IMPROVEMENT OF PREFERENTIAL CO OXIDATION ACTIVITY OVER CUO/COO\textsubscript{2}-CEO\textsubscript{2} CATALYSTS: EFFECT OF CO/CE RATIO

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ABSTRACT

A series of Co\textsubscript{2}O\textsubscript{3}-CeO\textsubscript{2} supports with different Co/Ce ratio have been synthesized by using polyethylene glycol (PEG) as a surfactant. The catalytic performance tests indicated the activity of the catalysts is better than the corresponding support. In addition, CuO/(0.7)Co\textsubscript{2}O\textsubscript{3}-CeO\textsubscript{2} displayed the best activity with 100% CO conversion and 93% O\textsubscript{2} selectivity at 120 °C. Furthermore, the stability test of CuO/(0.7)Co\textsubscript{2}O\textsubscript{3}-CeO\textsubscript{2} expressed the activity can be retained at 80% for 80 h at 100 °C. Catalysts and supports were characterized by BET, XRD, TPR and TPD techniques. Discussion of the results showed that the strongest lattice distortion and the best reducibility of Co O\textsubscript{2}-CeO\textsubscript{2} supports were both negative factors for the catalytic activity. More precisely, an appropriate Co/Ce ratio can restrain the stronger interaction between cobalt oxide and ceria to promote the formation of reducible copper species.

Keywords: Co/Ce ratio, CuO/Co\textsubscript{2}O\textsubscript{3}-CeO\textsubscript{2}, H\textsubscript{2}-rich gases, Preferential oxidation of CO.

INTRODUCTION

Proton-exchange membrane fuel cells (PEMFCs) have been extensively studied recently as a new power generation. Unfortunately, trace amount of CO in the hydrogen can poison the Pt-anode of PEMFC. To allow the PEMFC to perform optimally, the CO concentration should be lowered to a sub-ppm level before feeding (less than 100 ppm for CO-tolerant anode and 10 ppm for Pt anode). To date, several methods have been used for the CO removal, which included purification with metal membrane, preferential CO oxidation (CO-PROX), and CO methanation. Among these methods, CO-PROX is considered to be the most promising and economic one to remove the CO. Developing satisfactory CO-PROX catalysts has received tremendous interest and impressive progress has been achieved.

The noble metal catalysts (such as Pt, Au, etc.) have been found the most effective for CO-PROX. Nevertheless, the poor selectivity and high cost greatly limit their applications. Thus, non-precious metal-based CO-PROX catalysts have been developed rapidly. The copper oxide-based catalyst has been proposed as a promising catalyst for CO-PROX, owing to its low cost and high catalytic performance comparable to the noble metal catalyst. Generally, the optimum catalytic activity for CO-PROX over copper oxide-based catalysts can be achieved by creating easily reducible copper oxides. Many studies show that the redox property of copper oxide strongly depends on the natural properties of the supports, meaning that modifying the properties of supports may promote the formation of easily reducible copper oxides.

In previous reports, the CeO\textsubscript{2}-related supports have been extensively investigated due to their excellent oxygen storage capability. It is reported that support effect plays a significant role in enhancing catalytic properties by improving the dispersion of the active component or via strong interaction with the active sites. As a kind of CeO\textsubscript{2}-related support, CeO\textsubscript{2} mixed with other metal oxides (CeMO\textsubscript{x}) substances were widely used for supporting the copper oxide. The natural properties of CeMO\textsubscript{x} are related to the metal species, the ratio of Ce/M and the preparation method. Many metals have been introduced into CeMO\textsubscript{x}, such as Zr, Mn, Fe, Co, etc. In this work, we focused on the Co, because the CoO\textsubscript{2} exhibited a good CO oxidation activity and can inhibit the formation of surface carbonates. Moreover, the CuO/CoO\textsubscript{2}-CeO\textsubscript{2} catalysts are still less developed. Herein, by using PEG as surfactant, we synthesized a series of CoO\textsubscript{2}-CeO\textsubscript{2} supports with different Co/Ce ratio. CuO/CoO\textsubscript{2}-CeO\textsubscript{2} catalysts exhibited the expected excellent catalytic activities. Furthermore, the natural properties of CoO\textsubscript{2}-CeO\textsubscript{2} supports were characterized by N\textsubscript{2} adsorption/desorption, XRD, TPR and TPD, and the relationship between natural properties of composite oxide supports and reducibility of copper oxide was investigated.

