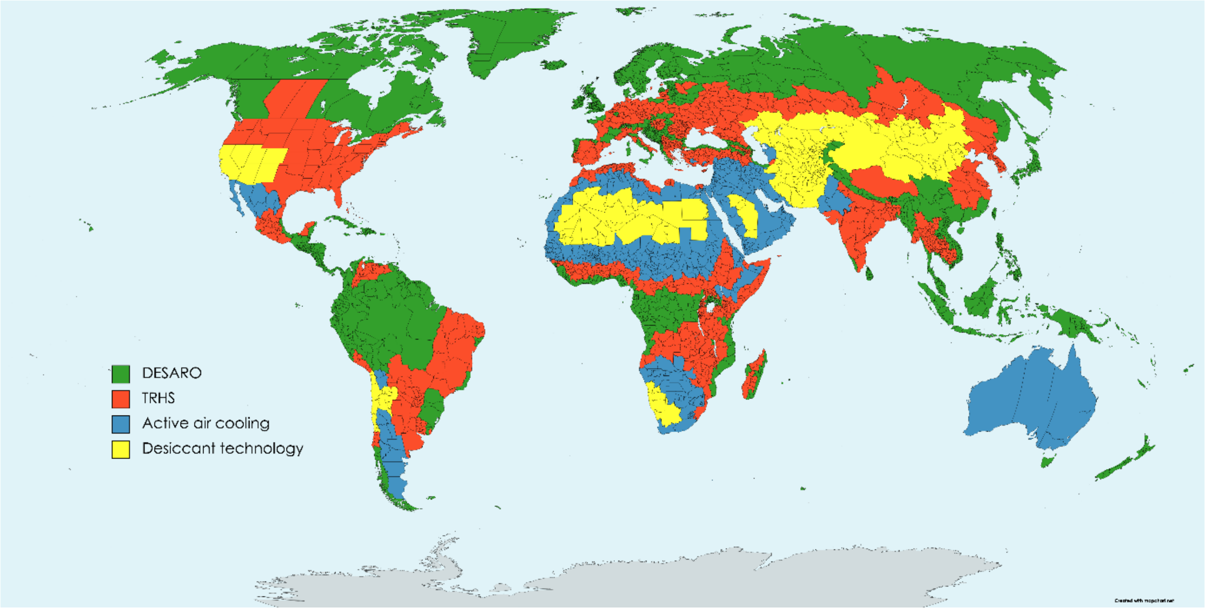
Keywords: Atmospheric water harvesting; desiccants; hygroscopic materials; water vapor adsorbents; thermo-responsive hydrophilicity switching polymers; deliquescent salt reverse osmosis; desalination; air cooling condensation

Fresh water production from atmospheric water vapor is a possible solution to local water scarcity, but the underlying processes are very energy demanding. Energy consumption of water-from-air technologies involving adsorption processes, thermo-responsive hydrophilicity switching polymers, air cooling processes, and reverse osmosis of deliquescent salt solutions are derived from energy balances. Estimates reveal that these technologies are uncompetitive when compared with conventional liquid fresh water sources. Water-from-air technologies become a viable option in the absence of local liquid water sources and when long-distance transport for socio-economic reasons is not an option. The usage of direct solar-driven technology for fresh water production from air is an attractive means to disentangle the local water-energy nexus. The optimal water-from-air technology depends on the climate, relative humidity, and temperature profiles and is presented on a world map, indicating the optimal geographic location for each technology.



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R&S-O12

An experimental study on the optimization of process parameters for super-dry reforming of methane

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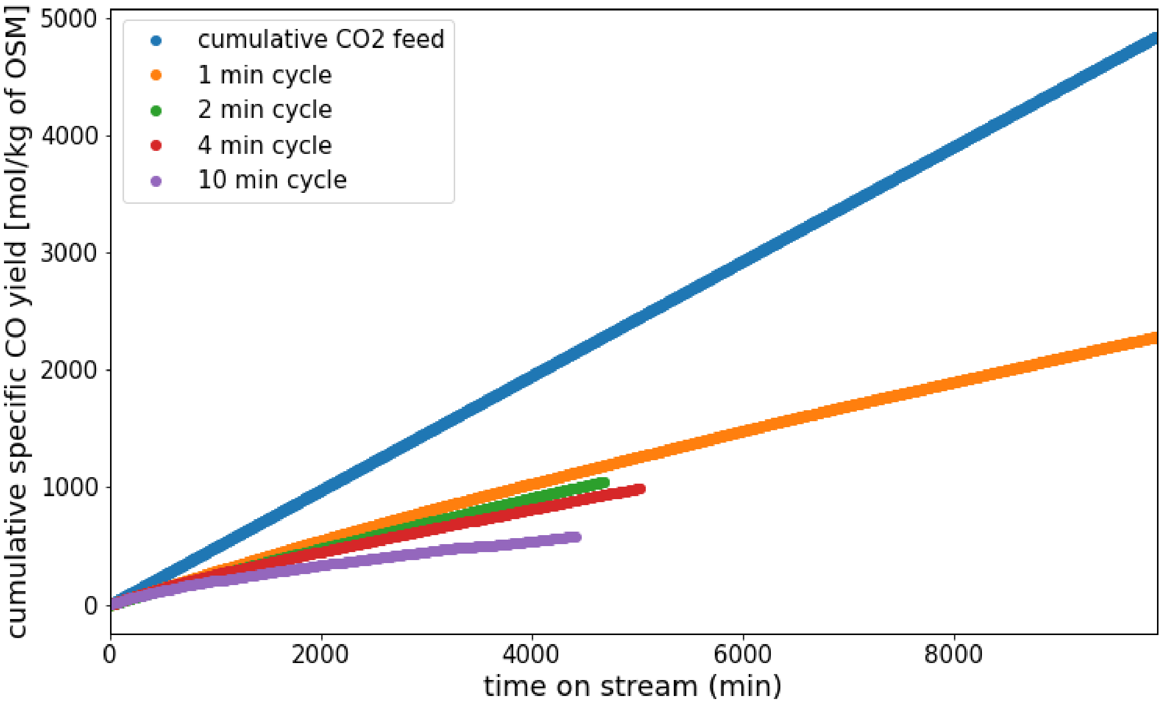
[1] *Ghent University, Belgium*

Keywords: CO2 capture and utilization; Chemical looping process; Sustainable engineering

Closing the carbon cycle in energy-intensive industries is a major objective for the EU to enable a climate-neutral, circular economy by 2050, as envisioned by the Green Deal. In order to achieve this, it is crucial to address greenhouse gas (GHG) emissions, for example by creating value chains to produce carbon-neutral fuels and chemicals starting from CO2. To this end, an intensified CO2 utilization process, named super-dry reforming (SDR), was developed by Buelens et al. [1]. SDR combines three major processes, i.e., dry reforming of methane, chemical looping redox reactions and calcium looping for CO2 capture. Compared to conventional dry-reforming, a conventional Ni-based catalyst can be used, since the operating conditions (1023 K, 101 kPa, 3:1 CO2/CH4 ratio) are thermodynamically unfavorable for carbon deposition, which results in less deactivation of the used catalyst. Moreover, the heat input required per mole of CO2 is 55 % lower (110 kJ mol-1 compared to 247 kJ mol-1), which makes this process also interesting from an energetic point of view. Per mole of methane three times as much CO2 can be converted, at the cost of hydrogen which is converted to water. However, when combined with green hydrogen, SDR can be a renewable, versatile and flexible source of syngas.

Currently, the Laboratory for Chemical Technology at Ghent University is building a super-dry reforming unit at pilot level, with a throughput of 1 kg CO2/h and a materials inventory of approximately 10 kg. This unit has two reactors in parallel, which are periodically switched between the reducing and oxidizing step. This allows to have continuous production of CO and inherent separation of H2O from CO and CO2. With more reactors in parallel, a permanent periodic regime, producing a steady stream of CO can be established [2].

The super-dry reforming process is optimized using a combination of experimental and modelling work. Experiments are performed focusing on the optimization of process parameters such as e.g. the length of the oxidation/reduction half-cycles. Experiments are carried out for a cycle length of 1, 2, 4 and 10 min. After each half-cycle, the reactor was purged for 1 min. Hence, for the same time on stream, a shorter cycle will have relatively less time where it is exposed to oxidizing or reducing gases. Remarkably, we observed that that shortest cycle length had the highest cumulative specific CO yield. This indicates that conversion of CO2 is fastest at the beginning of the oxidation half-cycle. For a cycle length of 10 min, significant deactivation of the oxygen-storage material (OSM) was observed. The ratio of the O-atoms in the feed to the exchangeable O-atoms in the OSM was larger than 1 in this case. Hence, these results show that deep reduction and deep re-oxidation have a negative effect on material stability. Deactivation mechanisms are further investigated through various characterization techniques such as (in situ) XRD and STEM-EDX.



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R&S-O13

Acidity and metal ratio effects on the low temperature hydrodeoxygenation of anisole over NiCu on SiO_2 and γ-Al_2O_3

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Keywords: Hydrodeoxygenation; Heterogeneous Catalysis; Ni-Cu catalysts; Biofuels; Biochemicals; Sustainable chemistry

The supply of fossil raw materials is finite and their use is linked to several environmental problems. Consequently, it is of utmost importance to investigate the conversion of renewable resources into valuable products. A high potential technology is the transformation of lignocellulosic biomass into fuels and value-added chemicals (i.e. BTX, cyclohexane, etc.). Several potentially viable routes have so far been explored, with biomass pyrolysis and aqueous phase catalytic processing among the most interesting. However, these routes typically result in a bio-oil which consists of highly oxygenated compounds. Due to the presence of unsaturated bonds and oxygen their stability, energy density, etc. is rather low, rendering them inadequate for direct use as biofuel. A hydrodeoxygenation (HDO) step is required to stabilize these components and make them suitable to be used as biofuels or other value-added products.

HDO has been a hot-topic for more than a decade and even longer, with the bulk of research focusing on the development of novel catalysts for the HDO of bio-compounds. Initially, research efforts mainly focused on noble metal catalysts, which have shown good performances, apart for rapid deactivation in some cases [1]. Hence, as an alternative transition metals, especially Ni- and/or Mo-based catalysts, have also been investigated [2]. Ni catalysts alloyed with Cu were promising in this respect, exhibiting a high hydrogenation ability in the low temperature range [3]. To bring these catalysts to industrial application, the NiCu catalyst itself as well as the reaction conditions should be optimized. This work focusses on the optimization of the NiCu catalyst in the low temperature regime (473 K), varying both the support and the Ni/Cu ratio.

Experimentally, the vapor-phase HDO of anisole has been assessed over NiCu catalysts, varying both the Ni/Cu ratio and the support. Both acidic γ-Al_2O_3 and neutral SiO_2 were used as supports to investigate the effect of acid sites on reaction mechanism in the low temperature range. The catalysts were characterized in detail via TPR, N_2-sorption, NH_3-TPD, TEM-EDX, XRD and XPS. The catalytic performance of the materials was assessed using a state-of-the-art High-Throughput Kinetics Screening set-up.

A link was established between the metal phases present on the catalysts and their performance. The presence of both a NiCu alloy phase and acid sites was found to be crucial for the low temperature hydrodeoxygenation of anisole to cyclohexane. Furthermore, the amount of Cu present in the alloy phase was important, as a Cu-rich alloy will be more active than a Ni-rich one. A pure Cu phase however is practically inactive, showing the necessity of having Ni atoms on the alloy surface.

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R&S-O14
Let the sun do your chores!

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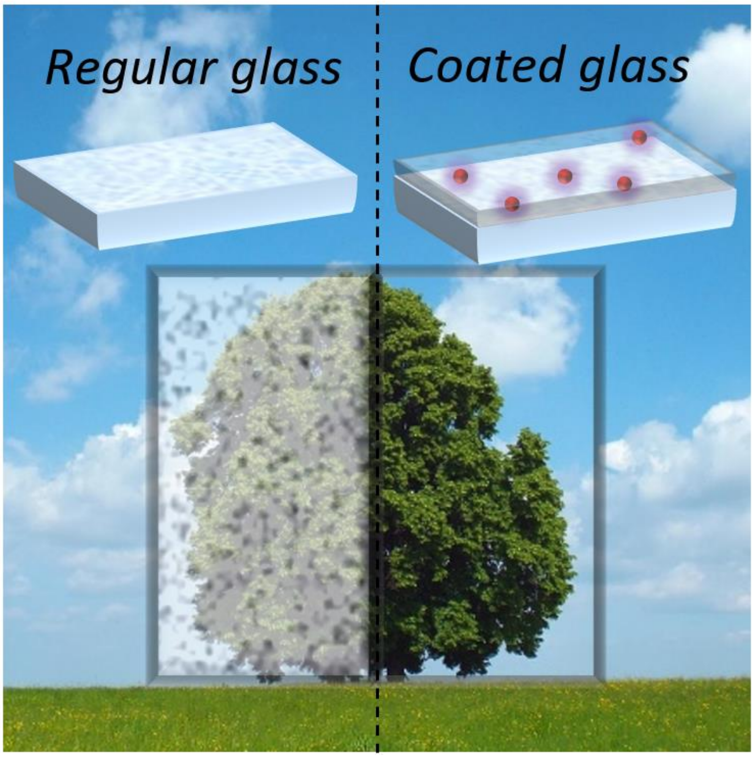
Keywords: Solar photocatalysis; plasmon embedded titania thin films; ISO; self-cleaning; air purification; water purification; antibacterial

Photocatalytic coatings are a promising technology against organic fouling in different forms as they can be applied as thin films on multiple substrates for various applications. To facilitate activity comparison, we considered ISO 27448, ISO 27447, ISO 22197-1,2 and ISO 10678 for self-cleaning, antibacterial, air (NOx, acetaldehyde) and water purifying properties respectively. Titania coatings with different plasmonic nanoparticles were tested along current commercial benchmarks, e.g. PilkingtonActivTM. Plasmonic nanoparticles are embedded into titania coatings to enhance their performance. They tackle the two main issues of titania as a photocatalyst, being (i) a low photoresponse in the solar spectrum, (ii) high charge-carrier recombination[1]. They increase the photoresponse by effectively using visible light and act as electron sinks, temporarily safeguarding excited electrons and preventing charge-carrier recombination. In a published article, we characterise these patented coatings (PCT/EP2018/079983) with an expanded photoresponse and improved photocatalytic (self-cleaning) activity[2]. The present work goes a step further and explores which plasmonic thin films are the most performant and readily compare them to commercial products following ISO tests. The results clearly show that the patented coatings outperform the commercial benchmark up to three times under UV-light. Under solar irradiation - adapting the ISO protocol – even higher improvements are expected.



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R&S-O15
Improved induction adsorptive CO2 capture process

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Keywords: Induction heating, CO2 capture

In the battle with climate change, cutting the use of fossil fuels and turning toward renewables is a major step. In this regard electrification of thermal processes in chemical industry holds a large potential for carbon footprint reduction via the use of green electricity and a decrease in energy intensity.

In this context, in our research, we have focused on the improvement of cycle steps in induction heating as an electrified alternative to conventional heating in Thermal Swing Adsorption processes to develop an effective electric cycle for carbon capture (Figure 1). In achieving this objective, extrudates of composite sorbents containing 13X zeolite and Fe3O4 (as the main ingredients) were prepared and subjected to heating quantification, equilibrium measurement, and dynamic ad/desorption experiments. Equilibrium measurements of CO2 and N2 adsorption isotherms confirmed that the mass adsorption capacity of the hybrid material decreases as the content of Fe3O4 increases, whereas the reduction in the adsorption capacity per unit volume of the extrudates is limited. This is due to the dense nature of Fe3O4, the content of 13X per unit volume of the sorbent with 20 wt% Fe3O4 is only 2% less than that of a sorbent with 10 wt% Fe3O4. With the aid of rapid inductive heating the desorption step could be completed in about 3 minutes, reducing the duration of the sorption cycles immensely.

The authors would like to acknowledge VLAIO for the financial support (HBC.2019.0109).

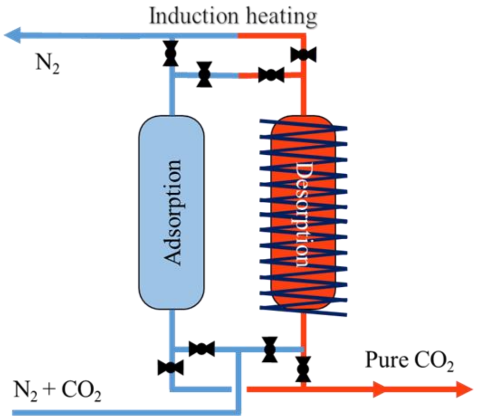

Figure 1: Illustrative description of CO2 desorption under induction heating

R&S-O16

Screening of biomass residue streams for their applicability as feedstocks for activated carbon production and their compliance as electrode material

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Keywords: Biomass residue strems; Activated carbon; Electrode material

Currently, activated carbon production still relies heavily on unsustainable feedstocks, e.g., coal or fresh wood. To be able to phase out these practices, biomass residue streams offer a valid alternative, both from an economic and ecological perspective. Therefore, this research screens different promising biomass streams for their potential to be converted into top-tier activated carbon. These should preferably have a well-developed porosity and high nitrogen content to maximize their energy storage capacity and potential applicability as electrode material in supercapacitors.

Seven different types of biomass were selected in this study based on their physicochemical characteristics (e.g., lignocellulosic composition and nitrogen content): Common ivy trimmings (CI), brewer's spent grain (BSG), Macadamia nut shells (MNS), chicken feathers (CF), coffee husks (CH) and the microalgae species Spirulina sp. (SP) and Chlorella vulgaris (CV). The biomass streams were transformed into biochars and activated carbons using a home-built stainless steel screw reactor [1,2]. Activated carbon was produced in a two step-process comprising a carbonization step at 700 °C in an inert atmosphere, followed by a physical activation step using CO2 at 800 °C. Biomass, biochars, and activated carbon were characterized for their ultimate and proximate analysis, biochemical composition, and elemental composition via inductively coupled plasma–atomic emission spectroscopy. Their surface functional groups were determined via FT-IR. Lastly, the porosity of the resulting activated carbons was measured via nitrogen physisorption experiments. The most promising activated carbons were incorporated in coin cell supercapacitors.

The results demonstrate the significant impact of the biomass's mineral composition on creating highly porous activated carbon structures. Furthermore, the overall activated carbon yields decreased for the samples with large ash fractions due to a relative increase in carbon burn-off. In terms of creating nitrogen-rich activated carbons, CF proved best with a resulting nitrogen content of 8.2%, in contrast with MNS, which exhibited the lowest percentage (0.54 %). However, in terms of porosity, this sample (MNS) outperformed the other investigated biomass streams with a BET specific surface area of 693.7 m2/g. A correlation between the activated carbon's porosity and their specific capacitance could be made when verifying the electrode material performance. Thus, the MNS-derived activated carbon performed best of the screened biomass streams with a specific capacitance of 53 F/g.

In conclusion, an investigation on the screening of different biomass residue streams was performed. It became clear that the low-ash content, lignocellulosic biomass MNS performed best compared to the other tested biomass streams. Future research should focus on combining different biomass streams to produce a highly porous nitrogen-rich biomass stream that would be perfectly suitable as electrode material.

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R&S-O17
Sodium aluminate-based materials as promising catalysts for biodiesel production

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Keywords: Catalysts; Biodiesel; Catalytic activity; material characterization

Fossil fuel dependence is nowadays at the heart of many international debates, ranging from environmental to geopolitical issues, it is clear that renewable energy plays a pivotal role in our society. Biodiesel, i.e. a mixture of fatty acid methyl esters (FAME) [1], is mainly produced through the transesterification of triglycerides via a homogeneously catalyzed process. Common catalysts as KOH, NaOH are largely available and cheap, however, the application is severely restricted by high recycle cost, soap formation and consequent loss of oil and problems of product separation [2]. It follows that heterogeneous basic catalysts could be easily recycled and reused overcoming many of these drawbacks. Although many base materials such as MgO, CaO, Na/SiO2, Ca/Mg-SBA-15 etc. have been investigates [3-4], it is still difficult to find efficient catalysts with an economic feasibility for the necessary scale up process. Sodium Aluminate, NaAlO2 (SA), is a promising candidate to overcome these limits because it is a solid strongly basic catalyst, cheap and easily available (byproduct of Boehmite industrial process). Furthermore because of its hygroscopic and corrosive nature, it is useful to incorporate it over a support. While sparse works have been found on the pure material [5-7], supporting it over a material with adequate morphological and textural properties is still matter of open research [8-9]. The aim of this work is to develop new Sodium Aluminate-based catalysts for transesterification reaction. To this purpose NaAlO2 was successfully incorporated with different impregnation methods on alumina and hydrotalcite supports. The so obtained materials were catalytically tested in the methanolysis reaction of commercial sunflower oil and compared with other common catalysts in this field. SA-based catalysts showed excellent performance, outcompeting other classical catalysts (i.e. MgO, Hydrotalcites) in terms of biodiesel production in the same reaction conditions. Furthermore, to correlate catalytic efficiency with morphological and surface properties, all the materials were deeply investigated by N2 physisorption, XRD, SEM, FT-IR, DRIFT, TPD. Characterizations techniques as TPD and DRIFTS show that the key role, in the catalytic behaviour of SA-based materials, is played by the quantity and strength of the basic sites. SA based materials possess a high number of basic sites capable to strongly deprotonate the methanol, forming methoxide ions able to attack the triglycerides chains.

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R&S-O18

NMRCoRe@CMWS as a node of convergence in molecular water science in Flanders

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Keywords: molecular water science; physicochemical characterisation; energy water nexus; NMR; X-ray science

Advancing molecular water science to provide innovative technological solutions is essential to sustain modern society and the primary goal of the Center for Molecular Water Science.[1] Solving the water energy nexus is key to enable society to meet its ever increasing demand for fresh water and enable carbonless energy production. Such developments call for a molecular-scale understanding of water. Understanding the structure and dynamics of the water hydrogen-bonding network is essential to grasp essential aspects of the processes driving our planet, its environment and the recently observed global climate change. This is a non-trivial task since even though water is everywhere and it appreciated as a simple molecule, the basic science of water has still to be completely understood. We are still unaware about its microstructure, i.e., exactly how water molecules organize themselves in the liquid form, at surfaces, and around biomolecules and polymers and how this organization evolves in time since water is clearly dynamic in nature with hydrogen bonds that form and dissolve on sub-picosecond timescales.

Unique, but fragmentary information on self-organization of water in its liquid form, at surfaces, and around biomolecules, is being harvested by physicochemical observations and a score of state-of-the-art techniques, Nuclear Magnetic Resonance (NMR), Electrochemical Impedance Spectroscopy (EIS), Dielectric Relaxation Spectroscopy (DRS), infrared, Raman and TeraHertz spectroscopy as well as X-ray and neutron scattering. Probing chemistry, chemical interactions and physical state, NMR is ideally positioned to serve as a node of convergence connecting observations from different sources into a unified model. [2]

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Poster Sessions

Poster session A: Wednesday October 12, 15:50-17:00 (Cafetaria)

Functional Materials (FM)		
FM-A01	Aerts Andreas	Development of responsive hydrogels for innovative treatment of osteoarthritis
FM-A02	AG Karthick Raj	Self-healing photoelectrocatalyst for selective oxidation of glycerol into valuable products
FM-A03	Arreguin Campos Mariana	Tough PEO based hydrogels for 3D printing and tissue engineering
FM-A04	Bazylevska Anastasiia	Bipolar electrochemistry for functionalization of 2D materials
FM-A05	Bhandary Subhrajyoti	Effect of chemical substitution on the construction of boroxine-based supramolecular crystalline polymers featuring B←N dative bonds
FM-A06	Billiet Naomi	Chemical solution-based synthesis of earth-abundant electrocatalysts for PEM water electrolysis
FM-A07	Borbás Balázs	Upconverting nanoparticles: energy transfer with dye molecules in suspensions and thin film systems
FM-A08	Chandrasekharan Vinodchandran	NMR studies of hydrogen-bonded water-aminium assemblies templating SAPO materials
FM-A09	De Meyer Pieter	Design of advanced anode materials for lithium ion batteries
FM-A10	De Vriendt Xeno	Quantifying delocalization and static correlation errors by imposing (spin)population redistributions through constraints on atomic domains
FM-A11	Debusschere Nele	Chemical solution synthesis of copper-based photocathode materials for photoelectrochemical reduction of CO2 to methanol
FM-A12	Dochain Denis	Innovative sol-gel routes to mesoporous bifunctional catalysts for the upgrading of bioethanol to butadiene
FM-A13	Driesen Sander	Combining hybrid hydrogels with peptide conjugation for targeted cartilage tissue engineering
FM-A14	Dumortier Loïc	A reactive force field for alumina systems

FM-A15	Ebrahimi Mahsa	Tailored network topology in mechanically robust double network hydrogels for 3D printing and injection
FM-A16	Giordano Luca	Study on Ga incorporation into InP quantum dots for laser application
FM-A17	Grachev Vladimir	Phase separation and stability of cotton and bacterial cellulose nanocrystals in the presence of various salts
FM-A18	Gutierrez Cisneros Carolina	Improvement of the mechanical performance of methacrylated alginate wound dressings through the addition of different crosslinking agents
FM-A19	Hamid Mouna	Advanced segmented block copoly(ether ester) for more sustainable polymer 3D printing
FM-A20	Houben Sofie	Dual network hydrogels with dynamic crosslinking possessing tuneable mechanical properties
FM-A21	Kavak Safiyye	3D investigation of metal-organic frameworks at atomic scale

Chemistry meets Biology (CB)		
CB-A01	Abdelhameed Shorok	Polyoxometalate ligand enables regioselective copper-mediated oxidative cleavage of protein
CB-A02	Borrego-Muñoz Paola	Anti-inflammatory effect of Izalpinin derived from Chromilaena leivensis: λ-carrageenan-induced pawa edema and in silico model
CB-A03	Cleirbaut Robine	Using UV-Vis spectroscopy and EPR as a tool to study the incorporation of heme proteins in titania
CB-A04	Declerck Kilian	Metal-oxo clusters as new class of nanozymes toward protein hydrolysis
CB-A05	Denijs Elias	Temperature triggered in situ tyrosine bioconjugation
CB-A06	Heirman Pepijn	The effect of plasma-induced oxidation on the interaction of inhibitory NK-cell receptors with their cancer cell ligands

CB-A07	Keskin Özlem Buse	Isolation, purification and structural characterization of siderophores from P. damselae subsp. piscicida
CB-A08	Keskin Özlem Buse	Growth and siderophore production in vritro P. damselae subsp. Piscicida under iron limitation
CB-A09	Krols Simon	Targeted AURKA degradation: towards new therapeutic agents for neuroblastoma
CB-A10	Lentink Sarah	Noncovalent complexes formed between hybrid polyoxometalates and proteins

Chemical Synthesis & Methodologies (CS&M)		
CS&M-A01	Ach Bram	Rapid aza-analoging of common carbocyclic scaffolds via a Diels-Alder/retro-Diels-Alder approach
CS&M-A02	Alizadeh Eslami Ali	A thermoreversible sol-gel route for the synthesis of ZrO2, CeO2, TiO2, and SnO2 catalysts used in the valeric acid ketonization
CS&M-A03	Bafti Arijeta	Influence of the titanium pretreatment on the yield titania nanotube properties
CS&M-A04	Beliš Marek	Nucleation and particle growth of poly(3-alkylthiophenes)
CS&M-A05	Bevernaege Kevin	Au(I) catalysed benzylic C-H amination with PTAD
CS&M-A06	Cruyssaert Ben	Exploration of synthesis and surface chemistry of colloidal alkaline-earth chalcogenides
CS&M-A07	Dadashova Narmin	Study of poloxo- and peroxometalates containing rare earth elements catalysts by physicochemical methods
CS&M-A08	Das Soumya Kumar	In-situ XRS and XES following Ni-Fe restructuring during methane dry reforming
CS&M-A09	De Vos Lobke	Development of polymeric hybrid scaffolds for corneal tissue engineering
CS&M-A10	Degroote Frederick	Exploring the synthetic utility of proton-free sulfur-mediated (3+2) cycloadditions
CS&M-A11	Demaerel Joachim	Synthesis of imidosulfur(IV) derivatives of sulfinate and sulfite esters via formal S-S bond insertion of dichloramines

CS&M-A12	Eloi Loïc	Synthesis and characterization of hybrid materials containing H-ZSM-5 and CeO2 for the one-step dehydration of 1,3-butanediol to butadiene
CS&M-A13	Górczyńska Sylwia	Chirality generation in triphenylmethane derivatives
CS&M-A14	Gries Aurelia	Determination of reaction enthalpies of synthesizing β-Li3PS4 in tetrahydrofuran
CS&M-A15	Hašková Lenka	Preparation of nature-based sulfoxides: alliin and its derivatives
CS&M-A16	Ilić Milica	Synthesis, biological evaluation and in silico ADMET prediction of 17α-picolyl and 17(E)-picolinylidene estra-1,3,5(10)-triene derivatives
CS&M-A17	Kalandia Givi	Polyoxometalate – pillararene hybrid for supramolecular polymer formation

Energy & Environment (E&E)		
E&E-A01	Ampe Adriaan	In-column modification of aminopropyl silica to produce highly performant stationary phases for Temperature-responsive liquid chromatography (TRLC)
E&E-A02	Beckwée Emile	Kinetics & thermodynamics of CH4 storage in solid aided clathrates
E&E-A03	Ciocarlan Radu-George	Modification of the surface chemistry of porous silica materials for gas storage applications
E&E-A04	De Geest Mitra	Clay-based structured composites for wastewater treatment through chromium removal
E&E-A05	Gueibe Christophe	Investigation of xenon adsorption in three types of porous materials
E&E-A06	Jia Yu-Wei	Simultaneous measurements of metals and PAHs using diffusive gradients in thin films (DGT) with an environmentally friendly binding layer
E&E-A07	Kajtazi Ardiana	ChromaRIM App: the new software in liquid chromatography to assist structural identification of small environmental solutes
E&E-A08	Kummamuru Nithin	Accelerated formation of methane hydrates in stainless steel beads packed reactor
E&E-A09	Lejaegere Charlotte	In-line gas chromatograph for ultra-trace level analysis of off-flavor compounds in water

E&E-A10	Lenaers Stijn	Large organic cations as stabilizing interlayer for hybrid perovskite solar cells

Chemical Processes & Reactor Technologies (CP&RT)		
CP&RT-A01	Arts Wouter	Stepping away from purified solvents in reductive catalytic fractionation, a step forwards towards a disruptive wood biorefinery process
CP&RT-A02	Bekele Beruk Alemu	Understanding the kinetics of 2,3-butanediol dehydration into 1,3-butadiene via kinetic modeling
CP&RT-A03	Bonheure Mike	Power-2-olefins: supersonic olefin production
CP&RT-A04	Bossier Sander	Plasma catalytic dry reforming of methane: how material properties influence conversion and kinetics – The PlasMaCatDESIGN project
CP&RT-A05	Ceulemans Sara	Effect of quenching on the afterglow temperature to improve CO2 conversion in a rotating gliding arc plasma reactor
CP&RT-A06	Den Haese Milan	Fully biobased-triblock copolymers generated using an unconventional oscillatory plug flow reactor
CP&RT-A07	Devos Cedric	A microfluidic batch reactor for quiescent multiphase paracetamol crystallization
CP&RT-A08	Gao Yujie	Ultrasensitive turn-on luminescence humidity sensor based on a perovskite/zeolite composite
CP&RT-A09	Garbarino Lucas Ivan	Mesoscale reaction-diffusion modelling of lignin solvolysis

Renewables & Sustainability (R&S)		
R&S-A01	Adeel Muhammad	Reducing the toxicity of crumb rubber granulates by encapsulation with (reclaimed) polymeric coatings
R&S-A02	Bleus Dries	Activated carbon adsorbers from NADES-extracted brewer’s spent grain and malt dust biomass
R&S-A03	Delabie Florian	Hemicellulose in the RCF biorefinery: towards a sustainable production of furfural in green solvents
R&S-A04	Hernandez Toribio Aitor	On the positioning of the internal catalyst in non-isocyanate polyurethanes: from faster exchange ratios to selective urea formation

R&S-A05	Jacobs Bram	Green two-step valorization of organosolv lignin: depolymerization and hydroxyalkylation
R&S-A06	Lubbe Foster	Drinking water from the air in South Africa

Poster session B: Thursday October 13, 15:10-16:20 (Cafetaria)

Functional Materials (FM)		
FM-B01	Lavendomme Roy	MoloVol: an easy-to-use tool for calculating cavity volumes and surfaces
FM-B02	Lenaerts Hilde	Designing metal oxide-based stationary phases for the separation of Ac-225 and Bi-213 for biomedical applications
FM-B03	Marcinskas Mantas	Organic semiconductors with phosphonic acid functional groups for application in photovoltaics
FM-B04	Maufort Arthur	Functionalization of 2D layered hybrid perovskites with benzotriazole-based organic ammonium salts
FM-B05	Misiakos Georgios	Structure-property investigation of Diels-Alder polymer networks
FM-B06	Misko Vyacheslav	Inverse solidification in active soft matter: towards new functional materials
FM-B07	Mohanty Sonali	Dual mode – thermometry and drug release vehicles based on hollow Y2O3:Er,Yb and Y2O2SO4:Er,Yb spheres
FM-B08	Mullaliu Angelo	Cutting-edge characterization tools for the in-depth investigation of functional materials
FM-B09	Mychinko Mikhail	The influence of size, shape, and defects on heat-induced alloying in individual Au@Ag core-shell nanoparticles
FM-B10	Naenen Viktor	Synthesis and characterization of high purity two-dimensional monolayer Ti3C2 MXenes
FM-B11	Ninakanti Rajeshreddy	Effect of tunable shell thickness on the plasmon-enhanced photocatalytic activity of (Au/Ag)@TiO2 core shell nanoparticles

FM-B12	Premcheska Simona	Effect of the synthetic route on the morphological and temperature-dependent photoluminescence properties of Na3ZrF7(Yb,Er) nanoparticles
FM-B13	Princen Ken	REVERSIGEL: REVERSIbly crosslinked hydroGELs for effective cardiac stem cell delivery
FM-B14	Radhakrishnan Sambhu	Hydrogen bonding with framework siloxane bonds drives liquid phase adsorption of primary alcohols in high-silica zeolites
FM-B15	Respekta Dobromił	Band alignment in InP/ZnSe core/shell quantum dots
FM-B16	Sasikumar Rahul	Multilevel nanoscale chemical patterning of graphite at different length scales
FM-B17	Svirskaite Lauryna Monika	N-type self-assembled semiconductors for application in photovoltaic devices
FM-B18	Tiryaki Aşkım Cansel	Optimization of sulforaphane extraction from cabbage seeds by ultrasound and microwave extraction methods
FM-B19	Van Bossele Laura	Strontium barium niobate thin layers as lead-free alternative for photonic applications
FM-B20	Van Hende Daria	The role of electron correlation on resonance effects
FM-B21	Zhu Jian	Boosted CO2 reduction of non-precious metal Ni@N-doped carbon electrocatalyst by regulating the synergies of Ni and N-doping

Chemistry meets Biology (CB)		
CB-B01	Balcaen Tim	Exploring contrast-enhancing staining agents for studying adipose tissue by means of contrast-enhanced computed tomography
CB-B02	Magdalenic Katarina	The natural product curcumin as a source of inspiration for the development of novel benzothiazepane-based cancer cell cytotoxic agents
CB-B03	Pappa Michaela	Chlorella sp. culture in coagulation and dissolved air flotation separation process using a poly-ε-lysine coagulant
CB-B04	Savic Nada	Controlling the reactivity of metal substituted polyoxometalates as artificial proteases through the

		interplay between surfactant and protein interactions
CB-B05	Sestic Tijana	Synthesis, structural characterization and in silico study of novel 4-azasteroid-17-hydrazone derivatives
CB-B06	Simms Charlotte	Introducing a second metal to Zr-MOF-808 to increase activity as an artificial peptidase
CB-B07	Swinnen Siene	Hydrolytic activity of Zr(IV) metal organic frameworks towards proteins in buffer solutions
CB-B08	Ul Haq Farhan	Deciphering the conformational landscape of ROS1 kinase using computational tools
CB-B09	Verdonck Jelle	Development of an analytical methodology for ultra-trace chromium speciation in biological fluids
CB-B10	Weckx Pasquinel	High temperature DOSY-NMR measurements allow for diffusion-based virtual separation in mixtures of less mobile biopolymers
CB-B11	Zhao Yuheng	Understanding the bone and vascular calcification related to type I collagen and Poly (ADP-ribose) in collagen tissues – a computational investigation

Chemical Synthesis & Methodologies (CS&M)		
CS&M-B01	Kheradmand Ezat	Ligand exchange quantification on colloidal InAs quantum dots
CS&M-B02	Lederer Mirijam	The influence of bases on thermal decomposition synthesis of LaF3
CS&M-B03	Lemaître Tom	Development of targeted Tb-161 radiolabeled nanoparticles
CS&M-B04	Liu Cuilian	Polyoxometalate based metal-organic assemblies towards supramolecular catalysis
CS&M-B05	Madhav Dharmjeet	Ultrasound assisted, bio-inspired CO2 mineralization to form CaCO3 with different morphology
CS&M-B06	Maes Diederick	Make and break: new thiol-thiol bonding and debonding platforms
CS&M-B07	Moussawi Mhamad Aly	Versatile post-functionalization strategy for the formation of symmetrical and non-symmetrical organic-inorganic polyoxometalate hybrids

CS&M-B08	Osmanova Sevinj	Effect of reaction conditions on the phase composition, magnetic and catalytic properties of MnOx-Na2WO4/SiO2 oxide system for oxidative conversion of methane
CS&M-B09	Osmanova Sevinj	Reactions of free radicals in catalytic oxidative conversion of methane based on in situ EPR/MS data
CS&M-B10	Radovanović-Perić Floren	Development of nanoporous crystalline thin films by spark plasma ablation deposition
CS&M-B11	Raes Arno	Sonochemistry as alternative route for the synthesis of black titania
CS&M-B12	Salazar Marcano David	Post-functionalization of hybrid hexavanadates as components in supramolecular systems
CS&M-B13	Talukdar Kristy	Sol-gel synthesis of Cu-based niobate for photoelectrochemical conversion of CO2
CS&M-B14	Van Hoey Wouter	Effect of templating on hydrothermal synthesis of Ce/Zr-oxide based catalysts for combustion of volatile organic compounds
CS&M-B15	Vaneeckhaute Ewoud	1H/D scrambling on functional groups of transition metal ligands enables conformational NMR analysis of homogeneous hydrogenation catalysts
CS&M-B16	Vermeeren Benjamin	Reductive amination of glycolaldehyde towards ethylene polyamines: selectivity control by fundamental mechanistic insight
CS&M-B17	Voets Lauren	SuFEx-enabled, chemoselective synthesis of triflates, triflamides and triflimidates

Energy & Environment (E&E)		
E&E-B01	Ma Tianhui	Biogeochemical cycle of Mercury (Hg) in sediment of the Scheldt Estuary and the Belgian Part of the North Sea (BPNS)
E&E-B02	Matranxhi Besarta	Assessment of the toxic potency and mutagenicity of soils from waste dumping sites in Wallonia, Belgium
E&E-B03	Mus Jorben	Randles circuit and performance analysis of a small proton exchange membrane fuel cell using current interrupt and electrochemical impedance spectroscopy techniques

E&E-B04	Pashayeva Ziyaret	Dissolution of cellulose in ionic liquids based on acetic acid
E&E-B05	Santos Sara	Solid micellar catalysts for CO2 hydrogenation to formate
E&E-B06	Stulens Sander	Synthesis of hollow mesoporous MOx spheres for enhanced confinement of polysulphides in lithium Sulfur batteries
E&E-B07	Vandeputte Delphine	Use of Cl/Br ratio as tracer for anthropogenic contamination in groundwater
E&E-B08	Vanderschaeghe Hannah	Thermo-responsive polymers for water harvesting from air
E&E-B09	Waly Sara	Artificial solar concentrators for renewable energy applications

Chemical Processes & Reactor Technologies (CP&RT)		
CP&RT-B01	Houllebergs Maarten	Dispersing carbomers, mixing technology matters!
CP&RT-B02	Hu Tianze	Investigation of dynamical aspects of molecular self-assembly and polymorphism on graphene using Raman spectroscopy
CP&RT-B03	Janssens Pieter	Dehydration of biomass-derived butanediols into green 1,3-butadiene: single-event microkinetic model construction and process design
CP&RT-B04	Lappa Foteini	Catalytic materials for CO2 conversion to heavier hydrocarbons
CP&RT-B05	Lataf Mohamed Amine	The synthesis and characterization of magnetic microwave absorbers for microwave-assisted pyrolysis
CP&RT-B06	Najafi Lahiji Mahsa	Pulse gas chromatography study of light olefin and paraffin adsorption
CP&RT-B07	Pourfallah Hesam	Computational fluid dynamics assisted reactive distillation design for the energy efficient dehydrogenation of liquid organic hydrogen carriers
CP&RT-B08	Torka Beydokhti Mostafa	Separation of zeolites with electrosedimentation
CP&RT-B09	Vandekerckhove Bavo	Practical actinometry in photoflow reactors

CP&RT-B10	Zanganeh Zinat	CO_2 hydrogenation to methanol over Au/ZnZrOx at high reaction temperatures

Renewables & Sustainability (R&S)		
R&S-B01	Meersseman Arango Hippolyte	Membrane-immobilized transaminase for intensified chiral amines production
R&S-B02	Mikolaitiene Austeja	Microalgae in fertilizers as a bioactive material to increase the sustainability of agroeco systems
R&S-B03	Morais Alysson	Multi-diagnostic NMR-dielectric characterization of water confined in hydrophobic pores
R&S-B04	Mortier Jonas	Co(salen)-catalyzed oxidation of para-substituted phenols towards benzoquinones: an experimental study of lignin model substrates
R&S-B05	Nees Marthe	The NCO cycle: heating up to the full recycling of PU waste.

FM-A01

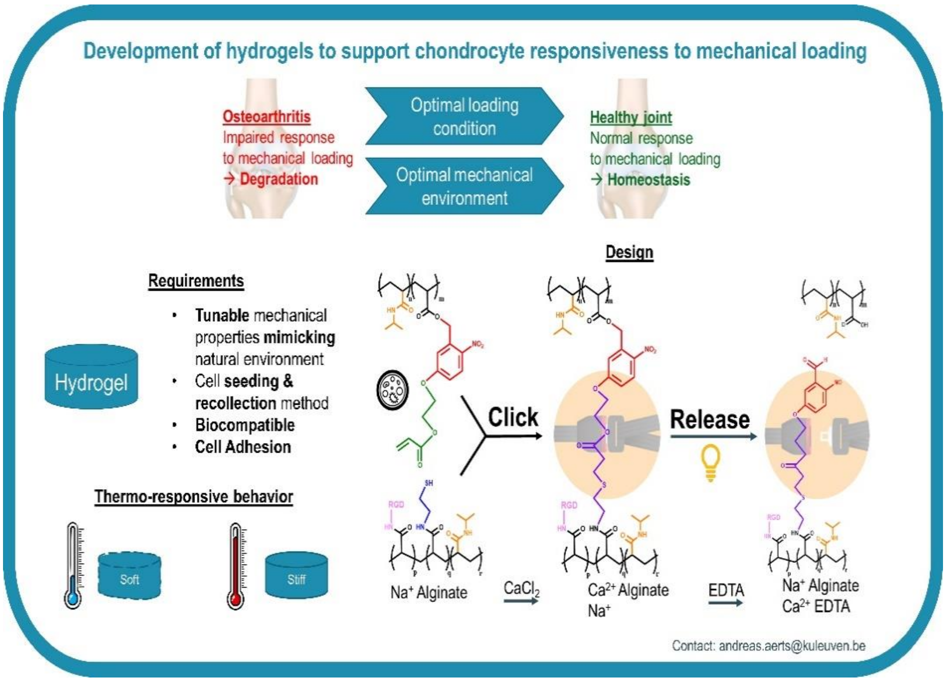
Development of responsive hydrogels for innovative treatment of osteoarthritis

Aerts Andreas[1]

[1] *KU Leuven, Belgium*

Keywords: Hydrogel; Thermoresponsive; Cell Culture; Osteoarthritis

Osteoarthritis has a high disabling impact on patients' lives and a high economic burden. To date, the only treatment for osteoarthritis consists of end-stage joint replacement. More insight into the role of the mechanical micro-environment on the impaired chondrocyte response upon mechanical loading will lead to the development of future effective exercise programs. To this end, a hydrogel with tuneable viscoelastic properties would revolutionize this work as it would allow to precisely modulate the micro-environment of the chondrocyte while leaving the cells in situ. A hydrogel consisting of thermoresponsive N-isopropylacrylamide polymers with an efficient cell seeding and recollection mechanism was developed in the form of a "click and release system". The click reaction consist of a biocompatible Michael-type reaction between a thiol and an acrylate functionality whereas a photo-labile o-nitrobenzyl moiety will be incorporated into this cross-linker to allow recollecting of the embedded cells on demand. A second alginate network cross-linked with calcium cations will be interwoven to obtain mechanical properties mimicking more closely native cartilage. First results of a proof-of-concept hydrogel network without the o-nitrobenzyl ester moiety will be presented. The ratio between thermoresponsive monomer and monomers designed to cross-link was successfully altered and the effect on solubility and thermoresponsive behaviour of their solutions was investigated. At the lowest incorporation ratio, a cloud point temperature of 26°C was obtained for both polymer solutions, which initially increased for the thiol containing polymers but sharply decreased for the acrylate containing polymers with increasing incorporation ratio. An optimized ratio of 97:3 was determined, hydrogels produced with this particular ratio had a swelling degree ranging from 100% to 400% at respectively 37°C and 4°C and a volume phase transition temperature around 21°C. Firm and elastic hydrogels are obtained at low temperature with a storage modulus of around 10 kPa, increasing the temperature increases the viscous behaviour of the hydrogels. More measurements are currently being carried out to more precisely characterize the mechanical properties of the hydrogel in function of temperature.



Development of hydrogels to support chondrocyte responsiveness to mechanical loading

Osteoarthritis
Impaired response to mechanical loading
→ **Degradation**

Optimal loading condition

Optimal mechanical environment

Healthy joint
Normal response to mechanical loading
→ **Homeostasis**

Requirements

- **Tunable** mechanical properties **mimicking** natural environment
- Cell **seeding & recollection** method
- **Biocompatible**
- **Cell Adhesion**

Thermo-responsive behavior

Design

Contact: andreas.aerts@kuleuven.be

FM-A02

Self-healing photoelectrocatalyst for selective oxidation of glycerol into valuable products

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Keywords: Glycerol Oxidation; Self-healing catalysis; Photoelectrochemical oxidation; Hydrogen

Glycerol is a major by-product of the biodiesel industry and low-cost source for many value-added C1 to C3 products. Currently, glycerol is converted into different value-added products by photocatalytic, thermocatalytic, electrocatalytic and photoelectrocatalytic methods [1]. The photoelectrocatalytic (PEC) oxidation of glycerol is attractive due to high product selectivity, its green character upon coupling with renewables, moderate and ambient reaction conditions while comparing with conventional high-temperature thermal catalysis, and also a high electron-to-product efficiency [2]. In this work, transition metal (Ni, Co, Fe) doped Bismuth vanadate (BVO) photoanodes are prepared by a two-step electrodeposition method. 10% Pt carbon on nickel foam was used as a dark cathode. Transition metal dopants on BVO form metal (Co, Ni) borate/phosphate active layer on the surface of BVO which prevents dissolution and regenerate the catalytic active surface, thus inducing a self-healing effect on the catalyst surface while testing in borate/phosphate buffer. The metal dopants display a synergetic effect of increased overall PEC performance and improved electronic conductivity of BVO. The glycerol oxidation is carried out in a customized membraneless two-electrode PEC flow cell with Re 83.9 in the presence of 0.1 M of glycerol in potassium borate buffer. The overall product selectivity to dihydroxyacetone is tuned by varying the different reaction parameters like applied potential, pH of the electrolyte, dopant ratio, and glycerol concentration.

[1] Wan Haibo et al, Electro-Oxidation of Glycerol to High-Value-Added C1-C3 Products by Iron-Substituted Spinel Zinc Cobalt Oxides. ACS Applied Materials and Interfaces, 14 (12), 14293–14301 (2022).

[2] Tateno Hiroyuki et al, Photoelectrochemical Oxidation of Glycerol to Dihydroxyacetone Over an Acid-Resistant Ta:BiVO4 Photoanode. ACS Sustainable Chemistry & Engineering, 10 (23), 7586–7594 (2022).

FM-A03
Tough PEO based hydrogels for 3D printing and tissue engineering

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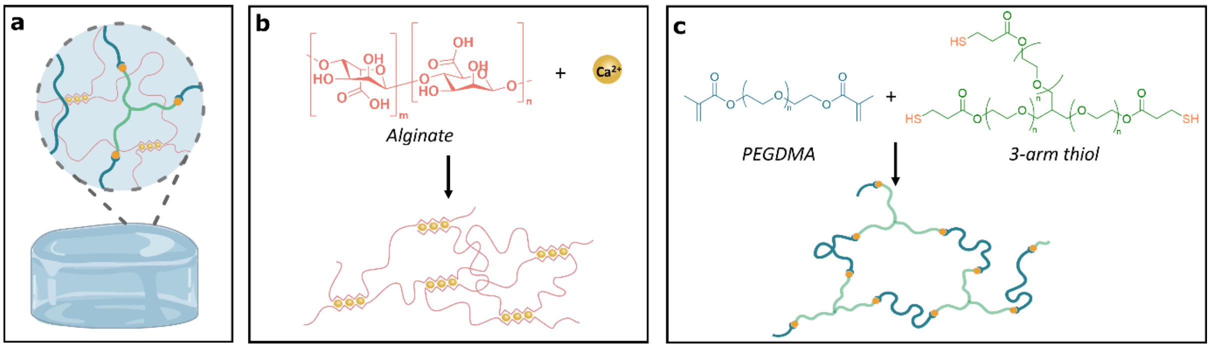
Keywords: hydrogels; tissue regeneration; 3D-printing; DN-hydrogels

As humans, injuries, diseases, and congenital malformations have always been part of our lives. Despite significant progress, pharmaceutical treatments often have limited efficacy. It is here where regenerative medicine and tissue engineering emerge, trying to provide solutions for treating severe injuries, where the body's response is not sufficient to restore comprehensive functionality. Nevertheless, mimicking native tissue is a formidable task.

Hydrogels are hydrophilic materials that can take up to thousands of times their dry weight in water. Due to their soft consistency and permeability to small molecules, hydrogels are attractive materials for regenerating tissue. Even though hydrogels are already being used in applications such as contact lenses, drug delivery, and wound dressing, the challenge of achieving mechanical integrity while incorporating other complex characteristics, and maintaining biocompatibility, still remains.

Double network hydrogels (DN hydrogels) are systems consisting of a combination of two different hydrogels. The contrasting properties of the two networks provide the material with exceptional mechanical properties. For instance, DN hydrogels have demonstrated mechanical properties comparable to the strength and toughness of cartilage.1 Despite the success in developing hydrogels with high mechanical performance, fabricating double network hydrogels that can be processed into complex three-dimensional (3D) structures continues to represent a challenge. Synthesizing DN hydrogels typically requires multiple steps, contrasting with the "one-pot" setup used for most injection/3D printing techniques. We tackle the problem with orthogonal crosslinking chemistry in two compatible networks. We employ both thiol-ene crosslinking and reversible ionic bonding (Figure 1). Thus, the selective reactivity of the two networks will potentially allow the formation of a double network hydrogel in a one-pot manner, which can further translate into the fabrication of complex 3D structures for the tailored treatment of various ailments.



FM-A04
Bipolar electrochemistry for functionalization of 2D materials

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[1] *KU Leuven, Belgium*

Keywords: 2D materials; functionalization; electrochemistry

After the isolation of the graphene monolayer 2D material have garnered great attention due to their unique properties. Covalent functionalization strategies are used to further finetune and improve these properties, which allows to integrate this material into a wide range of applications. However, these strategies need either highly reactive conditions, which do not guarantee a control over the degree and homogeneity of functionalization of the surface. Electrografting is a powerful tool known to modify a wide range of material in a controlled manner, by using said material as electrodes. Nevertheless, this method does not allow the functionalization of non-conductive surfaces and not much work has been done on 2D materials besides graphene. Recently, bipolar electrochemistry, a low cost, efficient and facile technique has been used to functionalize graphene material without the need to connect to a potentiostat. By applying a high voltage to the electrolyte cell, a gradient of the electric field occurs over the cell which induces the polarization of material placed between two electrodes. The polarization drives simultaneous reduction and oxidation reactions at the opposite poles of the placed material. This opens possibilities of functionalization of inert and semiconductor material, which opens new material with new properties. Furthermore, to achieve scalable production of modified 2D materials suitable for the high throughput needed for industrial application development of new production techniques are necessary. Bipolar electrochemistry has proven to be a promising method for the exfoliation from bulk to monolayer material. A wide range of material has been proven to be obtainable by such a method. The objective of this work is to then combine both exfoliation and functionalization in a one-pot method for the scalable production of new material with modified properties for facile production of 2D material in dispersion. The material is characterized by techniques such as Raman and AFM.

[1] Line Koefoed , Dodzi Zigah. et al. One-step preparation of bifunctionalized surfaces by bipolar electrografting. RSC Advances, 6 , 3882–3887, (2016)

[2] Yong Wang, Martin Pumera. et al. Nonconductive layered hexagonal boron nitride exfoliation by bipolar electrochemistry. Nanoscale, 10 , 7298-7303, (2018)

[3] Line Koefoed, Kim Daasbjerg, Functionalizing Arrays of Transferred Monolayer Graphene on Insulating Surfaces by Bipolar Electrochemistry. Langmuir, 32(25), 6289–6296

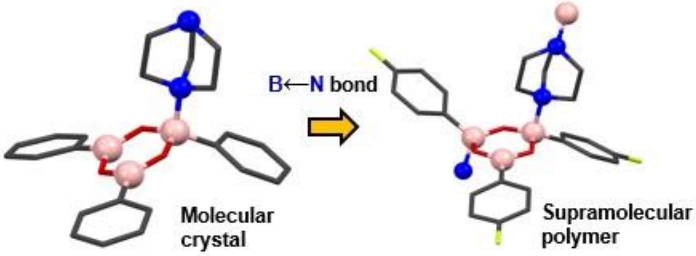
FM-A05
Effect of chemical substitution on the construction of boroxine-based supramolecular crystalline polymers featuring B←N dative bonds

Bhandary Subhrajyoti[1], *Van Hecke Kristof*[1]

[1] *Ghent University, Belgium*

Keywords: mechanochemistry; crystal engineering; dative bond; supramolecular polymer; quantum topology

The rational design and controllable synthesis of functional solid networks is one of the fundamental goals of materials science and crystal engineering. [1] Within the toolbox of crystal engineering, various weak non-covalent interactions have been utilized to connect molecular building blocks to achieve ordered network materials for various storage, and optoelectronic applications.[2-3] Recently, the B←N dative bond has emerged as a good alternative to traditional non-covalent and metal-coordinate bonds, to build supramolecular network/host-guest-based crystalline assemblies, for various applications. [4-5] Hence, it is of great interest to understand the structural and quantum topological aspects of B←N bonds, in different crystalline and chemical environments for further development of transition metal-free functional materials. Here we report the mechanochemical synthesis of five single-crystalline phenylboroxine and 1,4-diazabicyclo[2.2.2]octane (DABCO) ligand-based adducts, directed by boron-nitrogen dative bonds. By tuning the electronic features of the phenylboroxines by chemical modifications (-H/-OMe/-F/-Cl/-Br) at the para-position, the formation of the resulting bicomponent adducts can be controlled to obtain molecular to 1D polymeric crystalline materials. The electrostatic and quantum topological aspects of the B←N bonds reveal the origin for the different binding modes of the boroxine-DABCO adducts yielding molecular to polymeric structures.



