Copper supported on nanostructured mesoporous ceria-titania composites as catalysts for sustainable environmental protection: Effect of support composition

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Dedicated to Acad. Ivan Juchnovski on the occasion of his 80th anniversary

Mesoporous ceria-titania binary materials were used as a host matrix of nanosized copper oxide species. The obtained materials were characterized by XRD, nitrogen physisorption, UV-Vis, Raman, FTIR and temperature-programmed reduction with hydrogen. Their catalytic activity was tested in total oxidation of ethyl acetate and methanol decomposition to CO and hydrogen with a potential application in VOCs elimination and alternative fuels, respectively. The variations in the ceria-titania support composition affected the dispersion and the oxidative state of loaded copper species. The facilitated electron transfer between the copper species and ceria-titania support improved the catalytic activity in both catalytic processes and this effect could be successfully controlled by the Ti/Ce ratio in the samples.

Key words: Mesoporous nanostructured ceria-titania doped with copper, template-assisted hydrothermal synthesis, ethyl acetate oxidation, methanol decomposition.

INTRODUCTION

In the last decade methanol has been considered as suitable clean and efficient alternative fuel because it can be synthesized from biomass and other waste products by well-known technologies and easily converted to hydrogen or synthesis gas in case of need [1]. On the other hand, volatile organic compounds (VOCs) emitted from various industrial processes and transport activities are considered as an important class of air pollutants, and catalytic combustion is one of the most promising strategies for their elimination at relatively low temperatures [2]. An important step in the control of these catalytic processes is the development of highly efficient catalysts with controlled properties. Transition metal oxides are considered as appropriate alternative of noble metals and recently the main efforts are focused on the improvement of their electronic, surface and texture properties by the preparation of nanosized multi-component materials with well developed porous structure. The knowledge of the specific effects within the multi-component nanostructured metal oxides is prerequisite for the optimization of their properties. Recently, titanium oxide has received much attention due to its superior optical, electrical, mechanical and catalytic properties combined with non-toxicity and cost effectiveness [3]. The introduction of dopant into TiO₂ lattice may significantly affect the electronic band edges or introduce impurity states in the band gap [3]. It has been reported that the addition of ceria to titania decreases its particle size, increases the specific surface area and thermal stability, stabilizes the anatase phase, reduces the bandgap energy and improves the oxygen storage capacity via formation of oxygen vacancies. A lot of data in the literature demonstrates that the modification of TiO₂-CeO₂ mixed oxides with CuO increases the catalytic activity in oxidation processes due to improved dispersion of the supported nanoparticles and the textural characteristics of the composite materials [4-6]. It is known that factors such as the chemical nature of the support, the acid-base functionality, and the location of copper particles in mesoporous oxide matrix significantly affect the catalytic properties of the composite material [5]. CuO/CeO₂–TiO₂ has been reported as an active catalyst for SCR of NO by CO, in which ceria was incorporated into TiO₂ by using the conventional impregnation method [7]. Other authors reported that the catalytic performances of copper based catalysts for NH₃-SCR reaction are closely related to the texture and dispersion of copper oxide

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species, which are significantly influenced by the supports [8, 9].

The aim of current investigation is to study the effect of copper modification of mesoporous titania-ceria binary oxides. The effect of support composition on their catalytic behaviour in total oxidation of ethyl acetate as a representative 

**EXPERIMENTAL**

**Materials**

The titania-ceria samples were synthesized by template-assisted technique using Hexadecyl-N,N,N-trimethyl ammonium bromide (CTAB) as a template, hydrothermal treatment at 373 K and calcination at 773 K according to procedure described in [10]. The samples were denoted as xTiyCe, where x:y was the metal mol ratio, which in the bi-component samples was 2:8, 5:5 or 8:2. All initial titania-ceria materials were modified with copper by simple incipient wetness impregnation with aqueous solution of Cu(NO$_3$)$_2$·9H$_2$O in an appropriate amount to obtain 8 wt.% of copper. Then the samples were dried at ambient temperature and calcined with a heating step of 1 °C/min up to 773 K and dwelling time of 2 h.