EXPERIMENTAL DETAILS

Catalysts preparation

Pure CeO\textsubscript{2}, CoO\textsubscript{2} and CoO\textsubscript{2}-CeO\textsubscript{2} composite oxide supports were prepared by templating-precipitation method. The appropriate quantities of sodium hydroxide solution (0.5 mol/L) were added drop wise into a mixture solution of PEG (4 g/L), (NH\textsubscript{4})\textsubscript{2}Ce(NO\textsubscript{3})\textsubscript{6} and Co(NO\textsubscript{3})\textsubscript{6}·6H\textsubscript{2}O with a suitable molar ratio (Co/(Co + Ce) = 0.1~0.9), and then continue adding until pH of solution remained approximately at 10.0 under vigorous stirring. The mixture was stirred for 4 h, filtered and washed with deionized water. Obtained samples were dried at 100 °C overnight and then calcined at 500 °C for 4 h under air. All Cu-based catalysts were prepared through impregnation method. The supports were impregnated with an ethanol solution of copper nitrate for 24 h, followed by drying (100 °C, 12 h) and calcining (400 °C, 4 h).

CoO\textsubscript{2}-CeO\textsubscript{2} composite oxide was named as (x)CoO\textsubscript{2}-CeO\textsubscript{2} and the nominal value of Co/(Co + Ce) atomic ratio (x) represented for the Co content is 0.1, 0.3, 0.5, 0.7, 0.9, respectively. Based on our previous studies, the catalysts with 5.0 wt.% of CuO loading showed the best catalytic performance, therefore the CuO loading was maintained at this level and the catalysts were expressed as CuO/(x)CoO\textsubscript{2}-CeO\textsubscript{2}.

Catalyst characterization

N\textsubscript{2} adsorption isotherms of the samples were performed at -196 °C using an ASAP2020 analyzer (Micrometrics). BET analysis was used to determine the surface area and the average pore size was calculated by using the BJH formula from the desorption branch of the N\textsubscript{2} adsorption isotherm. Before each measurement, the samples were degassed at 200 °C in vacuum (0.13 Pa) for 5 h.

The crystalline structure of the solids was studied by Powder X-ray diffraction (PXRD) using a Brucker D8 diffractometer (operating at 40 kV and 30 mA) equipped with a Cu K\alpha radiation source. Diffraction intensity was measured in the 2θ ranges between 10 ° and 80 °, with a 2θ step of 0.02 ° for 8 s/point.

The surface atomic ratios of Co and Ce on the samples and the morphology change by the addition of Cobalt were measured by energy dispersive spectroscopy (EDS, Oxford instruments) attached to a scanning electron microscope (SEM, Quantam 200).

H\textsubscript{2}-TPR measurements were carried out on a Chemisorb 2750 instrument (Micrometrics). A 20 mg sample was pre-treated from room temperature to 300 °C under a helium flow (40 ml/min) at a rate of 10 °C/min for 1 h and then cooled down to room temperature. After this, the sample was heated to 600 °C at a rate of 10 °C/min under a flow of 5 vol.% H\textsubscript{2}/N\textsubscript{2} for recording the TPR spectra. The amount of H\textsubscript{2} uptake during the reduction was measured by a thermal conductivity detector (TCD). For H\textsubscript{2} consumption quantification, CuO (99.99%) was used as the calibration standard sample. In detail, 5, 10, 15, 20 and 25 mg CuO were employed to do H\textsubscript{2} under the same condition to achieve a plot of H\textsubscript{2} consumption amounts versus TCD integration areas, based on the following reaction equation:

\[
\text{CuO} + \text{H}_2 = \text{Cu} + \text{H}_2\text{O}
\]

The achieved plot was then used to quantify the H\textsubscript{2} consumption of CuO/CoO\textsubscript{2}-CeO\textsubscript{2} samples.
CO-TPD measurements were carried out on the same instrument with the H$_2$-TPR measurements. A 20 mg sample was pre-treated from room temperature to 300 °C under a helium flow (40 ml/min) at a rate of 10 °C/min for 1 h and then cooled down to room temperature. After this, CO was injected into the reactor until being saturated with CO. Then the samples were heated to 400 °C under a helium flow (50 ml/min) at a rate of 10 °C/min for recording the CO-TPD spectra.