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FM-A06

Chemical solution-based synthesis of earth-abundant electrocatalysts for PEM water electrolysis

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Keywords: /

Due to global warming, there is an urgent need for clean energy production. Hydrogen (H2) plays an important role in this story since it can function as energy storage chemical, clean fuel and feedstock. The reasons for this range of applications is that hydrogen is the element with the highest energy density, it has carbon dioxide (CO2) free combustion and functions as a feedstock chemical for several relevant chemicals such as ammonia and methanol. Therefore, research on cheap production methods of H2 that only use earth abundant materials and have limited CO2 emissions is necessary. A promising production method for H2 is water electrolysis making use of renewable energy sources. Water electrolysis produces H2 and O2 via the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER). This method does not release CO2 or other volatile by-products. Commercial water electrolysis methods are alkaline electrolysis and PEM (proton exchange membrane) electrolysis. The advantages of PEM electrolysis compared to alkaline electrolysis are higher energy efficiency, quick response, scalability and the possibility to work at elevated pressures. Unfortunately, PEM electrolysis still has some challenges. Namely, the high price and low abundancy of the electrocatalysts. The aim of this project is to select, synthesize, characterize and evaluate earth-abundant electrocatalysts for both HER and OER. There will be focused on metal sulfides for HER and metal oxides for OER. These materials will be synthesized by solution-based synthesis methods such as hydrothermal synthesis and sol-gel synthesis. The synthesis parameters will be varied to optimize the materials properties and morphology for PEM electrolysis. These properties and morphologies will be linked to the catalytic activity for water electrolysis and the stability of the material.

FM-A07

Upconverting Nanoparticles: Energy Transfer with Dye Molecules in Suspensions and Thin Film Systems

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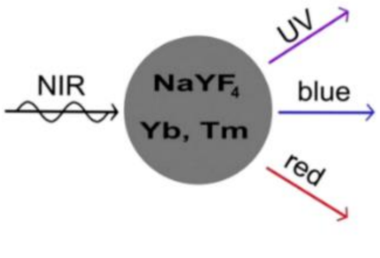
Keywords: upconverting nanoparticles; Rhodamine 6G; anti-Stokes emission; near-infrared excitation; chitosan matrix thin films

Recently, nano-scale functional materials have made advancements in many scientific fields: a new revolutionary approach is the application of upconverting nanoparticles (UCNPs) in photodynamic cancer therapy and solar cells.

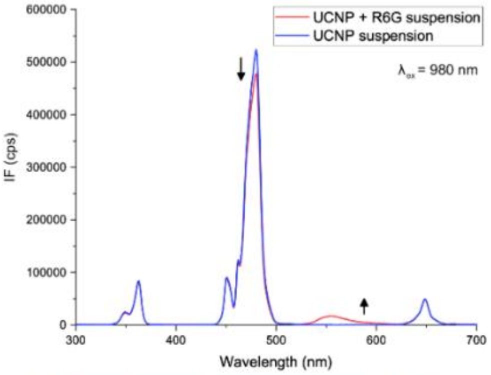
UCNPs show anti-Stokes emissions: under near-infrared excitation photons of higher energy (in the visible and UV range) are emitted (Figure 1). Furthermore, these emitted photons can later be absorbed by fluorescent dye molecules, which then transfer this energy to a semiconductor nanomaterial, e.g. TiO2.

NaYF4 : 20% Yb3+, 0.5% Tm3+ UCNPs were prepared via solvothermal synthesis. Both ethanolic and water-based suspensions showed intensive anti-Stokes emissions under NIR excitation. UCNP-containing thin-film model systems were prepared on glass substrates by spin-coating using water-based chitosan-matrix. The thin coatings showed significant upconversion emission intensities and energy transfer between the UCNPs and Rhodamine 6G (R6G) molecules was detected.

Experiments on the upconversion induced photodegradation of R6G via titania nanoparticles were conducted: the UCNPs showed energy transfer with both R6G molecules (Figure 2) and TiO2 nanoparticles under 980 nm excitation, the photodegradation of the dye molecules was measured with UV-Vis spectroscopy.



1. Figure: The upconversion phenomenon



2. Figure: Energy transfer between UCNPs and R6G molecules

FM-A08
NMR studies of hydrogen-bonded water-aminium assemblies templating SAPO materials

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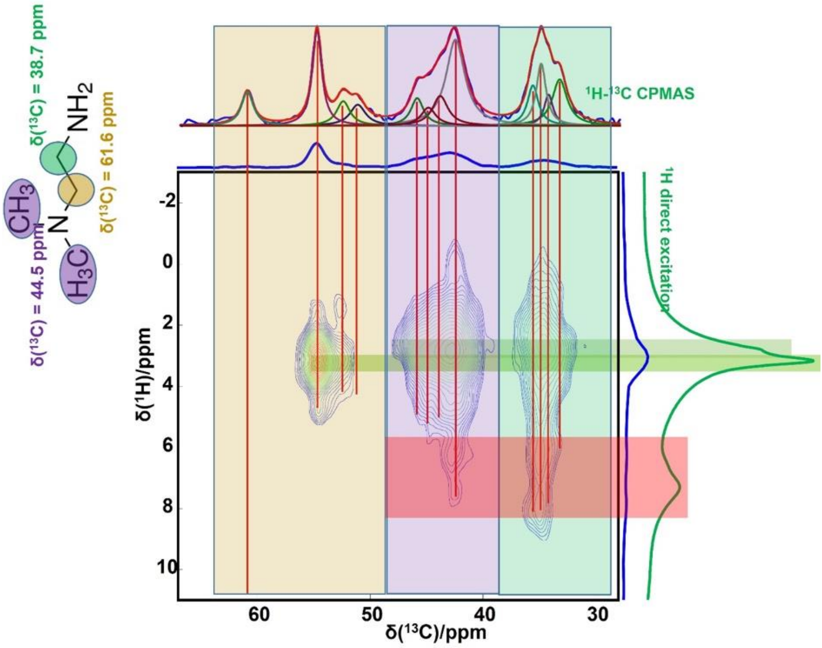
Keywords: NMR

Water plays a central role in the crystallization of a variety of organic, inorganic, biological, and hybrid materials. This is also the case of hydrothermal synthesis of zeolites and zeolite-like materials, an important class of industrial catalysts and adsorbents. However, structure direction by water in zeolite synthesis has never been clearly elucidated. Here we report the crystallization of phosphorous-based molecular sieves using rationally designed, hydrogen-bonded water-aminium assemblies, resulting in molecular sieves with crystallographic ordering of heteroatoms. We demonstrate that an assembly of 1:1 water-diprotonated N,N-dimethyl-1,2-ethanediamine acts as a structure-directing agent in the synthesis of a silicoaluminophosphate material with phillipsite topology, with the help of X-ray crystallography and multinuclear solid-state NMR spectroscopy. This concept of structure direction by water-containing supramolecular assemblies should be applicable to the synthesis of many classes of porous materials.



FM-A09
Design of advanced anode materials for lithium ion batteries

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Keywords: Li-ion batteries; Anode; High capacity; Silicon

Climate change is a widely acknowledged problem and one of its biggest driving forces is the emissions generated by internal combustion engine vehicles. Electrifying the vehicle fleet would go a long way towards solving the climate change issue. To make electric vehicles more attractive, it is necessary to increase the energy density of the batteries that power them. Nowadays, we can find graphite inside of these batteries' anodes. An increase in energy density can be realized by replacing graphite by silicon. The theoretical capacity of silicon (3572 mAh g-1) is ten times higher than graphite's (372 mAh g-1), making it an attractive alternative. Nonetheless, silicon has not been commercialized yet to the degree graphite has been. This is because silicon exhibits a large amount of swelling during operation, making it degrade quickly. That problem must be alleviated if silicon ever wants to see commercial application as an anode material. One way of doing this is by creating a composite with carbon which can compensate for that volume change. Hence, this project aims to employ a templating approach to synthesize silicon-carbon composite anode materials with a low degree of swelling and a high capacity intended to be used in addition to or as a replacement for graphite in Li-ion batteries.

FM-A10

Quantifying Delocalization and Static Correlation Errors by Imposing (Spin)Population Redistributions through Constraints on Atomic Domains

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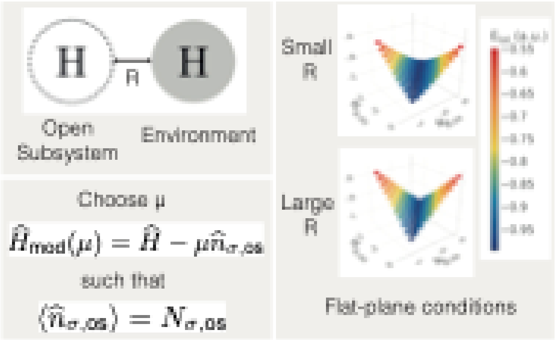
Keywords: Quantum chemistry; theoretical chemistry

The failure of many density functional approximations can be traced to their behavior under fractional (spin)population redistributions in the asymptotic limit toward infinite bonding distances, which should obey the flat-plane conditions. However, such errors can only be characterized sufficiently in terms of those redistributions if exact energies are available for many possible (spin)population redistributions at different bonding distances. In this study, we propose to model such redistributions by imposing (spin)populations on atomic domains by constraining full configuration interaction wave functions. The resulting N-representable descriptions of small hydrogen chains at different bonding distances allow us to computationally illustrate the effects of the flat-plane conditions in the limit to infinite bond distances, leading to more chemical insight into those flat-plane conditions. As the proposed methodology is able to capture the effects of the flat plane conditions, it could be used to generate the reference data that is required to measure the extent to which approximate methods violate the requirements of the exact functional, leading to a quantification of the delocalization and static correlation error of such methods.



FM-A11

Chemical solution synthesis of copper-based photocathode materials for photoelectrochemical reduction of CO2 to methanol

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Keywords: /

It is crucial to reduce CO2 emissions as climate change is a big issue that we are facing today. This is possible by converting the CO2 into a useful product, such as methanol. Solar energy can be used in combination with renewable electricity to provide the energy needed to convert CO2 using a photoelectrochemical system. We need semiconducting photoelectrodes which are low cost, non-toxic and stable to design such a system.1,2 These electrodes also require a suitable conduction band edge and the appropriate bandgap. The aim in this project is to design copper-based delafossite photocathode materials. Delafossites are ternary oxides with formula ABO2 with A being a monovalent metal cation, in this case Cu(I), and B a trivalent metal cation. 3,4 They are natural p-type semiconductors that, in comparison to cuprous oxide, have shown a higher electrochemical stability, improved hole mobility and are less susceptible to photodegradation. The focus in this research lies on the copper delafossite CuFeO2 and its solution-based synthesis. This material has shown high stability in aqueous environments, under reductive conditions and gives a higher conductivity compared to other delafossites. 1,5,6,7 The synthesis will focus on a chemical solution deposition process to produce thin films and a hydrothermal method to synthesize powders. X-ray diffraction (XRD) is used to determine the crystal structure and SEM/TEM are used to study the morphology and to determine the particle size. UV-vis is used to determine the bandgap energy. Afterwards, photocurrent measurements are conducted to study the photoelectrochemical characteristics of the materials.

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FM-A12

Innovative sol-gel routes to mesoporous bifunctional catalysts for the upgrading of bioethanol to butadiene

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Keywords: sol-gel; bifunctional; bioethanol; heterogeneous catalysis

Bioethanol production – from second generation biomass ideally – has been promoted by strong political incentives and is technologically sound. In parallel, butadiene is one of the compounds that is expected to suffer future shortage due to the shift towards shale gas from the traditional steam cracking of naphtha. Therefore, intensive research is currently conducted towards the direct catalytic conversion of ethanol to butadiene. The reaction is long known, and consists of a complex network of dehydrogenation, condensation and dehydration reactions catalysed respectively by redox and acid active sites that must operate in a balanced fashion to maximize the butadiene yield.1
In the highly versatile toolbox of sol-gel chemistry, non-hydrolytic sol-gel (NHSG) is particularly effective to synthesize mesostructured materials with tailored properties (texture, homogeneity, surface chemistry) and has already shown its potential to obtain effective catalysts.2-4
Here, NHSG was used to prepare bifunctional Ta-Cu-SiO2 catalysts via the acetamide elimination route ("Ac") and compare them with similar compositions obtained through the ether route ("Et"). Both pathways yielded mesoporous materials (Figure 1A; SSA≈600 m2 g–1; Vp≈0.1 mL g–1; Dp≈4.0 nm for the acetamide elimination route, SSA≈700 m2 g–1; Vp≈0.1 mL g–1; Dp≈7.0 nm for the ether route), with similar CuO crystallites size of around 20 nm. IR spectroscopy and XPS pointed to a successful Ta incorporation inside the silica matrix. For a given catalyst composition, the butadiene selectivity is systematically better with the catalysts obtained through the acetamide elimination route perform than those synthesized by the ether route (Figure 1B). After optimization of the Cu and Ta loading and achieving better balance between them, the best formulation (Ac-2Ta4Cu) reached an ethanol conversion of 75 % and a butadiene selectivity of 50 %. The overperformance of the acetamide route is currently attributed to a better active sites dispersion and proximity, where Cu nanoparticles are closer to more available Ta isolated sites, allowing for the long reaction mechanism to take place in a facilitating way and limiting unwanted by-products like ethylene.

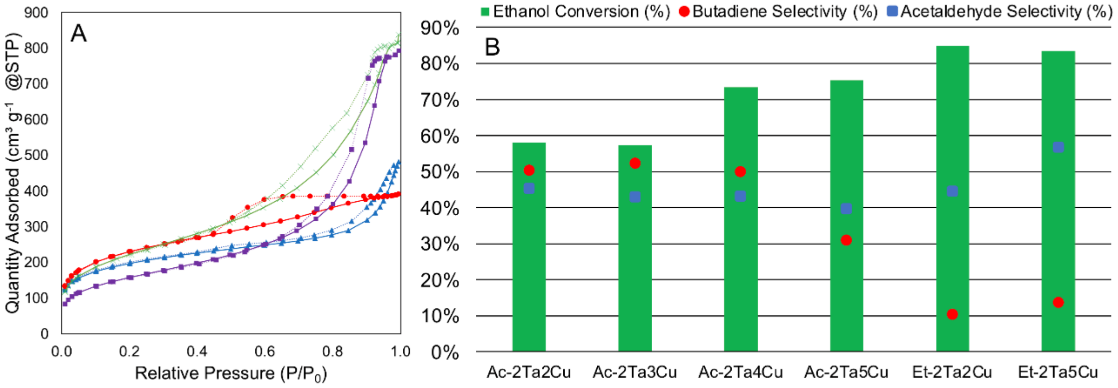

Figure 1 : (A) N_2-physisorption isotherms of Ac-2Ta2Cu (blue Δ), Ac-2Ta5Cu (red ○), Et 2Ta2Cu (green ×), Et-2Ta5Cu (purple □). Adsorption isotherms are plotted as solid lines, desorption isotherms are plotted as dotted lines; (B) Catalytic data at 325 °C, WHSV=1.10h^{-1}

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FM-A13

Combining hybrid hydrogels with peptide conjugation for targeted cartilage tissue engineering

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Keywords: Bioactive peptides; Double-network hydrogels; Regenerative medicine

Degenerative diseases like osteoarthritis affect millions of people worldwide. Hybrid hydrogels show great promise in tissue engineering applications as scaffolds for supporting native cartilage damaged from arthritis. Such gels can be designed and synthesized to be biocompatible and have outstanding mechanical properties, approaching the remarkable behavior associated with native cartilage tissue. However, further improvement in promoting tissue regeneration is needed. Previous work has shown that (poly)peptide-polymer conjugates can be tailored to promote cellular interactions. Integrating peptides into hybrid hydrogels in a controlled manner remains a formidable challenge. This is particularly true in gels that exhibit stimuli-responsive behavior (e.g., triggered gelation) and are thus amenable to relevant processing such as injection. This must be achieved while maintaining the necessary mechanical properties to support normal tissue function. This contribution focuses on hydrogel design using an adaptable hybrid, dual network synthetic scaffold whereby the building blocks are functionalized for specific attachment to peptides. The mechanical properties will be tuned to match those of native cartilage tissue. These results may pave the way toward dynamic materials which can be used to probe cellular interactions.

FM-A14
A Reactive Force Field for Alumina Systems

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Keywords: Molecular Modeling; ReaxFF; Catalysis; Aluminananoparticle assembly; transmission electron microscopy; electron tomography

Zeolites, microporous aluminosilicate minerals built from tetrahedral TO4 units where T corresponds to Si or Al, are widely used in the (petro)chemical industry and for biomass conversion. However, they are generally diluted with a binder like silica or alumina to adjust the catalyst's mechanical and chemical properties. Moreover, during the catalyst preparation, in the case of the alumina binder, the boehmite (β-Al2O3) polymorph is transformed into γ-Al2O3 in the calcination step. This change in morphology is also accompanied by a change in the hydration level.

However, the interaction between binder and zeolite remains poorly understood at the atomic level. While quantum mechanical DFT calculations become too CPU expensive to describe representative models of both the zeolite and alumina, empirical reactive force fields are very suitable. Yet, the lack of accurate force field parameters that can describe both different polymorphs of alumina (i.e. α , β and γ) as well the zeolitic system itself, incited us to setup a new ReaxFF force field able to describe both systems types. In this poster we present our strategy to optimize the ReaxFF force field parameters against an extensive training set. We use the robust CMA-ES algorithm for optimization, and propose a novel cost-function to handle a strong imbalance in training sets.

FM-A15

Tailored network topology in mechanically robust double network hydrogels for 3D printing and injection

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Keywords: Double network hydrogel; Mechanical properties; Injectability; Structure-property relationship;3D-printing

As a result of their unique characteristics, hydrogels have received enormous attention targeting diverse applications such as tissue engineering. However, a challenge that currently limits their widespread application as candidates for commercial biomaterials is their insufficient mechanical strength and toughness which prevent them to fulfill their role as load-bearing tissues. Moreover, a major gap still remains in the controlling of the complex behavior of hydrogels such as injectability and self-healing. Double network hydrogels can be considered as an approach to overcome the mentioned problems.

Our present work has focused on establishing a link between composition, processing, and properties in Alginate and polyethylene glycol (PEG) based hydrogels in which the network architecture and makeup are systematically varied. These hydrogels have been developed with target applications in 3D bioprinting, injection, and tissue engineering. A thorough investigation into the molecular structure/composition and the corresponding mechanical response has been carried out, which offers insight into the connection between crosslinking density and properties using a well-defined network scaffold. Our work highlights that the properties of the hydrogels can be readily and systematically tuned by controlling the composition and architecture and can introduce some properties such as injectability to hydrogels in order to make them competitive in the arena of regenerative medicine.

FM-A16
Study on Ga incorporation into InP quantum dots for laser application

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Keywords: /

Interest in InP QDs has increased exponentially during the last years since these materials offer an alternative to widely deployed CdSe QDs, which fall under restrictions issued for the use of Cd in consumer appliances. However, the photoluminescence efficiency of InP QDs is low, typically less than 1%, which makes the development of methods to prevent non-radiative relaxation after photo-excitation – so-called electron-hole pair recombination – imperative. Here, the most common approach is to shell InP QDs with a wider band-gap semiconductor. Until now, mostly so-called II-VI semiconductors, such as ZnSe and ZnS have been used, which often leads to +50% photoluminescence efficiencies, and even near 100% when multiple shells are used. However, the chemical mismatch between a III-V material like InP and a II-VI material such as ZnSe or ZnS can result in persistent defects at the core-shell surface, a situation that can be aggravated further by a mismatch in lattice constant. This results in a poor conservation of multi-excitons, which is an issue in view of the application of InP-based QDs as an optical gain material in lasers and amplifiers. It thus appears that such applications will require better shelling procedures. In this first study, we investigated the use of gallium to adjust the composition of the InP core. As GaP is a wider band-gap material than InP, a Ga-rich interface may better contain the electron-hole pair in the InP core. In addition, the smaller lattice parameter of GaP may help reducing lattice mismatch between core and shell, a second way a Ga-rich interface may reduce the formation of defects at the core/shell interface. Here, we show that the formation of InP QDs can be successfully adapted so as to InGaP QDs that can be overgrown by ZnS. We discuss the optical properties of the resulting materials, and give a first indication on the impact of a Ga-rich interface on multi-exciton recombination.

FM-A17

Phase separation and stability of cotton and bacterial cellulose nanocrystals in the presence of various salts

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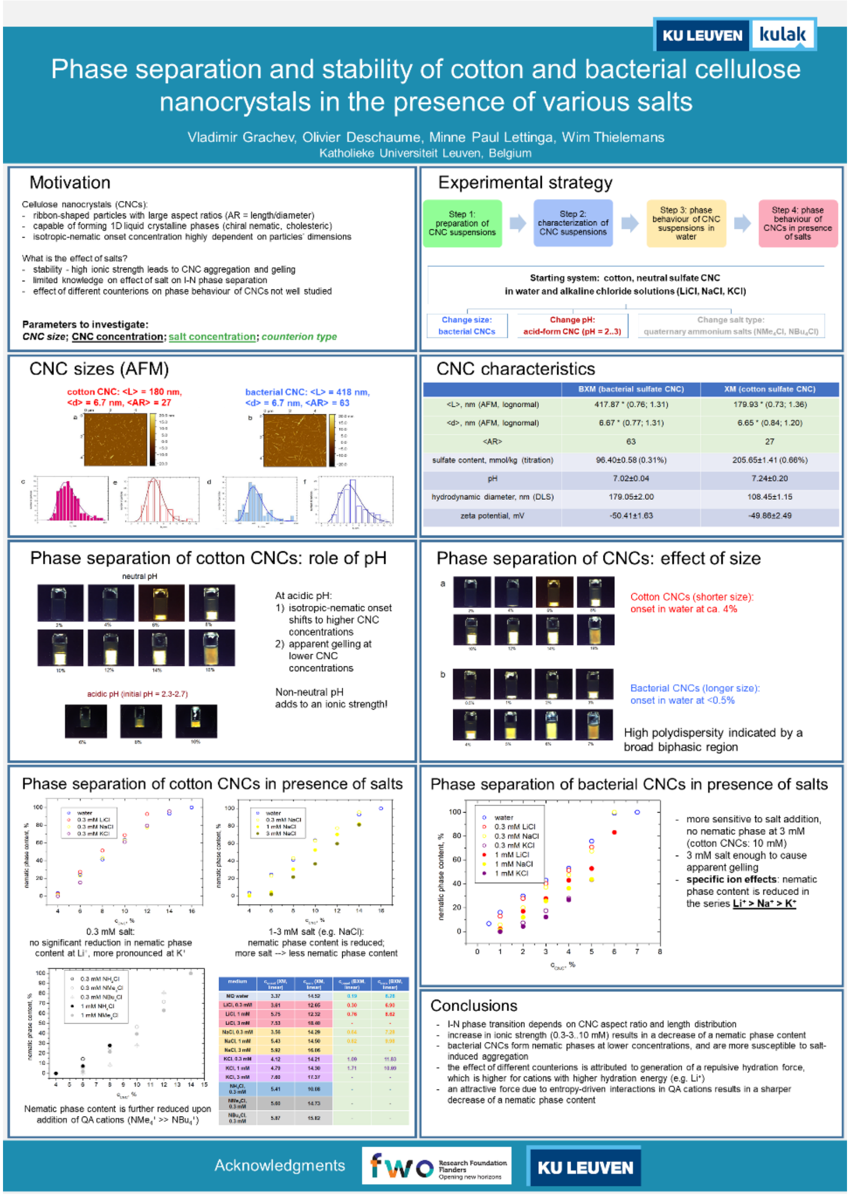
Keywords: nanocellulose; liquid crystals

Dependence of the phase equilibria of sulfated CNC suspensions derived from cotton and bacterial cellulose on the ionic strength and on the counterion type was determined. At a given ionic strength, the onset concentration of isotropic-nematic phase transition increased according to the series Li+ < Na+ < K+ < NH4+ < NMe4+ < NBu4+. For each counterion, increasing of the ionic strength resulted in a shift of the onset concentration. Equilibrium in phase separation was reached after 1 week for most of the CNC suspensions. The bacterial CNC suspensions were more susceptible to increases in the ionic strength than cotton CNC suspensions, phase separation was slower, and gelation appeared at lower salt content. This is attributed to a lower charge density on bacterial CNC surface and higher lengths of the extracted CNCs. The changes in phase behaviour in the presence of alkaline cations (Li+, Na+, K+) and NH4+ are mostly dependent on the extent of a depletive hydration force, while for NMe4+ and NBu4+ cations, the hydration force was partly counterbalanced by entropy-driven interactions.



KU LEUVEN kulak

Phase separation and stability of cotton and bacterial cellulose nanocrystals in the presence of various salts

Vladimir Grachev, Olivier Deschaume, Minne Paul Lettinga, Wim Thielemans
Katholieke Universiteit Leuven, Belgium

Motivation

Cellulose nanocrystals (CNCs):
- ribbon-shaped particles with large aspect ratios (AR = length/diameter)
- capable of forming 1D liquid crystalline phases (chiral nematic, cholesteric)
- isotropic-nematic onset concentration highly dependent on particles' dimensions

What is the effect of salts?
- stability - high ionic strength leads to CNC aggregation and gelling
- limited knowledge on effect of salt on I-N phase separation
- effect of different counterions on phase behaviour of CNCs not well studied

Parameters to investigate:
CNC size; **CNC concentration**; salt concentration; ***counterion type***

Experimental strategy

Step 1: preparation of CNC suspensions → Step 2: characterization of CNC suspensions → Step 3: phase behaviour of CNC suspensions in water → Step 4: phase behaviour of CNCs in presence of salts

Starting system: cotton, neutral sulfate CNC in water and alkaline chloride solutions (LiCl, NaCl, KCl)

Change size: bacterial CNCs

Change pH: acid-form CNC (pH = 2..3)

Change salt type: quaternary ammonium salts (NMe_4Cl, NBu_4Cl)

CNC sizes (AFM)

cotton CNC: <L> = 180 nm, <d> = 6.7 nm, <AR> = 27

bacterial CNC: <L> = 418 nm, <d> = 6.7 nm, <AR> = 63

CNC characteristics

	BXM (bacterial sulfate CNC)	XM (cotton sulfate CNC)
<L>, nm (AFM, lognormal)	417.87 * (0.76; 1.31)	179.93 * (0.73; 1.36)
<d>, nm (AFM, lognormal)	6.67 * (0.77; 1.31)	6.65 * (0.84; 1.20)
<AR>	63	27
sulfate content, mmol/kg (titration)	96.40±0.58 (0.31%)	205.65±1.41 (0.66%)
pH	7.02±0.04	7.24±0.20
hydrodynamic diameter, nm (DLS)	179.05±2.00	108.45±1.15
zeta potential, mV	-50.41±1.63	-49.86±2.49

Phase separation of cotton CNCs: role of pH

neutral pH

acidic pH (initial pH = 2.3-2.7)

At acidic pH:
1) isotropic-nematic onset shifts to higher CNC concentrations
2) apparent gelling at lower CNC concentrations

Non-neutral pH adds to an ionic strength!

Phase separation of CNCs: effect of size

Cotton CNCs (shorter size): onset in water at ca. 4%

Bacterial CNCs (longer size): onset in water at <0.5%

High polydispersity indicated by a broad biphasic region

Phase separation of cotton CNCs in presence of salts

0.3 mM salt:
no significant reduction in nematic phase content at Li^+, more pronounced at K^+

1-3 mM salt (e.g. NaCl):
nematic phase content is reduced;
more salt --> less nematic phase content

Nematic phase content is further reduced upon addition of QA cations (NMe_4^+ >> NBu_4^+)

medium	c_{onset} (XM, linear)	c[illegible] (XM, linear)	c_{onset} (BXM, linear)	c[illegible] (BXM, linear)
MQ water	3.37	14.52	0.19	6.28
LiCl, 0.3 mM	3.61	12.66	0.30	6.90
LiCl, 1 mM	5.75	12.32	0.76	8.62
LiCl, 3 mM	7.53	18.40	-	-
NaCl, 0.3 mM	3.56	14.29	0.64	7.28
NaCl, 1 mM	5.43	14.50	0.82	9.98
NaCl, 3 mM	5.92	16.06	-	-
KCl, 0.3 mM	4.12	14.21	1.09	11.83
KCl, 1 mM	4.79	14.30	1.71	10.69
KCl, 3 mM	7.60	17.37	-	-
NH_4Cl, 0.3 mM	5.41	10.08	-	-
NMe_4Cl, 0.3 mM	5.60	14.73	-	-
NBu_4Cl, 0.3 mM	5.87	15.82	-	-

Phase separation of bacterial CNCs in presence of salts

- more sensitive to salt addition, no nematic phase at 3 mM (cotton CNCs: 10 mM)
- 3 mM salt enough to cause apparent gelling
- **specific ion effects**: nematic phase content is reduced in the series **$Li^+ > Na^+ > K^+$**

Conclusions

- I-N phase transition depends on CNC aspect ratio and length distribution
- increase in ionic strength (0.3-3..10 mM) results in a decrease of a nematic phase content
- bacterial CNCs form nematic phases at lower concentrations, and are more susceptible to salt-induced aggregation
- the effect of different counterions is attributed to generation of a repulsive hydration force, which is higher for cations with higher hydration energy (e.g. Li^+)
- an attractive force due to entropy-driven interactions in QA cations results in a sharper decrease of a nematic phase content

Acknowledgments
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FM-A18

Improvement of the mechanical performance of methacrylated alginate wound dressings through the addition of different crosslinking agents

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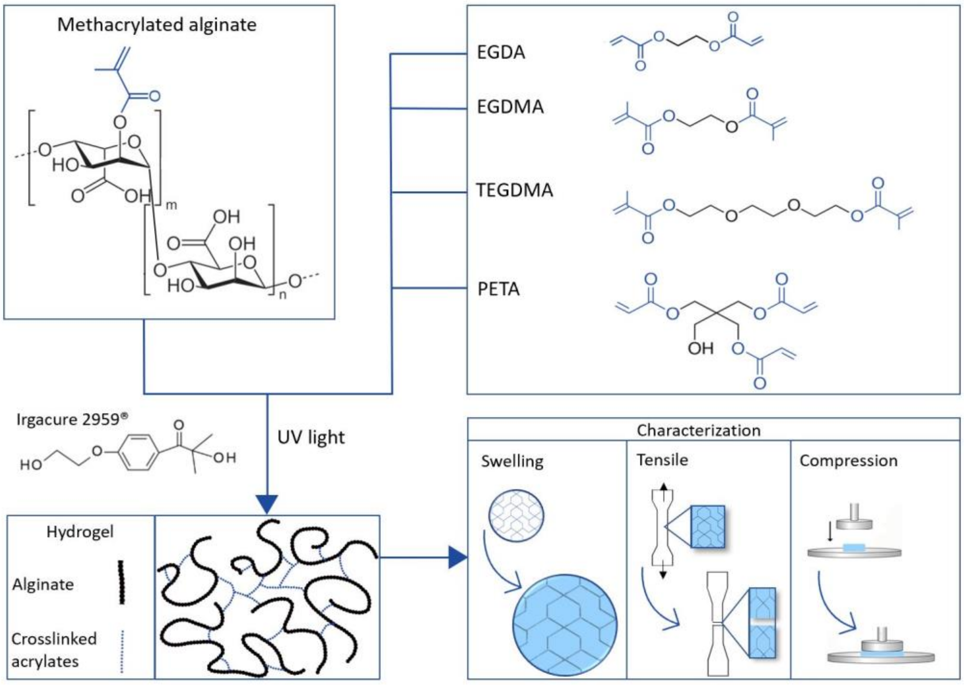
Keywords: Hydrogel; crosslinking; wound-dressing; mechanical performance; alginate

Diabetic patients have 15–25% probability to develop an ulcer, which is a chronic, non-healing wound where the skin disruption presents delayed and unsuccessful healing (Siddiqui & Bernstein, 2010). Studies indicate that 85% of foot amputations are preceded by such diabetic ulcers (Dahiru et al., 2016; Gianino et al., 2018; Khanolkar et al., 2008). This incidence is partly due to the fact that current ulcer treatment is unspecialized. If it was targeted to a specific need or condition, it could translate into adequate healing and a decrease of the amputation incidence. For this, wound dressing matrices that provide suitable healing conditions need to be engineered. A hydrogel is a type of wound dressing made of a hydrophilic polymeric structure whereby combinations of synthetic and/or natural polymers are used in their formulation to tune its properties and applications. Alginate-based hydrogels are an excellent choice as natural wound dressing material. This is because it is bioactive and it can provide biodegradability, optimal moisture vapor-transmission and exudate absorption with its inherent swelling properties (Huang et al., 2020). These allow to take-up wound fluid excess, increase the hemostatic capacity and activate the repair of damaged tissue. Moreover, the formed structure can contribute to the delivery of therapeutic compounds that target a specific insufficiency or condition (Varaprasad et al., 2020). However, a hydrogel made of pure alginate has low chemical stability, insufficient mechanical performance and does not have a controllable therapeutical capacity. For this reason, it is used together with other natural and synthetic materials which improve its applicability in wound treatment by achieving more flexible, yet mechanically stronger wound dressings (Ionita et al., 2013). Another important parameter which influences the mechanical strength is the type and extent of crosslinking. In particular, crosslinking by covalent bonds, in contrast to ionic crosslinking, enhances the mechanical performance and reduces degradation (Galli et al., 2018; Zhang et al., 2017). Furthermore, the presence of functional groups in alginate makes it versatile for blending and crosslinking which can contribute to hydrogel stability and moisture retention (Karri et al., 2016). Because of this, in the present research methacrylated alginate was used for its capacity to covalently crosslink upon exposure to UV-light. Still the mechanical performance is insufficient for wound dressing applications. For this reason, they were reinforced by the addition of one of four acrylated crosslinkers at two concentration ratios: ethylene diacrylate, ethylene glycol dimethacrylate, triethylene glycol dimethacrylate and pentaerythritol triacrylate. The resulting hydrogels were characterized and compared in terms of their water uptake capacity, degree of crosslinking and mechanical strength. The wound dressings that were obtained in this study, by the blending of crosslinkers, are meant to be used for the healing of diabetic ulcers. These dressings have improved mechanical capacity thanks to more extensive crosslinking through the enrichment of acrylate groups. This research shows that the strength of a biopolymeric material can indeed be tuned and enhanced by crosslinking with additive compounds at low concentrations. Although the swelling capacity is moderately reduced; the dressings can still contribute to a more effective wound repair by absorption of exudate, prevention of wound dehydration and enabling of oxygen permeation. The following step in this research is to confirm that the biological properties of alginate are kept in terms of biocompatibility, biodegradability and hemostasis. In conclusion, alginate is a leading biopolymer in the area of wound healing in the form of hydrogels, among others due to the retention of a moist environment around the wound, necessary to enable timely healing, and its compatibility with human tissue (Sun & Tan, 2013). This study shows a combination of the adequate blend and conditions to ensure its mechanical strength without losing its bioactive properties. Afterwards, the polymer matrix can be further enhanced so that it can control the delivery of active molecules.



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FM-A19
Advanced segmented block copoly(ether ester) for more sustainable polymer 3D printing

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Keywords: 3D printing; block copolymers; crystallization; waste reduction

Laser Sintering (LS) is a 3D printing process based on the layer-by-layer fusion of powders from – in most cases - crystallizable polymers.

One of the main problems encountered during 3D printing is the low reuse rate of the non-sintered polymer powder. Nowadays only ± 50% of the non-printed polymer powder in LS is recycled in a next printing run because most polymer powders tend to degrade when exposed to typical printing conditions. However, very recently, new segmented block copolymers based on polyester and polyether blocks have entered the LS market. It is claimed that they can be printed under classical LS conditions without suffering from degradation issues. Therefore, non-printed powder can more efficiently be re-used in a next printing run, which reduces the need for large portions of virgin powder material which in turn lowers the overall ecological footprint of this process.

A patent search in combination with chemical analyses revealed that the ester blocks in this new copolymer are based on a concatenation of 1,4-cyclohexanedicarboxylic acid with 1,4-cyclohexane dimethanol, leading to the polymer called PCCD. The polyether blocks are made from poly(tetrahydrofuran), PTHF. We also found out that the PCCD block is responsible for solidification via crystallization while the PTHF blocks remain liquid-like amorphous.

Interestingly, according to literature, pure PCCD is hardly crystallizable. [1] Because of its rather rigid nature, it crystallizes very slowly and therefore tends to vitrify upon cooling, already at very shallow cooling rates. In contrast, the crystallization rate of the blockcopolymer is surprisingly high. Most likely, the PTHF blocks increase the molecular mobility.

To gain a more fundamental insight into this matter, a series of PCCD homopolymers are synthesized with varying molar mass and cis/trans ratios of the cyclohexane moieties. The crystallization behavior is studied by thermal analysis and the material morphology by X-ray based methods.

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FM-A20
Dual network hydrogels with dynamic crosslinking possessing tuneable mechanical properties

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Keywords: Hydrogels; Double networks; Tissue engineering

N-acryloyl glycinamide (NAGA) has great potential as a building block for tough dynamic hydrogels as it is an acrylate monomer capable of forming dual hydrogen bonds with itself. This potential is illustrated in the range of mechanical properties obtainable for single network P(NAGA) hydrogels depending on the degree of entanglement and water content. These properties can be further altered by copolymerizing NAGA with other acrylate monomers to change the cumulative strength of the H-bonds. The same principle can be applied in dual network hydrogels. Poly(acrylate)/ alginate dual networks hydrogels were made using a variety of H-bonding acrylate monomers and the influence on the properties of the hydrogel were examined. The combination of a physically crosslinked poly(acrylate) network and an ionically crosslinked alginate network gives rise to a fully dynamic dual network hydrogel. This work describes an easy one-step, one-pot preparation method to prepare these gels making them also suitable for 3D printing.

Acknowledgments

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FM-A21
3D investigation of metal-organic frameworks at atomic scale

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Keywords: metal organic-frameworks; transmission electron microscopy

Metal-organic frameworks (MOFs) are porous and crystalline solids with high surface areas and porosities, good thermal and chemical stability as well as customizable chemistry.[1,2] Their properties make them ideal candidates for applications in various fields, such as catalysis,[3] gas storage, separation and purification,[4] and drug delivery.[5] However, characterization of these materials is not straightforward. Common characterization techniques, such as X-ray diffraction, provide information from bulk structures only. On the other hand, transmission electron microscopy (TEM) is a very suitable technique to investigate (nano)materials at a very local scale. Unfortunately, it is extremely challenging to apply TEM for imaging MOFs since they are highly beam sensitive materials. Here, we present high resolution TEM imaging of MIL-101(Cr) at the atomic scale using a direct electron detector camera and we will explore the use of a novel TEM technique: integrated differential phase contrast (iDPC).[6] Our results show that these new techniques enable to image MOFs in a more dose-efficient manner, compared to conventional techniques, such as high angle annular dark field scanning transmission electron microscopy (HAADF-STEM). By combining the novel techniques with electron tomography we are able to visualize the porous structure in 3D.

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FM-B01
MoloVol: An Easy-to-Use Tool for Calculating Cavity Volumes and Surfaces

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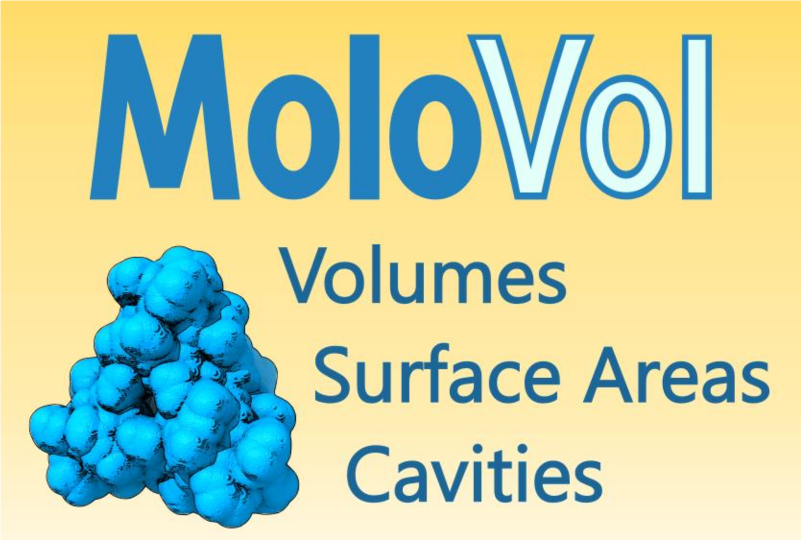
Keywords: computer program; volume; surface area; cavities; voids

Cavities are a ubiquitous feature of chemical structures encountered in various fields ranging from supramolecular chemistry to porous materials. They are involved in the encapsulation, transport, and transformation of guest molecules, thus necessitating a precise and accessible tool for estimating and visualizing their size and shape. MoloVol is a free, open-source software parametrizable through a user-friendly graphic interface developed for calculating a range of geometric features of chemical structures. MoloVol utilizes up to two spherical probes to define cavities, surfaces, and volumes. The general scope of the program utility and its algorithms were previously reported.[1] This poster presents the utility of MoloVol for the characterization of cavities in macrocycles, cage compounds, and porous materials. Molovol is available on Windows, macOS, and Linux distributions at https://molovol.com



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FM-B02

Designing metal oxide-based stationary phases for the separation of Ac-225 and Bi-213 for biomedical applications

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Keywords: inorganic materials; surface modification; sorption; radionuclide generator; Ac-225; Bi-213

Cancer is a disease that still kills nearly 10 million people every year [1] despite the countless existing treatments. The amount of novel therapies is growing every day and targeted alpha therapy is one of them. Herein, the patient is treated with a radiopharmaceutical that binds to the cancer cell and emits ionizing radiation to induce cell damage. Since alpha radiation has a very short range (only a few cell diameters), the healthy cells around the tumor are spared. Amongst a number of radioactive isotopes that can be used for this purpose, Bi-213 is a promising candidate because of its suitable half-life and well known chelation chemistry. Clinical trials with this isotope have already been performed in the past and results are very promising [2]. The biggest hurdle, however, is the Bi-213 production, which is now far from sufficient to implement this isotope in targeted alpha therapy on a large scale. The most commonly used generator for the separation of Ac-225 and Bi-213 is based on AG MP-50. This is a macroporous strong acid cation exchange resin composed of sulphonic acid groups attached to a styrene divinylbenzene copolymer backbone. The AG MP-50 generator has a high yield (>76% Bi-213), a very low breakthrough of Ac-225 (<2*10-5 %) and the Bi-213 elution is very fast (2-3 min). Despite these great advantages, the main disadvantage is its low radiation stability. The organic backbone and especially the link with the functional group is very susceptible to radiation damage, such that in normal operation conditions the performance of the generator will substantially decrease [3]. On the other hand, inorganic materials are known to be more resistant against radiation. Therefore, this contribution presents the study of surface modified inorganic materials and their performance towards Ac-225/Bi-213 separation. The materials under investigation are titania and zirconia, which are modified with phosphoric acid groups. Different analytical techniques such as zeta potential and ICP-MS are utilized to characterize the surface modification of the inorganic materials. Furthermore, the modified materials are subjected to a so-called ‘cold sorption’ test. Via this method, sorption properties such as separation efficiency, leaching stability and sorption capacity are evaluated by means of non-radioactive solutions of La and Bi. Ultimately, the actual Ac-225/Bi-213 sorption properties of the phosphoric acid-modified materials will be tested in a radiochemical laboratory.

The final goal of this research is to develop an improved direct Ac-225/Bi-213 generator material with high radiation stability and increased Bi-213 yield and purity to make targeted alpha therapy more available and to give cancer patients new hope for a better future.

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FM-B03

Organic semiconductors with phosphonic acid functional groups for application in photovoltaics

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Keywords: Synthesis; Hole transporting materials; Self-assembled monolayers; Photovoltaics

Organic semiconductors are integral to modern technologies and are commonly used in various devices, such as sensors, electronics, or photovoltaics. Usually, organic semiconductors benefit from synthesis versatility or solution-processing methods and can be successfully applied in thin-film optoelectronics. So far, a big number of different hole or electron transporting materials were introduced for application in organic solar cells, perovskite solar cells and other photovoltaics. Every photovoltaic system needs suitable charge transporting semiconductors and search for the optimal ones often leads to the performance increase as well as improvement of the other photovoltaic characteristics.

Promising strategy for further photovoltaics development is modification of organic semiconductors by incorporating specific functional groups, which can provide additional benefits or properties. Very recently, organic materials, containing phosphonic acid groups, such as 2PACz, MeO-2PACz, Me-4PACz or Br-2PACz, have been introduced as hole transporting materials, able to bond with metal oxide electrode. Therefore, these materials were employed as self-assembled monolayers (SAMs) in different photovoltaics and demonstrated very good power conversion efficiencies [1-3]. In this research several new organic semiconductors with phosphonic acid groups were synthesized and studied as SAM materials.

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FM-B04

Functionalization of 2D layered hybrid perovskites with benzotriazole-based organic ammonium salts

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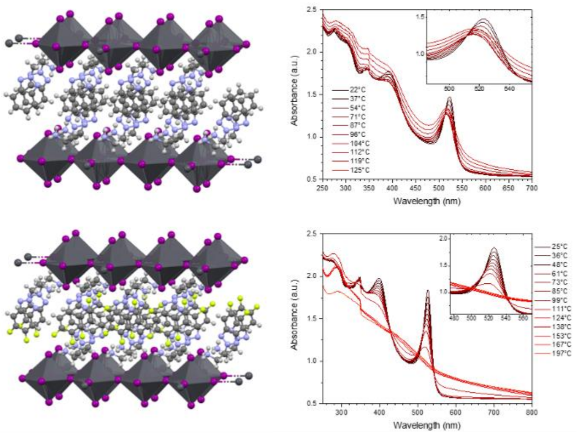
Keywords: Hybrid perovskites; benzotriazole; opto-electronic devices

2D layered hybrid perovskites are currently being investigated as an alternative to 3D hybrid perovskites, which suffer from limited stability against moisture, prolonged illumination, and temperature. In state-of-the-art 2D layered perovskites, butylammonium-based and phenethylammonium-based cations are still mostly employed. Although these organic cations succeed in stabilizing the perovskite, their insulating character lowers the charge carrier mobility and raises the exciton binding energy. These properties make 2D hybrid perovskites less competitive than their 3D counterparts, which limits the applicability of 2D layered perovskites in applications such as solar cells. This issue might be tackled by using larger organic cations with more pronounced opto-electronic properties, or by implementing dipole stacks or organic charge-transfer complexes in the organic layers.

In this work, benzotriazole-based organic cations are synthesized and subsequently successfully applied to 2D layered hybrid perovskites. The structural and opto-electronic properties of these perovskite thin films and single-crystals are investigated. It is shown that the synthesis of these cations is straightforward, and that the chromophore substituents and the alkyl tail length can be varied easily. Moreover, the electron-accepting character and the ease of substituent implementation render benzotriazole-based perovskites susceptible to organic layer engineering. This might significantly increase the charge transport properties of the perovskite as a whole, ultimately improving the performance in solar cells and photodetectors.



FM-B05
Structure-Property Investigation of Diels-Alder Polymer Networks

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Keywords: nanoparticle assembly; transmission electron microscopy; electron tomography

Diels-Alder (DA) polymer networks have attracted attention in recent years due to their potential for bridging the gap between thermoplastics and thermosets. Diels-Alder adducts are cleaved at elevated temperatures; Breaking these covalent bonds transforms the mechanical properties of the material, allowing it to be (re)processed. This has shown great promise in fused deposition modeling (FDM) since itcan adress one of the greatest drawbacks of the widely adopted AM technique being mechanical anisotropy. While cooling down after printing new DA bonds can be formed between layers whereas covalent interlayer bonding is not possible with current FDM materials. By using the well established furanmaleimide as a DA pair, there are different approaches to the architecture of these polymer networks i.e. furan groups can be incorporated into the polymer backbone or as pendand groups in this work.

By mixing bismaleimide (BM) crosslinkers in different proportions to the furan groups present, materials with a range of structures and properties can be made. The mechanical properties of the resulting materials depend on the flexibility and length of the repeating unit and of the bismaleimide. Ongoing research on a variety of building blocks is currently ongoing to produce a library of materials that will be evaluated for their mechanical properties, biocompatibility and 3D printing potential.

Structure-Property Investigation of Diels-Alder Polymer Networks

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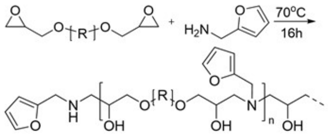

Figure 1: Ring-opening polymerization reaction to create a vaersatile backbone with furan pendant groups

Using the well-established furan-maleimide as a DA pair, there are different approaches to the architecture of these polymer networks i.e. furan groups can be incorporated into the polymer backbone or as pendant groups in this work (Fig. 1). By mixing bismaleimide (BM) crosslinkers in different proportions to the furan groups present, materials with a range of structures and properties can be made. The mechanical properties of the resulting materials depend on the flexibility and length of the repeating unit and of the bismaleimide. A proof-of-concept demonstration can be seen in Fig. 3 where two polymers (building blocks in Fig .2) are crosslinked with similar proportions of the same BM. The increased length of the repeating unit of PGDE results in a less densely crosslinked network giving rise to a completely different mechanical property profile. Ongoing research on a variety of building blocks is currently ongoing to produce a library of materials that will be evaluated for their mechanical properties, biocompatibility and 3D printing potential.

Diels-Alder (DA) polymer networks have attracted attention in recent years due to their potential for bridging the gap between thermoplastics and thermosets[1](Davidson, 2016 #1830). Diels-Alder adducts are cleaved at elevated temperatures; Breaking these covalent bonds transforms the mechanical properties of the material, allowing it to be (re)processed. This has shown great promise in fused deposition modelling (FDM) since it can address one of the greatest drawbacks of the widely adopted AM technique being mechanical anisotropy[2]. While cooling down after printing new DA bonds can be formed between layers[3] whereas covalent interlayer bonding is not possible with current FDM materials.

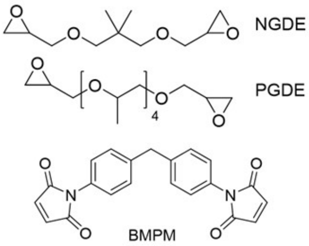

Figure 2: Compounds used in proof of concept

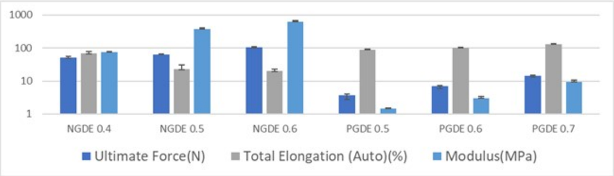

Figure 3: Tensile property comparison between NGDE and PGDE with different (0.4-0.7) furan/maleimide ratios.

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FM-B06
Inverse Solidification in Active Soft Matter: Towards New Functional Materials

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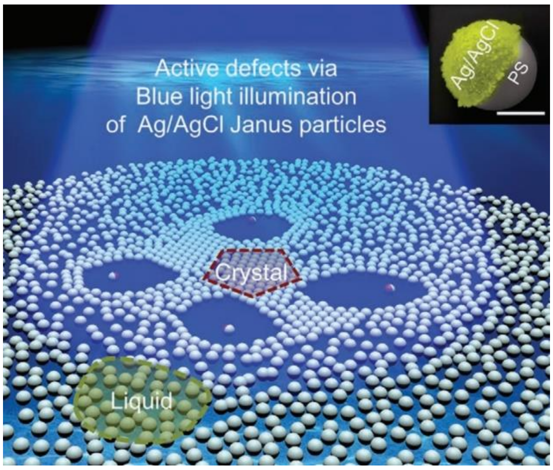
Keywords: Photocatalytic reaction; Active defects; Phase transition; Colloidal crystallization

Crystals melt when thermal excitations or the concentration of defects in the lattice is sufficiently high. The crystalline long-range order vanishes during melting. In contrast to this classical scenario of solid melting, a counter-intuitive behavior of the occurrence of crystalline long-range order in an initially disordered matrix has been demonstrated [1]. This unusual solidification is revealed in a system of passive colloidal particles accommodating chemically active defects – photocatalytic Janus particles. The observed inverse crystallization occurs when the amount of active-defect-induced fluctuations, which is the measure of the “effective temperature”, reaches critical value. The driving mechanism behind this unusual behavior is purely internal and resembles a blast-induced solidification. Here, the role of “internal micro-blasts” is played by the photochemical activity of defects residing in the colloidal matrix [2,3]. The defect-induced solidification occurs under non-equilibrium conditions: the resulting solid exists as long as a constant supply of energy in the form of ion flow is provided by the catalytic photochemical reaction at the surface of active Janus particle defects.

The observed amorphous-to-crystalline phase transition provides a novel insight into the collective effects in mixed colloidal systems of active and passive species. It offers versatile possibilities to address the processes of solidification in various systems brought out of equilibrium, including the formation of biomolecular condensates or biomineralization, transitions from amorphous to polycrystalline state in condensed matter, or the synthesis of materials under extreme conditions. We demonstrate that crystallization via internal drive due to the presence of active defects is accompanied by porosity of the resulting material. In this respect, the proposed crystallization mechanism allows to tailor mechanical properties of new functional materials by maintaining their electronic properties.



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FM-B07

Dual mode – thermometry and drug release vehicles based on hollow Y2O3:Er,Yb and Y2O2SO4:Er,Yb spheres

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Keywords: /

Doping, in general, is a widely used strategy in materials design that entails incorporating atoms or ions into host lattices to achieve desired properties and functions. Rare earth (RE3+) activated phosphors are gaining popularity due to their efficient luminescence, which can be used in cathode ray tubes (CRT), tricolor lamps, white light-emitting diodes (WLEDs), and field emission display (FED) devices, as well as in biomedical applications. In addition, such materials have been studied as potential temperature probes for use in luminescence thermometry. Trivalent erbium (Er3+) is a remarkable ion having upconversion properties due to its ladder-like energy levels, and it has been regarded as one of the most promising RE3+ candidates for luminescence thermometers due to its intense green emissions from thermally coupled 4S3/2 and 2H11/2 emitting levels. Furthermore, the RE3+ ion of choice is frequently combined with Yb3+ ion to benefit from its high absorption cross-section in the NIR, which favors energy transfer-induced upconversion processes to their RE3+ ions. Moreover, some of such phosphors are useful for drug delivery, due to their exceptional properties such as low density, large specific surface area, and good permeability, as well as their high loading capacity and diffusibility for drug molecules.

Here we describe the fabrication of Y2O3 hollow spheres doped with Yb3+ and Er3+ ions abide by the sequential templating process accompanying a simple hydrothermal treatment followed by heat treatment. In addition, we demonstrate the preparation of Y2O2SO4 doped with Yb3+ and Er3+ using a simple one-pot hydrothermal method. In this work these two different inorganic hollow phosphors were extensively investigated and showed to have excellent upconversion luminescence properties and could be effectively used as optical temperature sensors in the biological range (288.15 – 333.15 K). Additionally, they could be used for simultaneous drug delivery, employing doxorubicin (DOX) as a model cancer drug.

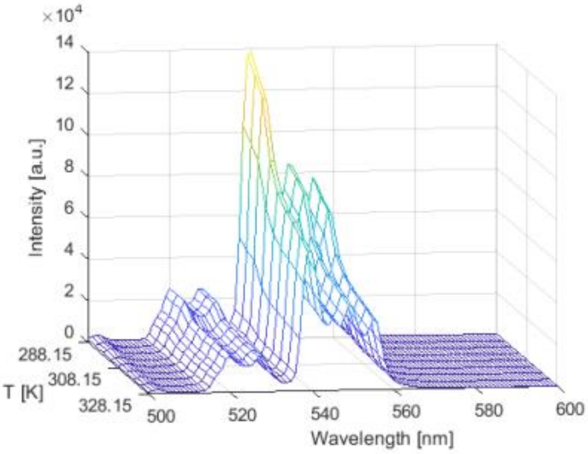

Figure 1 Emission map of $Y_2O_2SO_4$: Er,Yb hollow spheres measured in distilled water at varying temperatures (288.15 – 328.15 K).