**Methods of characterisation**

Specific surface area and pore volume data were collected from nitrogen adsorption-desorption isotherms measured at 77 K using a Quantachrome NOVA 1200 apparatus. Powder X-ray diffraction patterns were collected on a Bruker D8 Advance diffractometer with Cu Kα radiation using a LynxEye detector. FTIR spectra in the region of skeletal vibrations were recorded on a Bruker Vector 22 spectrometer at a resolution of 1–2 cm$^{-1}$, accumulating 64–128 scans and KBr pellets technique. The UV–Vis spectra were recorded on a Jasco V-650 UV-Vis spectrophotometer equipped with a diffuse reflectance unit. Raman spectra were acquired with a DXR Raman microscope using a 780 nm laser.

**Catalytic tests**

The catalytic oxidation of ethyl acetate was performed in a fixed bed flow reactor (0.030 g of catalyst) with a mixture of ethyl acetate in air (1.21 mol %) and WHSV of 100 h$^{-1}$. Methanol conversion was carried out in a fixed bed flow reactor (0.055 g of catalyst), argon being used as a carrier gas and methanol partial pressure of 1.57 kPa. On-line gas chromatographic analyses were performed for both reactions using an absolute calibration method and carbon based material balance.

**RESULTS AND DISCUSSION**

In order to obtain information for the textural characteristics of the studied materials, nitrogen physisorption measurements are done (Table 1). All materials were characterized with well-developed mesoporous structure and high specific surface area and pore volume. The addition of ceria to titania leads to an increase in the specific surface area and pore volume in comparison with the mono-component systems. Note, that the BET surface area of all CeO$_2$–TiO$_2$ samples overcomes that one if the samples were considered as a mechanical mixture of the individual oxides. This suggests for the existence of interaction between the studied metal oxides. The copper addition decreases the surface area and pore volume of titania-ceria supports, probably due to the incorporation of small CuO particles within the support pores. XRD patterns of all ceria-titania samples are presented in Fig. 1a and the data for phase composition, unit cell parameters and average crystallite size are listed in Table 1. For the pure TiO$_2$, only reflections of anatase (2θ=25.6°, 38.3°, 47.8° and 62.5°) were detected [11] (Fig. 1a, Table 1). For pure CeO$_2$, the strong reflections are attributed to cubic fluorite-like structure (2θ = 28.5°, 33.1°, 47.5°, 56.3° and 69.4°) with average crystallite sizes of 22 nm. Anatase phase was only registered when titania was doped with small amount of ceria (2Ce8Ti). However, the reflections were broader as compared to pure TiO$_2$, which evidences higher dispersion of TiO$_2$. With further increase of Ce content the reflections become weaker and wider, which indicates a decrease in the crystal size of TiO$_2$ (Table 1). For the Ce-rich samples (Fig. 1a) only reflections characteristic of cerianite CeO$_2$ could be detected. These reflections are slightly shifted to higher Bragg angles, which is due to a slight decrease of ceria unit cell parameter (Table 1). Taking into account that the radius of Ti$^{4+}$-ion is 0.74 Å, CN=6 and that one for Ce$^{4+}$-ion is 0.97 Å, CN=6, the latter observation could be assigned to the incorporation of smaller Ti$^{4+}$-ions into the ceria lattice [12,13]. XRD patterns of copper modified Ce-Ti materials are presented in
Fig. 1b. Typical anatase and fluorite phases were observed on Cu/TiO$_2$ and Cu/CeO$_2$ samples, respectively. The diffraction peaks in these samples at $2\theta = 35.5^\circ$, $38.5^\circ$ and $48.5^\circ$ are due to the presence of well crystallized CuO phase with monoclinic tenorite structure [5], probably located on the outer surface of mesoporous oxide support because of their relatively large crystal size (Table 1).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Space Group</th>
<th>Unit cell</th>
<th>Particles size, nm</th>
<th>BET m$^2$/g</th>
<th>Total Pore Volume, ml/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$</td>
<td>Anatase, syn Tetragonal – Body-centered I41/amd</td>
<td>3.786</td>
<td>17.4</td>
<td>85</td>
<td>0.29</td>
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<tr>