**Catalytic performance tests**

The CO oxidation reaction in H$_2$-rich gases was carried out with a flow reactor. In a typical run, steady-state catalytic activity was measured at each temperature with the reaction temperature raised from 60 to 260 °C in steps of 20 °C and 0.1 g catalyst was used. The space velocity was 18,000 ml/g min and the feed gas composition was 1 vol.% CO, 1.65 vol.% O$_2$, 50 vol.% H$_2$, and balanced in N$_2$ and was controlled with mass flow controllers. Excess O$_2$ was used to compare the activity of each catalyst distinctly. Product and reactant analysis were carried out by gas chromatography on-line equipped with a thermal conductor detector (TCD). Two columns were used in parallel: a molecular sieve (5A) column to quantify H$_2$, O$_2$, and CO and a carbon molecular sieve (TDX-01) column to quantify CO$_2$. No methane was detected under our experimental conditions. The CO conversion and selectivity are calculated as follows:

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

\[
\text{O}_2 \text{ selectivity (\%)} = \frac{0.5 (\text{CO}_{\text{in}} - \text{CO}_{\text{out}})}{(\text{O}_{2\text{in}} - \text{O}_{2\text{out}})} \times 100
\]

**RESULTS AND DISCUSSION**

The catalytic activity and selectivity over the CuO/CeO$_2$-CoO$_3$ composite oxides are much less O$_2$ selective to CO oxidation compared with the corresponding CuO/CeO$_2$ catalysts. The best result is attained over (0.5)Co$_3$O$_4$-CeO$_2$ for a CO conversion of 100% at 140 °C. There is a hypothesis that the catalytic activity can be regulated by properly modulating the Co/Ce ratio. Further, these results indicated that Co$_3$O$_4$-CeO$_2$ composite oxides might be good supports for CO-PROX reaction.

![Fig. 1](image1) Conversion profiles (a) and O$_2$ selectivity profiles (b) for CO oxidation over the CuO/CeO$_2$-CoO$_3$ catalysts: ■ CuO/CeO$_2$; ○ CuO/(0.1)Co$_3$O$_4$-CeO$_2$; ▲ CuO/(0.3)Co$_3$O$_4$-CeO$_2$; ◄ CuO/(0.5)Co$_3$O$_4$-CeO$_2$; ▶ CuO/(0.7)Co$_3$O$_4$-CeO$_2$; □ CuO/(0.9)Co$_3$O$_4$-CeO$_2$; ● Co$_3$O$_4$.

Fig. 1 shows the CO conversion and O$_2$ selectivity of Co$_3$O$_4$-CeO$_2$ composite oxides. We investigated the catalytic activity of Co$_3$O$_4$-CeO$_2$ composite oxides here in order to evaluate the effect of cobalt activity without copper active species. Similar to the previous reports $^{21-23}$, Co$_3$O$_4$ exhibited a certain activity for CO-PROX (100% CO conversion at 240 °C) while the CeO$_2$ displayed a disillusionary performance. The CO conversion increases with an increase of the Co/(Co+Ce) atomic ratios from 0.1 to 0.5, whereas after that the catalytic phenomenon is obtained oppositely along with a further increase of Co amounts. The best result is attained over (0.5)Co$_3$O$_4$-CeO$_2$ for a CO conversion of 100% at 140 °C. There is a hypothesis that the catalytic activity can be regulated by properly modulating the Co/Ce ratio. Further, these results indicated that Co$_3$O$_4$-CeO$_2$ composite oxides might be good supports for CO-PROX reaction.

![Fig. 2](image2) Conversion profiles (a) and O$_2$ selectivity profiles (b) for CO oxidation over the CuO/CeO$_2$-CoO$_3$ catalysts: ■ CuO/CeO$_2$; ○ CuO/(0.1)Co$_3$O$_4$-CeO$_2$; ▲ CuO/(0.3)Co$_3$O$_4$-CeO$_2$; ◄ CuO/(0.5)Co$_3$O$_4$-CeO$_2$; ▶ CuO/(0.7)Co$_3$O$_4$-CeO$_2$; □ CuO/(0.9)Co$_3$O$_4$-CeO$_2$; ● Co$_3$O$_4$.

