Promotional effect of CO pretreatment on CuO/CeO$_2$ catalyst for catalytic reduction of NO by CO

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Abstract: The CuO/CeO$_2$ catalysts were investigated by means of X-ray diffraction (XRD), laser Raman spectroscopy (LRS), X-ray photoelectronic spectroscopy (XPS), temperature-programmed reduction (TPR), in situ Fourier transform infrared spectroscopy (FTIR) and NO+CO reaction. The results revealed that the low temperature (<150 °C) catalytic performances were enhanced for CO pretreated samples. During CO pretreatment, the surface Cu$^+$/Cu$^0$ and oxygen vacancies on ceria surface were present. The low valence copper species activated the adsorbed CO and surface oxygen vacancies facilitated the NO dissociation. These effects in turn led to higher activities of CuO/CeO$_2$ for NO reduction. The current study provided helpful understandings of active sites and reaction mechanism in NO+CO reaction.

Keywords: CuO/CeO$_2$ catalysts; CO pretreatment; oxygen vacancies; NO reduction; rare earths

Copper-based catalysts have been widely reported in many catalytic reactions for their promising activities, especially CO oxidation, NO reduction and water-gas shift reaction$^{[1-6]}$. Many methods were considered to improve the catalytic properties of this system by inducing active species, changing the redox behaviors of copper phase$^{[7-9]}$ and their interactions with the supports$^{[6-10]}$. Among them, reductive pretreatment is widely applied$^{[1,11-14]}$. Generally, the reductive pretreatment of the catalysts could alter their physicochemical properties and change the catalytic activities. Martinez-Arias and Fernández-Garç et al. have detected low valence copper species in CO-TPR of CuO/Al$_2$O$_3$ and CuO/CeO$_2$/Al$_2$O$_3$$^{[11,12]}$. Tang et al. reported that the CeO$_2$/Co$_3$O$_4$ catalysts pretreated in H$_2$ under low-temperatures obtained both larger surface area and better activities for CO oxidation$^{[13]}$. Our group found that the activity of CuO/CeO$_2$/Al$_2$O$_3$ for CO oxidation was promoted after CO pretreatment$^{[14]}$. However, detailed mechanism of how the pretreatment influences the activities remains to be determined. On the other hand, CuO/CeO$_2$ catalysts have attracted numerous interests due to their activities for the abatement of exhaust gas from mobile emissions$^{[12,15]}$. Many attentions were also paid to the influence of preparation method$^{[16-18]}$, morphology$^{[19-21]}$, and modification$^{[22-24]}$ on the activities of catalysts containing CeO$_2$. The promoting effects of reductive pretreatment on the catalytic performances of ceria-contained catalysts for CO oxidation have also been reported$^{[11,13,14]}$. However, detailed researches on the course of enhancing reaction activities are still limited. In addition, the topic of pretreatment effect on catalytic reduction of NO by CO on CuO/CeO$_2$ is open for discussion.

In this regard, we used CO to pretreat CuO/CeO$_2$ catalysts and explored their catalytic performances in the NO+CO reaction. Characterizations including XRD, LRS, XPS, H$_2$-TPR and in situ FTIR were carried out to investigate the physical chemistry properties and NO and CO adsorption of the catalysts before and after pretreatment.

1 Experimental

1.1 Catalysts preparation

CeO$_2$ support was prepared via conventional precipitation method. Ce(NO$_3$)$_3$·6H$_2$O was dissolved in deionized water; then the aqueous solution was precipitated with an aqueous solution of NH$_3$·H$_2$O at room temperature until pH=10. The obtained suspension was aged at room temperature for 2 h, then centrifuged and washed with deionized water. The resulting materials were dried at 110 °C for 20 h and finally calcined at 500 °C for 5 h (heating rate was 3 °C/min) in air.

CuO/CeO$_2$ samples were prepared by impregnating CeO$_2$ support with an aqueous solution containing requisite
amount of Cu(NO$_3$)$_2$. The obtained slurry was stirred at room temperature for 2 h and then at 80 °C for 4 h, then dried at 110 °C for 12 h and finally calcined at 450 °C for 4.5 h.

CO pretreatment for CuO/CeO$_2$ catalysts was conducted in a quartz tube. Before switched to CO, each CuO/CeO$_2$ catalyst was pretreated in a N$_2$ stream at 300 °C for 0.5 h. After cooling down to room temperature, the catalyst was exposed to a CO-He stream (10% CO by volume, at atmospheric pressure) at a rate of 8.4 mL/min, and was heated at 150 °C for 1 h. The treated catalyst was cooled to room temperature in a N$_2$ stream. The resultant catalysts are denoted as xCuCe-CO, e.g., 05CuCe-CO corresponding to the CuO/CeO$_2$ with copper oxide loading amount of 0.5 mmol CuO/100 m$^2$ CeO$_2$ with CO pretreatment.

