available at www.sciencedirect.com

journal homepage: www.elsevier.com/locate/chnjc

Article

Understanding morphology-dependent $\text{CuO}_x\text{-CeO}_2$ interactions from the very beginning

Yuxian Gao ^{a,†}, Zhenhua Zhang ^{b,†}, Zhaorui Li ^a, Weixin Huang ^{a,*}

^a Hefei National Laboratory for Physical Sciences at the Microscale, Key Laboratory of Surface and Interface Chemistry and Energy Catalysis of Anhui Higher Education Institutes, CAS Key Laboratory of Materials for Energy Conversion and Department of Chemical Physics, University of Science and Technology of China, Hefei 230026, Anhui, China

^b Key Laboratory of the Ministry of Education for Advanced Catalysis Materials, Institute of Physical Chemistry, Zhejiang Normal University, Jinhua 321004, Zhejiang, China

ARTICLE INFO

Article history:

Received 20 October 2019

Accepted 29 November 2019

Published 5 June 2020

Keywords:

 CeO_2 nanocrystals $\text{CuO}_x/\text{CeO}_2$ catalysts

Metal-support interactions

CO oxidation

Morphology effect

ABSTRACT

Elucidation of the $\text{CuO}_x\text{-CeO}_2$ interactions is of great interest and importance in understanding complex $\text{CuO}_x\text{-CeO}_2$ interfacial catalysis in various reactions. In the present work, we have investigated structures and catalytic activity in CO oxidation of CuO_x species on CeO_2 rods, cubes and polyhedra predominantly exposing $\{110\}+\{100\}$, $\{100\}$ and $\{111\}$ facets by the incipient wetness impregnation method with the lowest Cu loading of 0.025%. The structural evolution of CuO_x species was found to depend on both the Cu loading and the CeO_2 morphology. As the Cu loading increases, CuO_x species are deposited preferentially on the surface defect of CeO_2 and then aggregate and grow, accompanied by the formation of isolated Cu ions, CuO_x clusters strongly/weakly interacting with the CeO_2 , highly dispersed CuO nanoparticles, and large CuO nanoparticles. The isolated Cu^+ species and CuO_x clusters weakly interacting with the CeO_2 were observed mainly on the O-terminated $\text{CeO}_2\{100\}$ facets. Meanwhile, more Cu(I) species are stabilized during CO reduction processes in $\text{CuO}_x/\text{c-CeO}_2$ catalysts than in $\text{CuO}_x/\text{r-CeO}_2$ and $\text{CuO}_x/\text{p-CeO}_2$ catalysts. The catalytic activities of various $\text{CuO}_x/\text{CeO}_2$ catalysts in CO oxidation vary with both the CuO_x species and the CeO_2 morphology. These results comprehensively elucidate the $\text{CuO}_x\text{-CeO}_2$ interactions and exemplify their morphology-dependence.

© 2020, Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

Published by Elsevier B.V. All rights reserved.

1. Introduction

Copper is used in catalysts for a wide variety of reactions, including CO oxidation, preferential CO oxidation under H_2 -rich steam, water-gas shift, methanol synthesis, and steam reforming [1–6]. CeO_2 , in view of its high oxygen storage capacity (OSC), ready redox cycle, and the ability to firmly anchor copper species from sintering [7–9], has been widely used as the

support, and the resulting $\text{CuO}_x/\text{CeO}_2$ catalysts, in which CuO_x represents all likely copper species (metallic Cu, Cu ions, Cu_2O and CuO) and their mixtures, have exhibited excellent catalytic performances in catalyzing various oxidation reactions of CO [10–16]. For examples, Avgouropoulos *et al.* [10] reported that the catalytic performance of CuO/CeO_2 catalyzed the preferential CO oxidation in excess H_2 was comparable to those of $\text{Pt}/\text{Al}_2\text{O}_3$ and $\text{Au}/\text{Fe}_2\text{O}_3$ catalysts. $\text{CuO}_x/\text{CeO}_2$ catalysts have

* Corresponding author. Tel/Fax: +86-551-63600435; E-mail: huangwx@ustc.edu.cn

[†] These authors contributed equally to this paper.

This work was supported by the National Natural Science Foundation of China (21525313, 21761132005), the Chinese academy of Sciences, and the Changjiang Scholars Program of Ministry of Education of China.

DOI: S1872-2067(19)63503-5 | <http://www.sciencedirect.com/science/journal/18722067> | Chin. J. Catal., Vol. 41, No. 6, June 2020

been demonstrated to be structurally sensitive, particularly in CO oxidation [17–27]. Liu et al. [28] firstly proposed that CO tended to chemisorb at the surface Cu(I) sites stabilized by the CuO-CeO₂ interaction during CO oxidation catalyzed by CuO_x/CeO₂ catalysts. Since then, various factors, such as compositions [22], preparation methods [29,30] and cerium precursors [31], have been investigated in detail to understand structure-activity relationship of CuO/CeO₂ catalysts in CO oxidation.

Recently the morphology of oxide nanocrystals has been demonstrated to strongly affect the oxide-involved catalysis [32–35]. According to the Wulff's rule [36], the morphology of a crystalline particle determines the crystal planes exposed on the surface, subsequently affects the surface compositions and geometric structures. CeO₂ nanocrystals with various types of morphologies, including cubes, octahedra, rods, wires, tubes, and polyhedra [37–42], have been successfully synthesized and used as catalysts and catalyst supports, in which morphology-dependent CeO₂ catalysis, including CuO_x/CeO₂ catalysis, has been well established [17,18,32–34,43–47]. Wang et al. [17] reported that sub-nanometer CuO_x clusters supported on CeO₂{110} facets were less active in catalyzing CO oxidation than those supported on CeO₂{111} facets due to a strongly bound Cu-[O_x]-Ce structure on CeO₂{110} facets. Lykaki et al. [18] employed CeO₂ rods, cubes and polyhedra to investigate the CeO₂ morphology effect on the structure and catalytic activity in CO oxidation of CuO/CeO₂ catalysts with a ~7.5% Cu loading. CuO/CeO₂ rods catalyst exhibited the highest catalytic activity, which was related with its abundance of weakly bound oxygen species, relative population of Cu⁺/Ce³⁺ redox pairs, and relative abundance of defects and oxygen vacancies.