Fig. 2 Conversion profiles (a) and O$_2$ selectivity profiles (b) for CO oxidation over the CuO/CeO$_2$-CoO$_3$ catalysts: ■ CuO/CeO$_2$; ○ CuO/(0.1)Co$_3$O$_4$-CeO$_2$; ▲ CuO/(0.3)Co$_3$O$_4$-CeO$_2$; ◄ CuO/(0.5)Co$_3$O$_4$-CeO$_2$; ▶ CuO/(0.7)Co$_3$O$_4$-CeO$_2$; □ CuO/(0.9)Co$_3$O$_4$-CeO$_2$; ● Co$_3$O$_4$.

The catalytic activity and selectivity over the series of CuO/CeO$_2$-CoO$_3$ catalysts as a function of the reaction temperature are depicted in Fig. 2. Obviously, the catalytic activities of CuO/CeO$_2$-CoO$_3$ catalysts are improved markedly when compared with the corresponding supports, indicating that copper is the main active species. The performance of catalysts formed a volcano curve with different atomic ratio. And the CuO/(0.7)Co$_3$O$_4$-CeO$_2$ catalyst possessed the best catalytic activity with 100% CO conversion and 93% O$_2$ selectivity at 120 °C. Moreover, it exhibited a broad temperature window of 100% CO conversion in the range from 120 °C to 240 °C. The Co$_3$O$_4$-CeO$_2$ composite oxides are much less O$_2$ selective to CO oxidation in the reactant gas mixture and even the (0.5)Co$_3$O$_4$-CeO$_2$ is unable to reach 100% CO selectivity during the reactant temperature. Meanwhile, all catalysts showed superior performance and almost every catalyst able to reach 100% CO selectivity during the reactant temperature. It is noteworthy that no methane formation here could be detected under our experimental conditions even when...
the temperature reached 240 °C, suggesting that the methanation could be suppressed in the catalysts.

The long-term stability of CuO/(0.7)CoO-CeO was also examined. As shown in Fig.3, the 80% CO conversion and 90% O2 selectivity of CuO/(0.7)CoO-CeO catalyst still maintained after 80 h, suggesting its excellent long-term stability. In order to further understand the relationship between the atomic ratio of Co/(Co+Ce) and the origin of high catalytic activity, N2 adsorption/desorption, PXRD, TPR, CO-TPD, and EDS characterizations were performed for all samples.

![Graph showing CO conversion and O2 selectivity over CuO/(0.7)CoO-CeO catalyst](image)

**Fig. 3** Effect of the time on stream on CO conversion (●) and O2 selectivity (■) for CO PROX reactions over CuO/(0.7)CoO-CeO catalyst (at 100 °C of reaction temperature). Reaction conditions: GHSV = 18,000 ml/h•gcat, 1 vol.% CO, 1.65 vol.% O2, 50 vol.% H2 and balanced in N2.

**Content determination**

Content determinations by ICP and EDS measurements are enumerated in Table 1 and Fig. S1 (Supporting information). As listed, CuO particles were well dispersed in all samples and the content was constant. Surface cobalt content increased with the ratio and the average surface Co content was similar with total actual value. All of the EDS curves of random three particles were well matched, which indicated that the metal oxide species were highly dispersed on the surface. Based on the highest performance of CuO/(0.7) CoO-CeO catalyst, it can be concluded that neither the surface content nor the capacity of cobalt is the major factor for catalytic performance.

**Table 1** Content determination of catalysts.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Content of Cu</th>
<th>Co/(Co+Ce) atomic ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>S[a] w%</td>
<td>T[b] w%</td>
</tr>
<tr>
<td>CuO/(0.1)CoO-CeO</td>
<td>3.67</td>
<td>5.02</td>
</tr>
<tr>
<td>CuO/(0.3)CoO-CeO</td>
<td>3.60</td>
<td>5.05</td>
</tr>
<tr>
<td>CuO/(0.5)CoO-CeO</td>
<td>3.81</td>
<td>5.05</td>
</tr>
<tr>
<td>CuO/(0.7)CoO-CeO</td>
<td>3.67</td>
<td>4.97</td>
</tr>
<tr>
<td>CuO/(0.9)CoO-CeO</td>
<td>3.78</td>
<td>4.98</td>
</tr>
</tbody>
</table>

[a] Surface atomic ratio (w%) and weight ratio (At%) by EDS analysis. [b] Total atomic ratio (w%) and weight ratio (At%) by ICP analysis