<td>Cu/TiO$_2$</td>
<td>Anatase, syn Tetragonal – Body-centered I41/amd</td>
<td>3.786</td>
<td>20.8</td>
<td>40</td>
<td>0.24</td>
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<tr>
<td></td>
<td>Tenorite</td>
<td>4.691</td>
<td>36.4</td>
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<td>3.419</td>
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<td></td>
<td>99.594</td>
</tr>
<tr>
<td>5Ce5Ti</td>
<td>Cerium oxide Cubic - Face center - Fm-3m</td>
<td>5.405</td>
<td>12.5</td>
<td>69</td>
<td>0.39</td>
</tr>
<tr>
<td>Cu/5Ce5Ti</td>
<td>Cerium oxide Cubic - Face center - Fm-3m</td>
<td>5.405</td>
<td>12.5</td>
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<td>0.39</td>
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<tr>
<td></td>
<td>Tenorite</td>
<td>4.716</td>
<td>45.8</td>
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<td>3.431</td>
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<td>99.578</td>
</tr>
<tr>
<td>2Ce8Ti</td>
<td>Anatase, syn Tetragonal – Primitive P42/mnm</td>
<td>3.784</td>
<td>5</td>
<td>166</td>
<td>0.62</td>
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<tr>
<td>Cu/2Ce8Ti</td>
<td>Anatase, syn Tetragonal – Primitive P42/mnm</td>
<td>3.793</td>
<td>7</td>
<td>102</td>
<td>0.49</td>
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<tr>
<td>8Ce2Ti</td>
<td>Cerium oxide Cubic - Face center - Fm-3m</td>
<td>5.409</td>
<td>17.0</td>
<td>55</td>
<td>0.30</td>
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<td>Cu/8Ce2Ti</td>
<td>Cerium oxide Cubic - Face center - Fm-3m Tenorite</td>
<td>5.407</td>
<td>16.8</td>
<td>38</td>
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<td>4.688</td>
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<td>99.323</td>
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<tr>
<td>CeO$_2$</td>
<td>Cerium oxide Cubic – Face center – Fm-3m</td>
<td>5.413</td>
<td>21.8</td>
<td>46</td>
<td>0.26</td>
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<tr>
<td>Cu/CeO$_2$</td>
<td>Cerium oxide Cubic – Face center – Fm-3m Tenorite</td>
<td>5.413</td>
<td>22.0</td>
<td>24</td>
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<td>5.130</td>
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<td>99.44</td>
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</table>
In the case of Cu/2Ce8Ti, the main reflections belonging to anatase phase appeared with low intensity and no reflections corresponding to CeO2 and CuO were observed. This observation indicates formation of highly dispersed metal oxide particles. Strong reflections attributable to cubic fluorite-like structure of CuO with average crystallite size of 40 and 45 nm, respectively (Table 1), were detected in the patterns of Cu/8Ce2Ti and Cu/5Ce5Ti. The observed decrease of the unit cell parameter for ceria components in copper containing samples (Table 1) as compared to pure CeO2 does not exclude partial substitution of Ce4+ ions by smaller Cu2+ ion (0.73 nm). According to [14] it is likely that part of Cu2+ ions entered into the CeO2 lattice to form a solid solution and the rest of Cu2+ formed CuO particles on the surface of CeO2.

FTIR analysis was conducted (not shown) in order to get more information for the studied materials. The spectrum of pure TiO2 sample consists of peaks at 460, 620 and the shoulder at 910 cm⁻¹, typical of anatase titania [12]. The broad and intensive band below 700 cm⁻¹ observed for the pure CeO2 sample is related to the Ce–O bond vibrations. The band around 1600 cm⁻¹ is due to adsorbed water molecules. The broad band in the interval 3100–3700 cm⁻¹ is assigned to O-H stretching vibrations. The broad and intensive band below 700 cm⁻¹ observed for the Cu/ CeO2 sample is assigned generally to Ce-O stretching vibrations in defect Ce-O-Cu structures [6]. This feature decreases for the mixed oxide materials, probably due to the creation of new contact between the different metal oxide nanoparticles. The registered variation in the intensity of the band in the 3100–3700 cm⁻¹ interval in the FTIR spectra of copper CeTi samples implies that the possible interaction between different oxides results in differences in the surface defects, which reflects on the amount of surface hydroxyl groups and adsorbed water (not shown).