In spite of a lot of previous studies, a comprehensive understanding of CuO_x-CeO₂ interactions still lacks. In this paper, we have prepared CuO_x/CeO₂ catalysts with Cu loadings of 0.025%–5% employing CeO₂ rods, cubes and polyhedra by the incipient wetness impregnation method. CeO₂ morphology-dependent structural evolutions of CuO_x species in various CuO_x/CeO₂ catalysts have been identified and correlated to the catalytic activity in CO oxidation. These results comprehensively elucidate the CuO_x-CeO₂ interactions and structure-activity relationship of CuO_x/CeO₂ catalysts.

2. Experimental

All chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd. and used without further purification. Commercial CeO₂ polyhedral nanoparticles (denoted as p-CeO₂) were purchased from Sigma Aldrich. 1% CO/Air, 5% H₂/Ar, 1% CO/Ar, Ar (99.999%), and 1% CO/Ar were purchased from Nanjing Shangyuan Industrial Factory and used without further purification. Ultrapure water (resistance > 18.5 MΩ) was used.

2.1. Catalyst synthesis

CeO₂ cubes (denoted as c-CeO₂) and rods (denoted as r-CeO₂) were synthesized followed the Mai et al.'s procedure [16]. In the typical method, 1.96 g Ce(NO₃)₃·6H₂O and 16.88 g

NaOH were respectively dissolved in 40 and 30 mL ultrapure water. Next the NaOH solution was added dropwise into the Ce(NO₃)₃ solution under continual stirring at room temperature. The acquired solution was stirred at room temperature for an additional 0.5 h and then transferred into a 100-mL Teflon bottle. The Teflon bottle was tightly sealed and hydrothermally treated in a stainless-steel autoclave at a desired temperature for 24 h (100 °C for cubes and 180 °C for rods). After cooling down to room temperature, the acquired precipitate was collected and washed with ultrapure water for 5 times and then dried in vacuum at 80 °C for 16 h. The final solid powder was calcined in a muffle oven at 500 °C for 4 h to synthesis CeO₂ cubes and rods.

The CuO_x/CeO₂ catalysts were prepared by a conventional incipient wetness impregnation method. Typically, the desired amount of Cu(NO₃)₂ solution was added dropwise to 0.3 g CeO₂ powders and ultrasonicated for 10 min at room temperature. Afterwards, the sample was kept at room temperature for 24 h and then dried at 80 °C for 12 h to obtain the catalyst precursor. The acquired catalyst precursor was calcined in a muffle oven at 500 °C for 2 h to synthesis the CuO_x/CeO₂ catalyst. The Cu loading (0.025–5 wt%) is adjusted by changing the concentration of added Cu(NO₃)₂ solution, and the acquired CuO_x/CeO₂ catalysts are denoted as x-CuO_x/b-CeO₂, in which 'x' represents the calculated Cu loading.

2.2. Catalyst characterization

The Cu loadings of various CuO_x/CeO₂ catalysts were determined by using a PerkinElmer Optima 7300 DV inductively coupled plasma atomic emission spectrometer (ICP-AES). BET specific surface areas of various CeO₂ morphologies were measured by using a Beckman Coulter SA3100 surface area analyzer. Before the measurement, the sample was first degassed at 300 °C for 5 h in a N₂ atmosphere. Power X-ray diffraction (XRD) patterns were conducted by using a Philips X'Pert PRO diffractometer using a nickel-filtered Cu K_α (λ = 0.15418 nm) radiation source with the operation voltage of 40 kV and operation current of 40 mA. X-ray photoelectron spectroscopy (XPS) measurements were performed by using an ESCALAB 250 high-performance electron spectrometer using monochromatized Al K_α (hν = 1486.7 eV) as the excitation source. The likely charging of samples was corrected by setting the binding energy of the adventitious carbon (C 1s) to 284.8 eV. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were obtained on a JEM-2100F high resolution transmission electron microscope with the electron acceleration energy of 200 kV. Visible Raman spectra were recorded in back-scattering configuration by using a LABRAM-HR Confocal Laser Raman spectrometer. Ar⁺ (514.5 nm) laser was employed as the excitation source.

H₂-TPR and CO-TPR experiments were performed by using a Micromeritics ChemiSorb 2750 instrument, in which 50 mg fresh sample was put into the U-shaped quartz microreactor and then heated at a rate of 10 °C·min⁻¹ with a flow rate of 20 mL·min⁻¹ in 5% H₂/Ar and 1% CO/Ar, respectively. The con-

sumptions of H_2 and CO were recorded by TCD and mass spectra (MS), respectively. X-ray absorption spectra (XAS) was conducted on the 14W1-XAFS beamline at Shanghai Synchrotron Radiation Facility (SSRF) operating at 3.5 GeV under “top-up” mode with a constant current of 220 mA.

In-situ diffuse reflectance infrared Fourier transformed spectroscopy (DRIFTS) of CO adsorption experiments were conducted on a Nicolet 6700 FT-IR spectrometer equipped with an in situ high-temperature reaction cell (Harrick Scientific Products, Inc.) in series mode with 256 scans and a resolution of 4 cm^{-1} with an MCT/A detector. 100 mg fresh samples were loaded on the sample stage of the reaction cell and purged with Ar at room temperature for 0.5 h. The backgrounds at different temperatures were first recorded under Ar atmosphere. For CO adsorptions, 1% CO/Air was purged into the reaction cell at different temperatures and kept for 0.5 h to reach the stable state. Subsequently, the DRIFTS spectrum was recorded.

2.3. Catalyst activity measurement

The catalytic activities of various CeO_2 and CuO_x/CeO_2 catalysts for the CO oxidation were evaluated with a fixed-bed flow reactor. 50 mg as-synthesized sample diluted with 50 mg SiO_2 was used and the catalytic reaction was conducted with the reaction gas that consisted of 1% CO/Air fed at a rate of $30\text{ mL}\cdot\text{min}^{-1}$. The sample was heated to the desired temperatures at a rate of $2\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ and kept at this temperature for 0.5 h until the catalytic reaction reached the steady state. The composition of the effluent gas was tested by an online GC-14 gas chromatograph. The CO conversion was calculated from the change in CO concentrations of the inlet and outlet gases.

3. Results and discussion

Representative TEM images of r- CeO_2 , c- CeO_2 and p- CeO_2 (Fig. 1 (A1)-(C1)) are similar to those previously reported

Fig. 1. Representative TEM images of r- CeO_2 (A1), c- CeO_2 (B1), and p- CeO_2 (C1); Representative TEM and HRTEM images of 5%- $CuO_x/r-CeO_2$ (A2, A3), 5%- $CuO_x/c-CeO_2$ (B2, B3), and 5%- $CuO_x/p-CeO_2$ (C2, C3) catalysts. Lattice fringes of 1.95–1.97, 2.69–2.71, and 3.11–3.13 Å respectively correspond to the spacing of $CeO_2\{220\}$, $CeO_2\{200\}$, and $CeO_2\{111\}$ (JCPDS 34-0394) crystal planes.

