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Article

Insights into facet-dependent reactivity of CuO–CeO₂ nanocubes and nanorods as catalysts for CO oxidation reaction

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ABSTRACT

Copper–ceria (CuO–CeO₂) catalysts have been known to be very effective for the oxidation of CO, and their chemical behavior has been extensively studied during the last decades. However, the effect of different CeO₂ crystal surfaces on the catalytic activity of CuO–CeO₂ for the oxidation of CO is still unclear and should be further elucidated. In this study, we deposited 1 wt% Cu on mostly {100}-exposed CeO₂ nanocubes (1CuCe NC) and mostly {110}-exposed CeO₂ nanorods (1CuCe NR), respectively. Both 1CuCe NC and 1CuCe NR have been used as catalysts for the oxidation of CO and achieved 100% and 50% CO conversion at 130 °C, respectively. The differences in the catalytic activity of 1CuCe NC and 1CuCe NR were analyzed using temperature-programmed reduction of H₂ and temperature-programmed desorption of CO techniques. The results confirmed the excellent reducibility of the 1CuCe NC catalyst, which was attributed to the weak interactions between Cu and the CeO₂ support. Moreover, *in situ* diffuse reflectance infrared Fourier-transform spectroscopy studies indicated that the {100} planes of 1CuCe NC facilitated the generation of active Cu(I) sites, which resulted in the formation of highly reactive Cu(I)–CO species during the oxidation of CO. Both the excellent redox properties and effective CO adsorption capacity of the 1CuCe NC catalyst increased its catalytic reactivity.

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1. Introduction

Owing to its great thermal stability, prominent redox properties, and efficient oxygen storage capacity, ceria (CeO₂), which is a versatile metal oxide, has been used for numerous applications, including three-way catalysis [1–4]. In particular, the controlled synthesis of well-defined CeO₂ nanoshapes, such as nanorods (NRs) [5,6], nanocubes (NCs) [7–9], and nanooc-

tahedrons [9] favors specific redox characteristics and catalytic properties. Engineering the surface chemistry of their well-defined stable facets, such as {111}, {110}, and {100}, could confer CeO₂ nanoshapes different physical and chemical properties [10,11]. In the last decade, a variety of technological approaches, such as *in situ* Raman spectroscopy, *in situ* diffuse reflectance infrared Fourier-transform spectroscopy (DRIFTS), nuclear magnetic resonance, and scanning transmission elec-

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tron microscopy (STEM) have been used to better understand the nature of the crystal facets of diverse CeO₂ nanostructures [9,12,13]. Consequently, it was determined that the order of the oxygen vacancies and their catalytic reactivities decreased as follows: {110}-exposed CeO₂ NR > {100}-exposed CeO₂ NC > {111}-exposed CeO₂ nanooctahedron.

According to previously published studies [14–17], when CeO₂ supports were loaded with different metals, the metal-support interactions have been important factors for tuning the electronic structure and dispersion of metal-support interfaces, which led to the significant enhancement in their catalytic performance. To date, many efforts have been made to elucidate the influence of different CeO₂ crystal surfaces on the metal-support interactions, particularly under reaction conditions [18–20], and it was concluded that {110}- and {100}-exposed CeO₂ NR presented superior catalytic properties compared with those featuring other morphologies [21–25]. Si et al. [18] revealed that CeO₂ NR was the most suitable support for stabilizing Au nanoparticles in Au/CeO₂ catalysts. Furthermore, Hu et al. [19] also proposed that Pd-supported CeO₂ NR exhibited strong reducibility, high surface oxygen mobility, and attained higher CO oxidation activity compared with CeO₂ NC. However, some researchers have determined that in some cases, CeO₂ NC was a better support than CeO₂ NR [26,27]. Thus, no consensus has been reached yet on the effect of the nanoshapes and crystal facets of CeO₂ on the catalytic CO oxidation capacity.

Researchers of different backgrounds have conducted more studies on Cu–CeO₂ catalysts than on other CeO₂-based materials. The synergistic effect of Cu and CeO₂ has been determined to play an important role for increasing the creation of high oxygen mobilities, which is beneficial for the catalytic properties [28,29]. We have recently demonstrated that Cu supported on {111}-exposed CeO₂ nanospheres, which were assumed to be inert surfaces in previous investigations [9,12,13], was very active and presented higher CO oxidation activity than CeO₂ NR with predominantly {110} exposed facets [30], which are known to be highly active surfaces. In addition, predominantly {100}-exposed CeO₂ NC has been used as support for Cu-based catalysts for the oxidation of CO [31]. However, more in depth systematic studies of the catalytic performance and chemical properties of Cu supported on the {100} and {110} crystal planes of CeO₂ should be conducted.

