Nanosized CuO–Zr\textsubscript{x}Ce\textsubscript{1\_x}O\textsubscript{y} aerogel catalysts prepared by ethanol supercritical drying for catalytic deep oxidation of benzene

Chaoquan Hu\textsuperscript{a,b}, Qingshan Zhu\textsuperscript{a,*}, Zheng Jiang\textsuperscript{a}

\textsuperscript{a} State Key Laboratory of Multiphase Complex System, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China
\textsuperscript{b} Graduate School of Chinese Academy of Sciences, Beijing 100049, China

\textbf{Abstract}

Nanosized CuO–Zr\textsubscript{x}Ce\textsubscript{1\_x}O\textsubscript{y} (0 ≤ x ≤ 0.5) solid solution oxide catalysts were prepared using a co-precipitation method followed with ethanol supercritical drying and calcination at 800°C. The structural characteristics and redox behaviors were investigated by using X-ray diffraction (XRD), transmission electron microscopy (TEM), Raman spectroscopy, and temperature programmed reduction (H\textsubscript{2}-TPR). The results revealed that the as-prepared samples not only possessed large specific surface areas, small crystal sizes and high homogeneity of constituents, but also exhibited high catalytic activity for the complete oxidation of benzene. The structural properties and the catalytic performances of the aerogel catalysts strongly depended on the Ce/Zr molar ratio. The most highly active catalyst, CuO–Ce\textsubscript{0.5}Zr\textsubscript{0.5}O\textsubscript{y}, could oxidize benzene at 300°C and kept robust in a 50 h long-term duration test, implying it would be a good and cost-effective alternative to noble metal catalysts for the complete oxidation of VOCs at lower temperatures.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Volatile organic compounds (VOCs) emitted from industrial production are an important class of air pollutants. Reduction of the VOCs emissions is a very important issue in the environment field since the emission standards are becoming increasingly stringent. Catalytic oxidation is one of the most important technologies for the abatement of VOCs at low concentrations in effluent streams [1,2]. Compared to the thermal oxidation, catalytic oxidation can operate at a relatively low temperature, which is helpful for reducing energy consumption and for avoiding the formation of toxic byproducts such as NO\textsubscript{x}. Supported noble metals are very active for the catalytic oxidation of VOCs [3,4]; however, the high cost and limited availability of the noble metals hamper their wide applications. Much effort has been made to prepare catalysts with high catalytic activities toward VOCs oxidation using cheap raw materials [5–8].

The unique features of oxygen storage capacity have made CeO\textsubscript{2} essential in numerous catalytic oxidation processes. Better redox properties than that of pure CeO\textsubscript{2} can be obtained by the incorporation of metal ions into the CeO\textsubscript{2} lattice forming Ce\textsubscript{1\_x}M\textsubscript{x}O\textsubscript{y} solid solutions, such as Ni, Pr, and Mn [9–13]. Recent reports have shown that the performance of Ce-based oxides for oxidation reactions is greatly enhanced by the incorporation of CuO into the CeO\textsubscript{2} lattice, and the activity of CeO\textsubscript{2} supported CuO catalyst for oxidation reactions is even comparable to those of the supported noble metals catalysts [14,15]. In recent years, doping ZrO\textsubscript{2} into CeO\textsubscript{2} has been extensively studied and it was found that the oxygen storage capacity, the redox property and the thermal resistance of the resulting mixed oxides Ce\textsubscript{1\_x}Zr\textsubscript{x}O\textsubscript{2} were greatly improved [16–20]. Thus, it is expected that CeO\textsubscript{2} with small amount of ZrO\textsubscript{2} supported CuO may show much better catalytic performance than CuO–CeO\textsubscript{2} for the catalytic oxidation of VOCs, such as catalytic activity and thermal stability.