**Structural properties of samples**

Fig. 4a compiles the XRD patterns of CoO-CeO supports with different atomic ratios. All of the samples present the characteristic peaks of fluorite structure of the CeO2 and spinel structure of the CoO2. The (0.1)CoO-CeO, (0.3)CoO-CeO, and (0.5)CoO-CeO supports mainly displayed the fluorite phases of CeO2, while the spinel phases of CoO2 were appeared mainly in (0.7) CoO-CeO and (0.9)CoO-CeO samples. Compared with the pure phases, these peaks became broader, and this indicated that the crystalite sizes of CeO2 and CoO2 were reduced in the composite oxides. The 2θ values of CeO2 (111) and CoO2 (311) diffraction are listed in Table 2. Compared with the corresponding pure phases, the diffraction peaks of CeO2 (111) slightly shift to higher 2θ value and CoO2 (311) shift to lower, which is accordance with the ionic radii of Ce3+ (0.970 nm) being larger than that of Co3+ (0.872 nm) and Ce2+ (0.658 nm). This reveals that the Ce and Co ions enter in the oxide lattices of each other. It is noteworthy that the distortion of oxide lattices is more and more obvious with the increase of Co/(Co+Ce) ratio until (0.7)CoO2-CeO2, which indicated that the interaction between CeO2 and CoO2 was existed factually and could be modified by modulating Co/ Ce atomic ratio.

![X-ray diffraction patterns of CeO2-CeO2 composite oxide (a) and CuO/CeO2-CeO2 catalysts (b): fluorite CeO2 (●) and spinel CeO2 ( ■).](image)

**Fig. 4** X-ray diffraction patterns of CeO2-CeO2 composite oxide (a) and CuO/CeO2-CeO2 catalysts (b): fluorite CeO2 (●) and spinel CeO2 ( ■).

XRD patterns of CuO/(0.4)CoO-CeO catalysts are shown in Fig. 4b and the crystallite size and 2θ values of CeO2 (111) and CoO2 (311) diffraction are also listed in Table 2. As revealed by the XRD patterns, no diffraction peaks of CuO species are observed in any studied samples, implying that the Cu ions may enter in the oxide lattices or well dispersed on composite oxides26-27. Further inspection of the XRD patterns displayed that the little shifts of CeO2 (111) and CoO2 (311) diffraction for CuO/CoO and CuO/CoO2 can be attributed to the incorporation of Cu into the CeO2 and CoO2 lattices. And the CuO/CoO2-CeO2 showed similar XRD patterns with corresponding CoO2-CeO2 supports. It suggests that the CuO might well disperse on the CoO2-CeO2 supports, which facilitates the CO-PROX.
Table 2 Physicochemical properties of CeO$_2$–Co$_3$O$_4$ composite oxides and CuO/Co$_3$O$_4$–CeO$_2$ catalysts.

