Enhanced Activity for CO Preferential Oxidation over CuO Catalysts Supported on Nanosized CeO₂ with High Surface Area and Defects

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Catalysts supported on nanosized CeO₂ with high surface area and defects exhibit high catalytic activity for CO preferential oxidation. Nanosized ceria (n-CeO₂) was synthesized by a facile method in 2-methylimidazolesolution. The characterization results of XRD, N₂ adsorption-desorption, Raman and TEM indicate that n-CeO₂ shows a regular size of 10 ± 1 nm, a high surface area of 130 m²·g⁻¹ and oxygen vacancies on the surface. A series of CuO/n-CeO₂ catalysts (CuCeO₃) with different copper loading were prepared for the preferential oxidation of CO in H₂-rich gases (CO-PROX). All CuCeO₃ catalysts exhibit a high catalytic activity due to the excellent structural properties of n-CeO₂, over which the 100% conversion of CO is obtained at 120 °C. The catalytic activity of CuCeOₓ catalysts increases in the order of CuCeO₁₂ < CuCeO₉ < CuCeO₆ < CuCeO₃. It is in good agreement with the order of the amount of active Cu⁰ species, Ce³⁺ species and oxygen vacancies on these catalysts, suggesting that the strength of interaction between highly dispersed CuO species and n-CeO₂ is the decisive factor for the activity. The stronger interaction results in the formation of more readily reducible copper species on CuCeO₉, which shows the highest activity with high stability and the broadest temperature “window” for complete CO conversion (120–180 °C).

Keywords: CO catalyst; nanosized ceria; oxygen vacancy; CO preferential oxidation

1. Introduction

Proton exchange membrane fuel cells (PEMFCs) are the most promising hydrogen-based fuel cell systems for commercial applications [1]. Hydrogen as fuel for PEMFCs should be almost free of CO to avoid the deactivation of cell Pt electrodes. However, the fed hydrogen produced by the reforming of hydrocarbon fuels, even after low-temperature water gas shift (WGSR) reaction, inevitably contains about 0.5–2.0 vol.% CO [2]. Thus, further CO removal in rich-H₂ gases is required. Among the various methods for CO removal, preferential oxidation of CO (CO-PROX) has been considered as the most efficient and low-cost one [3]. Many different types of catalysts for CO-PROX system have been reported in recent years [3–6]. Of the reported catalysts, CuO-CeO₂ couple oxide catalysts have attracted much attention because they are more active at low temperatures and have a lower cost compared to noble metal catalysts [3]. Ceria has high oxygen storing/releasing capacity and its structural properties play an important role in the catalytic performance of CuO/CeO₂ catalysts, such as surface area, pore structure and surface defects [7,8]. Many studies confirmed that the high activity of CuO/CeO₂ catalysts should be attributed to the strong interaction between highly dispersed CuO species and ceria [9–11]. The nano-scale CeO₂ with high surface area supports the dispersion of copper species and promotes the interfacial activity [12]. Surface defects and oxygen vacancies on ceria can enhance the interaction between copper species and CeO₂ [10–12]. Thus, nanosized CeO₂ with high surface area or surface defect supported CuO catalysts display superior activity for CO-PROX in comparison with usually used CuO/CeO₂ catalysts. Reis et al. [13] reported...
that CuO/CeO$_2$-nanocrystalline catalysts ($S_{\text{BET}} = 92 \text{ m}^2\text{ g}^{-1}$) with copper loading of 1.0 wt.% exhibited an improved reactivity for CO-PROX reaction. The high activity was closely related to the finely dispersed CuO species strongly interacting with CeO$_2$ nanocrystalline. Zou et al. [14] observed that CuO supported on ceria nanospheres ($S_{\text{BET}} = 133 \text{ m}^2\text{ g}^{-1}$) had a high low-temperature catalytic activity for CO PROX due to the formation of more active oxygen species on the surface of ceria nanospheres. Wang et al. [15] synthesized CuO/CeO$_2$-nanocrystal catalysts for CO-PROX. The catalyst calcined at 500 °C ($S_{\text{BET}} = 97 \text{ m}^2\text{ g}^{-1}$) shows the highest catalytic activity, because much surface lattice defects on CeO$_2$-nanocrystal supports strengthen the interaction between CuO and CeO$_2$.

The synthetic methods of nanosized CeO$_2$ most commonly reported in the literature are hydrothermal method and precipitation method in KOH, NaOH, or Na$_2$CO$_3$ solution [16–18]. The surface area of as prepared nanosized CeO$_2$ is generally small, and the residual K$^+$/Na$^+$ has a negative effect on the catalytic performance [19,20]. Moreover, Ce$^{3+}$/Ce$^{4+}$ precursors are completely oxidized in this reaction condition, which is unfavorable for the generation of surface defects.