Over the past few years, it has been recognized that nanosized materials offer significant promise as heterogeneous catalysts due to their high surface areas. One of the simple and effective strategies for preparing nanosized catalyst is the co-precipitation method, which usually consists of three steps: co-precipitation, drying and calcination. However, the conventional oven drying process always leads to their serious collapse of the structure of hydrogel due to the capillary stress caused by the surface tension of water. In contrast, under a supercritical state, the interface between vapor and liquid will disappear, thus eliminating the surface tension of the liquid. Therefore, if the hydrogel is dried under the supercritical state of a suitable liquid, the capillary stress will be eliminated, and the structure of the hydrogel can be maintained, which is beneficial to reduce the aggregation of the nanocrystals and the loss of surface area during the following calcination procedure [21–23], and thereby the number of active surface area sites may be increased.

In the present study, nanosized CuO–Zr\textsubscript{x}Ce\textsubscript{1\_x}O\textsubscript{y} aerogels with x in the range of 0–0.5 were prepared via a supercritical drying method and used as catalysts for the catalytic oxidation removal of benzene. Benzene is chosen as a model molecule of VOCs because it is widely...
used in modern industrial processes and difficult to be oxidized at relatively low temperatures. The as-prepared CuO–Zr,Ce1–xO aerogel catalysts were characterized by XRD, TEM, Raman spectra and H2–TPR techniques; their activities for deep oxidation of benzene were tested in a continuous-flow fixed-bed reactor.

2. Experimental section

2.1. Catalyst preparation

All the regents were of analytical grade and used as received without further purification. CuO–Zr,Ce1–xO aerogel catalysts were synthesized using the raw materials of Cu(NO3)2·3H2O, Ce(NO3)3·6H2O, ZrO(NO3)2·2H2O, NaOH and PEG. Cu(NO3)2·3H2O, Ce(NO3)3·6H2O and ZrO(NO3)2·2H2O with the defined molar ratios together with 5% PEG were dissolved into deionized water to form a solution with the metal ions concentration of 0.1 M. A 0.01 M NaOH solution was then added dropwise to the above solution under continuously vigorous stirring at room temperature until the metal ions were completely precipitated. The resultant hydrogel was aged for 2 h at room temperature, followed by filtering and repeatedly washing with deionized water and absolute ethanol to remove the free water involved in the hydrogel. The obtained gel was treated in an autoclave at the ethanol supercritical drying (SCD) condition of 260 °C and 8.0 MPa for 2 h. After the release of the ethanol vapor at 260 °C, the powder was cooled down to room temperature with a continuous argon flow. The resultant powders were further calcined in air at 800 °C for 2 h. The CuO content in all the catalysts was set to be about 5 wt.%.

2.2. Catalyst characterizations

The crystalline phase of the powder was analysed by an X-ray diffractometer (X’Pert MPD Pro, PANalytical, The Netherlands). The BET surface area of the sample was obtained at 77 K using an Autosorb-1 gas system (Quantachrome Instruments, USA). The BET surface area and the pore volume were calculated by using adsorption and desorption branches, respectively. Prior to each analysis, the sample was dried at 300 °C for 4 h under vacuum. The Raman spectrum was obtained on a LabRAM HR800 spectrometer (Horiba Jolin Yvon, France) equipped with a 514 nm single-frequency laser and a CCD detector at ambient temperature and moisture-free conditions. The sample was mounted in a spinning holder to avoid thermal damage during the scanning process. TEM images were taken on an H-700 electron microscope (Hitachi, Japan) at an accelerating voltage of 200 kV. All samples were crushed, dispersed in ethanol, and deposited on a microgrid prior to observation.

Temperature-programmed reduction (TPR) experiments were carried out using the CHEMBET 3000 adsorption instrument (Quantachrome, USA) equipped with a thermal conductivity detector (TCD). About 50 mg samples were loaded and dried under Ar atmosphere at 150 °C for 1 h. After the sample was cooled down to 50 °C, a reduction agent of 5% H2/Ar with a flow rate of 16 mL/min was introduced. The sample was heated up to 400 °C with a heating rate of 10 °C/min.

