CuO/CeO₂ catalysts: Redox features and catalytic behaviors

Xiaolan Tang, Baocai Zhang, Yong Li, Yide Xu, Qin Xin, Wenjie Shen *

State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences,
457 Zhongshan Road, P.O. Box 110, Dalian 116023, PR China

Received 11 July 2004; received in revised form 9 April 2005; accepted 20 April 2005
Available online 3 June 2005

Abstract

The reduction and oxidation features of nanostructured CuO/CeO₂ catalysts prepared by the deposition–precipitation method were extensively investigated by TPR, FT-IR and in situ XPS techniques. Both the chemical states of copper and the reduction degree of ceria could be well controlled during the reduction with hydrogen by adjusting the temperature. Noticeably, the fully reduced Cu₀ could be further oxidized into Cu⁺ in hydrogen by increasing the reduction temperature through the interaction between Cu₀ and lattice oxygen of ceria immigrating to the surface. Structure–reactivity relationship was established between the structural features of CuO/CeO₂ formed during the pre-reduction with hydrogen and its catalytic activities for CO oxidation. It was observed that reduction with hydrogen at 473–573 K, which leads to the full presence of metallic copper in the catalyst, gives rise to higher CO conversion. These phenomena were interpreted in terms of the reduction degrees of ceria, the changes of surface morphology and the chemical states of copper species. The interface oxygen activation as well as its transfer from the interface to the adsorbed reactant was found to play decisive roles in determining the reaction rate of CO oxidation.

© 2005 Elsevier B.V. All rights reserved.

Keywords: CuO/CeO₂; Redox features; Chemical states; Metal–support interaction; CO oxidation

1. Introduction

Cerium oxide has attracted much attention in environmental catalysis, either as effective promoter or supporting material based on its high oxygen-storage capacity and facile Ce⁴⁺/Ce³⁺ redox cycle [1–4]. The rapid growth in the applications and the characterization of CeO₂-containing catalysts in the past decade has been well documented [5–8]. It was widely noted that the activity and the selectivity of CeO₂-based catalysts are greatly enhanced not only by precious metals, but also by base metals, particularly copper. For instance, CuO/CeO₂ catalysts have been shown to be very active for CO oxidation, exhibiting specific activities far superior to the conventional copper-based catalysts and even comparable with or superior to platinum catalysts [8–10]. Another similar CuO/samaria-doped ceria catalyst was also reported to be highly active in total CO oxidation [5].

In principle, an excellent CuO/CeO₂ catalyst should have the abilities to facilitate the copper species in changing their valences and to supply suitable oxygen species. The so-called metal–support interaction between copper and ceria is often regarded as the key factor in determining the redox features and consequently, the catalytic behavior [11–17]. However, the complexity of the copper–ceria interaction still limits a detailed mechanistic understanding at the atomic level on how ceria affects catalytic features.

Several controversial views concerning the exact nature of the copper–ceria interaction in CuO/CeO₂ have been proposed recently. The redox features were extensively studied by the conventional temperature-programmed techniques and X-ray photoelectron spectroscopy to reveal some the variations in the chemical states of each component during reduction and oxidation processes. Zimmer et al. [2] explained the double-peak structure of H₂-TPR profiles as a stepwise reduction from Cu²⁺ to Cu⁺ and from Cu⁺ to Cu₀. In contrast, a direct reduction process of CuO to Cu₀ at temperatures below 473 K without the presence of Cu⁺
The intermediate was also suggested [18]. The correlation between the activity and the amount of highly reductive copper species was investigated by CO-TPR, with the conclusion that the reaction rates of CO oxidation strongly depend on the propensity of copper oxide species toward valence variations [19]. HRTEM and EXAFS studies of CuO/CeO2 under different redox atmospheres further demonstrated that the changes in the morphology and in the dispersion of copper species are also the most important factors that govern the catalytic performance [3,20–24].

The major objective of the present study is to investigate the distinct reduction and oxidation features of CuO/CeO2 catalyst prepared by the deposition–precipitation method. The copper–ceria interaction was characterized by quantitative H2-TPR, in situ XPS and FT-IR techniques. Since the metal–support interaction often plays a key role in determining the details of catalytic behavior; another objective of this investigation is to establish the relationship between the catalytic activity and the metal–support interaction by applying the CuO/CeO2 catalyst to the oxidation reaction of CO. The influence of reductive pretreatments at various temperatures on the reaction behaviors was extensively investigated, and some reaction pathways were accordingly proposed.