In this work, nanosized CeO$_2$ with high surface area and surface defects (n-CeO$_2$) was prepared in 2-methylimidazole solution. 2-methylimidazole can act as a stabilizer to limit particle growth and prohibit aggregation, and it is also expected to be a reducer to be oxidized by Ce$^{4+}$ and form Ce$^{3+}$ partly. The copper loading, as one of the important factors for preparation, has a great effect on catalytic performance for CuO/CeO$_2$ catalysts. Thus, n-CeO$_2$ supported CuO catalysts with different copper loading (3–12 wt.%) were prepared by impregnation method for CO-PROX. The samples were characterized by XRD, N$_2$ adsorption-desorption, TEM, H$_2$-TPR, XPS and Raman. The effects of structural parameters and copper content on catalytic activity were discussed.

2. Results and Discussion

2.1. Characterization of n-CeO$_2$ and p-CeO$_2$

Figure 1A shows the N$_2$ adsorption-desorption isotherm and pore size distribution of n-CeO$_2$ and p-CeO$_2$. Table 1 lists the BET surface areas, average pore diameters and lattice parameters of n-CeO$_2$ and p-CeO$_2$. Their N$_2$ adsorption-desorption isotherms both correspond to typical type IV isotherms. n-CeO$_2$ exhibits an H2-type hysteresis loop in the relative pressure ($P/P_0$) range from 0.4 to 1.0, suggesting the existence of mesopores due to the agglomeration of particles [10,17]. p-CeO$_2$ shows an H3-type hysteresis loop in the relative pressure ($P/P_0$) range from 0.8 to 1.0, which indicates the generation of irregular pores in p-CeO$_2$ [16]. From the inset of Figure 1A, we can see that n-CeO$_2$ shows a narrow distribution of pore size between 5 nm and 15 nm. For p-CeO$_2$, the pore size distribution is wider and in the range of 5–50 nm. As listed in Table 1, the pore volumes of n-CeO$_2$ and p-CeO$_2$ are 0.176 and 0.083 m$^3\text{ g}^{-1}$, and the average pore diameters are 5.6 and 18.7 nm, respectively. n-CeO$_2$ possesses a large surface area, reaching to 130 m$^2\text{ g}^{-1}$, while p-CeO$_2$ exhibits a relatively small surface area of 35 m$^2\text{ g}^{-1}$. The larger pore volume and smaller pore size benefit faster diffusion of reactant gas in catalysts. The larger surface area is beneficial to the high dispersion of copper species which can form more potential active sites.

![Figure 1](image-url). N$_2$ adsorption-desorption isotherms combined with the pore size distribution curves (inset) (A), XRD patterns (B) and UV-Raman profiles (C) of n-CeO$_2$ and p-CeO$_2$. 
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Table 1. Textural characteristics of p-CeO₂, n-CeO₂, CuO/p-CeO₂ and CuCeOX catalysts.

| Catalyst     | \( S_{\text{BET}} \) (m²·g⁻¹) | \( D_{\text{pore}} \) (nm) | \( V_{\text{pore}} \) (cm³·g⁻¹) | Lattice Parameters (nm) \(^a\) |
|--------------|-------------------------------|-----------------------------|-------------------------------|--------------------------------|
| p-CeO₂       | 35                            | 18.7                        | 0.083                         | 0.5414                         |
| n-CeO₂       | 130                           | 5.6                         | 0.176                         | 0.5417                         |
| CuCeO₃       | 95                            | 8.9                         | 0.187                         | 0.5411                         |
| CuCeO₆       | 94                            | 9.4                         | 0.198                         | 0.5409                         |
| CuCeO₉       | 92                            | 9.3                         | 0.186                         | 0.5425                         |
| CuCeO₁₂      | 86                            | 6.4                         | 0.130                         | 0.5417                         |
| CuO/p-CeO₂   | 24                            | 20.3                        | 0.051                         | 0.5413                         |

\(^a\) Obtained by using MDI Jade 5.0 software according to the data of XRD.