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FM-B08
Cutting-edge Characterization Tools for the In-Depth Investigation of Functional Materials

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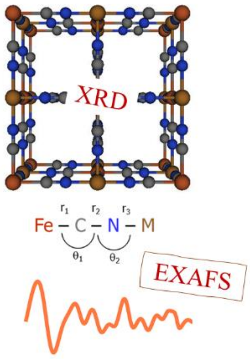
Keywords: Metal-organic frameworks; MOFs; XAFS; XRD; Spectroscopy

Functional materials can be defined as target-motivated materials, i.e., materials whose properties can be adjusted and optimized to serve a specific purpose.[1] Specific functions or properties can be fine-tuned through synthesis or by reshaping the functional material via post-synthetic modifications as simple as heat treatment.[2,3] In this context, metal-organic frameworks (MOFs) have attracted attention due to their ability to host ions in energy-related applications[4] as well as their excellent catalytic activity, also towards complex biomolecules such as proteins.[5] Determining the structure-activity relationship could help in tailoring certain properties: hence, identifying such features is crucial in developing state-of-the-art functional materials that can be utilized in several applications ranging from energy storage to bio-inspired catalysis.

Here, we present a few examples where a combination of advanced characterization tools was exploited to investigate and disclose fundamental structural properties as well as the reaction dynamics of Prussian blue analogs (PBAs) and metal-oxo cluster-based materials. In particular, X-ray Diffraction (XRD) and X-ray Absorption Fine Structure (XAFS) were coupled to explore the materials' long- and short-range order. Advanced analysis with a chemometric technique, i.e., Multivariate Curve Resolution with Alternating Least Squares algorithm (MCR-ALS), supported by ab initio spectra simulations, was performed to unfold the structure under investigation and correlated to the materials' performance.

Combining the complementary results and in-depth analysis thoroughly describes the structural features of the materials and fills the knowledge gap concerning the structure-activity relationship.



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FM-B09

The influence of size, shape, and defects on heat-induced alloying in individual Au@Ag core-shell nanoparticles

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Keywords: in situ electron tomography; bimetallic nanoparticles; 3D diffusion simulation; alloying dynamics

The development of colloidal synthetic techniques has allowed scientists to routinely produce bimetallic core-shell nanoparticles of various shapes, sizes, composition, and elemental distribution. These advancements enable precise control of specific optical properties based on surface plasmon resonance. In this manner. nanoplasmonic-based materials can be exploited for biosensing, photocatalysts, medicine, data storage, solar energy conversion, etc. However, operation in real conditions (e.g. at elevated temperatures) may cause particle reshaping and redistribution of metals between the core and shell of the particle, which in turn may gradually alter the properties of bimetallic nanoparticles. Hereby, a thorough understanding of the influence of the size, shape, and presence of is of great importance for the further development of nanoplasmonic-based technologies. The recently developed combination of fast electron tomography based on High Angle Annular Dark Field Scanning Transmission Electron Microscopy with in situ heating holders is a powerful approach to investigate heat-induced processes at the individual NP level, with high spatial resolution in 3 dimensions (3D). [1,2] Using this approach, we quantitatively investigated the influence of size, aspect ratio, core morphology and the presence of twin boundaries on heat-induced elemental redistribution in Au@Ag core-shell nanoparticles. More specifically, the elemental redistribution at high temperature in single-crystalline Au@Ag nanocubes with similar size and composition, but with different shapes of the core (truncated octahedra and sphere), was shown to be uniform along all directions and proceeding with similar kinetics. By performing 3D simulation of diffusion based on Fick's law, diffusion constants were found to be in the same range as the tabulated values for bulk Au-Ag alloys. [3] Moreover, our investigation indicated significantly faster alloying kinetics for pentatwinned Au@Ag nanorods in comparison to single-crystalline nanorods of comparable sizes and composition (Figure 1). This may be related to the presence of twinning planes, which cause the formation of distortions and vacant sites in the crystal lattice, facilitating diffusion of atoms. Finally, the influence of the core shape was demonstrated to be negligible in the case of two pentatwinned nanorods with different Au cores (rod and bipyramid). In conclusion, using fast electron tomography, we gained a fundamental insight into the nature of elemental diffusion at high temperature and its dependence on various factors, e.g. size, shape, and presence of twinning defects. We believe, that detailed knowledge of thermal stability and/or thermal degradation of bimetallic nanoplasmonic materials will drastically improve the application of these materials in the future.

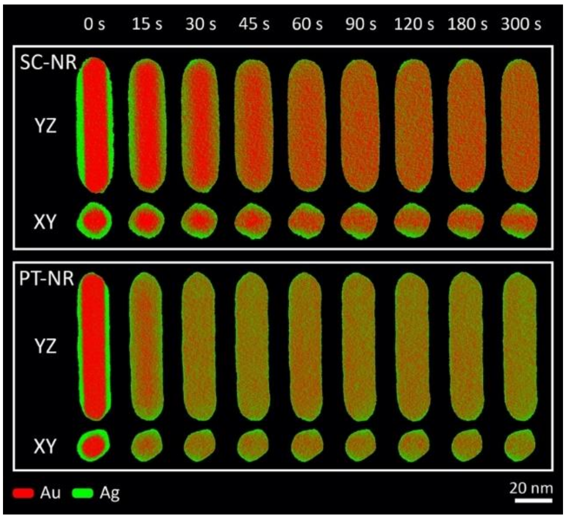

Figure 1. YZ- and XY-slices through the 3D reconstructions of elemental distribution in single crystalline (SC-NR, upper panel) and pentatwinned (PT-NR, lower panel) Au@Ag nanorods at different stages of alloying at 450 °C.

The project has received funding from European Research Council (ERC Consolidator Grant 815128, REALNANO) and European Commission (grant 731019, EUSMI).

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FM-B10

Synthesis and characterization of high purity two-dimensional monolayer Ti3C2 MXenes

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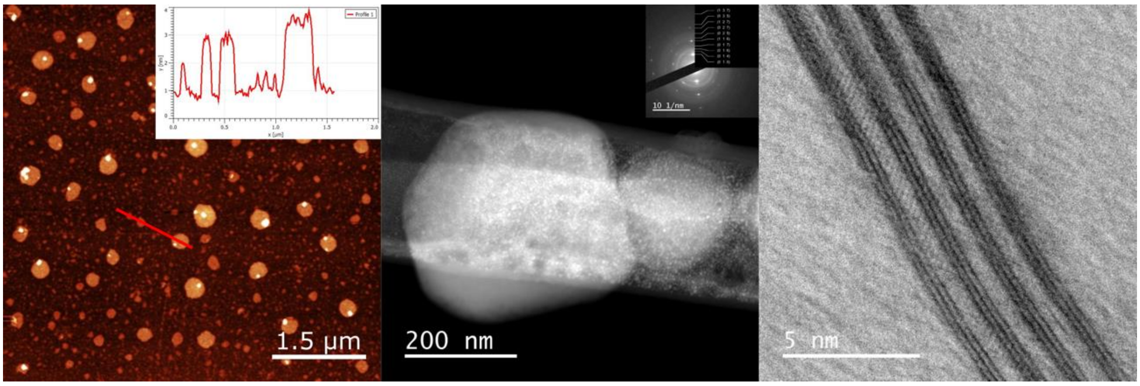
Keywords: MXenes; etching; synthesis; energy storage

MXenes are electrically conductive nanometric 2-D sheet-like transition metal carbides resulting from the chemical exfoliation of 3D MAX phases, such as Ti3AlC2. Their surface is terminated with functional groups (eg. -F/-Cl/-OH) and is tunable by adapting the synthesis method, allowing MXenes to be tailored towards the envisaged application. MXenes are developing an extreme interest as functional 2-D material in electrochemical applications, energy storage, catalysts, biomaterials and thermo-electrics. In this presentation we demonstrate the scalable synthesis of high purity monolayer Ti3C2 MXene using a modified LiF/HCl etching route. The relationship between the (traditional) synthesis routes and the induced impurities is identified and a dedicated purification and extraction methodology is proposed for counteracting these contaminations, drastically improving the quality and properties of the resulting MXene.



FM-B11

Effect of tunable shell thickness on the plasmon-enhanced photocatalytic activity of (Au/Ag)@TiO2 Core Shell Nanoparticles

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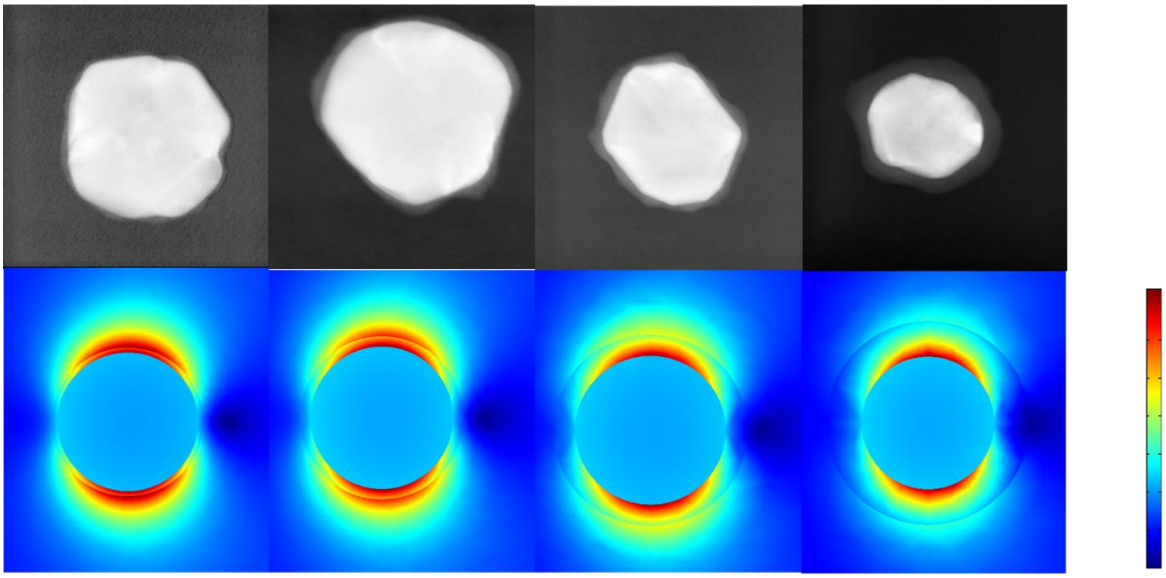
Keywords: Plasmonic nanoparticles; Photocatalysis; core shell

The use of gold and silver nanoparticles to boost the activity of TiO2 based photocatalysts by exploiting their plasmonic effect, has become a widely applied strategy to improve various solar light driven applications, such as photocatalytic air purification, self-cleaning surfaces, etc [1,2]. However, important experimental challenges arise when preparing and handling Ag-TiO2 or Au-TiO2 composite materials. Ag nanoparticles easily oxidize when exposed to air, and Au nanoparticles sinter together when treated at high temperatures, which is often required to calcine TiO2 into the appropriate anatase phase. Here, these limitations are overcome by stabilizing the plasmonic Au and Ag nanoparticles through the formation of a thin and uniform TiO2 shell, that also directly acts as the semiconducting photocatalyst. In this work, Au@TiO2 and Ag@TiO2 core shell nanoparticles have been studied by carefully varying the shell thickness at the nanometer scale. Slow hydrolysis of the titanium triethanolaminato isopropoxide precursor proved to be the key to accurately control the thickness of this TiO2 shell. Finite Element Method numerical simulations have previously shown that the near field enhancement is restricted to less than a few nanometers from the surface of a metal nanoparticle [3]. Also, in our work, photocatalytic stearic acid degradation tests revealed that the photocatalytic activity decreases by a factor of 2 when increasing the shell thickness from 2 nm to 15 nm. The dependance of plasmonic near field enhancement on the TiO2 shell thickness of around Au and Ag cores is further substantiated by means of surface enhanced Raman spectroscopy (SERS) using a probe of R6G molecules on Au@TiO2 and Ag@TiO2 thin films. A significant reduction in enhancement factor of SERS for a thicker TiO2 shells does invariably prove plasmonic nanoparticles with thinner shell thickness have a higher contribution from near field enhancement for photocatalysis. Results of photocatalytic activity in combination with SERS experiments and numerical simulations, prove that nanometer control of shell thickness can lead to the most efficient use of the near field enhancement effect of plasmonic nanoparticles in photocatalytic applications.



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FM-B12

Effect of the synthetic route on the morphological and temperature-dependent photoluminescence properties of Na3ZrF7(Yb,Er) nanoparticles

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Keywords: upconversion; lanthanides; nanoparticles; thermometry

Lanthanide-doped upconversion nanoparticles with sensitive and optically stable thermometric performance are becoming widely investigated in various scientific and industrial fields. Their tuneable dimensions and morphology, as well as their inherently advantageous structural parameters such as the low crystal lattice phonon energies, high chemical stabilities, sharp emission peaks, and relatively long emission lifetimes, make them frontrunners in many imminent applications for (bio)imaging, temperature sensing, and even theranostic purposes [1].

Despite significant research on fluoride host materials, Na3ZrF7 remains rarely and insufficiently investigated, even though it manifests some promising features like non-toxicity in contact with healthy cells and enhanced in vivo biodegradability to small non-toxic residues at lower pH values [2,3]. The insufficient insight is caused by a lack of much-needed systematic investigations of the most commonly exploited synthetic approaches such as coprecipitation, thermal decomposition, and solvothermal routes for this material.

In our present work, we investigate and compare how different synthetic routes and slight modifications of controlled parameters affect the morphology and the upconversion photoluminescence properties of the as-prepared nanoparticles. Such investigation is crucial to fully characterize and optimize the performance of this lanthanide-ion host matrix, especially for future biological applications.

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FM-B13
REVERSIGEL: REVERSIbly crosslinked hydroGELs for effective cardiac stem cell delivery

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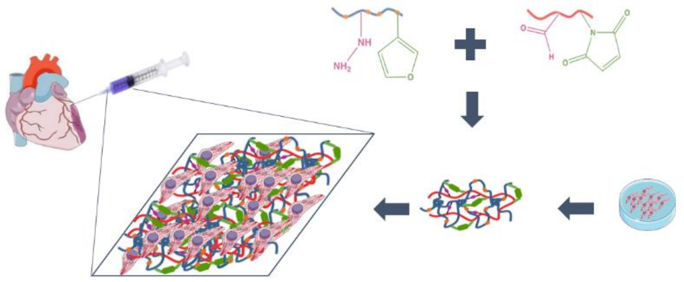
Keywords: Injectable, adaptable and in situ cross-linking hydrogels; Biotechnology; Dynamic covalent chemistry; Stem cells; Biomaterial; Tissue engineering

During a myocardial infarction heart tissue dies due to hypoxemia, disturbing the heart's function and potentially leading to heart failure, which is often fatal. Cardiac Atrial appendage Stem Cells (CASCs) are promising stem cells for heart tissue repair. However, stem cell-based therapies are limited by poor stem cell retention at the transplantation site. This work concentrates on developing an adaptable hydrogel that will facilitate CASCs transplantation and retention. The envisioned hydrogel will mimic the heart's extracellular matrix via two components: Elastin-Like Proteins (ELPs) and oxidised Hyaluronic Acid (HA) derivatives. ELPs are thermoresponsive proteins with (VPGXG)5 as core sequence, where X denotes any amino acid except proline. These ELPs can also contain short peptide sequences for cell adhesion. HA on the other hand offers synthetic versatility via its free carboxylic acids and alcohol groups, along with favourable biological properties like the promotion of angiogenesis and wound healing. Both components can be crosslinked by dynamic hydrazone bonds and via the ELPs' inherent LCST transition. Moreover, the hydrogels' mechanical properties can be further improved via in situ Diels-Alder cross-linking. To this end, SuFEx chemistry was applied to introduce orthogonal furan moieties along the ELP backbone being chemical handles for ultimately cross-link tuning with maleimide-decorated HA.



Evaluating Cardiac Appendage Stem Cell properties *in vitro* when embedded in newly developed hydrogels

FM-B14

Hydrogen Bonding with Framework Siloxane Bonds Drives Liquid Phase Adsorption of Primary Alcohols in High-Silica Zeolites

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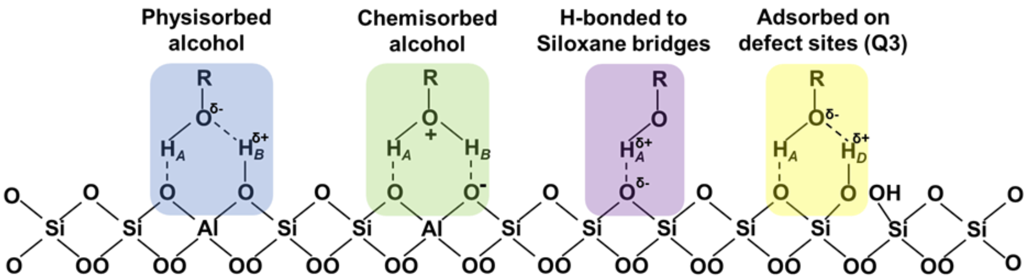
Keywords: Adsorption; Zeolites; Alcohols; Bio-alcohol separation

Liquid phase adsorption of C1-C8 1-alcohols on five MFI type zeolite samples with Si/Al ratio in the range of 11.5-140 and *BEA samples with Si/Al ratio of 12.5 and 150 was investigated using quantitative in situ nuclear magnetic resonance (NMR) spectroscopy. Alcohols were adsorbed as pure liquid and from D2O solutions. Additional ex situ NMR experiments were done on samples equilibrated with dilute aqueous 1-pentanol solutions. The saturation capacity reached pore filling. The number of adsorbed molecules largely exceeded the concentration of Brønsted acid sites and framework defects, previously identified as the preferential locations for alcohol adsorption from the gas phase. Using a combination of 1H direct excitation, 1H-13C CPMAS and 1H-29Si HETCOR NMR experiments, a new interaction mechanism was observed. In this mechanism , ethanol and larger alcohol molecules hydrogen bond to Si-O-Si siloxane oxygen atoms of the zeolite framework. Such mechanism co-exists with the traditionally accepted physisorption mechanisms. Hydrogen bonding to oxygen atoms of siloxane groups can explain why the saturation capacity of the zeolite pores using 1-pentanol as probe molecule does not correlate to the Brønsted acid and framework defect site concentrations and increases with increasing Si content of the zeolite framework. This demonstrates an increasing contribution of the newly discovered adsorption mechanism. Similar observations were made in *BEA type zeolites, hinting that hydrogen bonding to siloxane bridges could be a universal mechanism for liquid phase adsorption of long-chain alcohols on silicate-based zeolites. Hydrogen bonding of organic molecules with framework oxygen atoms may shed light on differences observed between oxidic hydrophobic adsorbents, generally exhibiting less pronounced hydrophobicity and monoatomic hydrophobic materials such as carbon.



FM-B15
Band alignment in InP/ZnSe core/shell quantum dots

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Keywords: Quantum dots; band alignment; transient absorption

Colloidal Quantum dots (QDs) have been a subject of research for over 30 years now. Thanks to their size-dependent optical properties, QDs found their way into applications in light display, lasers, photodetectors, and biomedicine. Recently, restrictions on the use of Cd made InP-based QDs emerge as an alternative to the widely deployed CdSe-based QDs. Similar to CdSe-based QDs, InP QDs are formed by a hot injection synthesis, and core/shell heterostructures such as InP/ZnSe can be formed to enhance optical properties, such as the photoluminescence quantum yield. To understand the different factors that determine these optical properties, linear and non-linear optical spectroscopy is most useful. By analyzing the interaction of QDs with light, extensive information on, for example, the energy and oscillator strength of the band-gap transition, the alignment of energy levels, the balance between radiative and non-radiative recombination, etc. can be obtained. In this study, we analyzed a set of InP/ZnSe/ZnS core/shell/shell QDs with different InP-core sizes using femtosecond pump-probe spectroscopy. The double shelling results in QDs with a near-unity photoluminescence quantum yield, but also raises the question as to how energy levels in core and shell interact. We show that this information can be derived from the transient absorption spectrum, i.e., the absorbance of the QDs after photo-excitation. By assigning the 4 different bleach bands to specific electronic transitions, we argue that the InP/ZnSe heterostructure is characterized by a straddling, so-called type 1, band alignment but with only a small energy offset between the InP and ZnSe valence-band edge. Upon decreasing the InP core diameter, hole delocalization within the ZnSe shell therefore becomes more pronounced; a trend that limits the range of emission colors InP/ZnSe core/shell QDs can address.

FM-B16

Multilevel Nanoscale Chemical Patterning of Graphite at Different Length Scales

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[2] *Meiji University, Japan*

Keywords: pattern-functionalization; covalent functionalization; electrochemical grafting

Chemical patterning of graphene and related 2D materials is relevant in several different domains of science and technology with exciting possibilities in electronics,[1] catalysis,[2] sensing, and photonics.[3] Such patterning can be achieved either using covalent or non-covalent approaches.[4] The covalent binding of chemical species to the surface enables robust functionalization however typically involves poor spatial control over the binding process due to the reactive chemistries involved. On the other hand, the non-covalent approach provides excellent control over the interfacial binding thanks to the weaker interactions involved in the process and to the principles of supramolecular chemistry, albeit does not provide as robust interface.

Here, we present a novel approach for chemical patterning of graphite using a combination of covalent and non-covalent approaches. Building on our previous work,[5] where self-assembled monolayers of linear alkanes were used as sacrificial masks for directing the covalent anchoring of aryl groups to the graphite surface in sub-10 nm arrays. We present an advanced design of a template alkane with modified terminal groups which allowed better pattern transfer fidelity in comparison to simple linear alkanes. We also explored the use of chronoamperometry instead of previously used cyclic voltammetry for the functionalization process, which enabled patterning of the graphite surface at two-different length scales: few hundred nanometers circular patterns interspersed with sub-10 nm linear arrays. The covalent chemical patterning process has been studied in detail using CV and CA measurements whereas the patterned substrates have been thoroughly characterized using Raman spectroscopy and scanning tunneling microscopy. The patterned surfaces have been employed for studying molecular self-assembly which revealed an intriguing "memory" effect.

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FM-B17

N-type self-assembled semiconductors for application in photovoltaic devices

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Keywords: electron transporting materials; semiconductor; naphthalene tetracarboxylic diimide; naphthalimide; solar cells.

Photovoltaics (PV) are devices of various structure, which convert solar energy directly to electricity by the photovoltaic effect in a semiconductor's junction [1]. High costs and insufficient conversion efficiencies are the major issues in the development of the photovoltaic devices to become a primary source of energy. Development of new charge transporting materials used for solar cells construction is necessary to reach high performances. Innovative way to increase device efficiency is application of self-assembled monolayers (SAM). SAMs can form ordered one-atom thick layer with well-defined orientation on the surface. The layout of directed organic semiconductors molecules maintain constant dipole moment, which influences charge transporting efficiency and the alignment of energy levels at the layers interface [2]. SAM materials have potential to surpass most of the traditional charge transporting materials due to their simple layer forming procedure, minimal material consumption, conformal target surface coverage and possibility to use materials with limited solubility in organic solvents.

In the last decade, naphtalenetetracarboxylic diimide (NDI) and naphthalimide (NI) derivatives have been widely used as electron transporting materials. NDI and NI solubility, photophysical and electronic behavior can be controlled by the incorporation of different functional groups on the core structure, which overall influences device photovoltaic properties [3]. So far, there isn't much data on successful incorporation of ETM SAMs in photovoltaic devices, indicating that there is still a lot of potential for n-type SAM semiconductors investigation.

In this work n-type semiconductors containing 1,4,5,8,-naphtalenetetracarboxylic diimide or 1,8-naphthalimide central fragment along with functionalized anchoring groups (quaternary ammonium, pyridine and sulfonic) were synthesized. These materials could be promising candidates for further photovoltaics development.

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FM-B18

Optimization of sulforaphane extraction from cabbage seeds by ultrasound and microwave extraction methods

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Keywords: Cabbage; Sulforaphane; Ultrasound Extraction; Microwave Extraction; Energy Consumption

The sulforaphane compound, which has a natural anticancer and antimicrobial effect, prevent the uncontrolled cell proliferation caused by cancer. Cabbage contains high level of dietary fibers, vitamins and sulforaphane. During this study, it was aimed to extract the sulforaphane from cruciferous cabbage seeds with the green extraction method of ultrasound and microwave techniques. It was also aimed to reveal the working of two extraction techniques and to optimize the conditions. At first, the samples were grounded and subjected to soxhalet extraction with n-hexane in order to remove the oily parts. After that, hydrolysis was carried out for 1 h at 25°C, at pH 7, by adding distilled water at a ratio of 1:2 sample: water (w/v). This process provides that all glucosinolate molecules in the mixture were hydrolyzed to sulforaphane with the help of the myrosinase enzyme. The resulting aqueous mixture was extracted with 65% ethyl acetate + 35% water. Anhydrous sodium sulfate was added to the mixture in order to remove excess water in the extracts and then the solvent was removed at 35°C. For ultrasound and microwave extraction methods, the effects of specific process variables on sulforaphane concentration [time (min), amplitude (%) and solvent/solid ratio (v/w) and time (min), power (W) and solvent/solid ratio (v/w)] and energy consumption were investigated, respectively. In case of targeting the maximum sulforaphane concentration, and acceptable energy consumption, the independent process variables of amplitude (%), power (W), solvent/solid ratio (v/w) and time (min) were optimized by desirability method.

Besides, glucosinolates at low pH values and in the presence of iron ions can be converted to sulforaphane nitrile, which has no positive effect on health and can be toxic to the cells. Therefore, it was analyzed even if sulforaphane nitrile was formed in the extracts, besides of the total phenolic substance, antioxidant capacity and extraction efficiency. As a result of this study, optimum processing conditions that provide the maximum sulforaphane concentration and acceptable energy consumption were found as 3 min extraction time, 26:1 solvent/solid ratio (v/w) and 100 W power in case of the microwave extraction method (7426.17 µg/g dry matter and 15.17 W) while, in ultrasound extraction method (7592.35 µg/g dry matter and 4.5 W), 5.21 minutes extraction time, 24:1 solvent/solid ratio (v/w) and 40.24% amplitude were determined as optimum values. When the results were evaluated, it was determined that the use of ultrasound extraction method for sulforaphane extraction gave more successful results.

This study was supported by TUBITAK with project number: 121O560.

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FM-B19

Strontium barium niobate thin layers as lead-free alternative for photonic applications

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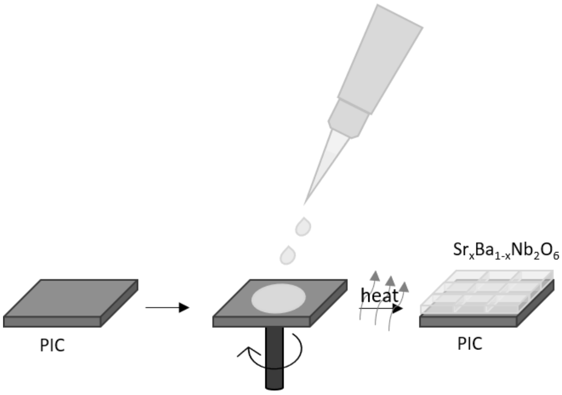
Keywords: Ferroelectric material; chemical solution deposition; strontium barium niobate

In our modern society people are able to communicate, generate and store enormous amounts of data. As a result, the amount of data traffic worldwide is increasing exponentially and outgrowing the available technology. Therefore, high-speed data communication has become a necessity. By integrating both electronic and photonic functions on a single chip, photonic integrated circuits (PICs) could function as a platform for data communication via optical means. Today, silicon and silicon-nitride materials are mostly used for integrated photonics. The possibilities of these platforms can be further enhanced by the addition of a ferroelectric layer as an active device for a hybrid system. Tuning of the signal can be accomplished by changing the refractive index of the active device. The most efficient way to integrate this ferroelectric layer is via direct layer growth on PICs. In this work, strontium barium niobate (SBN) as a promising ferroelectric material is used due to its high linear and non-linear electrooptic coefficients. For the direct integration of SBN on Si substrates, we have introduced a wet chemical solution deposition approach by means of spin-coating technique. The implementation of this wet chemical method facilitates molecular level control and low cost production of highly oriented ferroelectric thin films for integrated electro-optic devices.



FM-B20

The role of electron correlation on resonance effects

Van Hende Daria[1]*, Francisco Evelio*[2]*, Bultink Patrick*[1]*, Acke Guillaume*[1]*, Martín Pendás Angel*[2]

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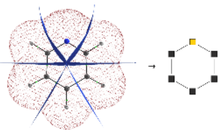
Keywords: electron correlation; conductivity; resonance; mesomerism

Electron delocalization (ED) measures and the oscillating pattern of their spatial decay rates are closely related to core chemical concepts such as resonance, mesomerism and aromaticity, and are known to be rather sensitive to electron correlation. It is widely accepted that the most reliable descriptors of aromatic behavior are based on ED indices, typically computed in the mean-field approximation. Studies on homogeneous systems have shown that oscillations disappear with increasing electron correlation as electrons become increasingly localized, thus destroying resonance and aromaticity. In this contribution we examine prototypical ionic Hubbard cyclic chains to model the effect of electron correlation on heteronuclear rings, comparing our results with those of actual calculations. We uncover a strong coupling regime in which the interplay between the heteroatom electronegativity and the strength of electron correlation leads to new electronic phases with enhanced delocalization which, if suitably synthesized, might lead to new aromatic molecules. ED descriptors emerge as useful tools to extract chemical information by quantifying global and local transitions between distinct electron organizations in the ground state.

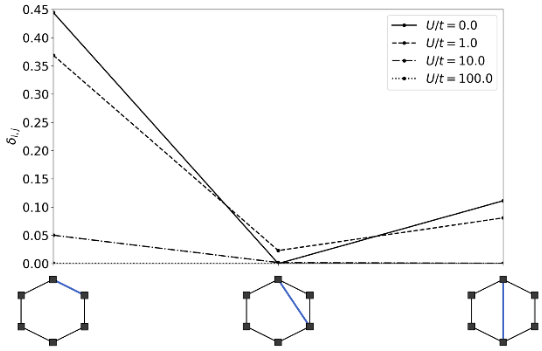
Introduction

- **Electron delocalization** (ED) explains chemical phenomena such as aromaticity and chemical bonding.
- The **oscillating pattern** of ED descriptors related to core chemical concepts such as resonance, mesomerism and aromaticity [1].
- How does **electron correlation** affect those aromaticity descriptors?
- Choose simplest Hamiltonian possible → Hubbard model Hamiltonian where the electron correlation is controlled through a **correlation parameter** U/t.



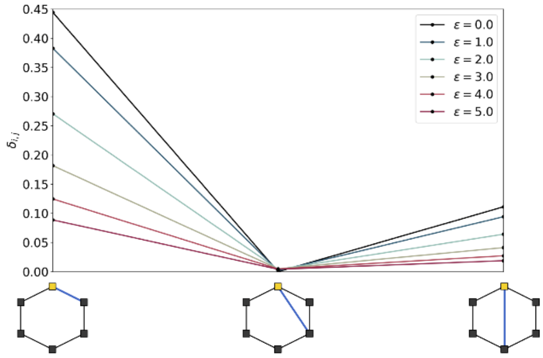
Individual factors reduce resonance effects

Static correlation



- $U/t = 0$:
  - Exact cancellation of $\delta_{1,3}$ due to destructive **quantum interference** effects.
  - Interference effects related to **resonance** theory and **mesomerism**.
- $U/t > 0$:
  - Electron correlation destroys the independent particle approximation.
  - Exact cancellation conditions are not met anymore.
  - **Oscillations gradually disappear** with increasing static correlation U/t.

An impurity



- **Oscillations gradually disappear** with increasing chemical potential ε.

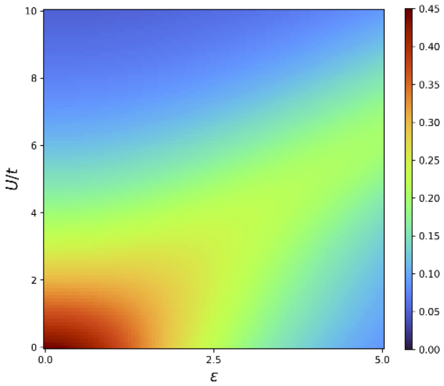
Theory

- Atoms in molecules (AIM) have a fluctuating number of electrons → **open quantum systems**.
- Define the delocalization index (DI) between atoms i and j as an **orbital-invariant** descriptor of electron delocalization through the statistics of the electron distribution [2].

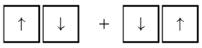
$$\delta_{i,j} = -2.0 \text{ covariance}_{i,j} \tag{1}$$

$$= -2.0 \sum_{i,j} (n_i - \overline{n}_i) \cdot (n_j - \overline{n}_j) \cdot p(n_i, n_j) \tag{2}$$

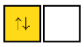
. . . but their interplay boosts electron delocalization



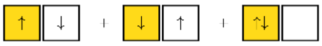
- On the $\varepsilon = 0$ axis: system moves from a metallic to a **Mott insulator** phase.



- On the $U/t = 0$ axis: **decreased covalency** as the polarity difference increases.



- At $U/t \approx \varepsilon$: **spontaneous dimerization** leads to increase in electron delocalization.



Conclusions

- Regions of high and low electron delocalization separate **distinct electron organizations** → DIs emerge as an important tool to **explain** the electronic structure and conductivity in chemical terms.

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GHENT UNIVERSITY

FM-B21

Boosted CO2 Reduction of Non-precious metal Ni@N-doped Carbon Electrocatalyst by Regulating the Synergies of Ni and N-doping

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Keywords: /

Excessive CO2 emission caused by anthropogenic activities has been declared as the main factor that contributes to climate change. Among the developed technologies like thermocatalysis, photocatalysis, etc. electrochemical CO2 reduction to fuels and feedstocks shows the superiorities that can be conducted under ambient conditions and easy scale-up.[1] However, selective conversion of CO2 to a specific reduction product in electrocatalysis still suffers from a high overpotential, a competitive hydrogen evolution reaction (HER), slow kinetics and low selectivity, and the process is sensitive to the catalysts' surface structure.[2] In this study, Ni catalyst decorated on a biomass-derived carbon (Ni@NC) was prepared by a sol-gel method followed by subsequent annealing. The architecture of the catalyst was optimized by N-doping and tuning the porosity with Zn sacrifice agent during the synthesis procedure. The prepared catalysts were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), and Nitrogen sorption. When evaluated as the cathode, the as-prepared samples show high CO Faradic efficiency, and gaseous CO and H2 that were detected by (Gas chromatography GC) are the main products. What is interesting is that a slight CH4 was detected. The results indicated that optimizing catalysts' structure by the synergies of Zn sacrifice agent and N-doping not only improved the CO(g) selectivity but also modified the interaction between catalyst surface and CO* intermediate for further reduction to CH4. This strategy opens a new window for developing a novel catalyst for electrochemical CO2 reduction to CO and more reduced products.

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Chemistry meets Biology

CB-A01

Polyoxometalate Ligand Enables Regioselective Copper-Mediated Oxidative Cleavage of Protein

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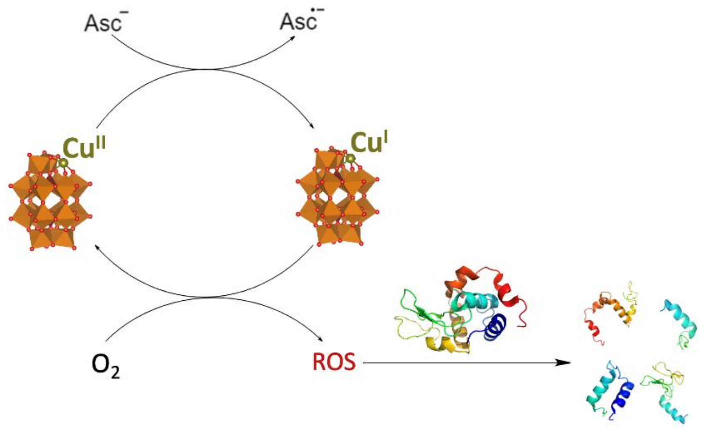
Keywords: copper; polyoxometalates; oxidative cleavage; regioselective; protein cleavage

Metal-catalyzed oxidation reactions (MCO) is one of the most applicable method to induce protein oxidative modifications (e.g., protein oxidation, protein oxidative cleavage and crosslinking), which are very essential technique for many applications in biotechnology and redox proteomics. However, a suitable ligand is needed to enable the metal to induce these oxidative modifications in a selective manner. A suitable ligand needs to show high stability and enhance the metal catalytic efficiency over a wide range of temperature and pH values. Herein, we studied the influence of the use of polyoxometalates (POMs) on the catalytic efficiency of Cu ions to induce protein oxidative cleavage. Cu-substituted POM (Cu-POM), α2-K8P2W17O61(Cu2+.OH2), (Cu(II)WD), in the presence of Asc, shows ability to selectively cleave hen egg white lysozyme (HEWL) and produce four peptide fragments. The oxidative cleavage of HEWL via Cu(II)WD/Asc is enhanced at low pHs, and at higher concentrations of Asc (2 mM) while less cleavage was observed if Cu(II)WD concentration > 0.1 mM. A detailed mechanistic investigation, through the use of different techniques such as electron paramagnetic resonance (EPR), hydrogen nuclear magnetic resonance (1H NMR), sodium dodecyl sulphate polyacrylamide gel electrophoresis (SDS-PAGE), of the cleavage of HEWL by CuWD/Asc revealed the crucial role played by POM to deliver the MCO reaction to cause protein cleavage regioselectively. CuWD showed high stability and integrity over different pH (5.0 - 8.5) and temperature values (25 – 60 ^{0}C). Further comparison of cleavage and binding sites of current system with previously reported HEWL cleavages by other MS-POMs (CeIV-, ZrIV- and HfIV-POM), and CuWD hydrolytic cleavage confirmed the POM enables a regioselective oxidative cleavage. We believe that this study will enables new applications for metal-substituted POMs (MS-POMs) to be used in introducing several protein oxidative modifications.


Asc⁻
Asc•⁻
Cu^II
Cu^I
O2
ROS

CB-A02

Anti-inflammatory effect of Izalpinin derived from Chromilaena leivensis: λ-carrageenan-induced pawa edema and in silico model

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[2] *Universidad del Bosque, Colombia*

[3] *Fundación Universitaria Juan N. Corpas, Colombia*

[4] *Universidad de Concepción, Chile*

Keywords: Anti-inflammatory; Chromolaena leivensis; flavonoinds; creatinine kinase; molecular docking; molecular dynamics

The flavonoid izalpinin was isolated from the aerial parts of Chromolaena leivensis. Its structural determination was carried out using MS and NMR spectroscopic techniques (1H, 13C). This compound was evaluated for its anti-inflammatory effect in a rat model on λ-carrageenan-induced plantar edema. Paw inflammation was measured at one-hour intervals for 7h following the administration of λ-carrageenan. Serum creatine kinase (CK) levels were evaluated, obtaining statistically significant results with the treatments at doses of 10 mg/kg (*$p<0.01$) and 20 mg/kg (**$p<0.005$). The anti-inflammatory effect of the compound was evaluated by plethysmography, and the results showed significant differences in the three concentrations (10 mg/kg, 20 mg/kg, 40 mg/kg) in the first and third hours after treatment. *$p<0.05$; ***$p<0.001$; ****$p<0.0001$ vs. the negative control group treated with vehicle (DMSO). Finally, molecular docking analysis revealed that izalpinin has a strong binding affinity for target proteins involved in the inflammatory process (COX-2, 5-LOX, NOS, 5-PLA2 and HAase). Molecular dynamics analysis allowed us to demonstrate that the ligand-protein complexes present acceptable stability, with RMSD values within the permitted range.

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CB-A03

Using UV-Vis spectroscopy and EPR as a tool to study the incorporation of heme proteins in titania

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Keywords: biosensors; EPR; UV-Vis spectroscopy; titania; heme proteins

Biosensors based on horseradish peroxidase (HRP) have shown to be promising for the detection of phenolic compounds [1]. The key in the development of this kind of devices concerns the immobilization of the proteins on suitable supports, with multiple factors influencing the efficiency of incorporation, such as temperature, pH, type of buffer, support, and the biochemical and biophysical properties of the protein itself. Mesoporous titania (TiO2) have shown promise to be used as support because of their biocompatibility [2].

In this study, we analyzed the incorporation of different heme proteins, like horse heart myoglobin (hhMb) and HRP, on different kinds of mesoporous and non-porous TiO2. We carefully checked the effect of various buffer solutions. While UV-Vis spectroscopy of the supernatant provides a facile way to detect the extent of incorporation of the protein, it does not reveal any information on its fate in/on the metal oxide. Using electron paramagnetic resonance (EPR) spectroscopy, the electronic and geometric structure of the active heme site can be investigated. EPR is also a valuable tool to detect paramagnetic centers in titania, such as Ti(III) and O2- (surface) centers. This is exploited in this work to understand how incorporation affects the active heme site of the protein as well as its influence on the surface sites. A different pH or different buffers are found to drastically affect the adsorption of the proteins as well as their structure and electrochemical activity. Therefore, it is important to take these factors into consideration when optimizing the adsorption process of heme proteins on mesoporous TiO2 for biosensor development.

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CB-A04
Metal-oxo clusters as new class of nanozymes toward protein hydrolysis

Declerck Kilian[1], *Savic Nada*[1], *Parac-Vogt Tatjana*[1]

[1] *KU Leuven, Belgium*

Keywords: nanozymes; metal-oxo cluster; proteomics

Nanozymes are nanomaterials with intrinsic enzyme-like properties, and have the ability to replace natural enzymes by mimicking their catalytically active centres. Compared to the natural enzymes, nanozymes have shown unique advantages such as high catalytic activity, low cost, high stability, and tuneable activity.[1,2] The selective hydrolysis of proteins is crucial for the application of nanozymes in biotechnology and proteomics, where trypsin currently represents the ‘golden standard’. However, trypsin produces fragments that are frequently too short and it only retains proteolytic activity under specific reaction conditions. Additionally, its frequent use in proteomics analysis may induce an oversampling of tryptic peptides and loss of sequence information as a result.[3] Therefore, our group has been developing Lewis acidic metal-oxo clusters as effective catalysts in middle-down proteomics applications.[4] In this study we report catalytic activity of the heterogeneous Zr(IV) metal-oxo cluster [Zr17O8(OH)24(OH2)12(HCOO)12(SO4)8] (Zr17) and the homogeneous [Zr6O4(OH)4(CH3CO2)12] (Zr6) metal-oxo cluster, toward the hydrolysis of myoglobin from equine skeletal muscle. The appearance of new fragments at lower molecular weight in sodium dodecyl sulphate polyacrylamide gel electrophoresis (SDS-PAGE) serves as indication to protein hydrolysis. Molecular interaction between the protein and the investigated metal-oxo clusters was evaluated by different techniques including circular dichroism (CD), ultraviolet-visible (UV-Vis) and tryptophan fluorescence spectroscopy. Moreover, 13C nuclear magnetic resonance (NMR) spectroscopy, infrared (IR) spectroscopy and inductively coupled plasma optical emission spectroscopy (ICP-OES) were employed to provide insight into the stability of the catalysts under the investigated reaction conditions.

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CB-A05
Temperature Triggered in situ Tyrosine Bioconjugation

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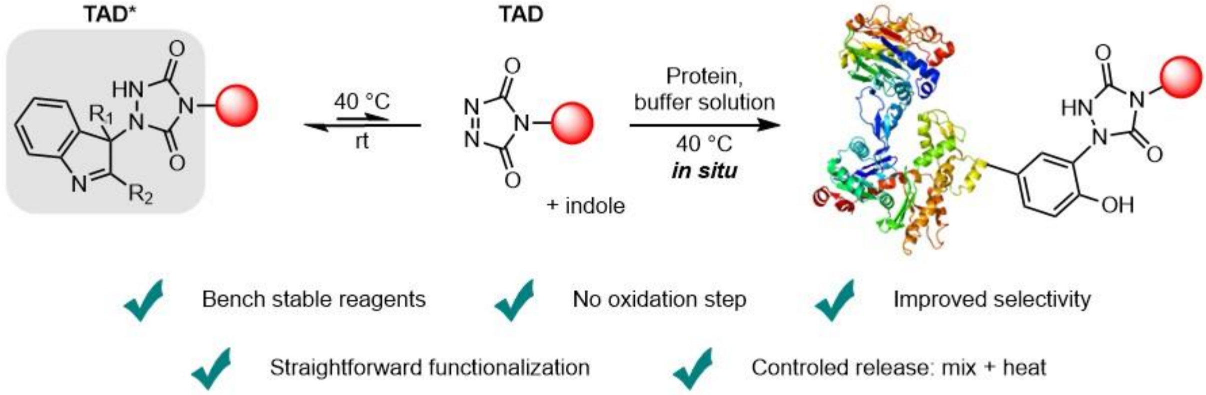
[1] *Ghent University, Belgium*

Keywords: Bioconjugation; Tyrosine; Triazolinedione; Protein modification

Protein conjugation has become a widely investigated research field as it is essential in a wide range of applications including imaging, protein function elucidation and targeted drug delivery [1]. Despite the increased importance for reliable methods towards synthetically modified proteins, it remains an ongoing challenge to develop strategies that can achieve high chemo- and site selectivity. Recently, triazolinedione (TAD) mediated tyrosine conjugation emerged as one of the fastest and most site specific bioconjugation techniques up to date [2]. Despite operational ease and reliability, TADs are very unstable by itself in aqueous medium and recently revealed off-target tryptophan modification [3]. Also, incompatibility of the biological payload with the corresponding urazole oxidation step limits their functionalization.

Here we introduce an in situ bioconjugation strategy involving protected TAD moieties (TAD*) which are bench-stable at room temperature, but deblock upon heating in aqueous medium, allowing controlled release and site-selective protein modification. In contrast to TAD, it was possible to synthesize a broad range of functional TAD*s exhibiting an improved shelf-life and solvent stability, via a straightforward one-pot procedure. Also, competition experiments showed an improved selectivity towards tyrosine at physiological pH, without any degradation products. Finally, site-selective modification of several proteins was achieved, demonstrating the generic potential of the TAD*-mediated bioconjugation strategy.



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CB-A06

The effect of plasma-induced oxidation on the interaction of inhibitory NK-cell receptors with their cancer cell ligands

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Keywords: plasma; immunotherapy; molecular dynamics

Our immune system naturally protects us against cancer. Natural killer (NK) cells, innate immune cells with the capability to directly kill malignant cells, play an important role in this cancer immunosurveillance. However, cancer cells can learn to evade this immune response, causing the growth of a tumour. The field of plasma-based immunotherapy aims to harness and improve this natural immune response through treatment with cold atmospheric plasma.[1] Previous research indicated that plasma treatment of skin cancer cells improves the ability of NK-cells to recognize and kill the cancer cells, which was attributed to the changed expression of surface ligands induced by reactive oxygen and nitrogen species (RONS) produced by the plasma.[2] Indeed, whether an NK-cell will attack or not is determined by the balance between activating and inhibiting signals received through binding of its surface receptors with these ligands on cancer cells. However, apart from intracellular effects, which can change the expression of ligands on the cancer cell surface, the RONS can also interact with the ligands already present on the cells, causing oxidation and conformational changes that may change their ability to bind their receptors.[3]

In this work, molecular dynamics simulations are used to investigate the effect of oxidation of cancer cell surface ligands HLA-Cw4 and HLA-E on their ability to bind their receptors on NK-cells, respectively KIR2DL1 and NKG2A/CD94. Both ligands send inhibitory signals to NK-cells upon binding, and previous research showed that plasma treatment can change their expression on cancer cells. Our simulations show that plasma-induced oxidation only slightly changes the binding free energy, which indicates that the improved NK-cell interaction induced by plasma treatment is mainly a result of the changed ligand expression, and not of oxidative damage done to the already expressed ligands.

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CB-A07
Isolation, purification and structural characterization of siderophores from P. damselae subsp. piscicida

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Keywords: siderophore; isolation; P. damselae subsp. piscicida; aptamer

Siderophore, in chemical terms, is a low-molecule-weighted metal chelating compound released by eukaryotic, prokaryotic, and higher organisms in an environment where iron is inadequate [1]. Siderophores have a wide variety of applications and study reports showing their importance in the world of biotechnology. They are used specifically as iron carriers and antibiotics to treat diseases such as cancer and malaria [2-4]. Photobacterium damselae subsp. piscicida (Phdp) is a pathogenic bacterium responsible for pasteurellosis outbreaks in aquaculture. From the past to the present, antibiotics used in the fight have lost their effect as a result of the development of multi-drug resistance to Phdp. This situation results in substantial fish deaths and economic losses in the aquaculture sector.

In these circumstances, our main goal is to isolate, purify and structural characterization of siderophores from P. damselae subsp. piscicida bacteria for the development of a specific aptamer. For this purpose, siderophore samples were produced as CAS dyed (metal bonded) and diluted 2 different metal-free media Basal medium (MM9; glucose, NH_4Cl, NaCl, casamino acid), Luria Bertani medium (LB). After the extraction procedures LB was found to be more suitable among the metal-free samples by thin layer chromatography method. Open column chromatography method with reversed phase silicagel adsorbent was preferred for isolation of siderophores from both CAS dyed and metal-free media. Advanced spectroscopic methods (1D, 2D-NMR, Mass) were used to determine the exact structure of isolated pure siderophores. The siderophore molecule, which is belonging to the geography of our country, will be isolated, purified and characterized for the first time by this project. With our further studies, a strategy to struggle Phdp epidemics that cause high economic losses in aquaculture will be developed.

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CB-A08

Growth and siderophore production in vritro P. damselae subsp. Piscicida under iron limitation

Eren Eroğlu, Asiye Esra[1]*, Keskin Özlem Buse*[1]*, Evran Serap*[1]*, Sarıkahya Nazlı*[1]*, Yaşa İhsan*[1]

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Keywords: P. damselae subsp. piscicida (Phdp); bacteria; siderophore; cytotoxic activities; hemolytic activities;apoptogenic activity

P. damselae subsp. piscicida (Phdp) is one of the most destructive bacterial pathogens in aquaculture, due to its wide geographical distribution, host range and massive mortality.[1] Various virulence factors have been identified in this bacterium, such as the synthesis of the plasmid-encoded exotoxin AIP56, which exhibits polysaccharide capsular material, extracellular products with phospholipase, cytotoxic and hemolytic activities, or apoptogenic activity against fish macrophages and neutrophils. An important virulence factor found in Phdp is the ability to obtain iron from the host by production of siderophores. These are low molecular weight compounds with the ability to chelate and dissolve $Fe3+$. Siderophore-$Fe3+$ complexes are transported to the bacterial cell by outer membrane receptors and specific transporters.[2]

Our main aim in the study is to investigate the relationship of Phdp siderophore production with growth and temperature in iron-restricted conditions. In this context, growth rates and siderophore secretion were investigated over 72 hours of growth in iron supplemented and iron restricted chemically defined media at two different temperatures, 15°C and 25°C. Siderophore production percentages were determined by the standard method (Chrome Azurol Sulfonate Assay, CAS) and also by the 96-well microplate method.[3] While growth rates decreased under iron restriction, siderophore production was detected in the exponential and stationary phases of growth. We have shown that siderophore synthesis in Phdp is two times more preferable at 15°C than at 25°C. The siderophore production potential of pathogenic Phdp strains isolated from fish farms in Turkey was demonstrated for the first time in this study. Our research results will contribute to the development of alternative methods in the fight against Phdp outbreaks.

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CB-A09

Targeted AURKA degradation: towards new therapeutic agents for neuroblastoma

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Keywords: AURKA; PROTACs; Neuroblastoma; Targeted Protein Degradation; MYCN

Neuroblastoma is a pediatric tumor of the sympathetic nervous system that arises during early embryonic development. Aurora kinase A (AURKA) is a well-established target in neuroblastoma (NB) due to its catalytic functions during mitosis and due to stabilisation of the key oncoprotein MYCN. Therefore, AURKA inhibition as a treatment for NB is actively being pursued. However, current inhibitors evidently trigger protein upregulation, possibly resulting in treatment resistance. Notably, classical inhibitors typically only target AURKA’s mitotic/catalytic functions. AURKA knockdown (opposed to inhibition) may overcome upregulation and may result in a more pronounced effect by additionally targeting AURKA's kinase scaffolding functions, including stabilization of MYCN.

Here, we make use of the Proteolysis Targeting Chimeras (PROTACs) technology to develop chemical tools to degrade AURKA. PROTACs are heterobifunctional small-molecule constructs that induce proximity between a protein of interest and an E3-ligase to drive ubiquitination and subsequent degradation by the proteasome system. Several PROTACs against AURKA were successfully designed and synthesized by connecting AURKA ligand MK-5108 with the E3-ligase recruiter thalidomide, via PEG-based linkers of varying lengths.

NGP cells were treated with 10, 100 and 1000 nM for 24h and AURKA levels were monitored via immunoblotting (Simple Wes). PROTAC SK2188 (4 PEG units) induces the most potent AURKA degradation at low nM concentrations (DC50: 2.3 nM). Moreover, AURKA reduction was associated with reduced MYCN levels upon treatment with SK2188 in a dose-dependent matter. Furthermore, relative to MK-5108, SK2188 efficiently induces replicative stress levels and DNA damage, and causes apoptosis at low nM concentrations. Next, compared to inhibitor MK-5108, antiproliferative effects of efficient AURKA PROTACs were significantly enhanced in NGP and IMR-32 cells (IC50: 32 and 22 nM respectively) and in patient-derived organoids, indicating clinical potential of AURKA-degraders.

[1] Muhammad Rishfi#, Simon Krols#, Fien Martens, Ellen Sanders, Aline Eggermont, Fanny De Vloed, Joshua Robert Goulding, Martijn Risseeuw, Jan Molenaar, Frank Speleman, Bram De Wilde, Serge Van Calenbergh*, Kaat Durinck*. Targeted AURKA degradation: towards new therapeutic agents for neuroblastoma. ChemRxiv, Preprint, Aug 19, 2022, DOI 10.26434/chemrxiv-2022-c7lzr

CB-A10

Noncovalent complexes formed between hybrid polyoxometalates and proteins

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Keywords: Polyoxometalates; proteins; electrostatic interactions

Polyoxometalates (POMs) are described as a class of negatively charged metal-oxygen clusters, generally formed by early transition metals in their highest oxidation state. Their versatile nature with respect to size, shape, polarity, acidity, redox potential and surface charge distribution, makes them very attractive for applications in various fields such as catalysis, medicine, materials science and hybrid materials. [1-3] Their versatile and tunable properties therefore make POMs ideal components for interactions with proteins. Due to their negative charge, three-dimensional shape and high polarity, they have been shown to exhibit specific interactions with positively charged protein surfaces [4]. This ability of POMs to specifically interact with proteins has been suggested to be the primary reason behind their well-documented biological properties that include antibacterial, antiviral, antiprotozoal, antidiabetic and anticancer activity [5–8].

Functionalization of POMs involves the covalent attachment of (bio)organic molecules to the inorganic core to form organic-inorganic hybrid POMs (HPOMs). In recent years the chemistry of hybrid POMs has developed very quickly [9–12], resulting in novel synthetic methodologies for the functionalization of POMs and producing many new types of POM based materials. HPOMs benefit from the synergistic properties of both the organic and inorganic components and as such may be tailored to achieve enhanced bioactivity, including enhanced interactions with proteins [13].