[43–47] in which r- CeO_2 , c- CeO_2 and p- CeO_2 were proposed to $\{110\}+\{100\}$, $\{100\}$ and $\{111\}$ facets, respectively. Corresponding XRD patterns of r- CeO_2 , c- CeO_2 , and p- CeO_2 (Fig. 2(A)) display typical diffraction peaks arising from the cubic fluorite phase structure of CeO_2 (JCPDS card No. 34-0394). The specific surface area was measured to be 69, 23 and $60\text{ m}^2/\text{g}$ for r- CeO_2 , c- CeO_2 , and p- CeO_2 , respectively.

The actual Cu loadings of CuO_x/CeO_2 catalysts were determined by ICP-AES (Table S1) to be very close to the calculated values. Figs. 1(A2)-(C2) and (A3)-(C3) show representative TEM and HRTEM images of various 5%- CuO_x/CeO_2 catalysts. CeO_2 nanocrystals in various 5%- CuO_x/CeO_2 catalysts retain their original morphologies quite well. The identified lattice fringes of 0.19, 0.27, and 0.31 nm in the HRTEM images of all the 5%- CuO_x/CeO_2 catalysts match with the spacing of $CeO_2\{220\}$, $\{200\}$ and $\{111\}$ crystal planes, respectively, while no Cu-associated lattice fringes can be observed. This could be due to the similar contrasts of CuO_x and CeO_2 under HRTEM mode and/or the high dispersion of CuO_x species on CeO_2 even at a Cu loading of 5 wt%.

Fig. 2(A) shows XRD patterns of various CuO_x/CeO_2 catalysts. No diffraction pattern of any likely CuO_x species could be observed in all the CuO_x/CeO_2 catalysts with the Cu loadings below 5%, suggesting the high dispersions of supported CuO_x species. The enlarged XRD patterns show weak $CuO(-111)$ and (111) diffraction peaks in the 5%- $CuO_x/c-CeO_2$ and 5%- $CuO_x/p-CeO_2$ catalysts but not in the 5%- $CuO_x/r-CeO_2$ catalyst, indicating a higher dispersion of CuO_x species on r- CeO_2 . The poorer dispersion of CuO_x on c- CeO_2 and p- CeO_2 can be likely attributed to the small specific surface area of c- CeO_2 and the relatively weak CuO_x interaction with the $CeO_2\{111\}$ facets exposed on p- CeO_2 , respectively.

Fig. 2. (A) XRD patterns of various CeO_2 and CuO_x/CeO_2 catalysts; (B) Cu K-edge XANES and their corresponding differentiated spectra (C) of various CuO_x/CeO_2 catalysts. Reference spectra of Cu, $Cu(NO_3)_2$, Cu_2O , and CuO are also included.

The nature of supported CuO_x species in various $\text{CuO}_x/\text{CeO}_2$ catalysts was examined by XAS. As shown in Fig. 2(B), the Cu K -edge XANES spectra of the CuO_x species supported on CeO_2 with different morphologies are quite similar. However, their corresponding differentiated spectra (Fig. 2(C)) show obvious differences. At the lowest Cu loading of 0.025%, 0.025%- $\text{CuO}_x/\text{c-CeO}_2$ catalyst exhibits a dominant Cu^+ feature while 0.025%- $\text{CuO}_x/\text{r-CeO}_2$ and 0.025%- $\text{CuO}_x/\text{p-CeO}_2$ catalysts exhibit dominant isolated Cu^{2+} species. These results demonstrate the dominance of isolated Cu ions in 0.025%- $\text{CuO}_x/\text{CeO}_2$ catalysts, but the Cu^{2+} precursor gets reduced into Cu^+ when supported on c- CeO_2 but not on r- CeO_2 and p- CeO_2 . This indicates the preferential occurrence of redox reaction between the Cu^{2+} precursor and the Ce^{3+} species associated with surface oxygen vacancies on c- CeO_2 during the catalyst preparation process. Similar redox reactions were observed to occur between the Nb^{5+} precursor and the Ce^{3+} species on c- CeO_2 and r- CeO_2 to produce the Nb^{4+} species [45,46] and between the Pd^{2+} precursor and the Ce^{3+} species created by surface reduction on p- CeO_2 to produce the $\text{Pd}(0)$ species [48]. Thus, c- CeO_2 exhibits much more Ce^{3+} species and associated surface oxygen vacancies that are capable of reducing the Cu^{2+} precursor than r- CeO_2 and p- CeO_2 , which should be related to the exclusive O-terminated $\text{CeO}_2\{100\}$ facets exposed on c- CeO_2 . The feature of isolated Cu^{2+} species dominates in the spectra of all three 0.05%- $\text{CuO}_x/\text{CeO}_2$ catalysts, and the CuO signal appears in the spectra of 0.1%- $\text{CuO}_x/\text{CeO}_2$ catalysts and further grows in the spectra of 0.5%- $\text{CuO}_x/\text{CeO}_2$ catalysts. These Cu K -edge XANES results demonstrate that as the Cu loading increases, the CuO_x species evolves from the isolated Cu^{2+} ions to the CuO species in $\text{CuO}_x/\text{r-CeO}_2$ and $\text{CuO}_x/\text{p-CeO}_2$, and from the isolated Cu^+ ions to the isolated Cu^{2+} ions and then the CuO species in $\text{CuO}_x/\text{c-CeO}_2$.

XPS was also used to characterize the CuO_x species in $\text{CuO}_x/\text{CeO}_2$ catalysts. Only the $\text{CuO}_x/\text{CeO}_2$ catalysts with the Cu loadings not lower than 0.5% show visible Cu $2p$ XPS spectra (Fig. 3). The Cu $2p_{3/2}$ binding energy of the CuO_x species locates at 934 eV in 0.5%- $\text{CuO}_x/\text{CeO}_2$ and 1%- $\text{CuO}_x/\text{CeO}_2$ catalysts and then shifts to 933.5 eV in 5%- $\text{CuO}_x/\text{CeO}_2$ catalysts. The CuO_x species with the Cu $2p_{3/2}$ binding energies at 934 and 933.5 eV can be assigned to the supported highly dispersed CuO clusters and large CuO nanoparticles, respectively [49–51]. These XPS results demonstrate the evolutions of the CuO_x species from highly dispersed CuO clusters to large CuO nanoparticles with

Fig. 3. Cu $2p$ XPS spectra of 0.5%- $\text{CuO}_x/\text{CeO}_2$ (A), 1%- $\text{CuO}_x/\text{CeO}_2$ (B), and 5%- $\text{CuO}_x/\text{CeO}_2$ (C) catalysts.

the increase of Cu loading from 0.5% to 5% in $\text{CuO}_x/\text{CeO}_2$ catalysts.

