IMPROVEMENT OF PREFERENTIAL CO OXIDATION ACTIVITY OVER $\text{CuO}/\text{Co}_3\text{O}_4\text{-CeO}_2$ CATALYSTS: EFFECT OF CO/CE RATIO

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ABSTRACT

A series of $\text{Co}_3\text{O}_4\text{-CeO}_2$ supports with different Co/Ce ratio have been synthesized by using polyethyleneglycol (PEG) as a surfactant. The catalytic performance tests indicated the activity of the catalysts is better than the corresponding support. In addition, $\text{CuO}/(0.7)\text{Co}_3\text{O}_4\text{-CeO}_2$ displayed the best activity with 100% CO conversion and 93% O_2 selectivity at 120 °C. Furthermore, the stability test of $\text{CuO}/(0.7)\text{Co}_3\text{O}_4\text{-CeO}_2$ expressed the activity can be retained at 80% for 80h 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 $\text{Co}_3\text{O}_4\text{-CeO}_2$ 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, $\text{CuO}/\text{Co}_3\text{O}_4\text{-CeO}_2$, H_2 -rich gases, Preferential oxidation of CO.

INTRODUCTION

Proton-exchange membrane fuel cells (PEMFCs) have been extensively studied recently as a new power generation ¹. 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) ^{2,3}. 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 ⁴. Developing satisfactory CO-PROX catalysts has received tremendous interest and impressive progress has been achieved ⁵⁻⁷.

The noble metal catalysts (such as Pt, Au, etc.) have been found the most effectual for CO-PROX ⁸⁻¹¹. 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 ¹²⁻¹⁵, 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 ^{12,14}, meaning that modifying the properties of supports may promote the formation of easily reducible copper oxides.

In previous reports, the CeO_2 -related supports have been extensively investigated due to their excellent oxygen storage capability ³. 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 ¹⁶. As a kind of CeO_2 -related support, CeO_2 mixed with other metal oxides (CeMO_x) substances were widely used for supporting the copper oxide. The natural properties of CeMO_x are related to the metal species, the ratio of Ce/M and the preparation method. Many metals have been introduced into CeMO_x , such as Zr, Mn, Fe, Co ¹⁷⁻²⁰. In this work, we focused on the Co, because the CoO_x exhibited a good CO oxidation activity and can inhibit the formation of surface carbonates. Moreover, the $\text{CuO}/\text{Co}_3\text{O}_4\text{-CeO}_2$ catalysts are still less developed. Herein, by using PEG as surfactant, we synthesized a series of $\text{Co}_3\text{O}_4\text{-CeO}_2$ supports with different Co/Ce ratio. $\text{CuO}/\text{Co}_3\text{O}_4\text{-CeO}_2$ catalysts exhibited the expected excellent catalytic activities. Furthermore, the natural properties of $\text{Co}_3\text{O}_4\text{-CeO}_2$ supports were characterized by N_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_2 , Co_3O_4 and $\text{Co}_3\text{O}_4\text{-CeO}_2$ 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), $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ with a suitable molar ratio ($\text{Co}/(\text{Co} + \text{Ce}) = 0.1\sim 0.9$), 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. And 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).

$\text{Co}_3\text{O}_4\text{-CeO}_2$ composite oxide was named as (x) $\text{Co}_3\text{O}_4\text{-CeO}_2$ 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 ^[6d, 8d] that 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 $\text{CuO}/(\text{x})\text{Co}_3\text{O}_4\text{-CeO}_2$.

Catalyst characterization

N_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_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 Bruker D8 diffractometer (operating at 40 kV and 30 mA) equipped with a Cu K α 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, Quanta 200).