2.3. Catalytic activity evaluation

The catalytic activity measurement was carried out in a fixed bed reactor with a diameter of about 6 mm. In each test run, 200 mg of catalyst diluted with appropriate amount of inert quartz beads (40–60 mesh) was placed at the center of the reactor. A thermocouple was located above the catalyst to monitor the reaction temperature. To prevent the physisorption of benzene in the initial stages of the test, the catalyst was pretreated at 120 °C for 30 min under the test flows of reactant mixture (1000 ppm benzene and 20 vol.% oxygen balanced by nitrogen). When a steady state was attained, the temperature was raised from 120 °C to the temperature of the complete conversion of benzene. The total flow rate was about 320 mL/min, corresponding to a GHSV of 96,000 mL·g−1·h−1. The benzene conversion was measured by determining the outlet concentration of benzene using a gas chromatograph (GC with a flame ionization detector (GC-9190, FID, China) and a GC with a TCD (SP-3420, BEIFEN, 13X and GDC-104 columns, China). The detection limit is 1 ppm for benzene and 5 ppm for carbon dioxide. In all reaction conditions, the carbon mass balances are in the range of 100±5%.

The benzene conversion was used as a measure of the catalytic activity of the catalyst in the present study and defined as follows:

\[
X_{\text{benzene}} = (\text{[benzene]}_{\text{in}} - \text{[benzene]}_{\text{out}}) / \text{[benzene]}_{\text{in}} \times 100\%
\]

where [benzene] was the concentration of benzene in the gas stream. Catalyst stability test for the CuO–Zr0.5Ce0.5O aerogel catalyst was carried out using the same equipment as the activity evaluation. The catalyst bed was first heated to 300 °C at which a complete benzene conversion was achieved, then decreased to 260 °C, and maintained constant at this temperature for about 50 h.

3. Results and discussion

3.1. Structural characteristics of CuO–Zr,Ce1–xO aerogels

Fig. 1 shows the XRD patterns of the as-prepared CuO–Zr,Ce1–xO aerogel powders calcined at 800 °C. The distinct fluorite oxide diffraction pattern of CeO2 can be seen in all samples. The samples with different amounts of ZrO2 show obvious broader diffraction peaks than the sample without ZrO2, indicating the decrease of the crystallite sizes of the samples caused by the doping of ZrO2. Furthermore, the position of CeO2 diffraction peaks gradually shifts to high 2θ values with increasing the ZrO2 amount, suggesting the formation of solid solution since the radius of Zr4+ ions (0.090 nm) is smaller than that of the Ce4+ ions (0.101 nm). The calculated results of the crystallite size and the cell parameter are summarized in Table 1. The average crystallite sizes of the samples were obtained according to the Scherrer equation by measuring the (111) diffraction of the cubic crystallites. Clearly, the crystallite size and the lattice parameter decrease with the increase of the ZrO2 amount in the samples, confirming that the ZrO2 incorporates into the CeO2 lattice. The formation of Ce–Zr solid solution can cause structural distortions inside CeO2, producing strain into the oxide lattice and facilitating oxygen vacancies formation.
synergetic effect between CuO and CeO$_2$, which may decrease its system calcined at 800 °C. The presence of bulk CuO would reduce the particles distributed randomly. CuO examined by TEM. It can be observed that aggregates of very small microstructure of the as-prepared aerogel samples was further the samples is consistent with that of the BET surface area. The samples were also summarized in the Table 1. It can be seen that the CuO diffraction peaks (Fig. 2.).