1.2 Catalytic characterizations

The powder X-ray diffraction patterns of samples were collected on a Philips X’pert X-ray diffractometer using Ni-filtered Cu K$_\alpha$ radiation ($\lambda=0.15408$ nm). The X-ray tube was operated at 40 kV and 40 mA. The data were collected in the 2θ range of 10°–80°.

Raman spectra were collected on a Jobin-Yvon (France-Japan) T64000 type Laser Raman spectroscope using Ar$^+$ laser beam, operating with an exciting wavelength of 516 nm and the laser power of 300 mW.

XPS analysis was performed on a PHI 5000 Versaprobe system, using Al K$_\alpha$ radiation (1486.6 eV) at an accelerating power of 25 W. All binding energies (BE) were referenced to the adventitious C1s at 285.0 eV.

1.3 Catalytic activity tests

The catalytic activity and selectivity of the catalysts were measured under steady state, involving a feed steam with a fixed composition, 5% NO, 10% CO and 85% He by volume as diluents. A quartz tube with 50 mg catalyst was used. The catalysts were pretreated in N$_2$ stream at 300 °C for 0.5 h and then cooled to room temperature; the mixed gas was then switched on. The reactions were carried out at different temperatures with a space velocity of 12000 h$^{-1}$. Two volumes and thermal conduction detections were used for analyzing the production. Volume A with Paropak Q for separating N$_2$O and CO$_2$, and volume B packed with 5A and 13X molecule sieve (40–60 M) for separating N$_2$, NO and CO.

2 Results and discussion

Fig. 1 shows the results of NO conversions and N$_2$ selectivity over the catalysts at different operation temperatures. When the operation temperature was relatively low (100 °C), CO pretreatment led to an enhancement of NO conversions of all catalysts. The enhancement extent decreases with the increasing of temperature. The NO conversions before and after CO pretreatment were almost the same when the temperature reaches 200 °C. However, as shown in the selectivity results (Fig. 1(b), (d), (f)), N$_2$ yields over the pretreated catalysts were greatly enhanced compared to the fresh catalysts in the range of 100–200 °C. To explore the stability of the CO-pretreated catalyst, the 05CuCe was used as a representative and the NO conversion and N$_2$ selectivity were collected at 200 °C for successive 20 h. The result is shown in Fig. 1(g), (h). It is found that both the NO conversion and N$_2$ selectivity can be well preserved, which suggests the good stability of the catalysts. To approach how the pretreatment result in such catalytic activity and selectivity, the physicochemical properties of CuO/CeO$_2$ catalysts were investigated as following.

XRD patterns of CuCe and CuCe-CO samples are shown in Fig. 2. No characteristic diffraction peaks for crystalline CuO$^{[10,25]}$ appear among 05CuCe and 10CuCe samples, indicating that CuO species were highly dispersed on CeO$_2$. CuO diffraction peaks were observed in 20CuCe. For the CO-pretreated samples, CuO diffraction peaks were not detected when the copper loading amounts were lower than 1.0 mmol/100 m$^2$ CeO$_2$, which was similar to the fresh samples. The characteristic diffraction peaks of crystalline CuO vanish in 20CuCe-CO, while peaks related to metallic copper$^{[10]}$ appears, suggesting that crystalline CuO was reduced to Cu$^0$. In order to further investigate the change of dispersed copper oxide species and ceria during CO pretreatment, Raman and XPS were performed.

The Raman spectra are shown in Fig. 3(a). All the spectra are dominated by a strong band at 445.0–461.8 cm$^{-1}$ attributed to triple degenerate F$_{2g}$ mode of fluorite-
Fig. 1 Results of NO conversion (%) (a, c, e) and N$_2$ selectivity (%) (b, d, f) over CuO/CeO$_2$ catalysts with different CuO loadings (The results of NO conversion (%) (g) and N$_2$ selectivity (%) (h) over 05CuCe catalysts collected at 200 ºC for successive 20 h)

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For the fresh samples, there is a weak band at around 600 cm$^{-1}$, corresponding to the presence of lattice defects and oxygen vacancies$^{[26,27]}$. This band blue shift and broaden after CO pretreatment, indicating the concentration of oxygen vacancies changed during the CO treatment. The relative intensities of 600 cm$^{-1}$ band are quantified in Fig. 3(b). Generally, the larger $I_{600}/I_{460}$ values suggest the more oxygen vacancies. As can be seen, the $I_{600}/I_{460}$ values of $x$CuCe-CO samples increase compared with those of $x$CuCe samples. Therefore, CO treatment induced the enhancement of oxygen vacancy concentration.

