

## Silica supported copper and cerium oxide catalysts for ethyl acetate oxidation

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### ARTICLE INFO

#### Article history:

Received 20 February 2013

Accepted 1 May 2013

Available online 14 May 2013

#### Keywords:

Copper ceria catalysts

Ethyl acetate oxidation

Active sites

### ABSTRACT

The formation of active sites in the silica supported copper and cerium oxide bi-component catalysts for total oxidation of ethyl acetate was studied by Nitrogen physisorption, XRD, XPS, UV–Vis, Raman, FTIR of adsorbed CO spectroscopies and TPR. It was found that the interaction between the copper oxide nanoparticles and the supported on the silica ceria ones is realized with the formation of interface layer of penetrated into ceria lattice copper ions in different oxidative state. This type of interaction improves the dispersion of copper oxide particles and provides higher accessibility of the reactants to the copper active sites even at low copper amount.

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### 1. Introduction

Recently, copper cerium oxide binary system have been intensively studied in various reactions, such as combustion of CO and methane, SO<sub>2</sub> reduction, hydrogen production by steam reforming of methanol, reduction of NO, decomposition of H<sub>2</sub>O<sub>2</sub>, wet oxidation of phenol, preference CO oxidation in excess of hydrogen, water gas shift reaction, and as additives in the three way catalysts for purification of automobile exhaust gas in order to reduce the cost of noble metals [1–13]. Although copper–cerium materials have been considered as effective oxidation catalysts, their performance in volatile organic compounds (VOCs) oxidation has been scarcely studied. Delimaris and Ioannides [14] and Hu et al. [4] demonstrated an optimum in copper content to achieve excellent catalytic activity in ethanol and ethyl acetate combustion, while no significant effect of copper addition to ceria was observed at low temperatures for toluene oxidation.

Up to now, most the investigations were focused on the behavior in bulk, non-supported materials, where copper oxide was doped with ceria or vice versa. It was found that the “intimate” contact between different metal oxide particles depends on the amount of both components as well as on the preparation and activation method used [15,16]. The formation of surface oxygen vacancies and facile Ce<sup>4+</sup>/Ce<sup>3+</sup> and Cu<sup>2+</sup>/Cu<sup>1+</sup> redox transitions as well as the increased copper oxide dispersion has been assumed as crucial points for the unique high catalytic activity of these materials [4–6,8,11]. In our

previous study, [17] we reported that ceria doping with small amount of copper by co-precipitation of nitrate precursors leads to significant incorporation of copper ions into the ceria lattice, which decreases their reducibility and catalytic activity in VOCs oxidation. It was assumed that the increase in the Cu/Ce ratio promotes the segregation of finely dispersed, easily reducible, and highly active copper oxide crystallites on ceria surface. Despite the large number of papers focused on the optimization of the intimate contact between copper and ceria ([3] and refs. therein), information on the effect of support is negligible [2,11,13]. Rao et al. [2] assumed higher interaction between different oxide species, which provided higher activity in CO oxidation, when they were supported on SiO<sub>2</sub> and ZrO<sub>2</sub> as compared to the Al<sub>2</sub>O<sub>3</sub> support. We demonstrated that copper ceria interaction could be restricted by the porous structure if mesoporous silica type SBA-15 was used as a support [17]. The aim of the current paper is to study the catalytic behavior of bi-component copper and cerium materials supported on conventional silica, where the role of pore structure is minimized. In order to clarify the formation of the catalytic active sites, data for selected bulk materials were used as reference.

### 2. Experimental

Copper and cerium supported on silica (Cabosil M5) materials with total metal content of 6 wt.% were prepared by impregnation of 1 g of silica with 0.5 M Cu(NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O and/or 0.25 M Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O aqueous solution in appropriate ratio, followed by drying at ambient temperature over night. Bulk analogs were obtained by precipitation of the corresponding nitrate precursors with a 2 M

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aqueous solution of KOH at a pH of 10.5. The powder samples were calcined at 773 K for 2 h and denoted as  $m\text{Cu}n\text{Ce}/\text{SiO}_2$  and  $m\text{Cu}n\text{-CeO}_x$  for the supported and bulk materials, respectively, where  $m/n$  corresponds to the ratio between the amount of different metals in wt.%.

