Effect of preparation procedure on the formation of nanosized mesoporous TiO$_2$–CeO$_2$ catalysts for ethyl acetate total oxidation and methanol decomposition

A. Mileva$^1$, G. Issa$^1$, J. Henych$^2$, V. Štengl$^2$, D. Kovacheva$^3$, T. Tsoncheva$^1$

$^1$Institute of Organic Chemistry with Centre of Phytochemistry, BAS, Bulgaria,
$^2$Materials Chemistry Department, Institute of Inorganic Chemistry AS CR
$^3$Institute of General and Inorganic Chemistry, BAS, Bulgaria

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Two series TiO$_2$–CeO$_2$ samples were synthesized using homogeneous precipitation with urea and template-assisted hydrothermal procedures. The samples were characterized by nitrogen physisorption, XRD, UV–Vis, Raman and TPR techniques. The catalytic properties of the obtained materials were studied in oxidation of ethyl acetate and methanol decomposition. The effect of preparation procedure on the phase composition, texture, structure and redox properties was discussed in close relation with the possibilities for fine tuning of their catalytic activity.

Keywords: Ti-Ce oxides, ethyl acetate total oxidation, methanol decomposition.

INTRODUCTION

Recently, the design and synthesis of nanostructured titanium oxide with high surface area, high thermal stability, and crystalline framework have attracted considerable interest because of their superior electrical, mechanical, optical and catalytic properties combined with non-toxicity and cost effectiveness [1]. Nowadays, titania is widely used in preparation of optical devices, pigment, bio-materials, gas sensors, electrodes, solar cells, catalysts for degradation of various pollutants [1, 2]. Different preparation techniques have been developed for effective control of titania properties for various applications [1, 2] and among them, doping with ceria have attracted particular attention due to its excellent redox chemistry and oxygen storage capacity [3]. The aim of present study is the preparation of series of nanostructured TiO$_2$–CeO$_2$ oxide materials two using homogeneous precipitation with urea and template-assisted hydrothermal synthesis. The obtained materials were characterized by nitrogen physisorption, XRD, Raman, UV–Vis and TPR. The catalytic properties were studied in methanol decomposition (MD) and total oxidation of ethyl acetate (EA) with an environmental potential as alternative clean and efficient fuel [4] and elimination of organic pollutants in air [5], respectively.

EXPERIMENTAL

Mono and bi-component titania and ceria materials were synthesized by hydrothermal procedure using CTAB as a structure directed template (HT) and homogeneous precipitation with urea technique (U) as was described in [4] and [6], respectively. The samples were denoted as xTiyCe$_M$, where x/y was the metal mol ratio and M was the preparation method used. The textural characteristics were collected from nitrogen adsorption-desorption isotherms measured at 77 K using a Coulter SA3100 instrument. Powder X-ray diffraction patterns were collected on a Bruker D8 Advance diffractometer with Cu K$_\alpha$ radiation using a LynxEye detector. Mean crystallite size were determined with the Topas-4.2 software package using the fundamental parameters peak shape description including appropriate corrections for the instrumental broadening and diffractometer geometry. The UV–Vis spectra were recorded on a Jasco V-650 UV-Vis spectrophotometer. Raman spectra were collected on a DXR Raman microscope using a 780 nm laser. The TPR/TG analyses were performed on a Setaram TG92 instrument in a flow of 50 vol% H$_2$ in Ar. Catalytic oxidation of EA was performed in a flow type reactor with a mixture of EA in air. Gas chromatographic analyses were done on a HP 5890 apparatus using carbon-based calibration. MD was carried out in a fixed bed flow reactor and Ar as a carrier gas. On-line gas chromatographic analyses

* To whom all correspondence should be sent: E-mail: aleksandra_bunalova@abv.bg

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were performed on HP apparatus equipped with flame ionization and thermo-conductivity detectors, on a PLOT Q column, using an absolute calibration method and a carbon based material balance.

RESULTS AND DISCUSSION

In Fig. 1a are presented nitrogen physisorption isotherms for the samples obtained by various techniques and the corresponding data are listed in Table 1. According to IUPAC classification the isotherms are of IV type, typical of materials with mesoporous structure. The observed differences in the shape of hysteresis loop indicate predominantly presence of cylindrical pores for TiO$_2$ HT and TiCe HT, cage-like pores for TiO$_2$ U and TiCe U and slit-like pores for CeO$_2$ HT and CeO$_2$ U.

![Fig. 1. Nitrogen physisorption isotherms (a) and XRD patterns (b) of TiCe materials.](image)

As compared to the hydrothermally obtained materials, the urea samples possess lower porous volume (Table 1) and higher specific surface area. Besides, an increase in the surface area and pore volume is also observed for both bi-component samples. Thus, the development of the mesoporous structure strongly depends on the preparation procedure and the initial phase composition. It is predominantly directed by the organic template used during the hydrothermal procedure and by the interparticles interaction for the urea assisted one and the effects are better pronounced for the binary oxides.