Fig. 4 shows Raman spectra of various CeO_2 and $\text{CuO}_x/\text{CeO}_2$ catalysts excited by lasers with the wavelength of 514.5 nm. A strong peak at 463–464 cm^{-1} and two weak peaks at 596 and 1176–1182 cm^{-1} were observed, corresponding to the F_{2g} , defect-induced mode (D), and second-order longitudinal modes of the cubic CeO_2 fluoride phase, respectively [52–54]. The $I_D/I_{F_{2g}}$ ratios were calculated to estimate the defect concentrations of CeO_2 in the $\text{CuO}_x/\text{CeO}_2$ catalysts. Fig. 4D shows the variations of $I_D/I_{F_{2g}}$ ratios of CeO_2 in the $\text{CuO}_x/\text{CeO}_2$ catalysts as a function of Cu loadings. The $I_D/I_{F_{2g}}$ ratio follows the order of r- $\text{CeO}_2 \approx$ c- $\text{CeO}_2 >$ p- CeO_2 , consistent with the previously reported results [44]. The supported CuO_x species strongly affect the $I_D/I_{F_{2g}}$ ratio of CeO_2 in $\text{CuO}_x/\text{CeO}_2$ catalysts. The $I_D/I_{F_{2g}}$ ratios of r- CeO_2 in $\text{CuO}_x/\text{r-CeO}_2$ catalysts and p- CeO_2 in $\text{CuO}_x/\text{p-CeO}_2$ catalysts decrease with the increase of Cu loading up to 0.05%, but then keep growing with the further increase of Cu loading. The $I_D/I_{F_{2g}}$ ratio of c- CeO_2 in $\text{CuO}_x/\text{c-CeO}_2$ catalysts decrease with the increase of Cu loading up to 0.1%, but then keep growing with the further increase of Cu loading. Comparing the evolution of the CuO_x species in $\text{CuO}_x/\text{CeO}_2$ catalysts, it can be deduced that the loading of isolated Cu ions on CeO_2 should decrease the density of defects while the loading of CuO species should create more defects. Furthermore, for various 5%- $\text{CuO}_x/\text{CeO}_2$ catalysts, the surface concentrations of oxygen vacancies are all increase significantly, indicating that big CuO nanoparticles, which have been proved spectroscopically, interacting with CeO_2 tremendously promotes the generation of surface defects. Thus, the isolated Cu ions seem to preferential-

Fig. 4. Visible Raman spectra of r- CeO_2 and various $\text{CuO}_x/\text{r-CeO}_2$ catalysts (A), c- CeO_2 and various $\text{CuO}_x/\text{c-CeO}_2$ catalysts (B), and p- CeO_2 and various $\text{CuO}_x/\text{p-CeO}_2$ catalysts (C); (D) The relevance of the $I_D/I_{F_{2g}}$ ratio to Cu loading on various CeO_2 and $\text{CuO}_x/\text{CeO}_2$ catalysts.

ly deposit at the defective sites of CeO_2 , likely the surface oxygen vacancies.

Fig. 5 shows H_2 -TPR profiles of various CeO_2 and $\text{CuO}_x/\text{CeO}_2$ catalysts. The CeO_2 nanocrystals (Fig. 5(A)) show typical surface reduction peaks (denoted as α peak) whose peak areas follow an order of $r\text{-CeO}_2 > p\text{-CeO}_2 > c\text{-CeO}_2$, agreeing with their specific BET surface areas. The loading of CuO_x species greatly promotes the reduction of CeO_2 , as demonstrated by the shift of the CeO_2 surface reduction peaks to the low temperatures, and such promotion effects depend on the nature of CuO_x species [55]. Meanwhile, additional reduction features related to the reduction of supported CuO_x species appear. Based on the reduction behaviors in the H_2 -TPR profiles, five types of supported CuO_x species on CeO_2 have been proposed [18,29,56–59], including isolated Cu ions (denoted as β peak), CuO_x clusters weakly interacting with the support (denoted as γ peak), CuO_x clusters strongly interacting with the support (denoted as δ peak), highly dispersed CuO nanoparticles (denoted as η peak), and large CuO nanoparticles (denoted as σ peak).

As shown in Fig. 5 B–H, the H_2 -TPR profiles of $\text{CuO}_x/\text{CeO}_2$ catalysts depend on the CeO_2 morphology. In $\text{CuO}_x/c\text{-CeO}_2$ catalysts, the reduction peaks are composed of $\alpha+\beta$ peak and shift gradually to the low temperature with the Cu loading increasing up to 0.1%. A sharp reduction peak emerges at 270 °C at 0.1% Cu loading and is composed of $\alpha+\delta$ peak since it is accompanied by the obvious weakening of α peak. This indicates that supported CuO_x clusters strongly interacting with CeO_2 are more capable of promoting the surface reduction of CeO_2 than supported isolated Cu ions. Notably, a very weak reduction peak locating at 150 °C also appears and is assigned to the γ peak [59] in which the involved Cu_xO clusters were proposed to weakly interact with surface oxygen species on CeO_2 . When the Cu loading reaches 0.2%, the $\alpha+\delta$ reduction peak further grows while the original α reduction peak at high temperature completely disappears. The $\alpha+\delta$ reduction peak shifts to low tem-

perature and saturates at 0.5% Cu loading, and the η peak corresponding to the reduction of highly dispersed CuO nanoparticles appears at lower temperatures than the $\alpha+\delta$ reduction peak and grows with the Cu loading, while the σ peak corresponding to the reduction of large CuO nanoparticles appears at higher temperatures than the $\alpha+\delta$ reduction peak at 5% Cu loading. Interestingly, a negative peak appears on $\text{CuO}_x/\text{CeO}_2$ catalysts with the Cu loading no more than 0.5%, especially on the catalysts with $p\text{-CeO}_2$ as support, which can be reasonably ascribed the reaction of hydroxyl groups on CeO_2 surface to produce H_2 at high temperature [60].