HPOMs offer several potential biological applications, including as protein crystallization agents as well as anti-tumor agents [14-16]. However, studies involving the interactions of POMs with proteins primarily involve either bare POMs or metal-substituted POMs [17-18]. This research therefore aims at unveiling the interactions between HPOMs and proteins. Such work has involved the synthesis of a library of HPOMs, which were characterized through a number of techniques including 1H NMR and 13C NMR, FTIR, ESI-MS, CHN elemental analysis and single crystal X-ray diffraction. Interaction studies of these HPOMs with proteins were then investigated via circular dichroism spectroscopy, tryptophan fluorescence and X-ray structure analysis of protein-HPOM complexes.

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CB-B01

Exploring contrast-enhancing staining agents for studying adipose tissue by means of contrast-enhanced computed tomography

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Keywords: Contrast-enhancing staining agents; contrast-enhanced computed tomography; virtual 3D histology; Bone marrow adipose tissue

While quantitative 2D histomorphometrical techniques and magnetic resonance imaging (MRI) allow obtaining crucial information about bone marrow adipose tissue (BMAT), they have limitations in terms of non-invasiveness and spatial resolution respectively. To overcome these shortcomings, we have used contrast-enhanced X-ray microfocus computed tomography (CECT) imaging, which applies contrast-enhancing staining agents (CESAs) to increase the X-ray attenuation of soft tissues (e.g. muscle tissue, adipose tissue, etc.). CECT has a better spatial resolution (sub-micrometer scale) compared to MRI and delivers a 3D dataset of the tissue of interest in a non-invasive manner. The current standard CESA for visualization of adipocytes (Ads) using CECT is osmium tetroxide ($OsO4$).[1-2] However, since $OsO4$ is highly toxic and rather volatile, a non-toxic alternative is desired. Moreover, decalcification of the tissue is necessary to obtain reliable results. To overcome the limitations of $OsO4$, the ContrasTTeam examined the 1:2 hafnium-substituted Wells-Dawson POM (Hf-WD 1:2 POM) as a novel non-invasive CESA for 3D BMAT visualization.[3] This CESA allows simultaneous visualization of Ads, vasculature and bone, but fails to reveal chemical properties of the Ads.

In this project we evaluated two additional CESAs (Hexabrix® and isotonic Lugol's iodine solution (IL)) apart from Hf-WD 1:2 POM, both individually and combined, for the quantitative structural analysis of BMAds in bovine muscle tissue (BMT) and murine caudal vertebrae (MCV). Results show that the negatively charged, hydrophilic CESAs are excluded by the apolar Ads, whereas certain iodine species in the IL solution can interact with these Ads. Interestingly, the grey values, depending on the concentration of iodine, are different for the Ads in BMT compared to MCV (Fig. 1). To investigate the origin of this difference, chemical analyses were performed on simple model systems and whole tissues. First, the iodination of L-tyrosine, 5-hexenoic acid and methyl-5-hexenoate in PBS was evaluated using nuclear magnetic resonance (NMR) spectroscopy. Second, the distribution behaviour of the iodine-containing components between PBS/1-octanol was determined. Third, high-resolution magic angle spinning (HR-MAS) NMR was used to obtain insight inthe degree of unsaturation in the fatty acid derivatives within both tissues. Current results indicate that there is a difference in degree of unsaturation between both tissues, however this cannot be the only explanatory variable for the observed difference in measured grey values. Therefore, lipidomics analysis of the tissues will be performed using LC-MS combined with NMR investigation on cell pellets of 5-hexenoic acid spiked cells (in vitro).

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CB-B02
The natural product curcumin as a source of inspiration for the development of novel benzothiazepane-based cancer cell cytotoxic agents

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Keywords: Curcumin; Benzothiazepanes; Cancer cell cytotoxicity; Pan-assay interference compounds (PAINS); Structure-activity relationship (SAR)

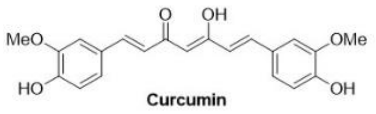
Cancer remains, to this day, one of the leading causes of death worldwide. According to the World Health Organisation, nearly 10 million deaths were attributed to some type of cancer in 2020. Therefore, new therapeutic treatments in oncology are still highly desirable.

Curcumin is a natural product, extracted from the rhizomes of the Curcuma longa plant. It has been used as a food additive predominantly in the South Asian cuisine for centuries, and it exerts a broad range of biological activities (antioxidant, anti-inflammatory, antimicrobial, anticancer…). With respect to its contribution to the field of cancer research, curcumin has shown to inhibit cancer cell proliferation, proving itself a potential drug candidate for further development.

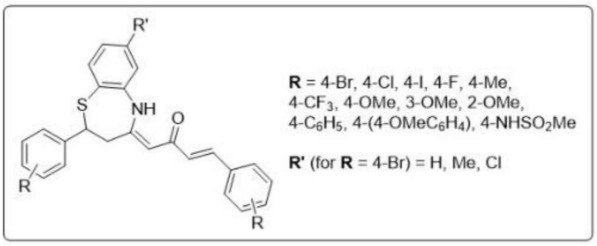
However, its low bioavailability, low stability and aspecific activity cannot be disregarded. Especially the aspecific activity is a matter of concern, as it plays a role in the pan-assay interference ("PAINS") properties exhibited by curcumin. Covalent and aspecific binding to target proteins, redox cycling resulting in peroxide formation, metal chelation and fluorescence interference are all examples that can lead to a false positive readout in assays.

Profound structural modifications of the curcumin scaffold are thus necessary to progress towards a more suitable drug candidate. Previous research in our group has led to the discovery of two unprecedented thiazepane-based derivatives with promising anticancer activity, considerably moving away from the traditional curcumin structure. The introduction of three-dimensionality to the molecule improved properties related to drug-likeness, such as solubility and bioavailability. In addition, PAINS-activity that can be attributed to the structural properties of the molecule could, in this way, be circumvented as well.

In that regard, we recently developed a small library of functionalized benzothiazepane systems to explore their biological activity in the context of cancer cell cytotoxicity. In this presentation, we will discuss the chemistry developed to allow the synthesis of these new molecules, their biological properties in terms of cytotoxicity against a panel of cancer cells, and some physicochemical properties, followed by concluding SAR insights and prospects for future research.



Curcumin



R = 4-Br, 4-Cl, 4-I, 4-F, 4-Me, 4-CF_3, 4-OMe, 3-OMe, 2-OMe, 4-C_6H_5, 4-(4-OMeC_6H_4), 4-$NHSO_2$Me

R' (for **R** = 4-Br) = H, Me, Cl

CB-B03

Chlorella sp. Culture in Coagulation and Dissolved Air Flotation Separation Process Using a Poly-ε-Lysine Coagulant

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Keywords: microalgae; poly-ε-lysine; dissolved air flotation

Harnessing the cultivation and utilization of different microalgae is an ongoing global project since microalgae grow via photosynthesis. They can build organic molecules from inorganic compounds and solar energy, which, compared to plants, results in nutritious biomass rich in protein with a low water footprint. Microalgae harvesting technologies have seen significant technological advancement in the latest years. This progress has improved the feasibility of the microalgal biorefinery since they lead to a great reduction in harvesting costs. Coagulation-based harvesting research is directed to biobased coagulants that are sustainable, harmless, efficient, and inexpensive. Polysaccharide bio-polymers herd the greatest part of research publications, while limited literature is available for protein-based coagulants [1]. It is hypothesized that protein and polypeptide coagulants could achieve high separation efficiencies due to their foaming properties.

A native Cuban Chlorella sp. strain (Universidad de Oriente, Cuba) was cultivated in BG-11 medium in 30L tubular photobioreactors. The growth was monitored on a dry weight basis, with an optical density of 750 nm [2]. Coagulation and dissolved air flotation (C-DAF) jar tests were conducted on day 6 of growth in late-exponential phase biomass resuspended in fresh medium to 0.15 g/L dry weight at pH 8. The jar testing consisted of a homogenization (10 min, 200 rpm) with the addition of poly-ε-lysine (PL) (molecular weight: 3.5–4.5 kDa, Carbosynth, Ltd., Compton, UK) and floc growth phase (20 min, 20 rpm) followed by DAF (450 kPa, 31% recycle ratio) (Platypus DAF jar tester, Aquagenics Pty Ltd, Australia) in 1 L. The separation efficiency (η%) is the difference in absorbance of the subnatant at 750 nm. Zeta-potential and pH were measured in the Zetasizer Nano (Malvern Panalytical, UK) and the Knick PH-meter 764 Multi-Calimatic, respectively [3]. Dissolved organic carbon (DOC) and total nitrogen (TN) were measured on the filtrate (0.45 μm PES membrane filter, VWR, Belgium) with the TOC-L analyser (Shimadzu, Germany). All solutions were freshly prepared for each experiment.

At 80 mg PL per g of algal biomass, there is a sudden increase in separation efficiency (89.5%), with the zeta potential increasing from -42.3 to -18.3 mV with weak foam formation. When increasing the dosage to 300 mg PL per g of algal biomass, the separation efficiency did not rise; the zeta potential increased slightly, reaching values closed to zero but did not become positive. The foam layer remained extremely thin. The pH dropped with an increasing dose of PL but did not go lower than 7. Similar observations were made by Noh et al. for a small-scale coagulation and sedimentation concept [4]. The PL is positively charged at pH 8 and of low molecular weight; thus, it successfully produces flocs of small size, around 80 μm. The weak foam formation could be explained due to the 100% ratio of hydrophilic residues to the total number of residues which does not support the interaction with the bubble-air interface even though it is known to be slightly negative [5]. Concluding, PL is prominent coagulant (electrostatic interactions with the cells) but not as efficient for flotation processes (weak hydrophobic interactions). Follow-up C-DAF tests with medium rich in organic matter could result in superior separation efficiencies since there might be a synergistic effect between the polypeptide and the extracellular organic matter.

Acknowledgments to FWO, which financially supported this study with an FWO junior fundamental research project (2020-2021, G050220N, 573k€) entitled “The presence of extracellular algal organic matter (AOM) in coagulation, flocculation and flotation processes for harvesting microalgae biomass: problem or opportunity?”

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CB-B04

Controlling the reactivity of metal substituted polyoxometalates as artificial proteases through the interplay between surfactant and protein interactions

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Keywords: polyoxometalates; hydrolysis; surfactants; protein; myoglobin

Selective hydrolytic cleavage of proteins is an important procedure in numerous biochemical applications.[1] Inspired by reports on the non-covalent, mainly electrostatic interaction between negatively charged polyoxometalates (POMs) and positive surface domains of proteins, our group introduced a conceptually new approach to the development of artificial proteases by using polyoxometalates (POMs) as ligands for Lewis acid active metal ions.2 Consequently, the POM does not only act as a ligand for the active metal ion, but due to its three-dimensional shape and negative charge it also induces the selectivity that is necessary for a controlled fragmentation of the polyamide backbone.[2] Furthermore, as it has been well known that surfactants can alter protein structure by interacting with specific regions of proteins. [3,4] Hence, in this study, the hydrolysis of horse heart myoglobin (Mb) was investigated in the presence of a Zr(IV)-substituted Keggin polyoxometalate – (Et2NH2)8[{α-PW11O39Zr-(μ-OH)(H2O)}2]·7H2O (Zr-K 2:2) – and three different surfactants which differ in structure and polarity: the ionic surfactant sodium dodecyl sulfate (SDS), as well as the zwitterionic surfactants N-dodecyl-N,N-dimethyl-3-ammonio-1-propanesulfonate (Zw3-12) and 3-[(3-cholamidopropyl)dimethylammonio]-1-propanesulfonate (CHAPS). Hydrolytic reactions were monitored by sodium dodecyl sulfate polyacrylamide gel electrophoresis (SDS-PAGE). The interactions of Mb with investigated surfactants and POM were explored by different techniques: Trp-fluorescence, circular dichroism, and UV-Vis spectroscopy as well as cyclic voltammetry (CV), while the characterization of micellar superstructure formation between protein/surfactant system and catalyst were explored using dynamic light scattering and electrical conductivity. The speciation of the catalyst in surfactant solutions was also followed by 31P Nuclear Magnetic Resonance Spectroscopy providing insight into its stability under reaction conditions.

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CB-B05
Synthesis, structural characterization and in silico study of novel 4-azasteroid-17-hydrazone derivatives

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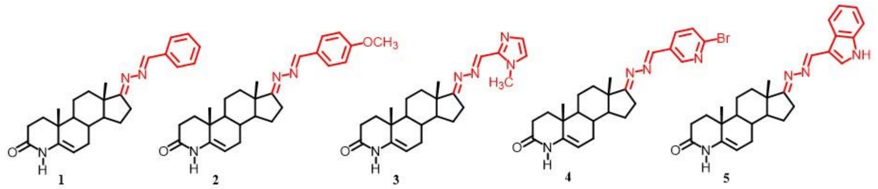
Keywords: 4-azasteroid; 17-hydrazone derivative; SwissADME; ProTox-II

Oncological diseases are one of the priority problems of modern society. Prostate and breast cancers are among the most frequently diagnosed cancers in men and women. The design of new semi-synthetic anticancer drugs without hormonal effect and with elucidated mechanism of action based on biologically active substances of natural origin is one of the most attractive tasks of modern medicinal chemistry [1]. Steroid hormones have a crucial role in the proliferation of both healthy and cancerous cells, so their structural modification might result in new effective antiproliferative compounds. Among the large and heterogeneous group of azasteroids, 4-azasteroids have attracted much interest. Many of them exhibit strong inhibition of human steroid 5α-reductase, such as finasteride and turosteride, two commercial drugs belonging to this class. Additionally, compounds with D-ring attached heterocyclic groups have been shown to possess a broad spectrum of biological activity towards tumor cells [2].

In this work, we combined the structural characteristics of 4-azasteroids and aromatic rings attached to the steroid nucleus via the azine function, in order to improve biological activity. All newly prepared compounds were characterized by 1H and 13C NMR spectroscopy, while compounds 1 and 2 were also analyzed by single-crystal X-ray diffraction.In silico ADME properties were predicted for all synthesized compounds by using the SwissADME tool, while in silico toxicology tests were performed with the ProTox-II web tool. Further in vitro investigation of biological activity is planned.



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CB-B06

Introducing a Second Metal to Zr-MOF-808 to Increase Activity as an Artificial Peptidase

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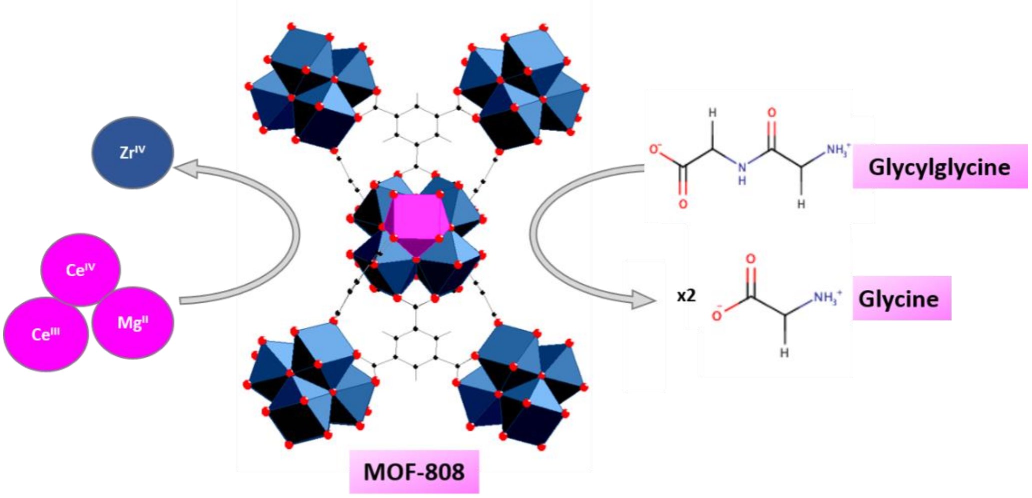
Keywords: MOF; Peptide; Bimetallic; Hydrolysis; Synthesis; Heterogeneous; Catalysis

Metal Organic Frameworks (MOFs), formed of organic linkers between metal-oxo clusters are highly crystalline materials with exceptionally high surface area, stability and a highly porous structure. Usually containing Lewis acidic metal ions within clusters, they are proving themselves as highly versatile and reusable catalysts for a huge range of reactions in different conditions. The ability of Zr-MOFs to catalyze hydrolysis of the highly stable peptide bond is well documented, along with the effect of linker variations,[1] connectivity, linker functionalization,[2] and synthesis conditions[3,4] being explored to boost activity. The 6 connected MOF-808 is exceptionally active towards this hydrolysis reaction, with a half-life of just 0.72 h.[5] Many other metal salts have been shown to be active towards peptide bond hydrolysis, with cerium salts being particularly active, as such, adding small amounts of Ce into UiO-66 boosts the reactivity of the MOF.[6] Building on our work with Zr-MOF-808, Ce-MOF-808 was expected to be even more exceptional that Zr-MOF-808, however suffers from a lack of stability in water. By incorporating Ce into Zr MOF-808, forming a bimetallic Zr/Ce-MOF-808, we hoped to capture the increased activity of cerium with the stability of zirconium in MOF-808. However, the activity of these bimetallic MOFs, synthesized with formic acid as the modulator were mediocre. EXAFS, PXRD and CV determined the oxidation state of Ce was affected by the presence of formic acid in the synthesis. By developing a novel synthesis route, employing green solvents at lower temperatures, the Ce(IV) state in bimetallic MOFs were preserved, boosting the reactivity of the material towards peptide bond hydrolysis. The presence of Ce(IV) in the MOF also reduces the interaction of peptide and MOF, reducing the amount of material lost through adsorption. This is corroborated with DFT calculations showing the interaction of peptide and Ce is less favorable than with Zr. This study has recently been expanded to investigate the post synthetic exchange of Mg(II) with Zr(IV) in MOF-808.[7] Curiously, this also results in increased activity towards peptide bond hydrolysis by lowering the activation energy of peptide bond hydrolysis, despite being less Lewis acidic.



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CB-B07
Hydrolytic Activity of Zr(IV) Metal Organic Frameworks towards Proteins in Buffer Solutions

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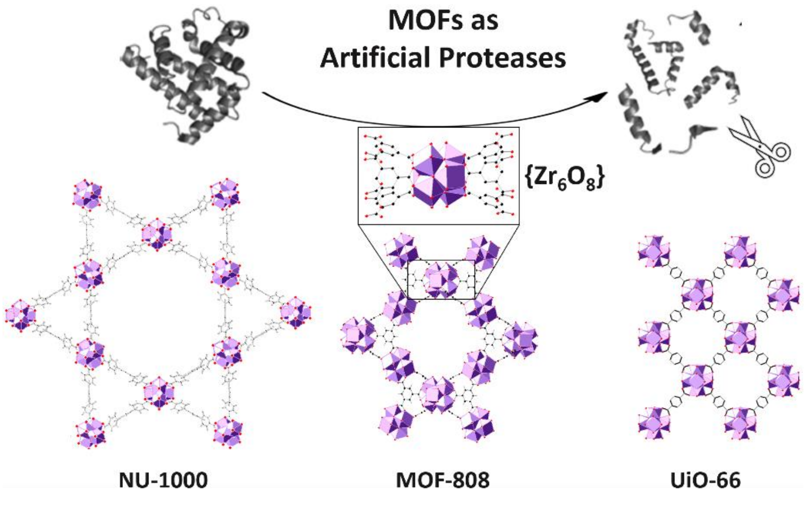
Keywords: MOF; Protein; Hydrolysis; Catalysis

Metal organic frameworks (MOFs) are hybrid inorganic-organic microporous, crystalline materials. MOFs are formed by metal nodes coordinated to organic ligands, therefore the combination of numerous different organic linkers with metal ions result in a large variety of possible MOF structures, affecting their pore size, hydrophobicity, reactivity, etc. Recently, we pioneered the use of Zr(IV)-based MOFs as very effective heterogeneous catalysts for hydrolysis of the peptide bond across a wide range of peptides at physiological pH and temperature. [1-4] Herein, we report on our first steps to establish a general protocol for the controlled, and selective hydrolysis of proteins by Zr(IV)-MOFs which can be combined with currently used techniques/protocols for protein analysis in proteomics and analytical biochemistry. To this end, the hydrolysis of various proteins by Zr(IV)-MOFs in different buffer solutions was followed by SDS-PAGE, while the adsorption of proteins onto the MOF could be probed with UV-VIS spectroscopy. The stability of MOFs in various buffer solutions before and after hydrolysis reactions was investigated with powder X-ray diffraction (PXRD), inductively coupled plasma optical emission spectrometry (ICP-OES) and scanning electron microscope (SEM). This research will enhance the potential of using Zr(IV)-MOF based nanozymes in the fields of proteomics and biotechnology.



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CB-B08

Deciphering the conformational landscape of ROS1 kinase using computational tools

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Keywords: Protein Kinase; ROS1; NSCLC

The aberrant function of protein kinases is often linked to human diseases, making them important targets of therapeutic relevance. In lung cancer, this is illustrated by several tyrosine kinases being targeted by small molecules for patient treatment. One of these tyrosine kinases, c - ros oncogene 1 (ROS1), is found to be rearranged in 1 ~ 2 % of patients. Rearrangements have been reported with multiple gene partners, resulting in constitutive activation of the ROS1 kinase domain. Hence, tyrosine kinase inhibitors (TKIs) are used as a treatment strategy against ROS1+ NSCLCs.

At the sequence level, ROS1 shares close similarity with anaplastic lymphoma kinase (ALK) and insulin receptor tyrosine kinase families. The native function of ROS1 has not been unveiled yet, and the natural ligand for ROS1 is not known to date. Due to limited ROS1 specific structural and experimental data, the study of wild-type (WT) ROS1 and ROS1 mutants is challenging. To address such challenges, we are using computational modeling and simulation methods to gain insights into structure and dynamics. We are employing existing ROS1 specific information where available, and of homologous kinases e.g., ALK.

Extensive reports are available for multiple kinases about the emergence of point mutations leading to reduction of TKI efficacy in patients, a principle that also applies to ROS1+ NSCLC. The low number of approved drugs to overcome these mutations, makes the problem crucial to address.

This study presents our work on molecular modeling to sample conformational changes on the kinase domain of ROS1 in the absence and presence of the selected mutations. For active WT conformation we directly use structural information from the Protein Data Bank (PDB). We selected PDB entry 3ZBF, which also serves a template for ROS1 mutants. Due to lack of inactive ROS1 structures, we applied homology modeling techniques, using the inactive ALK structure PDB entry 3L9P as a template for our models. Our study not only proposes parameters for analyzing WT ROS1, but also for studying clinically reported mutations. Also, we highlight signatures that can distinguish active and inactive states of ROS1 kinase.

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CB-B09

Development of an analytical methodology for ultra-trace chromium speciation in biological fluids

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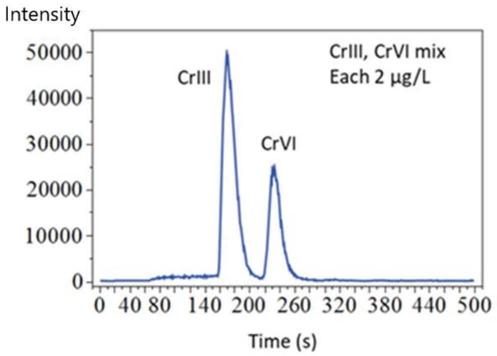
Keywords: hexavalent chromium; speciation; water

Chromium (Cr) is a transition element that exists in oxidation states ranging from - 2 to +6. The common stable ones in the environment are trivalent Cr(III) and hexavalent Cr(VI) chromium. Cr(III) is an important micronutrient for the human body, while Cr(VI) is highly toxic and carcinogenic. The environmental concentrations of both oxidation states are low. Due to the differences in toxicity between Cr(VI) and Cr(III) compounds, speciation of Cr is very important. Therefore, an improved sensitive and robust method for the simultaneous determination of Cr(III) and Cr(VI) in water samples (saliva, plasma, gastric juice, sweat and urine) has been developed. The method uses a hyphenated micro liquid chromatography (µLC) system coupled to inductively coupled plasma mass spectrometry (ICP-MS). The optimised method incorporates a pH adjusted EDTA complexation step to stabilise Cr(VI) and Cr(III). The µLC system uses an anion exchange micro-sized column to separate the Cr species. Cr(III) and Cr(VI) were separated with different retention times at 170 and 230 sec, respectively. The method was optimized and validated by spiking Cr(III) and Cr(VI) in various water samples. Furthermore, the method was validated using a drinking water proficiency testing material sample. The developed method can be used for rapid routine determination of chromium species with high precision and reliability.



CB-B10
High temperature DOSY-NMR measurements allow for diffusion-based virtual separation in mixtures of less mobile biopolymers

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Keywords: Biopolymers; DOSY-NMR; Virtual separation; WEAX; complex mixture analysis

Organic molecules and (bio-)polymers produced by biological and catalytic processes often occur as complex mixtures of structurally similar organic components. Identification and quantification of the individual components in complex mixtures is essential to chemical research and quality control in an industrial, biomedical or food safety setting. NMR spectroscopy achieves component identification by measuring the precession frequency of every NMR-active nucleus when the sample is placed in a magnetic field. This precession frequency deviates from an arbitrarily chosen reference due to a chemical shift that represents the influence of the neighbouring nuclei. The information transferred in this way allows to piece together a blueprint of the observed component.Mixtures of biopolymer components complicate this method, as overlap of crowded, near identical NMR spectra makes analysis difficult. Therefore, a physical separation can be beneficial to simplify the spectra. However, physical separation techniques may alter the chemical structure of the compounds, which influences the subsequent measurements and results.

Diffusion Ordered SpectroscopY (DOSY) is an NMR-based virtual separation technique, in which not the different compounds, but their corresponding spectra are distinguished and separated from each other. In particular, DOSY-NMR monitors the apparent self-diffusivity of each compound in solution. As such, differences in self-diffusion act as a separation tool to discriminate compounds virtually while retaining the mixture in its initial state.[1]The DOSY measurement, however, still contains a set of weaknesses. Firstly, the concentration of the observed compounds should be sufficiently low to simulate an infinite dilution and to avoid influencing the measured diffusivity. This is directly opposed by the need for high concentrations to counter for the inherent insensitivity of NMR signal generation. Additionally, when dealing with large, complex molecules, common in complex mixtures of biomolecules, a sufficiently high temperature is required to allow diffusion to occur in measurable quantity. Yet, DOSY-NMR is highly susceptible to temperature fluctuations, again leading to a compromise. Finally, small deviations in signal intensity of subsequent scans, due to small differences in alignment or changing homogeneity of the applied magnetic field can compromise the validity of the DOSY measurement. As such, repeatability and stability when employing DOSY-NMR are crucial.

In order to develop reproducible DOSY measurements, these weaknesses have been thoroughly analysed. High temperature DOSY measurements were performed on samples of water extractable arabinoxylan (WEAX), a family of dietary fibres present in wheat cell walls. They are suspected to have highly beneficial health effects on medical conditions including type II diabetes and certain cancers.[2,3] The WEAX compounds, with xylose backbone and varying arabinose substitution patterns, contain highly similar components with large molecular weights. Until now, these components could not be recorded with a sufficient resolution in the diffusion dimension.The concentration of WEAX in the samples has been optimised in order to allow sufficient diffusion to take place while simultaneously generating adequate signal intensity. Dissolution has been ensured to be rapid and thorough by making use of a high temperature water bath. The solvent used in the samples, D2O, also contains an amount of HDO, which generates a signal in the DOSY experiment. This signal was used as calibration of the results. An additional internal standard, DSS, has been added as secondary calibration. Several temperature settings were tested to allow selection of an optimum for both mobility of the compounds and stability of operations. Finally, an optimal lineshape and shimming was first sought, to ensure validity and repeatability.

This thorough manner of working allows the use of DOSY-NMR for more complex mixtures of high molecular weight compounds, enabling efficient structure elucidation and description of physical parameters in a single experiment without the need for a physical separation beforehand. As such, the original composition of the mixture can be studied more reliably. Such technological advances in mixture analysis consequently will always remain vital to the development of superior food products, safer pharmaceuticals and improved energy resources.

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CB-B11

Understanding the bone and vascular calcification related to type I collagen and Poly (ADP-ribose) in collagen tissues – a computational investigation

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Keywords: Multi-scale modeling; Spectroscopy; Biomineralization

Biomineralization is the process of a living organisms to produce mineralized tissues through the deposition of mineral particles. It leads to the formation of bones as a natural process, but sometimes becomes pathological when abnormal calcifications occur in the biological tissues, and thus leads to various diseases, particularly in the vasculature. To date, there is no ideal approach to prevent or reverse vascular calcification, since the chemical mechanism of biomineralization remains elusive. Understanding this fundamental and complex process will benefit both the research on bone formation and the treatment of vascular diseases, especially for high-risk patients with diabetes or chronic kidney diseases. Characterization methods such as SEM, TEM, and especially solid-state NMR are traditionally applied in the work to understand the biomineralization process at atomic and molecular level.[1] However, there is so far only a limited understanding of the processes occurring at molecular level, of the distribution of the mineral, of the morphology, and of the particular selectivity for calcium ions as the predominant metal ion in biomineralization. Further insight and studies are therefore necessary. Hydroxyapatite(HAp), collagen and Poly(ADP-ribose) are essential molecules involved in the calcification in the extracellular matrix. Type I collagen is the predominant construction material in bones, tendons and vasculatures, and it's capable of binding calcium ions since it is formed by amino acids. HAp, as a naturally existing mineral in bones, is found between and around collagen fibers. It forms spindle or plate crystals and is oriented in the same direction as the collagen fibers.[2] Calcium salts can aggregate on HAp surfaces, thus leading to the calcification in bones. Thus, it is of high relevance to study the interactions between collagen, calcium and HAp in order to understand the calcification process in bones. Furthermore, experimental evidence from a partner group shows that poly (ADP- ribose) (PAR) binds calcium ions selectively, and it is predicted that PAR would deliver those calcium ions to the collagen fibrils hole zones exclusively by binding to the collagen.[3] Increasing evidence shows that the PAR - collagen binding site is the collagen type I C-terminal, specifically the pi-stacked Tyr into which the adenine ring of PAR inserts, with an adjacent Arg in the collagen C-terminal having a charge interaction with the PAR. Since collagen molecule is constructed by two types of polypeptide chains (alpha 1 and alpha 2), there are two possible sites for the Arg-PAR interaction: one in the collagen alpha 1 chain, and one in the alpha 2 chain. However, the interaction mode and distribution among the sites remains unknown. Research also reveals the selectivity of PAR to calcium ions, since the diameter of the PAR-Ca dense liquid droplets increases monotonically when the calcium ion concentration increases, while this phenomenon is not present for other divalent metal ions. Therefore, detailed studies are needed to explain how calcium ions are selectively and locally concentrated around these substrates and why collagen fibrils are preferential sites for calcification. The primary goal of our study is therefore to develop novel theoretical models for collagen tissues in the process of calcification and to understand the structural and mechanical properties in the presence of Poly(ADP-ribose) and calcium ions in dense liquid phases. As the trial-and-error selection is unfeasible for such complex systems, our approach combines experimental and theoretical methods (DFT, MD). Through the calculation and simulation of spectroscopic (IR, Raman, NMR, diffractograms), structural, bonding, electronic and energetic properties, necessary and complementary information is provided to the experiments.

In my oral contribution I will present:

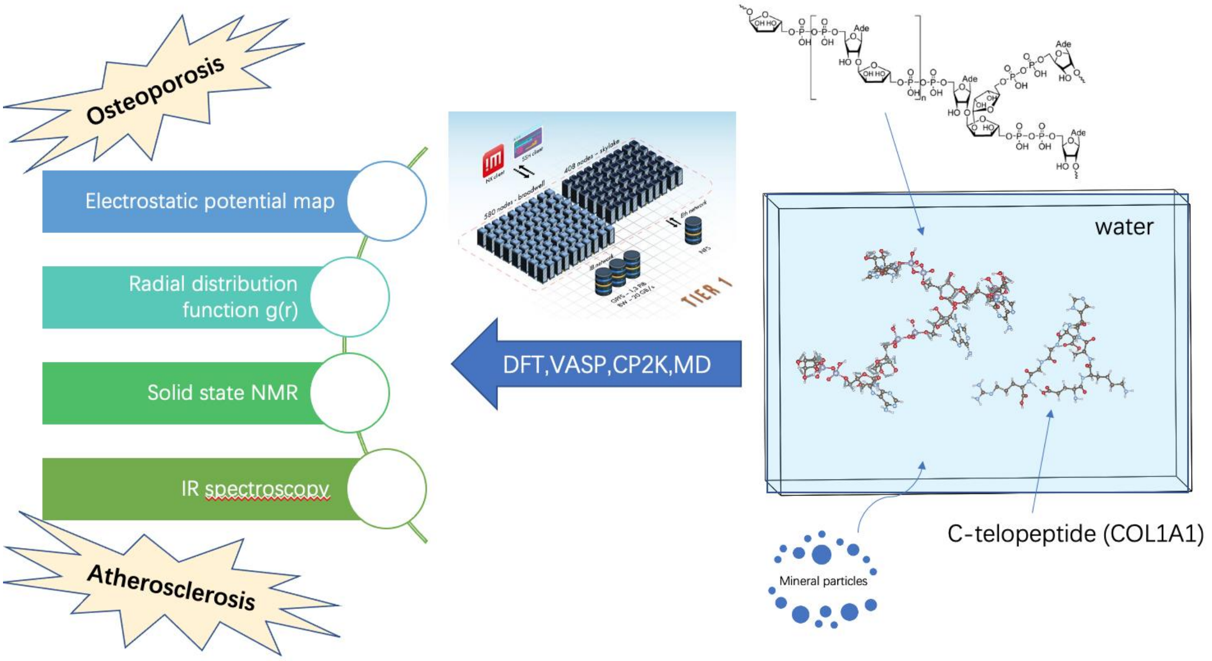
1) Recent outcomes concerning biomineralization and unfathomed questions;

2) The molecules involved in the process and previous research concerning their roles played in biomineralization: collagen, Poly(ADP-ribose), hydroxyapatite;

3) The methodology of the computational study: the design of the atomistic model, the choice of the parameters, simulations and the prediction of spectroscopic properties;

4) Computational results: structural geometries, bonding characterization, energies, spectroscopic properties (IR, solid-state NMR), comparison with experiment to unravel the interaction mechanisms;

5) Insight and solutions to prevent or reverse pathological calcifications.



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Chemical Synthesis & Methodologies

CS&M-A01

Rapid Aza-Analoging of Common Carbocyclic Scaffolds via a Diels-Alder/retro-Diels-Alder Approach

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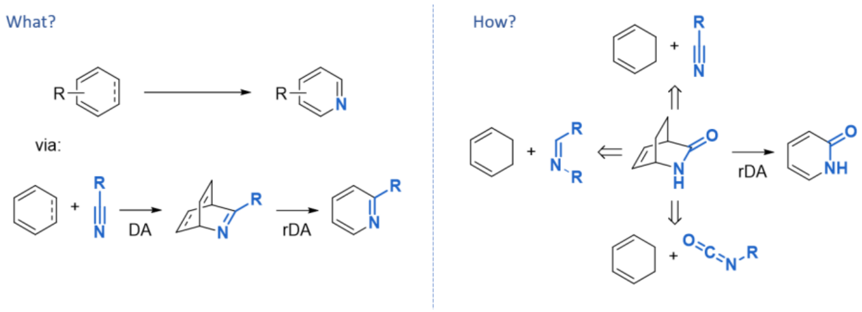
Keywords: late-stage functionalisation; atom swapping; cycloaddition; heterocycles

Nitrogen heterocycles are quite literally fundamental building blocks of life. Within the realm of the different types of molecules of primary metabolism, they can be considered as the champions of molecular recognition, making them part of the backbone of the vast majority of all small molecule drugs.[1] Today this heterocyclic scaffold is usually formed in the first few steps the synthesis of a specific scaffold or pharmacophore. Taking this active scaffold and decorating its periphery with different substituents is a powerful and often also quite feasible strategy in small molecule design and SAR studies.[2] Taking a scaffold, and performing single point substitutions not around the scaffold, but within the scaffold itself would actually be an even more powerful and highly complementary method for biology-driven compound synthesis. However, such an enabling transformation constitutes a highly challenging double substitution reaction, as it requires the controlled breaking of two carbon-carbon bonds, so that this atom can be excised and replaced. Current methods to construct N-heterocycles via atom swapping strategies are very limited, and typically require a lot of consecutive reaction steps. Here a new synthetic method to selectively substitute a carbon for a nitrogen within a given carbocyclic scaffold via a aza-Diels-Alder (DA)/retro-Diels-Alder (rDA) pathway will be explored.



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CS&M-A02

Thermoreversible sol-gel route for the synthesis of ZrO2, CeO2, TiO2, and SnO2 catalysts used in the valeric acid ketonization

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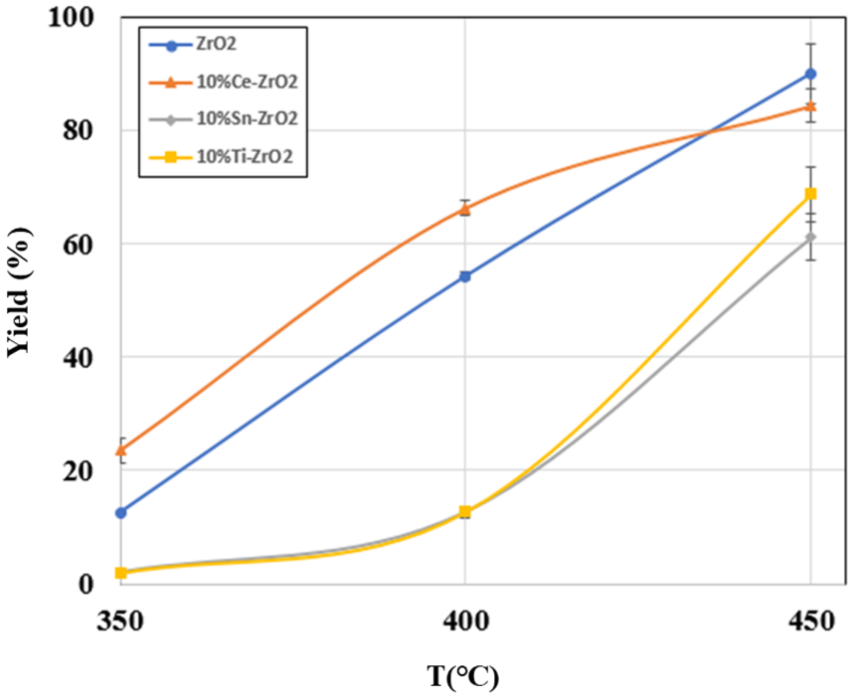
Keywords: Ketonization; Valeric Acid; Metal oxides; Thermoreversible Sol-Gel; Biofuels

Bio-oils could be upgraded via several processes such as aldol condensation [1], esterification [2], hydrodeoxygenation [3], and ketonisation [4] to achieve desirable properties such as suitable viscosity and rheology with higher energy content. The ketonization of carboxylic acids is highly relevant for the upgrading of bio-based streams to jet fuel grades. On the other hand, valeric acid is known as a lignocellulose-derived feedstock and an important platform chemical for production of bio-based fuels and fuel additives for the transportation sector [5, 6]. In the ketonization of valeric acid, oxygen content and acidity are reduced, while forming C-C bonds in order to produce 5-nonanone. Developing high performance heterogeneous catalysts for the ketonization reaction is important. Sufficient catalyst reducibility, high oxygen exchange capacity, and thermal strength are important parameters in the ketonization reaction [7] and in this regard amphoteric metal oxides owning high lattice energy have exhibited significant catalytic activity [8].

In this research the effect of different precursors of ZrO2 (Zr-oxynitrate hydrate, Zr-chloride, and Zr-isopropoxide) for the synthesis of ZrO2 was investigated. CeO2, TiO2, and SnO2 catalysts were also synthesized using a thermoreversible sol-gel route (TSG) as a simple and cost-effective method. Furthermore, the addition of 10% CeO2, TiO2, and SnO2 on the zirconia was studied. TGS is well-suited for using metal salts as cheap precursors. The method is carried out by dissolving the nitrate salts into water. To this solution, the surfactant F-127 was added as a pore-generating agent, at 3°C. At such temperature, F-127 exists in the form of unimer. Then, as the temperature increases, the unimers progressively form micelles with hydrophilic chains pointing toward the medium and hydrophobic central cores. Subsequently, the surfactant can aggregate to form gel. Meanwhile NH_4OH (28-30%) was also added to adjust the pH to 10. The catalyst was aged for 3 days at 60°C, and consequently it was washed and filtered with distilled water for several times. Then it was dried at 110°C overnight and calcined at 500°C for 4h with a heating ramp of 5°C/min. The synthesized catalysts were characterized by XRD, N2 Physisorption, NH3-TPD, and CO2-TPD. Leveraging on the TSG method, we obtained TiO2 catalyst with higher surface area (88 m^2/g), while the one obtained via the simple calcination reached 14 m^2/g only. These textural properties match with XRD data, showing very small crystallite sizes for TSG-made catalyst. The activity was measured (at T=350, 400, and 450°C) in a fixed bed tubular microreactor loaded with 50 mg of catalyst and fed with a stream of valeric acid (~5.5 mol%) in He (total flow of 60 ml/min). Products were analyzed using an online GC-MS. At T= 400°C, 10%Ce-ZrO2 catalyst showed higher yield among the synthesized catalysts. Selectivity to 5-nonanone remained very high (> 95%) and the total quantity of byproducts such as cis-4-nonene, 2-hexanone, 3-heptanone, and 2-octanone is negligible. In this study, space velocity is relatively high (20 h-1.gcatalyst-1) compared to previous reports[9]; this indicates a record specific productivity toward 5-nonanone for our TSG-made Ce-Zr-based catalyst.



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CS&M-A03

Influence of the titanium pretreatment on the yield titania nanotube properties

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Keywords: titania nanotubes; thin-film; anodization

Perovskite solar cells (PSCs) have attracted much research interest due to their advantageous photovoltaic performance. Their properties include for example high carrier mobility, wide optical absorption range, and high power conversion efficiency (PCE). In commonly used planar PSCs, the perovskite layer is sandwiched between the electron and hole transport layers (ETL and HTL). Usually, various inorganic metal oxides, such as TiO2, ZnO, and SnO2, are used as ETLs in PSCs. TiO2, the most studied ETL material, can be fabricated by various methods to produce the final titania layer with different shapes and morphology [1,2]. For advantageous nanostructured titania, a simple and cheap preparation procedure, by electrochemical oxidation of Ti-foil or a Ti-film yields a high-quality dense array of vertically aligned titania nanotubes [3]. Here we identified that the properties of the titanium substrate are important for the final properties of the ETL, and thus for the solar cell itself.

In this work, the synthesis of TiO2 nanotubes by the anodization method is reported, as well as the influence of the (pre)treatment conditions on the resulting samples. We compare the TiO2 nanotubes prepared by electrochemical oxidation of titanium-foils and Ti-film generated by magnetron sputtering on glass substrates. The samples were prepared by pretreating the substrates in different atmospheres and at different temperatures, which provided better insight into the resulting shape and length of the prepared nanotubes, as well as their subsequent features. In the microscopy results we describe the morphology of the titania nanostructures obtained by anodization process. Different methods such as grazing incidence X-ray diffraction (GIXRD) and Kelvin probe force microscopy (KPFM) were employed for systematic characterization. Finally, the electrical properties of the samples were investigated using the solid-state impedance spectroscopy (SS-IS) method.

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CS&M-A04
Nucleation and particle growth of poly(3-alkylthiophenes)

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Keywords: nucleation; organic polymers; SAXS

Nucleation – the initial step of the crystallization – is still rather unexplored, while this step has a major impact on the outcome [1]. One of the possible systems for studying nucleation are organic polymers, namely polythiophenes, where nucleation and particle growth has recently been examined by non-linear optics (NLO) [2].

In this research, dynamic small-angle X-ray scattering (SAXS) experiments are used for nanoscale information about size, structure and morphology of monomers/aggregates in the initial stages of the particle growth. In total, 3 different poly(3-alkylthiophenes) were studied by sealing various concentrations of the polymer in a mixture of a THF solvent and MeOH anti-solvent. The polymer mixtures were dissolved by heating, and the aggregation with subsequent particle formation was observed during the cooling period. In-house trials were succeeded by synchrotron experiments at the ESRF BM26 beamline.

Results are showing differences in particle formation between the types of the polymers, based on the concentration, side-chain, presence of defects in the backbone of the polymer or the ratio of solvent/anti-solvent in the mixture. Aggregation of polymers is also observed prior to the precipitation of particles. In conclusion, these experiments, together with work in the field of NLO, are providing deeper insight in particle formation of organic materials.

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CS&M-A05
Au(I) catalysed Benzylic C-H amination with PTAD

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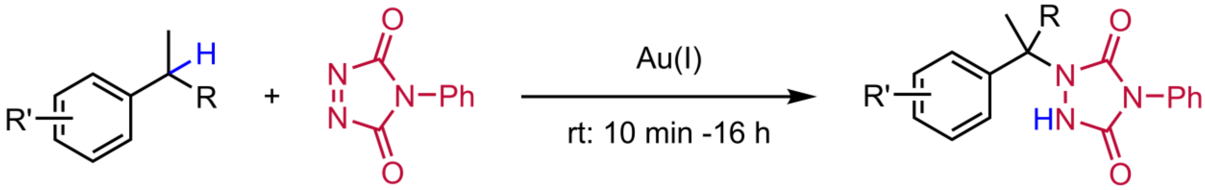
Keywords: CH insertion; TAD; gold; Au; catalysis

Triazolinediones (TAD) are highly reactive dienophiles and also have a limited intrinsic reactivity towards amination of activated CH-bonds.[1]

Here, we report that this CH-amination reactivity can be significantly enhanced by mild gold(I)-catalysis. Simple alkyl-substituted aryls serve as substrates for room temperature benzylic CH-aminations.

In this poster we show the catalyst optimisation and the substrate scope.



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CS&M-A06

Exploration of synthesis and surface chemistry of colloidal alkaline-earth chalcogenides

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Keywords: Semiconductor Nanocrystals; Colloidal Synthesis; Surface Chemistry

AECs are composed of a IIa metal (Mg, Ca, Sr) and S or Se (X), feature large bandgaps positioned in the UV and are commonly used as hosts for emissive ions. AEC nanocrystals could therefore be used as UV emitters, or scatter-free emitters based on lanthanide ions. Moreover, while most AEC crystallize in the rocksalt structure, MgX can also be grown as zinc blende crystals with lattice parameters that come close to those of commonly examined and used IIb-VI chalcogenides or III-V pnictides, such as CdSe and InP. Hence, AECs could extend the range of materials to form core/shell heterostructures out of these compounds. However, such implementations of AECs are hampered by the limited knowledge of the colloidal synthesis and the surface chemistry of these compounds. Here, we report on possible routes to synthesize these materials and the resulting surface termination of AECs by organic ligands, for which we take the formation of CaS as a starting point. We show that ~12 nm large CaS nanocubes can be formed by reacting calciumacetate and diphenylthiourea in a mixture of oleylamine (OLA), trioctylamine and oleic acid (OA). Using Nuclear Magnetic Resonance (NMR) and infrared (IR) spectroscopy, we demonstrate that such as-synthesized CaS nanocubes are terminated by a dense shell of oleate ligands, which are unequally packed at the surface, and small traces of OLA. Although the base doesn't show much interaction with the surface, titrations involving OA and 1-undecenoic acid point out initial slow dynamics between the bound oleate ligands and a created free pool of carboxylic acid which leads to a reorganization of the surface coverage. Apart from providing detailed insight in the surface chemistry of CaS NCs, this work shows that known approaches and concepts to analyze and rationalize the interaction between colloidal nanocrystals and surface-active ligands can be extended to AEC nanocrystals.

CS&M-A07

Study of poloxo- and peroxometalates containing rare earth elements catalysts by physicochemical methods

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Keywords: polyoxometallates; rare earth elements; catalysis; dioxolanes

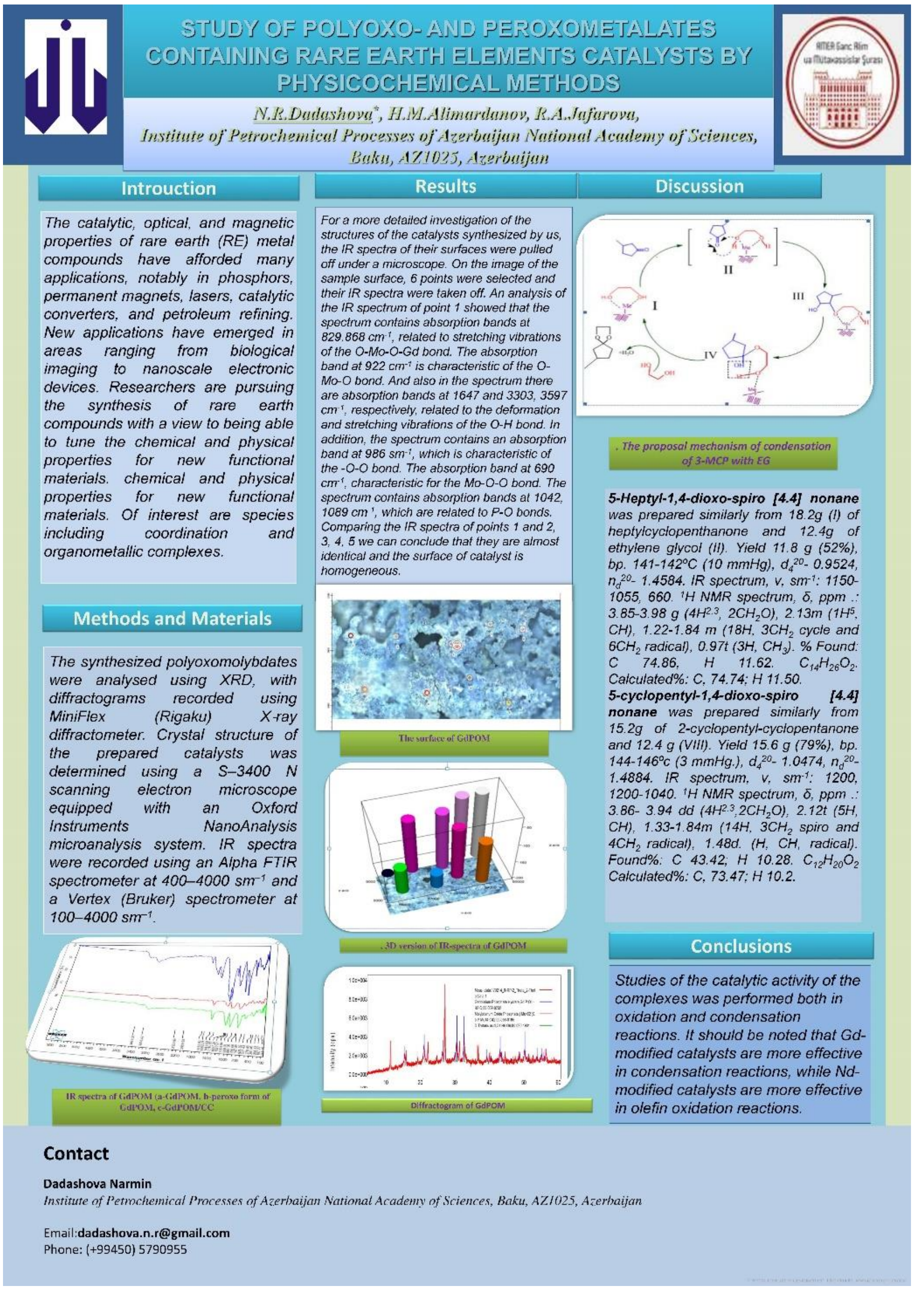
The catalytic, optical, and magnetic properties of rare earth (RE) metal compounds have afforded many applications, notably in phosphors, permanent magnets, lasers, catalytic converters, and petroleum refining. New applications have emerged in areas ranging from biological imaging to nanoscale electronic devices. Researchers are pursuing the synthesis of rare earth compounds with a view to being able to tune the chemical and physical properties for new functional materials. chemical and physical properties for new functional materials. Of interest are species including coordination and organometallic complexes [1,2].

To study the structure of the samples of polyoxo- and peroxometallates of phospohotungsten and molybdenum- XPO4(MeO(O2)2)4), (where X= Gd, Nd, La, Me= Mo,W) FTIR, EPR, and TGA methods of analysis have been used.

For a more detailed investigation of the structures of the catalysts synthesized by us, the IR spectra of their surfaces were pulled off under a microscope. On the image of the sample surface, 6 points were selected and their IR spectra were taken off. An analysis of the IR spectrum of point 1 showed that the spectrum contains absorption bands at 829.868 cm-1, related to stretching vibrations of the O-Mo-O-Gd bond. The absorption band at 922 cm-1 is characteristic of the O-Mo-O bond. And also in the spectrum there are absorption bands at 1647 and 3303, 3597 cm-1, respectively, related to the deformation and stretching vibrations of the O-H bond. In addition, the spectrum contains an absorption band at 986 sm-1, which is characteristic of the -O-O bond. The absorption band at 690 cm-1, characteristic for the Mo-O-O bond. The spectrum contains absorption bands at 1042, 1089 cm-1, which are related to P-O bonds. Comparing the IR spectra of points 1 and 2, 3, 4, 5 we can conclude that they are almost identical and the surface of catalyst is homogeneous.

Thermograms of complexes are characterized by an endothermic effect associated with the lost of water and by an exothermic effect associated with the decomposition of peroxo compounds and release of oxygen (140 °C). This proves the assumption that water enters the inside sphere and dimer (or tetramer) forms of peroxotungstate (peroxomolybdate) complexes containing gadolinium and neodymium are formed. The results of TGA are in good agreement the results of FTIR spectroscopy about the hydrophobic nature of the catalyst.

Studies of the catalytic activity of the complexes was performed both in oxidation and condensation reactions. It should be noted that Gd-modified catalysts are more effective in condensation reactions, while Nd-modified catalysts are more effective in olefin oxidation reactions.



STUDY OF POLYOXO- AND PEROXOMETALATES CONTAINING RARE EARTH ELEMENTS CATALYSTS BY PHYSICOCHEMICAL METHODS

N.R.Dadashova, H.M.Alimardanov, R.A.Jafarova,*
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Introuction

The catalytic, optical, and magnetic properties of rare earth (RE) metal compounds have afforded many applications, notably in phosphors, permanent magnets, lasers, catalytic converters, and petroleum refining. New applications have emerged in areas ranging from biological imaging to nanoscale electronic devices. Researchers are pursuing the synthesis of rare earth compounds with a view to being able to tune the chemical and physical properties for new functional materials. chemical and physical properties for new functional materials. Of interest are species including coordination and organometallic complexes.

Methods and Materials

The synthesized polyoxomolybdates were analysed using XRD, with diffractograms recorded using MiniFlex (Rigaku) X-ray diffractometer. Crystal structure of the prepared catalysts was determined using a S–3400 N scanning electron microscope equipped with an Oxford Instruments NanoAnalysis microanalysis system. IR spectra were recorded using an Alpha FTIR spectrometer at 400–4000 sm^{-1} and a Vertex (Bruker) spectrometer at 100–4000 sm^{-1}.

IR spectra of GdPOM (a-GdPOM, b-peroxo form of GdPOM, c-GdPOM/CC

Results

For a more detailed investigation of the structures of the catalysts synthesized by us, the IR spectra of their surfaces were pulled off under a microscope. On the image of the sample surface, 6 points were selected and their IR spectra were taken off. An analysis of the IR spectrum of point 1 showed that the spectrum contains absorption bands at 829.868 cm^{-1}, related to stretching vibrations of the O-Mo-O-Gd bond. The absorption band at 922 cm^{-1} is characteristic of the O-Mo-O bond. And also in the spectrum there are absorption bands at 1647 and 3303, 3597 cm^{-1}, respectively, related to the deformation and stretching vibrations of the O-H bond. In addition, the spectrum contains an absorption band at 986 sm^{-1}, which is characteristic of the -O-O bond. The absorption band at 690 cm^{-1}, characteristic for the Mo-O-O bond. The spectrum contains absorption bands at 1042, 1089 cm^{-1}, which are related to P-O bonds. Comparing the IR spectra of points 1 and 2, 3, 4, 5 we can conclude that they are almost identical and the surface of catalyst is homogeneous.