It should be noted that no diffraction peaks of CuO crystallites can be detected for all samples calcined at 800 °C. The CuO diffraction peaks were previously observed in many CuO–Zr$_x$Ce$_{1−x}$O$_y$ samples after calcination at 800 °C [24–26]. To our best knowledge, this is the first report of the absence of CuO diffraction peaks for the Cu–Ce–Zr system calcined at 800 °C. The presence of bulk CuO would reduce the synergetic effect between CuO and CeO$_2$, which may decrease its catalytic activity for oxidation reactions. Thus, the nanocrystalline catalyst prepared by the ethanol supercritical drying is believed to have a better structural stability than those prepared by the conventional methods. This result also indicates that the preparation method has great effect on the chemical and physical properties of the catalyst. It has been widely accepted that the skeleton of the original hydrogel is almost kept intact in the aerogel, as in the supercritical drying process, the in hydrogel is almost kept intact in the aerogel, as in the supercritical adsorption bands at approximately 462, 600 and 1125 cm$^{-1}$ are observed for all the samples. It is well known that the adsorption peak at 462 cm$^{-1}$ is ascribed to the Raman active F$_{2g}$ mode of CeO$_2$ cubic lattice, which can be viewed as a symmetric breathing mode of the oxygen atoms around cerium ions [30]. The weak and broad band observed near 600 cm$^{-1}$ and the second-order peak at 1125 cm$^{-1}$ can be attributed to oxygen vacancies, which results from the replacement of Ce$^{4+}$ by metal ion with different radius[31]. These results indicate that part of CuO was incorporated into the CeO$_2$ lattice for the CuO–CeO$_2$ sample and did not segregate even after calcination at 800 °C. It should be noted that the band located at 462 cm$^{-1}$ becomes broader and weaker with the increase of the ZrO$_2$ loading. The most probable interpretation of the broadening of the band is the presence of more oxygen vacancies, which was related to a change of the CeO$_2$ environment in the presence of ZrO$_2$ due to the formation of solid solutions [34]. Thus, it is reasonable to conclude that the Zr–Ce–O formed a solid solution in the CuO–Zr$_x$Ce$_{1−x}$O$_y$ samples, which is consistent with the above XRD results.

3.2. Redox property of CuO–Zr$_x$Ce$_{1−x}$O$_y$ aerogels

Temperature-programmed reduction has been widely used to characterize oxygen storage/release behavior of CeO$_2$-based materials [35]. The TPR profiles of the as-prepared CuO–Zr$_x$Ce$_{1−x}$O$_y$ aerogels are shown in Fig. 5. It can be seen that the hydrogen consumption of all the samples can be roughly divided into two reduction peaks named $\alpha$ and $\beta$, respectively. The presence of two reduction peaks is similar to the reduction behavior of CuO–CeO$_2$ reported by many investigators [36]. It has been pointed out that the peak $\alpha$ may be originated from the reduction of oxygen in close contact with ceria and the peak $\beta$ may be attributed to bulk copper oxide species which are less associated with ceria.

The quantitative analysis of the reduction peaks was further carried out and the results are shown in Table 1. The data for hydrogen uptake during the TPR (Table 1) show that the amount of the consumed hydrogen is larger than the one corresponding to the reduction of CuO to Cu, indicating the reduction of CeO$_2$ also took place alongside with the CuO reduction. Furthermore, the H$_2$ consumption increases with the increase of the ZrO$_2$ content in the catalysts, indicating that the reduction of Ce$^{4+}$ to Ce$^{3+}$ becomes easier with the incorporation of ZrO$_2$. It should be noted that the reduction temperatures of the CuO–CeO$_2$–ZrO$_2$ samples systematically shifted to lower regions with increasing the ZrO$_2$ content. The decrease of the reduction temperature may be caused by the following two factors.

---

Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mean crystallite size (nm)</th>
<th>Lattice parameter (nm)</th>
<th>Surface area (m$^2$/g)</th>
<th>Pore volume (cm$^3$/g)</th>
<th>$\text{H}_2$ uptake (mmol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5%CuO– CeO$_2$</td>
<td>48</td>
<td>0.5404</td>
<td>22.5</td>
<td>0.10</td>
<td>0.79</td>
</tr>
<tr>
<td>5%CuO–Zr$<em>0.1$Ce$</em>{1-x}$O$_y$</td>
<td>15</td>
<td>0.5360</td>
<td>124.2</td>
<td>0.88</td>
<td>1.20</td>
</tr>
<tr>
<td>5%CuO–Zr$<em>0.3$Ce$</em>{1-x}$O$_y$</td>
<td>14</td>
<td>0.5349</td>
<td>127.4</td>
<td>0.89</td>
<td>1.31</td>
</tr>
<tr>
<td>5%CuO–Zr$<em>0.5$Ce$</em>{1-x}$O$_y$</td>
<td>9.8</td>
<td>0.5327</td>
<td>139.4</td>
<td>0.96</td>
<td>1.35</td>
</tr>
<tr>
<td>5%CuO–Zr$<em>0.7$Ce$</em>{1-x}$O$_y$</td>
<td>9.3</td>
<td>0.5320</td>
<td>151.7</td>
<td>1.08</td>
<td>1.42</td>
</tr>
<tr>
<td>5%CuO–Zr$<em>1$Ce$</em>{0.5}$O$_y$</td>
<td>9.0</td>
<td>0.5281</td>
<td>162.0</td>
<td>1.15</td>
<td>1.65</td>
</tr>
</tbody>
</table>