Nitrogen physisorption data were obtained in a Micromeritics ASAP 2000 instrument. Powder X-ray diffraction patterns were collected on a Bruker D8 Advance diffractometer with Cu K $\alpha$  radiation. The average metal oxide crystallite size was evaluated according to the Scherrer equation. The UV–Vis spectra were recorded on a Jasco V-650 UV–Vis spectrophotometer. X-ray photoelectron spectra were collected using a SPECS spectrometer with a 150 MCD-9 detector and using a nonmonochromatic Al K $\alpha$  (1486.6 eV) X-ray source. Spectra were recorded using analyzer pass energy of 30 eV, an X-ray power of 200 W, and under an operating pressure of  $10^{-9}$  mbar. During data processing of the XPS spectra, binding energy (BE) values were referenced to C1s peak (284.5 eV). Spectra treatment has been performed using the CASA software. Selected XPS measurements were done in the UHV chamber of ESCALAB-Mk II (VG Scientific) electron spectrometer. Raman spectra were recorded using a Renishaw system 1000, equipped with argon ion laser (532 nm). IR spectra of adsorbed CO were recorded at 97 K with a Nexus 8700 FTIR spectrometer using a DTGS detector and acquiring at  $4\text{ cm}^{-1}$  resolution. An IR cell allowing in situ treatments in controlled atmospheres and temperatures from 97 K to 773 K has been connected to a vacuum system with gas dosing facility. For IR studies, the samples were pressed into self-supported wafers and treated at 423 K in vacuum ( $10^{-5}$  mbar) for 1 h. After activation, the samples were cooled down to 97 K under dynamic vacuum conditions followed by CO dosing at increasing pressure (0.4–8.5 mbar). IR spectra were recorded after each dosage. In order to evaluate the stability of the IR bands, the samples have been submitted to dynamic vacuum conditions after maxima CO dosing and the evolution of the intensity of each IR band has been recorded with time.

The TPR/TG (temperature-programmed reduction/thermogravimetric) analyses were performed in a Setaram TG92 instrument. Typically, 40 mg of the sample was placed in a microbalance crucible and heated in a flow of 50 vol%  $\text{H}_2$  in Ar ( $100\text{ cm}^3\text{ min}^{-1}$ ) up to 773 K at  $5\text{ K min}^{-1}$  and a final hold-up of 1 h. The weight loss during the reduction was calculated on the base of TPR–TG curves, and the values were normalized to one and the same catalyst weight (40 mg).

The oxidation of ethyl acetate was performed in a flow type reactor with 1.21 mol% ethylacetate in air and WHSV of  $300\text{ h}^{-1}$ , using 0.03 g of catalyst. GC analyses were done on a HP 5890 apparatus using carbon-based calibration.

### 3. Results and discussion

#### 3.1. Structural characterization of the initial materials

XRD patterns of all silica supported materials are presented in Fig. 1. Well defined reflections typical of  $\text{CeO}_2$  face centered cubic fluorite phase (PDF files 34-0394) with average crystallite size of about 5 nm are registered for  $\text{Ce}/\text{SiO}_2$  (Fig. 1 and Table S1). The broadening of these reflections for all bi-component materials indicates an increase in ceria dispersion (Table S1). The sharp reflections observed for all copper containing materials reveal the presence of CuO phase with monoclinic tenorite structure (PDF 48-1548) and particle size about 20–30 nm. The preservation of ceria unit cell parameters after copper addition (Table S1) does not indicate formation of solid solution [1,11].