H_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_2/N_2 for recording the TPR spectra. The amount of H_2 uptake during the reduction was measured by a thermal conductivity detector (TCD). For H_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_2 under the same condition to achieve a plot of H_2 consumption amounts versus TCD integration areas, based on the following reaction equation:

The achieved plot was then used to quantify the H_2 consumption of $\text{CuO}/\text{Co}_3\text{O}_4\text{-CeO}_2$ 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/h·g_{cat}, and the feed gas composition was 1 vol.% CO, 1.65 vol.% O₂, 50 vol.% H₂ and balanced in N₂ and was controlled with mass flow controllers. Excess O₂ 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 H₂, O₂ and CO and a carbon molecular sieve (TDX-01) column to quantify CO₂. No methane was detected under our experimental conditions. The CO conversion and selectivity are calculated as follows:

$$\text{CO conversion (\%)} = (\text{CO}_{\text{in}} - \text{CO}_{\text{out}}) / \text{CO}_{\text{in}} \times 100$$

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

RESULTS AND DISCUSSION

Catalytic performance

Fig. 1 Conversion profiles (a) and O₂ selectivity profiles (b) for CO oxidation over the CeO₂-Co₃O₄ composite oxides: ■ CeO₂; ○ (0.1)Co₃O₄-CeO₂; ▲ (0.3)Co₃O₄-CeO₂; ◇ (0.5)Co₃O₄-CeO₂; ◀ (0.7)Co₃O₄-CeO₂; □ (0.9)Co₃O₄-CeO₂; ● Co₃O₄.

Fig. 1 shows the CO conversion and O₂ selectivity of Co₃O₄-CeO₂ composite oxides. We investigated the catalytic activity of Co₃O₄-CeO₂ composite oxides here in order to evaluate the effect of cobalt activity without copper active species. Similar to the previous reports²¹⁻²³, Co₃O₄ exhibited a certain activity for CO-PROX (100% CO conversion at 240 °C) while the CeO₂ displayed a disillustory 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)Co₃O₄-CeO₂ 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 Co₃O₄-CeO₂ composite oxides might be good supports for CO-PROX reaction.

Fig. 2 Conversion profiles (a) and O₂ selectivity profiles (b) for CO oxidation over the CuO/CeO₂-Co₃O₄ catalysts: ■ CuO/CeO₂; ○ CuO/(0.1)Co₃O₄-CeO₂; ▲ CuO/(0.3)Co₃O₄-CeO₂; ◇ CuO/(0.5)Co₃O₄-CeO₂; ◀ CuO/(0.7)Co₃O₄-CeO₂; □ CuO/(0.9)Co₃O₄-CeO₂; ● CuO/Co₃O₄.

The catalytic activity and selectivity over the series of CuO/Co₃O₄-CeO₂ catalysts as a function of the reaction temperature are depicted in Fig. 2. Obviously, the catalytic activities of CuO/Co₃O₄-CeO₂ catalysts are improved markedly when compared with the corresponding supports, indicating that copper is the main active species. The performance of catalysts formed a volcanic curve with different atomic ratio. And the CuO/(0.7)Co₃O₄-CeO₂ catalyst possessed the best catalytic activity with 100% CO conversion and 93% O₂ 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 Co₃O₄-CeO₂ composite oxides are much less O₂ selective to CO oxidation in the reactant gas mixture and even the (0.5)Co₃O₄-CeO₂ 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)Co₃O₄-CeO₂ was also examined. As shown in Fig.3, the 80% CO conversion and 90% O₂ selectivity of CuO/(0.7)Co₃O₄-CeO₂ 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.

Fig. 3 Effect of the time on stream on CO conversion (●) and O₂ selectivity (■) for CO PROX reactions over CuO/(0.7)Co₃O₄-CeO₂ catalyst (at 100 °C of reaction temperature). Reaction conditions: GHSV = 18,000 ml/h·g_{cat}, 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)Co₃O₄-CeO₂ 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.