$^a$ Nominal loading of CuO = 0.63 mmol/gcat.
First, the BET surface area of the CuO–Zr$_x$Ce$_{1-x}$O$_y$ samples increases with the ZrO$_2$ loading. The higher surface area favors the accessibility of H$_2$ and reduction of the sample by H$_2$. Second, the formation of Ce–Zr–O solid solution results in a distortion of the mixed oxides, which can allow a higher mobility of the lattice oxygen. Thus, the reduction is no longer confined to the surface but extended deep into the bulk, which may also accelerate the reduction process and lower the reduction temperature.

![TEM images](image)

**Fig. 3.** TEM images of the as-prepared CuO–Zr$_x$Ce$_{1-x}$O$_y$ catalysts calcined at 800 °C: (a) $x = 0.0$, (b) $x = 0.1$, (c) $x = 0.2$, (d) $x = 0.3$, (e) $x = 0.4$, (f) $x = 0.5$.

![Raman spectra](image)

**Fig. 4.** Raman spectra of the as-prepared CuO–Zr$_x$Ce$_{1-x}$O$_y$ catalysts calcined at 800 °C.

![TPR profiles](image)

**Fig. 5.** TPR profiles of the as-prepared CuO–Zr$_x$Ce$_{1-x}$O$_y$ aerogels.
3.3. Catalytic performance of CuO–ZrₓCe₁₋ₓO_{y} aerogels

The light-off curves over the as-prepared CuO–ZrₓCe₁₋ₓO_{y} aerogels are shown in Fig. 6. It can be seen that the benzene conversion increased with increasing the reaction temperature for all the catalysts. No product of selective oxidation is observed for all the catalysts. As shown in Fig. 6, the catalytic activity of CuO–CeO_{2} catalyst for the benzene oxidation is much lower than that of the catalysts doped with ZrO_{2}. Furthermore, the catalytic activity for the benzene oxidation increases with increasing the ZrO_{2} content in the catalyst. Among these catalysts, the CuO–Zr_{0.5}Ce_{0.5}O_{y} is found to be the most active for the catalytic oxidation of benzene. The comparison of the catalytic performance for benzene oxidation between CuO–Zr_{0.5}Ce_{0.5}O_{y} catalyst and the reported catalysts is shown in Table 2. Taken the calcination temperature of the catalyst, GHSV, and the 100% conversion temperature (denoted by T_{100%}) into account, the as-prepared CuO–Zr_{0.5}Ce_{0.5}O_{y} aerogel catalyst exhibits excellent catalytic performance for the benzene oxidation. However, due to the lack of general agreement on the experimental parameters, it is difficult to make direct comparison among the data reported in the literature [37–40].

The catalytic performances of the catalysts may be related to many factors, such as structure and surface area, etc. It is well known that the higher surface area can afford more unsaturated coordination sites exposed to gas molecules and increase the catalytic activity. Thus, it is reasonable that the catalytic activity for the benzene oxidation increases with increasing the ZrO_{2} content in the catalyst due to the increase of the BET surface area and the more available active sites. In addition, the incorporation of ZrO_{2} modifies the fluorite lattice and creates oxygen vacancy, which can accelerate the dissociation of oxygen molecules on the surface and increase the mobility of the lattice oxygen. Thus, a higher catalytic performance would be also expected with increasing the ZrO_{2} loading for the CuO–Zr_{x}Ce_{1−x}O_{y} (0 ≤ x ≤ 0.6) aerogel catalysts due to the generation more amounts of the oxygen vacancy and the enhanced mobility of the lattice oxygen.