In order to verify this assumption, Raman spectra were collected (Fig. 2a). The spectra of all supported copper containing samples present three main peaks at around 275, 330 and  $619\text{ cm}^{-1}$ , typical of CuO phase [1]. The intense peak at  $466\text{ cm}^{-1}$

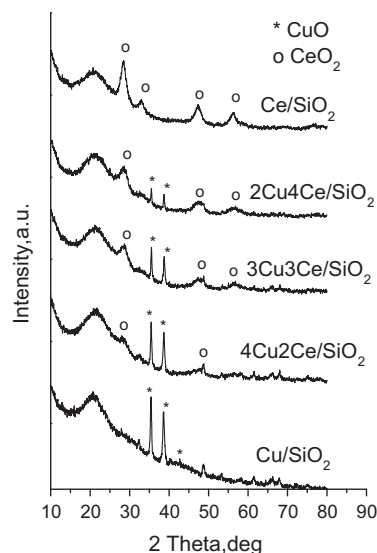


Fig. 1. XRD patterns of silica supported materials.

in ceria containing materials is assigned to F2g mode of  $\text{CeO}_2$  fluorite structure [8]. We would like to stress on the broadening and slight red shift of the position of the main  $\text{CeO}_2$  peak for all bi-component samples. A simultaneous increase in the intensity of the peak at ca.  $610\text{ cm}^{-1}$  is also observed in  $\text{CeO}_2/\text{SiO}_2$  sample. Generally, this peak is assigned to the formation of oxygen vacancies due to the replacement of  $\text{Ce}^{4+}$  by metal ion with different valence [1,8–10]. Accordingly, the observed effects could be assigned to ceria dispersion increase and/or to interaction between different metal oxide nanoparticles with creation of oxygen vacancies.

The UV–Vis spectroscopy is sensitive to the changes in metal ions environment and has been used to obtain more information (Fig. 2b). The peak at around 350 nm in  $\text{Ce}/\text{SiO}_2$  spectrum is typical of  $\text{O}^{2-} \rightarrow \text{Ce}^{4+}$  CT transitions [2]. The observed blue shift of this peak for  $\text{Ce}/\text{SiO}_2$  in comparison with bulk  $\text{CeO}_2$  indicates the higher dispersion of cerium in supported materials. The absorption in the 240–320 nm and 600–800 nm regions in the spectrum of  $\text{Cu}/\text{SiO}_2$  is related to  $\text{O}^{2-} \rightarrow \text{Cu}^{2+}$  CT and  $d-d$  transitions, respectively, of crystalline CuO [1]. The observed changes in the 350–500 nm region for all bi-component materials confirm the assumption done above of the existence of strong interaction between metal ions and/or to the increase in metal oxides dispersion.

More precise information for the state of metal ions was obtained by FTIR spectra of adsorbed CO (Fig. 3). The IR spectra of CO adsorption on both  $4\text{Cu}2\text{Ce}/\text{SiO}_2$  and  $2\text{Cu}4\text{Ce}/\text{SiO}_2$  samples shows an intense IR band at  $2157\text{ cm}^{-1}$  together with bands at  $2123\text{ cm}^{-1}$  and  $2133\text{--}2135\text{ cm}^{-1}$ . The band at  $2157\text{ cm}^{-1}$  is related to CO interacting with silanol groups in accordance with the corresponding shift in the hydroxyl region [18], whereas the IR bands at  $2123\text{ cm}^{-1}$  and  $2135\text{ cm}^{-1}$  can be assigned to  $\text{Ce}^{3+}$  ions in different coordination environments [19–21], in accordance with the high sensitivity of CO as probe molecule [22]. The latter IR band ( $2135\text{ cm}^{-1}$ ) can also be associated with physisorbed CO, but we can neglect this assignment taken into account the high stability of the band during evacuation. Comparing the IR spectra of both  $4\text{Cu}2\text{Ce}/\text{SiO}_2$  and  $2\text{Cu}4\text{Ce}/\text{SiO}_2$  samples, higher amount of  $\text{Ce}^{3+}$  ions can be deduced in the  $4\text{Cu}2\text{Ce}/\text{SiO}_2$  sample. On the other hand, a blue asymmetry is observed on the IR band of the  $4\text{Cu}2\text{Ce}/\text{SiO}_2$  sample at low CO coverage (shoulder at  $2172\text{ cm}^{-1}$  in spectra c) which is associated with very small amount of  $\text{Cu}^+$  ions [23]. Thus, we can conclude in the coexistence of reduced copper and cerium species which should be related to an interaction between both metals [5,12].

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