In this study, we investigated in detail the facet-dependent properties of Cu-based catalysts supported on CeO₂ NC and NR for the CO oxidation reaction. Very small amounts of Cu (1 wt%) were deposited on CeO₂ nanostructures, hereafter 1CuCe, and the adsorption of CO on different crystal planes of CeO₂ and the synergistic effect between Cu and the CeO₂ support were investigated. In contrast with previously reported findings, the catalytic properties of Cu supported on {100}-exposed CeO₂ NC were superior to those of Cu supported on {110}-exposed CeO₂ NR. Using multiple tests, it has been concluded that the CO adsorption capacity of 1CuCe NC {100} was higher than that of 1CuCe NR {110} because the increased reducibility of 1CuCe NC facilitated the formation of abundant Cu(I)-CO species, which was essential for the increase in catalytic activity.

2. Experimental

2.1. Synthesis of catalysts

2.1.1. Preparation of CeO₂ NC

In this study, analytical grade chemicals and reagents were used directly, without purification. A modified version of the procedure described by Lyu et al. [32] was used to hydrothermally synthesize the CeO₂ NC support. For a typical synthesis, 7.5 g ammonium acetate and 7.5 mL glacial acetic acid were dissolved in 30 mL water to obtain a buffer solution. Then, 1.63 g cerium(III) nitrate hexahydrate was added to the prepared buffer solution under stirring for 10 min. The solution was diluted to 64 mL, transferred into a 100 mL Teflon-lined stainless-steel autoclave, and then it was heated to 220 °C for 24 h. The mixture was centrifuged, and the obtained precipitate was washed with deionized water and dried at 80 °C for 12 h; the final product was denoted as CeO₂ NC. Afterward, half of the amount of CeO₂ NC powder was calcined at 400 °C for 4 h to compare the chemical behavior of uncalcined and calcined samples.

2.1.2. Preparation of CeO₂ NR

The CeO₂ NR support was prepared using the procedure described by Wang et al. [30]. For the typical synthesis of CeO₂ NR, 1.3 g cerium(III) nitrate hexahydrate and 14.4 g sodium hydroxide were dissolved in 20 and 40 mL deionized water, respectively, under stirring for 30 min. The solutions were mixed, and the obtained slurry was hydrothermally treated at 100 °C for 24 h. The subsequent steps were identical to those followed for the preparation of CeO₂ NC. The resulting sample was denoted as CeO₂ NR.

2.1.3. Preparation of Cu–CeO₂ catalysts

Cu–CeO₂ catalysts were synthesized using the deposition precipitation method, as described by Wang et al. [30]. In detail, 0.50 g CeO₂ powder was dissolved in 25 mL deionized water under stirring. Suitable amounts of copper(II) nitrate trihydrate were dissolved in 12.5 mL deionized water, and the solutions were added dropwise to the CeO₂ solution. After the pH was adjusted to 9 using sodium carbonate aqueous solution, the stirring was continued for 30 min, and the resulting suspension was maintained at ambient temperature for 1 h. The final products were obtained via filtration followed by washing with deionized water (1 L), drying at 75 °C and calcination at 400 °C for 4 h. Lastly, the samples prepared by depositing Cu on uncalcined CeO₂ and CeO₂ calcined at 400 °C were denoted as xCuCe NC and xCuCe NR, and the catalysts prepared using calcined CeO₂ supports were symbolized as xCuCe NC 400-400 and xCuCe NR 400-400, where x = 1 is the Cu loading ($x = [\text{Cu}/\text{CeO}_2]_{\text{wt}} \times 100\%$) in wt%.

2.2. Characterization of as-prepared catalysts

The morphological characterization of the catalysts was performed using transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM)

analyses utilizing a JEM-2800 (JEOL) instrument with the accelerating voltage of 200 kV. Energy dispersive X-ray spectroscopy (EDX) elemental mappings were obtained using the same JEM-2800 (JEOL) instrument, which was equipped with an EDX spectrometer and was operated in STEM mode. The actual Cu contents of the as-prepared samples were determined using a SUPRA 55 (Zeiss) scanning electron microscopy (SEM) device with the acceleration voltage of 5.0 kV.

Powder X-ray diffraction (XRD) patterns were obtained using an X'pert3 (PANalytical) powder diffractometer with Cu $K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) that was operated at 40 kV and 40 mA. N₂ sorption isotherms of the prepared catalysts were obtained using an SSA-4200 (Builder) instrument, and the specific surface areas (A_{BET}) of the catalyst samples were evaluated using the Brunauer–Emmett–Teller (BET) method.

To examine the reducibility of the as-prepared samples, temperature-programmed reduction of hydrogen (H_2 -TPR) analysis was conducted using a PCSA-1000 (Builder) adsorption instrument. For a typical measurement, 30 mg catalyst was placed in a U-shaped quartz cell and was pretreated with purified O₂ gas at 300 °C for 30 min. After pretreatment, the samples were cooled to room temperature by purging them with Ar gas followed by heating to 400 °C (temperature ramp of 5 °C·min⁻¹) under 5% H₂/Ar balance gas mixture (flow rate of 30 mL·min⁻¹). The corresponding H₂ consumption data were collected using a thermal conductivity detector.