Similar reduction peaks were also observed in the H_2 -TPR profiles of $\text{CuO}_x/r\text{-CeO}_2$ and $\text{CuO}_x/p\text{-CeO}_2$ catalysts, but evolved in different ways. The most obvious difference is that the α reduction peak can remain in $\text{CuO}_x/p\text{-CeO}_2$ and $\text{CuO}_x/r\text{-CeO}_2$ catalysts up to the Cu loading of 0.2% but in $\text{CuO}_x/c\text{-CeO}_2$ catalysts up to 0.05%. This indicates that supported CuO_x species on $c\text{-CeO}_2$ should be more extensively promote the surface reduction of CeO_2 than those on $r\text{-CeO}_2$ and $p\text{-CeO}_2$. This could be likely related with the much smaller surface area of $c\text{-CeO}_2$ than $r\text{-CeO}_2$ and $p\text{-CeO}_2$. Another noteworthy difference is that the very weak γ reduction observed firstly in 0.1%- $\text{CuO}_x/c\text{-CeO}_2$ does not appear for all $\text{CuO}_x/p\text{-CeO}_2$ catalysts and for $\text{CuO}_x/r\text{-CeO}_2$ catalysts till the Cu loading of 1%. On one hand, this indicates the formation of Cu_xO clusters weakly interacting with surface oxygen species mainly on O-terminated $\text{CeO}_2\{100\}$ facets exposed on $c\text{-CeO}_2$ but barely on the (Ce, O)-terminated $\text{CeO}_2\{111\}$ and $\{110\}$ facets. On the other hand, this indicates that the CuO_x species is preferentially deposited on the $\{110\}$ facets of $r\text{-CeO}_2$ and then on the $\{100\}$ facets.

Various CeO_2 and $\text{CuO}_x/\text{CeO}_2$ catalysts were also characterized by CO-TPR (Fig. 6). It can be seen that the reduction of CeO_2 by CO is easier than by H_2 . This can be attributed to the fact that CO only needs molecular adsorption to reduce CeO_2

Fig. 5. H_2 -TPR profiles of various CeO_2 and $\text{CuO}_x/\text{CeO}_2$ catalysts.

Fig. 6. CO-TPR profiles of various CeO₂ and CuO_x/CeO₂ catalysts.

while H₂ needs to dissociatively adsorb to reduce CeO₂. Three main reduction peaks appear at 350, 475, and 700 °C, corresponding to the reductions of surface CeO₂ (denoted as α peak), surface hydroxyl groups on CeO₂, and bulk CeO₂, respectively [61]. In addition, p-CeO₂ displays a sharp reduction peak at 180 °C, which could be related with the reduction of oxygen species adsorbed on p-CeO₂ surface. This suggests that although mainly exposing the {111} facets, p-CeO₂ has certain amount of defective sites capable of adsorbing oxygen, likely relevant to the presence of particles with irregular shapes. The loading of CuO_x species promotes the reduction of CeO₂ by CO, and the reduction peaks of various CuO_x species, including isolated Cu ions (denoted as β peak), CuO_x clusters weakly interacting with the support (denoted as γ peak), CuO_x clusters strongly interacting with the support (denoted as δ peak), highly dispersed and large CuO nanoparticles (denoted as η peak), appear in order in the CO-TPR profiles [62,63].

One interesting observation is that the initial reduction rates of CuO_x/r or c or p-CeO₂ catalysts vary with the Cu loadings. They are highest for CuO_x/p-CeO₂ catalysts with the Cu loadings up to 0.1%, due to the weakest interaction between dominant isolated Cu ions with the CeO₂{111} facets exposed on p-CeO₂; and they are highest for CuO_x/c-CeO₂ catalysts of the Cu loadings with 0.2% and 0.5%, consistent with the appearance of CuO_x clusters weakly interacting with the support in CuO_x/c-CeO₂ catalysts; and they are highest for CuO_x/r-CeO₂ catalysts of the Cu loadings with 1% and 5%, suggesting that the CuO nanoparticles are most facily reduced on r-CeO₂.

Another interesting observation is that the low-temperature reduction peak areas of CuO_x/c-CeO₂ catalysts below 200 °C are much smaller than those of CuO_x/r-CeO₂ and CuO_x/p-CeO₂ catalysts with similar Cu loadings. This can be attributed to the dominant Cu⁺ species in CuO_x/c-CeO₂ catalysts with low Cu loadings whose consumption of CO is less than that of Cu²⁺ dominant in CuO_x/r-CeO₂ and CuO_x/p-CeO₂ catalysts, and as

demonstrated below, to the low-temperature reduction of CuO nanoparticles mainly to Cu⁺ species in CuO_x/c-CeO₂ catalysts with high Cu loadings but mainly to Cu(0) in CuO_x/r-CeO₂ and CuO_x/p-CeO₂ catalysts. The Cu⁺ intermediate in CuO_x/c-CeO₂ catalysts is further reduced by CO at elevated temperatures. This indicates that the Cu⁺ species interacts more strongly with the CeO₂{100} facets exposed on c-CeO₂ and is subsequently more stable than with the CeO₂{110} and {111} facets respectively exposed on r-CeO₂ and p-CeO₂.

Fig. 7 shows in situ DRIFTS spectra of CO adsorption on various CuO_x/CeO₂ catalysts at different temperatures. It is well established that the CO only adsorb at the Cu⁺ site but barely at the Cu²⁺ and Cu(0) sites at room temperature and above [64]. No CO adsorption could be observed on the CuO_x/CeO₂ catalysts with the Cu loadings below 0.05%, likely due to the very weak signals beyond the detection sensitivity of the employed IR spectrometer. For the CuO_x/CeO₂ catalysts with the Cu loadings no less than 0.05%, reductions of supported CuO_x species occur during CO adsorption processes, giving the vibrational features of adsorbed CO dependent both on the CeO₂ morphologies and adsorption temperatures. Totally two vibrational features of adsorbed CO were observed at 2099–2103 and 2091–2095 cm⁻¹, which were previously assigned to CO adsorbed at the Cu⁺ species derived from the CuO_x clusters strongly interacting with CeO₂ or highly dispersed CuO nanoparticles and at the Cu⁺ species derived from the CuO_x clusters weakly interacting with CeO₂, previously [23,50,65–67].

