Mesoporous ceria–zirconia–alumina nanocomposite-supported copper as a superior catalyst for simultaneous catalytic elimination of NO–CO

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A series of transition metal (Mn, Fe, Co, Ni, Cu and Ag) oxides supported on ceria–zirconia–alumina nanocomposite catalysts were prepared through wetness impregnation method. The catalytic performance of these catalysts were evaluated in the catalytic elimination of NO–CO. Activity results revealed supported copper catalyst gave the optimal catalytic activity, which was related to high dispersion of copper species (XRD and Raman), low-temperature reducibility (TPR), and more oxygen vacancies (DRS).

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1. Introduction

The catalytic removal of nitrogen oxides (NOx) from engines is one of the greatest challenges in the field of environmental catalysis, owing to much stricter emission regulations adopted by most of the developed and developing countries in the world [1]. Transition metals and their oxides have been tried as active components for the substitution of noble metal catalysts in the simultaneous catalytic elimination of NO with CO, which is one of the central reactions occurring in automotive catalytic converters where both reactants are undesirable pollutants [2]. The reactions can be represented by:

\[ \text{NO} + \text{CO} \rightarrow 1/2\text{N}_2 + \text{CO}_2 \] (1)

\[ \text{N}_2\text{O} + \text{CO} \rightarrow \text{N}_2 + \text{CO}_2 \] (2)

γ-Alumina, belonging to a metastable “transition” alumina polymorph, is one of the most commonly used catalyst support materials in the widespread applications from petroleum refining to automotive emission control. CeO2–ZrO2 solid solution is an indispensable component that acts as an oxygen storage/release material in the three-way catalysts. Owing to the presence of synergetic interaction between alumina and CeO2–ZrO2 solid solution, many authors systematically investigated the structure, texture, redox, thermal stability, and oxygen storage capacity of the combination of alumina and Ce1−xZrxO2 prepared from different methods [3–14]. These results showed that ceria–zirconia–alumina system exhibited improved OSC, enhanced textural properties, and higher sintering-resistant in comparison with Ce–Zr solid solution or alumina alone. In addition, as stated by Toyota’s scientists, this new advanced Ce–Zr–Al composite oxide system has potentially become the 3rd oxygen storage material for automotive catalysts [8,10,11]. Thus, it is significant to study Ce–Zr–Al nanocomposite-based catalysts for catalytic elimination of NO with CO.

Previously, we studied the structure, reducibility, catalytic activity of CuO/Al2O3, CuO/CeO2/Al2O3, CuO/Ce1−xZrxO2/Al2O3 catalysts prepared by impregnation method [15–17]. Herein, mesoporous ceria–zirconia–alumina nanocomposite was prepared by oxidative co-precipitation. Then, the nitrates of transition metal as precursors were used to impregnating Ce–Zr–Al oxides support to obtain the targeted catalysts. The objective of this work is to compare the difference in catalytic activity and characterize these catalysts’ structure, reducibility, and the interaction of transition metal oxide–support by means of XRD, Raman, H2–TPR, and UV–Vis DRS.

2. Experimental

2.1. Catalyst preparation

In this work, ceria–zirconia–alumina (hereafter as CZA) nanocomposite was prepared by the oxidative co-precipitation method as reported elsewhere [10]. A requisite amount of Ce(NO3)3·6H2O, Zr(NO3)4·5H2O and Al(NO3)3·9H2O were dissolved in distilled water and hydrogen peroxide of 1.1 times of cerium was added.
Fig. 1. N$_2$O yield, CO conversion, and N$_2$ yield over the oxidized (a, b, c) and reduced (d, e, f) catalysts as a function of reaction temperature.
into the salt solution. Next, the excess ammonia (25%) was slowly dropped to the mixture solution with vigorously stirring until pH = 10. The resulting solution was kept in stirring for 1 h, aged overnight, filtered and washed three times with distilled water. The obtained pale yellow press cake was dried at 110 °C for 12 h, followed by calcination at 600 °C for 5 h. The CZA nanocomposite consisted of 80 wt.% γ-Al2O3 and 20 wt% CeO2–ZrO2 mixed oxide with Ce/Zr molar ratio of 1:1.