Temperature-programmed desorption of carbon monoxide (CO-TPD) measurements were performed using an LC-D200 M (Ametek) apparatus equipped with a mass spectrometer. First, 100 mg sample was pretreated at 300 °C for 1 h under synthetic air followed by cooling to room temperature via purging with He gas. Then, each sample was introduced into a 2% CO/Ar balance gas mixture for 30 min to determine the amount of CO adsorbed on the sample. This was followed by another purging with He gas to remove the adsorbed species. The temperature was increased to 800 °C (temperature ramp of 10 °C·min⁻¹) under He gas flow, and then the CO desorption signals were monitored using a mass spectrometer.

Raman spectra of the prepared catalysts were recorded using a Lab RAM HR800 (HORIBA Jobin Yvon) spectrometer under the laser excitation of 633 nm. The signals were collected in the Raman region of 200–800 cm⁻¹. An Axis Ultra spectrometer with Al $K\alpha$ (222 W) radiation and the C 1s peak at 284.8 eV was used for X-ray photoelectron spectroscopy (XPS) analysis.

The *in situ* DRIFTS experiments were performed using a Vertex 70 (Bruker) Fourier-transform infrared spectrometer equipped with a mercury-cadmium-telluride detector by cooling the samples with liquefied N₂. The adsorption–desorption behavior of CO on the as-prepared catalysts was investigated using the CO-N₂-CO-O₂ system for *in situ* DRIFTS measurements at 30 and 100 °C. Prior to the *in situ* DRIFTS experiments, 30 mg sample powder was pretreated at 300 °C for 30 min under synthetic air flow (21% O₂ and N₂ balance) followed by cooling to 30 °C under purging with purified N₂ gas. The background spectra were collected under N₂ purging; the spectral resolution was 4 cm⁻¹. After purging with N₂ gas for 30 min, the sample was placed in a container with the reaction gas

mixture (1% CO, 20% O₂, and N₂ balance) for 30 min to determine the CO adsorption intensity. This was followed by N₂ gas purging and CO readsorption by aging the sample for 30 min during each step. Afterward, the sample was added to a container with 1% O₂/N₂ balance gas mixture.

2.3. Catalytic performance tests

The catalytic activity for the oxidation of CO was measured in a quartz fixed bed reactor. In detail, 50 mg catalyst sample was added to the reactor that contained the gas mixture (1% CO, 20% O₂, and N₂ balance; flow rate of 67 mL·min⁻¹ and gas hourly space velocity of 80 400 mL·g_{cat}⁻¹·h⁻¹) and the test was performed in the temperature range of 30 to 300 °C. Prior to the activity test, the samples were activated at 300 °C in air. The composition of the gas stream from the reactor was determined online using a non-dispersive infrared (IR) spectrometer (Gasboard-3500). The conversion of CO was evaluated as follows:

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

where $[\text{CO}_{\text{in}}]$ and $[\text{CO}_{\text{out}}]$ are the inlet and outlet CO concentrations, respectively. The time dependence of the catalytic performance was investigated at 100 °C under the same operating conditions mentioned above. The Arrhenius plots of the reaction rate were obtained by collecting data in the CO conversion interval of 5% to 15%.

3. Results and discussions

3.1. Morphological characterization of as-prepared catalysts

To identify the morphology and crystal facets of the as-synthesized catalysts, TEM, HRTEM, and STEM analyses were conducted. The TEM images in Figs. 1a and 1d illustrate the well-defined nanostructures of the 1CuCe NC and 1CuCe NR catalysts. The 1CuCe NC catalyst consisted of cube-shaped nanostructures ranging in size from 10 to 30 nm. The length of the NRs of the 1CuCe NR catalyst was approximately 50 to 200 nm and their diameter was approximately 10 nm. The HRTEM images revealed that the 1CuCe NC catalyst presented the main interplanar spacings of 0.27 and 0.20 nm (Fig. 1b), which corresponded to the {100} and {110} facets, respectively. Conversely, the 1CuCe NR catalyst exhibited 0.19 and 0.27 nm lattice fringes, which corresponded to the {110} and {100} facets, respectively (Fig. 1e) [30,33]. Thus, it was concluded that 1CuCe NC comprised a large amount of {100}-dominant surfaces that were truncated at the cube corners by {110} planes, and 1CuCe NR was mainly enclosed by the exposed facets of the {110} and {100} surfaces [18–20]. Both 1CuCe catalysts maintained their well-defined morphologies after the CO oxidation reaction (Fig. S1). Moreover, no Cu species were detected in the spectra of the catalysts, which indicated that the deposited Cu species were well dispersed on the CeO₂ supports. Thus, in this work, the structures of the as-prepared and used catalysts matched those of CeO₂ NCs and NRs. The STEM-EDX mapping images (Figs. 1c and 1f) combined with the HRTEM results demonstrated the good distribution of the Cu deposited on the

Fig. 1. (a) Transmission electron microscopy (TEM), (b) high-resolution transmission electron microscopy (HRTEM), and scanning transmission electron microscopy–energy-dispersive X-ray electron spectroscopy (STEM-EDX) mapping images of 1CuCe NC; (d) TEM, (e) HRTEM and (f) STEM-EDX of 1CuCe NR.