At a Cu loading of 0.05%, CO adsorption peak appears at 2099–2103 cm⁻¹ only at 150 °C, indicating the occurrence of reduction of CuO_x clusters strongly interacting with CeO₂ into Cu⁺ at this temperature, consistent with the CO-TPR results. At a Cu loading of 0.1%, this peak appears obviously at 100 °C for CuO_x/c-CeO₂, much weaker for CuO_x/p-CeO₂ and does not appear for CuO_x/r-CeO₂. The CO adsorption peak significantly grows at 150 °C, demonstrating a more extensive reduction of

Fig. 7. In situ DRIFTS results of CO adsorption on various $\text{CuO}_x/\text{CeO}_2$ catalysts at 30 °C (black), 100 °C (red), and 150 °C (blue).

supported CuO_x species into Cu^+ . These observations suggest that the interaction of CuO_x clusters with various CeO_2 surfaces follows an order of $\text{CeO}_2\{110\}$ facets exposed on r- CeO_2 > $\text{CeO}_2\{111\}$ facets exposed on p- CeO_2 > $\text{CeO}_2\{100\}$ facets exposed on c- CeO_2 .

An obvious CO adsorption peak at 2095 cm^{-1} appears for CO adsorption on 0.2%- $\text{CuO}_x/\text{c-CeO}_2$ at RT but not on 0.2%- $\text{CuO}_x/\text{r-CeO}_2$ and 0.2%- $\text{CuO}_x/\text{p-CeO}_2$, corresponding to the facile reduction of CuO_x clusters weakly interacting with the support that only forms in $\text{CuO}_x/\text{c-CeO}_2$ catalysts. An additional much stronger CO adsorption peak appears at 2103 cm^{-1} for CO adsorption on 0.2%- $\text{CuO}_x/\text{c-CeO}_2$ at 100 °C. This feature also appears for CO adsorption on 0.2%- $\text{CuO}_x/\text{r-CeO}_2$ and 0.2%- $\text{CuO}_x/\text{p-CeO}_2$ at 100 °C, but with much weaker intensities.

The CO adsorption behavior on 0.5%- $\text{CuO}_x/\text{c-CeO}_2$ is similar to that on 0.2%- $\text{CuO}_x/\text{c-CeO}_2$. On 1%- $\text{CuO}_x/\text{c-CeO}_2$, CO adsorption at RT gives a strong peak at 2095 cm^{-1} . This strong peak should arise from CO adsorption at the Cu^+ species derived from the highly dispersed CuO nanoparticles, instead of from the CuO_x clusters weakly interacting with CeO_2 observed in the case of 0.2%- $\text{CuO}_x/\text{c-CeO}_2$ and 0.5%- $\text{CuO}_x/\text{c-CeO}_2$. Thus we tend to assign the feature at 2095 cm^{-1} herein to CO adsorbed at the Cu^+ site coexisting with CuO, i.e., the partially reduced CuO. Our assignment is supported by the observation that the vibrational feature shifts to 2103 cm^{-1} upon CO adsorption at 100 °C at which temperature supported CuO nanoparticles are more extensively reduced than at RT. The vibrational feature at 2095 cm^{-1} also appear for CO adsorption at RT on 0.5%&1%- $\text{CuO}_x/\text{r-CeO}_2$ and 0.5%&1%- $\text{CuO}_x/\text{p-CeO}_2$ that contain few CuO_x clusters weakly interacting with the support. When the adsorption temperature increases to 100 °C, this feature almost disappears and a strong peak appears at 2099–2102 cm^{-1} , indicating the reduction of more extensive reduction of the highly dispersed CuO nanoparticles.

It can be seen from Fig. 7 that the intensity of CO vibrational peaks for CO adsorption at adopted temperatures always follow an order of $\text{CuO}_x/\text{c-CeO}_2 \gg \text{CuO}_x/\text{p-CeO}_2 \gg \text{CuO}_x/\text{r-CeO}_2$; however, the reduction peak at the same temperature ranges in the CO-TPR profiles is weakest for $\text{CuO}_x/\text{c-CeO}_2$ (Fig. 6). These results suggest that the fraction of the reduction of supported CuO_x species into Cu^+ below 150 °C follows an order of

$\text{CuO}_x/\text{c-CeO}_2 \gg \text{CuO}_x/\text{p-CeO}_2 \gg \text{CuO}_x/\text{r-CeO}_2$ while the fraction of the reduction of supported CuO_x species into $\text{Cu}(0)$ follows a reverse order of $\text{CuO}_x/\text{c-CeO}_2 \ll \text{CuO}_x/\text{p-CeO}_2 \ll \text{CuO}_x/\text{r-CeO}_2$. These results suggest that the $\text{Cu}^{2+}\text{-CeO}_2(100)$ (c- CeO_2) interaction is weaker than the $\text{Cu}^+\text{-CeO}_2(100)$ (c- CeO_2) interaction so that the Cu^+ intermediate can be stabilized during the reduction of Cu^{2+} by CO, whereas the $\text{Cu}^{2+}\text{-CeO}_2(110)$ (r- CeO_2) interaction is stronger than the $\text{Cu}^+\text{-CeO}_2(100)$ (c- CeO_2) interaction so that the Cu^{2+} is reduced to $\text{Cu}(0)$ by CO.

CO oxidation was used as a probe reaction to investigate the catalytic performance of various CeO_2 and $\text{CuO}_x/\text{CeO}_2$ catalysts. As shown in Fig. 8, the relative catalytic activities among CeO_2 and $\text{CuO}_x/\text{CeO}_2$ catalysts vary with both the Cu loading and the CeO_2 morphology. p- CeO_2 and $\text{CuO}_x/\text{p-CeO}_2$ catalysts are most active among bare CeO_2 and $\text{CuO}_x/\text{CeO}_2$ catalysts with Cu loadings up to 0.1%; $\text{CuO}_x/\text{c-CeO}_2$ catalysts are most active among $\text{CuO}_x/\text{CeO}_2$ catalysts with Cu loadings up of 0.2% and 0.5%; $\text{CuO}_x/\text{r-CeO}_2$ catalysts are most active among $\text{CuO}_x/\text{CeO}_2$ catalysts with Cu loadings no less than 1%. Similar results were also previously reported [18,67]. We found that the orders of catalytic activities of various catalysts with different CeO_2 morphologies follow very well with those of their corresponding initial reduction rates in CO-TPR profiles (Fig. 7). Thus CO oxidation over CeO_2 and $\text{CuO}_x/\text{CeO}_2$ catalysts follows the MvK mechanism, which has been well documented in the literatures [17–27]. The catalytic activities of 0.025%- $\text{CuO}_x/\text{CeO}_2$ and 0.05%- $\text{CuO}_x/\text{CeO}_2$ catalysts are relatively lower than those of bare CeO_2 , ascribed to the decrease of surface oxygen defects (Fig. 4). These results also demonstrate that CO oxidation catalyzed by $\text{CuO}_x/\text{CeO}_2$ catalysts is sensitive to both Cu and CeO_2 structures.