2. Experimental

2.1. Catalyst preparation

The CeO2 support was prepared by precipitation of Ce(NO3)3·6H2O aqueous solution with the addition of ammonia aqueous solution at 333 K until the pH of the mixture was greater than 9.0 under vigorous stirring. The precipitant was then aged in the mother liquid for 4 h, followed by filtration and washing with distilled water. The obtained solid was dried at 373 K for 10 h and calcined at 723 K for 4 h in air.

The CuO/CeO2 catalyst was prepared by the deposition–precipitation method with the copper loading of 5% by weight. Briefly, the CeO2 powder was first suspended in an aqueous solution containing an appropriate amount of Cu(OAc)2·H2O. Then, a 0.25 M Na2CO3 aqueous solution was gradually added to the suspended solution containing CeO2 and copper precursor at 343 K until the pH of the mixed solution reached 9.0. The mixture was further aged for 1 h under vigorous stirring, during which copper hydroxide was exclusively precipitated on the surface of CeO2. The resulting solid was washed with hot distilled water, dried at 373 K for 10 h and subsequently, calcined in air at 723 K for 4 h.

2.2. Characterization

The powder X-ray diffraction (XRD) patterns were recorded using a Rigaku D/MAX–RB with Cu Kα radiation operated at 40 kV and 100 mA.

The specific surface areas (S_BET) of the catalysts were calculated from a multipoint Brunauer–Emmett–Teller (BET) analysis of the nitrogen adsorption isotherms at 77 K recorded on a Micrometrics ASAP 2000 instrument. The copper particle sizes of the catalysts were measured by the CO pulse titration method at room temperature using a CHEMBET 3000 adsorption instrument. One hundred-milligram samples were reduced in 5 vol.% H2/Ar for 1 h at 573 K, and then purged with He for 30 min at 473 K. After cooling down the samples to room temperature CO pulse titrations were carried out.

The temperature-programmed reduction measurements were carried out in a CHEMBET 3000 adsorption system equipped with a TCD detector. Each sample of 100 mg CuO/CeO2 was loaded and pretreated in He flow at 673 K for 1 h to remove the adsorbed carbonates and hydrates. After cooling down the sample to room temperature and introducing the reduction agent of 5 vol.% H2/Ar, we programmed the temperature to rise at a ramp of 10 K/min. For some cases, a sample experienced the preliminary TPR process was further subjected to re-oxidation with 20 vol.% O2/N2 at different temperatures for 1 h, then purged with He flow at 673 K for 30 min to remove the adsorbed oxygen species. Further TPR performances were conducted after cooling down the samples to room temperature.

FT-IR spectra were recorded with a Fourier transformation spectrometer (Nicolet Impact 410) with a resolution of 4 cm⁻¹, using 64 scans per spectrum in the region of 4000–1000 cm⁻¹. CuO/CeO2 samples were pressed into a thin self-supporting wafer and put it into a quartz IR cell with CaF2 windows; in the cell they were subjected to reduction with flowing hydrogen for 2 h at 473 and 773 K, respectively. After evacuation at ambient temperature for 10 min, and subsequently cooling down to 143 K, IR spectra were recorded by exposing the treated samples to CO of 15 Torr.

X-ray photoelectron spectroscopy analyses were performed with an ESCALAB MK-II spectrometer (VG Scientific Ltd., UK) using Al Kα radiation (1486.6 eV) operated at an accelerating voltage of 12.5 kV. The powder samples were pressed into thin discs and mounted on a sample rod placed in a pretreatment chamber, in which the catalysts were reduced by flowing hydrogen at 373–773 K for 2 h. Then the sample was transferred into the analysis chamber where the spectra of Cu 2p, Cu L3VV, Ce 3d and O 1s levels were recorded. The XPS measurement of CuO/CeO2 catalyst after CO oxidation reaction at 373 K for 10 h was also carried out. Charging effects were corrected by adjusting the binding energy of C 1s to 284.6 eV.

2.3. Activity tests

The catalytic activity tests were performed under atmospheric pressure in a continuous flow fixed-bed reactor. Samples of 200 mg (40–60 mesh) were placed between two layers of quartz wool inside a quartz tube (i.d. = 6 mm).
Prior to catalytic reactions, the catalysts experienced various pretreatments with different procedures. CO oxidation reaction was performed at 298–393 K with a feed composition of CO/O$_2$/He = 1/1/98 (vol.%). The total feed gas flow rate was 43 ml/min, corresponding to a gas hourly space velocity (GHSV) of 10,000 h$^{-1}$. Effluents from the reactor were on-line analyzed by a Varian 3800 gas chromatograph equipped with TCD and FID detectors. Combined 13X molecular and Haysep D packing columns were used to detect the CO, CO$_2$ and O$_2$.

