

(141d) Role of CeO₂ In the Total Oxidation of Toluene Over CuO-CeO₂/Al₂O₃

Unmesh Menon¹, Vladimir V. Galvita¹, Hilde Poelman¹, Vitaliy Bliznuk² and Guy B. Marin¹, (1) Laboratory for Chemical Technology, Ghent University, Ghent, Belgium, (2) Department of Material Science and Engineering, Ghent University, Ghent, Belgium

Introduction

Benzene, toluene and xylene (BTX), are considered to be three major carcinogens and their emission in the environment has to be controlled. Among the destructive technologies, catalytic oxidation is the most promising approach for the abatement of Volatile Organic Compounds (VOCs) owing to its advantages including high efficiency, low operating temperature and no secondary pollution [1]. The performance of the catalyst determines the effectiveness of this technique.

Supported or unsupported noble metal catalysts are used for complete oxidation of VOCs, but high costs limit their wide application, thus giving way to transition metal oxides such as copper oxide. These are less active at lower temperatures but present comparable activity at higher temperatures and have high catalyst loading capabilities [2-6].

However, a pure copper-based catalyst is less active and stable in the presence of water vapor and/or CO₂ in the gas mixture. At the same time, copper catalysts promoted by ceria show better catalytic performance for the complete oxidation of toluene, propane, benzene and p-xylene than unpromoted copper catalysts [7,8] as well as improved activity in the presence of oxidation products CO₂ and water [9]. Ceria as a promoter for supported CuO has shown several advantages: (a) ceria stabilizes the dispersion of the active component [10,11]; (b) metal/ceria interactions strongly affect their redox and catalytic properties; (c) ceria also acts as an oxygen storing component due to the presence of mixed oxidation states (3+/4+) of cerium; (d) copper-doped CeO₂ can improve the oxygen storage capacity, diffusivity and redox properties, which are attributed to the formation of structural defects.

However, it is still unclear how copper and ceria interact with each other and promote catalytic activity. The questions addressed in this study are: (1) Assistance of CeO₂ in the oxidation of reduced copper species, (2) the crucial copper species inducing the copper & Ceria interaction, (3) the active sites of copper & Ceria system for toluene oxidation, (4) the role of ceria in decreasing the negative effect of the presence of water and CO₂, (5) the enhancement of catalytic activity due to copper & Ceria interaction

In this study the binary mixed oxide, CuO-CeO₂/g-Al₂O₃, has been investigated in detail in comparison to its corresponding single-oxide components CuO/g-Al₂O₃, CeO₂/g-Al₂O₃ in order to correlate catalytic activity towards total oxidation of toluene with their physicochemical characterization. A transient response technique with millisecond time scale [12] was used to investigate the catalytic activity and influence of H₂O and CO₂ on the catalytic behavior. The structure of the catalysts was investigated by the use of high resolution electron microscopy (HRTEM), selected area electron diffraction (SAED), X-ray diffraction (XRD) and X-ray absorption Spectroscopy (XAS).

Experimental procedure

The CuO-CeO₂/γ-Al₂O₃, CuO/γ-Al₂O₃ and CeO₂/γ-Al₂O₃ catalysts were synthesized via impregnation of γ-Al₂O₃ with Cu(NO₃)₂·2.5H₂O and/or Ce(NO₃)₄·9H₂O precursors, followed by drying at 357K for 8h and calcination above 973 K for 8h in air. 10mg of 250-500nm particles were used for experiments to determine the catalytic activity.

The selected area electron diffraction (SAED) and high resolution electron microscopy (HREM) of the samples were carried out in a transmission electron microscope (TEM) operating at 300 kV (Jeol, JEM-2200FS).

The temporal analysis of products (TAP) experiments are performed in a quartz micro-reactor, with 33mm bed-length and 4.75mm inner diameter, evacuated to 10⁻⁴ - 10⁻⁵ Pa. A very small amount of reactant molecules (~10⁻⁹ mol), which is ~5 orders less than the active sites in the catalyst, is pulsed into the reactor by means of two high-speed pulse valves. The products and reactants at the outlet of the reactor are monitored by a quadrupole mass spectrometer. A temperature range of 723K - 873K is covered. To study the activity of the CuO-CeO₂/γ-Al₂O₃, CuO/γ-Al₂O₃ and CeO₂/γ-Al₂O₃ catalysts towards toluene total oxidation, experiments were performed over O₂ pre-treated catalysts by pulsing C₇H₈ with and without di-oxygen in the feed. Typically, a stoichiometric ratio of di-oxygen to toluene, 9:1, was used in the mixture C₇H₈/O₂/Ar, when experiments were conducted in the presence of di-oxygen.

In situ XAS experiments were performed at the SAMBA beam line of the SOLEIL synchrotron. X-ray absorption near edge (XANES) spectra were recorded with 1s time resolution during H₂ reduction and reoxidation with CO₂ and water at both the Cu K (8979 eV) and Ce L_{III} edge (5723 eV).