Figure 1B displays the XRD patterns of n-CeO₂ and p-CeO₂. As seen in Figure 1B, the strong diffraction peaks at 28.5, 33.1, 47.5 and 56.3° are clearly observed in n-CeO₂ and p-CeO₂, and match well the standard diffraction peaks for fluorite ceria (JCPDS 34-0394). For p-CeO₂, the lattice parameter is 0.5414 nm, which is consistent with that of pure ceria. The lattice parameter of n-CeO₂ is 0.5417 nm, a little larger than that of p-CeO₂, implying that a portion of larger-radius Ce³⁺ ions (ionic radius 0.1143 nm) substitute Ce⁴⁺ (0.907 nm) in the n-CeO₂ lattice. The substitution can result in the formation of lattice defects and oxygen vacancies on the surface of n-CeO₂ [21]. UV-Raman characterization was performed to further obtain the information about oxygen vacancies in n-CeO₂ and p-CeO₂. As shown in Figure 1C, n-CeO₂ and p-CeO₂ display an intense band at about 464 cm⁻¹ responding to the characteristic F₂g vibration (Ce-O-Ce stretching) of fluorite structure CeO₂. As compared with p-CeO₂, n-CeO₂ has a slight peak shift towards lower wavenumber, which is associated with the lattice expansion and the generation of oxygen vacancies. Moreover, a peak at 590 cm⁻¹ related to oxygen vacancy for n-CeO₂ was clearly observed, which confirms the presence of oxygen vacancy in n-CeO₂.

TEM and HRTEM images of n-CeO₂ are presented in Figure 2. As shown in Figure 2A, n-CeO₂ displays an irregular polyhedral shape with the size of 10 ± 1 nm. Structural details can be seen from Figure 2B. Most of the spacing of lattice fringe in n-CeO₂ is around 0.305 and 0.270 nm, which correspond to the (111) and (200) planes of CeO₂, respectively. The selective area (red square, Figure 2B) HRTEM image is shown in Figure 2C. As can be clearly seen in the magnified image of the white square I and II in Figure 2C, several regions (dark pits in the red ellipses) show the quite different contrast which should be associated with the defects caused by the substitution of Ce³⁺ into n-CeO₂ lattice and the formation of oxygen vacancies. The oxygen vacancies favor the adsorption and activation of surface oxygen species, and further increase the catalytic activity of catalysts for CO oxidation.

2.2. Characterization of CuO/p-CeO₂ and CuCeOX Catalysts

Figure 3 shows the \( N₂ \) adsorption-desorption isotherm and pore size distribution of CuO/p-CeO₂ and CuCeOX catalysts. CuO/p-CeO₂ exhibits a type IV isotherm with H3-type hysteresis loop. All of the CuCeOX catalysts display a typical type IV isotherm accompanied by an H2-type hysteresis loop, indicating that the porosity structures are maintained in CuCeOX catalysts. As listed in Table 1, the surface area and pore volume of CuO/p-CeO₂ decrease obviously in comparison with p-CeO₂. The surface areas of CuCeOX decrease to about 90 m²·g⁻¹ and the average pore diameters increase slightly as compared with n-CeO₂. The increase of copper loading from 3% to 9% causes a slight enhancement in pore volume which decreases sharply when the copper loading further increases to 12%. Figure 4 displays the XRD patterns of CuO/p-CeO₂ and CuCeOX catalysts. As can be seen from Figure 4, all CuO/p-CeO₂ and CuCeOX catalysts show the same peaks with n-CeO₂. No typical characteristic peaks of CuO are detected for all CuCeOX catalysts, implying the well-dispersion of CuO species [22]. However, the diffraction peaks of CuO at 35.6° and 38.7° are observed over CuO/p-CeO₂, indicating the existence of the bulk CuO, which may be related to the small surface area of p-CeO₂. The inset of Figure 4 shows that the diffraction peak of CeO₂ (111) shifts slightly to higher 2θ values for CuCeOX catalysts with
the increase of copper loading. Meanwhile, the calculated lattice parameters of ceria in 
CuCeO\(_x\) decrease slightly with the increase of Cu loading from 3% to 9% (listed in Table 1), 
suggesting that a portion of copper ions are incorporated into n-CeO\(_2\) lattices. It can further 
increase the defect concentration on n-CeO\(_2\) surface to improve the oxygen mobility, which 
is favorable for redox properties of catalysts [21,22]. With the copper loading increasing to 
12%, the lattice parameter has no evident change compared to n-CeO\(_2\), indicating that the 
excessive loading of copper species probably blocks the incorporation of Cu\(^{2+}\) ions into the 
lattice of CeO\(_2\).

![Figure 3](image)

Figure 3. N\(_2\) absorption-desorption isotherm (A) and pore size distribution (B) of CuO/p-CeO\(_2\) and CuCeO\(_x\) catalysts. 