A series of transition metal (Mn, Fe, Co, Ni, Cu and Ag) oxides supported on CZA nanocomposite catalyst were prepared using the corresponding nitrate by conventional wetness impregnation method. The transition metal loading amount relative to CZA nanocomposite support is 5 wt%. The mixture was kept stirring for 3 h and evaporated at 100 °C. The resultant materials were first dried at 110 °C for 12 h and then calcined at 500 °C for 3 h. For simplification, these catalysts were denoted as MCZA, where M represents Mn, Fe, Co, Ni, Cu, and Ag, respectively.

### 2.2. Catalyst characterization

Textural properties of CZA were obtained by N2 adsorption-desorption at 77 K on a Micrometrics ASAP-2020. The sample was degassed at 300 °C for 4 h before the analysis. Desorption branch of the isotherm was used for the BJH pore distribution. TEM images were obtained using a JEOL JEM-2100 microscope operating at 200 kV. The sample was dispersed in ethanol and kept in ultrasonic bath for 15 min.

XRD patterns were recorded on a Philips X’Pert Pro diffractometer, equipped with a Ni-filtered Cu Kα radiation (0.15418 nm). The X-ray tube was operated at 40 kV and 40 mA. The mean grain sizes (D_XRD) were determined from XRD line broadening measurements using the Debye–Scherrer equation, D_XRD = Kλ/βcosθ, where λ is the X-ray wavelength, θ is the diffraction angle, K is the particle shape factor, Pore diameter (nm)

### Table 1

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>T10°C NO Conv.</th>
<th>T50°C NO Conv.</th>
<th>T90°C NO Conv.</th>
<th>T10°C CO Conv.</th>
<th>T50°C CO Conv.</th>
<th>T90°C CO Conv.</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnCZA-O</td>
<td>154</td>
<td>230</td>
<td>285</td>
<td>406</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>FeCZA-O</td>
<td>142</td>
<td>212</td>
<td>240</td>
<td>265</td>
<td>292</td>
<td>315</td>
</tr>
<tr>
<td>CoCZA-O</td>
<td>207</td>
<td>374</td>
<td>&gt;450</td>
<td>&gt;450</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>NiCZA-O</td>
<td>246</td>
<td>235</td>
<td>310</td>
<td>&gt;450</td>
<td>&gt;450</td>
<td>–</td>
</tr>
<tr>
<td>CuCZA-O</td>
<td>100</td>
<td>165</td>
<td>223</td>
<td>283</td>
<td>278</td>
<td>–</td>
</tr>
<tr>
<td>AgCZA-O</td>
<td>100</td>
<td>128</td>
<td>176, 345</td>
<td>422</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>MnCZA-R</td>
<td>276</td>
<td>312</td>
<td>425</td>
<td>&gt;450</td>
<td>450</td>
<td>–</td>
</tr>
<tr>
<td>FeCZA-R</td>
<td>243</td>
<td>284</td>
<td>345</td>
<td>396</td>
<td>&gt;450</td>
<td>&gt;450</td>
</tr>
<tr>
<td>CoCZA-R</td>
<td>170</td>
<td>259</td>
<td>326</td>
<td>&gt;450</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>NiCZA-R</td>
<td>260</td>
<td>293</td>
<td>380</td>
<td>&gt;450</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>CuCZA-R</td>
<td>134</td>
<td>132</td>
<td>220</td>
<td>242</td>
<td>260</td>
<td>320</td>
</tr>
<tr>
<td>AgCZA-R</td>
<td>162</td>
<td>349</td>
<td>&gt;450</td>
<td>&gt;450</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

a MnCZA-O represents the oxidated MnCZA catalyst.
b MnCZA-R represents the reduced MnCZA catalyst.
c T10, T50, and T90 are defined as the temperature at 10%, 50%, and 90% of NO/CO conversion.