Catalysts	Content of Cu		Co/(Co + Ce) atomic ratio	
	S ^[a] . wt %	T ^[b] . wt %	S ^[a] . At %	T ^[b] . At %
CuO/(0.1)Co ₃ O ₄ -CeO ₂	3.67	5.02	7	8
CuO/(0.3)Co ₃ O ₄ -CeO ₂	3.60	5.05	25	28
CuO/(0.5)Co ₃ O ₄ -CeO ₂	3.81	5.05	42	37
CuO/(0.7)Co ₃ O ₄ -CeO ₂	3.67	4.97	71	65
CuO/(0.9)Co ₃ O ₄ -CeO ₂	3.78	4.98	91	92

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

Structural properties of samples

Fig. 4a compiles the XRD patterns of Co₃O₄-CeO₂ supports with different atomic ratios. All of the samples present the characteristic peaks of fluorite structure of the CeO₂ and spinel structure of the Co₃O₄. The (0.1)Co₃O₄-CeO₂, (0.3)Co₃O₄-CeO₂ and (0.5)Co₃O₄-CeO₂ supports mainly displayed the fluorite phases of CeO₂, while the spinel phases of Co₃O₄ were appeared mainly in (0.7)Co₃O₄-CeO₂ and (0.9)Co₃O₄-CeO₂ samples. Compared with the pure phases, these peaks became broader, and this indicated that the crystallite sizes of

CeO₂ and Co₃O₄ were reduced in the composite oxides. The 2θ values of CeO₂ (111) and Co₃O₄ (311) diffraction are listed in Table 2. Compared with the corresponding pure phases, the diffraction peaks of CeO₂ (111) slightly shift to higher 2θ values and Co₃O₄ (311) shift to lower, which is accordance with the ionic radii of Ce⁴⁺ (0.097 nm) being larger than that of Co²⁺ (0.082 nm) and Co³⁺ (0.065 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)Co₃O₄-CeO₂, which indicated that the interaction between CeO₂ and Co₃O₄ was existed factually and could be modified by modulating Co/Ce atomic ratio.

Fig. 4 X-ray diffraction patterns of CeO₂-Co₃O₄ composite oxide (a) and CuO/CeO₂-Co₃O₄ catalysts (b): fluorite CeO₂ (★) and spinel Co₃O₄ (●).

XRD patterns of CuO/Co₃O₄-CeO₂ catalysts are shown in Fig. 4b and the crystallite size and 2θ values of CeO₂ (111) and Co₃O₄ (311) 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 oxides^{24,25}. Further inspection of the XRD patterns displayed that the little shifts of CeO₂ (111) and Co₃O₄ (311) diffraction for CuO/CeO₂ and CuO/Co₃O₄ can be attributed to the incorporation of Cu into the CeO₂ and Co₃O₄ lattices. And the CuO/Co₃O₄-CeO₂ showed similar XRD patterns with corresponding Co₃O₄-CeO₂ supports. It suggests that the CuO might well disperse on the Co₃O₄-CeO₂ supports, which facilitates the CO-PROX.

Table 2 Physicochemical properties of CeO₂-Co₃O₄ composite oxides and CuO/Co₃O₄-CeO₂ catalysts.