As can be seen from the TEM and HRTEM images of CuCeO\(_9\) presented in Figure 5A, 
B.; CuCeO\(_9\) maintains the original shapes of n-CeO\(_2\) after the loading of CuO and mainly 
exposes (111) and (200) planes of CeO\(_2\). No CuO crystallite or amorphous CuO on the 
surface can be found in Figure 5B. Combined with the result of XRD, it is confirmed that 
the copper species exist as highly dispersed CuO species, which may be related to the high 
surface area of n-CeO\(_2\).
The reduction peaks for n-CeO$_2$ and p-CeO$_2$ both show two reduction peaks over 200 °C, corresponding to the reduction of surface and bulk oxygen species of CeO$_2$ [17], respectively. The surface defects on n-CeO$_2$ facilitate the formation of more active oxygen species. Thus, the reduction peaks for n-CeO$_2$ obviously shift toward lower temperature compared to those for p-CeO$_2$. All CuCeO$_x$ catalysts and CuO/p-CeO$_2$ exhibit two reduction peaks below 200 °C, denoted as $\alpha$ and $\beta$, respectively. As shown in Table 2, the H$_2$ consumption for CuCeO$_x$ catalyst increases with the increase of copper loading. Thus, the overlapped reduction peaks below 200 °C mainly belong to the reduction of copper species with a strong interaction with CeO$_2$, while the peak $\beta$ should be ascribed to the reduction of copper species incorporated into CeO$_2$ and large CuO clusters weakly interacted with CeO$_2$. In addition, CuO/p-CeO$_2$ also shows a reduction peak at 210 °C, denoted as peak $\gamma$, which should be assigned to the reduction of bulk CuO. It agrees well with the characterization of XRD. No peak belonging to the reduction of bulk CuO can be found in CuCeO$_x$ catalysts, which is consistent with the results of XRD and TEM. Usually, the position of reduction peaks can be evaluated to determine the strength of the interaction between CuO and CeO$_2$. The lower temperature of reduction peaks results in the stronger interaction between copper species and CeO$_2$ [11]. For CuO/p-CeO$_2$, the temperature of reduction peaks is significantly higher than that of CuCeO$_x$ catalysts, which may be due to the formation of bulk CuO on p-CeO$_2$ inhibiting the interaction between copper species and p-CeO$_2$. For CuCeO$_x$ catalysts, the temperature of peak $\alpha$ and $\beta$ gradually decreases with the copper loading increasing from 3% to 9%, indicating that the interaction between highly dispersed CuO and n-CeO$_2$ is enhanced gradually. The more highly dispersed CuO and more defects on the surface of n-CeO$_2$ can enhance the interaction to lower the reduction temperature of peak $\alpha$ and $\beta$. With the copper loading further increasing to 12%, the temperature of peak $\alpha$ and $\beta$ shifts to higher temperatures at 127 °C and 147 °C, respectively. It is probably because that excessive accumulation of copper species results in the formation of larger CuO clusters,
which decreases the strength of interaction between copper species and n-CeO$_2$. CuCeO$_9$ shows the lowest reduction temperature of peak $\alpha$ and $\beta$, implying that the strength of interaction between copper species and n-CeO$_2$ in CuCeO$_9$ is the strongest and the copper species in CuCeO$_9$ are more readily reducible than those on other catalysts.

![Figure 6. H$_2$-TPR profiles of n-CeO$_2$, p-CeO$_2$, CuO/p-CeO$_2$ (A) and CuCeOX catalysts (B).](image)

Table 2. H$_2$ consumption amount $^a$ and reduction temperature of CuO/p-CeO$_2$ and CuCeOX catalysts.

| Catalysts       | $\alpha$ Peak | $\beta$ Peak | $\gamma$ Peak | Total            |
|-----------------|---------------|--------------|---------------|------------------|
|                 | Peak Temp. (°C) | H$_2$ Cons. (µmol g$^{-1}$) | Peak Temp. (°C) | H$_2$ Cons. (µmol g$^{-1}$) | Peak Temp. (°C) | H$_2$ Cons. (µmol g$^{-1}$) | H$_2$ Cons. (µmol g$^{-1}$) |
| CuO/p-CeO$_2$   | 142           | 632          | 185           | 648              | 210             | 713                       | 1993                      |
| CuCeO$_3$       | 124           | 468          | 136           | 513              | -               | -                         | 981                       |
| CuCeO$_5$       | 121           | 616          | 133           | 851              | -               | -                         | 1467                      |
| CuCeO$_9$       | 111           | 716          | 127           | 1291             | -               | -                         | 2007                      |
| CuCeO$_{12}$    | 127           | 667          | 147           | 1775             | -               | -                         | 2442                      |

$^a$ CuO (99.99%) was used as the calibration standard sample for H$_2$ consumption.