UV–vis diffuse reflectance spectra of individual TiO2 and CeO2 oxides and their composites are presented in Fig. 2a. Only one adsorption edge which corresponds to the band transition at about 355 and 314 nm was detected in the spectra of TiO2 and CeO2, respectively. It is clearly seen, that ceria doping of titania results in shift of the adsorption edge to the visible region. The observed red shift was most pronounced for 2Ce8Ti sample and decreased with the increase of ceria content. In accordance with [15] this could be due to the formation of new energy level within the band gap of TiO2. The absorption in the range of 240–320 nm and 600–800 nm regions for all copper modification is related to O2−→Cu2+ CT and d–d transitions, respectively, of crystalline CuO [6] (Fig. 2b). In accordance with the XRD and nitrogen physisorption data, the observed changes in the 350–500 nm region for all copper modifications confirm the assumption done above for the existence of strong interaction between the different metal ions and/or the increase in the metal oxides dispersion.

In order to obtain more information for the type of interaction between metal oxide nanoparticles, Raman spectra were recorded (Fig. 3a).
The Raman spectrum of TiO$_2$ consisted of well defined Raman shifts at 143 cm$^{-1}$ (E1g), 195 cm$^{-1}$ (E2g), 396 cm$^{-1}$ (B1g), 514 cm$^{-1}$ (A1g) and 637 cm$^{-1}$ (E3g), which are typical of pure anatase structure [16]. In case of mixed CeTi samples, the observed decrease in the intensity of the main peak, typical of titanium oxide accompanied with its slight broadening could be due to particle size decrease, which is in accordance with the XRD data (Fig. 1a, Table 1). The spectrum of CeO$_2$ showed the main Raman shift at 463 cm$^{-1}$ (E2g) typical of CeO$_2$ [12]. The additional band at 600 cm$^{-1}$ was generally assigned to the presence of oxygen defects in the ceria lattice. For the bi-component CeTi materials, a slight shifting and broadening of the main Raman-active mode accompanied with a decrease in its intensity is detected (Fig. 3a). This could be assigned to partial replacement of Ce ions with Ti ones, resulting in Ce-O bonds shortening and formation of smaller crystallites with defect structure. In the case of 2Ce8Ti sample, no peaks of CeO$_2$ are observed. The Raman bands corresponding to CuO was absent for all copper catalysts, indicating that CuO was in highly dispersed state, consistent with the XRD results. The observed slight blue shift of the Raman E1g mode to 150 cm$^{-1}$ for copper modifications could be an indication for the changes in the environment of titanium ions in anatase lattice (Fig. 3b). The appearance of such a non-stoichiometric structure of titania could be due to the formation of distinct atomic defects like Ti$^{3+}$, interstitial Ti$^{4+}$, or oxygen vacancies [15]. A slight red shift of the position of the band at 463 cm$^{-1}$, combined with significant decrease in the intensity and increase of the half-width is observed for all Cu/CeTi materials, suggesting strong interaction between CuO and CeO$_2$ (Fig. 3b). At the same time the disappearance of the main CuO peaks and a significant increase of the relative intensity of the peak at 600 cm$^{-1}$ is
observed. Generally, the latter feature is assigned to the formation of oxygen vacancies due to the replacement of Ce$^{4+}$ by metal ion with different valence.

In Fig. 4 are presented data from the TPR analyses. The reduction of pure CeO$_2$ was initiated just above 657 K. The observed weight loss with further temperature increase up to 773 K corresponded to about 10% reduction of Ce$^{4+}$ to Ce$^{3+}$ ions, probably from the surface [12] (Fig. 4a).

The reduction effect for the bi-components samples is larger in comparison with pure CeO$_2$ and starts at lower temperature. For 5Ce5Ti higher reduction ability as compared to 8Ce2Ti is detected, which could be assigned to the increase of the number of titanium ions, incorporated in ceria lattice. However, the reduction became more difficult with further increase of titania content (2Ce8Ti), but it remains still easier as compared to the pure CeO$_2$.