Fig. 2. N2 adsorption-desorption isotherms (a), small-angle XRD pattern (b), and the TEM images (c, d) of ceria-zirconia-alumina nanocomposite support.
factor, usually taken as 0.89, and $\beta$ is full width at half maximum in radians.

H$_2$-TPR experiments were performed in a quartz U-type reactor, and 50 mg sample was used for each measurement. Prior to the reduction, the catalyst was pretreated in N$_2$ stream at 100 °C for 1 h and then cooled to room temperature. After that, H$_2$–Ar mixture (7% H$_2$ by volume) was switched on, and the temperature increased gradually with ramp of 10 °C/min. In addition, the TPR of the same sample was carried out for several redox cycles. Oxygen storage capacity (OSC) of solid catalyst was estimated based on the area under the peak up to 650 °C.

Raman spectra were collected on a JOBIN YVON type Laser Raman spectroscopy using Ar$^+$ laser beam. The Raman spectra were recorded with an excitation wavelength at 488 nm and the laser power at 25 mW.

UV–Vis DR spectra were collected from a Shimadzu UV–Vis–NIR 3600 spectrophotometer. The spectra were recorded in the range from 200 to 1000 nm using BaSO$_4$ as a reference.

2.3. Catalyst testing

The catalyst testing was performed in a fixed quartz reactor. The NO reduction with CO was investigated under steady state, involving a fixed feed with a gas composition of NO 5%, CO 10% and He 85% by volume as a carrier gas at a space velocity of 12,000 h$^{-1}$. For each measurement, 50 mg catalyst was pretreated in N$_2$ stream at 100 °C for 1 h and then be cooled to room temperature. After that, the valve gear was switched to the reaction gas. Volume A was packed with Paropak Q for separating CO$_2$ and N$_2$O. In addition, the reduced catalysts obtained from H$_2$-treatment at 700 °C for 1 h were also tested under the same conditions.

3. Results and discussion

3.1. Catalytic reaction data (NO–CO model reaction)

Fig. 1a–c showed the N$_2$O yield, CO conversion, and N$_2$ yield over the oxidized catalysts as a function of temperature, respectively. For N$_2$O yield profile, the results indicated that N$_2$O was formed during the initial stage at lower temperature, and with the increase in reaction temperature the yield of N$_2$O reached a maximum. Further increase in temperature, however, induced a gradual decrease in the amount of N$_2$O until reaching zero. However, the maximum of N$_2$O yield over these MCZA catalysts corresponds to different reaction temperatures. The trend of activity in term of light-off temperature ($T_{50}$ of NO conversion) is (AgCZA)$<$CuCZA$<$FeCZA$<$MnCZA$<$NiCZA$<$CoCZA, as listed in Table 1. CuCZA sample gave the highest NO conversion in high-temperature region ($T>250$ °C). Regarding CO conversion expressed in $T_{50}$, it displayed an order of FeCZA$<$CuCZA$<$MnCZA$<$AgCZA$<$NiCZA$<$CoCZA, in agreement with the sequence of NO conversion in some extent. In addition, all studied samples displayed a low N$_2$ yield (<25%) below 250 °C. Upon increasing the reaction temperature, CuCZA sample showed better performance than others as shown in Fig. 1c.

To evaluate the activity of the reduced catalysts, Fig. 1d–f exhibited the catalytic performance expressed in N$_2$O yield, CO conversion, and N$_2$ yield, respectively. From these curves, it was obvious that the N$_2$O yield showed a peak top and the latter two expressions (CO conversion, N$_2$ yield) increased with increasing temperature over these reduced catalysts. Among them, the activity of the reduced CuCZA sample was higher than the others, which was also confirmed by light-off temperatures shown in Table 1. In addition, we have also performed the reaction experiment with a stoichiometric condition between the oxidative and reducing agents (5% NO–5% CO balanced He) to observe the influence of NO/CO ratio on the catalytic performance (Supplementary information). It can be noted that the similar trend of activity was obtained. Moreover, CuCZA sample still exhibits good catalytic activity under this reaction condition. Integrating the above analysis, we can conclude that CuCZA is a superior catalyst for catalytic elimination of NO with CO.