3. Results

3.1. Surface area and structure

The BET surface area of the prepared CeO$_2$ support was measured to be 103.5 m$^2$/g, and the deposition of copper caused a significant decrease in the specific surface area to 85.2 m$^2$/g. However, further reduction of the CuO/CeO$_2$ catalyst with hydrogen only slightly changed the surface areas, no remarkable decrease can be observed. The BET surface area of the sample, which experienced reduction with hydrogen even at 773 K, still remained 83.1 m$^2$/g.

XRD measurements only showed the distinct fluorite oxide diffraction patterns of CeO$_2$ in the as-prepared and reduced samples. No detectable diffractions of copper crystallines can be observed, suggesting the extremely high dispersion of copper on the surface of CeO$_2$. The average crystallite size of ceria was 9.3 nm in the as-prepared catalyst, calculated from the peak at 28.6° of the XRD pattern using the Scherrer equation, while the corresponding value slightly increased to 10.1 nm after reduction with hydrogen at 773 K.

The Cu particle size of the as-prepared catalyst measured by CO absorption was 5.9 nm, while the particle size of copper in the catalyst reduced at 773 K only slightly increased to 6.6 nm, indicating the presence of slight copper sintering. However, it should be noted that the evaluated particle sizes of Cu are relative values because the CO can be adsorbed on the ceria phase as well, especially in the presence of metals, giving rise to partial reduction of ceria [25]. Nevertheless, the results of CO pulse titration still indicated that only slight sintering of Cu occurred in CuO/CeO$_2$ after reduction with hydrogen even at 773 K.

3.2. Temperature-programmed reduction

Fig. 1 shows the H$_2$-TPR profiles of CuO, CeO$_2$ and CuO/CeO$_2$ catalyst. Pure CuO showed a single reduction peak at 588 K. For CeO$_2$ alone, the hydrogen consumption took place at 701 K, which is usually attributed to the surface reduction of ceria. The total hydrogen consumption amount was calculated to be 701.1 μmol/g$_{\text{cat}}$, corresponding to a stoichiometric change in the composition of CeO$_2$ to CeO$_{1.87}$. However, the reduction behavior of ceria was dramatically changed in the presence of copper. CuO/CeO$_2$ catalyst exhibited two overlapped reduction peaks at 413 and 446 K, respectively, with a total hydrogen consumption of 1014.7 μmol/g$_{\text{cat}}$. This amount of hydrogen consumption greatly exceeded the amount required for the quantitative reduction of CuO to Cu (about 787.0 μmol/g$_{\text{cat}}$). This fact, together with the disappearance of the low temperature peak at 701 K, which was present in CeO$_2$ alone, indicated that excess hydrogen was used to remove the readily reducible oxygen in the surface layer of ceria.

As pointed out by recent studies, the TPR profiles of CuO/CeO$_2$ become reproducible only after the first preliminary TPR measurement [26]. This lack of reproducibility implied that an irreversible change in the morphology of dispersed copper on cerium oxide occurred during the first reduction process, which could be attributed to the re-distribution of copper species if new sites of low energy become available during the reduction process. In order to obtain further information to highlight the nature of this irreversible change, we further re-oxidized the sample subjected to the preliminary TPR process with 20 vol.% O$_2$/N$_2$ at 300–773 K, followed by another TPR measurement. As shown in Fig. 2, the TPR profiles of the samples after these re-oxidation treatments were greatly modified when compared with the results of the preliminary measurement. Both the hydrogen uptake and the temperature of reduction peaks were changed, depending on the temperature of re-oxidation. Table 1 summarizes the peak temperature and the amount of hydrogen consumed of each reduction peak. Clearly, re-oxidation at 300 K already caused almost the majority of copper and surface ceria to be oxidized, and a re-distribution of copper species was observed with reduction peaks at 413, 447 and 477 K.
representing the presence of three types of copper species. The more easily reduced $\alpha$ peak was assigned to the reduction of amorphous CuO clusters closely interacting with CeO$_2$. The $\beta$ peak may be due to an overlap of the reduction of the bulk-like CuO and the surface CeO$_2$, and the $\gamma$ peak to the segregated CuO crystalline [22,27,28]. Similarly, the re-oxidation at 573 and 773 K also led to the re-distribution of copper species, three distinct reduction peaks of Cu species can be distinguished, with the $\beta$ and $\gamma$ peaks slightly moving toward higher temperatures. In addition, the hydrogen uptake at higher temperature gradually increased and the corresponding value at lower temperature decreased. Noticeably, after re-oxidation at 773 K, the $\alpha$ peak dramatically decreased while the $\beta$ and $\gamma$ peaks significantly increased. This may suggest that re-oxidation at higher temperature helps in the formation of separated CuO crystalline and the migration of CuO clusters into bulk ceria during the reduction–oxidation cycle. When the hydrogen consumption is monitored, it can be found that the total amount of hydrogen consumption also strongly depends on the re-oxidation temperatures.