CeO₂ supports for both catalysts.

3.2. Catalytic performance of as-prepared samples

The catalytic performance of the 1CuCe NC and 1CuCe NR catalysts for the oxidation of CO was investigated. The light-off curves for the catalytic performance of the 1CuCe catalysts for the oxidation of CO are presented in Fig. 2a. Significant differences were observed between the catalytic activities of 1CuCe NC and 1CuCe NR. As depicted in Fig. 2a, 1CuCe NC achieved 100% CO conversion when the temperature was as low as 130 °C. By contrast, at the same temperature, 1CuCe NR only reached 50% CO conversion. This contradicted one of the previously published reports where the catalytic performance of predominantly {110}-exposed CeO₂ NR was superior to those of other CeO₂ morphologies [21–23,25]. Conversely, catalyst with CeO₂ NC supports have been reported to exhibit the worst

performance for the oxidation of CO [18–20]. However, in this study, the CO oxidation activity of 1CuCe NC was significantly higher than that of 1CuCe NR. Steady-state performance tests were carried out at 100 °C, and the corresponding results are depicted in Fig. 2b. The steady-state measurements for the conversion of CO were in line with those of the light-off test; the 1CuCe NC and 1CuCe NR catalysts were stable and maintained the CO conversion values of 67% and 23%, respectively. Furthermore, we also obtained the Arrhenius plots of the reaction rates (Fig. 3) in the CO conversion range below 15%. The apparent activation energy values of 1CuCe NC and 1CuCe NR were 46.8 and 53.7 kJ·mol^{−1}, respectively, and the activation energy values of both catalysts were approximately identical. Although the catalytic performances of 1CuCe NC and 1CuCe NR were significantly different, the EDX elemental analysis results revealed that both catalysts presented similar Cu contents: 1.2 and 1.3 wt% for 1CuCe NC and 1CuCe NR, respec-

Fig. 2. (a) Light-off curves of CO conversion for CO oxidation reaction and (b) steady state performance of 1 wt% Cu deposited on CeO₂ nanocubes (1CuCe NC) and 1 wt% Cu deposited on CeO₂ nanorods (1CuCe NR) catalysts (test conditions: 50 mg catalyst and gas hourly space velocity of 80 400 mL·g_{cat}^{−1}·h^{−1}).

Fig. 3. Arrhenius plots of 1 wt% Cu deposited on CeO₂ nanocubes (1CuCe NC) and 1 wt% Cu deposited on CeO₂ nanorods (1CuCe NR) catalysts. Here E_a is the activation energy and r_{CO} is the rate of CO oxidation.

tively (Table 1). Thus, it was proposed that the superior catalytic performance of 1CuCe NC was attributed to the disparate Cu–CeO₂ interaction, and also the unique chemical properties that derived from this interaction.

3.3. Textural properties of as-prepared catalysts

The XRD patterns of the fresh and used 1CuCe NC and 1CuCe NR catalysts are compiled in Fig. 4a. All the diffraction peaks typically assigned to the fluorite cubic structure of CeO₂ (JCPDS 34–0394) were detected in the XRD spectra of all samples. This was in good agreement with the results of previous studies, and the peak intensities for the {111}, {200}, {220}, and {311} crystal planes of the 1CuCe NC catalyst were relatively higher than those of the 1CuCe NR one [10,33]. Owing to the very low Cu content of the as-prepared samples and the good dispersion of Cu species on the CeO₂ surface, no Cu species signals were detected for either catalyst [30].

The textural properties obtained using N₂ sorption experiments are compiled in Table 1. In line with the findings of previously published papers [18–23], the A_{BET} value of 1CuCe NR (104 m²·g^{−1}) was more than two times higher than that of

Table 1

Cu content, Brunauer–Emmett–Teller (BET) specific surface area (A_{BET}), and reduction temperature (T_R) values for temperature-programmed H₂ reduction (H₂-TPR) reaction of 1 wt% Cu deposited on CeO₂ nanocubes (1CuCe NCs) and 1 wt% Cu deposited on CeO₂ nanorods (1CuCe NRs).

Sample	Cu content ^a (wt %)	A_{BET} ^b (m ² ·g ^{−1})	T_R ^c (°C) of α , β peaks
1CuCe NC	1.2	41	205
1CuCe NR	1.3	104	237, 353

^a Obtained using energy-dispersive X-ray spectroscopy. ^b Determined using BET testing. ^c Data collected from H₂-TPR analysis.

1CuCe NC (41 m²·g^{−1}). In previous reports, A_{BET} has been generally considered to be an important factor for determining catalytic activity [34,35]. However, in our study, we demonstrated that catalytic performance did not depend on A_{BET} . The N₂ sorption isotherms and pore size distribution plots indicated that the textural properties of the 1CuCe NC and 1CuCe NR catalysts were different. According to previously published literature [33], the 1CuCe NC and 1CuCe NR catalysts presented type IV N₂ sorption isotherms with H2 and H3 hysteresis loops, respectively, which indicated the presence of mesopores (Fig. S2).