Samples	BET (m ² ·g ⁻¹)	Average pore volume (cm ³ ·g ⁻¹)	Average pore diameter (nm)	CeO ₂ (111)		Co ₃ O ₄ (311)	
				2θ	Crystallite size (nm) ^[a]	2θ	Crystallite size (nm) ^[a]
CeO ₂	139.6	0.14	3.4	28.42	7.8	--	---
(0.1)Co ₃ O ₄ -CeO ₂	115.3	0.12	4.3	28.56	3.7	NA	NA
(0.3)Co ₃ O ₄ -CeO ₂	190.4	0.16	3.4	28.61	3.7	36.78	11.9
(0.5)Co ₃ O ₄ -CeO ₂	176.4	0.43	9.7	28.61	3.7	36.75	15.0
(0.7)Co ₃ O ₄ -CeO ₂	95.0	0.20	10.1	28.59	3.8	36.82	14.6
(0.9)Co ₃ O ₄ -CeO ₂	77.9	0.12	5.2	NA ^[b]	NA ^[b]	36.72	15.7
Co ₃ O ₄	29.2	0.098	13.4	--	--	36.93	25.6
CuO/CeO ₂	112.3	0.17	6.1	28.53	7.1	--	--
CuO/(0.1)Co ₃ O ₄ -CeO ₂	100.6	0.12	4.7	28.56	3.7	NA ^[b]	NA ^[b]
CuO/(0.3)Co ₃ O ₄ -CeO ₂	168.1	0.16	3.7	28.61	3.7	36.75	16.3
CuO/(0.5)Co ₃ O ₄ -CeO ₂	136.0	0.36	10.6	28.63	3.8	36.72	15.9
CuO/(0.7)Co ₃ O ₄ -CeO ₂	119.3	0.33	11.2	28.57	3.8	36.80	16.2
CuO/(0.9)Co ₃ O ₄ -CeO ₂	106.8	0.15	5.6	NA ^[b]	NA ^[b]	36.72	15.8
CuO/Co ₃ O ₄	25.0	0.076	12.1	--	--	36.84	24.9

[a] Estimated from CeO₂ (111) and Co₃O₄ (311) face by Scherrer equation.
[b] Not available due to weak XRD peaks.

Fig. 5 N₂ adsorption/desorption isotherm (a) and pore size distribution (b) of CuO/CeO₂-Co₃O₄ catalysts

Fig.5 and Fig.S2 (Supporting information) demonstrate the N₂ adsorption/desorption isotherms and pore size distributions of CuO/Co₃O₄-CeO₂ samples. The CuO/Co₃O₄-CeO₂ samples showed similar N₂ adsorption/desorption isotherms and pore size distributions with the corresponding supports. Thus, the CuO/Co₃O₄-CeO₂ samples were taken as the examples to describe the results of N₂ adsorption/desorption characterization. All CuO/Co₃O₄-CeO₂ samples exhibited type-IV isotherms, indicating the existence of mesopores in the samples. The pore volumes of (0.5)Co₃O₄-CeO₂ and (0.7)Co₃O₄-CeO₂ 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)Co₃O₄-CeO₂ 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)Co₃O₄-CeO₂ 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 CeO₂ and Co₃O₄ in the composite oxide are smaller than those in their pure phases (7.1 nm for CeO₂ and 19.6 nm for Co₃O₄), suggesting that the formation of Co₃O₄-CeO₂ composite oxide was helpful to prevent the sintering of Co₃O₄ and CeO₂.^{26,27}

The reduction performance of supports and catalysts

Table 3 H₂ consumption amount and reduction temperature of CuO/Co₃O₄-CeO₂ catalysts.

Catalysts	α peak		β peak		γ peak	
	H ₂ cons ($\mu\text{mol}\cdot\text{g}^{-1}$)	Peak temp (°C)	H ₂ cons ($\mu\text{mol}\cdot\text{g}^{-1}$)	Peak temp (°C)	H ₂ cons ($\mu\text{mol}\cdot\text{g}^{-1}$)	Peak temp (°C)
CuO/CeO ₂	810	202	595	213	--	--
CuO/(0.1)Co ₃ O ₄ -CeO ₂	690	201	534	210	--	--
CuO/(0.3)Co ₃ O ₄ -CeO ₂	884	209	1042	224	352	255
CuO/(0.5)Co ₃ O ₄ -CeO ₂	1302	211	782	222	911	260
CuO/(0.7)Co ₃ O ₄ -CeO ₂	412	162	864	191	7271	265
CuO/(0.9)Co ₃ O ₄ -CeO ₂	333	201	1169	237	5474	316
CuO/Co ₃ O ₄	225	212	852	252	17059	429