The Arrhenius plots of CO oxidation catalyzed by various CeO_2 and $\text{CuO}_x/\text{CeO}_2$ catalysts were plotted in order to gain insight into the active structure of various $\text{CuO}_x/\text{CeO}_2$ catalysts (Figs. S1–S3), from which the apparent activation energy (E_a) and apparent pre-exponential factor ($\ln(A)$) values, respectively relating to the intrinsic activity and the density of active sites, were derived and summarized (Tables S2–S4). The $\ln(A)$ increases with the Cu loading, particularly, it increases are linearly related with the Cu loading for $\text{CuO}_x/\text{CeO}_2$ catalysts with similar E_a (Fig. S4). However, the E_a changes in a complex way

Fig. 8. Catalytic performance of various CeO_2 and $\text{CuO}_x/\text{CeO}_2$ catalysts in the CO oxidation.

along with the nature of supported CuO_x species. Fig. 9 shows the variations of E_a as a function of the Cu loadings and corresponding supported CuO_x species. It can be seen that the E_a of $\text{CuO}_x/\text{CeO}_2$ catalysts with supported isolated Cu ions, except 0.05%- $\text{CuO}_x/\text{c-CeO}_2$, does not vary much from that of corresponding CeO_2 catalysts, implying that their active structures contributing to the catalytic activity remain as CeO_2 while the supported isolated Cu ions should act as spectators.

The E_a of $\text{CuO}_x/\text{CeO}_2$ catalysts with supported CuO_x clusters and CuO particles is obviously larger than that of CeO_2 , indicating that their active structures contributing to the catalytic activity should be the $\text{CuO}_x\text{-CeO}_2$ interface. In $\text{CuO}_x/\text{r-CeO}_2$ catalysts, the E_a keeps increasing as the supported Cu species evolves from supported CuO_x clusters to supported highly-dispersed CuO nanoparticles and then supported CuO nanoparticles. In $\text{CuO}_x/\text{c-CeO}_2$ catalysts, the E_a remains similar for the Cu loadings of 0.05%–0.2%, and then increases to similar values for the Cu loadings of 0.5%–5%. These observations indicate that although with different supported CuO_x species, the dominant active structures in 0.05–0.2%- $\text{CuO}_x/\text{c-CeO}_2$ catalysts and in 0.5–5%- $\text{CuO}_x/\text{c-CeO}_2$ catalysts are the same, respectively as supported CuO_x clusters- CeO_2 interface and sup-

ported CuO nanoparticles- CeO_2 interface. Therefore, the isolated Cu^+ species dominant in as-prepared 0.5%- $\text{CuO}_x/\text{c-CeO}_2$ catalyst likely restructures into supported CuO_x clusters during CO oxidation. In $\text{CuO}_x/\text{p-CeO}_2$ catalysts, the E_a keeps increasing as the supported Cu species evolves from supported CuO_x clusters to supported highly-dispersed CuO nanoparticles but then decreases with the formation of supported CuO nanoparticles. These results reveal the complex $\text{CuO}_x\text{-CeO}_2$ interfacial catalysis in CO oxidation.

In the $\text{CuO}_x\text{-CeO}_2$ interfacial catalysis in CO oxidation, a key step is the formation of CO_2 by the reaction of CO adsorbs at the Cu^+ sites derived from the reduction of CuO_x species with surface lattice oxygen of CeO_2 [19]. The E_a is mainly determined the reactivity of surface lattice oxygen of CeO_2 , i.e., the reducibility of CeO_2 , while the $\ln A$ is mainly determined by the density of $\text{Cu}^+\text{-CeO}_2$ interface. The $\ln A$ reasonably increases with the Cu loading; however, the general observations that the E_a increases with the Cu loading suggests that the intrinsic reactivity of surface lattice oxygen of CeO_2 should be suppressed by the loading of CuO_x . Such a suppressing effect not only depends on the nature of various CuO_x species that follows an order of as $\text{CuO nanoparticles} > \text{CuO}_x \text{ clusters} > \text{isolated Cu ions}$, but also

Fig. 9. The relevance of the calculated E_a value and Cu loading/structure of CuO_x species on $\text{CuO}_x/\text{r-CeO}_2$ (A), $\text{CuO}_x/\text{c-CeO}_2$ (B), and $\text{CuO}_x/\text{p-CeO}_2$ (C) catalysts.

vary with the morphology and surface structures of CeO₂.

4. Conclusions

In summary, employing CuO_x/CeO₂ catalysts with different CeO₂ morphologies (rods, cubes and polyhedra) and Cu loadings (0.025%–5%) prepared by incipient wetness impregnation method, we have successfully identified morphology-dependent CuO_x-CeO₂ interaction and catalysis in CO oxidation. The surface defects of CeO₂ are preferentially occupied by the CuO_x species with the formation of isolated Cu ions. As the Cu loading increases, the CuO_x clusters strongly/weakly interacting with the CeO₂, highly dispersed CuO nanoparticles, and large CuO nanoparticles form sequentially in CuO_x/CeO₂ catalysts. However, the isolated Cu⁺ ions and CuO_x clusters weakly interacting with the CeO₂ are formed mainly on c-CeO₂ due to the exposed unique O-terminated {100} facets. The interaction of CuO_x clusters with various CeO₂ surfaces follows an order of CeO₂{110} facets exposed on r-CeO₂ > CeO₂{111} facets exposed on p-CeO₂ > CeO₂{100} facets exposed on c-CeO₂. The Cu²⁺-c-CeO₂ interaction is weaker than the Cu²⁺-r-CeO₂ interaction so that the Cu⁺ intermediate can be stabilized during the reduction of Cu²⁺ by CO, whereas the Cu²⁺-r-CeO₂ interaction is stronger than the Cu⁺-r-CeO₂ interaction so that the Cu²⁺ is reduced to Cu(0) by CO. CO oxidation catalyzed by CuO_x/CeO₂ catalysts follows the MvK mechanism and is sensitive to both Cu and CeO₂ structures. These results not only comprehensively elucidated the morphology-dependent CuO_x-CeO₂ interaction but also greatly deepen the fundamental understanding of CO oxidation reactions catalyzed by CuO_x/CeO₂ catalysts.