To further study the structure of the 1CuCe NC and 1CuCe NR catalysts, their Raman spectra before and after the CO oxidation reaction were obtained and the results are illustrated in Fig. 4b. All samples displayed the typical features of triply degenerate F_{2g} mode at approximately 465 cm^{−1}, which is the F_{2g} band position of fluorite CeO₂ [21]. The intensities of the Raman peaks of 1CuCe NC were significantly higher than those of 1CuCe NR. Previously published studies indicated that the small shoulder band at approximately 600 cm^{−1} could be assigned to the oxygen defect sites [3,31,33]. However, in our study, no peaks for defect related features were identified in the Raman spectra of the 1CuCe NC or 1CuCe NR catalysts. In addition, no segregated copper oxide phases, which typically occur at 292 and 340 cm^{−1} were detected in the spectra of the catalysts [30]. This suggested that the supported Cu species were finely dispersed on the surface of CeO₂, which was in good agreement with the above-mentioned results.

Fig. 4. (a) X-ray diffraction patterns and (b) Raman spectra of 1 wt% Cu deposited on CeO₂ nanocubes (1CuCe NC) and 1 wt% Cu deposited on CeO₂ nanorods (1CuCe NR) catalysts.

3.4. XPS surface analysis

We used XPS analysis to investigate the surface chemical composition of the 1CuCe catalysts. Figs. 5a and 5d represent the Cu 2*p* XPS spectra of the fresh and used 1CuCe NC and 1CuCe NR catalysts. Two main broad peaks that corresponded to Cu 2*p*_{1/2} and Cu 2*p*_{3/2} were observed in the XPS profiles of all samples. According to the literature, the peaks at the binding energies of 932.5 and 933.5 eV corresponded to the Cu⁺/Cu⁰ states and Cu²⁺ species, respectively [30,31,36]. Therefore, it could be concluded that the 1CuCe NC catalyst contained more Cu⁺/Cu⁰ species than the 1CuCe NR one. Figs. 5b and 5e display the Ce 3*d*_{5/2} and Ce 3*d*_{3/2} XPS profiles of the 1CuCe catalysts. The peaks of the Ce 3*d*_{5/2} and Ce 3*d*_{3/2} spectra were labeled as *v'*, *v''*, and *v'''* and *u'*, *u''*, and *u'''*, respectively. As previously reported in the literature [21,26], the concentrations of Ce³⁺ ions of 1CuCe catalysts of different morphologies were similar, regardless of their oxygen vacancy defects.

Taking into account the data previously reported in the literature [37,38], different types of oxygen species, namely surface adsorbed and surface lattice oxygen, strongly affected the reactivity of the catalysts and the nature of the reaction pathways. Figs. 5c and 5f illustrate the presence of two intense peaks in the O 1*s* XPS profiles of the fresh and used 1CuCe NC and 1CuCe NR catalysts. The O_α peaks at the binding energies of 531.3 and 531.1 eV were attributed to the adsorbed oxygen or carbonate species, and the O_β peaks at 529.5 and 529.2 eV represented the surface lattice oxygen [37,38].

3.5. Reducibility of as-prepared catalysts

The reduction properties and chemical behavior of the 1CuCe catalysts were determined using H₂-TPR analysis. The

1CuCe NC catalyst exhibited only one intense reduction peak (α) at 205 °C, which was assigned to the weak interaction between the dispersed Cu and CeO₂ support [30] (Fig. 6a). Conversely, two well-separated reduction peaks at 237 and 353 °C were detected for the 1CuCe NR catalyst (Fig. 6a) at much higher temperatures than those of the 1CuCe NC catalyst. Using the data reported in a recently published study [39] and the XRD, Raman, STEM, and HRTEM results, the α peak of the 1CuCe NR catalyst was attributed to the reduction of the well-dispersed copper oxide species, and the β peak could be ascribed to the strong interactions of Cu-[O_x]-Ce structure. The reduction properties of the 1CuCe NC and 1CuCe NR catalysts were significantly different and depended on the shapes of the CeO₂ crystals; moreover, their reducibility was strongly correlated with their catalytic performances. The reduction temperatures of the 1CuCe NC and 1CuCe NR catalysts are listed in Table 1. The reducibility of the 1CuCe NC catalyst was relatively higher than that of the 1CuCe NR catalyst, which was in agreement with their catalytic performances.

3.6. CO-TPD analysis of CO adsorption properties of as-prepared catalysts

Fig. 6b depicts the CO₂ desorption profiles of the as-prepared catalysts, which were obtained using CO-TPD analysis. Two CO₂ formation peaks were observed for both the 1CuCe NC and 1CuCe NR catalysts, but the desorption temperatures were different for the two catalysts. The initial peak for the formation of CO₂ over the 1CuCe NC catalyst occurred at the low temperature of 213 °C and was accompanied by the shoulder peak at 653 °C. Conversely, the corresponding peaks of the 1CuCe NR catalyst occurred at much higher temperatures: 307 and 724 °C, respectively. These results indicated that the de-

Fig. 5. (a) Cu 2*p*, (b) Ce 3*d*, and (c) O 1*s* X-ray photoelectron spectroscopy (XPS) profiles of 1 wt% Cu deposited on CeO₂ nanocubes (1CuCe NC) catalyst and (d) Cu 2*p* (e) Ce 3*d* and (f) O 1*s* XPS profiles of 1 wt% Cu deposited on CeO₂ nanorods (1CuCe NR) catalyst.