<table>
<thead>
<tr>
<th>Samples</th>
<th>BET (m$^2$·g$^{-1}$)</th>
<th>Average pore volume (cm$^3$·g$^{-1}$)</th>
<th>Average pore diameter (nm)</th>
<th>CeO$_2$ (111) Crystallite size (nm)$^\text{[a]}$</th>
<th>Co$_3$O$_4$ (311) Crystallite size (nm)$^\text{[a]}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeO$_2$</td>
<td>139.6</td>
<td>0.14</td>
<td>3.4</td>
<td>28.42</td>
<td>7.8</td>
</tr>
<tr>
<td>(0.1)Co$_3$O$_4$–CeO$_2$</td>
<td>115.3</td>
<td>0.12</td>
<td>4.3</td>
<td>28.56</td>
<td>3.7</td>
</tr>
<tr>
<td>(0.3)Co$_3$O$_4$–CeO$_2$</td>
<td>190.4</td>
<td>0.16</td>
<td>3.4</td>
<td>28.61</td>
<td>3.7</td>
</tr>
<tr>
<td>(0.5)Co$_3$O$_4$–CeO$_2$</td>
<td>176.4</td>
<td>0.43</td>
<td>9.7</td>
<td>28.61</td>
<td>3.7</td>
</tr>
<tr>
<td>(0.7)Co$_3$O$_4$–CeO$_2$</td>
<td>95.0</td>
<td>0.20</td>
<td>10.1</td>
<td>28.59</td>
<td>3.8</td>
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<tr>
<td>(0.9)Co$_3$O$_4$–CeO$_2$</td>
<td>77.9</td>
<td>0.12</td>
<td>5.2</td>
<td>NA$^\text{[b]}$</td>
<td>NA$^\text{[b]}$</td>
</tr>
<tr>
<td>Co$_3$O$_4$</td>
<td>29.2</td>
<td>0.098</td>
<td>13.4</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>CuO/Co$_3$O$_4$</td>
<td>112.3</td>
<td>0.17</td>
<td>6.1</td>
<td>28.53</td>
<td>7.1</td>
</tr>
<tr>
<td>CuO/(0.1)Co$_3$O$_4$–CeO$_2$</td>
<td>100.6</td>
<td>0.12</td>
<td>4.7</td>
<td>28.56</td>
<td>3.7</td>
</tr>
<tr>
<td>CuO/(0.3)Co$_3$O$_4$–CeO$_2$</td>
<td>168.1</td>
<td>0.16</td>
<td>3.7</td>
<td>28.61</td>
<td>3.7</td>
</tr>
<tr>
<td>CuO/(0.5)Co$_3$O$_4$–CeO$_2$</td>
<td>136.0</td>
<td>0.36</td>
<td>10.6</td>
<td>28.63</td>
<td>3.8</td>
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<tr>
<td>CuO/(0.7)Co$_3$O$_4$–CeO$_2$</td>
<td>119.3</td>
<td>0.33</td>
<td>11.2</td>
<td>28.57</td>
<td>3.8</td>
</tr>
<tr>
<td>CuO/(0.9)Co$_3$O$_4$–CeO$_2$</td>
<td>106.8</td>
<td>0.15</td>
<td>5.6</td>
<td>NA$^\text{[b]}$</td>
<td>NA$^\text{[b]}$</td>
</tr>
<tr>
<td>CuO/Co$_3$O$_4$</td>
<td>25.0</td>
<td>0.076</td>
<td>12.1</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

[a] Estimated from CeO$_2$ (111) and Co$_3$O$_4$ (311) face by Scherrer equation.
[b] Not available due to weak XRD peaks.

**Fig. 5** N$_2$ adsorption/desorption isotherm (a) and pore size distribution (b) of CuO/Co$_3$O$_4$–CeO$_2$ catalysts.

Fig. 5 and Fig. S2 (Supporting information) demonstrate the N$_2$ adsorption/desorption isotherms and pore size distributions of CuO/Co$_3$O$_4$–CeO$_2$ samples. The CuO/Co$_3$O$_4$–CeO$_2$ samples showed similar N$_2$ adsorption/desorption isotherms and pore size distributions with the corresponding supports. Thus, the CuO/Co$_3$O$_4$–CeO$_2$ samples were taken as the examples to describe the results of the CuO/Co$_3$O$_4$–CeO$_2$ samples. The CuO/Co$_3$O$_4$–CeO$_2$ samples exhibited type-IV isotherms, indicating the existence of mesopores in the samples. The pore volumes of (0.5)Co$_3$O$_4$–CeO$_2$ and (0.7)Co$_3$O$_4$–CeO$_2$ are larger than that of other samples. In addition, both of them displayed broader pore size distributions than other samples. The larger pore volume and broader pore size distribution are in favour of CO-PROX. The surface area and crystallite size calculated by Scherrer equation are summarized in Table 2. The BET surface area increased along with an increase of atomic ratio in the first instance and the CuO/(0.3)Co$_3$O$_4$–CeO$_2$ catalyst gave the highest surface area among all catalysts, while after that a further increase of the atomic ratio resulted in a decrease of the surface area. However, the CuO/(0.3)Co$_3$O$_4$–CeO$_2$ catalyst didn’t show the best performance, indicating that the performance of catalysts was not directly related to the BET surface. The crystallite sizes of CeO$_2$ and Co$_3$O$_4$ in the composite oxide are smaller than those in their pure phases (7.1 nm for CeO$_2$ and 19.6 nm for Co$_3$O$_4$), suggesting that the formation of Co$_3$O$_4$–CeO$_2$ composite oxide was helpful to prevent the sintering of Co$_3$O$_4$ and CeO$_2$.
The reduction performance of supports and catalysts

