

Catalytic oxidation of volatile organic compounds over cerium-copper oxide catalysts

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Abstract

Over 300 chemicals are designed as volatile organic compounds (VOCs) by the U.S. Environmental Protection Agency and most of them are highly toxic/carcinogenic substances that contribute to photochemical smog, global warming and so on. Therefore, VOCs are carefully regulated and different technologies have been developed to control their release to the atmosphere [1]. Catalytic oxidation is one of the most widely used techniques to control VOCs emissions at relatively low temperatures: it is less fuel intensive compared to thermal oxidation and it is highly versatile with the possibility to treat waste streams with different VOC concentrations and effluent flow rates [2].

It is generally accepted that the oxidation of VOCs over transition metal oxides, such as CuO- CeO₂ systems, occurs according to a Mars-van Krevelen type mechanism and proceed through lattice oxygen (nucleophilic attack) of the solid catalysts [3]. Therefore, the molecular oxygen is only required to reoxidize the reduced catalyst surface [4].

The redox activity of CuO-CeO₂ catalysts is created by the ability to reduce and re-oxidize both CuO and CeO₂, which is enhanced by a strong interaction between these phases. Indeed, CuO-CeO₂ is a more efficient catalyst for VOC total oxidation than the corresponding single metal oxides. This means that a synergistic effect between CuO and CeO₂ can be observed using a MvK model to describe the kinetic data. In this work, several CuO-CeO₂ catalysts with different Cu/Ce contents (denoted hereafter as Cu_xCe_{1-x} where x indicates the Cu/Cu+Ce atomic ratio) have been synthesized by the solution combustion synthesis (SCS) and their catalytic activity has been examined in the total oxidation of ethylene as probe molecule. The prepared catalysts have been characterized by complementary techniques, including powder XRD, FE-SEM, N₂ physisorption at -196 °C, H₂-TPR, XPS and IR spectroscopy.

The Cu_xCe_{1-x} catalysts have specific surface areas and total pore volumes in the range of 34-73 m²g⁻¹ and 0.04-0.25 cm³g⁻¹, respectively. The largest surface area and pore volume values are observed for the Cu_{0.15}Ce_{0.85} catalyst, whereas further increase of Cu content leads to worse values of textural properties, in agreement with previous studies. The specific surface areas for pure CeO₂ and CuO are 69 m²

g^{-1} and $4 \text{ m}^2 \text{g}^{-1}$, respectively. XRD patterns have shown that a cubic fluorite lattice structure of CeO_2 ($Fm3m$ symmetry) appear with all samples, as well as reflections of the CuO phase occur in the addition to those of ceria, as the increase of copper leads to the formation of bulk CuO particles. Figure 1 shows a representative FE-SEM image of the $\text{Cu}_x\text{Ce}_{1-x}$ catalysts, in which is possible to observe relatively uniform agglomerates of particles (diameter of ca. 100-150 nm).

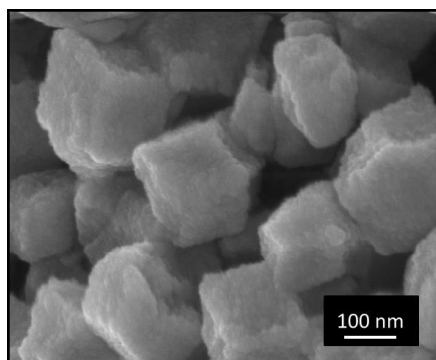


Figure 1. FE-SEM image of the $\text{Cu}_{0.6}\text{Ce}_{0.4}$ catalyst.

The oxidation activity of $\text{Cu}_x\text{Ce}_{1-x}$ catalysts has been evaluated in the total oxidation of ethylene with a gas hourly space velocity of 19100 h^{-1} and a W/F value of 0.03 g h l^{-1} . The conversion of ethylene to CO_2 as function of temperature is shown in Figure 2. All the prepared catalysts display positive ethylene conversion trends for an increasing reaction temperature. However, different conversion values can be observed. The most active catalyst is $\text{Cu}_{0.6}\text{Ce}_{0.4}$ and complete oxidation of ethylene to CO_2 occurs at ca. 450°C . Further increase of Cu content diminishes the catalytic activity. The lowest ethylene conversion is achieved for pure CeO_2 . As a whole, $\text{Cu}_x\text{Ce}_{1-x}$ catalysts show better activities compared to pure CuO and CeO_2 likely due to their easier reducibility and redox properties, as revealed by H_2 -TPR and XPS analysis. Therefore, the most active powder catalyst ($\text{Cu}_{0.6}\text{Ce}_{0.4}$) was then deposited on a cordierite-type monolith through a novel direct synthesis (Figure 3) and tested for the total oxidation of the VOCs. The $\text{Cu}_{0.6}\text{Ce}_{0.4}$ -based monolith exhibited high activity towards the total oxidation of VOCs, which is comparable to that obtained with powdered $\text{Cu}_{0.6}\text{Ce}_{0.4}$.

Since industrial emissions usually contain mixtures of VOCs, studies on the catalytic activity of a single probe molecule of VOC only partially represent the possible catalyst applications. Therefore, further investigations are currently under investigations for mixture of VOC (namely, ethylene, propylene and toluene).

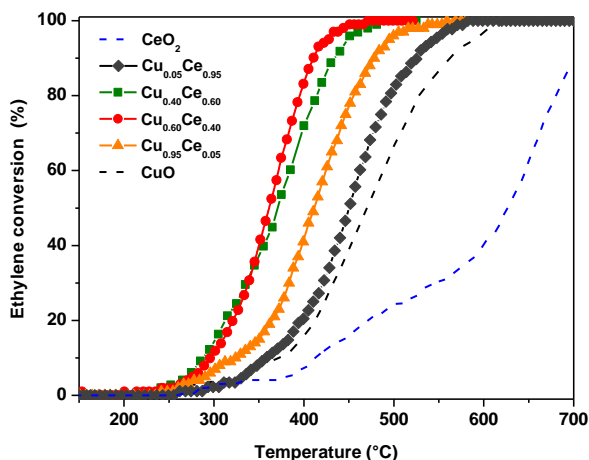


Figure 2. Conversion of ethylene to CO_2 as a function of temperature.

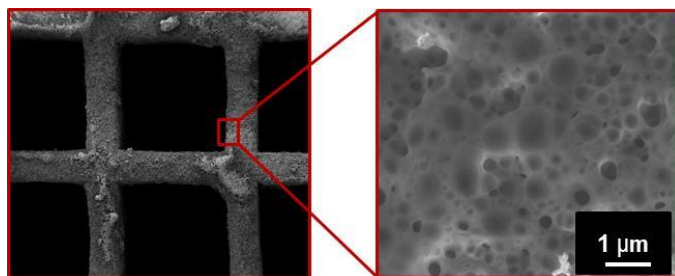


Figure 3. $\text{Cu}_{0.6}\text{Ce}_{0.4}$ based monolith catalyst obtained by means of direct synthesis (via SCS route).

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References

- [1] Ertl G., Knözinger H., Schüth F., Weitkamp J., *Handbook of Heterogeneous Catalysis* (2nd ed.), Wiley-VCH, Weinheim (2008) 2394-2411..
- [2] Taylor S.H., *Top. Catal.* 52 (2009) 457.
- [3] Balcaen V., Poelman H., Poelman D., Marin G.B., *J. Catal.* 283 (2011) 75-88.
- [4] Piumetti M., Fino D., Russo N., *Appl. Catal. B* 163 (2015) 277-287.

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