TPR profiles of the Co₃O₄-CeO₂ supports (shown in Fig. 6a) indicated that the reduction behavior of composite oxides is affected strongly by the Co/Ce ratio. Pure CeO₂ hardly can be reduced during the examined temperature range, while the pure Co₃O₄ exhibits two reduction peaks γ_1 and γ_2 , which can be assigned to the step-wise reduction *via* Co₃O₄ to CoO and CoO to Co²⁸, respectively. And the ratio of the peak area of γ_1 to γ_2 is close to the ratio of two-step theoretical reduction of Co₃O₄ (1:3.07). For the Co₃O₄-CeO₂ composite supports, ζ reduction peak appears, which might be attributed to

the reduction of Co²⁺ interacting with ceria or the reduction of surface oxygen species of ceria accompanying with Ce⁴⁺ to Ce³⁺ reduction²⁹. 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 ζ peak overlaps with γ_2 . These changes in the reducibility might be caused by the change of interaction between Co₃O₄ and CeO₂, which is in agreement with the XRD analysis. Among the Co₃O₄-CeO₂ supports, the (0.5)Co₃O₄-CeO₂ exhibits the best reduction property, which result in its highest CO removal activity.

Fig. 6 H₂-TPR profiles of CeO₂-Co₃O₄ composite oxides (a) and CuO/CeO₂-Co₃O₄ catalysts (b).

The H₂-TPR profiles of CuO/Co₃O₄-CeO₂ catalysts are depicted in Fig. 6b and table 3. Obviously, three (α , β and γ) peaks can be observed. Peaks of α and β are attributed to the reduction of the CuO species, α peak corresponds to the reduction of highly dispersed CuO particles which have strong interaction with CeO₂-Co₃O₄ composite oxides, while β peak corresponds to bulk CuO and partial CeO₂¹⁰⁻¹². And γ 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 α and β are becoming lower and the area becomes larger until CuO/(0.7)Co₃O₄-CeO₂ catalyst. However, the reduction temperature of γ peak shifts higher and the area becomes larger. This should be due to the enhancement of the Co content. CuO/(0.7)Co₃O₄-CeO₂ 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)Co₃O₄-CeO₂. As revealed by XRD and TPR analysis results of Co₃O₄-CeO₂

supports, the distortion of oxide lattices was more and more obvious with the increase of Co/Ce ratio except for $(0.7)\text{Co}_3\text{O}_4\text{-CeO}_2$, and the $(0.5)\text{Co}_3\text{O}_4\text{-CeO}_2$ 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 $\text{CuO}/(0.7)\text{Co}_3\text{O}_4\text{-CeO}_2$, we further inspected the natural properties of $(0.7)\text{Co}_3\text{O}_4\text{-CeO}_2$ support. It revealed that $(0.7)\text{Co}_3\text{O}_4\text{-CeO}_2$ 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 $\text{Co}_3\text{O}_4\text{-CeO}_2$ supports and $\text{CuO}/\text{Co}_3\text{O}_4\text{-CeO}_2$ catalysts are given in Fig. 7. The TPD spectra of the $\text{Co}_3\text{O}_4\text{-CeO}_2$ 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 literature¹⁷, 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 CO_2 desorption, which likely formed by the decomposition of the surface carbonates that have resulted from CO adsorption. The CO_2

desorption peak might be lower owing to the formation of new CO adsorption and oxidation sites involving copper oxides (CuO_x) and cobalt oxides (CoO_x). It is interesting that the lower peaks shifted to lower temperature with the increase of Co_3O_4 loadings, while the higher temperature peak shifted to higher temperature after the $\text{Co}/(\text{Co} + \text{Ce})$ is 0.5. The TPD profiles of $(0.1)\text{Co}_3\text{O}_4\text{-CeO}_2$, $(0.3)\text{Co}_3\text{O}_4\text{-CeO}_2$ and $(0.5)\text{Co}_3\text{O}_4\text{-CeO}_2$ oxides differed significantly from the spectra of $(0.7)\text{Co}_3\text{O}_4\text{-CeO}_2$ and $(0.9)\text{Co}_3\text{O}_4\text{-CeO}_2$ samples in the intensity of two peaks. Thus, only a proper $\text{Co}/(\text{Co}+\text{Ce})$ 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 $\text{Co}/(\text{Co}+\text{Ce})$ in $\text{Co}_3\text{O}_4\text{-CeO}_2$ composite oxides impacted the quantity and strength of CO desorption.