The XPS spectra of Cu 2p, O 1s and Ce 3d of CuO/p-CeO$_2$ and CuCeOX catalysts were displayed in Figure 7 and the results derived by XPS are summarized in Table 3. According to Table 3, the actual Cu content in CuCeOX catalysts is far higher than that in bulk. Combined with the results of XRD and TEM, it suggests that a large amount of copper species are highly dispersed on the surface of CuCeOX catalysts. The Cu 2p spectra of CuCeOX and CuO/p-CeO$_2$ are shown in Figure 7A. The main peak at around 933.5, combined with the shake-up satellite in the range of 938–947 eV, is assigned to the existence of Cu$^{2+}$, and the weak peak at 931.0 eV represents the presence of the Cu$^+/Cu^{0}$ species [31]. Considering that CuO/p-CeO$_2$ and CuCeOX catalysts were calcined in air during the preparation process, the existence of Cu$^{0}$ seems to be impossible. The formation of Cu$^{+}$ can be induced by the synergistic interaction between copper and ceria species during the calcining process [14,32]. Thus, most copper species are present in Cu$^{2+}$ state and a small amount in Cu$^+$ state for CuO/p-CeO$_2$ and CuCeOX catalysts. The reduced degree of copper species can be estimated by the ratio of the intensity of the shake-up satellite peaks to that of the main Cu 2p$\frac{3}{2}$ Peaks ($I_{sat}/I_{mp}$). The lower $I_{sat}/I_{mp}$ values imply higher reduced degree of copper species on the surface [33]. According to the $I_{sat}/I_{mp}$ values listed in Table 3, the relative amounts of Cu$^+$ increase in the order of CuO/p-CeO$_2$ < CuCeO$_{12}$ < CuCeO$_5$ < CuCeO$_9$ < CuCeO$_3$ < CuCeO$_{0}$ < CuO. Figure 7B shows the O 1s XPS spectra of CuO/p-CeO$_2$ and CuCeOX catalysts. In addition to a main peak $O_{latt}$ at 529.7 eV attributed to the lattice oxygen of CuO and CeO$_2$, a shoulder peak $O_{ads}$ at higher binding energy $\sim$531.4 eV assigned to the adsorbed oxygen or hydroxyl/carbonate species is observed [34]. The relative surface concentration of $O_{latt}$ can be calculated by the ratio of peak area. The value of $O_{latt}/(O_{latt} + O_{ads})$ listed in Table 3 displays a slight decrease...
with the increase of surface Cu content, suggesting that the coverage of CuO results in the decrease of lattice oxygen content on the surface of CuO/p-CeO$_2$ and CuCeO$_X$ catalysts.

![Figure 7](image_url)

**Figure 7.** XPS spectra of CuO/p-CeO$_2$ and CuCeO$_X$ catalysts: (A) Cu 2p; (B) O 1s; (C) Ce 3d.

**Table 3.** ICP and XPS results of CuO/p-CeO$_2$ and CuCeO$_X$ catalysts.

| Catalysts | Ce$^{3+}$/(Ce$^{3+}$+Ce$^{4+}$) (%) | $I_{sat}/I_{mp}$ | $O_{sat}/O_{total}$ (%) | Cu Content (wt.%) $^a$ | Cu/Cu+Ce (at.%) $^b$ | $A_{SSd}/A_{460}$ |
|-----------|----------------------------------|----------------|------------------------|------------------------|----------------------|-----------------|
| CuO/p-CeO$_2$ | 11.79 | 0.41 | 74.63 | 8.9 | 28.8 | 0.15 |
| CuCeO$_3$ | 16.61 | 0.35 | 79.42 | 3.1 | 18.3 | 0.23 |
| CuCeO$_9$ | 17.83 | 0.32 | 76.52 | 5.9 | 25.0 | 0.28 |
| CuCeO$_9$ | 20.82 | 0.27 | 72.96 | 8.9 | 29.3 | 0.39 |
| CuCeO$_{12}$ | 16.23 | 0.38 | 69.42 | 11.8 | 32.9 | 0.18 |

$^a$ Actual Cu content (wt.%) determined by ICP. $^b$ Surface atomic ratio Cu/Cu+Ce determined by XPS.

Usually, the spectrum of Ce 3d can be resolved into eight components, and two groups of spin-orbital multiplets are labeled as u and v, corresponding to Ce 3d$_{3/2}$ and Ce 3d$_{5/2}$, respectively. As shown in Figure 7C, the bands labeled u' (903.0 eV) and v' (884.5 eV) represent the 3d$_{10}$4f$_1$ initial electronic state corresponding to Ce$^{3+}$, while the other six bands labeled u'' (917.0 eV) and v'' (898.5 eV), u'' (907.8 eV) and v'' (889.4 eV), u (901.0 eV) and v (882.6 eV) are associated with Ce$^{4+}$. Obviously, Ce$^{4+}$ and Ce$^{3+}$ species coexist in CuO/p-CeO$_2$ and CuCeO$_X$ catalysts. As reported, the concentration of Ce$^{3+}$ is directly related to the amount of oxygen vacancies [35]. Generally, the ratio of Ce$^{3+}$ can be estimated from the relative area of u' and v' peaks to the area of Ce 3d region according to the following equation [36]:

$$\text{Ce}^{3+} (\%) = \frac{S(u') + S(v')}{\sum S(u) + S(v')} \times 100\%$$

It can be seen from Table 3 that the Ce$^{3+}$ ions’ percentage of CuO/p-CeO$_2$ is obviously lower than that of CuCeO$_X$ catalysts. For CuCeO$_X$ catalysts, the percentage of Ce$^{3+}$ ions firstly increase with the copper loading increasing from 3% to 9%, and then decreases when the copper loading further increases to 12%. The highest relative concentration of Ce$^{3+}$ is observed in CuCeO$_9$, which means the most oxygen vacancies exist in CuCeO$_9$. It is also confirmed by UV-Raman results discussed below. CuCeO$_9$ contains higher amounts of Ce$^{3+}$ and Cu$^{+}$ species, which implies that the redox cycles between Cu$^{2+}$/Cu$^+$ and Ce$^{3+}$/Ce$^{4+}$ are more facile to occur in CuCeO$_9$ than in other catalysts. Thus, CuCeO$_9$ is expected to exhibit excellent activity for CO-PROX reaction.

As shown in Figure 8, all CuCeO$_X$ catalysts display an intense band at about 460 cm$^{-1}$ and a slight downshift compared to n-CeO$_2$. The shift is most likely due to the change of the fluorite crystal structure caused by the strong interaction between copper species and n-CeO$_2$ [25]. Copper species incorporating into CeO$_2$ also results in lattice defects and formation of oxygen vacancies. The broad peak related to oxygen vacancies at 584 cm$^{-1}$ is observed in all CuCeO$_X$ catalysts. CuO/p-CeO$_2$ also shows a weak peak at about 584 cm$^{-1}$ as compared with p-CeO$_2$. The relative concentration of oxygen vacancies can be evaluated by the ratio of peaks area between 584 cm$^{-1}$ and 460 cm$^{-1}$ (noted as
According to $A_{584}/A_{460}$ ratios listed in Table 3, the relative concentration of oxygen vacancies follows the order of CuCeO$_9$ > CuCeO$_6$ > CuCeO$_3$ > CuCeO$_{12}$ > CuO/p-CeO$_2$, which is in good agreement with the results of XPS characterization. CuCeO$_9$ possess more oxygen vacancies as compared with other catalysts. For CuCeO$_{12}$ and CuO/p-CeO$_2$ catalysts, the generation of large CuO clusters and bulk CuO on the surface prevent copper ions from incorporating into CeO$_2$ lattice to form oxygen vacancies to some extent. Oxygen vacancies can provide the site for the adsorption and activation of O$_2$ [17]. The reaction of $O_2 + 2O_{\text{vacancy}} = 2O_{\text{lattice}}$ is an important step of the CO-PROX reaction mechanism [38]. Thus, the presence of more oxygen vacancies has a positive effect on the activity of CuCeO$_X$.

![Figure 8. UV-Raman spectra of CuO/p-CeO$_2$ and CuCeO$_X$ catalysts.](image)

### 2.3. Catalytic Performance

The catalytic performance of the n-CeO$_2$, p-CeO$_2$, CuO/p-CeO$_2$ and CuCeO$_X$ catalysts for CO-PROX reaction is shown in Figure 9A,B. It can be seen that the CO conversion of n-CeO$_2$ is higher than that of p-CeO$_2$ and the CO conversion for both of them is lower than 20% in the temperature range investigated. CuO/p-CeO$_2$ shows lower CO conversion compared to CuCeO$_X$ catalysts, which achieves a complete CO conversion at 160 °C. All CuCeO$_X$ catalysts are rather active for the CO-PROX reaction. The CO conversion increases dramatically with increasing the reaction temperature in the range of 40–100 °C, and reaches 100% at 120 °C for all CuCeO$_X$ catalysts, and then begins to decrease slightly above 140–180 °C due to the competitive H$_2$ oxidation. The activity of CuCeO$_X$ catalysts for CO-PROX is enhanced gradually with the content of copper increasing from 3% to 9%, followed by a small decrease for CuCeO$_{12}$ catalyst. CuCeO$_5$ shows higher activity as compared with other CuCeO$_X$ catalysts, for which the CO conversion approaches 100% at 100 °C with O$_2$ selectivity of 100%. It also shows the broadest temperature “window” for complete CO conversion, from 120 °C to 180 °C. The selectivity of O$_2$ shows a contrary trend compared to CO conversion, and decreases with the increase of reaction temperature. When the reaction temperature is higher than 120 °C, the competing adsorption of H$_2$ and CO occurs in the CO PORX atmosphere [39]. Higher temperature facilitates the oxidation of H$_2$ and results in the decrease of the selectivity of oxygen to CO$_2$. The results of stabilities test over CuCeO$_5$ catalyst are shown in Figure 9C. No obvious decline was observed in the conversion of CO in 54 h, indicating that the redox feature of CuCeO$_5$ is quite stable.