Table 3 $H_2$ consumption amount and reduction temperature of CuO/Co$_3$O$_4$–CeO$_2$ catalysts.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>$\alpha$ peak</th>
<th>$\beta$ peak</th>
<th>$\gamma$ peak</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$H_2$ cons (µmol·g$^{-1}$)</td>
<td>Peak temp ($^\circ$C)</td>
<td>$H_2$ cons (µmol·g$^{-1}$)</td>
</tr>
<tr>
<td>CuO/Co$_3$O$_4$</td>
<td>810</td>
<td>202</td>
<td>595</td>
</tr>
<tr>
<td>CuO/(0.1)Co$_3$O$_4$–CeO$_2$</td>
<td>690</td>
<td>201</td>
<td>534</td>
</tr>
<tr>
<td>CuO/(0.3)Co$_3$O$_4$–CeO$_2$</td>
<td>884</td>
<td>209</td>
<td>1042</td>
</tr>
<tr>
<td>CuO/(0.5)Co$_3$O$_4$–CeO$_2$</td>
<td>1302</td>
<td>211</td>
<td>782</td>
</tr>
<tr>
<td>CuO/(0.7)Co$_3$O$_4$–CeO$_2$</td>
<td>412</td>
<td>162</td>
<td>864</td>
</tr>
<tr>
<td>CuO/(0.9)Co$_3$O$_4$–CeO$_2$</td>
<td>333</td>
<td>201</td>
<td>1169</td>
</tr>
<tr>
<td>CuO/Co$_3$O$_4$</td>
<td>225</td>
<td>212</td>
<td>852</td>
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</tbody>
</table>

TPR profiles of the Co$_3$O$_4$–CeO$_2$ supports (shown in Fig. 6a) indicated that the reduction behavior of composite oxides is affected strongly by the Co/Ce ratio. Pure CeO$_2$ hardly can be reduced during the examined temperature range, while the pure Co$_3$O$_4$ exhibits two reduction peaks $\gamma_1$ and $\gamma_2$, which can be assigned to the step-wise reduction via Co$_3$O$_4$ to CoO and CoO to Co$^{2+}$, respectively. And the ratio of the peak area of $\gamma_1$ to $\gamma_2$ is close to the ratio of two-step theoretical reduction of Co$_3$O$_4$ (1:3.07). For the Co$_3$O$_4$–CeO$_2$ composite supports, $\zeta$ reduction peak appears, which might be attributed to the reduction of Co$^{2+}$ interacting with ceria or the reduction of surface oxygen species of ceria accompanying with Ce$^{4+}$ to Ce$^{3+}$ reduction. Before increasing the ratio to 0.5, the reductive peaks shift to the lower temperature range. When further increasing the ratio, the temperature shift higher instead. And the $\zeta$ peak overlaps with $\gamma_2$. These changes in the reducibility might be caused by the change of interaction between Co$_3$O$_4$ and CeO$_2$, which is in agreement with the XRD analysis. Among the Co$_3$O$_4$–CeO$_2$ supports, the (0.5)Co$_3$O$_4$–CeO$_2$ exhibits the best reduction property, which result in its highest CO removal activity.

Fig. 6 $H_2$-TPR profiles of CeO$_2$–Co$_3$O$_4$ composite oxides (a) and CuO/CeO$_2$–Co$_3$O$_4$ catalysts (b).

The $H_2$-TPR profiles of CuO/Co$_3$O$_4$–CeO$_2$ catalysts are depicted in Fig. 6b and Table 3. Obviously, three ($\alpha$, $\beta$ and $\gamma$) peaks can be observed. Peaks of $\alpha$ and $\beta$ are attributed to the reduction of the CuO species, $\alpha$ peak corresponds to the reduction of highly dispersed CuO particles which have strong interaction with CeO$_2$–Co$_3$O$_4$ composite oxides, while $\beta$ peak corresponds to bulk CuO and partial CeO$_2$.$^{10-12}$ And $\gamma$ peak can be assigned to the reduction of supports. In the present work, copper is totally reduced in all catalysts according to the amounts of hydrogen consumed and the reduction peaks are more and more difficult to be distinct due to the overlap of individual in the high Co content. With increasing of Co/Ce ratio, the reduction temperatures of $\alpha$ and $\beta$ are becoming lower and the area becomes larger until CuO/(0.7)Co$_3$O$_4$–CeO$_2$ catalyst. However, the reduction temperature of $\gamma$ peak shifts higher and the area becomes larger. This should be due to the enhancement of the Co content. CuO/(0.7)Co$_3$O$_4$–CeO$_2$ catalyst exhibits the lowest reduction temperature of CuO species and the largest total hydrogen consumption. The easily reducible copper oxide and abundant of easily reduced supports are highly active sites for CO-PROX, which can explain the best catalytic performance of CuO/(0.7)Co$_3$O$_4$–CeO$_2$. As revealed by XRD and TPR analysis results of Co$_3$O$_4$–CeO$_2$.
supports, the distortion of oxide lattices was more and more obvious with the increase of Co/Ce ratio except for (0.7)CoO₂CeO₂, and the (0.5)CoO₂CeO₂ showed the best reducibility. This suggested that the strongest lattice distortion and the best reducibility of supports were not benefit to create easily reducible copper oxides. It is contrary to commonly believed idea that easily reducible supports can promote the copper oxide-based catalyst activity for CO-PROX. To learn more about the reducible copper oxide in CuO/(0.7)CoO₂CeO₂, we further inspected the natural properties of (0.7)CoO₂CeO₂ support. It revealed that (0.7)CoO₂CeO₂ support exhibited relative small crystallite size, large pore volume and broad pore size distribution, which might be helpful to form the copper oxide easily to be reduced.