Fig. 6. (a) Temperature-programmed reduction of H₂ profiles and (b) CO₂ desorption peaks obtained using temperature-programmed desorption of CO analysis of 1 wt% Cu deposited on CeO₂ nanocubes and nanorods (1CuCe NC and 1CuCe NR, respectively) catalysts.

sorption of CO₂ over the 1CuCe NC catalyst occurred easier than over the 1CuCe NR catalyst. Furthermore, the peak intensity for the formation of CO₂ at low temperature was much stronger for the 1CuCe NC catalyst than for the 1CuCe NR catalyst. Song et al. [40] proposed that the amount of CO₂ formed directly correlated with the concentration of oxygen present on the surface of the catalyst. This indicated that the content of surface oxygen of the 1CuCe NC catalyst was significantly higher than that of the 1CuCe NR catalyst. Accordingly, these abundant surface oxygen species facilitated the formation of CO₂, and then, the facile desorption of CO₂ contributed to the superior catalytic performance of the 1CuCe NC catalyst compared with that of the 1CuCe NR catalyst. Thus, it was demonstrated that the adsorption of CO significantly depended on the crystal planes of the CeO₂ nanostructures and was favored on the 1CuCe NC with predominantly {100} exposed facets.

3.7. *In situ* DRIFTS analysis of as-prepared catalysts

To gain a more in depth understanding of the CO adsorption mechanism on the as-synthesized 1CuCe NC and 1CuCe NR catalysts, *in situ* DRIFTS spectra were recorded at 30 and 100 °C. According to the literature [41–43], the adsorption bands observed in the ranges of 2200–2140, 2140–2100, and 2100–2000 cm⁻¹ indicated the adsorption of CO on Cu(II), Cu(I)-CO, and Cu(0)-CO sites, respectively. Furthermore, Guo et al. [44] proposed that the CO adsorption peak at 2094 cm⁻¹ should be ascribed to the Cu(I)-CO species and was attributed to the strong interactions between the small copper oxide species and CeO₂ support, while the peak at 2109 cm⁻¹ was attributed to the larger copper oxide clusters.

In our study, the adsorption of CO on the reduced Cu(I) sites (Cu(I)-CO species) was observed at 2103 and 2107 cm⁻¹ for the 1CuCe NC and 1CuCe NR catalysts, respectively (Figs. 7a and 7e). The initial CO adsorption peaks at 2092 and 2096 cm⁻¹ that were observed for the 1CuCe NC and 1CuCe NR catalysts could be ascribed to the small copper oxide species [44] or the shift of the weakly adsorbed oxygen species that attached on the Cu(I) defect sites [30]. The intensity of the CO adsorption bands of the 1CuCe NC catalysts was higher than that of the 1CuCe NR catalyst (Figs. 7a and 7e). The shoulder peak at 2174 cm⁻¹,

which was attributed to gaseous CO was only observed for the 1CuCe NR catalyst. However, no extra peak for gaseous CO was identified for the 1CuCe NC catalyst, which implied the strong carbonyl adsorption on the Cu(I) site [30]. The *in situ* DRIFTS profiles in this study revealed to the adsorption of CO on the Cu(II) sites did not occur for both the 1CuCe NC and 1CuCe NR catalysts. Using previously reported information, it was concluded that the abundant Cu(I)-CO adsorption sites were thermally more stable than the Cu(0) or Cu(II)-CO sites and their presence enhanced the catalytic properties of the material [28,45]. Thus, we considered that the Cu(I)-CO adsorption sites should be the active sites of both the 1CuCe NC and 1CuCe NR catalysts. During the N₂ purging process, the intensities of the carbonyl bands in the *in situ* DRIFTS profiles of the 1CuCe NC and 1CuCe NR catalysts gradually decreased and completely disappeared after 450 s (Figs. 7b and 7f). The CO adsorption abilities during the readsorption steps after N₂ purging were similar to those described in the former CO adsorption steps, that is, the peak intensities in the *in situ* DRIFTS profiles of the 1CuCe NC catalyst were still higher than those of the 1CuCe NR catalyst (Figs. 7c and 7g). Subsequently, the rapidly fading CO adsorption peaks were associated with the O₂ flowing step than the N₂ purging process (Figs. 7d and 7h). This should be ascribed to the increase in the reactivity of the Cu(I)-CO adsorption sites owing to the induction of oxygen gas [46].