![Fig. 3. XRD patterns (a), TPR profiles (b), and OSC data (c) of these catalysts studied.](image-url)
3.2. Characterizations of CZA nanocomposite support (N$_2$ sorption, low-angle XRD, TEM)

Fig. 2a showed N$_2$ adsorption–desorption isotherms and the corresponding BJH pore size distribution of CZA nanocomposite support. It can be seen that the isotherm is typical IV as defined by IUPAC, which belongs to mesoporous materials due to the texture of inter-nanoparticles mesoporosity and confirmed by small-angle XRD pattern with a broad peak at 1–3° (Fig. 2b). H$_2$-type hysteresis loop with a sloping adsorption branch and a relatively steep desorption branch were observed at the relative pressure ($P/P_0$) of 0.4–0.8. This hysteresis loop is characteristic for interstice pore structure stacked by nanoparticles. The inset gave pore size distribution of CZA and it had the two maximum centered at 3.1 and 4.6 nm, respectively. This suggested the heterogeneity of the particle size of alumina and ceria–zirconia solid solution as confirmed by the following wide-angle XRD results.

To observe the general morphology and microstructure of mesoporous CZA nanocomposite, TEM experiments have been performed and the representative images were shown in Fig. 2b and c. From the TEM’s globe view (Fig. 2c), it does not clearly show the presence of highly ordered mesopores, but reveals a rather wormlike structure resulting from closely aggregated metal oxide nanoparticles. This is in agreement with N$_2$ sorption. Furthermore, for CZA nanocomposite at high magnification (Fig. 2d), it mainly contains one kind of periodicity of lattice fringes (~0.302 nm), which was compatible with the distance expected between the (111) reticular plane of Ce$_{0.5}$Zr$_{0.5}$O$_2$ solid solution (~3 nm) due to the displacement of Ce$^{4+}$ ions (0.97 Å) by the smaller Zr$^{4+}$ ions (0.84 Å). This is in good agreement with XRD diffraction database (JCPDS 38-1436) and the results obtained from literature [3]. Regarding the MCZA catalysts, similar behaviors can be observed from XRD results, namely, only the presence of diffraction peaks of Ce$_{0.5}$Zr$_{0.5}$O$_2$ solid solution and $\gamma$-Al$_2$O$_3$. Moreover, transition metal oxides were highly dispersed or small crystalllite on CZA nanocomposite under XRD detection limitation, as confirmed by the absence of characteristic diffraction.

Fig. 3b showed the typical H$_2$-TPR profiles of MCZA catalysts. For CZA nanocomposite, there was a small hump at ca. 340 °C, attributed to the reduction of surface Ce$^{4+}$ [18]. It was noted that CuCZA catalyst only presented one peak at around 220 °C, which was composed of oxygen consumption from highly dispersed copper species interacting with CZA and the surface layers reduction of CZA [17,19]. However, two peaks at 330 and 405 °C have been assigned to the sequential reduction of Mn species (Mn$^{4+}$→Mn$^{3+}$→Mn$^{2+}$) for MnCZA catalyst. FeCZA catalyst exhibited an obvious leading asymmetric peak, started from 250 °C and centered at 400 °C. This could be explained by the possibility that the interaction between Fe species and CZA nanocomposite caused the overlap phenomena of the reduction peaks. The CoCZA and NiCZA samples both showed multiple reduction peaks above 300 °C associated with the change of oxidation state of Co or Ni, and a negative peak at ca. 200 °C. The latter may be due to low temperature H$_2$ desorption [20]. There is no observed reduction peak at AgCZA catalyst, suggesting the as-prepared Ag catalyst was mostly metallic state. Integrating the above analysis, MCZA catalysts exhibited different reducibilities, which were related to the intrinsic redox of transition metal oxide and interaction of transition metal oxide and CZA nanocomposite support. In addition, according to some relevant literatures [21,22], the total OSC data derived from H$_2$-TPR integrated peak area was plotted in Fig. 3c. The histogram clearly indicated that CuCZA sample showed the highest oxygen-removal from Cu oxide and CZA itself.