XPS experiments were conducted to investigate the surface composition and elementary valences. Fig. 4 shows the Cu 2p spectra of the samples. Apparently, most copper species in the fresh samples were in a +2 oxidation state. For the pretreated samples, the Cu 2p$_{3/2}$ peaks of 05CuCe and 20CuCe shift from 933.1 to around 931.1 eV, which is attributed to the appearance of low valence copper species$^{[9,27]}$. Moreover, the shake-up peaks for Cu$^{2+}$ at 936.0–945.8 eV nearly disappear. These changes indicate the formation of Cu$^+$ or/and Cu$^0$ species after CO treatment. The Cu-LMM Auger spectra were recorded to further verify the valence state of copper. For the fresh samples, the copper species mainly exist as Cu$^{2+}$ at 569.2 eV (Fig. 4(b)). For the pretreated samples, the Auger spectra of pretreated samples could be resolved into two peaks at 570.4 and 568.2 eV, which is expected for Cu$^+$ and Cu$^0$, respectively$^{[9,28]}$. Thus the copper species were mainly Cu$^+$ and Cu$^0$ after CO pretreatment.
The surface composition change of the support were monitored by Ce 3d XPS (Fig. 4(c)). The surface cerium was mostly present in a +4 oxidation\[^9\]. There are an increase in the intensities of $v'$ and $u'$ for the treated samples. As calculated in Table 1, for all the CuCe-CO samples, the relative intensities of $v'$ and $u'$ to the other six bands increase. This reveals that the surface ratio of Ce$^{3+}$ to Ce$^{4+}$ of the samples was enhanced. Combined with the Raman results, it is reasonable to propose that some Ce$^{4+}$ was reduced to Ce$^{3+}$ during CO treatment process and the surface oxygen vacancies formed.

The O 1s spectra (Fig. 4(d)) were performed to analyze the surface oxygen species. The major band O' at 529.9 eV is assigned to characteristic oxygen of the metal oxide, and the band O'' at higher binding energy is resulted from adsorbed oxygen species\[^9,26\]. For all the samples, the intensities of O' decrease after CO pretreatment, indicating that some surface lattice oxygen was removed. The O/(Cu+Ce) atomic ratios are shown in Table 1. For 10CuCe and 20CuCe, this ratio decrease after CO pretreatment, but for 05CuCe it increase a little. The decrease of surface oxygen concentration was probably due to the formation of reduced copper and cerium species or surface oxygen vacancies. Since the loading amount of copper oxide is relatively low on 05CuCe, there may be more active sites for chemisorbed CO$_2$, O$_2$ and H$_2$O. This may be the reason for high oxygen concentration on 05CuCe.
Table 1 XPS analysis of the surface compositions for CuO/CeO₂ catalysts

<table>
<thead>
<tr>
<th>Sample</th>
<th>Atomic concentration (at.%)</th>
<th>Atomic ratio</th>
<th>Cu(II) (%)</th>
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<tr>
<td></td>
<td>C</td>
<td>O</td>
<td>Cu</td>
</tr>
<tr>
<td>05CuCe-CO</td>
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<td>20CuCe-CO</td>
<td>25.42</td>
<td>50.53</td>
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</table>

**Fig. 5 TPR results of CuCe and CuCe-CO samples**

**H₂-TPR** was performed to compare the difference in the reduction properties of CuCe and CuCe-CO samples (Fig. 5). For 05CuCe, two reduction peaks appear at 127 and 149 °C. As discussed in XRD section, all the copper species were well dispersed on the surface of ceria in this sample. Therefore, the two peaks can be assigned to the stepwise reduction of dispersed CuO: Cu²⁺→Cu⁺ and Cu⁺→Cu⁰, respectively [29]. When the CuO loading is 1.0 and 2.0 mmol/100 m² ceria, a new reduction peak at about 172 °C appears, corresponding to the reduction of crystalline CuO [15,22]. However, for 10CuCe, this peak only appears as a weak shoulder, implying that the crystalline CuO exists as small CuO cluster, which is not detectable for XRD characterization. In addition, surface oxygen from ceria is also known to take part in this reduction process [30], and its reduction peak is proposed to overlap with the reduction peak of Cu⁺→Cu⁰ or crystalline CuO.

Following CO pretreatment, the reduction peaks of Cu²⁺ nearly disappears, indicating that Cu²⁺ was reduced to lower valence copper species. The reduction peaks for Cu⁺ and surface oxygen from ceria shift to lower temperature. This shift is probably related to the hydrogen spillover effect of metallic copper clusters formed during CO treatment. On the surface of metallic copper, H₂ can be disassociated into more active H and thus promotes the reducibility of Cu⁺ and surface ceria. As shown in CuCe-CO profiles, the reduction peak present at lower temperatures (147, 140, 138 °C) with the increase in CuO loading. This is in accordance with the hydrogen spillover effect because larger amount of CuO loading would be reduced to metallic copper clusters of bigger size, which in turn led to stronger hydrogen spillover. As a result, the reduction of surface oxygen of ceria along with Cu⁺ were facilitated after CO pretreatment, and copper species were present mainly as Cu⁺/Cu⁰ in CuCe-CO samples, which complement the Raman and XPS results.