To explore the temperature-dependent adsorption behavior of CO, the *in situ* DRIFTS spectra of the 1CuCe NC and 1CuCe NR catalysts were recorded at 100 °C, and the results are presented in Fig. 8. The Cu(I)-CO peaks of both the 1CuCe NC and 1CuCe NR catalysts at 100 °C were much stronger than those detected at 30 °C. These results were in good agreement with the light-off performance of the catalysts. Moreover, the peaks ascribed to the adsorption of CO in the spectra of both catalysts during N₂ and O₂ purging disappeared much faster from the spectra obtained at 100 °C than from the profiles obtained at 30 °C (Fig. 8). These phenomena indicated that the oxidation ability of the adsorbed CO was higher when the temperature was higher, which was in agreement with the CO oxidation activities of the 1CuCe NC and 1CuCe NR catalysts.

3.8. Discussion

Fig. 7. *In situ* diffuse reflectance infrared Fourier-transform spectroscopy profiles of (a)–(d) 1 wt% Cu deposited on CeO_2 nanocubes (1CuCe NC) and (e)–(h) 1 wt% Cu deposited on CeO_2 nanorods (1CuCe NR) catalysts during CO adsorption, N_2 purging, CO readsorption, and O_2 purging, respectively, at 30 $^\circ\text{C}$.

In this study, we attempted to elucidate the mechanism of CO oxidation on the crystal planes of the 1CuCe NC and 1CuCe NR catalysts. Using HRTEM measurements, we established that the 1CuCe NC and 1CuCe NR catalysts presented mainly {100} and {110} exposed planes, respectively (Figs. 1b and 1e). Using the data from the HRTEM, STEM, XRD, and Raman analyses, it was determined that the Cu deposited on the as-prepared catalysts was well-dispersed on the surface of the CeO_2 supports. Moreover, the H_2 -TPR and CO-TPD analyses results demonstrated the superior reducibility and CO chemisorption ability and also the higher amount of surface oxygen of the 1CuCe NC catalyst than that of the 1CuCe NR catalyst toward the formation of Cu(I)-CO species (Fig. 6). Based on the *in situ* DRIFTS profiles (Figs. 7 and 8), the intensities of the CO adsorption peaks of the 1CuCe NC catalyst were significantly higher than those of the 1CuCe NR catalyst, and these results were consistent with their catalytic activities. Combining the *in situ* DRIFTS data with the CO-TPD results, it was concluded that the adsorption of CO on the Cu sites supported on the {100} planes of CeO_2 was favored over the adsorption on the {110} facets of

CeO_2 .

Some recently published papers indicated that CeO_2 NCs and NRs tended to feature {111} exposed facets when they were pretreated via calcination at high temperature [47,48]. Thus, to gain insight into the surface transformation effect, we also investigated the catalytic activity of 1CuCe NC 400-400 and 1CuCe NR 400-400 (Fig. S3). The catalytic performances of 1CuCe NC 400-400 and 1CuCe NC were similar (Fig. S3). By contrast, the CO oxidation properties of 1CuCe NR 400-400 and 1CuCe NR differed significantly. As illustrated in Fig. S3b, the 1CuCe NR 400-400 catalyst presented superior CO oxidation performance and slightly higher activity than the 1CuCe NC 400-400 catalyst at higher temperature (approximately 120 $^\circ\text{C}$). Therefore, we proposed that after calcination, the original crystal planes of the CeO_2 NR could transform into other types of facets, which were difficult to identify [30]. Consequently, we could hypothesize that the effect of surface reconstruction on the catalytic properties was more significant for the CeO_2 NRs than for CeO_2 NCs. The CO chemisorption properties of the 1CuCe NR 400-400 and 1CuCe NC 400-400 catalysts (Fig. S4)

Fig. 8. *In situ* diffuse reflectance infrared Fourier-transform spectroscopy profiles of (a)–(d) 1 wt% Cu deposited on CeO₂ nanocubes (1CuCe NC) and (e)–(h) 1 wt% Cu deposited on CeO₂ nanorods (1CuCe NR) catalysts during CO adsorption, N₂ purging, CO readsorption, and O₂ purging, respectively, at 100 °C.

were consistent with their CO oxidation performance.

The intensities of the CO adsorption peaks in the *in situ* DRIFTS profiles of the 1CuCe NC 400-400 catalyst (Fig. S5) were stronger than those of the 1CuCe NR 400-400 catalyst (Fig. S6). These results were similar to those obtained for the 1CuCe NC and 1CuCe NR catalysts (Figs. 7 and 8, respectively). The catalytic performances of the 1CuCe NC, 1CuCe NR, 1CuCe NC 400-400, and 1CuCe NR 400-400 were in good agreement with the intensities of their CO adsorption peaks obtained using *in situ* DRIFTS measurements and CO-TPD analysis. Moreover, Wu et al. [25] have recently reported that the different IR band intensities of diverse CeO₂ nanostructures appeared to be correlated with their specific surface areas and surface structures [25]. In our study, the 1CuCe NC catalyst presented more intense CO adsorption bands than the 1CuCe NR catalyst despite the lower surface area exposed by NCs compared with that exposed by NRs. These results indicated that A_{BET} was not the most important property that affected catalytic performance. From the XPS and *in situ* DRIFTS results, it was concluded that the presence of abundant Cu(I) sites on the surface of the

1CuCe NC catalyst facilitated the adsorption of CO via the formation of Cu(I)-CO species. Thus, we inferred that CO molecules preferentially adsorbed on the Cu sites of the 1CuCe NC catalyst with predominantly exposed {100} planes than on those of the 1CuCe NR with predominantly {110} exposed surfaces.