All $\text{CuO}/\text{Co}_3\text{O}_4\text{-CeO}_2$ catalysts showed two CO desorption peaks. In contrast, the introduction of Cu species made desorption peaks shift to lower temperature, thus indicating the stronger adsorption of CO in ternary catalysts than CuO/CeO_2 , $\text{CuO}/\text{Co}_3\text{O}_4$ and $\text{Co}_3\text{O}_4\text{-CeO}_2$ oxides. The interaction was more positive to the reaction³⁰. The areas of these peaks give an interesting transformation. Take EDS and TPR results into account, an individual CeO_2 phase formed on the surface at lower Co_3O_4 contents which reduced active Cu–Co–Ce–O clusters in surface. A proper cobalt loading was necessary to form Cu–Co–Ce–O surface clusters, which was in agreement with our data.

Fig. 7 TPD profiles of $\text{CeO}_2\text{-Co}_3\text{O}_4$ composite oxides (a): a' CeO_2 ; b' $(0.1)\text{Co}_3\text{O}_4\text{-CeO}_2$; c' $(0.3)\text{Co}_3\text{O}_4\text{-CeO}_2$; d' $(0.5)\text{Co}_3\text{O}_4\text{-CeO}_2$; e' $(0.7)\text{Co}_3\text{O}_4\text{-CeO}_2$; f' $(0.9)\text{Co}_3\text{O}_4\text{-CeO}_2$; g' Co_3O_4 and TPD profiles of $\text{CuO}/\text{CeO}_2\text{-Co}_3\text{O}_4$ catalysts (b): a CuO/CeO_2 ; b $\text{CuO}/(0.1)\text{Co}_3\text{O}_4\text{-CeO}_2$; c $\text{CuO}/(0.3)\text{Co}_3\text{O}_4\text{-CeO}_2$; d $\text{CuO}/(0.5)\text{Co}_3\text{O}_4\text{-CeO}_2$; e $\text{CuO}/(0.7)\text{Co}_3\text{O}_4\text{-CeO}_2$; f $\text{CuO}/(0.9)\text{Co}_3\text{O}_4\text{-CeO}_2$; g $\text{CuO}/\text{Co}_3\text{O}_4$.

CONCLUSION

Employing the templating technique, a series of $\text{Co}_3\text{O}_4\text{-CeO}_2$ 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, $\text{CuO}/\text{Co}_3\text{O}_4\text{-CeO}_2$ catalysts exhibited a better CO-PROX activity than the corresponding supports. Among these samples, the $\text{CuO}/(0.7)\text{Co}_3\text{O}_4\text{-CeO}_2$ displayed the best activity with 100% CO conversion and 93% O_2 selectivity at 120 °C, and the excellent activity was still maintained after reaction for 80 h. The inspection of $\text{CuO}/\text{Co}_3\text{O}_4\text{-CeO}_2$ and $\text{Co}_3\text{O}_4\text{-CeO}_2$ samples revealed that the strongest lattice distortion and the best reducibility of $\text{Co}_3\text{O}_4\text{-CeO}_2$ 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.

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REFERENCES

1. J. Han, H. J. Kim, S. Yoon, H. Lee, *J. Mol. Catal. A: Chem.* 335, 82 (2011).
2. H. Igarashi, T. Fujino, M. Watanabe, *J. Electroanal. Chem.* 391, 119 (1995).
3. Q. Fu, H. Saltsburg, M. Flytzani-Stephanopoulos, *Science* 301, 935 (2003).
4. E. D. Park, D. Lee, H. C. Lee, *Catal. Today* 139, 280 (2009).
5. O. Pozdnyakova, D. Teschner, A. Woetsch, J. Krohnert, B. Steinhauer, H. Sauer, L. Toth, F. Jentoft, A. Knopgericke, Z. Paal, *J. Catal.* 237, 1 (2006).