The surface of GdPOM

. 3D version of IR-spectra of GdPOM

Diffractogram of GdPOM

Discussion

. The proposal mechanism of condensation of 3-MCP with EG

***5-Heptyl-1,4-dioxo-spiro [4.4] nonane** was prepared similarly from 18.2g (I) of heptylcyclopenthanone and 12.4g of ethylene glycol (II). Yield 11.8 g (52%), bp. 141-142°C (10 mmHg), d_4^{20}- 0.9524, n_d^{20}- 1.4584. IR spectrum, v, sm^{-1}: 1150-1055, 660. ^1H NMR spectrum, δ, ppm .: 3.85-3.98 g ($4H^{2.3}$, $2CH_2O$), 2.13m ($1H^5$, CH), 1.22-1.84 m (18H, $3CH_2$ cycle and $6CH_2$ radical), 0.97t (3H, CH_3). % Found: C 74.86, H 11.62. $C_{14}H_{26}O_2$. Calculated%: C, 74.74; H 11.50.*

***5-cyclopentyl-1,4-dioxo-spiro [4.4] nonane** was prepared similarly from 15.2g of 2-cyclopentyl-cyclopentanone and 12.4 g (VIII). Yield 15.6 g (79%), bp. 144-146°c (3 mmHg.), d_4^{20}- 1.0474, n_d^{20}- 1.4884. IR spectrum, v, sm^{-1}: 1200, 1200-1040. ^1H NMR spectrum, δ, ppm .: 3.86- 3.94 dd ($4H^{2.3}$,$2CH_2O$), 2.12t (5H, CH), 1.33-1.84m (14H, $3CH_2$ spiro and $4CH_2$ radical), 1.48d. (H, CH, radical). Found%: C 43.42; H 10.28. $C_{12}H_{20}O_2$ Calculated%: C, 73.47; H 10.2.*

Conclusions

Studies of the catalytic activity of the complexes was performed both in oxidation and condensation reactions. It should be noted that Gd-modified catalysts are more effective in condensation reactions, while Nd-modified catalysts are more effective in olefin oxidation reactions.

Contact

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CS&M-A08

In-situ XRS and XES following Ni-Fe restructuring during methane dry reforming

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[1] *Ghent University, Belgium*

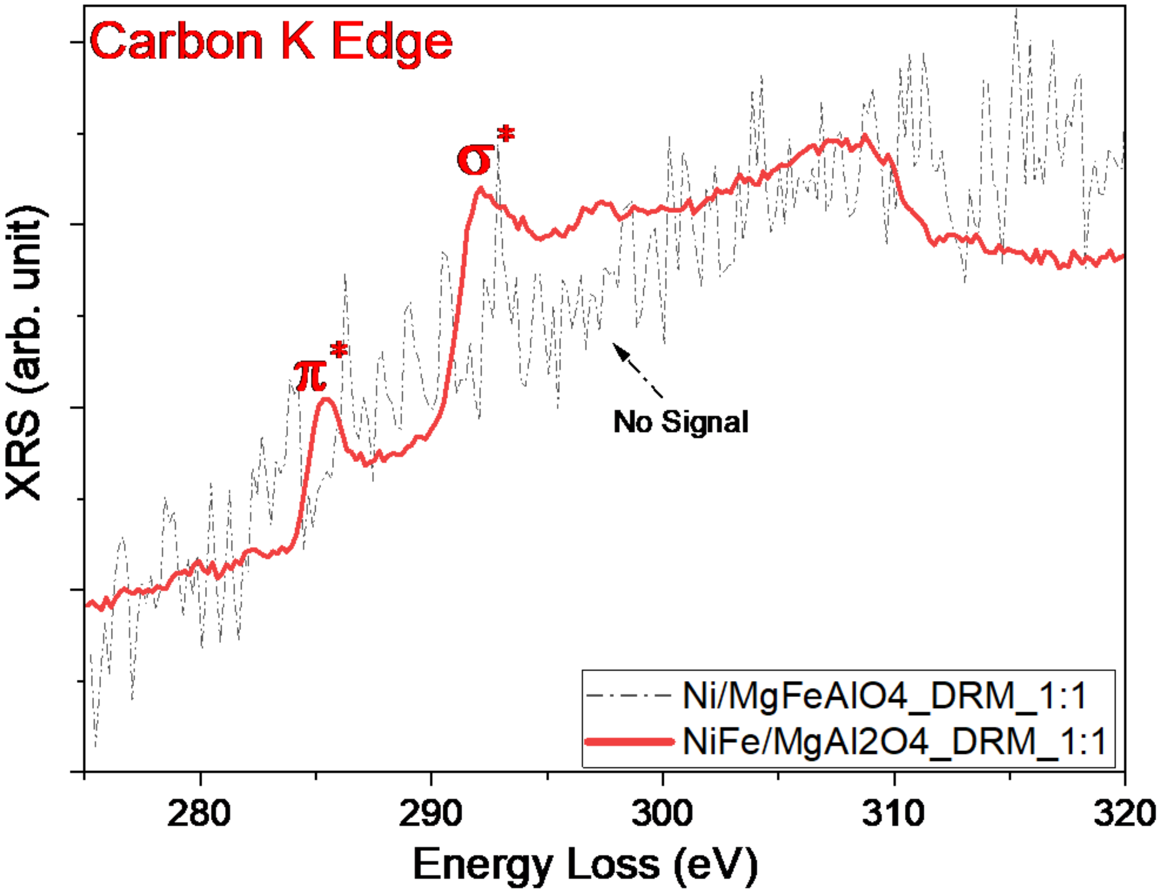
Keywords: Dry reforming of Methane; Ni-Fe alloy formation; Redox behaviour

To reduce the effect of greenhouse gases on our environment, an efficient catalyst (Ni/MgFeAlO4) has been developed, which is able to convert the most concerned greenhouse gases CO2 and CH4 into syngas by methane dry reforming (DRM) with least possibility of coke formation. In recent work, Fe incorporation into a spinel MgAl2O4 support yielded a more carbon-resistant catalyst (NiFe/MgFeAlO4) than NiFe/MgAl2O4, because it provided lattice oxygen to remove deposited carbon through both FeOx, extracted from the active NiFe alloy phase, along with O supplied from the support when reducing Fe3+ to Fe2+.[1] Synchrotron-based ex-situ X-ray Raman Scattering (XRS) confirmed that in reduced MgFeAlO4, up to 50% of Fe is present as Fe2+, providing support redox functionality.[2]

Here, the changes occurring to Ni/MgFeAlO4 during alloy formation and DRM have been investigated by in-situ XRS and X-ray Emission Spectroscopy (XES). XRS probes the soft O K and L2,3 edges of Mg and Al through hard X-rays (~10 keV). XES gives access to valence to core (VtC) transitions for transition metals like Ni and Fe, yielding info about oxidation state, bond lengths and neighbouring elements.

For the Ni/MgFeAlO4 material, a change is observed in the O signal, particularly in the ratio of shoulder/main peak during CH4 reduction and subsequent CO2 oxidation, which indicates the excitation of O1s electrons above Fermi level into the Mg/Al3sp and the Fe4sp band, hybridized with O2p states. For Al L2,3, a similar change in ratio of shoulder/main peak occurs upon reduction, related to the spinel inversion parameter. A regular wet impregnated NiFe/MgAl2O4 showed massive coke formation after DRM with CO2:CH4 = 1:1 ratio. In contrast, Ni/MgFeAlO4 exposed to the same coking conditions, did not suffer from C deposition, yielding no C signal at all (Figure 1).

At the Ni and Fe K edges, XES was recorded in parallel to the multi-element XRS acquisitions. For NiFe/MgAl2O4, comparison with Ni and Fe references showed that Ni went into metallic state (~Ni foil) during reduction, while returning towards Ni2+ after CO2 oxidation (~Ni(NO3)2). The XES Fe Kβ2,5 signal varied more subtly. During DRM with CO2:CH4 = 1:1, the Ni signal took up position in between metal and oxide state. As for Fe, a clearly different signal was obtained during DRM, with lower main intensity in Kβ2,5 and a sloping pre-edge towards Kβ". In contrast, the Ni/MgFeAlO4 material showed variation in the main peak shape and intensity, but no sloping pre-edge. These features, derived from successful in-situ XRS and XES characterization in DRM, allow to reveal the functionality of O2-, Al3+, Ni2+ and Fe3+ in MgFeAlO4 during reaction. The electronic variation and structural modification in Ni/MgFeAlO4 show why Fe incorporation in the support is beneficial to its use as catalyst for DRM.



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CS&M-A09
Development of polymeric hybrid scaffolds for corneal tissue engineering

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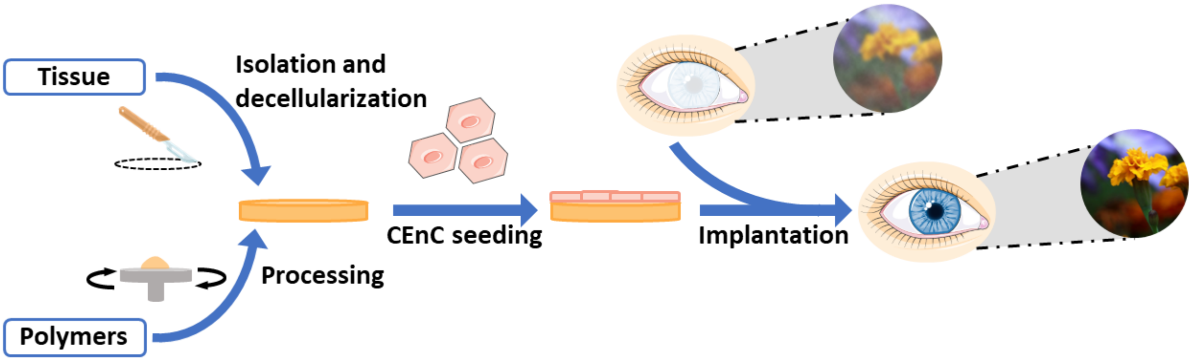
Keywords: Corneal endothelial tissue engineering; gelatin; poly(lactic acid)

The cornea is a transparent, dome shaped membrane that is part of the outer layer of the eye. It is composed of 5 layers; the epithelium, the Bowman's layer, the stroma, the Descemet's membrane and the endothelium. Several diseases or trauma can lead to opacification of the cornea, resulting in an impaired vision or even blindness. Corneal blindness is the fourth leading cause of blindness worldwide, affecting around 23 million people.[1] Currently, the only treatment for corneal endothelial diseases, a collective term referring to all conditions that cause the degeneration of the corneal endothelium and thereby lead to a dysfunctional cornea, involves a transplantation with tissue from cadaveric donor eyes. Because of the limited availability of the latter, researchers are investigating donor independent strategies to replace a diseased corneal endothelium. Alternative treatments in development include scaffold-free methods (such as endothelial cell injection and transplantation of a sheet of corneal endothelial cells (CEnCs)) and scaffold-based approaches. In the latter, a tissue engineered graft is produced consisting of a structural support and a layer of corneal endothelial cells.[2] The properties of the natural Descemet's membrane (e.g. transparency, Young's modulus, thickness, etc.) are used as benchmark for the scaffold since it functions as natural basement membrane of the CEnCs. Eventually, the implant should replace the original endothelium and Descemet's membrane in order to restore the patient's vision.

In this research, it is aimed to develop an artificial Descemet's membrane mimic on which CEnCs can be grown to produce a tissue engineered endothelial graft. To this end, a material needed to be developed that is, among others, mechanically strong enough for the surgical implantation and cell interactive to allow the formation of a monolayer of CEnCs. Therefore, a gelatin derivative was modified with poly(D,L-lactic acid) (PDLLA) grafts to combine the properties of both materials. First, methacrylamide groups were introduced on the gelatin (Gel-MOD) to enable crosslinking of the material. The degree of substitution was ranging from 70 to 90 %. Then, grafting was realized by using the remaining functional groups on gelatin as macroinitiator for the ring opening polymerization of PDLLA. Optimization indicated that a temperature of 65°C, a reaction time of 48-52 hours, 2 equivalents of the organocatalyst 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) and precipitation or dialysis in acetone were the most optimal conditions for this reaction. The obtained Gel-MOD-PDLLA was characterized using 1H-nuclear magnetic resonance, thermogravimetric analysis, differential scanning calorimetry and rheology. It was found that the MM of the PDLLA grafts ranged from 280 to 3200 g/mol. Rheology was performed to determine the crosslinking kinetics. The introduction of the PDLLA grafts prevented gel-MOD crosslinking, most likely due to steric hindrance.

Via spin coating, the produced materials were processed into functional membranes which showed a transparency over 96% for the entire visual spectrum. This transparency is sufficiently high for the application. Further evaluation of both the material (e.g. the influence of the MM of the PDLLA grafts on the mechanical properties) and the membrane (thickness, diffusion, etc.) is necessary to obtain a scaffold with adequate properties that can serve as a basement membrane for CEnCs.



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CS&M-A10
Exploring the Synthetic Utility of Proton-free Sulfur-mediated (3+2) Cycloadditions

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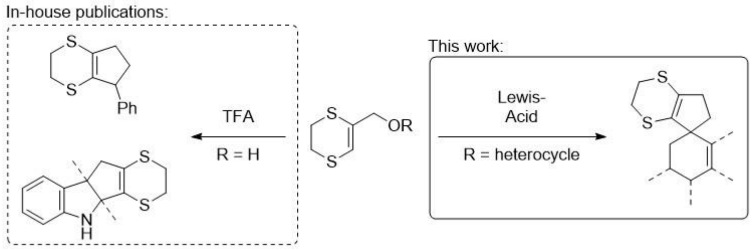
Keywords: Cycloaddition; sulfur; cationic; proton-free

Building on previous research into sulfur-mediated (3+2) cycloadditions, this poster showcases recent improvements for a versatile cyclopentannulation procedure.

Here is described how the reported reaction conditions have previously set hard limits on the substrate scope, what various options were considered and explored in the development of different cation precursors, and some exciting hints at the new possibilities that have presented themselves along this journey.



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CS&M-A11

Synthesis of Imidosulfur(IV) Derivatives of Sulfinate and Sulfite Esters via Formal S-S Bond Insertion of Dichloramines

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[2] *RWTH Aachen University, Germany*

Keywords: imination; imidosulfur; sulfur chemistry

The sulfinimidoyl (S(O)=NR) unit is the aza analogue of the sulfonyl (SO_2) group and is found in medicinally relevant structures such as sulfoximines and sulfonimidamides. These carbon-bound sulfur(VI) structures are often prepared via oxidation of the corresponding iminosulfur(IV) precursors. However, when replacing the carbon substituents with more heteroatoms on the sulfur core, this process becomes unviable due to unavailability of the starting materials. Here, we show that N-protected iminosulfur(IV) derivatives can be prepared easily from lower-valent, commercially available sulfur species. Sulfinimidate esters (with one alkoxy group on sulfur) and imidosulfite esters (with two alkoxy groups) were thus accessible from disulfides or elemental sulfur, respectively. The other starting materials consist of dichloramines, which are responsible for introduction of the N-substituted aza group and the oxidation to S(IV), and alcohols, which take the place of the alkoxy ester. These little-known sulfi(na)te functional groups could then be oxidized to sulfur(VI) sulfonimidoyl structures such as sulfonimidates, or the all-heteroatom-substituted imidosulfate esters. Various other transformations of the sulfur(IV) structures were possible, making them a useful platform to a variety of S(=NR)-containing functional groups.

CS&M-A12

Synthesis and characterization of hybrid materials containing H-ZSM-5 and CeO2 for the one-step dehydration of 1,3-butanediol to butadiene

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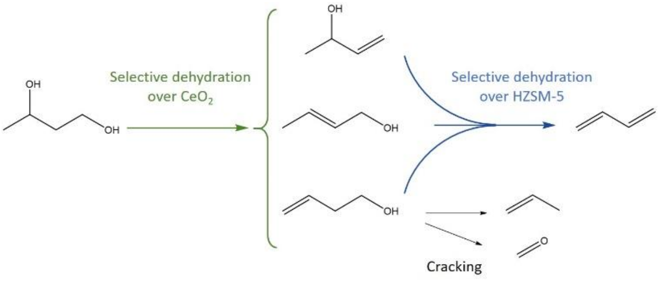
Keywords: hybrid catalyst; nano-HZSM-5; CeO2; 1,3-butanediol dehydration; butadiene

The selective dehydration of 1,3-butanediol (1,3-BDO), which can be obtained from biomass fermentation, is being investigated as a potential sustainable route to produce butadiene (BD), which is currently obtained via naphtha steam cracking. Acid zeolites were reported in literature as promising catalysts (yields up to 57% for H-ZSM-5 with Si/Al ratio 260) [1]. The main byproduct during this reaction is propylene, which is obtained from the cracking side reaction of the intermediate 3-buten-1-ol. To suppress side reactions, weaker acid sites can be introduced by incorporating boron in the zeolite framework. However, obtaining the intermediates selectively over acid zeolites is challenging [2]. Instead, CeO2 can catalyze the reaction of 1,3-BDO towards unsaturated alcohols, which are readily dehydrated to BD over acid zeolites [3]. Vecchini et al. described a process for the conversion of 1,3-BDO to BD using two different reactors for consecutive dehydration steps (in which the first and the second reactor contain ceria and zeolite respectively) with an overall BD yield of 70% [4]. To accomplish the one-step dehydration of 1,3-BDO to BD in a single reactor with high yields, a hybrid catalyst (a catalyst with two different dehydration functions) is needed. An overview of the desired reaction pathway is depicted in Figure 1.

In this present work, a set of nanosized (B-)H-ZSM-5 zeolites with varying Si/Al (15 – 150) and B/Al (0-1) ratios are successfully synthesized to tune the acid strength. In order to increase the yield, hybrid materials containing nanosized H-ZSM-5 zeolites and CeO2 are synthesized. The ceria is expected to provide the selective production of unsaturated alcohols, while the zeolites contain the Brønsted acid sites with medium strength to accomplish the reaction of the C4 unsaturated alcohols to BD with high selectivity.



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CS&M-A13
Chirality generation in triphenylmethane derivatives

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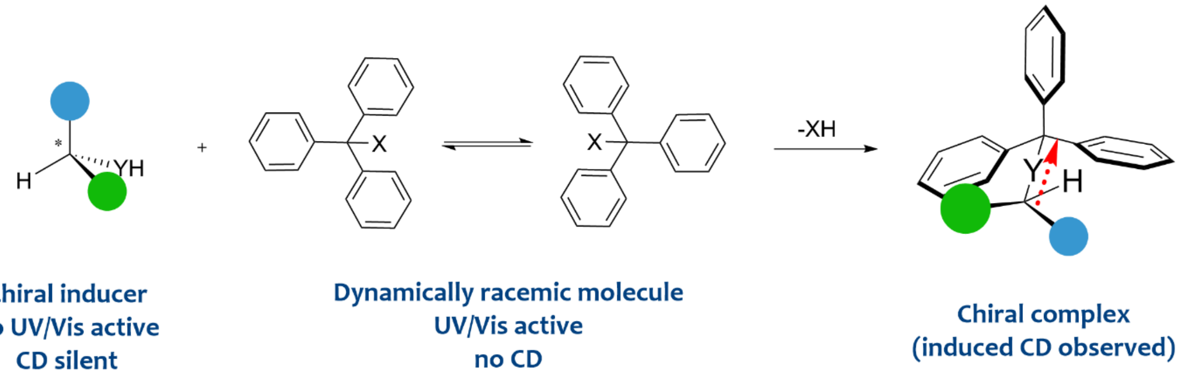
Keywords: chirality; chromophore probe; ECD spectroscopy

The triphenylmethyl group (trityl, Tr), of a unique propeller-shape structure, has found numerous applications in organic chemistry. For example, trityl can be used as a protecting group for primary alcohols, amines or thiols [1].

However, the Tr group can be used, both, as a reagent and a chromophore probe. In one step, a stereogenic center is generated, of stereochemistry, which can be determined using the phenomenon of induction and transfer of chirality from a permanent chiral element to a conformationally labile propeller [2].

This phenomenon can be easily monitored by electronic circular dichroism (ECD) spectroscopy. In order to demonstrate the chirality transfer series of optically active triphenylmethane derivatives were synthesized in which the trityl group is attached directly to the stereogenic center or is located at a distance of one methylene group. Measured ECD spectra show significant Cotton effects in the absorption area of the trityl group, confirmed efficient chirality transfer from inductor to the reporter [3].

The work was supported by grant no. POWR.03.02.00-00-I026/16 co-financed by the European Union through the European Social Fund under the Operational Program Knowledge Education Development.



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CS&M-A14

Determination of reaction enthalpies of synthesizing β-Li3PS4 in Tetrahydrofuran

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Keywords: Synthesis; Sulfide Solid Electrolyte; Batteries; Calorimetry

All-solid-state batteries are considered the next generation in battery technology due to increased energy and power density as well as freedom of design, e.g. constructing batteries in bipolar stacks. Solid-state electrolytes offer advantages over conventional liquid electrolytes, such as greater thermal safety, because of high melting points, and higher mechanical strength, which is believed to suppress growth of lithium dendrites and therefore opens up the possibility of using a lithium metal anode. One promising material group are sulfides, of whom crystalline β-lithium thiophosphate (β-Li3PS4) gathered much attention over the last years due to its good ionic conductivity and the opportunity of using a wet-chemical synthesis route.

The wet-chemical synthesis route offers the advantage of facilitated scaling up the production. For safe scaling-up, it is important to examine the synthesis route thermally to handle exothermic and endothermic processes. While uncontrolled heat or gas development of exothermic reactions can cause damage on the reaction equipment and severe safety issues, an exaggerated heat dissipation can slow down the process. For endothermic reactions, it is necessary to provide the reagents with enough energy to facilitate and accelerate the reaction while considering the thermal stability of the reactants.

In this work, the synthesis of β-Li3PS4 in tetrahydrofuran (THF) is examined thermally. The synthesis consist of three chemical process steps carried out under inert atmosphere. Firstly, lithium sulfide and phosphorus pentasulfide are mixed in THF to form a Li3PS4-THF co-crystal as an intermediate product. Secondly, THF is removed by heat-treatment under formation of amorphous Li3PS4. Lastly, the amorphous powder crystallizes to β-Li3PS4 at elevated temperature. A reaction calorimeter was used to determine the reaction enthalpy of the first step. A mixing vessel with a membrane allows to examine the process under inert atmosphere. Differential scanning calorimetry was used to determine the enthalpies of the two following synthesis steps. These findings contribute to develop a scaled-up synthesis route for β-Li3PS4.

CS&M-A15

Preparation of nature-based sulfoxides: alliin and its derivatives

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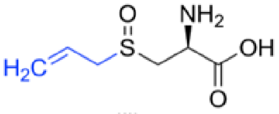
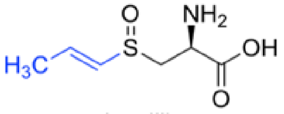
Keywords: alliin; preparation; alkylation; oxidation; antimicrobial

Resistance to antibiotics is becoming currently a more significant issue. A possible approach to deal with this problem proposes Allium plants with a self-protective mechanism against pathogens and microorganisms such as garlic or onion. Sulfur compounds are mainly responsible for this mechanism. One of the advantages of these compounds is their fast degradation rate, which prevents the development of bacterial resistance [1,2]. In this work, we focused on the sulfur compound allicin, which forms by converting sulfoxides by the enzyme alliinase [3]. Therefore, we aimed to prepare and optimize the synthesis of allicin precursors, namely alliin and its derivates, isoalliin, butiin, and benzyliin (fig. 1). These precursors can be prepared in two steps. In the first step, L-cysteine is alkylated to the corresponding S-alkyl-L-cysteine. The second step involves oxidation with hydrogen peroxide to (±)-L-sulfoxide. The tested parameters included the type and amount of catalyst, temperature, and the molar ratio of starting materials for the alkylation step. The chosen catalysts were ammonium hydroxide solution, sodium hydroxide solution, and sodium. Several oxidation agents were tested in the case of oxidation, particularly hydrogen peroxide and tetraisopropyl orthotitanate with tert-butyl hydroperoxide. Furthermore, the effect of the amount of oxidation agent and temperature on the reaction course was studied. All of the above mentioned precursors have been successfully prepared, and will be used for the topical application in follow-up research.

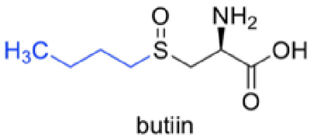
This work was supported from the OP RDE registration no.: CZ.02.2.69/0.0/0.0/19_073/0016928“, funded by the ESF.



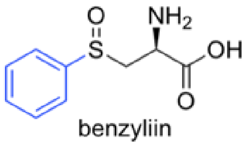
alliin



isoalliin



butiin



benzyliin

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CS&M-A16
Synthesis, biological evaluation and in silico ADMET prediction of 17α-picolyl and 17(E)-picolinylidene estra-1,3,5(10)-triene derivatives

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Šestić Tijana[1]*, Jakimov Dimitar*[1]*, Kuzminac Ivana*[1]

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Keywords: steroids; medicinal chemistry; cytotoxicity; estrogen receptor

Steroid compounds belong to a fundamental class of natural signaling molecules with a very high potential for the treatment of many types of diseases. Design and synthesis of new potential selective antitumor agents with a high degree of inhibition of neoplastic cell growth is one of the aims of modern medicinal chemistry. The heterocyclic ring modification at the C17 position of the steroidal molecule plays an important role in biological activity. With this in mind, we have synthesized and evaluated the potential antitumor activity of four novel and one previously synthesized 17α-picolyl and 17(E)-picolinylidene estrane derivatives, starting from estrone and its methyl ether. For all synthesized compounds we analyzed in silico ADMET properties using the online SwissADME tool and ProToxII virtual lab. Since these modifications were conducted on steroid compounds, their relative binding affinities for the ligand-binding domains of estrogen receptor α and β and androgen receptor were determined using fluorescent assay in yeast, in order to establish the molecular basis of their activity. The antiproliferative activity of all synthesized compounds was examined on six tumor and one normal cell line using an MTT assay.

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CS&M-A17

Polyoxometalate – Pillararene Hybrid for Supramolecular Polymer formation

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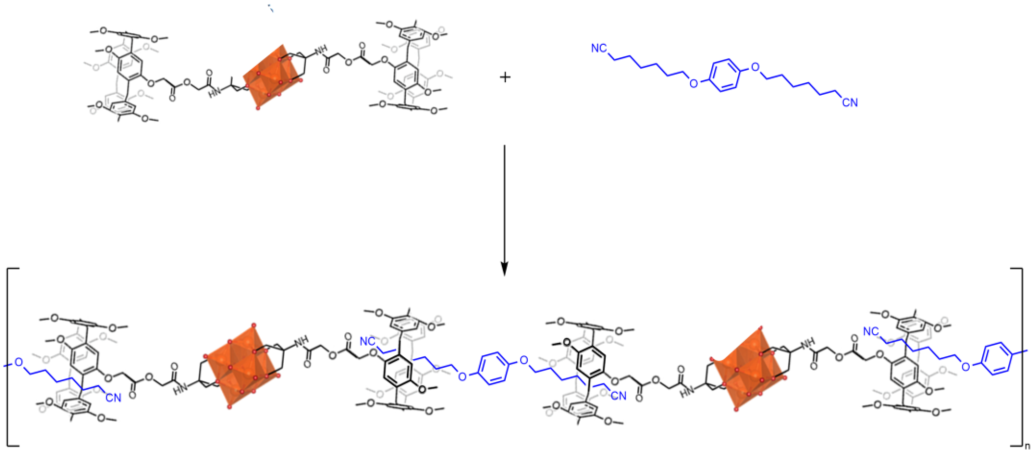
Keywords: Polyoxometalates; Pillararenes; Supramolecular Structures

Macromolecular systems based on supramolecular chemistry have attracted the interest of many scientist due to their dynamic properties. The ability of some supramolecular materials to respond to physical or chemical changes in their environment due to reversible non-covalent bonding interactions has prompted the development of "smart" materials with many potential applications.[1] In this regard, supramolecular networks based on pillararenes, which are a novel member of the container-type macrocycle family that can undergo host-guest interactions, have recently attracted much attention.[2] On the other hand, polyoxometalates (POMs), which are negatively charged metal oxygen nanoclusters, are interesting candidates for embedding into a supramolecular network since their interesting magnetic, electronic, and catalytic properties expands potential application of such structures even further.[3] As a result, a novel POM-pillararene hybrid was synthesized, which, upon addition of a guest functionality, can form a supramolecular network, which would benefit from the redox and catalytic properties of the Lindqvist hexavanadate {V6O19} (V6) structure. Moreover, reversibility of the system should be possible given the type of interaction between host-guest moieties.



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CS&M-B01
Ligand Exchange Quantification on Colloidal InAs Quantum Dots

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[1] *Ghent University, Belgium*

Keywords: Colloidal Quantum dots; Surface Chemistry; Ligands

The exploitation of III-V colloidal quantum dots (QDs) in optoelectronic devices is rapidly increasing due to their unique photophysical properties. While the implementation of InAs colloidal QDs in optoelectronics requires a deep understanding of their surface binding motif, less studies have paid considerable attention to revealing the surface chemistry of this group of binary quantum dots compared to the more prevalent II-VI and IV-VI groups. Among those few studies, an acid-based mediated ligand exchange has been previously reported for tetrahedrally-shaped InAs QDs by introducing the surface to aliphatic acids, resulting in partial replacement of the surface by the conjugate bases in an X-for-X manner [1]. In this regard, we have applied the same mechanism to further analyze the surface chemistry of recently developed InAs QDs synthesized by utilizing the simultaneous role of In(I)Cl as both the precursor and the reducing agent. It turns out that introducing the surface of such InAs QDs to an alkanethiol (Dodecanethiol) and a carboxylic acid (Undecylenic acid) leads to the formation of Oleylammonium chloride salt which has been validated by a series of H-NMR spectra as well as X-ray photoelectron spectroscopy. It was therefore revealed that the surface consists of X-type Chloride anions together with [OlNH2] as L-type ligands. While there is an exchange going on the surface with the exposed acids, there will be only a partial displacement of the initial surface moieties, resulting in a surface covered by thiolate and carboxylate groups. The fact that two different synthesis procedures lead to the same surface chemistry reactions is an appealing outcome that could be used later on to develop a more insightful realization of InAs QDs surface chemistry as a candidate for infrared-based optoelectronic devices.

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CS&M-B02
The Influence of bases on thermal decomposition synthesis of LaF3

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Keywords: nanomaterials; schlenk line; thermal decomposition; LaF3; nanothermometry

Nanothermometry is a fast-developing field of research due to the need of remote, precise, reliable and non-invasive temperature sensing in real time. This is both important for research, aswell as for industrial applications. However, new nanomaterials suitable for nanothermometry are often difficult to design as the synthesis might be challenging to control, and the fine-tuning of morphology, crystallinity and size is a sophisticated task. Schlenk line based synthesis are a well-known and frequently used route to grow nanoparticles for nanothermometry. However, reports on LaF3 synthesized employing a Schlenk line based thermal decomposition route are very rare.

In this presentation we will overview our work carried out on the preparation of nanosized and well-dispersed LaF3 and the influence of different bases, namely LiOH, KOH, NaOH and NaF, used in a thermal decomposition Schlenk line synthesis.

It has been reported before that an increase in the respective base and with it the pH value was assumed to accelerate the release of CF3COO- ions.[1] Chien et.al linked this to an accelerated growth of LaF3 nanocrystals. Using varied reaction conditions we have worked to optimize the best synthesis route for the development of the nano-sized LaF3.

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CS&M-B03
Development of targeted Tb-161 radiolabeled nanoparticles

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Keywords: nanoparticles; therapy; radionuclides; cancer; target; Tb-161

Currently applied cancer therapeutic strategies focus on the non-specific destruction of cells growing uncontrollably. This implies that rapidly dividing noncancerous cells may also be damaged in the process. However, there is now a greater emphasis on targeted radionuclide therapies designed to recognize, target, and damage only the desired cells.

Tb-161 is gathering more interest in recent years as a therapeutic radionuclide thanks to its favorable decay properties. It decays via the emission of β-particles with a half-life of 6.9 days. Those energetic electrons (average energy = 154 keV) have a maximum tissue range of 0.29 mm and a linear energy transfer (LET) around 0.32 keV/mm. Additionally, Tb-161 releases a significant amount of Auger/conversion electrons during decay, leading to a much higher dose being delivered locally compared to Lu-177 which possesses similar decay characteristics but does not emit Auger/conversion electrons. The simultaneous emission of γ-rays makes Tb-161 a high-potential theranostic radionuclide.

Radionuclides are traditionally transported to the tumor by the means of a chelating molecule coupled to a targeting vector. However, trans-chelation may occur, leading to the potential release of free radionuclides in the organism and hence to the accumulation in non-targeted organs. Furthermore, the dose effectively delivered to the tumor may be relatively low because of the fast renal clearance of such therapeutic agents. Targeted nanoparticles, containing the theranostic radionuclide Tb-161, are thus being developed to address these issues.

Our work focuses on the synthesis of core-shell nanoparticles via thermal decomposition of lanthanide salts, their silanization, functionalization with a targeting vector, and finally their characterization. Results show that core-shell NaGdF4@NaGdF4:Tb3+ nanoparticles could be produced with a size around 16 nm with a silica coating thickness in the order of a few nanometers. We also showed that modified folic acid could be easily coupled to the surface of silica-coated nanoparticles using the so-called “thiol-click” chemistry. The synthesis involving Tb-161 doped nanoparticles is currently being carried out to investigate their radiochemical behavior.

CS&M-B04
Polyoxometalate Based Metal-Organic Assemblies Towards Supramolecular Catalysis

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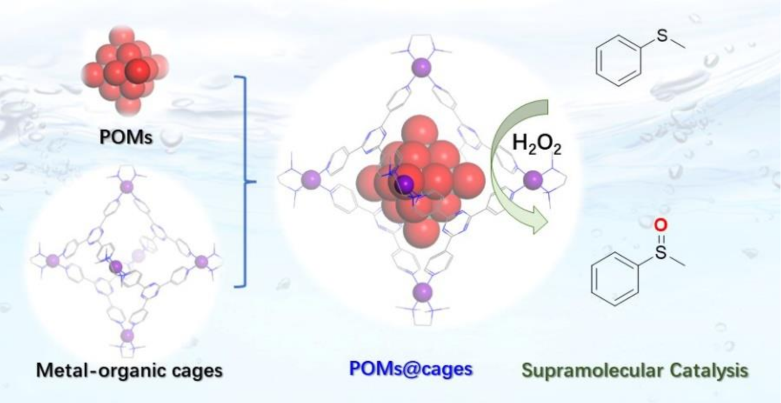
[1] *KU Leuven, Belgium*

Keywords: Polyoxometalate; Metal-Organic cage; Supramolecular Catalysis

Polyoxometalates (POMs) represent a unique class of anionic metal-oxygen clusters with special characteristics such as thermal stability, high negative charges, remarkable redox abilities, optical and magnetic properties that have been extensively investigated for various applications ranging from catalysis, medicine, electrochemistry, photochromism, and magnetism.[1] However, the functionalization and applications of inorganic POMs are often hampered by several drawbacks, such as a limited ability to modify their structures, low pH and hydrolytic stability, and the poor solubility of most alkali-POMs salts in organic solvents. With regard to this, developing supramolecular approaches in POMs chemistry could provide great advancements to overcome these drawbacks. Creating supramolecular POMs assemblies with controlled structures will advance their functionalization at the molecular level and result in great tunability of their properties. Herein, we have shown that cationic metal-organic cages could provide an ideal platform for encapsulating POMs to stabilize structures and extend functions. The water-soluble octahedral M6L4 metal-organic cages and Lindqvist [M6O19]2- (M = Mo or W) or organic-inorganic polyoxometalate hybrids [R-V6O13]2- are capable form POMs@hosts complex through a host-guest formation, which were characterized by 1D, 2D nuclear magnetic resonance (NMR) spectroscopy, electrospray ionization mass spectrometry (ESI-MS) and UV-Vis, and computational simulations. While the Mo6O19@Pd6L4, polyoxometalates are supported on water-soluble cages and can be efficient catalysts for green and selective sulfoxidation in an aqueous medium(see figure below). Moreover, our preliminary results indicate that improvement of the hydrolytic stability of POMs through metal-organic cages opens the potential for synthesizing elusive POMs (i.e., [V6O19]6-).



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CS&M-B05

Ultrasound assisted, bio-inspired CO2 mineralization to form CaCO3 with different morphology

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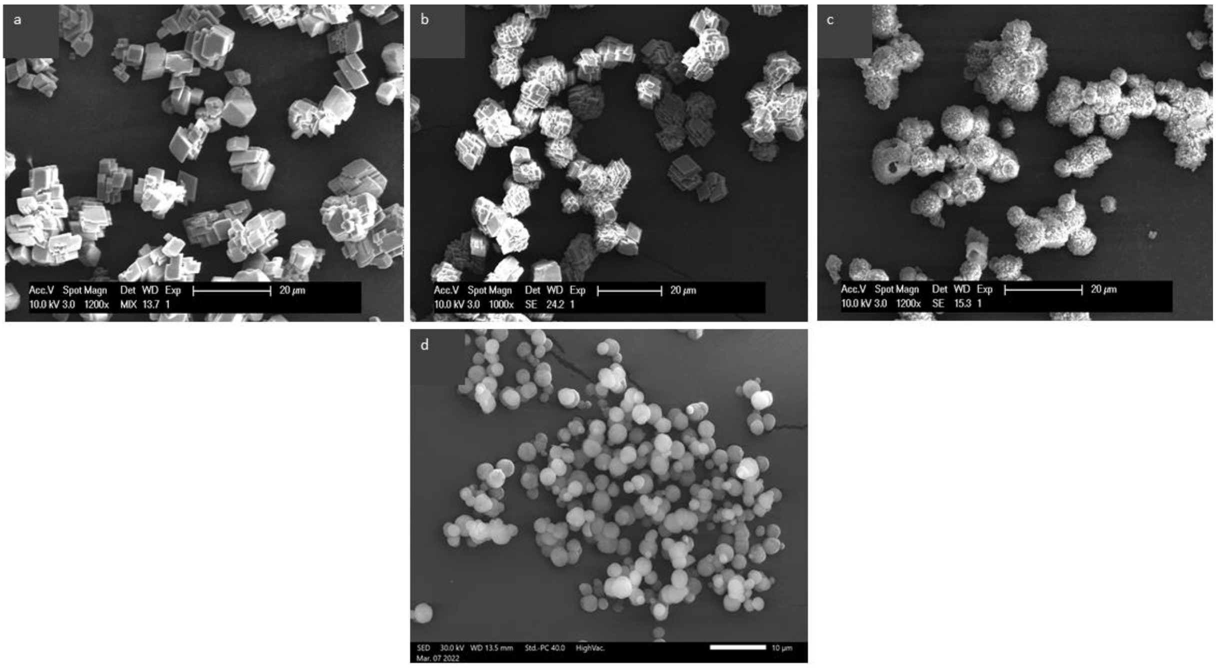
Keywords: CO2 utilization; CO2 mineralization; Crystallization; Biomimetic mineralization; Ultrasound

Global warming due to the increasing concentration of greenhouse gases, particularly CO2, is one of the most concerning challenges the world is facing right now [1]. CO2 mineralization, where CO2 gas is reacted with alkaline earth metal ions to form stable carbonates, is a promising technique for CO2 capture, utilization, and long-term storage. However, due to the large abundance of natural calcium carbonate (CaCO3), and advanced milling techniques, micron ranged CaCO3 is produced economically via the top-down method making the bottom-up methods (mineralization or precipitation) less economically interesting. We take inspiration from the natural formation of carbonate in organisms (mussels, nacre, etc.) via controlled crystallization (using environmental CO2) in a marine environment to form CaCO3 particles with different morphology [2]. We use water-soluble polymers combined with ultrasound to control the crystallization and tune the particle size, shape and polymorphs. CaCO3 particles with different properties could have advanced applications in water purification, biomedical materials development, drug delivery, catalysis and adsorbent giving the economic added value to them [3].



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CS&M-B06
Make and Break: New Thiol-Thiol bonding and debonding platforms

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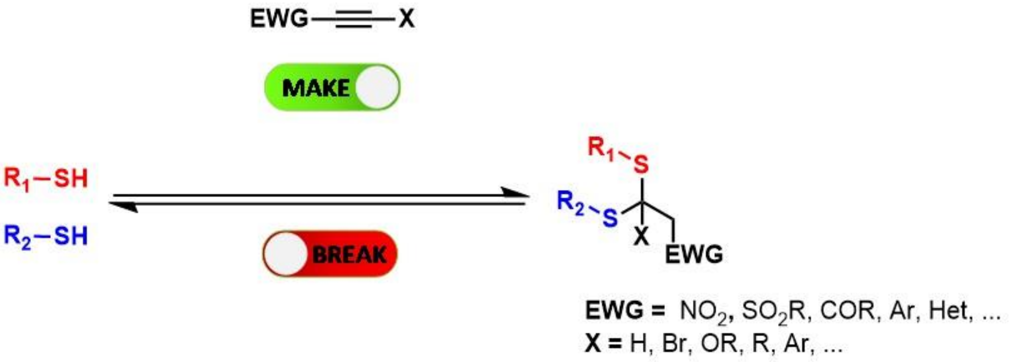
Keywords: Dynamic covalent chemistry; Click and unclick chemistry; Bioorthogonal chemistry; Thiol-Michael addition

Sulphur-based chemistry has attracted chemists in various fields and has become a hot topic over the years. Thanks to the inherent reactivity profile of sulphur containing molecules, applications range from a biological to synthetic and material context. In proteins, cysteine residues are targeted by various reactive groups to trigger a certain response. Michael acceptors such as maleimides, vinyl sulfones, etc. are mostly used for this purpose.[1] Additionally, sulphur-based chemistries are frequently used in a polymer context. The main work horses in this field being the thiol-ene and thiol-yne radical reactions.[2] Recently, we have developed a reversible thiol-yne platform based on two consecutive thiol-Michael click reactions.[3] Starting from an alkynone we proved the synthesis of initial thioacetal formation in which we later demonstrated the reversible nature of thioacetal exchange via a base catalysed mechanism. Furthermore, this thioacetal exchange showed to be easily tuneable depending on the electron deficiency of the corresponding thioacetal. Additionally, several ways of breaking the thioacetal moiety are now being developed to further expand the application scope in the fields of bioconjugation and specialty polymer design.



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CS&M-B07
Versatile post-functionalization strategy for the formation of symmetrical and non-symmetrical organic-inorganic polyoxometalate hybrids

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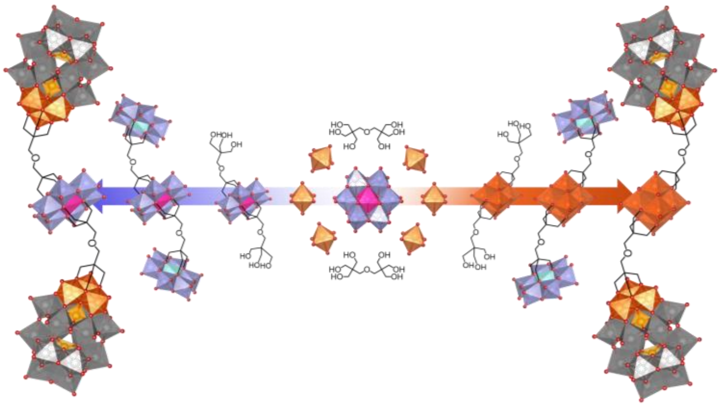
[1] *KU Leuven, Belgium*

Keywords: polyoxometalates; organic-inorganic hybrids

Polyoxometalate (POM) chemistry provides access to nanoscopic objects that resemble inorganic-shaped cavitands as cubes, cylinders, spheres... Such compounds are obtained through the association of building blocks from the dynamic library of metalates through the condensation of molybdates or tungstates in acidic medium. Grafting organic ligands onto these all-inorganic clusters gives access to a wider variety of POMs with interesting properties and potential applications in several areas covering biology,[1] electronics,[2] catalysis[3] and much more.[4] Despite the great advances in the field, the design and fabrication of new POMs with interesting properties remains an essential task and a challenge for research nowadays. In this context, we have developed a versatile post-functionalization strategy that allows combining multiple types of metal-oxo clusters in a single hybrid molecule.[5] Initially, simple hybrid POMs are developed as building-blocks that are later employed in the formation of symmetrical and non-symmetrical heterometallic hybrids through post-functionalization. This strategy illustrates the flexibility of POMs and the unlimited potential that can be unlocked through the combination of several metals in a single hybrid further expanding their physical and chemical properties.



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CS&M-B08

Effect of Reaction Conditions on the Phase Composition, Magnetic and Catalytic properties of MnOx-Na2WO4/SiO2 Oxide System for Oxidative Conversion of Methane

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Keywords: Oxidative Conversion of Methane; SEM/EDS; electron magnetic resonance (EMR); X-ray diffractometry (XRD)

MnOx-Na2WO4/SiO2 oxide samples based on a mesoporous silica matrix synthesized using tetraethoxysilane (TEOS), cetyltrimethylammonium bromide (CTAB) as precursors were prepared, characterized by scanning electron microscopy with energy dispersive elemental analysis (SEM/EDS), X-ray diffractometry (XRD), electron magnetic resonance (EMR), N2 adsorption-desorption measurements and tested as catalyst for the reaction of oxidative conversion of methane (OCM). The SEM microphotographs of the samples were shown below.

The SEM images show significant changes in the surface structure of the samples after the reaction. EDS data indicate the presence of manganese and tungsten and the effect of the reaction mixture on their distribution in the samples. The significant changes of the values of specific surface area and pore volume of samples after 15 hours working in OCM reaction were observed (116.8 m2/g and 0.590 cm3/g - before and 46.1 m2/g and 0.232 cm3/g - after). Two set of EPR spectra for the samples with g = 2.01-2.1 and hyperfine constant of ~ 94 G (nuclear spin I = 5/2 for 55Mn, six lines (2I + 1 = 6) before and with unresolved hyperfine structure and $\Delta H \sim 600$ G after the reaction belongs to MnOx, most likely to Mn2O3 nanoparticles are observed

EDS data show, if the ratio of the amount of Mn/W in the sample before the reaction is >1, but after exposure to the reaction mixture, it is <1. Taking into account EPR data it can be unambiguously stated that the state and distribution of manganese change significantly under the influence of the reaction mixture. Based on the EDS data, we can confirm, that under the influence of the reaction medium, the surface of the catalyst is enriched with tungsten centers.

Acknowledgements: This work is funded by the European Union's Horizon 2020 research and innovation program under grant agreement No.814557. The authors are grateful to Richard Heyn (SINTEF, Oslo, Norway) for help in measuring the texture characteristics of the samples.

It is shown that the MnOx-Na2WO4/SiO2 catalyst used consists of MnOx, Na2WO4, MnWO4, and SiO2 phases. It is assumed that at OCM reaction temperature of 750–850 °C, one of these phases, Na2WO4, is in a molten state (the melting and decomposition temperatures of Na2WO4 are 696 and 1200 °C, respectively), and under the reaction conditions Na2WO4 covers the surface of crystalline SiO2, forming “liquid glass” from the products of the reaction of MnOx with Na2WO4. This example shows the features of high-temperature reactions catalyzed by multicomponent systems, the components of which are in different aggregate states under the reaction conditions. The EMR and SEM/EDS data indicate a noticeable effect of the reaction conditions on the surface structure and the distribution of catalytically active components in the catalyst structure. The results of the study of samples subjected to various redox pre-treatments using scanning electron microscopy in combination with elemental analysis, X-ray diffractometry and electron magnetic resonance turned out to be key, which made it possible to suggest the formation of a liquid-like phase under the conditions of the OCM reaction, most likely the sodium tungstate, enveloping as continuous layer the granules of SiO_2 carrier in crystalline modification of cristobalite and/or tridymite with products of reaction MnO_x with Na_2WO_4 dispersed in this “liquid”. MnO_x-Na_2WO_4/SiO_2 system contains two types of active oxygen capable of interacting with methane molecules. One of them is the oxygen of the MnO_x oxide structures, the second is the oxygen of the anion $(WO_4)^{2-}$. Most likely, in the catalytic process, the charge state of tungsten remains unchanged and tungsten remains in the highest oxidation state in the form of tungstate ions. Moreover, as noted above, during EDS studies under the action of a methane-oxygen reaction mixture at a ratio of $CH_4/O_2 = 2$ or more, the catalyst surface is enriched in tungsten and depleted in manganese, and catalytic measurements in this case show a decrease in the catalytic activity of the samples, its deactivation. It was shown that the activity of catalyst decrease as a function of OCM reaction duration and CH_4/O_2 ratio on approximately 15% for 10 hours working of catalyst and $CH_4/O_2= 4$ ratio.

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CS&M-B09
Reactions of Free Radicals in Catalytic Oxidative Conversion of Methane Based on in situ EPR/MS Data

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Keywords: oxidative conversion of methane (OCM); NaMnW/SiO2 catalyst; EPR spectroscopy

Based on the data of EPR spectroscopy in combination with mass spectroscopy of the gas-phase products of the oxidative condensation of methane (OCM), the stages with the participation of methyl radicals on the surface and in the gas phase are determined, which make it possible to control the OCM process. The key homogeneous stages that determine the selectivity of the OCM process have been identified, and the kinetics of the formation-decomposition reactions of methyl peroxide radicals (CH3• + O2 ↔ CH3O2•) has been studied. The data obtained make it possible to consider within the framework of a unified scheme all the main stages of this reaction occurring both on the surface and in the gas phase. It is shown that in the considered heterogeneous-homogeneous process the stages of formation of free radicals and final products can be spatially separated. A stepwise scheme of methane oxidation in the presence of oxide catalysts is proposed. The regularities of the process of reoxidation of OCM catalysts, approaches to the design of spatially separated active particles in multicomponent catalysts, which are responsible for the generation of radical particles and their selective transformation, are also considered. Using the example of a multicomponent oxide catalyst NaMnW/SiO2 for this reaction, which, according to X-ray phase analysis, consists of the MnOx, Na2WO4, and SiO2 phases, it was shown that at the OCM reaction temperature, that is, 750-850 °C, one of these phases, the Na2WO4 phase, is in the molten state (manganese oxides - MnO, Mn2O3, MnO2 and SiO2 have a melting point above 850 °C), i.e. under the conditions of this reaction, we have, one might say, pseudo-liquid Na2WO4, covering the surface of crystalline SiO2 (with cristobalite and / or tridymite structure) in the form of a film, and nanosized MnOx particles in it, according to EPR data. This example demonstrates interesting features of high-temperature reactions, in this case, OCM reactions catalyzed by multicomponent systems, the components of which are in different states of aggregation under the reaction conditions. Such systems for the OCM process can significantly improve the selectivity to hydrocarbons C2.

Acknowledgements: This work is funded by the European Union's Horizon 2020 research and innovation program under grant agreement No.814557. The authors are grateful to Richard Heyn (SINTEF, Oslo, Norway) for help in measuring the texture characteristics of the samples.

CS&M-B10

Development of nanoporous crystalline thin films by Spark Plasma Ablation Deposition

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Keywords: spark plasma discharge; ablation; metallic oxides

Spark plasma discharge deposition or as we like to call it Spark Plasma Ablation Deposition (SPAD) is a novel method capable of preparing clean nanoparticle easily. Instantaneous sublimation of electrode material (target) is induced by a very high voltage that ionizes the carrier gas between the electrodes, creating metal vapour which then condensates into primary nanoparticles [1]. By coupling the ablation device with an chamber where impaction deposition takes place, we were able to produce various stoichiometric and non-stoichiometric thin films from different conductive materials. Here we report on how the different average high energy plasma states (created by different sparking conditions and oxygen concentration in the carrier gas, both within the boundaries of the method) affect the crystallinity and chemical composition of metallic oxide thin films. Specifically we ablated Cu, Ti, V, W, Mo, Li and Mn targets. Plasma was monitored by optical emission spectroscopy while the film morphology was characterized by microscopy techniques (AFM, SEM) through thickness, surface roughness and particle size. Moreover, we tried to clarify the overall mechanisms of nanoparticle oxidation through standard (GIXRD, XPS) and advanced (GISAXS, TEM) characterization techniques. All of the films show good nanoporosity and controllable chemical composition, however we find that the order of crystallinity and degree of particle aggregation highly depend on the nature of the ablated system.

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CS&M-B11
Sonochemistry as alternative route for the synthesis of black titania

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Keywords: Black Titania; Titanium Dioxide; Sonochemistry; Oxygen Vacancies

Titanium dioxide (TiO2) is by far the most widely studied and commercialized semiconductor for photocatalytic applications. Despite its popularity, the material's photocatalytic activity is limited by its low surface area and wide band gap (3.2 – 3.7 eV), which only allows activation by UV light. Tremendous effort has therefore been put both in nanostructuring of titania, as well as in narrowing the band gap, with the aim of obtaining more beneficial surface areas, and the ability to utilize also a part of the visible light region of the solar spectrum for photocatalytic reactions. A narrower band gap is conventionally achieved through metal or non-metal doping, resulting in a characteristic color of such modified TiO2 materials. Ever since it was demonstrated that exposure of TiO2 to high temperatures (> 400 °C) in a reducing environment resulted in oxygen vacancies and Ti3+ sites in TiO2, giving the material a deep black colour, the field of 'colored' TiO2 has seen an explosive growth in interest. Because these lattice disorders can enhance the photocatalytic activity, many have set their sights on synthesizing 'black TiO2' through alternative methods, while understanding the resulting structure-activity relation. Many synthesis routes are still plagued by a high energy requirement and demanding chemical reaction environment.

As a unique alternative mild and facile synthesis route, we use ultrasonic irradiation to introduce varying degrees of disorder in the TiO2 lattice. The process relies on acoustic cavitation phenomena, in which many small gas bubbles are created, grow, and implode on microsecond scale. This leads to local temperatures up to 5000 K and pressures up to 500 bar in the microenvironment of the bubble, which gives ultrasonically synthesized TiO2 its exceptional physicochemical properties. First results from our research group show almost a 10-fold increase in specific surface area for materials that underwent sonochemical treatment. In this work, we further investigate the influence of various synthesis parameters on the properties of the resulting black TiO2 materials.