To obtain additional surface information, the catalysts were characterized by surface-sensitive Raman technology. Fig. 4 showed the Raman spectra of CZA nanocomposite-supported transition metal oxide catalysts. CZA nanocomposite support showed an extremely weak band at ca. 485 cm$^{-1}$, which was attributed to F$_2g$ vibration mode of the ceria fluorite structure. However, the position and FWHM
of this band changed in the CZA nanocomposite when compared to pure ceria with a strong Raman peak at 465 cm\(^{-1}\). This would be explained by weak crystallizability of ceria–zirconia solid solution and lattice defects arising from zirconia or alumina incorporation into the ceria matrix [14]. In addition, a small hump at ca. 600 cm\(^{-1}\) was slightly observed, associated with the presence of the oxygen vacancies on the surface of ceria [23]. These above-mentioned features could be observed at the MCZA catalysts. Besides these peaks associated with CZA support, the catalysts showed some characteristic peaks of transition metal oxide, such as MnCZA at 650 cm\(^{-1}\) of MnOx [24], CoCZA at 524, 692 cm\(^{-1}\) of CoO\(_2\) [25], and AgCZA with multiple peaks. This suggested the presence of small crystallites that could not be detected by XRD. However, the Raman spectrum obtained for CuCZA sample was very similar to that of the CZA support, and it was not possible to discern any signal related to copper species, indicating high dispersion of these species, without formation of any copper crystalline phase.

Based on the previous reports [26] and therein, CZA deconvolution in Fig. 5a exhibited three absorption maxima located at 242, 280, and 350 nm in its DRS, attributed to \(\text{O}^{2-} \rightarrow \text{Ce}^{3+}, \text{O}^{2-} \rightarrow \text{Ce}^{4+}\) charge transfer transitions, and interband transitions, respectively. Regarding MCZA samples (Fig. 5b), a broad and unresolved absorption band with different edges (450, 483, 489 and 685 nm for AgCZA, NiCZA, CuCZA and FeCZA, respectively) could be observed, which was different with CZA support. Interestingly, the relative intensity of \(\text{O}^{2-} \rightarrow \text{Ce}^{3+}\) (\(\alpha\), 230 nm) in CuCZA sample was higher than that of the others and revealed the presence of more oxygen defects (act as NO dissociation sites) caused by more Ce\(^{3+}\) due to charge compensation [14,27]. This may be one reason that CuCZA showed higher activity. For CoCZA sample, it contained a broad and intense band at 550–900 nm due to d–d transitions of CoO\(_2\). CuCZA sample also consisted of a symmetric band at 550–1000 nm due to d–d transitions of dispersed Cu\(^{2+}\) (3d\(^8\)), located in distorted octahedral coordination environment of O-containing ligands [28].

4. Conclusions

Simultaneous elimination of NO and CO over various transition-metal catalysts with mesoporous ceria–zirconia–alumina nanocomposite as support was investigated. The results indicated that CZA nanocomposite was composed of Ce\(_{0.5}Zr_{0.5}O_2\) solid solution (~3 nm) and nanocrystallite γ-Al\(_2\)O\(_3\) (5–8 nm). Among these catalysts studied, supported copper catalyst showed better catalytic performance than others did, which was due to the presence of strong interaction between copper and CZA support and causing the formation of highly dispersed copper species with lower temperature reducibility and more oxygen vacancies.

Supplementary materials related to this article can be found online at doi:10.1016/j.catcom.2011.05.002.

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References


Fig. 5. UV–Vis DRS profiles of (a) ceria-zirconia-alumina nanocomposite support and (b) the catalysts studied.