6. Y. Yoshida, Y. Mitani, T. Itoi, Y. Izumi, *J. Catal.* 287, 190 (2012).
7. E. V. Ramos-Fernandez, C. Pieters, B. van der Linden, J. Juan-Alcañiz, P. Serra-Crespo, M. W. G. M. Verhoeven, H. Niemantsverdriet, J. Gascon, F. Kapteijn, *J. Catal.* 289, 42 (2012).
8. C. S. Polster, R. Zhang, M. T. Cyb, J. T. Miller, C. D. Baertsch, *J. Catal.* 273, 50 (2010).
9. L.H. Chang, N. Sasirekha, Y.W. Chen, *Catal. Commun.* 8, 1702 (2007).
10. H. Wang, H. Zhu, Z. Qin, F. Liang, G. Wang, J. Wang, *J. Catal.* 264, 154 (2009).
11. Y. Huang, A. Wang, L. Li, X. Wang, D. Su, T. Zhang, *J. Catal.* 255, 144 (2008).
12. D. Gamarra, C. Belver, M. Fernandez-Garcia, A. Martinez-Arias, *J. Am. Chem. Soc.* 129, 12064 (2007).
13. M. Turco, G. Bagnasco, C. Cammarano, L. Micoli, M. Lenarda, E. Moretti, L. Storaro, A. Talon, *Appl. Catal., B* 102, 387 (2011).
14. C. S. Polster, H. Nair, C. D. Baertsch, *J. Catal.* 266, 308 (2009).
15. F. Zhang, C. Chen, W.m. Xiao, L. Xu, N. Zhang, *Catal. Commun.* 26, 25 (2012).
16. S. Ivanova, V. Pitchon, C. Petit, V. Caps, *ChemCatChem* 2, 556 (2010).
17. C. T. Campbell, *Science* 309, 713 (2005).
18. K. Sirichaiprasert, A. Luengnaruemitchai, S. Pongstabodee, *J. Am. Chem. Soc.* 32, 915 (2007).
19. Z. Zhao, X. Lin, R. Jin, Y. Dai, G. Wang, *Catal. Sci. Technol* 2, 554 (2012).
20. L. Gong, L. T. Luo, R. Wang, N. Zhang, *J. Chil. Chem. Soc.* 57, 1048 (2012).
21. A. A. Firsova, T. I. Khomenko, A. N. Il'ichev, V. N. Korchak, *Kinet. Catal.* 49, 682 (2008).
22. P. Bera, A. Hornés, A. L. Cámara, A. Martínez-Arias, *Catal. Today* 155, 184 (2010).
23. Z. Lenzion-Bieluñ, M. M. Bettahar, S. Monteverdi, D. Moszyński, U. Narkiewicz, *Catal. Lett.* 134, 196 (2010).
24. H. Wang, H. Zhu, Z. Qin, G. Wang, F. Liang, J. Wang, *Catal. Commun.* 9, 1487 (2008).
25. M. P. Woods, P. Gawade, B. Tan, U. S. Ozkan, *Appl. Catal., B* 97, 28 (2010).
26. M. Kang, *Appl. Catal., A* 251, 143 (2003).
27. C.W. Tang, C.C. Kuo, M.C. Kuo, C.B. Wang, S.H. Chien, *Appl. Catal., A* 309, 37 (2006).
28. Q. Guo, Y. Liu, *Appl. Catal., B* 82, 19 (2008).
29. Q. Guo, S. Chen, Y. Liu, Y. Wang, *Chem. Eng. J.* 165, 846 (2010).
30. J.Y. Luo, M. Meng, J.S. Yao, X.G. Li, Y.Q. Zha, X. Wang, T.Y. Zhang, *Appl. Catal., B* 87, 92 (2009).