According to the previous studies [38,40,41], the mechanism of CO-PROX over CuO/CeO$_2$ can be explained as follows: CO is adsorbed on the surface of highly dispersed CuO species at CuO-CeO$_2$ interfacial regions firstly and forms Cu$^+$-CO species. Cu$^+$-CO reacts with lattice oxygen nearby to produce CO$_2$ accompanied by the generation of oxygen vacancies. Simultaneously, Ce$^{3+}$ and Cu$^{2+}$ are reduced into Ce$^{4+}$ and Cu$^+$. Then, gaseous oxygen is adsorbed on the vacancies and activated to lattice oxygen species. During the process, Ce$^{3+}$ and Cu$^+$ transform into Ce$^{4+}$ and Cu$^{2+}$, respectively. Highly dispersed CuO species are the active site and CeO$_2$ acts as an oxygen supplier. Oxygen vacancy also plays an important role to provide the activated site for O$_2$. The more highly dispersed CuO species and oxygen vacancies on the surface of n-CeO$_2$ can promote the redox equilibrium...
of Ce$^{4+}$ + Cu$^+$ ↔ Ce$^{3+}$ + Cu$^{2+}$, and then enhance the CuO-CeO$_2$ interaction in CuO/CeO$_2$ catalysts. The results of structural characterization indicate that n-CeO$_2$ possesses a large surface area and large amount of oxygen vacancies, which favor the high dispersion of CuO species on the surface and the enhancement of interaction between copper species and n-CeO$_2$ supports. According to the reaction mechanism mentioned above, the high performance of CuCeO$_X$ catalysts should be related to the structural properties of n-CeO$_2$. CuCeO$_9$ possesses a higher content of active Cu$^+$ species, more Ce$^{3+}$ and oxygen vacancies, leading to the stronger interaction between highly dispersed CuO species and n-CeO$_2$, which apparently promotes the activity for CO-PROX.

Figure 9. Catalytic performance (the amount of catalyst is 100 mg, under the space velocity of 60,000 mL/(gcat·h) with a feed gas of 1.5 vol.% CO, 1.5 vol.% O$_2$, 47 vol.% H$_2$ and 50 vol.% N$_2$): CO conversion (A) and CO$_2$ selectivity (B) of n-CeO$_2$, p-CeO$_2$, CuO/p-CeO$_2$ and CuCeO$_X$ catalysts; Variation of CO conversion with time over CuCeO$_9$ at 100 °C (C).

3. Materials and Methods

3.1. Catalyst Preparation

Nanosized CeO$_2$ was synthesized by precipitation method. A total of 18.8 mmol of cerium (III) nitrate was dissolved in 20 mL distilled water, and then added dropwise to 100 mL aqueous solution containing 0.5 mol of 2-methylimidazole. The resultant suspension was stirred for about 6 h at 70 °C. After cooling to room temperature naturally, the precipitate was collected through centrifugation, washed with distilled water and ethanol several times and dried at 100 °C for 8 h. Then, the product was calcined in air at 500 °C for 4 h. The obtained sample was named as n-CeO$_2$. For the purpose of comparison, p-CeO$_2$ was prepared using NaOH solution (pH = 10) as precipitator by the same method.

The CuO-based catalysts were prepared by impregnation method. An appropriate amount of n-CeO$_2$ was impregnated with an ethanol solution of copper acetate for 24 h, followed by drying at 80 °C for 8 h. Subsequently, the resultant solids were calcined in air for 4 h at 500 °C. The nominal contents of Cu were 3 wt.%, 6 wt.%, 9 wt.% and 12 wt.%, respectively. The corresponding catalyst samples were labeled as CuCeO$_X$, where X stands for the loading of copper (wt.%). For the purpose of comparison, CuO/p-CeO$_2$ catalyst was prepared using the same method with the copper loading of 9 wt.%.