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CS&M-B12

Post-functionalization of hybrid hexavanadates as components in supramolecular systems

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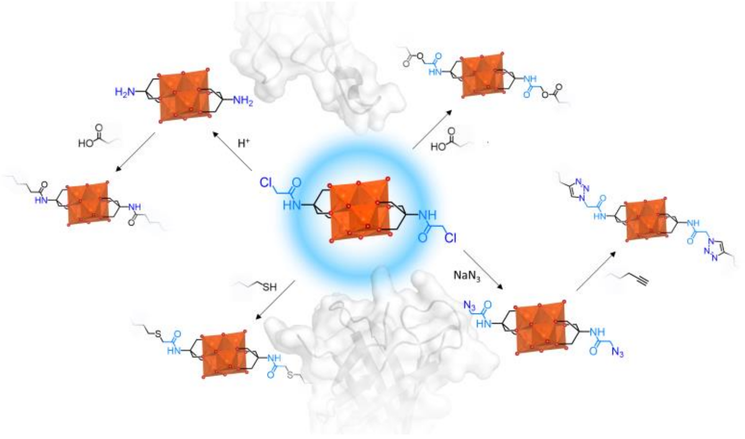
Keywords: hybrid; post-functionalization; supramolecular; polyoxometalates; hexavanadates; proteins

The synthesis of increasingly complex hybrid (bio)organic-inorganic compounds that synergistically combine the properties of both organic and inorganic components is a challenging task that is highly important in the formation of functional materials. In this respect hybrid polyoxometalates (HPOM) – a family of anionic metal-oxo nanoclusters functionalized with organic ligands – have demonstrated great potential in recent years, particularly due to their ability to undergo post-functionalization reactions with a wide range of organic moieties.[1,2] The Lindqvist hexavanadate structure, {V6O19} (V6), is particularly interesting due to its redox and catalytic properties.[3] However, V6 HPOMs have not been explored as extensively as other HPOMs due to the limited viable post-functionalization platforms available. Hence, [V6O13{(OCH2)3CNHCHOCH2Cl}2] (V6-Cl) was synthesized as a new platform for the derivatization of V6 structures via nucleophilic substitution that can also be altered in functionality to expand the types of possible post-functionalization reactions to amidation and azide-alkyne cycloaddition (click reaction). The potential of V6-Cl as a versatile post-functionalization platform was demonstrated with substrates of varying complexity, which were selected based on their relevance towards the increasing interest in HPOM-based motifs for supramolecular self-assembly.[4] Moreover, the supramolecular interactions of V6 HPOMs with proteins and their self-assembly as a result of post-functionalization with biologically active protein-binding substrates was also investigated.



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CS&M-B13
Sol-gel synthesis of Cu-based niobate for Photoelectrochemical conversion of CO2

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Keywords: CO2; photocathode; photoelectrochemistry

Solar-driven CO2 reduction presents a potential solution to deal with the global energy crisis and global warming. Photoelectrochemistry is one of the potential technologies to convert carbon dioxide into chemical fuels using sunlight. The key steps to conduct this process are the multi-electron transfer reactions in an efficient way for oxygen evolution reaction (OER), and carbon dioxide reduction using holes and electrons generated in an illuminated semiconductor [1]. Challenges of CO2 reduction generally lie in finding appropriate photo-active material which contains suitable band edge positioning, high charge carrier mobility and good stability in the aqueous medium. The objective of this study is to convert CO2 into valuable fuels using the synergistic photoelectrochemical (PEC) technology [2]. In this perspective, a p-type Cu-based transition metal-oxide semiconductor will be synthesized, characterized and used as a photocathode for photoelectrochemical (PEC) reduction. The focus of this research is synthesizing ternary p-type Cu-oxides as photocathode by means of an aqueous solution-gel route. The deposition conditions (number of layers and concentration of the solution) of the spin coat method to prepare the metal oxide thin films will be investigated. Furthermore, TGA and Raman spectroscopy will be performed to analyze the thermal decomposition of the precursors and phase formation of the synthesized metal oxide [3].

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CS&M-B14

Effect of templating on hydrothermal synthesis of Ce/Zr-oxide based catalysts for combustion of volatile organic compounds

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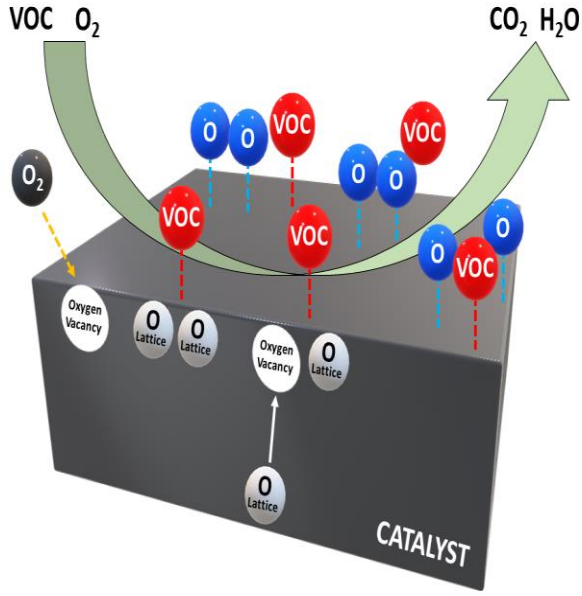
Keywords: Hydrothermal synthesis; Template; Ce/Zr-oxide catalysts; VOC combustion

Volatile organic compounds (VOCs), which by definition are organic compounds with a boiling point ≤ 250 °C at atmospheric pressure, are amongst the major contributors to global air pollution. VOCs are emitted from a wide variety of sources and play an important role in aerosol, photochemical smog and ground-level ozone formation, hence contributing to global climate change. Besides their impact on the environment, VOCs also pose a threat towards human health, since many VOCs are carcinogenic, mutagenic and teratogenic. Due to their toxic nature, strict regulations regarding VOCs emissions have been implemented. To comply with these regulations, efficient techniques of VOCs elimination from poluted air, including adsorption, membrane separation, thermal oxidation, (photo)catalytic combustion, have attracted extensive research. From these methods, catalytic combustion is believed to be the most promising due to its low cost, low operational temperature (200 – 500 °C) and limited formation of by-products.[1]

At present, noble metal based catalysts are considered to be the most efficient for the VOCs abatement. However, the high cost of these materials has led scientific research towards exploring cheaper transition metal oxide containing catalysts. Ceria and cerium based materials have been widely used in catalytic processes (CO-PROX, automotive three-way-catalysis, water-gas shift reaction, etc.) owing to their high redox activity and oxygen storage capacity (OSC). The latter is caused by the presence of lattice defects in the crystal structure, which induce oxygen mobility. As a result, besides Langmuir-Hinshelwood (L-H) and Eley-Rideal (E-R) also Mars-van Krevelen (MVK) mechanisms can be activated in the oxidation reactions. Hence, this is why ceria and cerium based materials are of specific interest for the VOCs combustion.

According to literature, the OSC of the widely used ceria can be enhanced significantly by incorporating zirconium ions in the crystal lattice. The smaller size of a Zr4+ cation (ionic radii of 0.84 Å compared to 0.97 Å for Ce4+) modifies the cubic fluorite structure of CeO2, which results in an enhanced OSC and oxygen mobility, improving the redox properties of the material.[2] Moreover, the addition of zirconia also improves the thermal stability of ceria. Therefore, in this research focus is put on the synthesis of Ce/Zr-oxide based catalysts for the VOCs combustion.

In order to prepare Ce/Zr-oxide materials, usually one of the following methods is used: sol-gel synthesis, hydrothermal synthesis or impregnation. However, the vast majority of Ce/Zr-oxide materials obtained using these methods have specific surface areas that do not exceed 100 m²/g.[3] Higher specific surface areas are of interest because it allows the deposition of more active elements and their higher dispersion. Generally, when one wants to obtain a material with a higher specific surface area template-based synthesis methods are preferred. However, such methods require a specific temperature treatment to eliminate the template and the residual organic components formed upon decomposition of the template. Therefore, in this research, the influence of a template in a hydrothermal synthesis method for Ce/Zr-oxide based catalyts has been investigated. The synthesis was performed using an ionic template (cetyltrimethylammonium bromide) or a non-ionic template (Pluronic P123) as well as in the absence of a template. The influence of the synthesis method on the material properties was studied in detail and reported.



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CS&M-B15
1H/D scrambling on functional groups of transition metal ligands enables conformational NMR analysis of homogeneous hydrogenation catalysts

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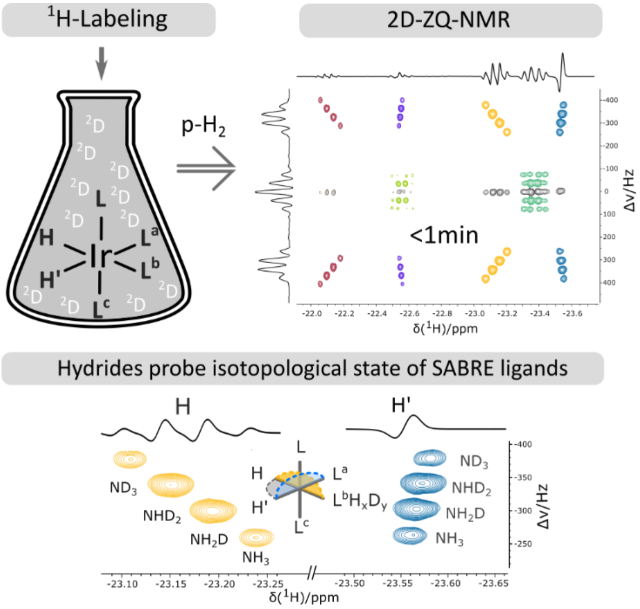
Keywords: NMR; Hydrides; Transition metals; Parahydrogen; Stereo-chemistry

Reaction pathways of transition metal catalysts for hydrogenation and spin transfer highly rely on the stereo-specific coordination of the dihydrogen molecule and the substrate to the active metal center. In a catalytic cycle catalytic complexes evolve transiently. Intermediates occur at concentrations too low to allow detection and structure elucidation, limiting experimental options to understand and improve the catalysis. Using parahydrogen as the source of hydrogen, hydride species on the catalyst can be observed with extremely high sensitivity enabling complete elucidation of the identity and stereochemistry of the active complexes using 1H-NMR. Adding a small concentration of protons to an otherwise deuterated reaction medium, spontaneous 1H/D scrambling encodes ligands with exchangeable protons with a unique isotopological label, enabling structure elucidation without requiring the presence of a sensitive or isotope labelled NMR active hetero-atom. Isotopological labelling enables to discriminate and identify all active hydride complexes containing hyperpolarized hydrides and provides access to their relative concentrations as they are encoded in the unique isotopological fingerprint of each complex. Using rapid 2D zero quantum NMR spectroscopy full chemical characterization of catalyst conformations is possible in less than a minute. The new methodology and interpretation of the 2D zero quantum spectra is explained and demonstrated on the example of isotopologically labelled Ir complexes with pyridine, benzylamine and ammonia as ligands. [1]



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CS&M-B16

Reductive amination of glycolaldehyde towards ethylene polyamines: selectivity control by fundamental mechanistic insight

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Keywords: green chemistry; heterogeneous catalysis; biomass; reductive amination; glycolaldehyde

Amines, such as alkanolamines (AA) and polyamines (PA), are an omnipresent class of chemicals in today's industry. Their market demand has rapidly increased in recent years due to their use in coatings, polyurethane synthesis and applications in waste water treatment and acid gas scavenging. However, the current production of AAs and PAs can still ameliorate in terms of green chemistry and sustainability since it depends on oxiranes (mostly ethylene oxide) or chlorinated hydrocarbons (mostly ethylene chloride) as carbon substrates. Recently, in collaboration with industry, our research group published a critical review discussing the substitution of ethylene oxide by glycolaldehyde (GA), a biomass-derived structural analogue. Interestingly, the unique asymmetric functionality of GA enables to produce either an AA or PA product via the same reductive amination reaction pathway. Consequently, selectivity control, i.e. driving the reaction towards the desired AA or PA, while also minimizing undesired side reactions, is of essential importance. Although the production of bio-based amines from GA has gained increasing interest in the past few years, almost all current research has been devoted to the formation of AAs, whereas PAs have attracted less attention since their formation process is not straightforward. This study addresses this research gap by aiming to extend and deepen current knowledge of the reaction mechanism and influential reaction conditions, in order to drive product selectivity towards these PA products. Validation of the proposed reaction pathway and identification of the main reaction intermediates resulted in a threefold strategy - each of which applies to an individual reaction step in the pathway - to increase PA selectivity.

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CS&M-B17
SuFEx-Enabled, Chemoselective Synthesis of Triflates, Triflamides and Triflimidates

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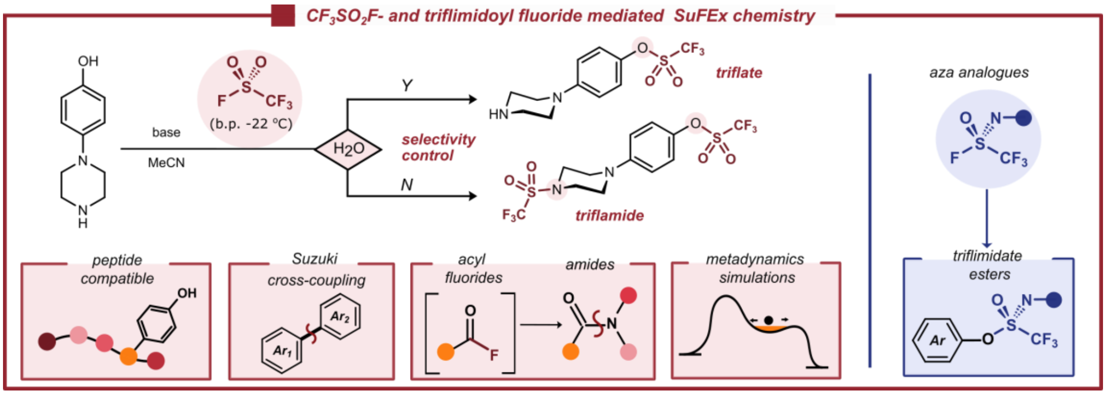
Keywords: /

Sulfur(VI) Fluoride Exchange (SuFEx) chemistry has emerged as a next-generation click reaction, designed to assemble functional molecules quickly and modularly [1]. Here, we report the ex situ generation of trifluoromethanesulfonyl fluoride (CF3SO2F) gas in a two chamber system based on our former work [2], and its use as a new SuFEx handle to efficiently synthesize triflates and triflamides. This broadly tolerated protocol lends itself to peptide modification or to telescoping into coupling reactions. Moreover, redesigning the SVI–F connector with a S=O → S=NR replacement, furnished the analogous triflimidoyl fluorides as SuFEx electrophiles, which were engaged in the synthesis of rarely reported triflimidate esters. Notably, experiments showed H2O to be the key towards achieving chemoselective trifluoromethanesulfonation of phenols vs. amine groups, a phenomenon best explained—using ab initio metadynamics simulations—by a hydrogen bonded termolecular transition state for the CF3SO2F triflylation of amines.



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Energy & Environment

E&E-A01

In-column modification of aminopropyl silica to produce highly performant stationary phases for Temperature-responsive liquid chromatography (TRLC)

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Keywords: nanoparticle assembly; transmission electron microscopy; electron tomography

Temperature-responsive liquid chromatography (TRLC) allows for extensive tuning of retention through use of temperature alone, enabling to replace mobile phase gradients by temperature gradients.1 As a result, application of these stationary phases provides a green alternative to conventional methods by opening the possibility for analysis under isocratic and aqueous conditions.2 This is achieved by application of stationary phases containing temperature-responsive polymers, which reversibly change their surface from hydrophilic to hydrophobic upon increase in temperature. By making use of reverse temperature gradients, the retentive ability of these stationary phases can be reduced by lowering the temperature during analysis. However, for TRLC to truly become competitive to conventional modes of liquid chromatography, further improvements into column efficiency and stability are required. It was hypothesized that the limitation in efficiency lies with the inherent issue of swelling and deswelling of the polymer during the packing procedure, causing irregularities into the column, consequently leading to a reduction in column efficiency. To combat this, a new manufacturing procedure was attempted, in which the modification of the silica was performed after initial packing with aminopropyl-silica particles. This was tested by a flow-through setup, where a solution of temperature-responsive polymer was flown through the column to achieve in-column grafting of the polymer onto the particles. Additionally, the remaining aminopropyl groups on the silica particles were end-capped by flowing through acetic anhydride to further improve the stability of the obtained columns. Initial findings showed that this flow-through modification is not only possible, but also yielded a higher efficiency in terms of achievable number of plates with these columns. Additionally, it was observed that end-capping of the stationary phase was possible after packing as well, which further increased the stability of the column.

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E&E-A02

Kinetics & thermodynamics of CH4 storage in solid aided clathrates

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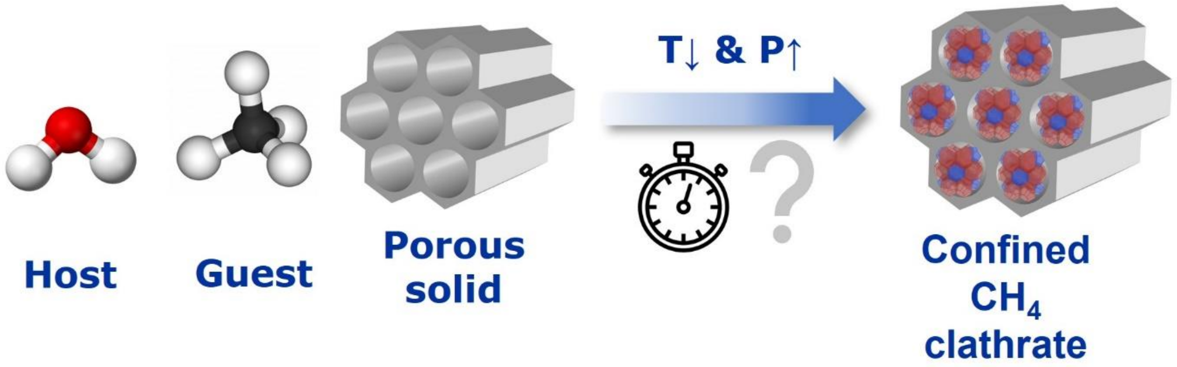
Keywords: Methane; clathrate; hydrate; gas storage; mesoporous silica

Clathrate hydrates are inclusion compounds consisting of a host lattice, formed by hydrogen bonded water molecules, in which gas molecules, such as CH4, CO2 and H2 can reside. Typically, these structures are formed at elevated pressures and temperatures around or below the freezing point of water. In the past, clathrates were merely regarded an obstacle in gas and oil transportation due to spontaneous formation in pipelines leading to flow assurance problems. Recently, however, they have received increased attention as medium to store gases, given their non-explosivity, environmentally benign nature, moderate storage conditions, low production cost, low risk of handling and high volumetric storage capacity, i.e. up to 160 m3 CH4 (at 0 °C and 1 bar) is stored in 1 m3 CH4 clathrate [1].

Clathrate formation in bulk water is hampered by low water to hydrate conversions, high pressures to initiate formation and slow nucleation and growth kinetics. A promising solution is the use of nanoporous materials to confine the water phase. Under nanoconfinement, the gas-liquid interface is increased compared to bulk water, allowing clathrate formation to occur at milder conditions, with improved kinetics and with increased gas storage [2]. However, while plenty of research has been devoted to identifying moderately hydrophobic mesoporous materials as optimal clathrate formation promotors in terms of formation pressure and gas uptake, quantitative kinetic data of confined clathrate nucleation, growth and reformation is greatly underrepresented. Yet this is crucial for the potential of clathrates as a future energy storage medium.

Two high-pressure experimental setups were developed in-house to quantitively monitor the kinetics and thermodynamics of solid aided clathrate formation. A gravimetric system was constructed by changing the electronics and software of a magnetic suspension balance, allowing the highly accurate and direct monitoring of gas uptake/release kinetics during clathrate formation/dissociation, respectively. A robust volumetric system was built to mimic the future gas uptake/release process in a storage vessel. Hence, the poster will cover results of nucleation, growth and reformation of methane clathrates aided by mesoporous silica (hydrophobized SBA-15) showing the effect of temperature, pressure, water loading and multiple reformations on the kinetics and thermodynamics of methane clathrate formation.



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E&E-A03

Modification of the surface chemistry of porous silica materials for gas storage applications

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Keywords: methane clathrates; hydrophobic silica; energy storage

Hydrophobic silica materials found their way in many applications (as unique component or in composites), including inks, coatings, paintings, separation media, defoamers, storing materials, plastics, cosmetics etc.

One of the most recent and interesting utilization of hydrophobic silica is related with the storage of methane (CH4) or carbon dioxide (CO2). Immediately, one can divide these two domains in energy storage direction (CH4-like molecules) and carbon capture and storage direction (CCS, CO2 molecule). Methane or carbon dioxide hydrates are an ice-like substance formed when CH4 and H2O or CO2 and H2O combine at low temperature and moderate pressure. Under these conditions, the water molecules are forming cage-like structures, in which the CH4 or CO2 can be stored. On top of this, it was shown that these types of hydrates are able to form at milder conditions if the ice cages are formed in a confined space, defined by specific porous materials, like silica or carbon-based. In order for the hydrates to form in these well-defined spaces, the surface chemistry of the materials must be very carefully controlled. If the surface is too hydrophilic, the water will adhere too strongly to the walls of the material and the hydrates formation will be inhibited. On the contrary, if the surface is too hydrophobic, the water will not be able to diffuse inside the pores and to form the ice-like cages.[1]

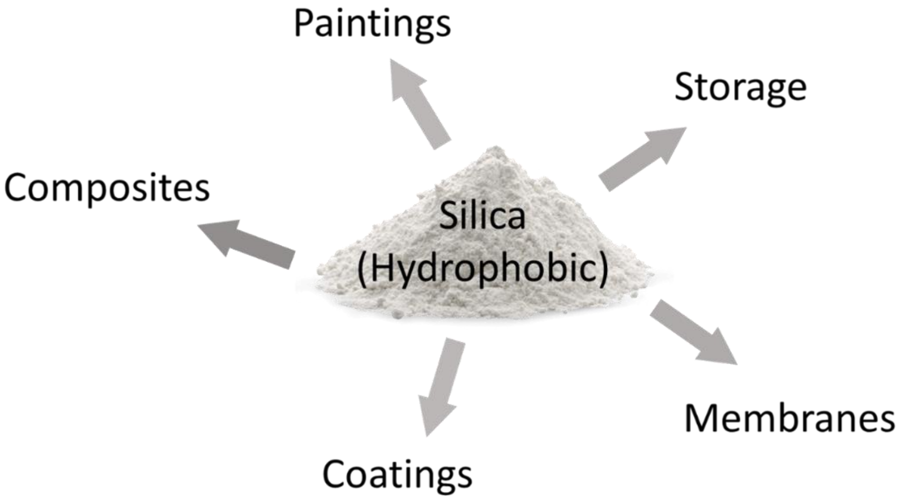
In this study, a series of micro/meso-porous silica materials (SiO¬2) are modified with different silanes, in order to control the surface properties. In the first step, ordered siliceous materials with mesopores (> 2 nm) and high pore volume are developed, of the type MCM-41 and SBA-15, by templated hydrothermal synthesis. By the use of different templates the pore size of the materials can be varied in the mesoporous range as well as the ratio micro/mesopores present. On top of this, by the additional use of swelling agents during the synthesis the pore size can be further enlarged (towards macropore formation), forming foam-like structures (3D-pore network, mesoporous cellular foam MCF). Finally, a KIT-6 SiO2 material with bi-continuous mesostructured and large ordered domains is modified for its unique combination of micro-meso pores.[2][3]

Secondly, the hydrophobisation of the silicas is performed in the presence of organosilanes of general formula R3SiX. Here, besides the type of the modifier molecule, the amount of the molecules on the surface represents a very important parameter for the surface properties. The materials developed are characterised by physisorption (porosity analysis), thermal analysis (thermal stability and crystal phase changes), X-ray diffraction (crystallinity and pore ordering), elemental analysis, SEM/TEM, and FT-IR and spectroscopy. The surfaces of the hydrophobic materials will be characterised in detail by elemental analysis (O, C, N). The hydrophobic surface properties of the materials will be assessed by water sorption measurements.

Moreover, the modification degree of porous materials in number of organic groups per nm^2 (groups/nm^2) will be approximated and quantified from thermal and physisorption analyses taking into account the weight loss of the burned carbon group and using the following formula:

(groups/〖nm〗^2)=(wt%(R)*N_A)/(MM(R)*S_BET)

in which wt%(R) is the weight loss percentage in g/100 g of sample of removed organic groups as measured in TGA, MM(R) is the molar mass of the carbon group, SBET (N2/Ar-sorption) is the surface area of the unmodified SiO2 and NA is Avogadro's constant. The experimental error is estimated to 0.1 groups/nm^2.



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E&E-A04

Clay-based structured composites for wastewater treatment through chromium removal

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Keywords: Chromium compounds; Clay-based structured composites

Skin irritation, chronic ulcers and lung cancer are only a few of the problems associated with chromium pollution, which is caused by the waste disposal of industrial processes such as metallurgy and dyeing. On a worldwide basis, 14,730 tons was emitted in the mid-90s and Cr6+ and Cr3+ are the two most abundant forms of the pollutants [1]. The Cr3+ compounds are less harmful to the environment due to its weak solubility in water and its limited ability to permeate organisms' cell membranes. Unfortunately, the more toxic form (i.e. Cr6+) can be formed from Cr3+ when atmospheric oxygen or organics are available.

A multitude of remediation methods are at hand to treat the chromium polluted wastewaters, with the adsorption process being considered as an effective and economical technique. The suitability of the method can be attributed to the flexibility in design and operation and re-usable treated effluents are often obtained. Consequently, the adsorption process was selected for this project, with the focus being on using structured clay-based adsorbents. Large scale applicability is aimed at by the shaping of the active materials and clay-based adsorbents are used due to their ability to remove heavy metal species through adsorption and ion exchange [2]. The work is a part of the H2020 EU-India Pavitra Ganga project and aims at improving the current wastewater treatment systems for implementation under Indian conditions. The sorbent composition was adapted with regard of the chromium speciation and the relative concentrations and the sorption performance were evaluated. The final goal is to ensure that wastewater loaded with Cr can be re-used for irrigation after the treatment.

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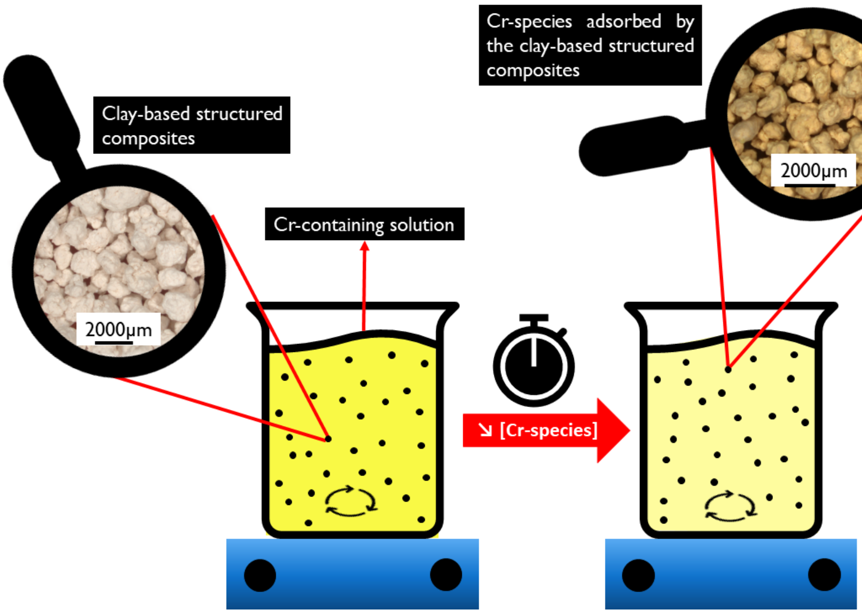

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E&E-A05
Investigation of xenon adsorption in three types of porous materials

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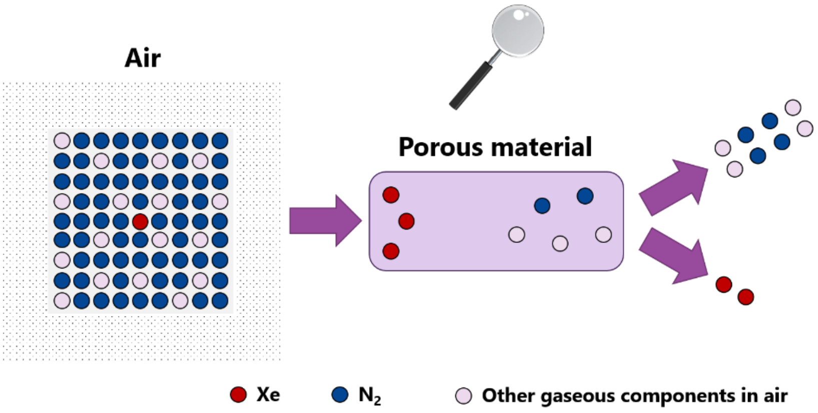
Keywords: Xenon; Adsorption; Activated Carbon; Silver-exchanged Zeolite; Metal-Organic Framework

The recovery of xenon from atmospheric air, based on highly efficient and selective adsorption, could replace the current cost-intensive cryogenic distillation generally used for xenon production. In addition, adsorption improvements for the measurement of ultra-low levels of radioactive xenon in the atmosphere could increase the capability of the verification system for the Comprehensive Nuclear-Test-Ban Treaty (CTBT). In the same context, enhanced radioactive xenon trapping systems at civilian nuclear installations could also improve the verification capability, as this would further reduce the atmospheric radioactive xenon background.

Activated carbon has been used for more than 60 years in the nuclear industry to recover radioactive xenon from gaseous effluents. About 20 years ago, researchers have demonstrated that some silver-exchanged zeolites had a higher Xe adsorption capacity at low Xe-partial pressures. The lack of knowledge on the durability of these zeolites did not yet allow their use with highly radioactive gas streams. More recently, some metal-organic frameworks have been demonstrated to be quite selective for xenon over other gas components, which could open a new opportunity in these fields. Ideally, adsorbents that are capable of trapping large amounts of xenon whilst being highly selective for xenon are looked for. In addition, these adsorbents should be durable against multiple temperature swing adsorption cycles as well as against severe irradiation.

In this poster, the measurement of xenon breakthrough curves over a range of conditions, used for the investigation of the Xe adsorption properties, will be presented and the results obtained on the three types of adsorbents will be discussed. Other characterization techniques (e.g. liquid nitrogen adsorption and thermal gravimetric analysis) used to support such research, through the identification of promising materials and to investigate their durability, will be addressed.



E&E-A06

Simultaneous measurements of metals and PAHs using diffusive gradients in thin films (DGT) with an environmentally friendly binding layer

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Keywords: DGT; Metals; PAHs; CALUX

The Diffusive Gradients in Thin Films (DGT) technique is an in situ and preconcentration method which has been widely developed to measure either inorganic or organic contaminants using different resin layers in aquatic environment. However, it was never considered to use a single resin, containing multiple functional groups, for simultaneous determination of inorganic and organic compounds by a universal passive sampler. A new DGT sampler using an environmentally friendly Capterall Mersorb (CM) binding layer for simultaneous measurements of ten trace metals (Cd, Zn, Cr, Mn, Co, Ni, Cu, Pb, Ag, Hg) and three Platinum group elements (PGEs) (Pd, Pt, Rh) was established in this study using DGT with. The binding kinetics of each element in a mixed solution indicated a rapid uptake by the CM resin gels. The capacities of CM gel for Cd, Zn and Cu were 381, 320 and 202 µg disc-1 respectively, which were comparable to chelex-100 resin gel, which is commonly used for trace metal sampling in DGT. Moreover, CM-DGT was combined with a chemically activated luciferase gene expression bioassay (CALUX) to measure polycyclic aromatic hydrocarbons (PAHs) in aquatic systems. CALUX bioassay measures the sum of biological and toxicological effects of PAHs, instead of individual compound concentration. Benzo[a]pyrene (BaP) as the model of PAHs, has been efficiently uptaken by CM gel. The combination of DGT and CALUX bioassay shows a great potential to measure the group of PAHs compounds in situ and at very low concentration levels. Therefore, this novel DGT sampler provides a possibility to simultaneously determine inorganic and organic contaminants for the first time in aquatic systems.

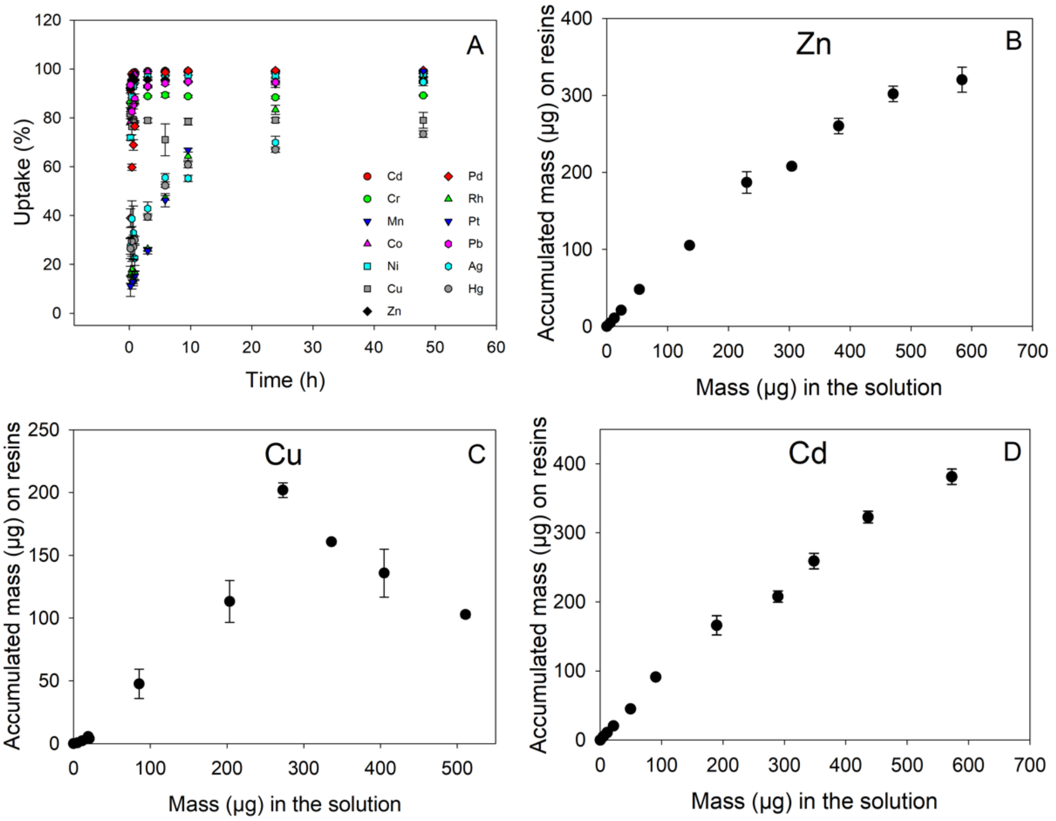

Figure 1. Uptake percentage (%) of metals by CM resin in 500 µg L^{-1} solutions containing 0.05 M NaCl (A). Accumulated mass (µg) of Zn (B), Cu (C) and Cd (D) on CM resin gel discs by deployment for 16 h in solutions containing mixed elements of Zn, Cu and Cd in a concentration range of 5–600 µg.

E&E-A07

ChromaRIM App: the new software in liquid chromatography to assist structural identification of small environmental solutes

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Keywords: HPLC-HRMS; Quantitative Structure- Retention Relationship model; In silico prediction; Retention index; structural elucidation

Over the past decade, high-performance liquid chromatography, coupled with high-resolution mass spectrometry (HPLC-HRMS), has been increasingly used in the analysis of environmental and treated wastewater samples. An important development therein has been the expanding ability of HRMS to elucidate the elemental composition of unknown environmental solutes. However, HRMS predictions software cannot always reliably predict the elemental composition of (larger) molecules while structural information obtained by MS remains limited. This hinders the identification and structural characterization of unknowns.

In this research, a Quantitative Structure- Retention Relationship (QSRR) modeling technique is used to build a predictive chromatographic retention index model (ChromaRIM) to support the structural elucidation procedure of unknowns where HRMS data and experimental retention indices are obtained. The developed predictive algorithm is purely based on RPLC retentive data and molecular descriptors, which allow confirmation and/or invalidation of the possible structural formulas through the implementation of the optimized predictive retention index equation. A number of molecular descriptors were thereby compared and eventually used in a broadly applicable equation in the intended chemical space for retention index prediction. The model was specifically designed to operate under easily transferrable generic linear gradients on one of the most frequently used stationary phases in HPLC and UHPLC. The novelty of this work is that it represents a complete, fully transferrable retention index-based workflow, effectively allowing to narrow down the possibilities in de novo structural elucidation of carbon, hydrogen, or oxygen-containing organic solute (< 500 Da). As a proof-of-concept, the methodology was further tested with both known and unknown solutes of various micropollutants that are of wastewater treatment relevance.

ChromaRIM offers the prospect for the near future transfer of the complete workflow into integrated LC-MS software to assist in the structural identification of unknowns, via comparison of the experimental and predicted retention of all hypothesized structures. The transferability of the approach concomitantly seeds the development of the long overdue, yet necessary, broadly applicable retention index databases in RPLC.

E&E-A08

Accelerated formation of methane hydrates in stainless steel beads packed reactor

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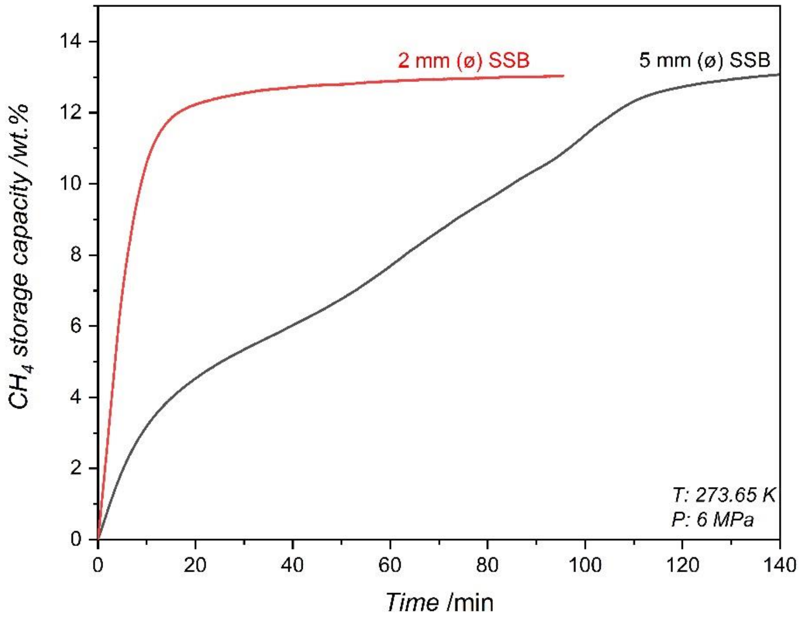
Keywords: Methane hydrates; Gas hydrates; Hydrate formation; Gas storage; Energy storage

Clathrate hydrates have received a lot of attention as a viable option for large-scale methane (CH4) storage. In lieu of using nanoconfinement to enhance nucleation sites and hydrate growth as in porous materials, whose synthesis is often associated with high costs and poor batch reproducibility, this fundamental work proposes a new approach for promoting CH4 hydrates in an unstirred reactor packed with stainless steel beads (SSB), where the interstitial space between the beads was exploited for enhanced hydrate growth. At 273.65 K, 275.65 K, 277.65 K and an initial pressure of 6 MPa, SSB of two diameters, 5 mm and 2 mm, were used as a packed bed to investigate their effects on CH4 hydrate formation. The thermal conductivity of SSB packing potentially aided hydrate growth by expelling the hydration heat. The experiments conducted in both 5 mm and 2 mm SSB packed bed reactors showed a maximum gas uptake of 0.147 mol CH4/mol H2O at 273.65 K with water to hydrate conversion of 84.42% with no significant variation. The results revealed a promotion effect on the kinetics of CH4 hydrate formation in the unstirred reactor packed with 2 mm SSB due to the availability of more interstitial space offering multiple nucleation sites for CH4 hydrate. This research shows that the use of expensive or intricate porous materials can be rendered obsolete by exploiting the interstitial voids in the packing of cheap and widely available SSB as a promising alternative material for enhancing the kinetics of artificial CH4 hydrate synthesis.



E&E-A09

In-line gas chromatograph for ultra-trace level analysis of off-flavor compounds in water

Lejaegere Charlotte[1], *De Prins Michiel*[1], *Verheyden Loes*[1], *Martens Johan*[1]

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Keywords: /

Geosmin and 2-methylisoborneol are well known off-flavor compounds causing product quality problems in drinking water or product produced in aquaculture at ultra-low concentrations. The off-flavors are harmless but the sensitivity of people towards them makes them problematic and undesired.[1] The compounds are chemically inert and hardly biological degradable, making common removal methods such as filtration and sedimentation ineffective.[2] The use of highly sensitive analytical devices to detect these ultralow concentrations is a must. Both geosmin and 2-methylisoborneol can be measured successfully using mass spectroscopy. However, these specialized analytical devices cannot be employed in-line at drinking water or aquaculture production facilities and will only be found in specialized analytical labs. The development of a simple analytical device that can be mounted in-line, and on-line, in a production environment would be a big step forward.

A selective adsorbent for both geosmin and 2-methylisoborneol is investigated via a screening. The optimal parameters for a selective adsorbent are derived and by tuning the hydrophilic-hydrophobic balance the affinity is maximized. A more complex water matrix, e.g. water from an aquaculture plant, does not affect the selectivity towards geosmin and 2-methylisoborneol. At concentrations of 100 ppt (parts per trillion), more than 99 % of both compounds is adsorbed by the adsorbent.

A pre-concentration module with a packed bed of the selective adsorbent is created in a solid phase extraction-like setup. The packed bed configuration resulted in the best adsorption due to complete contact of the adsorbent and the water sample. This is necessary as the concentration of both off-flavor compounds is incredibly low. Extraction of the compounds from the packed bed is realized by using an extraction solvent with an affinity of the off-flavor compounds higher than the affinity to the packed bed. By screening multiple extraction solvents, extractions close to 100 % are acquired.

An in-line and/or on-line analysis system consisting of a pre-concentration module and gas chromatograph (with flame ionization detector) is developed for the analysis of geosmin and 2-methylisoborneol in water systems. Selective adsorption on the packed bed is obtained in the pre-concentration module and followed by an extraction solvent that passes over the bed. The extraction liquid with higher concentrated off-flavor compounds is transferred to the detector for concentration determination. This technique has major advantages over current available techniques since it does not require complex analysis equipment to achieve traces of the off-flavor compounds and can be placed directly in the production environment. At optimal conditions, a concentration of one part per trillion can be measured from a water volume of 100 mL with an in-line routine analytical device.

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E&E-A10

Large organic cations as stabilizing interlayer for hybrid perovskite solar cells

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Keywords: Perovskite; Solar cells

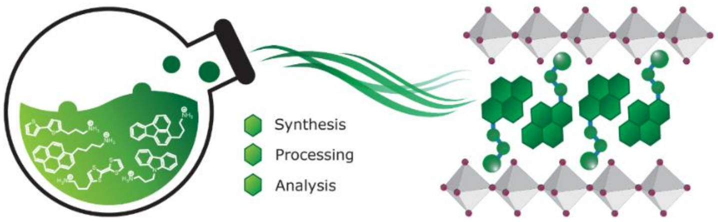
The emergence of perovskite solar cells (PSCs) has led to the development of a PV technology combining both a high power conversion efficiency (PCE) and potential low fabrication cost.[1] Their PCE has increased enormously from an initial value of 3.8% in 2009 to 25.5% in 2021.[2] Furthermore, recent research activities worldwide focus on the implementation of highly efficient hybrid perovskite solar cells as top cell in tandem solar cells with silicon solar cells as bottom cell. Such approaches have resulted in tandem solar cells with PCEs up to 29.1%[3].

These perovskite solar cells (PSCs) are based on hybrid organic-inorganic perovskites (HOIPs), materials integrating both worlds of organic and inorganic chemistry. Perovskites are generally described by the chemical formula ABX3 and possess the crystal structure of CaTiO3. In this structure, a small monovalent organic cation (A) (e.g. methyl ammonium) is surrounded by eight corner-sharing BX6-octahedra with B being a divalent metal ion such as Pb2+ and X a halogen ion.

Despite their exceptional properties and high record efficiencies, the environmental instability of 3D HOIPs towards moisture and temperature is, unfortunately, still one of the major drawbacks to face before the large-scale commercialization of PSCs can be initiated.[4]

The addition of small amounts of larger organic cations (e.g. butyl ammonium and phenyl ethyl ammonium) as a sort of insulating 2D perovskite interlayer has drastically increased the stability of PSCs over the past few years without a significant loss in cell efficiency. The HyMaD research group, however, focuses on the synthesis of large ammonium cations which are also organic chromophores, this way creating perovskite materials in which the organic part can have semi-conductive properties instead of merely acting as an insulating interlayer. Such cations may not only passivate traps but may also act as Hole Transport Layers (HTLs) or Electron Transport Layers (ETLs) and thus improve the performance of PSCs by a combined functionality.

In a recent collaboration with Imec both BTBT and Carbazole ammonium salts were tested as a bottom interlayer in p-i-n perovskite solar cells. In these devices, the use of the BTBT derivative significantly increased the open-circuit voltage boosting the power conversion efficiency (PCE) from 16.6% to 18.6%. Additionally, the devices retained 89% of the initial PCE after 250 hours at 25% relative humidity and 95% after 1 hour under continuous MPP tracking (MPPT).



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E&E-B01

Biogeochemical cycle of Mercury (Hg) in sediment of the Scheldt Estuary and the Belgian Part of the North Sea (BPNS)

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Keywords: Hg and MeHg concentrations; sediment porewater and solid phase; DGT; bioavailable

Mercury (Hg) is one of the most toxic elements in natural and urbanised environments and monomethylmercury (MeHg) is the most health concern due to its bioaccumulation and biomagnification along the food chain. Coastal and estuarine zones are often the specific sites of high Hg contamination due to the anthropogenic. The BPNS (Belgian Part of the North Sea) has suffered a long-term, recurrent metallic pollution by atmospheric deposition, direct wastewater discharge from coastal industries and input of the Scheldt Estuary which is enriched in trace metals originating from its watershed and especially from the industrial site of Antwerp. Sediment functions both as a sink of Hg accumulation and a source of Hg release to surface water. In addition, sediment can also record both historical and current Hg contamination in aquatic systems if the vertical profile of Hg in sediment available (solid phase). More research has been done on Hg contamination in sediment solid phase, however the Hg and MeHg concentrations in sediment porewater are normally low (at ng/L level) and the conventional methodology (centrifugation and filtration, or Rhizon extraction) to sample Hg and MeHg in porewater cannot always produce accurate results especially for MeHg. The passive sampling technique of Diffusive Gradients in Thin-films (DGT) is a suitable technique preconcentrating labile Hg and MeHg from porewater and then be analyzed by Advance Mercury Analyzer (AMA) for total Hg concentrations and Gas Chromatography coupled with Atomic Fluorescence Spectrometry (GC-AFS) for MeHg concentrations. The total Hg concentration in porewater samples (from classic sampling method) can be analysed with Cold Vapor-Atomic Fluorescence Spectrometry (CV-AFS) after oxidation and reduction of samples. In addition, different from porewater extraction, DGT is a powerful tool to measure labile fractions of Hg and MeHg due to the pore size of the diffusive gel (10-20 nm) in sediment porewater and the labile fraction of Hg and MeHg measured by DGT is potentially bioavailable in aquatic systems. While the exchange of Hg between solid and dissolved phases can affect the labile Hg concentration both in water and sediment. Mercury and MeHg distribution between different phases in sediment systems can be also studied in this way. In the two Belgica campaigns in March 2020 and March 2021 in the Scheldt estuary and the BPNS, both classic porewater and DGT sampling were carried out and Hg and MeHg concentration profiles were obtained by these two sampling methodologies. Relatively high total Hg concentrations were observed both in sediment porewater (10 to 90 ng/L) and solid phase (93 to 406 µg/kg) at sampling station S15 (upper Scheldt estuary and close to the industrial zone of Antwerp, salinity was around 5). The labile Hg concentrations (DGT measured) were ranged from 2 to 35 ng/L in the porewater at S15. However, lower total Hg concentrations were found in sediment porewater (3 to 43 ng/L) and solid phase (31 to 147 µg/kg) at sampling station SV (Close to Zeebrugge harbor in the BPNS, salinity was around 29). In SV, labile Hg concentrations were fluctuated around 11 ng/L. The range of MeHg is from 0.5 to 3.6 ng/L at S15 and from 0 to 1.0 ng/L at SV. High MeHg concentrations are related to the sediment environment and the concentration of total Hg in porewater.

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E&E-B02

Assessment of the toxic potency and mutagenicity of soils from waste dumping sites in Wallonia, Belgium

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Keywords: CALUX; AMES Test; soil pollution; toxicity; mutagenicity

Soil pollution caused by human activities is an alarming issue that puts pressure on soil health and its capacity to provide ecosystem services. Thousand man-made chemical compounds with potential toxicity have been released and deposited on the earth's surface, posing a great threat to human, plant, and animal health. Some pollutants break down in soils over time, however others such as persistent organic pollutants (PCDD/Fs, dl-PCBs, and PAHs) remain for very long times. The latter even at low exposure levels can exert toxic responses and can alter processes and functions of the endocrine system. The full risks of these chemicals and their various mixes are not yet fully known.

In this study, the toxic potency and the mutagenicity of high risk contaminated soils from waste dumping sites in Wallonia, Belgium were assessed. A combined approach of bioanalytical assays (AhR/ER – CALUX) and the AMES test was applied in the subset of soil samples collected in 2020-2021 from seven sampling points in Wallonia, Belgium.

The AhR-CALUX potency estimates ranged from 4 to 613±88 µg-BEQs/g d.w. for PCDD/Fs, from 18 to 241±35 µg-BEQs/g d.w. for PCBs, and from 3 to 140±28 µg-BEQs/g d.w. for PAHs. These results significantly exceed the guide values recommended for soils by EU/US policy makers. The ER-CALUX potency estimates were below determination levels. However, antagonistic activity (blocker) was detected, which could prevent full determination of the agonist activity/potency.

The mutagenicity of the soil samples was conducted in Salmonella typhimurium strains TA98, TA100, in the presence and absence of the S9 metabolic activation. The results revealed one soil sample as mutagenic, for the TA100 strain in the presence of the S9 metabolic activation while 5 soil samples were found mutagenic for the tests of the TA98 strain both with and without S9 metabolic activation.

The present results indicate mutagenicity and toxic potency for the soils on Belgian waste dumping sites due to the chemical compounds present. These polluted soils can be a major input pathway of the organic contaminants to the ecosystems, harming human health and well-being, wildlife and negatively affecting food, water, and air quality. Therefore, monitoring them is of high importance. The combined approach used in this study could be useful to monitor different genotoxic and/or toxic compounds in environmental samples and could be used to better evaluate the environmental quality of soils.

E&E-B03

Randles Circuit and Performance Analysis of a Small Proton Exchange Membrane Fuel Cell using Current Interrupt and Electrochemical Impedance Spectroscopy Techniques

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Keywords: PEMFC; CI; EIS; Randles models

Climate change urges scientists, engineers and politicians to find realistic solutions that substantially reduce the emission of anthropological greenhouse gases (GHG) in order to meet the climate neutrality target of the European Union by 2050 [1]. Several options are hereby considered, such as ammonia or hydrogen fuels [2], but also the sustainable production of hydrocarbon fuels combined with carbon dioxide management comprising carbon sequestration using storage (CCS) or utilisation (CCU) [3, 4].

In the transportation sector, which is a major contributor to the emissions of GHG and involving road, air and maritime traffic [5], there is nowadays a strong impetus toward electrification employing batteries. These can be charged using green electricity generated from solar, hydro, wind or even ocean energy. However, batteries have a rather limited gravimetric and volumetric energy density [6], which curtails the autonomy of the system when the latter must remain economically justifiable or even practicable. For this reason, hybrid electric power trains using hydrogen-based fuel cells offer an attractive solution. As the system load profiles are usually highly dynamic, only Proton Exchange Membrane Fuel Cells (PEMFC) appear eligible at this time. These fuel cells work on relatively low temperatures and can cope adequately with varying load profiles when used in a hybrid configuration with batteries or supercapacitors and buck/booster DC-DC converters if a constant output voltage is desired. The integration of the PEMFC into a wider electric environment therefore necessitates the knowledge of at least the Randle circuit of the fuel cell and the components with which it interacts. These circuits can be established by i.a. the current interrupt (CI) method or the more involved electrochemical impedance spectroscopy (EIS) technique. They yield valuable insight into the performance and the degradation of the components, which is specifically relevant for the fuel cell (the degradation is mostly situated near the membrane electrode assembly (MEA) of the fuel cell) [6, 7]. Detection and quantification of the degradation is fundamental in the development of the necessary mitigation strategies, which must result in a more reliable operation, and a prolonged optimal performance of the examined component.

The presentation will give an overview of the aforementioned characterisation techniques applied to a small PEMFC and discuss the test bed setup. The Randles models will be established and compared, and the performance of the fuel cell will be described under varying operating conditions.

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E&E-B04

Dissolution of cellulose in ionic liquids based on acetic acid

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Keywords: Green chemistry; cellulose; ionic liquids; biorenewable

In recent decades, a great effort has been made to find sustainable and alternative energy sources due to the rapidly growing demand for energy and the depletion of fossil fuels. Therefore, the development and utilization of natural polymers have been attracted increasingly and the most abundant and important biorenewable resource for fuels, chemicals, and materials biopolymer on the earth is cellulose [1].

The fact that cellulose is a renewable resource, the willingness to develop new cellulose materials is daily increase, however, many of the technologies currently used in the processing of cellulose are undesirable from an environmental point of view. Because cellulose is insoluble in water and common organic solvents, ongoing research worldwide aims to find new, efficient and green solvent systems and efforts are focused on the use of ionic liquids (ILs) to dissolve cellulose [2].

As a new class of greener solvents, some ILs have been found to be able to dissolve cellulose under relatively mild conditions. Besides, compared with volatile organic solvents, ILs have many unique properties such as a broader selection of anion and cation combinations, negligible vapor pressure, non-flammability, wide liquid range, enhanced electrochemical and thermal stabilities, and strong dissolution ability for various organic and inorganic materials [3,4].

Here, we present the results of our studies of cellulose dissolution in ionic liquids of various combinations. We have studied the influence of the cationic part of the ionic liquid on the process of cellulose dissolution. We used ionic liquids of different combinations, where acetic acid was used as an anion part with various cations (N-methylpyrrolidone, di-, tri-, butylethylamines). The solubility of cellulose was studied at a temperature of 80-100 °C for 24 hours at various concentrations of cellulose (1-20%) in ionic liquids. Based on a number of studies, we found that cellulose dissolves well in an ionic liquid-based on N-methylpyrrolidone and acetic acid.

The process of cellulose dissolution in ionic liquids was confirmed by 1H, 13C NMR and IR spectroscopy data. Thus, comparing the IR spectra of pure ionic liquids and a solution of cellulose in an ionic liquid, we found that the spectrum of the latter demonstrates new absorption bands at 1042 cm-1 and 3377 cm-1, characteristic of C–O and H–O bonds, respectively, which are absent in pure ionic liquid.

An identical picture is observed in the 1H, 13C NMR spectrum. Thus, in 1H NMR, new signals of protons of CH2O, CHO groups are observed in the area of 3.37–3.64 ppm. (multiplet form), and in 13C NMR signals of carbon atoms in the range of 62.38 ppm., 71.96 ppm. respectively.

The obtained data have a considerable practical interest related to the simplification of cellulose processing technology.

DISSOLUTION OF CELLULOSE IN IONIC LIQUIDS BASED ON ACETIC ACID

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Introduction

In recent decades, a great effort has been made to find sustainable and alternative energy sources due to the rapidly growing demand for energy and the depletion of fossil fuels. Therefore, the development and utilization of natural polymers have been attracted increasingly and the most abundant and important biorenewable resource for fuels, chemicals, and materials biopolymer on the earth is cellulose.

Because cellulose is insoluble in water and common organic solvents, ongoing research worldwide aims to find new, efficient and green solvent systems and efforts are focused on the use of ionic liquids (ILs) to dissolve cellulose.

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Ionic Liquids
- Non-flammable
- low viscosity
- Low vapor pressure
- Non-volatile nature
- Tuneable Properties
- High Thermal Stability

Key Factors
- Cellulose Polymerization and Crystallinity
- Lignin Structure and Composition
- Hemicellulose Crosslinking
- Accessible Surface Area and Porosity

Value-added Products
- Cellulose
- Lignin
- 5-HMF
- Furfurals
- Levulinic Acid
- Total Reducing Sugars

Results and discussion

Here, we present the results of our studies of cellulose dissolution in ionic liquids of various combinations. We have studied the influence of the cationic part of the ionic liquid on the process of cellulose dissolution. We used ionic liquids of different combinations, where acetic acid was used as an anion part with various cations (N-methylpyrrolidone, di-, tri-, butylethylamines). The solubility of cellulose was studied at a temperature of 80-100 °C for 24 hours at various concentrations of cellulose (1-20%) in ionic liquids. Based on a number of studies, we found that cellulose dissolves well in an ionic liquid-based on N-methylpyrrolidone and acetic acid.

The process of cellulose dissolution in ionic liquids was confirmed by IR and 1H, 13C NMR spectroscopy data. Thus, comparing the IR and NMR spectra of pure ionic liquids and a solution of cellulose in an ionic liquid, we found that the spectrum of the latter demonstrates new absorption bands at 1042 cm^{-1} and 3377 cm^{-1}, characteristic of C–O and H–O bonds and new signals of protons of CH2O, CHO groups in the range of 3.37–3.64 ppm. (multiplet form), signals of carbon atoms in the range of 62.38 ppm., 71.96 ppm. respectively, which are absent in pure ionic liquid.

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E&E-B05
Solid Micellar Catalysts for CO2 hydrogenation to formate

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Keywords: /

Solid micellar catalysts (SOMIC) are a new class of complex heterogeneous catalytic materials. Ru@MCM-41, the first SOMIC to be synthesized and characterized, consists of Ru(III) single atom sites and silanoxo base sites incorporated into the walls of MCM-41 and both stabilized by quaternary ammonium surfactants inside the pores.[1] Lab-scale batch experiments showed promising results for CO2 hydrogenation to formate at 90 °C, reaching formate concentrations up to 4 M in a water-free environment, thereby mimicking state-of-the-art homogeneous Ru catalysts, but with superior stability and recyclability.[2-4] The performance of Ru@MCM-41 was next evaluated in continuous-flow using Robinson-Mahoney 3-phase reactor.

High selectivity to formate was also observed in flow conditions, reaching a formate concentration of 0.3 M at 70 °C for a feed of 1.3 M tri-ethylamine (TEA) and a CO2 and H2 total pressure of 46 bar. However, the catalyst gradually loses its activity after 72 hrs. Analysis of the liquid product indicates a gradual loss of the CTA+ surfactant from the pores of the material over the duration of the flow experiment, likely due to an exchange with protonated TEA. Separate batch experiments indeed show that exchange of the surfactant with ammonium chloride significantly decreases the activity.[1] Follow-up experiments and small modification to the SOMIC synthesis are being evaluated to enhance the stability of these materials.

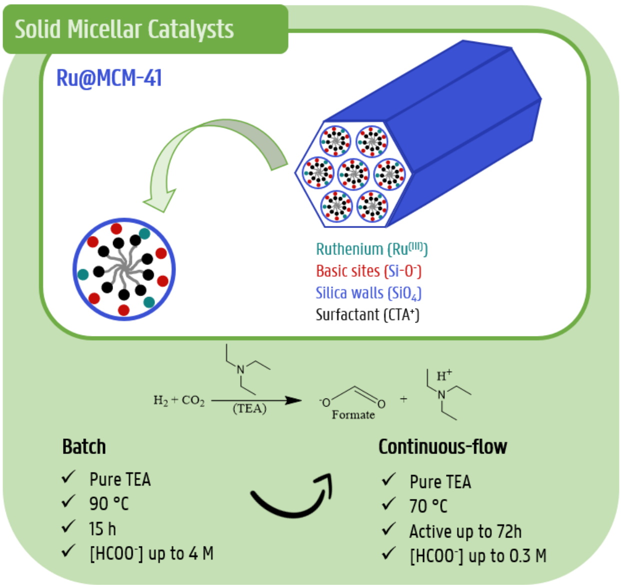

Figure 1. Representation of the CO_2 hydrogenation reaction to formate (in batch and continuous-flow conditions) using Ru@MCM-41.

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E&E-B06

Synthesis of hollow mesoporous MOx spheres for enhanced confinement of polysulphides in lithium Sulfur batteries

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Keywords: Lithium sulfur battery

With the energy density of lithium ion batteries reaching their theoretical limits, researchers have moved their interest to other systems [1,2]. Lithium Sulfur batteries (LSB) are regarded as one of the more promising next-generation energy storage systems due to the ultra-high theoretical energy density of 2600 Wh/kg and the cheaper predicted cost to fabricate these batteries. Unfortunately, the premature end-of life and reaching the theoretical capacity in LSBs are problematic compared to other batteries [3]. The problems arising in LSBs are mainly caused by the insulating nature of the sulfur cathode, sluggish electrochemical kinetics, and severe shuttle effect associated with polysulfide intermediates. To cope with the negative effects and improve the performance of LSBs, a variety of transition metal-based materials (including metal oxides, metal nitrides and metal sulfides) have been incorporated in the cathode as host material [4]. More specifically, core-shell structured sulfur composite nanoparticles (NPs) and their various derivatives have been widely investigated as a promising cathode material for LSBs [5]. They possess a unique set of features for suppressing the shuttle effect including accommodation of the volume change in the sulfur electrode, and providing abundant active sites for Lithium polysulfide (LiPS) capture and conversion [6–8]. While a wide variety of procedures are available for the synthesis of hollow mesoporous particles, it remains difficult to synthesize hollow nanospheres with good uniformity [9]. Here, a variety of hollow metal oxide mesoporous nanospheres are rationally designed and synthesized to serve later as sulfur host in the cathode of LSBs [10]. The sulfur incorporation strategy for these hollow spheres is investigated and optimized so that a large amount of sulfur is effectively incorporated in the hollow structures.

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E&E-B07

Use of Cl/Br ratio as tracer for anthropogenic contamination in groundwater

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Keywords: Wastewater reuse; Tracer; Cl/Br ratio; Ion Chromatography

Due to climate change, in the future droughts will become more prevalent and supply of drinking water will become increasingly challenging [1]. A possible way to limit this, could be the reuse of treated wastewater in agriculture by infiltration of the soil. However, this can currently not be applied due to a lack of knowledge concerning the possibility of the presence of bacteria, viruses, inorganic and organic contaminants in this wastewater, which could reduce the water quality [2]. So, before this can safely be applied, research is needed to guarantee that the reuse of wastewater does not cause contamination of groundwater and soil. A 5 year lasting project (IRP, VUB) started in 2020 at an agricultural field next to the WasteWater Treatment Plant (WWTP) in Kinrooi (North-Eastern Belgium) and the small surface water system, Abeek, in which the WWTP discharges. Here, water coming from the effluent of the WWTP will be infiltrated in the field to increase the groundwater level in a controlled way. A monitoring program of different contaminants (both organic and inorganic) has been carried out in both groundwater, and surface water (including effluent of the WWTP) to determine background levels of these contaminants, and during the infiltration, this monitoring continues. For this type of study, it is of the utmost importance to find a reliable tracer to understand the dynamics between the groundwater in the field and surface water (effluent and influent of the WWTP) and determine the origin of fluctuations of contaminant concentrations. Determining the chloride to bromide mass or molecular ratio (Cl/Br) is a possible way to achieve this since both Cl and Br ions have been proven to show close to ideal conservative behavior. This means that processes such as dilution, evaporation and mixing affect both ions to an equal extend keeping the ratio intact [3–6]. In this project, bromide and chloride anions are analysed using Ion Chromatography. The analytical challenge lays in the low concentrations of bromide in the water samples with a concentration difference of two orders of magnitude between bromide and chloride concentration. A new method was developed to perform this analysis by increasing the sensitivity of the instrument and lowering the calibration range. Quality control and assurance are currently being carried out for validation. Using this method, water samples taken before and after the infiltration are analysed. Bromide concentrations at lower than 1 mg/L are detected, which is to be expected for groundwater [4]. Although the results so far indicate that the use of the Cl/Br ratio for this research is reliable as tracer, more research is needed to confirm this and is currently being carried out. In conclusion, Cl/Br ratio as tracer for dynamics of ground- and surface water has shown promising results. This was especially challenging because of the low concentration of bromide in the water which could successfully be measured by the improved method.

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E&E-B08

Thermo-responsive polymers for water harvesting from air

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Keywords: water; water vapor; thermo-responsive polymers

Water scarcity affects two-thirds of the world's population, and it is an increasing issue in western developed countries. Periods of drought and excessive water usage are examples of respectively natural and anthropogenic causes of low water availability. An increase in human population, a continued depletion of groundwater and a diminishing water quality impact future water supply. Plenty of water is available on Earth, but only 0.025% of all this water is readily accessible for human consumption. Most water on Earth is not directly useful because the water is too saline, present in the form of snow, ice or vapor, or is located in deep underground aquifers. A large but currently untapped water reservoir is atmospheric water vapor. Utilizing the ubiquitous water vapor is a key element in solving water scarcity as fresh water can be provided at any time and any place. The concept of harvesting water vapor from the air to produce clean fresh water is therefore an imaginative solution to the water scarcity problem.[1,2]

Coping with deteriorating water quality has led to the construction of wastewater treatment plants which has resulted in higher energy demand in the water sector. The latest technology introduced in the water sector is seawater desalination with reverse osmosis (RO), which is again a more energy-intensive option. The implementation of water-from-air techniques falls in line with the continued energy intensification of the water sector. However, the implementation of the popular desiccant-based technology would be a serious deviation from the observed trend. The water phase transitions during desorption and condensation of desiccant technology make this method intrinsically too energy-intensive and the prospects of energy efficiency improvements are constrained by thermodynamic limitations. The same conclusion holds for active cooling, which utilizes mature refrigeration technology. A radical decrease in the energy requirements of water-from-air technology is necessary to bridge the energy gap with conventional liquid water supply methods.[2]

The thermo-responsive hydrophilicity switching (TRHS) polymers concept uses thermo-responsive polymers (TRPs) that release the absorbed water vapor directly in liquid form upon heating, avoiding the energy-intensive desorption and condensation water phase transitions during water production with conventional desiccants. This novel method has the potential to drastically reduce the energy requirements of water-from-air technology. Suitable materials should absorb water at night when it is cooler and relative humidity (RH) high and release it during the daytime at moderate temperatures. In this case, no additional energy other than sunlight is required for water capturing, storage and delivery, the water harvesting cycle of these materials is schematically visualized in Figure 1.2 TRPs are a class of stimuli-responsive or intelligent polymers, that possess the ability to change their physical and/or chemical properties in response to environmental changes in e.g., temperature, pH, mechanical force, and electromagnetic fields. The most extensively studied and best understood stimuli is temperature. The most well-known thermo-responsive polymer is poly(N-isopropylacrylamide) (PNIPAM), because its hydrophilicity switching temperature is around 34°C, which is close to our body temperature, making it an interesting drug delivery vehicle. The polymer chains of thermo-responsive polymers undergo a conformational reorganization when the temperature exceeds the lower critical solution temperature

(LCST), causing the captured water to leak out of the material by the reduction in volume during the reversible polymer chain collapse.[2,3]

Figure 1 provides a visualization of the thermo-response behavior of a water-swollen PNIPAM sample. The polymer which contains absorbed liquid water was heated to 40°C, at which a visible shrinking of the gel and water expulsion from the gel is observed. The minimum amount of water that needs to be absorbed in a PNIPAM hydrogel to enable the expulsion of liquid water at 40°C was determined to be approximately 1 g of water per gram of dried polymer. However, pure freeze-dried PNIPAM only absorbs 0.24 g/g water vapor at 90% RH and 25°C, which is insufficient to harvest liquid water from the polymer by exploiting the thermo-response phenomenon. Hence, the water absorption capacity of the PNIPAM polymer must be enhanced in the vapor phase. In 2019 Zhao et al. published an article reporting their Super Moisture-Absorbing Gel (SMAG), which combines the thermo-responsive PNIPAM with chloride doped poly-pyrrole (PPy-Cl). Their gel absorbs reportedly an astonishing amount of water 3.4 and 6.7 g/g at 60 and 90 % RH, respectively. However, the underlying reason for the extremely large water absorption properties achieved by Zhao et al. cannot be explained by the inclusion of PPy-Cl in the polymer network as this component takes up even less water than PNIPAM. According to their results, PPy-Cl absorbs only 0.19 g/g at 90 % RH which is in line with the measured water absorption of 0.14 g/g at 90% RH of synthesized samples. Reproduction of the SMAG according to their synthesis method, however, only results in water-absorbing capacities of 0.25-0.35 g/g at 90% RH, only a fraction of the reported values which is expected when the separate capacities of the polymers are considered. So far, the reproduction of the results has been unsuccessful, even with the author's consultation, raising questions about the repeatability and robustness of their methods, placing the potential of thermo-responsive polymers as water harvesting from air materials in a renewed perspective.[3]

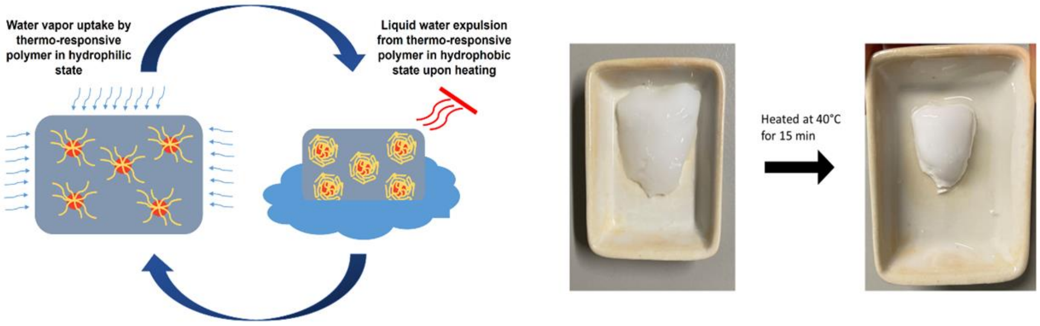

Figure 1: (Left) Water harvesting cycle of a thermo-responsive material. The thermo-responsive hydrophilicity switching material ad(ab)sorbs water vapor at low temperature and releases liquid water by hydrophilicity switching upon heating. (Right) Thermo-responsive reaction of a water swollen PNIPAM sample at 40°C.[2]

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E&E-B09

Artificial Solar Concentrators for Renewable Energy Applications

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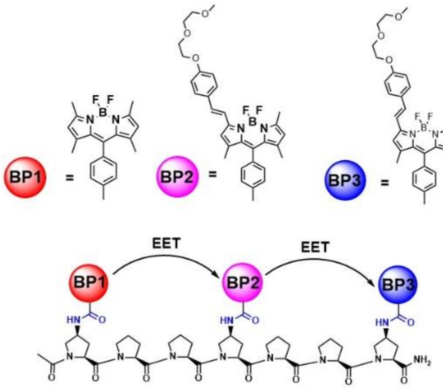
Keywords: /

Photosynthesis is the generic term which is used to describe the disparate ways in which natural organisms convert sunlight into a usable chemical fuel. Interest in natural LHCs has stimulated the growth of artificial analogues in which chromophores have been arranged in a logical sequence likely to assure electronic energy transfer.1,2 Inspired by natural LHCs, several systems mimic assemblies are known based on dendrimers, MOFs and peptides. Oligoproline is a superlative platform to meet such challenges, as it is rigid and has the advantage of controlling secondary structure. The BODIPY subunit has been extensively used as the antenna in artificial photosynthetic systems3. Consequently, linking BODIPY molecules with various chromophores made it possible to synthesise donor/acceptor systems for a variety of applications such as energy transfer cassettes and artificial light harvesting arrays4.

Herein, we presenting a synergistic programme for the design of Artificial Solar Concentrators in which a variety of fluorescent Bodipy dyes are organized on a left-handed proline-II helix in such a way that favourable cascade-type electronic energy transfer (EET) occurs. New donor-acceptor LHCs belongs to the family of BODIPY chromophores linked covalently to oligoproline assemblies via coupling of BODIPY chromophoric subunits contain a terminal proline unit which allows the control of the orientation and distance between chromophores. The newly synthesized dyads were fully characterized. Steady-state measurements of the new LHCs thoroughly studied in DCM revealed good overlap between emission of donor with absorption of acceptor. Efficient (EET) is observed for the new synthesized dyads, which is manifested selective photoexcitation of the donor BODIPY moiety resulted in the quenching of the donor emission followed by the appearance of (acceptor) emission.



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CP&RT-A01

Stepping away from purified solvents in reductive catalytic fractionation, a step forwards towards a disruptive wood biorefinery process

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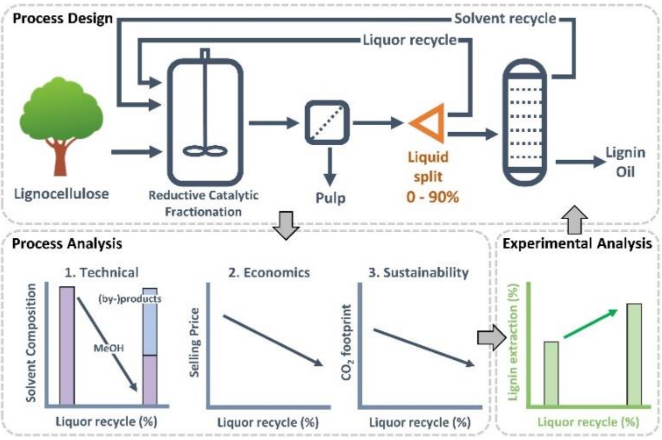
Keywords: reductive catalytic fractionation; process simulation; TEA; LCA

Lignin-first reductive catalytic fractionation (RCF) is an emerging biorefinery technology that successfully converts lignocellulose into useful fractions, including the transformation of lignin into a bio-oil rich in functionalized phenolics. We present here a novel industrial-scale process that achieves to drastically reduce the costs and the CO2 footprint of RCF biorefining through an innovative recycle system, in which the reaction liquor, enriched with lignocellulose-derived components and products viz., (i) methyl acetate, formed by hemicellulose deacetylation, (ii) water, released from the lignocellulose matrix, and (iii) crude lignin oil are partially recycled to the reactor without exhaustive purification of the pristine solvent methanol. This leads to unique solvent mixtures of methanol, methyl acetate, water and the crude lignin oil compared to pure solvent systems (e.g., methanol or methanol/water), commonly used in RCF. A key parameter, the load on the crude oil distillation column for solvent recuperation, was systematically varied in this RCF biorefinery, designed to convert 150 kt wood (on dry basis) per year. The minimum selling price (MSP) and the global warming potential (GWP) of the lignin oil product were then consistently evaluated using techno-economic analysis (TEA) and life cycle assessment (LCA) at varying distillation loads. With a 60 % reduction in both operational and capital expenses, when the load on the distillation column is reduced by 75%, the MSP of the lignin oil decreases from 2500 to 1200 €.t-1. Accordingly, the GWP decreases from 1.25 to 0.9 kgCO2.kg-1 as emissions associated with fuel consumption are limited. These model results were verified in lab-scale experiments that reflect the simulated reaction conditions. RCF with a solvent system comprising methanol, methyl acetate, water and crude lignin oil enhances the lignin extraction, stimulates hemicellulose co-extraction and produces novel lignin oil phenolics by partially acetylation of propanol sidechains. A parameter study of the reaction time and temperature showed that the lignin oil MSP and GWP can further diminish to 650 €.t-1 and 0.8 kgCO2.kg-1, respectively, when the reaction time is halved, from 2 to 1 h as the capital expenses for the large-volume reactors are drastically cut thereby, covering minimal losses in lignin oil revenues.


Process Design
Solvent recycle
Liquor recycle
Lignocellulose
Reductive Catalytic Fractionation
Pulp
Liquid split 0 - 90%
Lignin Oil
Process Analysis
1. Technical
Solvent Composition
(by-)products
MeOH
Liquor recycle (%)
2. Economics
Selling Price
Liquor recycle (%)
3. Sustainability
CO2 footprint
Liquor recycle (%)
Experimental Analysis
Lignin extraction (%)
Liquor recycle (%)

CP&RT-A02
Understanding the kinetics of 2,3-butanediol dehydration into 1,3-butadiene via kinetic modeling

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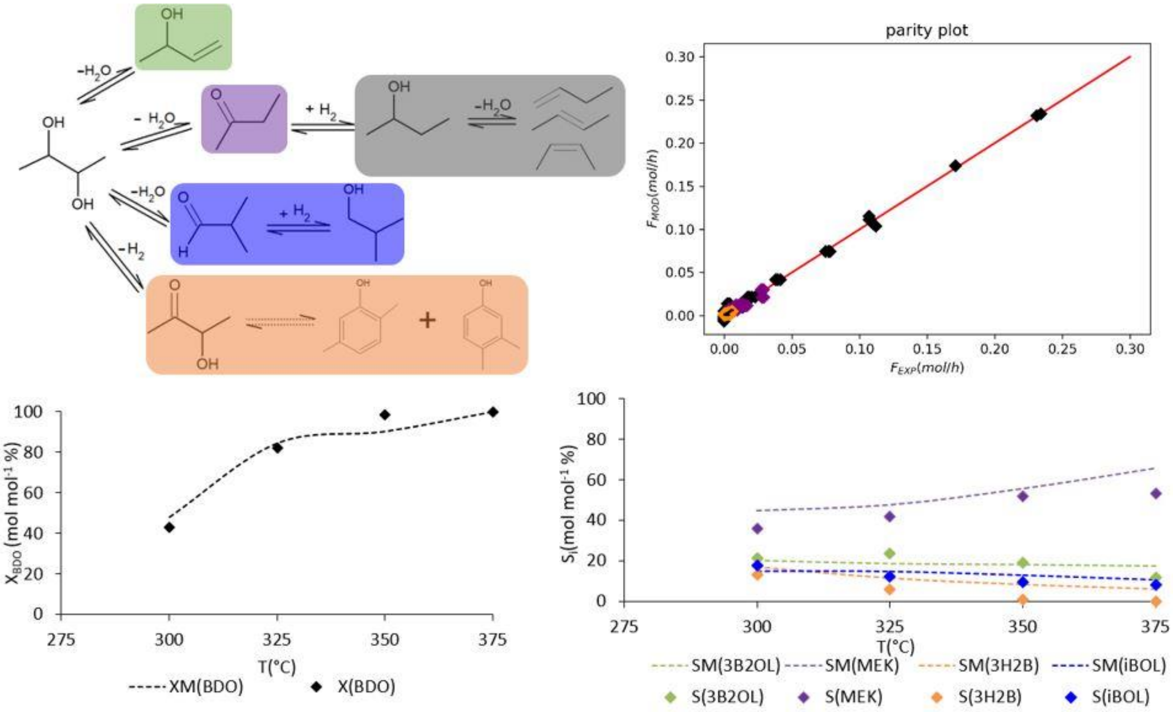
Keywords: bio-based feedstock; green BD production; ZrO2; kinetic modeling

The selective dehydration of 2,3-butanediol (BDO) is currently being investigated as a potential renewable route for green 1,3-butadiene (BD) production [1]. The BDO conversion towards BD comprises two consecutive dehydrations, with 3-buten-2-ol (3B2OL) as intermediate. The 1st dehydration is the crucial one, as it may not only lead to the desired intermediate but also to the stable methyl ethyl ketone [2]. Consequently, optimizing the first step is critical for maximal BD formation. ZrO2 is a unique metal oxide that has the essential acid-base concerted sites to catalyze the formation of 3B2OL via 1,2 elimination [1]. Using the so-called hydrothermal synthesis method, it is possible to maximize the acid-base concerted sites of adequate strength on a ZrO2 surface, resulting in a 3B2OL selectivity up to 42% (mol/mol). A fundamental understanding of the reactions occurring over the acid-base concerted sites of the ZrO2 catalyst surface via kinetic modeling will allow better catalyst design and identification of optimal operating conditions.

A systematic set of experiments were performed in a wide range of operating conditions in absence of transport limitations in a Berty reactor, allowing to determine the effect of temperature (300 - 375°C), space time (28 1130 kg.s/mol), inert-to-feed ratio (1 - 8 mol/mol) at a total pressure of 10 bar. The parameters constituting the Langmuir-Hinshelwood Hougen-Watson type kinetic model are determined via regression to the experimental data using the commercially available Athena Visual Studio software. The resulting model is globally significant, with an F-value above 1000, greatly exceeding the tabulated one of 4; all the parameters are statistically significant, and the multiple correlation coefficient, R squared amounted to 0.99. The kinetic model construction resulted in a clear understanding of the reaction network, in particular with respect to the adsorption of BDO on the acid and acid-base concerted sites. These differences in adsorption configuration of BDO for 3B2OL and MEK formation were represented by differences in adsorption enthalpies. Estimation of these adsorption enthalpies for the formation of MEK and 3B2OL amounted to -123 kJ/mol and -174 kJ/mol respectively, indicating the critical need to tune the adsorption properties of the catalyst. Furthermore, the model reproduces the experimental data well, capturing important trends such as the increase in selectivity towards 3B2OL with decreasing reaction temperature and increasing space-time. This is attributed to the enhancement of BDO adsorption on those acid-base concerted sites facilitating the formation of 3B2OL at lower temperature given the higher adsorption enthalpy.



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CP&RT-A03
Power-2-Olefins: supersonic olefin production

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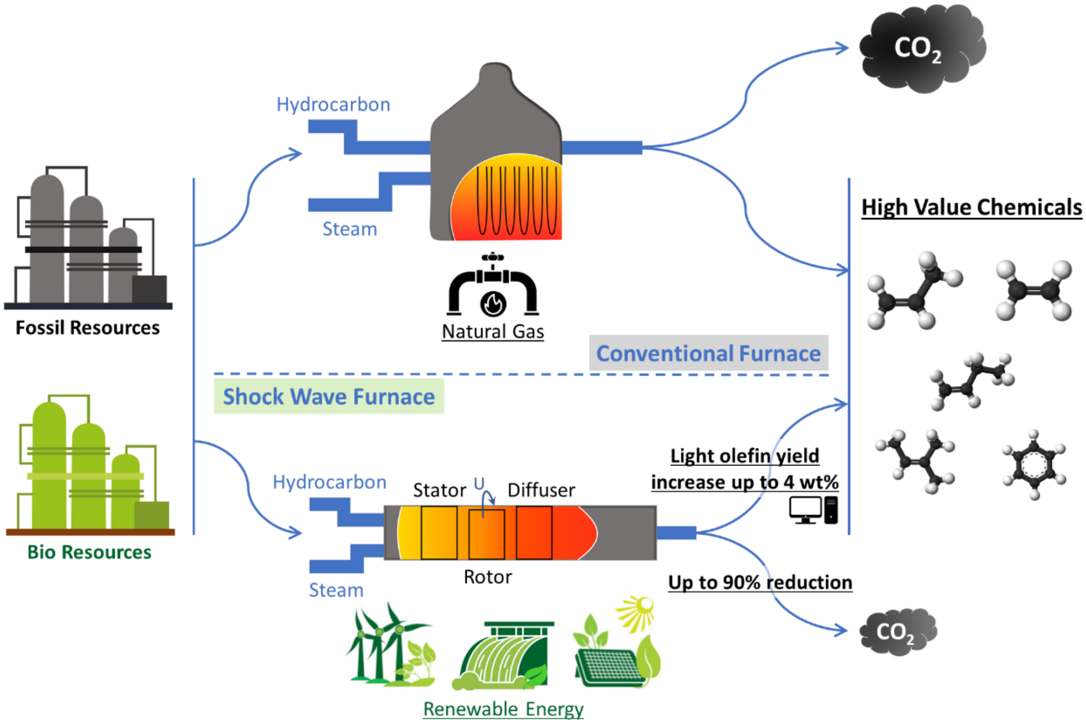
Keywords: Power-2-Heat; Sustainable Olefin Production; Reactor Simulations; Computational Fluid Dynamics; Turbomachinery

Our world is facing huge challenges. Climate change, a problem created by people that goes far beyond national borders, requires a coordinated solution with drastic mindset changes at all levels of our current society. It is, therefore, undebatable that the current worldwide society requires an economic vision wherein renewable energy and circularity thrive. In this respect, an essential and crucial role is reserved for the chemical industry provided that it becomes CO2-neutral. Electrification of the (chemical) process industry offers a solution if combined with the usage of renewable and/or recycled raw materials and carbon capture utilization and/or storage. This transition would, however, require massive quantities of cheap net zero-carbon electricity. Nevertheless, this prerequisite alone is not sufficient to shift from conventional to electrified processes. Current chemical plants are not designed for swift integration of electricity. Yet, electrification does offer an opportunity to completely reinvent -often outdated- production processes to enhance energy efficiency and product yield and thus profit margins [1].

In this respect, a turbomachine-like reactor design -originally developed by Vladimir Andreevich Bushuev in 1998 [2]- has been computationally assessed focusing on the production of light olefins. In this design, the inlet and outlet are connected with a vaneless spaced duct in which multiple stages are positioned. A stage comprises a stator followed by a rotor and a diffuser. By utilizing high-speed rotation, the reactor provides the required kinetic energy -reaching supersonic levels- to the fluid, which is subsequently transformed into heat upon the reduction of flow velocity (i.e. subsonic velocities in the vaneless space) in the diffuser cascade. Specifically, this movement generates stationary shockwaves across which the flow decelerates from supersonic to subsonic velocities over a very small length (a few micrometers). Hence, velocity is being traded for enthalpy, resulting in heating times for shock-heated gases in the order of nanoseconds. Behind the diffuser cascade, a vaneless space is situated where residence time, turbulence, and temperature are sufficiently large for the chemical reactions to take place. After this vaneless space, another stage is implemented and the process repeats itself until the desired conversion is reached within a continuous process.

As a proof of concept, 0D/1D reactor models have been developed in the open-source software Cantera [3] to assess the potential of turbomachine-like reactors and to compare it to the potential of conventional Millisecond furnaces. Additionally, 3D non-reactive steady-state simulations were performed to provide the established 0D/1D reactor models with more accurate temperature, pressure, and residence time distribution profiles for improved yield predictions. The results have shown that this turbomachine-like reactor design, compared to a conventional Millisecond furnace, could enhance the propylene and ethylene yields up to 4 wt%.



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CP&RT-A04

Plasma Catalytic Dry Reforming of Methane: How Material Properties Influence Conversion and Kinetics – The PlasMaCatDESIGN Project

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Keywords: non-thermal plasma; DRM; plasma catalysis; CO2 Utilization

Although much research is being conducted on plasma-assisted heterogeneously catalysed CO2 conversion and some general concepts and literature data are available, systematic and detailed knowledge of the impact of material properties with respect to catalytic control (efficiency, space time yield and selectivity) in the plasma is currently insufficient.[1] Recent literature is starting to fill in some gaps through detailed catalyst characterization [2-4], but the study of the impact of material properties on the kinetics of the overall CO2 conversion reactions are often missing In the PlasMaCatDESIGN project, we aim to study material-activity correlations through controlled and systematic catalyst synthesis and detailed characterization, not only linking reagent conversion and product selectivity/yield, but also reaction kinetics, to catalyst properties. This knowledge is necessary to allow crucially needed knowledge-based catalyst design.

An essential part of this project is thus the systematic and controlled synthesis of catalytic materials, structured at different length scales (from macro to nano). These materials are thoroughly characterized using typical methods, e.g., XRD, N2-sorption, SEM(-EDX), TGA-MS, NH3-TPD, CO2-TPD, CH4-TPD, DRIFTS and Raman, before and after plasma catalysis. For plasma catalysis, less common methods such as Hg intrusion porosimetry, TPO-MS, TPR-MS, and cyclic TPR-TPO/TPO-TPR are also employed.

A coaxial dielectric barrier discharge (DBD) reactor is employed to perform the plasma catalytic conversion of CH4 and CO2 (known as dry reforming of methane; DRM). It is the simple geometry of a coaxial DBD set-up that allows for use of catalysts in the plasma discharge. The plasma catalytic process is studied using a GC to study conversion and selectivity/yield, thermocouples are inserted before and after the plasma to measure the overall gas temperature and several electrical components are used to evaluate the plasma power, current, Lissajous figure shape, number of discharges per half cycle and the transported charge per discharge in function of the applied voltage and AC frequency.[5] Results show a clear impact of the catalytic element applied. Both positive and negative impact on conversion, selectivity and kinetics have been obtained via deposition of different active elements.

Acknowledgements

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CP&RT-A05

Effect of quenching on the afterglow temperature to improve CO2 conversion in a rotating gliding arc plasma reactor

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Keywords: plasma CO2 conversion; afterglow gas cooling; quenching nozzle; extra gas inlet; modelling

Due to global warming, there is a large interest in lowering the concentration of CO2 in the atmosphere. This can be achieved by capturing the CO2 and storing it (Carbon Capture and Storage, CCS), but a more interesting approach is to use the captured CO2 to create fuels and chemicals (Carbon Capture and Utilization, CCU). A promising way to do this is by the use of plasma, which has important advantages over other CO2 conversion techniques, e.g. it does not require any rare earth metals, the plasma can be created using renewable electricity and it can instantly be switched on and off [1]. The aim in plasma conversion of CO2 is to simultaneously obtain a high conversion and a high energy efficiency, which is why different methods to increase both are being investigated. One way to do this is by quenching in the afterglow, i.e. immediately cooling down the gas after the plasma reactor. This will limit the recombination of CO and O2 molecules back into CO2, which lowers both the conversion and the energy efficiency. It has already been shown through simulations that quenching the gas in the afterglow can improve the results [2], and experiments in a microwave reactor and a thermal plasma reactor have also reported better conversions or energy efficiencies [3,4]. In this research, we investigate the effect of quenching in a rotating gliding arc (RGA) reactor. This type of reactor creates a warm plasma, causing dissociation of CO2 mainly by thermal reactions, it can operate at atmospheric pressure and, in contrast to a classical gliding arc reactor, it has a 3D geometry, enabling more gas to pass through the discharge zone.

To investigate the effect of quenching in the afterglow, we created a thermal model of an RGA reactor. In this model, we assumed that the plasma is in local thermodynamic equilibrium, we mimicked the plasma by a heat source and at this stage we included no reactions in order to keep the model as simple as possible, while still obtaining valuable insights. There are different methods of cooling the afterglow, two of which we tested in our RGA model: the use of a quenching nozzle and the addition of an extra gas inlet after the reactor that supplies room temperature gas. We investigated two nozzles that have a different smallest diameter, 1 mm and 2 mm, and an extra inlet at two different positions in the afterglow. For both the nozzle and the extra inlet, we varied the power of the heat source and the gas flow rate and looked at the effect they have on the temperature drop. We found that the gas cools down for both quenching methods compared to the temperature in the reactor when no cooling is present and that the smallest nozzle gives the best cooling results for every simulated power and flow rate. In further research we hope to experimentally validate these results.

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CP&RT-A06
Fully biobased-triblock copolymers generated using an unconventional oscillatory plug flow reactor

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Keywords: Polymerization; flow reactor; block copolymers; oscillatory plug flow

Producing polymers in continuous flow offers significant advantages in terms of efficiency, scalability, and safety. Using conventional tubular flow reactors to synthesize polymers comes with some challenges, especially related to maintaining narrow residence time distributions (RTD) when operating with viscous fluids. Laminar flow is typically observed in tubes with restricted dimensions, and significant wall effects result in the broadening of the molar mass distributions. We envisioned that such a limitation can be overcome by the use of an oscillatory flow reactor (OFR). This work describes the use of a novel plate-type OFR to improve continuous-flow polymerization reactions for the first time. The reactor plate is equipped with millimeter-scale cubic pillars, and when combined with a superimposed oscillatory flow regime, pro- motes turbulent flow to circumvent detrimental wall effects during polymerizations. Additionally, the pulsatile flow intensifies mixing, and careful tuning of the pulsation amplitude and frequency lead to improved (i.e., narrowed) residence time distributions, a crucial parameter when synthesizing complex block polymer scaffolds in continuous flow. This innovative principle of implementing OFRs for improved continuous polymerization reaction is demonstrated with the benchmark ring-opening polymerization of lactide, a well-known renewable monomer. Thorough characterization using the reactor system reveals the relationships between process conditions and molecular attributes, including target molar mass and dispersity (Đ). Further, the OFR enabled the streamlined preparation of a series of block polymers with variable composition and low dispersity in a single experiment by judiciously adjusting the independent inlet feed rates. Finally, the OFR system allows for simple scaling without affecting the critical process parameters. As a result, a multi-gram synthetic protocol was achieved employing a biobased hydroxyl telechelic poly(β-farnesene) macroinitiator in the ring-opening polymerization of lactide to generate fully renewable ABA-type triblock copolymers.

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CP&RT-A07
A microfluidic batch reactor for quiescent multiphase paracetamol crystallization

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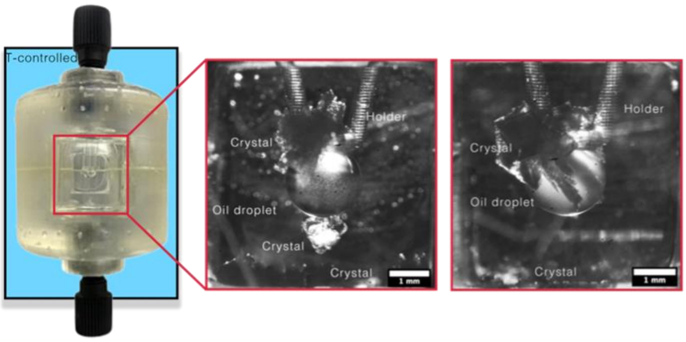
[1] *KU Leuven, Belgium*

Keywords: Microfluidic; multiphase; crystallization; quiescent

The presence of a liquid-liquid interface in a chemical reactor can accelerate the reaction or crystallization kinetics, increase the yields and make new pathways possible. Microfluidic reactors offer extreme control by confining the solution in a small volume. We present a temperature-controlled platform consisting of six 3D-printed microfluidic batch reactors (V=1.5mL each) for multiphase crystallization in quiescent conditions. The batch reactor has a holder which descends into the solution which is used to keep an oil droplet in place. The onset of crystallization is monitored in situ using a camera installed on a motorized rail, with a size detection limit of approximately 100µm and a temporal resolution of 2min20s.

The mean induction time for nucleation in the presence of the oil droplet interface is 17.8±6.5h. Nucleation was expected to occur on the liquid-liquid interface, but in approximately 60% of the experiments nucleation started on the holder and in 30% on the bottom of the crystallizer. This is surprising, considering that the holder is printed in the same material and thus has the same roughness as the rest of the crystallizer. Shortly after (<0.5h) detection of the first crystal, crystals in other locations were detected, occasionally on the droplet's interface. Our results suggest that multiple nucleation events took place in short succession, even though there was no active mixing in the solution. This is in contradiction with the single nucleus mechanism hypothesis, which predicts that nucleation and growth of a single large crystal is the first step in the nucleation process.Although the first crystal did not nucleate on the solution-oil interface, the presence of the oil droplet did significantly decrease the mean induction time. For experiments without droplet, nucleation only occurred in approximately 15% of the experiments before 48h. Also in those experiments multiple crystals were detected in close succession.

Our results show that the presence of a heterogeneous interface increases nucleation rates, even when the interface itself does not serve as a nucleation site. The mechanism behind this peculiar observation is yet to be explored. In addition, the occurrence of multiple nucleation events in close succession, in the absence of active mixing, suggests that the first nucleation event may cause a relaxation effect in the solution which catalyzes nucleation.



CP&RT-A08
Ultrasensitive Turn-on Luminescence Humidity Sensor Based on a Perovskite/Zeolite Composite

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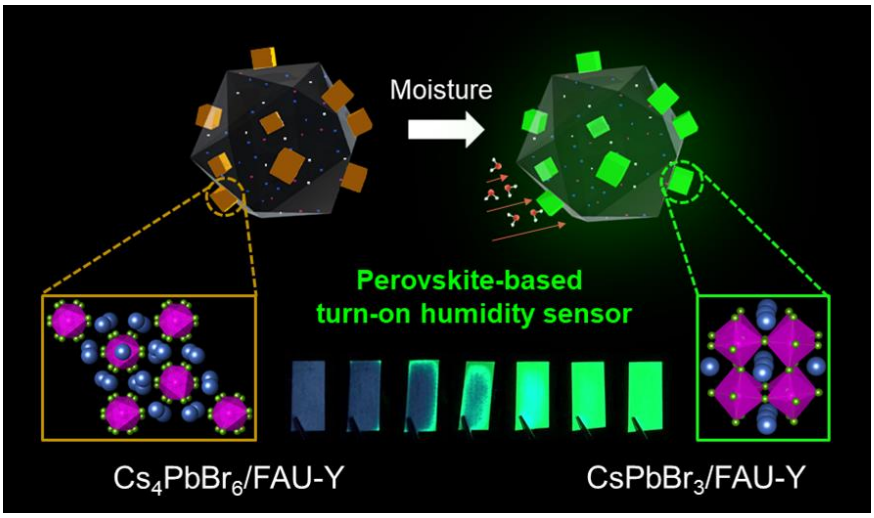
Keywords: turn-on humidity sensor; perovskite; high sensitivity

Recently, the detection and quantification of humidity have attracted great interest, but for fluorescence sensing of humidity, it is still a challenge to achieve high performance. [1,2] Here, we report an ultrasensitive and high-performing luminescence humidity sensor based on perovskite/zeolite composite, Cs4PbBr6/FAU-Y. The zeolite FAU-Y acts as a support for dispersing amorphous Cs4PbBr6 nanoparticles (11 ± 2 nm), which rapidly undergo a moisture-mediated transformation into a highly luminescent CsPbBr3 perovskite, due to the hydrophilic nature of the zeolite substrate. The composite exhibits strong fluorescence response ((I-I0)/I0) (992 for 98% RH, 91.7 for 7% RH), good linearity and low detection limit (0.56% RH) while producing highly reproducible and stable optical signals. Test paper embedded with the moisture-sensitive composite yields a simple and reliable naked-eye method for detecting moisture exposure within anhydrous products and dry storage environments. This work showcases a unique concept to develop turn-on humidity sensors based on the bright metal halide perovskite luminescence, thus promoting innovative practical applications outside their typical scope of applications such as solar cells, photodetectors, or light emitting diodes (LEDs).



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CP&RT-A09
Mesoscale reaction-diffusion modelling of lignin solvolysis

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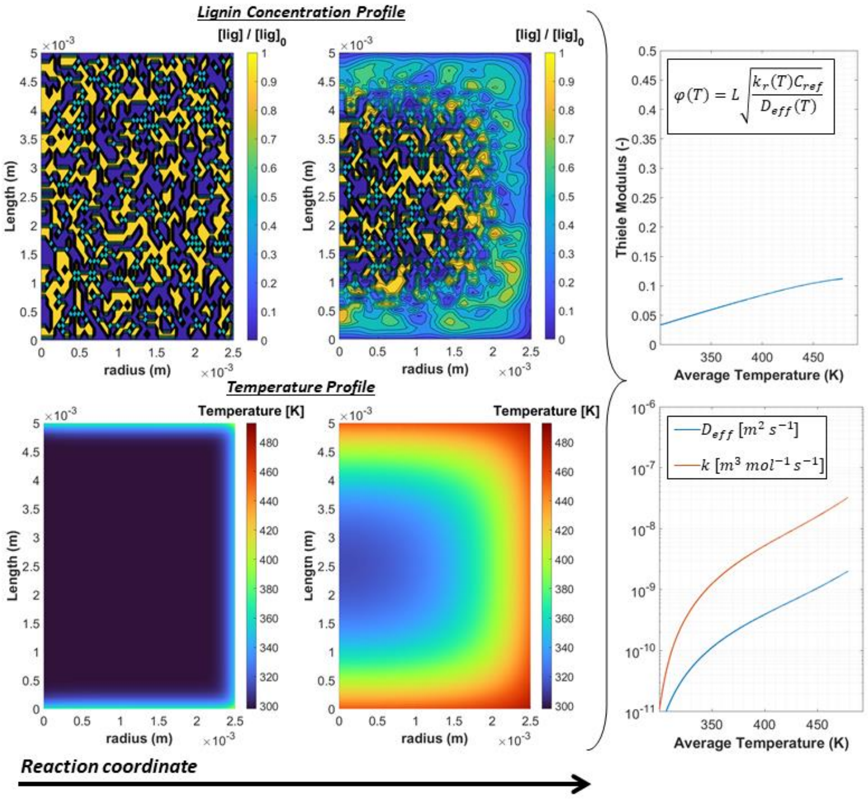
Keywords: Lignin Solvolysis; Intrinsic Kinetics

Lignin is a complex and abundant bio-polymer that represents the largest source of renewable aromatics on earth, as it comprises 15-25 wt. % of lignocellulosic biomass. Lignin extraction from the plant cell wall via solvolytic transformations is a critical first step for further lignin valorization, e.g. via Reductive Catalytic Fractionation (RCF), where the whole biomass is used as feedstock. Determining the intrinsic kinetics of lignin solvolysis is challenging since transport phenomena competes on similar time scales and governs the effective rates of delignification. Mesoscale modelling to study lignin solvolysis has been recently reported in literature, where the particle domain is represented either by a simplified approach (1D) [1] or using more complex 3D representations of the biomass [2-3]. On the one hand, 1D modelling is not capable of capturing the anisotropy effect and geometries are oversimplified, thus minimizing the computational effort at the expense of reducing the fundamental understanding of the underlying phenomena. On the other hand, 3D modelling provides a more realistic and detailed description of the particle domain at the expense of higher computational costs and their formulation are rather case-specific, which makes them not easily applicable to different biomass types. For instance, an advance characterization of the biomass tissue microstructure is required to recreate the complex solid domain in 3D, which is specific for each case-study.

This work presents a comprehensive mesoscale reaction-diffusion model which, based on Darcy's law and Fick's second law, describes the solvolytic extraction of lignin from the lignocellulosic biomass, assuming uniformly distributed pores. The resulting set of partial differential equations are numerically solved via finite difference approximations in a computationally less demanding 2D domain, which represents the symmetry plane along the axial coordinate of a cylindrical biomass pellet. Pseudo-second order kinetics based on a specific lignin species is assumed to describe the solvolytic extraction of lignin from the biomass, and effective rates of delignification are calculated using apparent kinetic data extracted from literature [1-2]. Therefore, the lignin fraction in the biomass is assumed to be constituted by repeating units of a single lignin species used as a reference to quantify the degree of delignification. This hypothesis enables the estimation of the effective diffusivity through the porous media using the well-established Stokes-Einstein equation. Moreover, external mass and heat transfer coefficients are calculated via robust correlations [4-5]. The solvent environment plays an important role for the diffusion of lignin fragments, as the polymer extension can be correlated with the solvent characteristics, e.g. polarity, through power law relationships according to the Flory theory [6]. The use of process simulators, e.g. ASPEN Plus, enables the acquisition of reliable thermochemistry data of the solvent environment when non-idealities play an important role, such as in highly concentrated polar solvents. The different regimes of lignin solvolysis, i.e. kinetically-limited, intermediate and diffusion-limited regime, can be quantitatively identified via the Thiele modulus (φ). To this end, the reaction-diffusion model presented in this work has been developed to simulate the solvolytic extraction of lignin of various biomass feedstocks (hardwood, softwood and herbaceous) under different solvent environments, aiming to identified the conditions to extract transport-independent kinetic data from experiments. Figure 1 illustrates the effect of particle size in the extent of delignification and the regime type at which solvolysis occurs, being based on the kinetic data of hardwood delignification reported elsewhere [3]. Accordingly, solvolysis proceeds under a kinetically-limited regime for small-scale particles, i.e. smaller than 1 mm length.



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CP&RT-B01
Dispersing Carbomers, Mixing Technology Matters!

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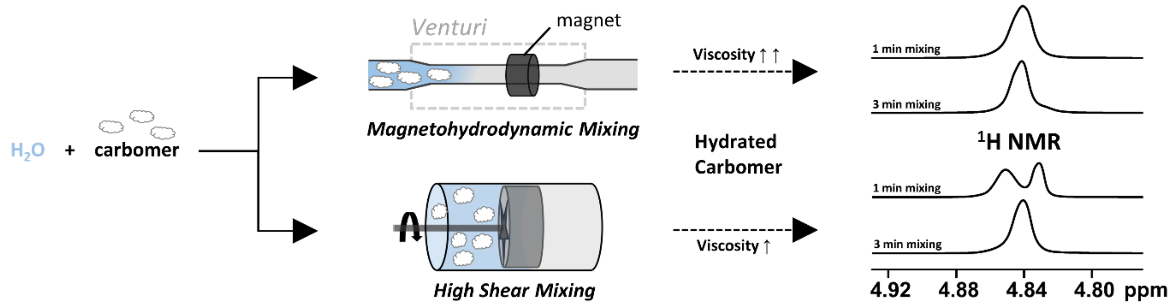
Keywords: Carbomer hydration; carbomer hydrogel preparation; high shear mixing; magneto-hydrodynamic mixing; nuclear magnetic resonance spectroscopy

Polymer based hydrogels are widely applied in the cosmetic, pharmaceutical, paint, and food industries. Their unique visco-elastic properties and low toxicity renders them very attractive as thickening, suspending, dispersing, and stabilizing agents [1]. Carbomer hydrogels, in particular, have come in high demand since the start of the COVID-19 pandemic as they are often used for preparing hand sanitizing hydro-alcoholic gels. Hydrogels are typically prepared by using high shear mixers to mix the carbomer powder with water and an alkaline neutralizing agent, such as amines [2,3]. High shear mixers (HSM) are not only energy-intensive, the applied shear can also physically and chemically damage the hydrated polymer chains, resulting in a permanent viscosity loss [3]. This work explores magneto-hydrodynamic (MHD) mixing as a radical new approach for preparing high viscosity carbomer dispersions. The MHD mixing principle is based on the application of a magnetic field on a fluid stream flowing in a turbulent flow regime [4]. Experimental observations revealed that the magnetic field is responsible for additional shear, electrostatic, tensile and oscillatory forces. Pairing of turbulent flow with electromagnetic forces creates powerful conditions for dispersing powders, enhancing fragmentation, de-agglomeration, hydration and solubilization [4]. Using MHD mixing, carbomer dispersions with higher viscosity and increased storage modulus were obtained compared to conventional HSM. 1H NMR spectroscopy demonstrated this to be induced by a different water distribution, accompanied by lower ionization and higher degradation of the polymer in case of high shear mixing [5]. Subsequent neutralization of the carbomer dispersion with triethanolamine (TEA) enabled to adjust the pH of the mixture and tune the viscosity of the hydrogel. Using HSM, the TEA concentration was limited to 0.2 wt.% TEA as the gel became too viscous, i.e. 6,800 mPa·s, and the flow dropped from 12 to 0.3 m3/h. MHD mixing on the other hand enabled to reach TEA concentrations up to 1.0 wt.%, with viscosities in excess of 16,520 mPa·s, while operating at a steady flow of 7.8 m3/h. In general, hydrogels prepared with HSM exhibited a lower viscosity than comparable samples prepared with MHD. 1H NMR allowed to rationalize the difference in performance the degradation of the added TEA and additional damage to the carbomer backbone in the case of HSM. The choice for magneto-hydrodynamic mixing over other conventional mixing methods might also be beneficial in other application areas and therefore merits further exploration.



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CP&RT-B02
Investigation of dynamical aspects of molecular self-assembly and polymorphism on graphene using Raman spectroscopy

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Keywords: self-assembly; dynamical; polymorphism

Self-assembly at the liquid-solid interface is a highly dynamic process that typically proceeds via three distinct stages: slow nucleation is followed by rapid growth and eventually slow ripening.[1] The formation of an organic self-assembled molecular network (SAMN) on solid support holds great potential for the bottom-up fabrication of nanomaterials. To achieve a desirable SAMN structure, many experimental variables have been described, such as temperature, concentration, and solvent. However, it is still difficult to predict and control the structures because a thorough understanding of the thermodynamics and kinetics of the assembly process is missing. Herein, Raman spectroscopy has been used to study the dynamical self-assembly of 1,12-diaminododecane (DAD) at the graphene/ tetradecane interface. Since the adsorption of DAD causes n-type doping of graphene [2], we reasoned that changes in the G-peak position [Pos(G)] of graphene exposed to the solution of DAD will allow us to investigate the dynamical aspects of the self-assembly process. We observed some time-dependent changes in the position of the G peak of graphene and discuss potential reasons for the observed changes.

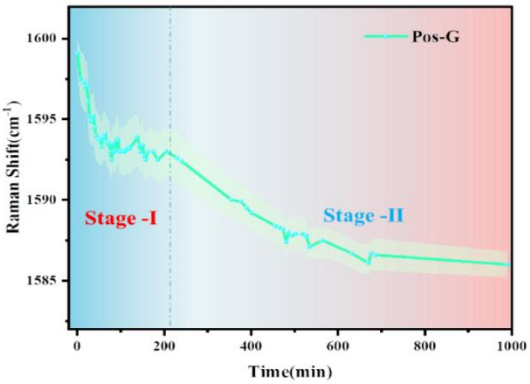

Figure 1. (a) Plots of Pos(G) versus time. These plots suggest that variation in the doping behavior as a function of time under liquid\solid interface.

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CP&RT-B03
Dehydration of biomass-derived butanediols into green 1,3-butadiene: Single-Event MicroKinetic model construction and process design

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Keywords: Single-Event MicroKinetic modeling; process design; 1,3-butanediol dehydration; 1,3-butadiene

1,3-Butadiene (BD) is a key building block for the polymer industry and is currently mainly produced as a by-product of the energy-intensive steam cracking. As there is a tendency to move towards lighter steam cracking feedstocks (e.g., ethane instead of heavier naphtha), less BD is produced through the latter process and novel production processes are needed to meet the increasing BD demand. Moreover, the steam cracking process generates more than one ton of CO2 per ton of BD. [1]

Contemporary research therefore pursues the development of sustainable on-purpose BD production which rely on biomass(-derived) feedstocks such as butanediols. 1,3-butanediol (13BDO) is of particular interest as it does not compete in other processes while it is readily available from the bio-catalytic hydrolysis of 2nd generation biomass resources such as paper waste. [2]

As shown in Figure 1, the experimentally observed chemo-catalytic dehydration kinetics of 13BDO into BD can be reproduced by a single-event microkinetic (SEMK) model [3]. In agreement with the observations of Lee et al. [4], 13BDO readily dehydrates into a mixture of three buten-ol species with 3-buten-1-ol as the major isomer. Upon full conversion of 13BDO, the dehydration of these isomers then yields BD. Side-product formation was accurately accounted for through the catalytic cracking of 3-buten-1-ol and the isomerization of 3-buten-2-ol into propylene (and formaldehyde) and methyl-ethyl-ketone respectively.

Due to its fundamental nature, the SEMK model's applicability extends to operating conditions well beyond the parameter space from which the model parameters were determined. As such, the model can pin-point optimal operating conditions and guide the overall process design when imbedded into a process simulator. As we will show in this presentation, these are key advantages when developing an economically viable green BD process.

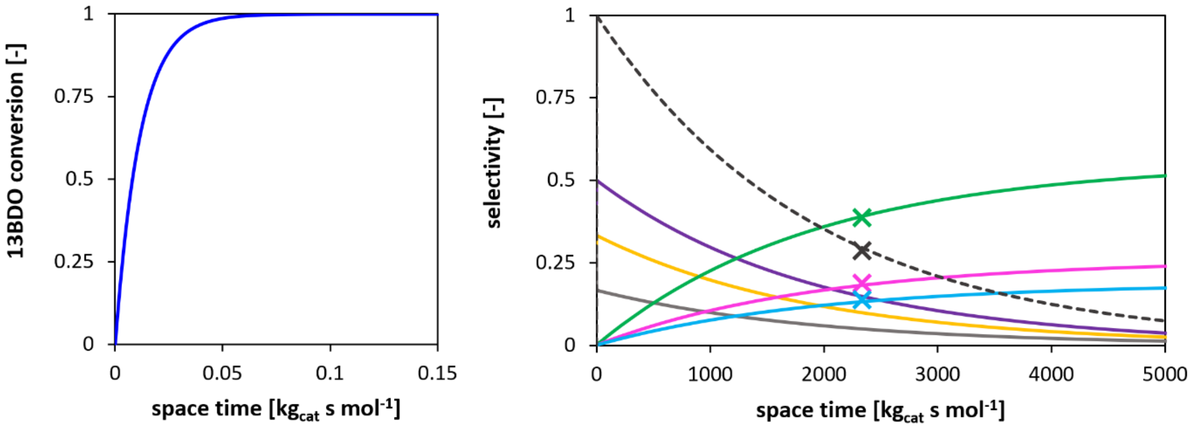

Figure 1: conversion profile of 13BDO (left, —) and selectivity profiles (right, at full 13BDO conversion) of 1,3-butadiene (—), methyl-ethyl-ketone (—), propylene (—), 3-butene-1-ol (—), 2-buten-1-ol (—), 3-buten-2-ol (—) and the sum of the buten-ol selectivities (– –) as a function of space time at T = 573 K and p_{tot} = 1 atm. The experimentally detected (mixture of) species at a space time of 2.3 10^3 kg_{cat} s mol^{-1} as reported by Lee *et al.*[4] are also shown (×).

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CP&RT-B04
Catalytic materials for CO2 conversion to heavier hydrocarbons

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Keywords: carbon dioxide; catalysis; hydrocarbons

The global energy and climate crisis have raised the demand of new alternatives to produce green fuels, especially for transport where electrification is hard (e.g. aviation). Paraffins produced directly from CO2 hydrogenation in a one step reaction is an attractive way to obtain carbon-neutral fuels.

Methanol production from syngas and methanol conversion to gasoline are two well-studied procedures but replacing syngas with CO2 and converting it to a specific range of paraffinic hydrocarbons (methanol-intermediated) has not yet been examined to a great extent. Literature study shows results on a preliminary level, especially when targeting longer alkanes. Those recent advances in catalytic materials indicate that beta zeolite enhanced with Cu or Zn is a very efficient way for methanol conversion to hydrocarbons. In addition, In and Co in combination with beta zeolite result in high selectivity to C4-C7 isoparaffins for the direct CO2 to hydrocarbons reaction. We aim to investigate the role of different zeolites (different pore size or framework) on the products distribution while targeting even longer hydrocarbons. The first experiments are being conducted. The goal is to enhance both the conversion of CO2 and the selectivity and study the pathways that occurring, such as oligomerization.

With this poster we are targeting a presentation of the state of the art on this one-step process based on literature, in combination with some experimental results based on our screening of innovative materials supported on different zeolites, especially with large pores, to allow hydrocarbon chain growth.

CP&RT-B05

The synthesis and characterization of magnetic microwave absorbers for microwave-assisted pyrolysis

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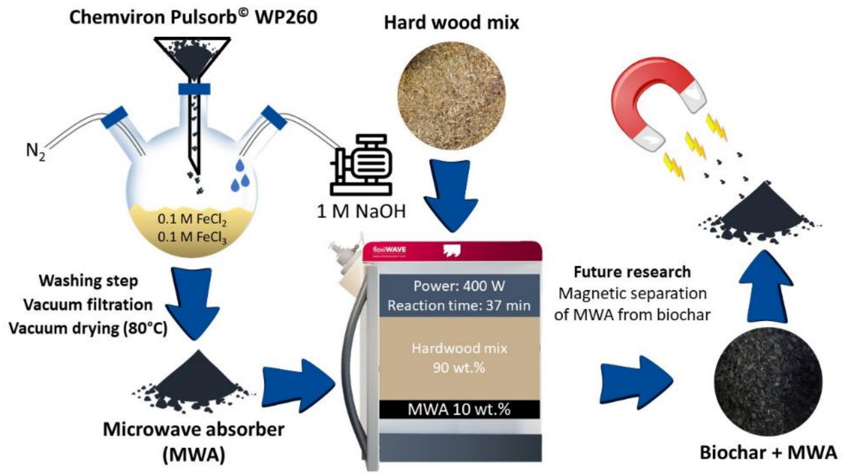
Keywords: magnetic activated carbon; microwave absorber; pyrolysis; biochar; hardwood

Microwave absorbers (MWAs) are materials with the capability to convert microwaves into heating energy due to their high dielectric permittivity and/or magnetic permeability. Due to these properties, these materials are able to generate heat from microwave energy upon absorption. In this study, various microwave absorbers were used for microwave-assisted pyrolysis of hardwood. The microwave absorbers used in this study originated from commercial activated carbon (Chemviron's pulsorb WP260 AC) and were modified through magnetite (Fe3O4) addition. Three variables (magnetite addition level: 5 and 20 wt.%, addition method: in-situ co-precipitation and physical blending and washing agent: water and ethanol/water) were tested. The resulting microwave absorbers were evaluated on the pyrolysis performance of hardwood in a Milestone Flexiwave microwave reactor (Power: 400 W; Residence time: 37 min; Pressure: 100 – 500 mbar; Total reactor loading: 20 g) with 10 wt.% MWA addition. The biochar yield varied from 24 wt.% and 89 wt.% and seemed to be significantly influenced by the synthesis method rather than Fe3O4 level. The microwave absorbers with physically blended Fe3O4 resulted in the best pyrolysis performance. All other modified MWAs performed less than the original commercial WP260 AC sample. The resulting biochars from the experiments with physically blended Fe3O4 WP260 and WP260 were characterized by elemental composition (C,H,N,S,O and ash content) after physical separation from the MWA. Furthermore, the concentration of 16 priority polycyclic aromatic hydrocarbons (PAHs) in the selected biochars were evaluated. The results suggest that physical Fe3O4 blending seems to cause a reduction of total PAHs content, mainly by reduction of the pyrene content in the biochar. Future experiments will involve the study concerning the possibility of magnetic separation of the MWA from the produced biochar. This will provide us more possibilities when scaling up the microwave-assisted pyrolysis process.



CP&RT-B06

Pulse Gas Chromatography Study of Light Olefin and Paraffin Adsorption

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Keywords: Light hydrocarbons; Metal-organic frameworks; Inverse gas chromatography; Selectivity

The separation of the light olefin and paraffin mixtures is one of the energy-intensive and expensive processes in the industry. More efficient olefin/paraffin separation processes could contribute to the reduction of carbon footprint in the chemical industry [1-3]. Alternative separation methods that allow lower energy consumption are adsorption and membrane-based processes. In particular, mixed-matrix membrane-based processes (MMM) allow for good tuning of permeability and selectivity, due to a combination of kinetic and equilibrium effects in polymer matrix and embedded porous solid particles [4]. It is widely reported that MMM filled by metal-organic frameworks (MOFs) can selectively separate olefins from paraffins [5,6]. In order to design an efficient MMM, understanding the separation performance of membrane constituents is highly beneficial. In this work, we used inverse gas chromatography (IGC) as a facile method to estimate adsorption thermodynamics parameters (i.e. Henry constants and isosteric heats of adsorption of C2/C3 olefins and paraffins over ZIF-8 and MOF-808 samples. The Henry constants demonstrate that ZIF-8 is a paraffin-selective adsorbent, but with rather low thermodynamic selectivities. On the other hand, MOF-808 has a different behavior. In addition, the van ‘t Hoff plots confirmed the good linearity and reliability of the measured data.

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CP&RT-B07

Computational Fluid Dynamics assisted reactive distillation design for the energy efficient dehydrogenation of Liquid Organic Hydrogen Carriers

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Keywords: Liquid Organic Hydrogen Carrier (LOHC); Reactive Distillation (RD); Computational Fluid Dynamics (CFD); Multiphase Counter-current Flow; Unstructured Packed Bed; OpenFOAM

The main impediment to the commercial deployment of Liquid Organic Hydrogen Carrier (LOHC) is the significant heat requirements at high temperatures (300 °C) for H2 release. However, by decreasing the dehydrogenation pressure, it is possible to operate at temperatures as low as 200 °C, making it possible to couple the process with plentily available low-grade waste heat. Dehydrogenation at low pressure using reactive distillation (RD) also solves the issue of catalyst deactivation by the liquid product due to slow desorption. In the proposed RD, H2-rich LOHC vapor and H2-poor LOHC liquid phases flow counter-currently (so that the dehydrogenation catalyst can stay wet, a requirement for commercial dehydrogenation catalysts). As with trickle beds, counter-current operation is challenging as the window of operation between flooding and weeping is very narrow. On top of that, the flooding risks are increased due to the high flow rate of H2 produced (up to 12 moles per mole LOHC). As part of this project, we present the results of our Computational Fluid Dynamics (CFD) study establishing the window of operation for counter-current operation using spheres as packing and catalyst material. The next steps involve the use of high voidage packing material and an induction-based backup heating system to cope with the almost isothermal operation required for the RD, coupled with the endothermic reaction enthalpy.

The preliminary design of the RD unit for H12-BT/H0-BT LOHC will be carried out by Fenske-Underwood-Gilliland (FUG) method. Then several CFD simulation cases will be run in OpenFOAM software to investigate the flow behavior of counter-current flow of H12-BT and H0-BT components on the surface of an unstructured packed bed generated by Blender software. Finally, the outcomes of the CFD simulations are deployed and flooding condition, wettability, and maldistribution of liquid are monitored to optimize the RD unit.

This study is conducted as a part of the BE-HyFE project which is a Belgian academic collaboration project to facilitate using of hydrogen in the energy transition sector.

CP&RT-B08
Separation of Zeolites with Electrosedimentation

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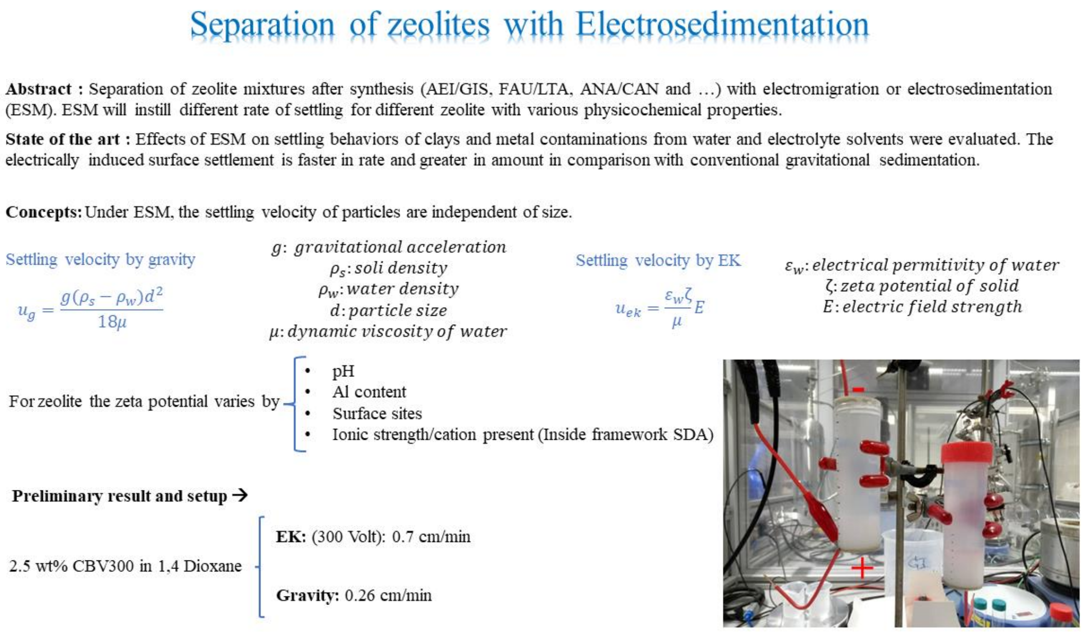
[1] *KU Leuven, Belgium*

Keywords: Zeolite; separation; electrosedimentation

Controlling the polymorphism in zeolite synthesis is a crucial factor for catalysis. The formation of unwanted polymorphs during the synthesis can hamper the application, which is specifically the case for catalytic efficiency (side products). It has been proven that often just a single framework excels for a specific task. The separation and purification of zeolites now needs (harsh) post-synthetic processes (e.g. washing with HCl). Indeed, new approaches for the post-synthetic separation of zeolites are in demand. Here we explore electrosedimentation for the separation of zeolite mixtures. Electrokinetic sedimentation will instill different rates of settling for zeolites with different physicochemical properties, such as density, surface charge, and Al-content.

Electrokinetic sedimentation has been used for removing clayey soils and metal contamination from water and different electrolyte solvent. One of the major problems in conventional gravitational settling is that the rate of settling for fine particles (clayey particles; size ≤5µm) is very slow. It has been seen that electrosedimentation is faster in settling rate and greater in magnitude in comparison with gravitational settling [1,2].



Separation of zeolites with Electrosedimentation

Abstract : Separation of zeolite mixtures after synthesis (AEI/GIS, FAU/LTA, ANA/CAN and …) with electromigration or electrosedimentation (ESM). ESM will instill different rate of settling for different zeolite with various physicochemical properties.

State of the art : Effects of ESM on settling behaviors of clays and metal contaminations from water and electrolyte solvents were evaluated. The electrically induced surface settlement is faster in rate and greater in amount in comparison with conventional gravitational sedimentation.

Concepts: Under ESM, the settling velocity of particles are independent of size.

Settling velocity by gravity

$$u_g = \frac{g(\rho_s - \rho_w)d^2}{18\mu}$$

g: *gravitational acceleration*
ρ_s: *soli density*
ρ_w: *water density*
d: *particle size*
μ: *dynamic viscosity of water*

Settling velocity by EK

$$u_{ek} = \frac{\varepsilon_w \zeta}{\mu} E$$

ε_w: *electrical permitivity of water*
ζ: *zeta potential of solid*
E: *electric field strength*

For zeolite the zeta potential varies by

- pH
- Al content
- Surface sites
- Ionic strength/cation present (Inside framework SDA)

Preliminary result and setup →

2.5 wt% CBV300 in 1,4 Dioxane

EK: (300 Volt): 0.7 cm/min

Gravity: 0.26 cm/min

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CP&RT-B09

Practical Actinometry in Photoflow Reactors

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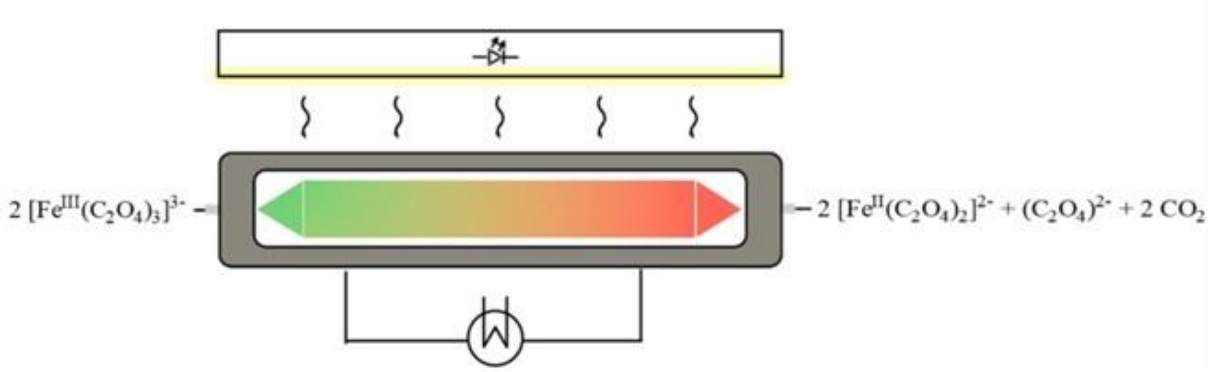
Keywords: actinometry; ferrioxalate; photochemistry; flow chemistry; photon flux; HANU 2X 15 reactor; Vapourtec UV-150 reactor

Accurate determination of the photon flux is of major importance to evaluate and characterize photochemical reactor setups. Knowing the photon flux ensures reproducible reactor operation and facilitates predictable scale-up. Over the past years, flow reactors have proven to be the key enabling technology for photochemistry to become relevant on production scales. This mainly due to mitigation the limited penetration depth of photons in typical batch reactors. However, due to the practical drawbacks of the widely accepted standard for photon flux determination (ferrioxalate actinometry) concerning precipitation and gas formation at higher conversion, reliable actinometry in flow reactors is still challenging. In this work, three practical approaches for ferrioxalate based determination of the photon flux are presented which address these problems. These ‘dimmed emitter’, ‘segment based’ and ‘time-resolved’ methods thus allow photon flux determination in flow reactors with higher irradiated volumes and more powerful light sources, which is of utmost importance in the context of future scale-up.



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CP&RT-B010
CO2 hydrogenation to methanol over Au/ZnZrOx at high reaction temperatures

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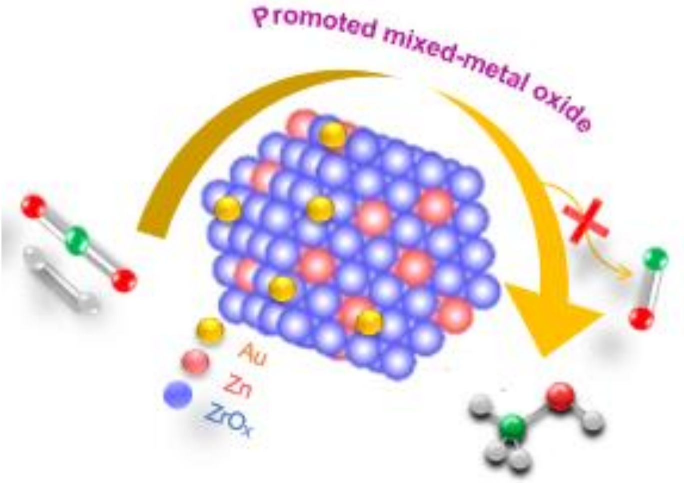
Keywords: CO2 hydrogenation; Methanol; Metal oxide; High temperature

One way to mitigate the carbon dioxide emissions causing global warming and climate change is heterogeneous catalytic hydrogenation of CO2 to valuable products, particularly methanol [1-2], and consequently to lower olefins (C2-C4=) over a tandem catalyst [3-4] which provides an environmentally-friendly raw material for the polymer industries. However, in the CO2 hydrogenation reaction, high temperature favors the competing RWGS reaction, conflicting with olefin production which is feasible at high temperatures owing to the rapid kinetics of C–C bond formation [5-6]. In this respect, the design of efficient and selective hydrogenation catalysts at high temperatures is required.

Among the metal oxides which have been used for methanol synthesis [7-8], ZrO2 showed inferior activity in the CO2 hydrogenation reaction, which was promoted by zinc incorporation through the coprecipitation method, transforming the monoclinic and tetragonal zirconia into cubic phase, increased surface area, and pore volume, and enhanced CO2 adsorption capacity. Eventually, high selectivity to methanol was observed over a promoted Au/ZnZrOx catalyst in a high-pressure plug flow reactor at temperatures above 300 ˚C, reaching methanol formation of 0.24 gMeOH.gcat-1.h-1 at 325 ˚C and 45 bar in a feed with H2/CO2=4 and GHSV=21000 ml.gcat-1.h-1. However, high CO2 conversion at 350 ˚C, directed the reaction to the RWGS reaction, resulting in a decrease in methanol selectivity and formation which proved to be compensated by calcining the mixed-metal oxide at higher temperatures around 650 ˚C. Catalyst/experimental conditions modification is being evaluated to enhance methanol selectivity followed by performing experiments in a tandem reactor in the combination of zeolites.



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Renewables & Sustainability

R&S-A01

Reducing the toxicity of crumb rubber granulates by encapsulation with (reclaimed) polymeric coatings

Adeel Muhammad[1], *Vande Velde Christophe*[1], *Vuye Cedric*[1], *Blom Johan*[1], *Bergmans Jef*[2], *Dardenne Freddy*[1], *Billen Pieter*[1]

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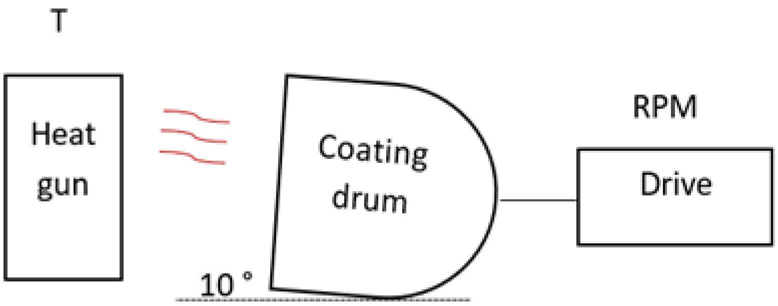
Keywords: Crumb Rubber; Zinc Leaching; Coatings; Ecotoxicity

Globally two billion tires are manufactured annually. Waste tire management is a global environmental concern due to the non-biodegradability and lack of an environmentally friendly method for disposing and reusing end-of-life tires (ELTs). Because ELTs contain approximately 1-2 % zinc by weight, the leaching of zinc, next to several organic pollutants, is a serious environmental concern and limits their applications as crumb rubber (CR) in sports fields, artificial turf, and as an additive in asphalt pavements. In tackling the problem of zinc leaching from CR from ELTs, one of the potential routes is immobilization by coating the granulates. Prior reports gave a glimpse of the potential but use expensive virgin materials, are not tested according to Flemish regulations (column leaching tests), and are not tested for weathering, or total ecotoxicity. In this study, we developed a variety of polymer coatings that can reduce the leaching of zinc by 82-91%, and even up to 99%, very far below the Flemish environmental limit value of 2.8 mg/kg dry matter, and reduce the ecotoxicity to aquatic life. With the current knowledge, a variety of polymer-based coatings, among which polyurethanes (to which specific additives could be added) can be tuned to various desired applications. A techno-economic estimate shows that the main component of the total coating cost is the coating material itself. With the current formulations (i.e. 10% by mass of coating), which are not optimized, making the coatings would require an additional cost of 80 to 300 EUR per ton CR, depending on the selected coating material. However, this price will decrease by making the coatings thinner (there is still a sufficient margin given the outstanding leaching results) and by using recycled materials. For sustainable performance, the latter is in our opinion imperative.



R&S-A02

Activated carbon adsorbers from NADES-extracted brewer’s spent grain and malt dust biomass

Bleus Dries[1], Joos Bjorn[1,2], Hardy An[1,2], Marchal Wouter[1], Vandamme Dries[1]

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Keywords: Biomass; valorisation; pyrolysis; adsorption materials; activated carbon

This investigation elaborates on a sustainable two-step valorization method for obtaining specialty bio-chemicals and activated carbon materials from biomass side products of the beer brewing industry. Two specific biomass streams are investigated: Brewer’s spent grain (BSG), a nutrient- and antioxidant-rich [1] side product obtained after the beer brewing process (3.4 million tons per annum in the EU [2]), and malt dust (MD), an underexplored biomass stream obtained from the barley malting process. As a two-step valorization route, antioxidant phenolic compounds are first hydrothermally extracted from these biomass streams using non-toxic, bio-based natural deep eutectic solvents (NADES), after which the spent biomass is further pyrolyzed and activated to obtain activated carbon (AC) adsorption materials . These biomass-based AC are proposed as a promising tool for separation of phenolic extracts and NADES solvent recuperation. [3-5]

Dry biomass was extracted using a hydrothermal extraction method at 120°C. Two choline chloride-based NADES solvents (malic acid:choline chloride, glycerol:choline chloride) were evaluated for their efficiency against a ‘conventional’ acetone-water solvent mixture. Filtered extracts were analysed on HPLC for contents of four major phenolic components (caffeic acid, syringaldehyde, p-coumaric acid and ferulic acid). Next, the spent biomass was pyrolyzed at 700 °C, and physically activated using CO2 at 800 °C. The produced AC were then analysed using nitrogen physisorption experiments to obtain their BET (Brunauer–Emmett–Teller) specific surface area, scanning electron microscopy for surface morphology, ultimate (CHNSO) analysis, and thermogravimetric analysis for volatiles and ash content determination. To test the applicability of AC for separation of solutes from NADES solvents, preliminary batch ad- and desorption tests were performed.

Hydrothermal extractions performed with NADES generally offered favourable results for both biomass streams (22.3 µg/g caffeic acid, 4.7 µg/g syringaldehyde, 91.8 µg/g p-coumaric acid and 272.0 µg/g ferulic acid for BSG, 33.5 µg/g caffeic acid, 6.5 µg/g syringaldehyde, 17.2 µg/g p-coumaric acid and 42.3 µg/g ferulic acid for MD). These results are in line with, or exceed the findings of earlier studies [6-7]. Results also showed that the hydrothermal process using NADES solvent could serve as a valid alternative to extraction methods with classical solvents. Elemental analysis, ICP-OES and FT-IR analysis showed (slight) alterations in the physico-chemical properties of AC obtained from spent biomass. BET surface areas of the produced AC’s reached up to 1658 m2/g for BSG biomass, and up to 1198 m2/g for malt dust, representing an uptick of 16% and 33% over the untreated biomass AC from each stream, respectively.

In conclusion, through the proposed two-step valorisation method of BSG and MD biomass, phenolic anti-oxidant compounds were successfully extracted from BSG and malt dust biomass streams, using green solvents and a novel hydrothermal extraction method. Secondly, the obtained AC’s from spent biomass were characterized with excellent surface areas that exceeded those of untreated biomass. Physisorption tests will be performed to indicate the ad- and desorption capacity of the produced AC.

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R&S-A03

Hemicellulose in the RCF Biorefinery: Towards a Sustainable Production of Furfural in Green Solvents

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[1] *KU Leuven, Belgium*

Keywords: Furfural; Carbohydrate conversion; Green chemistry; Solvent effects; Biorefining

Furfural is a highly useful chemical for all kinds of applications. It mainly serves as a platform chemical for making a wide range of valuable products, ranging from general commodity chemicals used in food, flagrance and agricultural industry, to fuel additives and plastics with unique high temperature properties. Current synthesis of furfural from sugars employs soluble acids in water, which is corrosive and polluting, while the yield amounts only 50% based on the theoretical carbon mass. Present research investigates the role of organic solvents in the conversion of hemicellulose from real biomass to furfural. Solvents have chemical and physical properties (e.g. H-bridge formation character, polarity, permittivity,…) which not only determine the solubility, but can also promote chemical reactions. By deeper understanding of these solvent effects in furfural production, a targeted identification of the best performing solvents can be made. This could lead to a continuous process with high steady state furfural yields. The research also explores its sustainable integration within a larger biorefinery scheme. In this way, it aims to contribute substantially to the development of a new generation of furfural production form second generation sugars.

R&S-A04

On the positioning of the internal catalyst in Non-Isocyanate Polyurethanes: from faster exchange ratios to selective urea formation

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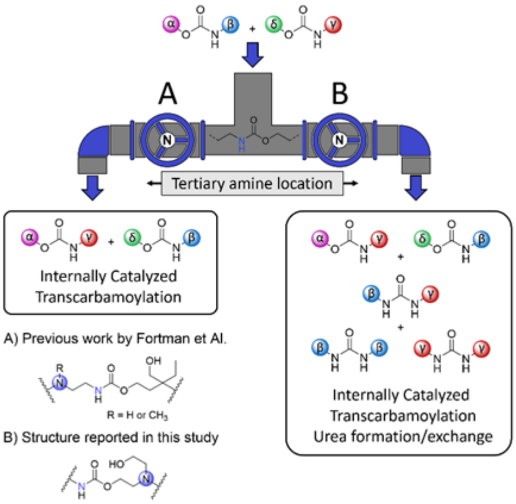
Keywords: covalent adaptable network; polyhydroxyurethane; non-isocyanate polyurethane; internal catalysis

We developed a novel methodology to provide non-isocyanate polyurethane-based covalent adaptable networks (CANs)[1], with embedded tertiary amines that serve as internal catalytic moieties for the dynamic bond exchange processes. For the CAN design, multifunctional N-substituted 8-membered cyclic carbonates, which can be ring-opened by macromolecular amines, were used. Several model reactions were conducted to investigate transcarbamoylation bond exchange reactions at elevated temperatures and assess the influence of catalytic moieties within the urethane structure. This led to the design of a non-isocyanate PU CAN[2] wherein the position of the internal catalyst was changed with respect to previous reported polyhydroxyurethane CANs,[3] while maintaining close proximity to the dynamic carbamate linkages.



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R&S-A05

Green two-step valorization of organosolv lignin: depolymerization and hydroxyalkylation

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Keywords: organosolv lignin; liquid phase reforming; hydroxyalkylation; glycerol carbonate

INTRODUCTION

Growing concerns about climate change and the reliability of our society on non-renewable fossil sources asks for a drastic solution: the transition from a fossil-based economy towards a sustainable one. Lignin, an aromatic biopolymer incorporated in lignocellulose biomass and with a wide variety of functionalities, can play a key role in this approach for several reasons: the abundancy of lignin in nature, being not directly competitive with the food supply chain and the prospect of a growing increase in commercial availability. Today, though, lignin is mistakenly regarded as waste with only 2% being used as inexpensive filler material due to certain drawbacks of lignin in the application level such as the structural complexity and low reactivity and solubility.

PURPOSE

In this work, a two-step valorization strategy is proposed by turning the organosolv lignin feedstock into a low molecular weight product with increased functionality by batch-wise liquid phase reforming at lab scale followed by the hydroxyalkylation with glycerol carbonate to turn all OH functionalities into 1,2-diols (and in a lesser extent 1,3-diols).

The 1st step consists of a reductive depolymerization in absence of external H2 (i.e., liquid-phase reforming) to reduce the structural complexity and increase the phenolic OH concentration of the lignin feedstock by cleaving ether bonds and to increase the phenolic OH content and assess possible occurring side reactions (e.g., hydrodeoxygenation).

The 2nd step aims to convert all OH functionalities into 1,2-diols by using non-toxic glycerol carbonate (as an alternative to toxic epoxides) resulting in a final lignin with more uniform functionality and thus a more improved reactivity for polymer synthesis at application level.

METHODS

Organosolv lignin was depolymerized by a mild reductive depolymerization in ethanol/water (70/30 v/v) with or without formic acid as an in situ H2 source and in presence or absence of Pd/Al2O3 as catalyst. Several process parameters in this depolymerization were systematically varied to gain insight in the depolymerization. The depolymerized organosolv lignin was characterized in depth (e.g., molecular weight via GPC and OH functionalities via 31P-NMR) to assess the various process conditions on the liquid phase reforming products.

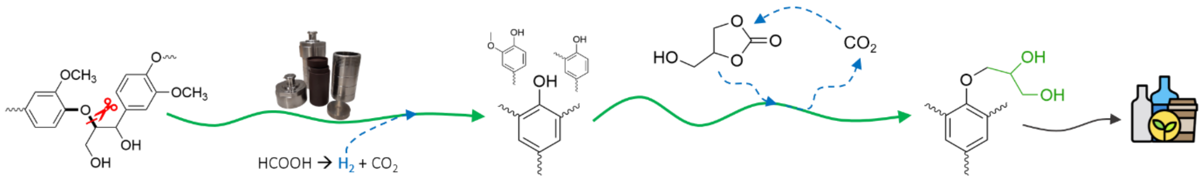
Next, the hydroxyalkylation was investigated which was divided into 2 stages. The 1st stage involved the modification of polymeric organosolv lignin with glycerol carbonate to obtain an optimal set of parameters (T, t) accompanied with an optimized work-up procedure. The 2nd stage comprised of applying the hydroxyalkylation procedure to depolymerized organosolv lignin to investigate the effect of molecular weight and presence of different OH functionalities on the hydroxyalkylation.

RESULTS AND CONCLUSION

In this research, the two-step valorization strategy of lignin was found to be a promising path to obtain a low molecular weight lignin with more uniform functionalities, namely 1,2-diols.

For the depolymerization, a higher formic acid and/or catalyst loading improved the depolymerization resulting in a decrease of the MW of organosolv lignin feedstock in the range of 41% - 81. By using formic acid and/or Pd/Al2O3, the depolymerization mechanism was either primarily acid-catalyzed or followed mainly a reductive pathway. By studying the concentration of different OH functionalities, it was elucidated that upon hydrogenolysis other side reactions take place (e.g., hydrodeoxygenation and esterification).

By modifying both organosolv lignin and depolymerized organosolv lignin with glycerol carbonate, the OH functionalities were successfully turned into 1,2-diols. In addition, the increase in aliphatic OH concentration is much higher for the depolymerized organosolv lignin which supports the use of the two-step valorization strategy. However the original aliphatic OH content could not be determined with 31P-NMR spectroscopy and the expected total OH content of all hydroxyalkylated samples was not met which indicates side reactions occurred during the modification and should thus be further investigated.



R&S-A06
Drinking water from the air in South Africa

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Keywords: water-from-air; thermoresponsive polymers; performance modelling of water harvesting technologies; weather data; deliquescent salt reverse osmosis; water scarcity

The concept of drinking water harvested on demand directly from the air has captured the imagination of researchers and entrepreneurs. Different technologies show potential in this regard. These include thermoresponsive polymers, desiccants, deliquescent salt reverse osmosis, and active air cooling. However, water harvesting processes are energy intensive and the performance of water-from-air technologies in outdoor conditions is underexplored. An understanding of the performance of water-from-air technologies in outdoor conditions is crucial if these technologies are ever to be implemented as a go-to solution in water scarce areas.

In this study we apply an outdoor water harvesting model to weather data from the Witzenberg valley in South Africa. The model used attempts to give a more realistic estimation of the performance of water-from-air technologies in real-life conditions. The short-term variability of the weather influences the specific yield of the technologies. This has not been taken into account with previously published water-from-air models. The model employed in this study aims to address this shortcoming and runs on ten-minute averaged weather data. A weather station has been installed to collect data as input to the model. The technologies are modelled to operate according to the day-night cycle by capturing water during the night and releasing it during the day. The research results report the estimated amount of water produced and energy required for different water-from-air technologies in outdoor conditions.

R&S-B01

Membrane-immobilized transaminase for intensified chiral amines production

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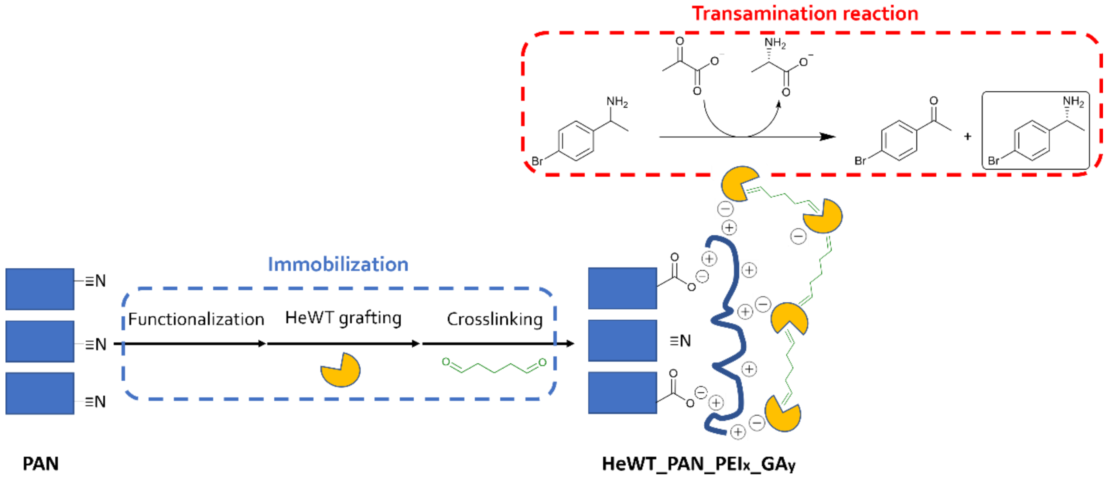
Keywords: transaminase; enzyme immobilization; chiral amines; membrane technology

Chiral amines are essential building blocks to manufacture high-value active pharmaceutical ingredients. Their synthesis often involves non-green processes requiring expensive homogeneous catalysts and high-energy inputs [1]. Hence, amine transaminases (ATAs) have gained considerable attention lately, as their use in transaminations provide greener routes to produce chiral amines with excellent enantioselectivity. Industrial applications of ATAs remain however scarce and restricted to batch processes in which ATAs are employed as non-reusable homogenous biocatalysts [2]. To overcome this limitation, more versatile heterogenized biocatalysts able to operate in continuous flow have been designed [3,4]. Importantly, most targeted transaminations are strongly limited by unfavourable thermodynamics. One strategy to shift the equilibrium towards high chiral amine yields is the set-up of integrated reaction-purification processes. In this context, coupling transamination with membrane technology in an enzyme membrane reactor is of particular interest, as it could allow the selective removal of products during operation. Enzymes onto polymeric membranes has already been reported, e.g. with lipase or glucose oxidase but not transaminase. As proof of concept, we present the immobilization of an ATA from Halomonas elongata (HeWT) onto polyacrylonitrile-based membranes (PAN) and its application to catalyze a model transamination (batch kinetic resolution of 4-bromo-α-methylbenzylamine ; Figure 1). To this end, the PAN surface was chemically modified and then coated with polyethyleneimine (PEI) to host the enzyme. Eventually, glutaraldehyde (GA) was used to cross-link the loosely attached HeWT and thus prevent their leaching from the membrane's surface. The obtained immobilized biocatalyst successfully performed subsequent catalytic cycles and showed negligible HeWT leaching. The decisive parameters impacting the enzyme specific activity were then assessed. As a result, we aim to demonstrate the use of a novel immobilized transaminase support material well-suited for upcoming operations, that pave the way to intensified biocatalytic processes for chiral amines production.



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R&S-B02

Microalgae in fertilizers as a bioactive material to increase the sustainability of agroeco systems

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Keywords: fertilizers; granules; micro-algae; algae; binders

As the world's human population increases, so does the consumption of various products, including food. As a result, the use of fertilizers is growing, and the soil is increasingly depleted and degraded. Micro and macro-organisms balance in soil is a key factor for soil sustainability because much of the synthesis, degradation of organic matter and the uptake of plant nutrients from fertilizers depend on the activity of the bioactive substances (microorganisms). Organic algae fertilizers are considered as a potential alternative to conventional synthetic fertilizers because they are rich in macronutrients, micronutrients, proteins, carbohydrates and vitamins, which directly help in improving the growth and yield of crop plants [1,2]. Therefore, to use effective concentrated fertilizers and maintain soil fertility, health and sustainability, fertilizers with biologically active substances such as algae and various bacteria are being developed [3].

In this work, using urea, microalgae (Fig. 1a) and binders such as molasses, cellulose and starch, concentrated and environmentally friendly nitrogen fertilizers were developed (Fig.1b).

Microalgae (15% w/w) were used as a potential source of microorganisms suitable to produce slow release biofertilizers. Bioactive nitrogen fertilizers were granulated using a drum granulator and adding different binders, and their properties (static compressive strength, pH, bulk density, etc.) were evaluated and compared with urea.

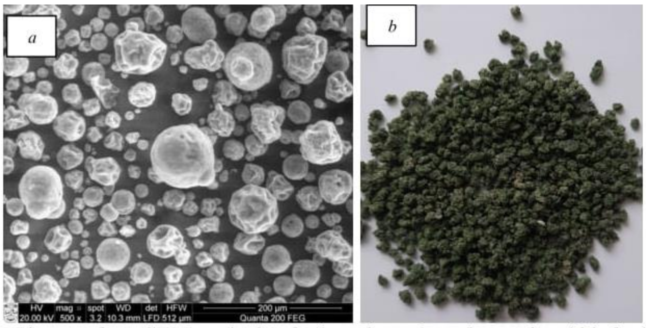

Fig. 1. Photos of: *a* –SEM analysis of microalgae; *b* – of granulated biofertilizers

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R&S-B03

Multi-diagnostic NMR-dielectric characterization of water confined in hydrophobic pores

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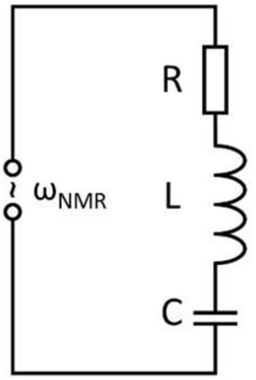
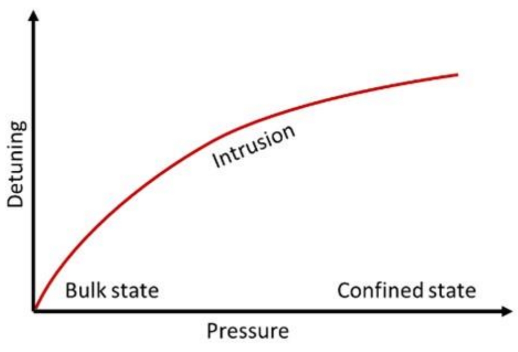
Keywords: water; confinement; NMR spectroscopy; hydrophobic pores; dielectric properties

Confinement of water in hydrophobic pores reshapes its hydrogen bonding structure, modifying its dielectric constant and solvation power [1,2]. Turning water into a tunable solvent using the WATUSO principle, [2], i.e., altering its solvent properties through hydrophobic nano-confinement, is a technology that finds straightforward applications in gas storage, catalysis and in the design of green chemical processes. Changes in the number and length of the hydrogen bonds of water under confinement cause its dielectric constant to decrease. Inside 3 nm thick slit-like cavities, the effective dielectric constant of water decreases to values as low as 3, while bulk water features a dielectric constant of 80 [3]. Changes in the hydrogen bond length of water under confinement can be sensitively probed by the chemical shift in 1H Nuclear Magnetic Resonance spectroscopy (NMR). Introduction of a dielectric medium, i.e. a sample, in an NMR coil modifies the probe circuit. This causes detuning of the probe, and is corrected for in NMR measurements, but it can also be exploited to gain access to the dielectric properties of the sample. This rather unexplored effect can transform NMR spectrometers into multi-diagnostic characterization tools, with the ability to simultaneously characterize the spectral and dielectric properties of solid and liquid samples. In this work we report on the modeling of sample-coil interactions in NMR spectrometers to extract the changes in the dielectric properties of water confined in hydrophobic pores. The circuit alteration upon sample introduction into the NMR probe and/or intrusion of water into the pores was modelled to obtain information about the changes in the effective dielectric properties of water intruded into hydrophobic pores through the increase in pressure caused by sample spinning. Pore penetration results in a modified relative permittivity of the water phase as seen in the detuning of the probe.





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R&S-B04

Co(salen)-catalyzed oxidation of para-substituted phenols towards benzoquinones: an experimental study of lignin model substrates

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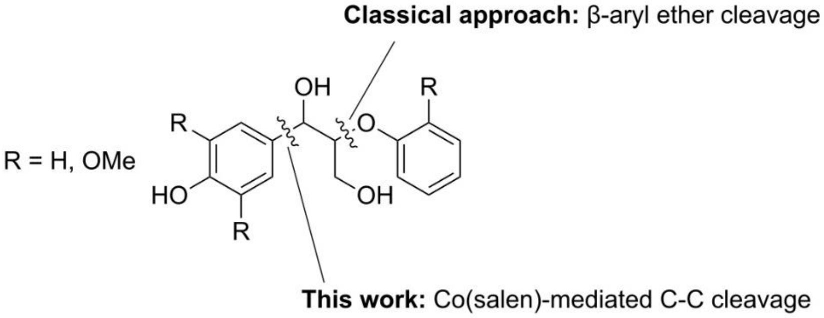
Keywords: Lignin; oxidation; Transition metal catalysis

Lignin is a renewable feedstock that is abundantly present in the plant cell wall. Despite the potentially valuable phenolic moieties present in the structure, valorization techniques are still limited and most of the lignin is burned as fuel. Since β-O-4 ether bonds account for 50-65% of the interunit linkages in native lignin, most research towards lignin valorization focuses on the cleavage of these β-aryl ethers. However, after lignin is removed from its matrix via various biorefining processes, the amount of phenolic -OH units can increase up to 70%. Focusing on transforming these substituted phenol groups would more accurately address the challenge of lignin valorization.

In literature, Co(salen) has been shown to oxidatively break C-C bonds between the α-carbon and the aromatic ring, yielding various quinones from dimeric model substrates.[1] To this respect, Co(salen)-catalyzed oxidation of monomeric lignin model substrates is further examined. New reaction conditions were found that show promising results compared to the current best performing batch process.[2] The catalytic oxidation was also performed in continuous flow, providing intensified oxidation conditions and more accurate process control.



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R&S-B05

The NCO cycle: heating up to the full recycling of PU waste

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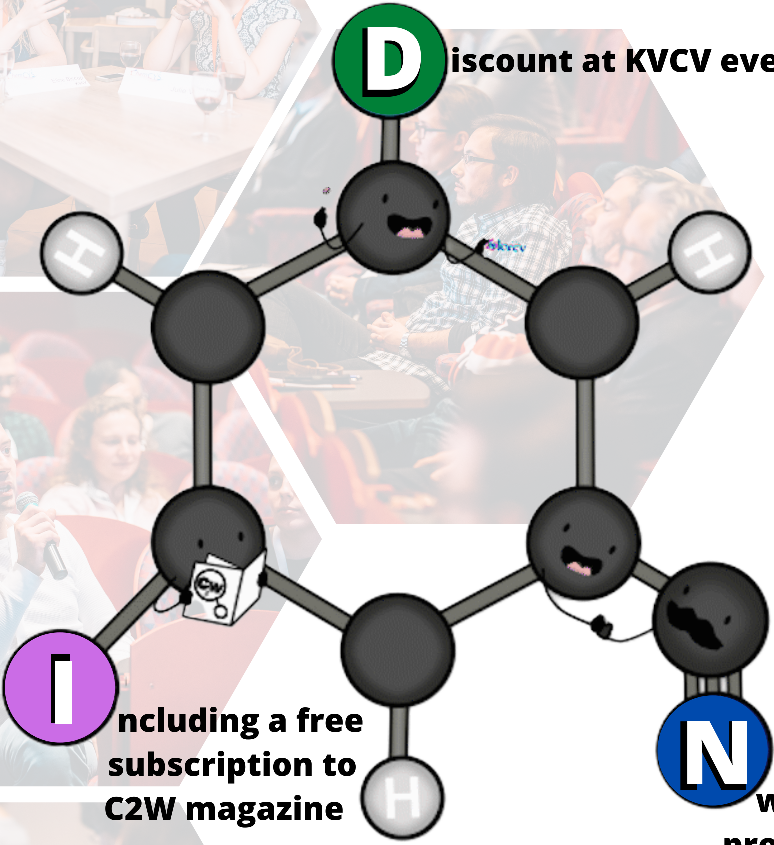
Keywords: polymer recycling; organic chemical synthesis; Polymer reaction engineering

The circularity of plastics is a topic of great interest today. The same is also true for the circularity of polyurethane (PU), one of the most versatile polymers on the market today. PUs are a class of mostly thermoset polymers, produced by a condensation of di-(or poly)isocyanates with polyols (polyfunctional alcohols). Since mechanical recycling leads to inferior products, research into chemical recycling methods is on the rise. The most promising chemical recycling technique is split-phase glycolysis which results in a pure polyol phase and a glycol/dicarbamate phase. However, to date, this approach only focusses on the recovery ofpolyols, neglecting the recycling potential of the dicarbamate phase, which makes up 10-40 % of the PUR mass. This project aims to extend the existing chemolysis processes into a two-step process that can recover both polyols and isocyanates from PU waste, thus completing the isocyanate cycle in a rather short loop. Since the chemolysis of PU has already been extensively discussed in the literature, focus was first laid on the recovery of the isocyanates from model carbamates by thermolysis. The structure of the carbamate and the reaction conditions during recovery were varied. The reaction products formed during this isocyanate recovery were analyzed by Fourier-transform infrared spectroscopy (FTIR), gel permeation chromatography (GPC), high-performance liquid chromatography (HPLC) and proton nuclear magnetic resonance (1HNMR). Subsequently, the entire two-step process was tested and analyzed starting from PU waste foam to polyols and isocyanates. The first experiments of the recycling process were successful in recovering the polyols and a small amount of isocyanates. Other valuable chemicals were also formed during the process that could be used in various applications. Although to date only a small amount of isocyanates could be recovered in the two-step recycling process, the yield could be increased by using appropriate catalysts, solvents and separation techniques. In addition, the by-products obtained from the process may be used in new applications. The new two-step recycling process might therefore be an opportunity to help close the isocyanate cycle.



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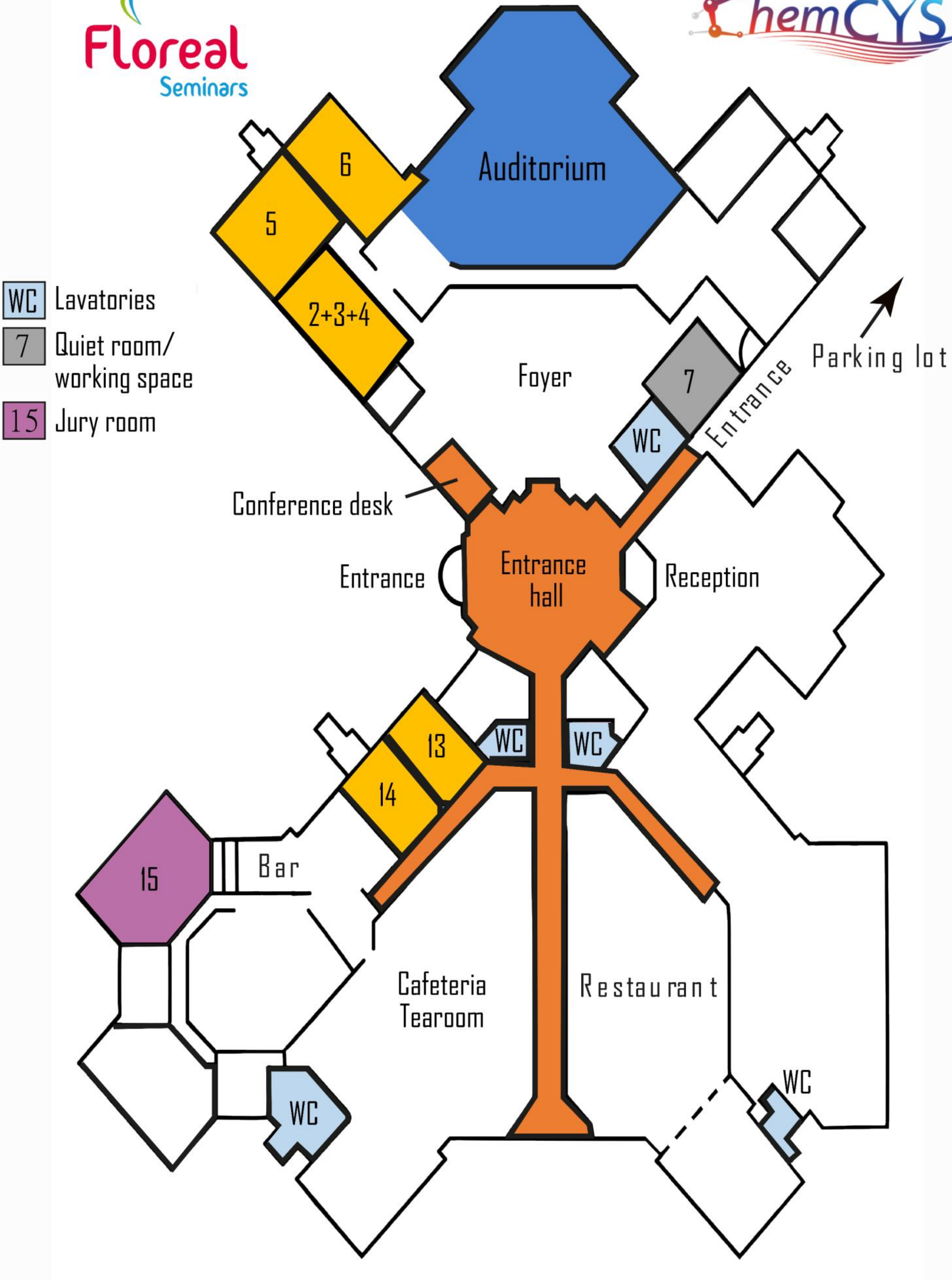

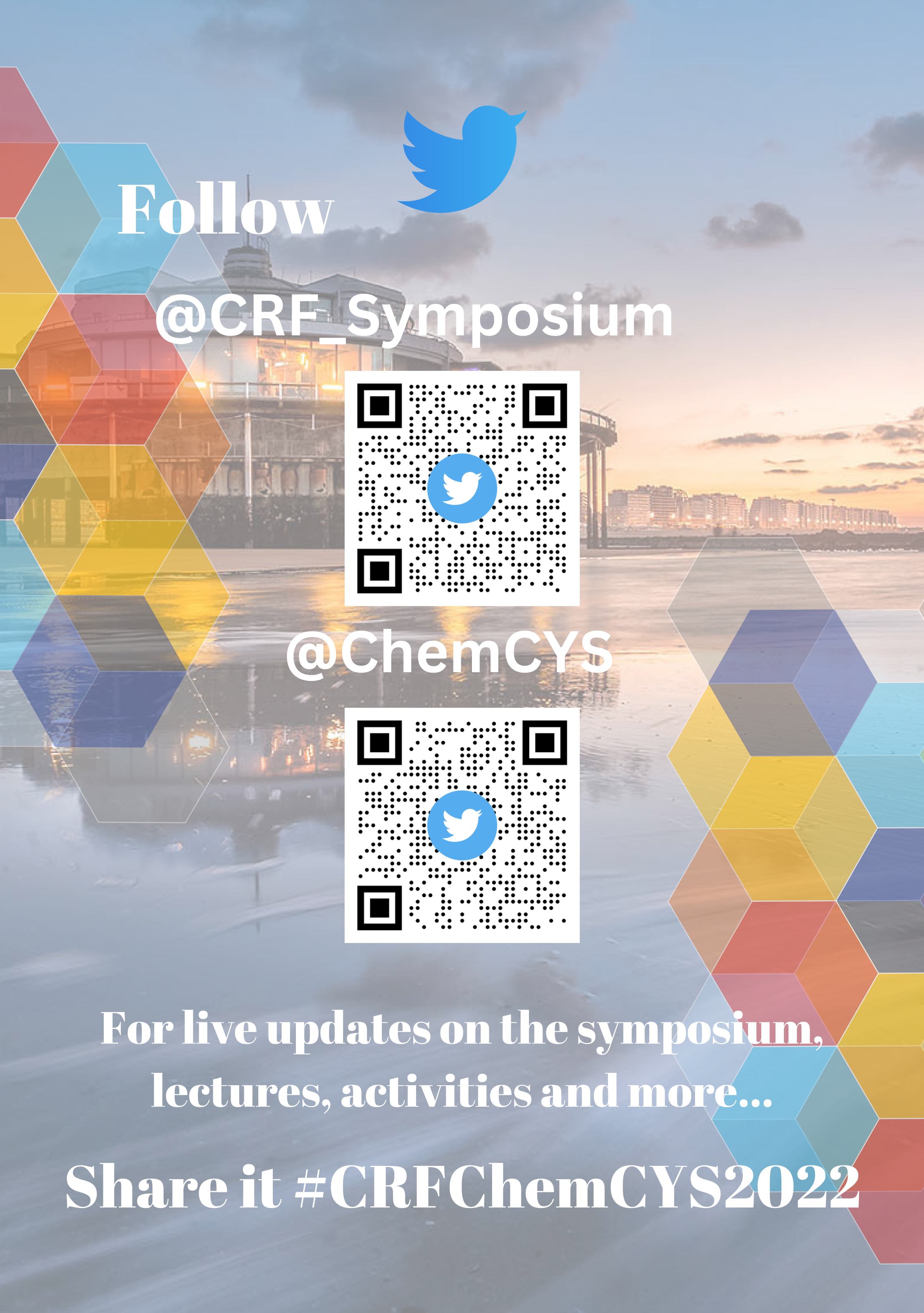

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