Results

XRD analysis of the CuO-CeO₂/γ-Al₂O₃ catalyst shows that alumina and ceria have a crystallite diameter of about 5 nm. At the same time CuO presents single crystals of about 100nm. From the STEM and SAD images the CuO single crystal units of ~100nm were confirmed, while CeO₂ appeared as 100nm clusters of nanocrystallites. EDX line scans were undertaken through specific regions of a STEM frame, displaying the elements present along the line (see Fig.1). The line scan proves that in addition to the large CuO crystallites, CuO is also present inside the CeO₂ clusters as small sized species. In situ XANES measurements at the Ce L_{III} and Cu K edge yield direct evidence that CeO₂ in the CuO-CeO₂/γ-Al₂O₃ catalyst is reduced by H₂ at similar temperature as the CuO phase. Fig. 2 shows XANES results which confirm partial reoxidation of ceria by water. Whereas, CuO is not reoxidised by water.

The toluene oxidation experimental data indicate that the reaction is carried out according to a redox Mars-van Krevelen mechanism. Lattice oxygen atoms from the surface of the catalyst are consumed by toluene and oxygen vacancies are created. These vacancies are filled by the oxygen atoms that diffuse from the bulk to the surface of the catalyst or by di-oxygen. It is shown that the degree of reduction of the metal oxide determines to a large extent its performance for VOCs oxidation. The presence of water or CO₂ on the catalyst surface decreases the rate of regeneration of the reduced catalyst by di-oxygen. Furthermore, if water and/or CO₂ are present in the gas phase, the rate of desorption from the surface becomes slower due to the high partial pressure of water in the gas phase.

The activity of the CuO-CeO₂/Al₂O₃ catalyst increases in the presence of H₂O or CO₂. On the other hand, CuO/Al₂O₃ showed loss of activity in the presence of H₂O. There was no significant change in activity on CuO/Al₂O₃ and CeO₂/Al₂O₃ when co-feeding toluene with CO₂.

Conclusions

Two CuO phases exist in the CuO-CeO₂/Al₂O₃ catalyst: large ~100nm crystals, not contacting CeO₂ and small CuO species dispersed upon and incorporated into clusters of CeO₂ nano-crystallites with size ~5nm.

The effect of CeO₂ on the catalytic activity can be explained by two factors. First, ceria stabilizes the dispersion of the active component, i.e. a smaller crystallite size of the CuO phase on the support becomes one of the key factors in determining the chemical reactivity. Second, incorporation of copper into the CeO₂ lattice can form Ce_{1-x}Cu_xO_{2-d} solid solution which also has high activity and reducibility at low temperatures compared to CuO or CeO₂ alone. The promoting effect of ceria is found to be more pronounced at low temperatures.

Adding H₂O or CO₂ into the C₇H₈/O₂ mixture increases the catalytic activity of CuO-CeO₂/Al₂O₃ catalyst by producing lattice oxygen species from reoxidation of ceria by CO₂ or H₂O. Over the CuO/Al₂O₃ catalyst the re-oxidizing role of CO₂ or H₂O co-fed with toluene is insignificant.

Acknowledgement

This work was supported by a Concerted Research Action (GOA) of Ghent University and the Long Term Structural Methusalem Funding by the Flemish Government'.

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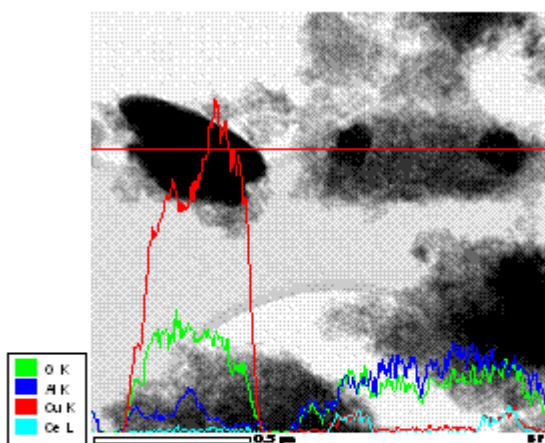


Fig. 1 EDX line scans through a STEM frame on the CuO-CeO₂/Al₂O₃ catalyst

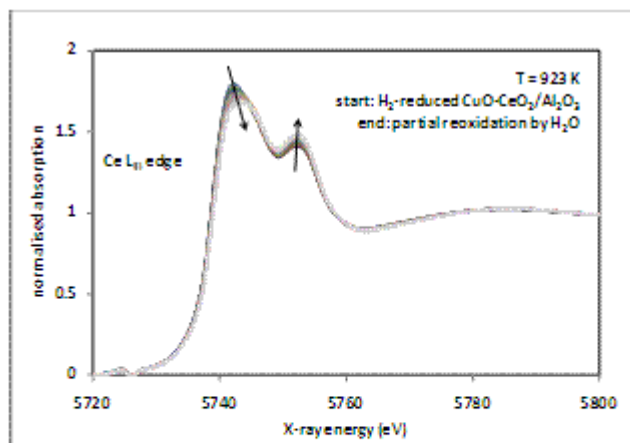


Fig. 2 CO₂ yield and ratio of CO₂ yields vs reaction temperature for experiments with and without H₂O in the feed over CuO-CeO₂/Al₂O₃ catalyst

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