When the re-oxidation temperature increased from 300 to 573 K, the total amount of hydrogen consumed increased steadily from 1239.3 to 1400.6 $\mu$mol/g$_{\text{cat}}$. This can be understood by considering that the oxidation treatment at 573 K oxidized Ce$^{3+}$ in the vicinity of copper species, and thus more hydrogen was consumed. When the re-oxidation was performed at 773 K, the H$_2$ consumption amount decreased slightly to 1330.3 $\mu$mol/g$_{\text{cat}}$. This could be interpreted as a variation of distribution of copper species caused by the migration of surface copper species to bulk and the formation of separated CuO crystalline. Thus, less Ce$^{3+}$ on the interface can be re-oxidized. However, it was pointed out recently that with Cu on ceria-based materials, there is not always a correspondence between H$_2$O formation and H$_2$ consumption. This was interpreted as a “hydrogen storage” phenomena in which hydrogen is initially utilized for copper oxide reduction, then stored in some form on the support to be used for its reduction at higher temperature [29]. The results of TPR measurement still are qualitatively and semi-quantitatively indicative of the variations of distribution and texture during the reduction process.

For further investigating the reproducibility of redox ability of CuO/CeO$_2$, we performed the third TPR measurement again by re-oxidizing of the sample that had experienced previous TPR-oxidation (573 K)–TPR cycle at 573 K. As shown in Fig. 2, the result clearly demonstrated that this TPR profile showed very good reproducibility with the previous one, suggesting that the re-distribution of copper species is reversible under this circumstance, while only the first reduction process with hydrogen leads to the irreversible re-distribution of copper species.

### 3.3. X-ray photoelectron spectroscopy

Fig. 3 shows the X-ray photoelectron spectra of Cu 2p and Cu L$_{3}$VV Auger for the as-prepared catalyst and the reduced samples. For the as-prepared sample, as shown in Fig. 3, the spectra of Cu L$_{3}$VV Auger can be resolved into two peaks at 917.3 and 918.5 eV. The kinetic energy at 917.3 eV closely corresponded to the value expected for CuO. Together with the presence of Cu 2p$_{3/2}$ binding energy at 933.8 eV and the relatively large satellite peak, the copper valences in the as-prepared sample could be comprehensively assigned to the evolution of CuO, while the minor presence of Cu$^0$ at 918.5 eV was mainly due to the slight

### Table 1

Summary of TPR results over CuO/CeO$_2$ after re-oxidations

<table>
<thead>
<tr>
<th>Re-oxidation temperature (K)</th>
<th>$\alpha$ consumption (µmol/g$_{\text{cat}}$)</th>
<th>$\beta$ consumption (µmol/g$_{\text{cat}}$)</th>
<th>$\gamma$ consumption (µmol/g$_{\text{cat}}$)</th>
<th>Total amount (µmol/g$_{\text{cat}}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh</td>
<td>534.9 (413)</td>
<td>479.8 (446)</td>
<td>–</td>
<td>1014.7</td>
</tr>
<tr>
<td>300</td>
<td>437.3 (413)</td>
<td>447.9 (447)</td>
<td>318.1 (477)</td>
<td>1239.3</td>
</tr>
<tr>
<td>573 (first)</td>
<td>197.7 (420)</td>
<td>510.7 (462)</td>
<td>692.2 (494)</td>
<td>1400.6</td>
</tr>
<tr>
<td>573 (second)</td>
<td>204.3 (419)</td>
<td>521.0 (463)</td>
<td>684.0 (495)</td>
<td>1409.3</td>
</tr>
<tr>
<td>773</td>
<td>45.8 (417)</td>
<td>554.2 (460)</td>
<td>730.3 (499)</td>
<td>1330.3</td>
</tr>
</tbody>
</table>
photoreduction of CuO in the spectrometer. After reduction at 373 K, the peak at 917.5 eV ascribed to Cu$^{2+}$ significantly decreased, while the intensive peak at 918.5 eV that corresponded to Cu$^{0}$ increased. This fact clearly suggested that the transformation of Cu$^{2+}$ into Cu$^{0}$ occurred to some degree during the reduction, and Cu$^{2+}$ and Cu$^{0}$ co-existed in sample. When the reduction was performed at 473 K, the position of the main peak was shifted to 918.5 eV, indicating that CuO was almost reduced to Cu$^{0}$. This is in good agreement with the observations in the TPR profiles that the majority of the copper oxides were completely reduced to metallic copper at temperatures below 473 K. With further increase in the reduction temperature to 673 K, however, some of the Cu$^{0}$ was re-oxidized to Cu$^{+}$ with the kinetic energy at 914.0 eV. As previously reported [3], when the copper is highly dispersed and in intimated contact with the supports, Cu 2p$_{3/2}$ energies, particularly Cu Auger parameters, may deviate significantly from the corresponding bulk values. This large negative shift of kinetic energy implied the difference in copper coordination. On further raising the reduction temperature up to 773 K, the peak at 918.5 eV representing Cu$^{0}$ completely disappeared, and only the peaks at 914.0 and 917.3 eV can be observed, suggesting the dominant presence of Cu$^{+}$ species. Therefore, we can conclude that the Cu$^{0}$ formed at 473 K was almost completely re-oxidized to Cu$^{+}$ during the reduction processing with hydrogen at 773 K.

Fig. 4 shows the O 1s spectra for the as-prepared CuO/CeO$_{2}$ and the samples after the reduction with hydrogen at different temperatures. In addition to the presence of the main peak at 529.5 eV of oxygen in ceria, an apparent shoulder peak at 531.6 eV representing the lattice oxygen vacancies was observed. This kind of lattice oxygen vacancies...
Vacancies can be attributed to such highly polarized oxide ions at the surface (and interfaces) of the nanocrystals with an unusual low coordination [29]. With the increase in the reduction temperature, the intensity of the O 1s peak initially increased and then dropped gradually after passing the maximum at 473 K. The XPS spectra of Ce 3d are shown in Fig. 5. It is well known that the interpretation of the Ce 3d photoemission spectra is not straightforward due to the hybridization between the Ce 4f levels and the O 2p states [30–36]. A favorable method which considers the relative intensity of the \( u_0 \) (\( v_0 \)) and \( u' \) (\( v' \)) peaks to the intensity of Ce 3d region was applied to estimate the reduction degrees of ceria [30]:

\[
\text{Ce(III)}(\%) = \frac{100 \times [S(u_0) + S(v_0) + S(u') + S(v')]}{\sum [S(u) + S(v)]}
\]

Table 2 summarizes the Ce(III)% values as well as the atomic surface compositions. For the as-prepared sample, a certain amount of Ce\(^{3+}\) existed (about 22%), partly attributed to photoreduction of CeO\(_2\). The Ce(III)% of the used sample was 22.8%, close to the corresponding value of the as-prepared sample. As the reduction temperature increased, the Ce(III)% rapidly increased, and the value reached 37.7% at around 473 K. Further increase in the reduction temperature, Ce(III)% only slightly increased to 44.8% after reduction at 773 K. This may imply that the most of the surface ceria were reduced around 473 K, accompanied with the reduction of Cu\(^{2+}\) to Cu\(^0\).

**Table 2**

<table>
<thead>
<tr>
<th>Reduction temperature (K)</th>
<th>Atomic ratio</th>
<th>( I_{sat}/I_{pp} )(^b) (Cu 2p)</th>
<th>Ce(III) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh</td>
<td></td>
<td></td>
<td>22.0</td>
</tr>
<tr>
<td>Used(^a)</td>
<td>0.56</td>
<td>0.11</td>
<td>22.8</td>
</tr>
<tr>
<td>373</td>
<td>0.51</td>
<td>0.11</td>
<td>24.2</td>
</tr>
<tr>
<td>473</td>
<td>0.37</td>
<td>0.09</td>
<td>37.7</td>
</tr>
<tr>
<td>573</td>
<td>0.35</td>
<td>0.10</td>
<td>40.1</td>
</tr>
<tr>
<td>673</td>
<td>0.39</td>
<td>0.11</td>
<td>41.5</td>
</tr>
<tr>
<td>773</td>
<td>0.39</td>
<td>0.11</td>
<td>44.8</td>
</tr>
</tbody>
</table>

\(^a\) The sample subjected to the CO oxidation reaction for 10 h at 373 K.

\(^b\) The ratio of the intensity of the satellite peak to those of the principal peak (Cu 2p).

**Fig. 5** XPS spectra of Ce 3d for the as-prepared and the reduced CuO/CeO\(_2\) catalyst.

**Fig. 6** Cu/Ce ratio and Ce(III)% for CuO/CeO\(_2\) at different reduction temperatures.
depletion of lattice oxygen, which reversibly promoted the migration of lattice oxygen to surface. After reduction at 673 K, a slight increase in the Cu/Ce atomic ratio was observed, suggesting that copper migrated from the bulk ceria toward the surface accompanied by a further reduction of the CeO$_2$ surface. Hence, it can be concluded that the surface composition is also strongly influenced by the hydrogen reduction temperatures, together with significant changes of chemical states of copper and cerium.

3.4. In situ FT-IR

Fig. 7 shows the IR spectra of CO adsorbed at 143 K on the catalysts subjected to pre-reduction with hydrogen at 473 and 773 K, respectively. For the as-prepared sample, a narrow peak appearing at 2108 cm$^{-1}$ suggests the presence of Cu$^{2+}$ carbonyls. Hydrogen reduction at 473 K caused an apparent red shift phenomena with the band position of CO adsorption at 2088 cm$^{-1}$, which can be ascribed to Cu$^{0}$ carbonyl. After reduction at 773 K, the band position of CO adsorption shifted to 2068 cm$^{-1}$. Because Cu$^{+}$ carbonyls usually show a significantly higher stability than Cu$^{0}$ and Cu$^{2+}$ carbonyls [17], the presence of highly stable CO adsorption at 2068 cm$^{-1}$ even after RT evacuating suggested that this peak could be attributed to Cu$^{+}$ carbonyls. The interaction of the metallic copper particles with the underlying support would be the reasonable explanation for the shift of wavenumber. Although it is well agreed that the wavenumber increases with the copper oxidation state [6], the unusual low wavenumber of Cu$^{+}$ carbonyls may be due to one of the following two reasons. One possibility is that the water produced during the reduction with H$_2$ accounts for the low wavenumber of Cu$^{+}$ carbonyl [36]. The other possibility is that the vibration frequency of Cu$^{+}$ carbonyls decreases by increasing the degree of reduction around the Cu$^{+}$ adsorption center [24]. Therefore, it can be seen that the as-prepared catalyst and the reduced catalysts showed absolutely different IR spectra of CO adsorptions. Variations in the frequency of these carbonyls have been related to the changes in the chemical states and coordination environments of the copper species.

3.5. Activity measurements

The effect of pretreatment procedures on the catalytic activities of CuO/CeO$_2$ for CO oxidation reaction was tested. Fig. 8 shows the CO conversion as a function of temperature over the CuO/CeO$_2$ catalysts pre-reduced at different temperatures. It can be seen that the catalytic performance depended on pretreatment conditions, and that an apparent difference appeared in the temperature range of 333–353 K. The complete oxidation was achieved at 373 K for the catalyst experiencing reduction treatment below 673 K, while the corresponding value only arrived at 91% after reduction at 773 K. Fig. 9 further compares the conversions of CO at 333 and 353 K over the CuO/CeO$_2$ catalysts subjected to different pretreatments with hydrogen. Obviously, mild reductive pretreatment of CuO/CeO$_2$ was found to increase the activity slightly. The catalysts that experienced hydrogen reduction at 473 and 573 K exhibited the highest catalytic activity with CO conversion of about 42% at 333 K and 88% at 353 K. But the catalysts reduced at higher temperatures resulted in less CO conversion at the same reaction temperature.
4. Discussion

4.1. Redox features of CuO/CeO₂

Compared with the TPR profile of pure CuO characterized by a single peak at around 588 K, the copper species in CuO/CeO₂ were reduced at significantly lower temperatures, indicating the remarkable influence of CeO₂. The redox potentials of copper species in ceria were measured and found to be much lower than the potentials of bulk CuO, suggesting that less energy is required to reduce the copper species in CeO₂ than in the case of CuO [38]. Meanwhile, the presence of copper also notably promoted the reduction ability of ceria, especially the surface ceria, as can be seen from the combination of CuO reduction and surface ceria reduction in the preliminary TPR measurements of CuO/CeO₂. However, it should be emphasized that significant irreversible re-distribution of copper species took place during this preliminary reduction process. Only after these treatments during which the most stable contact between copper and ceria was found, the reduction and oxidation could become reversible. As demonstrated by the following re-oxidation and TPR measurements, changes in the copper–ceria contact was observed with the formation of three types of copper species. This might be one of the main reasons for the previously reported controversial redox properties of CuO/CeO₂ catalysts.

Concerning the generation of Cu⁺ species during hydrogen reduction at 773 K, we proposed that the redox behavior of CuO/CeO₂ is an associated process. Both the reduction and the re-oxidation proceeded in a synergistic way in which copper and ceria participated in the redox behavior of each other, particularly in the re-distribution of copper species. The reducibility of Ce⁴⁺ to Ce³⁺ enhanced the flexibility of copper ions, resulting in different valences by maintaining the electronic neutrality of the lattice. Starting from the as-prepared CuO/CeO₂ catalyst, most of the copper was initially in the fully oxidized Cu²⁺ state, and hydrogen reduction forced CuO to transform into metallic copper at 473 K, and subsequently to Cu₂O with the interaction with cerium oxide at 773 K. IR spectra of CO adsorption on the samples reduced at 473 and 773 K provided further evidence for the stable existence of Cu⁰ at 473 K and Cu⁺ at 773 K, respectively. The apparently low frequency of carbonyls after reduction at 773 K meant that the Cu⁺ adsorption centers were surrounded by high proportion of Ce³⁺. This specific coordination environment relates with the reaction equilibrium (Ce⁴⁺ + Cu⁰ → Ce³⁺ + Cu⁺). Therefore, the change of copper valences in CuO/CeO₂ can be put forward in a sequential manner (Cu²⁺ → Cu⁰ → Cu⁺) under hydrogen by gradually increasing the reduction temperatures with Cu⁺ as the most stable specie at 773 K. Clearly, this reduction sequence does not agree well with the previous results, which concluded that Cu⁰ was always the final species under severe reductive atmosphere [21,36,38,39]. Tschöpe et al. [26] reported that the copper component in the intimate mixture with cerium oxide could be readily reduced to Cu⁺ with hydrogen at 473 K and 100% Cu⁰ at 673 K. Lamonier et al. also observed Cu⁺ to be predominant when CuO/CeO₂ was reduced with hydrogen at 423 K, and all of the copper species were completely reduced to Cu⁺ at 673 K [37,40]. This result comprehensively elaborated that the strong metal–support interaction in CuO/CeO₂ could lead to abnormal stability of Cu⁺ under severe reductive conditions [41]. These differences might originate from different preparation routes, which may cause significant differences in the structure of the final catalyst, and thus, in the copper–ceria interaction.

The interaction between the Ce⁴⁺/Ce³⁺ and the Cu²⁺/Cu(²⁻⁵⁺) couples take place at boundaries of nanocrystalline ceria (CeO₂₋ₓ). The Cu²⁺ in CuO/CeO₂ was directly reduced to metallic copper at 473 K. Along with this, some surface Ce³⁺ was reduced with the generation of Ce²⁺ as well. With further increase in the reduction temperature, the Cu⁰ was re-oxidized to Cu⁺. The most likely elucidation for the re-oxidation of Cu⁰ to Cu⁺ during hydrogen reduction at 773 K is the diffusion of lattice oxygen to the surface to oxidize the copper overlayers.

4.2. Reaction pathway of CO oxidation

Combining the reaction data of CO oxidation with structural characterizations of CuO/CeO₂ catalyst, one can easily establish the correlations between the copper valence states and the copper–ceria interface and the catalytic performances. It is widely known that the oxidation state of supported transition metal species has an important effect on the activity in various catalytic reactions [17]. As a result, the rates of CO oxidation depend strongly on the valence of
copper. Therefore, it can be expected that the electronic interaction between copper and ceria would lower the reaction temperature due to the enhancement of the redox activity. CeO₂ can be readily reduced and can shift rapidly between the +3 and +4 state and vice versa simultaneously, copper species in the CuO/CeO₂ catalyst also has the ability to undergo rapid cycling among different oxidation states.