3.2. Characterization

Inductively coupled plasma optical emission spectroscopy (ICP-OES) was employed to determine the content of Cu in catalysts, which was carried out on Agilent 720. X-ray diffraction (XRD) measurements were performed on a Bruker D8 Advance instrument (Bruker, Billerica, MA, USA) with Cu Kα radiation and operated at 40 kV and 40 mA. N$_2$ adsorption-desorption isotherms were measured on Micromeritics Tristar II plus equipment (Micromeritics, Norcross, GA, USA) at −196 °C. Before the measurement, the samples were degassed at 200 °C in vacuum (0.13 Pa) for 5 h. The surface areas and pore size distribution were determined by Brunauer–Emmett–Teller ( BET) method and Barrett–Joyner–Halenda (BJH) formula, respectively. Transmission electron microscopy (TEM) observations were carried out on a Thermo Fisher Scientific Talos F200X transmission electron microscope (Thermo Fisher, Waltham, MA, USA) at 200 kV. The sample was pretreated and held on a copper grid. H$_2$ temperature-programmed reduction (H$_2$-TPR) measurements were carried
out on Micromeritics AutoChem II 2920. The 100 mg of sample was pretreated with He at 200 °C for 1 h, and then cooled to 50 °C. After that, the test was performed within the flow of 10% H₂/Ar (40 mL·min⁻¹) by heating up to 400 °C at a rate of 10 °C·min⁻¹. The X-ray photoelectron spectra (XPS) were obtained using a Thermo Fisher Scientific Escalab 250Xi spectrometer with monochromatic Al Kα radiation (1486.6 eV) as the excitation X-ray source. All binding energies (BE) were referenced to the adventitious C 1s at 284.6 eV.

UV-Raman spectra were recorded in Thermo Fisher Scientific Dxr2xi Evolution Raman spectrometer with a He-Gd laser of 325 nm excitation wavelength and a measurement range of 100–2000 cm⁻¹.

3.3. Activity Test

The catalytic activity was measured by packing 100 mg catalyst in a fixed-bed quartz micro-reactor at atmospheric pressure. The composition of reaction gas was 1.5 vol.% CO, 1.5 vol.% O₂, 50 vol.% H₂ and 47 vol.% N₂, and the space velocity was 60,000 mL/(g·cat·h). The gas composition was analyzed by an online Fuli GC-9670 gas chromatograph equipped with a thermal conductivity detector (TCD), using TDX-01 column for separating CO₂ and 13X molecular sieve column for separating O₂, N₂ and CO. The conversion of CO and the selectivity of O₂ were calculated as follows:

$$\text{CO conversion} = \left(\frac{[\text{CO}]_{\text{in}} - [\text{CO}]_{\text{out}}}{[\text{CO}]_{\text{in}}}\right) \times 100\%$$

$$\text{O}_2 \text{ selectivity} = \frac{0.5 \times ([\text{CO}]_{\text{in}} - [\text{CO}]_{\text{out}})}{[\text{O}_2]_{\text{in}} - [\text{O}_2]_{\text{out}}} \times 100\%$$

4. Conclusions

In this work, nanostructure CeO₂ (n-CeO₂) was synthesized by a facile method only using Ce(NO₃) and 2-methylimidazole as materials. For comparison, p-CeO₂ was prepared in NaOH solution by the same method. As compared with p-CeO₂, n-CeO₂ as prepared exhibits a higher surface area of 130 m²·g⁻¹ and possesses more surface defects, which must be associated with the role of 2-methylimidazole in the formation of n-CeO₂. The soluble Ce³⁺ was oxidized by O₂ to form a hydrated Ce⁴⁺ formulated Ce(H₂O)ₓ(OH)ₙ(4−x)⁺. 2-methylimidazole can act as a template agent in this process to prevent the aggregation of Ce(H₂O)ₓ(OH)ₙ(4−x)⁺ effectively, and was also used as a reducer to obtain Ce³⁺ from Ce⁴⁺. Using n-CeO₂ as supports, a series of CuO-based catalysts (CuCeOₓ) with different copper loading were prepared and tested for CO-PROX system. The increase of copper loading has no obvious effect on the structural properties of CuCeOₓ catalysts. All CuCeOₓ catalysts exhibit a large surface area, which leads to a high dispersion of CuO species on the surface of catalysts. More oxygen vacancies on CuCeOₓ induced by intrinsic surface defects on n-CeO₂ are in favor of the interaction between the highly dispersed CuO and n-CeO₂. These may be the main reasons for their high activity for CO-PROX reaction. CuO/p-CeO₂ catalyst was prepared with the copper loading of 9 wt.% for comparison. The smaller surface area of p-CeO₂ increases the aggregation of copper species to form large CuO clusters and bulk CuO which contribute less to the catalytic activity. The lower oxygen vacancy density on p-CeO₂ reduces the oxygen mobility. Thus, CuO/p-CeO₂ shows a lower CO conversion compared to CuCeOₓ catalysts. The activity of CuCeOₓ catalysts for CO-PROX follows the order: CuCeO₉ > CuCeO₆ > CuCeO₃ > CuCeO₁₂, which is consistent with the amount of Ce³⁺ species, Cu⁺ species and oxygen vacancies on the catalysts. CuCeO₉ exhibits the highest catalytic performance. The copper species on CuCeO₉ are more readily reducible due to the stronger interaction between the highly dispersed copper species and n-CeO₂.
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