Fig. 7 shows the Arrhenius-type plots for the benzene oxidation over the CuO–CeO_{2} and CuO–Ce_{0.5}Zr_{0.5}O_{y} catalysts. The apparent activation energy (AAE) of the reaction over CuO–CeO_{2} and CuO–Ce_{0.5}Zr_{0.5}O_{y} is 78.5 and 67.4 kJ/mol, respectively. Obviously, the addition of ZrO_{2} to the CuO–CeO_{2} mixed oxide caused the decrease of the apparent activation energy for benzene oxidation due to the increase of the oxygen mobility.

3.4. Stability test of CuO–ZrₓCe₁₋ₓO_{y} catalyst

A long-term stability test over the CuO–ZrₓCe₁₋ₓO_{y} catalyst was performed to evaluate the stability of the catalytic activity. The benzene conversion with time on stream over the CuO–ZrₓCe₁₋ₓO_{y} catalyst is shown in Fig. 8. The result shows that the conversion of benzene remained at about 98% and no obvious deactivation was observed for up to 50 h, indicating that the catalytic performance of the CuO–ZrₓCe₁₋ₓO_{y} catalyst for benzene oxidation is well sustained.

Table 2
Comparison of the catalytic performance for benzene oxidation between the as-prepared CuO–ZrₓCe₁₋ₓO_{y} aerogel catalyst and the reported catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Calcination temperature (°C)</th>
<th>Benzene concentration (ppm)</th>
<th>GHSV (mL g⁻¹ h⁻¹)</th>
<th>T_{100%} (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuO–ZrₓCe₁₋ₓO_{y} (this work)</td>
<td>800</td>
<td>1000</td>
<td>96000</td>
<td>300</td>
</tr>
<tr>
<td>La₀.₅Sr₀.₅MnOₓ⁺</td>
<td>600</td>
<td>500</td>
<td>20000</td>
<td>340</td>
</tr>
<tr>
<td>LaCoO₃</td>
<td>700</td>
<td>1700</td>
<td>60000</td>
<td>400</td>
</tr>
<tr>
<td>Pt/Zr–La₉</td>
<td>600</td>
<td>1050</td>
<td>20000</td>
<td>210</td>
</tr>
<tr>
<td>LaMnO₃</td>
<td>800</td>
<td>2000</td>
<td>14000</td>
<td>&gt;360</td>
</tr>
</tbody>
</table>

* From Ref. [37].
* From Ref. [38].
* From Ref. [39].
* From Ref. [40].
* The unit is h⁻¹.
4. Conclusions

Nanosized CuO–Zr$_x$Ce$_{1-x}$O$_y$ ($0 \leq x \leq 0.5$) aerogel catalysts were prepared by a simple co-precipitation method followed by subsequent ethanol supercritical drying and thermal processing steps. The as-prepared samples possessed large specific surface areas, small crystal sizes and high homogeneity of constituents even after calcination at 800 °C. Structure analysis revealed that ZrO$_2$ incorporated into the CeO$_2$ lattice, which remarkably modified the structural and textural properties of the final product. H$_2$-TPR suggests the presence of two different CuO species: highly dispersed CuO and CuO in the CeO$_2$ lattice, which remarkably modiﬁed the structural and textural properties of the final product. H$_2$-TPR suggests the presence of two different CuO species: highly dispersed CuO and CuO in the CeO$_2$ lattice. All the as-prepared CuO–Zr$_x$Ce$_{1-x}$O$_y$ ($x>$0) aerogel catalysts with high surface areas exhibited highly catalytic activities for the deep oxidation of benzene, and the CuO–Zr$_{0.5}$Ce$_{0.5}$O$_y$ catalyst showed the best catalytic activity. The CuO–Zr$_{0.5}$Ce$_{0.5}$O$_y$ catalyst showed an excellent stability of the catalytic performance for benzene oxidation during a long-term stability test of 50 h. It is believed that the CuO–Zr$_{0.5}$Ce$_{0.5}$O$_y$ aerogel catalyst is a good and cost-effective alternative to noble metal catalysts for the complete oxidation of VOCs at lower temperatures.

Acknowledgment

We would like to express our gratitude for financial support from National Natural Science Foundation of China (grant No. 20821092 and 20736004).

References