The most interesting result was that the reduction with hydrogen at 473–573 K is sufficient to obtain a high catalytic activity toward CO total oxidation. This is occasionally in good accord with the abundances of Cu⁰ species and lattice oxygen on the surface. The catalyst reduced with hydrogen at 373 K showed lower catalytic activity. The reason was supposed to be the depletion of lattice oxygen on the surface by H₂ at 373 K [42], while this reduction temperature is not enough to facilitate the oxygen migration from bulk to surface and the formation of oxygen vacancies. Reduction at higher temperatures also obviously decreased the catalytic performances. As XPS results showed, with the increase in the reduction temperature, the intensity of the Olat peak initially increased, and then dropped gradually after passing the maximum at 473 K. So, excess reduction will cause the decrease of the amount of lattice oxygen vacancies on the surface. In addition, further reduction may happen at the sites of ceria far away from copper species, which are relatively difficult to be reduced and have marginal effects on the transportation of oxygen. Thus, the decrease of catalytic activity could be mainly attributed to the variations in the copper valence and the coordination environment of copper species.

The spectrum of the sample experiencing the CO oxidation reaction was similar to that of the as-prepared catalyst. However, a slight increase in Iₘagnet/Iₚp value was observed, indicating that part of Cu⁰ was oxidized to Cu²⁺ during the reaction process, and that most of the copper was in a fully oxidized Cu²⁺ state. As shown in Table 2, after the catalyst was subjected to CO oxidation reaction at 373 K for 10 h, the Cu/Ce and Ce/O ratios obviously increased. This suggested that the finely dispersed copper species in the CeO₂ migrated toward the surface during the CO oxidation process. In addition, the consumption of surface lattice oxygen also led to the increase of Cu/Ce and Ce/O ratios. Comparing to the as-prepared sample, the used sample presented the lower Olat peak, implying that the lattice oxygen vacancies are correlated with the reaction pathway of CO oxidation. Therefore, it is possible to propose that reduction at 473–573 K is necessary and enough to achieve an appropriate perimeter interface where the metallic Cu sites closely contact ceria. This perimeter interface is probably responsible for the effective proceeding of the reactions. As illustrated in Scheme 1, the reaction pathway for CO oxidation involves surface reaction at the copper–CeO₂ interface where CO adsorbs onto the metallic copper, and reacts with the adsorbed active oxygen species nearby. The role of the support is to activate O₂ to or to provide sites at the interface around copper particles for activating O₂.

Either the lattice oxygen (path 1) derived from ceria or the activated superoxide ions (O₂⁻) generated on the copper–CeO₂ interface (path 2) can react with the adsorbing CO to form CO₂. Interface activation plays a determining role with Cu⁰ effectively adsorbing CO, and with CeO₂ on the interface serving as dissociation centers for oxygen molecules. Once the surface oxygen is consumed, oxygen vacancies, which lie close to the copper species, can accept oxygen from bulk diffusion in catalyst lattice or gaseous oxygen. It is important to note that the CO oxidation concerns redox couples: Cu²⁺/Cu(2−δ)⁺ and Ce⁴+/Ce³+. This process of electron transfer activates the lattice oxygen nearby the copper species. By contrast, higher reduction temperatures than 473–573 K would modify the copper–ceria interface dramatically, with the formation of Cu⁺ species and the decrease of lattice oxygen on the surface. Consequently, the strong adsorption of CO on Cu⁺ and the inhibition of oxygen activation would result in less CO conversion.

5. Conclusions

Appropriate metal–support interaction can lead to optimization of the catalytic system with greatly promoted redox features, in which both copper and ceria participated in the redox cycle of each other. The preliminary reduction process with hydrogen led to irreversible re-distribution of copper species, only after which the redox process can become reversible. However, the Cu particle size remained rather stable during the redox cycles, only slight copper sintering could be observed.

A strong reduction temperature dependence of copper chemical states in the as-prepared CuO/CeO₂ catalyst was observed. A sequential change in copper states (Cu²⁺ → Cu⁰ → Cu⁺) occurred during reduction with hydrogen by gradually increasing the reduction temperatures. Especially, Cu⁺ can stably exist as the dominant copper species after reduction treatment with hydrogen at 773 K.

A reaction pathway in CuO/CeO₂ system for CO oxidation was proposed involving surface reaction at the copper–CeO₂ interface, where CO adsorbed onto the metal...
and the lattice oxygen derived from ceria or the activated superoxide ions ($O_2^-$) on the copper–CeO$_2$ interface. The CuO/CeO$_2$ system reduced at 473–573 K with H$_2$ achieved the most effective interface to adsorb the reactant and to activate oxygen molecules, and in turn, gave the highest catalytic activities for CO oxidation.

Acknowledgment

We are grateful to Dr. Zili Wu for assistance with the in situ FT-IR measurements and analysis.

References