**In situ** FTIR of NO and CO co-absorption on CuCe and CuCe-CO were performed to address the surface species under simulative reaction condition (Fig. 6). For all samples, three types of NO absorption species were produced: linear nitrite (1277 cm⁻¹), monodentate nitrate (1456 cm⁻¹) and bridged nitrate (1623 cm⁻¹) [18,23,25]. The CO adsorption show two bands at 2101 cm⁻¹ for CO-Cu⁺ and 2143 cm⁻¹ for (CO)₂-Cu⁺; and CO₂ adsorption present at 2360 cm⁻¹ [18,23,25]. Compared with CO, NO preferentially interact with CuCe and CuCe-CO samples at low temperature. For 05CuCe, the band for linear nitrite (1277 cm⁻¹) slightly decreased when the temperature reached 150 °C. The band for bridged nitrate (1623 cm⁻¹) shifted to 1601 cm⁻¹ and disappeared at 175 °C. Meanwhile, CO species (2102 and 2143 cm⁻¹) appeared at 150°C. For 05CuCe-CO, the band for linear nitrite became evidently weaker from 125 °C; the bridged nitrate (1601 cm⁻¹) disappeared at 125 °C. This indicates that the adsorbed NOx species were activated and were easier to decompose on 05CuCe-CO sample. Simultaneously, the bands for CO species (2101 and 2143 cm⁻¹) could be observed in low temperature region and were apparently stronger than those in the fresh sample. Intensity change of CO₂ adsorption band (2360 cm⁻¹) from 125 to 150 °C was also increased for 05CuCe-CO sample. Therefore, the pretreated samples interacted with CO more strongly. In addition, the change of surface NOx species concentrations were always accompanied with the change of surface CO₂ concentrations. Similar results could be observed in the spectra of 20CuCe and 20CuCe-CO samples.

Combined with the Raman and XPS results, it is deduced that the promotional effect of reductive atmosphere treatment resulted from the enhanced concentration of surface oxygen vacancies of ceria and Cu⁺/Cu⁰ species. The oxygen vacancies facilitated NO decomposition, and Cu⁺ were active sites for CO adsorption. Additionally, the dissociations of NO would eliminate the oxygen vacancies, thus the regeneration of oxygen vacancies is essential to maintain the catalytic activities for NO decomposition. As discussed in TPR results, the reduction of surface oxygen of ceria was facilitated after CO pretreatment, i.e., the regeneration of oxygen vacancies was also promoted. Consequently, the NO conversions were promoted at low temperature (100°C). However, at higher temperature (>100 °C), NO adsorption species were unstable and CO adsorption species became dominant. Surface ceria was reduced by CO to give out oxy-
Fig. 6 *In situ* FTIR results of NO and CO co-adsorption on 05CuCe (a), 05CuCe-CO (b), 20CuCe (c) and 20CuCe-CO (d) samples from 50–300 °C

...gen vacancies, therefore enough NO decomposition active sites were generated without CO pretreatment. Thus, there were no great differences between catalytic activities of CuCe and CuCe-CO samples at higher temperatures.

It is worth noting that CuCe-CO samples maintain higher N₂ selectivity than CuCe samples in the region of 100–200 °C. As is well established, there are two ways for the production of N₂ in NO+CO reaction: one is the combine between N atoms from NO dissociation; another is the reaction between N₂O and CO activated by Cu⁺ [1]. As discussed above, the population of oxygen vacancies was similar between fresh and treated samples under reaction condition at higher temperatures. However, CuCe-CO samples still possessed more Cu⁺ species. In such case, N₂O would have greater chance to react with Cu⁺-CO, which is consistent with the greater CO oxidation on 05CuCe-CO than on 05CuCe. It is thus reasonable that the N₂ selectivity of 05CuCe-CO was much larger than that of 05CuCe (>100 °C) with quite similar NO conversions.

3 Conclusions

The present work investigated the influence of CO pretreatment on the catalytic performance, reduction and adsorption of CuO/CeO₂. The activities and selectivity for NO reduction by CO were greatly promoted. XRD, LRS, XPS and TPR results indicated the formation of low valence copper species and surface oxygen vacancies during CO pretreatment. The redox properties of catalysts were also influenced. *In situ* FTIR results suggested that CO treatment changed the NO and CO adsorption on CuO/CeO₂ and NO decomposition was facilitated. These factors were responsible for the promot-
ing activity and selectivity.

References:


