

## VOC oxidation over copper doped ceria nanocatalysts

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Excessive emissions of volatile organic compounds (VOCs) into the environment, which mainly result from different industrial plants and motor vehicles, greatly affect the quality of the air and thus the quality of life. There are currently many technologies that keep the concentration of volatile organic compounds in the atmosphere below the allowed limits. The catalytic oxidation of volatile organic compounds has been intensively investigated since the 1970s with the aim of finding efficient catalysts and suitable reactors.

Traditional noble metal catalysts, like Pt or Pd, although the most active for the oxidation of hydrocarbons, are expensive and extremely susceptible to poisoning, especially when employed at moderate working temperatures. Cerium(IV) oxide or ceria (CeO<sub>2</sub>) is a very good alternative due to its low cost, good mechanical properties, thermal stability, poisoning resistance, and, most importantly, high oxygen storage and release capacity stemming from the fast and facile reversible redox reaction between cerium(IV) and cerium(III) cations inside the ceria crystal lattice.

Many studies have shown that it is not easy to predict the behaviour of a mixture based on the oxidation process of a single component, because the performance of the catalyst is influenced by several factors. Some authors state that during catalytic oxidation of a mixture of volatile organic compounds, the process may be inhibited, while others believe that certain molecules of volatile organic compounds may be activated if mixed with other molecules and may change the selectivity [1].

Therefore, in this work, pure and copper doped ceria (Cu<sub>x</sub>Ce<sub>1-x</sub>O<sub>2</sub>, x = 0, 0.1, 0.3 and 0.4) nanoparticles were prepared using the hydrothermal method, thermally treated at 500 °C for 2 hours and thoroughly characterized. The catalytic activity of powder catalysts was tested in the fixed bed reactor at various working conditions using single VOC compound, toluene, and VOC mixture BTEX (benzene, toluene, ethylbenzene, and o-xylene). Catalytic oxidation was carried out at atmospheric pressure, at different temperatures, with a constant total flow rate of the reaction mixture and constant inlet toluene (210 ppm), and BTEX (each compound ca 45 ppm) concentrations. Copper doped ceria showed higher activity compared to pure ceria, as was expected. Characteristic temperature, T<sub>90</sub>, at which 90% VOC conversion was achieved indicates that generally higher temperatures were needed for single toluene oxidation than for individual compounds in BTEX mixture, except for benzene (on copper doped ceria catalysts) which showed to be the most difficult BTEX component to oxidize due to its known stable structure (Table 1.). This could indicate that toluene oxidation is greatly improved when BTEX mixture was oxidised rather than individual toluene compound.

To further explore the statement, the intrinsic catalytic activity (mg of converted VOC compound g<sup>-1</sup> h<sup>-1</sup>) was calculated according to the following equation:

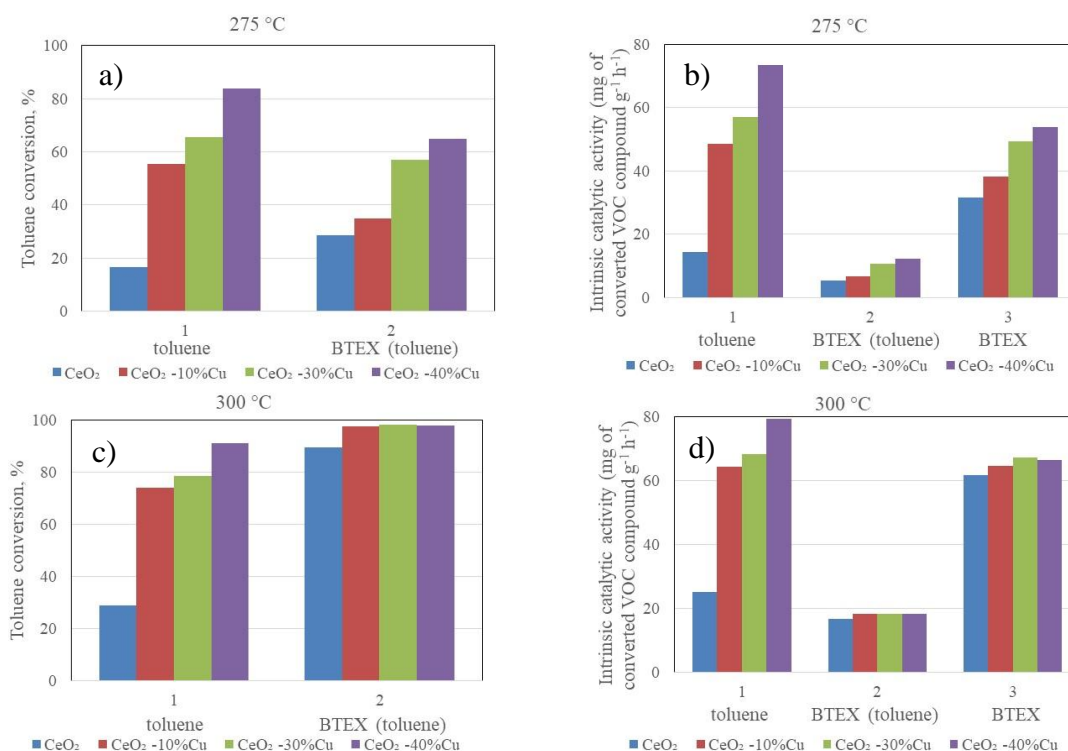
$$\frac{[mg]}{[g * h]} = \frac{X_A * Q_m}{m_{cat} * 100}$$

where X<sub>A</sub> represents the conversion of toluene at a given temperature (%); Q<sub>m</sub>, the VOC component mass flow (mg h<sup>-1</sup>); m<sub>cat</sub>, the catalyst mass (g).

**Table 1.** Temperatures corresponding to 90 % conversion of single toluene and BTEX compounds for all analysed catalysts.

	$T_{90}, ^\circ\text{C}$				
	toluene	BTEX (benzene)	BTEX (toluene)	BTEX (ethylbenzene)	BTEX (o-xylene)
CeO <sub>2</sub>	>450	362	300	292	292
CeO <sub>2</sub> -10%Cu	345	355	295	288	288
CeO <sub>2</sub> -30%Cu	335	350	292	278	278
CeO <sub>2</sub> -40%Cu	295	355	292	270	270

At the selected temperatures of 275 and 300 °C toluene conversions and intrinsic catalytic activities were compared. At higher temperature toluene conversion increases showing higher toluene conversions achieved within mixture than individual toluene compound (Figure 1a and 1c), but intrinsic catalytic activity remains lower for mixture than individual toluene compound (Figure 1b and 1d), although it increases at higher temperature.



**Figure 1.** Toluene conversion and intrinsic catalytic activity comparison within mixture and individual toluene compound at 275 °C (a and b) and at 300 °C (c and d).

The exception to these observations is pure CeO<sub>2</sub>, showing both higher toluene conversion and intrinsic catalytic activity at selected temperatures when BTEX mixture was used. This indicates that further research is needed to further explore whether toluene oxidation is inhibited or activated when BTEX mixture is used over pure and doped ceria catalysts.

[1] Burgos et al., Deep oxidation of VOC mixtures with platinum supported on Al<sub>2</sub>O<sub>3</sub>/Al monoliths, Appl. Catal., B 38 (2002) 251-258.

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