4. Conclusions

The facet-dependent CO oxidation properties over 1CuCe NC {100} and 1CuCe NR {110} catalysts have been analyzed using various techniques. Catalytic evaluation studies revealed that 1CuCe NC {100} displayed excellent CO oxidation activity, compared with 1CuCe NR {110}. Consequently, it was demonstrated that the catalytic performance did not correlate with the specific surface area. Using H₂-TPR and CO-TPD analyses, we demonstrated that the excellent reducibility and high concentration of surface oxygen which were attributed to the synergism between Cu and the CeO₂ support contributed to the superior performance of 1CuCe NC. The facet dependence of

the adsorption of CO molecules on abundant reduced Cu(I) sites was investigated using XPS and *in situ* DRIFTS testing, and it was concluded that the adsorption of CO molecules on the abundant reduced Cu(I) sites was the critical factor for the combination with surface oxygen. Therefore, we concluded that the 1CuCe NC catalyst with a large number of exposed {100} facets was much more active for the oxidation of CO than the 1CuCe NR catalyst with {110} exposed surfaces, which was considered to be the most active catalyst among previously reported CeO₂ catalysts of different morphologies.

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Graphical Abstract

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Insights into facet-dependent reactivity of CuO–CeO₂ nanocubes and nanorods as catalysts for CO oxidation reaction

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The presence of abundant Cu(I) site expedites the adsorption of CO on 1CuCe NC {100} owing to the formation of Cu(I)–CO species; consequently, the facile CO₂ desorption contributes to the catalytic performance of 1CuCe NC {100} being superior to that of 1CuCe NR {110}.

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CO氧化反应中的二氧化铈晶面效应

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摘要: 二氧化铈(CeO_2)因其具有较强的储放氧能力, 被用作氧化还原反应的催化材料. 自2005年, 研究者制备出形貌可控的 CeO_2 纳米棒、纳米立方体和纳米多面体, 在 CeO_2 形貌控制及构效关系研究方面取得长足发展. 各种结构表征手段包括原位拉曼(*in situ* Raman)、原位傅里叶变换红外光谱(*in situ* DRIFTS)、核磁共振(NMR)和电镜等被用来研究不同形貌 CeO_2 的表面结构和在催化反应中的活性差异. 一般的活性规律为 CeO_2 纳米棒($\{110\}/\{100\}$) > 纳米立方体($\{100\}$) > 纳米多面体($\{111\}/\{100\}$).

近年来, 负载型 CeO_2 催化剂因其能稳定分散金属, 通过金属-载体相互作用调控界面电子结构并表现出优异的催化活性而引起广泛关注, 其中晶面效应在负载型 CeO_2 催化体系中显得较为复杂. 铜铈催化剂被认为是经济有效的CO氧化催化剂, 然而由于制备和测试条件差异导致的 CeO_2 晶面对铜铈催化剂催化CO氧化活性的影响规律并不统一. 我们之前的研究工作发现纳米棒 CeO_2 - $\{110\}$ 晶面上的 $\text{Cu}-[\text{O}_x]-\text{Ce}$ 结构不利于形成 Cu(I) , 而纳米颗粒 CeO_2 - $\{111\}$ 晶面上的 CuO_x 团簇很容易形成 Cu(I) , 从而对CO催化氧化极为有利, 这与纯载体 CeO_2 的规律并不一致. 与此同时, 对于铜负载的 CeO_2 纳米棒(NR)及纳米立方体(NC)所体现的性质及活性差异缺少系统深入的研究.

在上述工作基础上, 我们采用沉积沉淀法在 CeO_2 NR及 CeO_2 NC上负载1% wt的铜分别得到1CuCe NR和1CuCe NC, 并对所合成催化剂的结构和吸附性能进行了表征. 高分辨透射电镜(HRTEM)照片显示, CeO_2 纳米棒主要暴露 $\{110\}$ 晶面, 而 CeO_2 纳米立方体以 $\{100\}$ 晶面为主. 催化测试结果表明, 1CuCe NC在130 °C时CO已完全转化为 CO_2 , 而相同温度下1CuCe NR只有50%转化. 进一步通过氢气程序升温还原(H_2 -TPR)和一氧化碳程序升温脱附(CO-TPD)分析发现, 1CuCe NC催化剂具有较强的还原性且表面氧化物含量高. 此外, X射线光电子能谱(XPS)和*in situ* DRIFTS研究表明, 1CuCe NC促进 Cu(I) 位点生成, 导致活性 $\text{Cu(I)}-\text{CO}$ 物种增多, 这些优异的化学性质导致其具有较高的催化CO氧化活性.

关键词: $\text{CuO}-\text{CeO}_2$ 催化剂; 晶面效应; CO催化氧化; 氧化还原性质; 活性位

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