Thus, TPR results clearly demonstrate the existence of interaction between different metal oxide species in bi-component materials, which results in the presence of more readily reducible ceria crystallites, interacting with titania. In Fig. 4b are presented data from the TPR analyses of the copper modifications. Cu/TiO$_2$ exhibits reduction peak with a maximum at about 470 K, which corresponds to one step reduction of Cu$^{2+}$ to metallic copper [4].

The appearance of two reduction peaks for Cu/CeO$_2$ centered at 385 and 439K could be assigned to the reduction of Cu$^{2+}$ ions in different environment and/or differently dispersed CuO particles (Fig. 4b). Two reduction effects are observed also for all mixed copper samples, indicating the existence of at least two types of copper species (Fig. 4b). Note that the ratio between them changes with Ce/Ti ratio with a tendency to an increase in the relative part of the low-temperature effect with ceria amount decrease. In accordance with the XRD data, this could be due to the improved dispersion of ceria in the vicinity of titania.

In Fig. 5 are presented temperature dependencies of total oxidation of EA. Beside CO$_2$, which is the most important product of EA oxidation, ethanol (EtOH), acetaldehyde (AA), acetic acid (AcAc) and ethene is also registered as by-products. For CeTi samples the ethyl acetate oxidation is initiated above 500 K and 80–100% conversion is achieved at 650 K. Among all materials, pure ceria exhibits the highest catalytic activity. Besides, on this material high selectivity to EtOH (47%) is observed. The lowest catalytic activity combined with high selectivity to AA (25%), EtOH (22%) and ethene (18%) is registered for TiO$_2$ sample. The improvement of the selectivity to CO$_2$ for all binary materials clearly indicates dominant effect of redox over the acid-base properties for these materials [2]. With the exception of Cu/CeO$_2$, all copper modifications exhibited improved catalytic activity in total oxidation of ethyl acetate to CO$_2$ in comparison with the corresponding supports (Fig. 5b).

![Fig. 4. TPR-DTG patterns of CeTi (a) and Cu/CeTi (b) materials.](image-url)
Fig. 5. Ethyl acetate conversion of CeTi (a) and Cu/CeTi (b) materials.

Note the decrease in the catalytic activity with the increase in Ce/Ti ratio in the support. Taking into account the nitrogen physisorption measurements this could be due to a decrease in the BET surface area (Table 1).

The temperature dependencies of methanol conversion and selectivity to CO and hydrogen for titania and ceria samples are presented in Fig. 6a. Besides CO, which formation is directly related to hydrogen production from methanol, CO$_2$, CH$_4$, dimethyl ether (DME) and C$_2$-C$_3$ hydrocarbons are registered as by-products. All materials exhibit catalytic activity above 500-550 K. The monocomponent CeO$_2$ sample possesses extremely low catalytic activity and about 50% selectivity to CO due to the formation of CH$_4$ (Fig. 6a).

The main by-products during the methanol decomposition on TiO$_2$ materials are DME (about 50%) and hydrocarbons (about 17%) which clearly indicates existence of high acidic functionality. Here, well pronounced trend to deactivation with the temperature increase for this material is detected, which could be due to the deposition of non-desorbable products. The binary CeTi materials demonstrate improved catalytic activity and stability at higher temperatures as compared to the individual oxides (Fig. 6a).

Their relatively low selectivity to CO is due to the contribution of methane (about 30%) and DME (30-40%) as by-products. Copper modifications demonstrated improved catalytic activity in methanol decomposition as compared to ceria-titania supports only in case of relatively low Ce/Ti ratio of the support (Fig. 6b). The complex temperature dependency of their catalytic activity indicates changes in the catalytic active sites under the reaction medium.

CONCLUSION

High surface area mesoporous ceria-titania binary materials can be successfully synthesized using template assisted hydrothermal technique. Binary oxide supports exhibit improved dispersion, high surface area and pore volume combined with excellent oxygen mobility. As a result, a significant increase in the catalytic activity and selectivity in total oxidation of ethyl acetate to CO$_2$ and methanol decomposition to syngas is achieved.
Small additives of copper to ceria and/or titania oxides promotes their catalytic activity in total oxidation of ethyl acetate and methanol decomposition to syngas, but this effect is strongly influenced by support composition. The lower Ce/Ti ratio promotes the catalytic activity both in ethyl acetate oxidation and methanol decomposition in a higher extent.

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