Fig. 1b shows the XRD patterns of titania and ceria materials. The diffraction peaks in the pattern of TiO$_2$ HT and TiO$_2$ U are indexed to anatase phase of TiO$_2$ [2] with average crystallite size of about 17 nm and 13 nm, respectively. The diffraction figures for both CeO$_2$ materials are typical of cubic fluorite-like structure of cerianite [3] with average crystallite size of 10-13 nm. Ceria with average crystallite size of 12 nm is only registered phase for TiCe H, while a mixture of anatase and ceria with average crystallite size of 5 and 7 nm, respectively, is found for TiCe U. The observed decrease of unit cell parameters for the ceria components in binary materials (5.403Å for TiCe-HT and 5.401Å for TiCe-U) as compared to pure CeO$_2$ samples (5.416 Å for CeO$_2$-HT and 5.414 Å for CeO$_2$-U) does not exclude partial substitution of Ce$^{4+}$ ions by smaller Ti$^{4+}$ ions.

In Fig. 2 are presented Raman spectra of TiCe materials, obtained by various procedures. The Raman shifts at 143 cm$^{-1}$(E$_{1g}$), 195 cm$^{-1}$(E$_{2g}$), 396 cm$^{-1}$(B$_{1g}$), 514 cm$^{-1}$(A$_{1g}$) and 637 cm$^{-1}$(E$_{3g}$) in the spectra of both TiO$_2$ samples demonstrate presence of pure anatase phase [7]. Only one Raman-active E$_{2g}$ mode, centered at about 463 cm$^{-1}$, which is typical of cubic structure, is detected for both ceria materials [3].

### Table 1. Nitrogen physisorption data of TiCe materials.

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET $m^2g^{-1}$</th>
<th>$V_1$ $cm^3g^{-1}$</th>
<th>$T_{50%}$, K</th>
<th>$T_{30%}$, K</th>
<th>SA, EA $mol.m^{-2}$</th>
<th>SA, MD $mol.m^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$ HT</td>
<td>85</td>
<td>0.29</td>
<td>660</td>
<td>662</td>
<td>0.29</td>
<td>0.37</td>
</tr>
<tr>
<td>TiO$_2$ U</td>
<td>97</td>
<td>0.19</td>
<td>651</td>
<td>630</td>
<td>0.23</td>
<td>0.54</td>
</tr>
<tr>
<td>TiCe HT</td>
<td>99</td>
<td>0.45</td>
<td>586</td>
<td>685</td>
<td>0.60</td>
<td>0.37</td>
</tr>
<tr>
<td>TiCe U</td>
<td>117</td>
<td>0.30</td>
<td>574</td>
<td>661</td>
<td>0.65</td>
<td>0.53</td>
</tr>
<tr>
<td>CeO$_2$ HT</td>
<td>46</td>
<td>0.26</td>
<td>560</td>
<td>730</td>
<td>1.74</td>
<td>0.43</td>
</tr>
<tr>
<td>CeO$_2$ U</td>
<td>76</td>
<td>0.07</td>
<td>535</td>
<td>604</td>
<td>1.09</td>
<td>0.60</td>
</tr>
</tbody>
</table>

*BET-surface areas; $V_1$-pore volume; $T_{50\%}$-temperatures for 50% conversion of ethyl acetate (EA); $T_{30\%}$-temperatures for 30% conversion of methanol decomposition (MD); *SA-specific catalytic activity
is typical of pure ceria phase. The shift in the main absorption edges for both individual oxides indicates higher dispersion for the hydrothermally obtained materials. The red shift of the curves for the bi-component TiCe materials could be due to the formation of new energy level within the band gap of TiO2 and/or presence of highly dispersed ceria. Substitution of Ti ions in ceria lattice is not excluded as well.

TPR-TG profiles of hydrothermally and urea obtained TiCe samples are compared in the 450–770 K region (Fig. 3b). The observed weight loss for CeO2 HT (0.18 mg) and CeO2 U (0.08 mg) corresponds to the reduction of Ce4+ to Ce3+ and it is about 10 and 4 %, respectively. The reduction effects for the TiCe-HT (0.55 mg) and TiCe-U (0.38 mg) are larger in comparison with the pure CeO2 samples and they are also detected at lower temperature. In accordance with the other physicochemical measurements, this indicates increased mobility of lattice oxygen which could be due to the improved dispersion and distortion of ceria lattice during the titanium incorporation. The reduction behaviour for all materials is not in a simple relation to their specific surface area. Thus, the facile reduction for the hydrothermal samples is probably related to their higher dispersion, well developed mesoporous structure and homogeneous phase composition.