**CO adsorption property of the catalysts**

CO-TPD curves of CoO₂CeO₂ supports and CuOCoO₂CeO₂ catalysts are given in Fig. 7. The TPD spectra of the CoO₂CeO₂ composite oxides consisted of two broad overlap peaks: the first peak appeared in the temperature range from 30 to 100 °C, and the second one existed in the range from 150 to 300 °C. According to literature, the peak occurred at 100 °C was due to CO desorption, and the one observed in the temperature range from 200 to 500 °C was due to CO₂ desorption, which likely formed by the decomposition of the surface carbonates that have resulted from CO adsorption. The CO₂ desorption peak might be lower owing to the formation of new CO adsorption and oxidation sites involving copper oxides (CuO) and cobalt oxides (CoO). It is interesting that the lower peaks shifted to lower temperature with the increase of CoO₂ loadings, while the highest temperature peak shifted to higher temperature after the Co/(Co + Ce) is 0.5. The TPD profiles of (0.1)CoO₂CeO₂, (0.3)CoO₂CeO₂, and (0.5)CoO₂CeO₂ oxides differed significantly from the spectra of (0.5)CoO₂CeO₂ and (0.9)CoO₂CeO₂ samples in the intensity of two peaks. Thus, only a proper Co/(Co+Ce) atomic ratio in the system would form Co–Ce–O clusters in the surface which was active to CO adsorption and oxidation. It is indicated that the atomic ratio of Co/(Co+Ce) in CoO₂CeO₂ composite oxides impacted the quantity and strength of CO desorption.

All CuOCoO₂CeO₂ catalysts showed two CO desorption peaks. In contrast, the introduction of Cu species made desorption peaks shift to lower temperature, thus indicating the stronger absorbed of CO in ternary catalysts than CuOCoO₂CeO₂, CuOCoO₂CeO₂, and CoO₂CeO₂ oxides. The interaction was more positive to the reaction. The areas of these peaks give an interesting interaction of the ternary system, which could promote the formation of active sites involving copper oxides (CuO) and cobalt oxides (CoO). The two peak ratios except for (0.7)CoO₂CeO₂ catalyst are given in Fig. 7.

Employing the templating technique, a series of CoO₂CeO₂ samples were synthesized by modulating the Co/Ce ratio and used for supporting copper oxide. These samples were applied for the CO-PROX. As expected, CuOCoO₂CeO₂ catalysts exhibited a better CO-PROX activity than the corresponding supports. Among these samples, the CuO/(0.7)CoO₂CeO₂ displayed the best activity with 100% CO conversion and 93% O₂ selectivity at 120 °C, and the excellent activity was still maintained after reaction for 80 h. The inspection of CuOCoO₂CeO₂ and CoO₂CeO₂ samples revealed that the strongest lattice distortion and the best reducibility of CoO₂CeO₂ supports were not favorable to create easily reducible copper oxides. And the formation of easily reducible copper oxides may relate to the crystallite size, large pore volume and broad pore size distribution of supports. It should be expressed that an appropriate Co/Ce ratio of the supports could restrain the strongest interaction of the ternary system, which could promote the formation of active species. Further research concerning this subject is proceeding.

**CONCLUSION**

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REFERENCES