In Fig. 4 are presented temperature dependencies of total oxidation of EA on various materials. Beside CO2, which is the most important product of EA oxidation, (Fig. 4b), ethanol (EtOH), acetaldehyde (AA), acetic acid (AcAc) and ethene are also registered as by-products. For both series of samples the ethylacetate oxidation is initiated above 500 K and 80–100% conversion is achieved at 650 K. Among all materials, both pure mono-
component ceria compounds exhibit lowest $T_{50}$ (Table 1) which indicates their high catalytic activity. Besides, on these materials high selectivity to EtOH is observed. The lowest catalytic activity combined with high selectivity to AA, EtOH and ethene is registered for both TiO$_2$ samples. The binary materials possess intermediate catalytic activity as compared to the individual oxides and here high selectivity to ethanol is also observed. A common feature is the higher activity for all urea obtained materials as compared to their hydrothermally prepared analogues. In order to ignore the impact of the differences in the specific surface area of the samples, the specific catalytic activity as conversion per unit BET was calculated (Table 1). Surprisingly, here urea samples exhibit lower or similar SA to the HT analogues indicating that the observed catalytic behaviour is strongly related to the improved surface area during the urea synthesis.

![Fig. 4. Ethyl acetate conversion (a) and selectivity to CO$_2$ (b) of TiCe materials.](image)

It was well established that for many oxide systems, the total oxidation of EA is a step-wise process including hydrolysis to EtOH and AcAc and their further oxidation via Mars van Krevelen mechanism [5]. The improvement of the selectivity to CO$_2$ for the binary materials and for all urea obtained ones clearly indicates the dominant effect of the surface redox over the acid-base properties for these materials, which is obviously regulated both by the preparation method and the substitution of ceria with Ti.

The temperature dependencies of methanol conversion and CO selectivity for titania and ceria samples are presented in Fig. 5. Besides CO, which is the most important product from the decomposition, CO$_2$, CH$_4$, dimethyl ether (DME) and C$_2$-C$_3$ hydrocarbons are registered as by-products. All materials exhibit activity above 500-550 K. The temperatures at which 30% conversion is achieved (Table 1.) demonstrate high catalytic activity combined with 90% selectivity to CO due to the formation of CO$_2$ for CeO$_2$. Just the opposite, the HT obtained analogue possesses extremely low catalytic activity and about 50% selectivity to CO due to the formation of CH$_4$.

![Fig. 5. Methanol conversion (a) and selectivity to CO (b) of TiCe materials.](image)

The main by-products during the methanol decomposition on both TiO$_2$ materials are DME (about 50%) and hydrocarbons (about 17% for TiO$_2$ HT) which clearly indicates existence of high acidic function. Here, well pronounced trend to deactivation with the temperature increase for both materials is detected, which could be due to the deposition of non-desorbable products. Both binary materials demonstrate improved catalytic activity and stability at higher temperatures as compared to the individual oxides. Their relatively low selectivity to CO is due to the contribution of methane (about 30%) and DME (30-40%) as by-products. All urea materials exhibit higher catalytic activity as compared to their HT analogues. The higher values of the specific activity for the urea samples (Table 1.) strongly evidences that their higher catalytic activity is not in simple relation with the improved specific surface area.

Thus the variations in the SA values (Table 1.) as well as the differences in the selectivity for both catalytic processes urge the authors to assume more complex effect than the expected one from the differences in the specific surface area. The XRD, Raman, UV-Vis and TPR analyses demonstrate higher dispersion for the hydrothermally obtained materials, which can also influence the degree of substitution of Ti in ceria lattice for binary materials. This can affect the generation of oxygen
vacancies and cerium and titanium ions in lower oxidative state [1]. As a result changes in the surface acidic-base and redox properties and the related with them catalytic behaviour of the solids is expected (Figs. 4, 5). The complexity of this process needs more detail analysis with appropriate techniques and further investigation is in progress.

CONCLUSION

By using homogeneous precipitation with urea and template-assisted hydrothermal procedures, nanosized titania-ceria materials with high specific surface area and pore volume were successfully prepared. The strong interaction between CeO$_2$ and TiO$_2$ as well as the crystallization of particles in the nanoscale improve the redox properties of the TiO$_2$–CeO$_2$ mixed oxides. The control of the catalytic activity and selectivity requires fine tuning of the phase composition, texture, structure, morphology and surface properties which could be tuned by the preparation method used. The hydrothermal method provides the formation of more homogeneous, better dispersed materials with higher mesopore volume, but their lower specific surface area provides lower catalytic activity in ethyl acetate oxidation and methanol decomposition as compared to the urea synthesized materials.

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