References

- [1] A. A. Gokhale, J. A. Dumesic, M. Mavrikakis, *J. Am. Chem. Soc.*, **2008**, 130, 1402–1414.
- [2] D. Gamarra, A. L. Camara, M. Monte, S. B. Rasmussen, L. E. Chinchilla, A. B. Hungria, G. Munuera, N. Gyorffy, Z. Schay, V. C. Corberan, J. C. Conesa, A. Martinez-Arias, *Appl. Catal. B*, **2013**, 130, 224–238.
- [3] H. Bao, W. Zhang, Q. Hua, Z. Jiang, J. Yang, W. Huang, *Angew. Chem. Int. Ed.*, **2011**, 50, 12294–12298.
- [4] R. Van Den Berg, G. Prieto, G. Korpershoek, L. I. Van Der Wall, A. J. Van Bunningen, S. Lægsgaard-Jørgensen, P. E. de Jongh, K. P. de Jong, *Nat. Commun.*, **2016**, 7, 13057.
- [5] G. Huang, B. J. Liaw, C. J. Jhang, Y. Z. Chen, *Appl. Catal. A*, **2009**, 358, 7–12.
- [6] W. Huang, W. X. Li, *Phys. Chem. Chem. Phys.*, **2019**, 21, 523–536.
- [7] C. Sun, D. Xue, *Phys. Chem. Chem. Phys.*, **2013**, 15, 14414–14419.
- [8] T. Montini, M. Melchionna, M. Monai, P. Fornasiero, *Chem. Rev.*, **2016**, 116, 5987–6041.
- [9] S. W. Yu, H. H. Huang, C. W. Tang, C. B. Wang, *Int. J. Hydrogen Energy*, **2014**, 39, 20700–20711.
- [10] G. Avgouropoulos, T. Ioannides, C. Papadopolou, J. Batista, S. Hocevar, H. K. Matralis, *Catal. Today*, **2002**, 75, 157–167.
- [11] G. Sedmak, S. Hocevar, J. Levec, *J. Catal.*, **2003**, 213, 135–150.
- [12] J. A. Rodriguez, J. Graciani, J. Evans, J. B. Park, F. Yang, D. Stacchiola, S. D. Senanayake, S. Ma, M. Pérez, P. Liu, J. F. Sanz, J. Hrbek, *Angew. Chem. Int. Ed.*, **2009**, 121, 8191–8194.
- [13] J. Graciani, K. Mudiyanse, F. Xu, A. E. Baber, J. Evans, S. D. Senanayake, D. J. Stacchiola, P. Liu, J. Hrbek, J. F. Sanz, J. A. Rodriguez, *Science*, **2014**, 345, 546–550.
- [14] H. Yen, Y. Seo, S. Kaliaguine, F. Kleitz, *Angew. Chem. Int. Ed.*, **2012**, 51, 12032–12035.
- [15] M. Konsolakis, *Appl. Catal. B*, **2016**, 198, 49–66.
- [16] C. Deng, A. Huang, X. Zhu, Q. Hu, W. Su, J. Qian, L. Dong, B. Li, M. Fan, C. Liang, *Appl. Surf. Sci.*, **2016**, 389, 1033–1049.
- [17] W.-W. Wang, W.-Z. Yu, P.-P. Du, H. Xu, Z. Jin, R. Si, C. Ma, S. Shi, C.-J. Jia, C.-H. Yan, *ACS Catal.*, **2017**, 7, 1313–1329.
- [18] M. Lykaki, E. Pachatouridou, S. A. C. Carabineiro, E. Iliopoulou, C. Andriopoulou, N. Kallithrakas-Kontos, S. Boghosian, M. Konsolakis, *Appl. Catal. B: Environ.*, **2018**, 230, 18–28.
- [19] F. Yang, J. Graciani, J. Evans, P. Liu, J. Hrbek, J. F. Sanz, J. A. Rodriguez, *J. Am. Chem. Soc.*, **2011**, 133, 3444–3451.
- [20] S. Yao, K. Mudiyanse, W. Xu, A. C. Johnston-Peck, J. C. Hanson, T. Wu, D. Stacchiola, J. A. Rodriguez, H. Zhao, K. A. Beyer, K. W. Chapman, P. J. Chupas, A. Martínez-Arias, R. Si, T. B. Bolin, W. Liu, S. D. Senanayake, *ACS Catal.*, **2014**, 4, 1650–1661.
- [21] K. Koizumi, K. Nobusada, M. Boero, *Phys. Chem. Chem. Phys.*, **2017**, 19, 3498–3505.
- [22] A.-P. Jia, S.-Y. Jiang, J.-Q. Lu, M.-F. Luo, *J. Phys. Chem. C*, **2010**, 114, 21605–21610.
- [23] A. Martínez-Arias, M. Fernández-García, O. Gálvez, J. M. Coronado, J. A. Anderson, J. C. Conesa, J. Soria, G. Munuera, *J. Catal.*, **2000**, 195, 207–216.
- [24] L. Qin, Y.-Q. Cui, T.-L. Deng, F.-H. Wei, X.-F. Zhang, *ChemPhysChem*, **2018**, 19, 3346–3349.
- [25] X. Zheng, X. Zhang, X. Wang, S. Wang, S. Wu, *Appl. Catal. A*, **2005**, 295, 142–149.
- [26] S. Sun, D. Mao, J. Yu, Z. Yang, G. Lu, Z. Ma, *Catal. Sci. Technol.*, **2015**,

Graphical Abstract

Chin. J. Catal., 2020, 41: 1006–1016 doi: S1872-2067(19)63503-5

Understanding morphology-dependent CuO_x-CeO₂ interactions from the very beginning

Yuxian Gao, Zhenhua Zhang, Zhaorui Li, Weixin Huang*
University of Science and Technology of China;
Zhejiang Normal University

This paper comprehensively elucidated the morphology-dependent CuO_x-CeO₂ interaction and catalysis in CO oxidation with the Cu loadings of 0.025%–5%.

- 5, 3166–3181.
- [27] H. Bao, Z. Zhang, Q. Hua, W. Huang, *Langmuir*, **2014**, 30, 6427–6436.
- [28] W. Liu, M. Flytzani-Stephanopoulos, *Chem. Eng. J.* **1996**, 64, 283–294.
- [29] J. Sun, L. Zhang, C. Ge, C. Tang, L. Dong, *Chin. J. Catal.*, **2014**, 35, 1347–1358.
- [30] H. Shang, X. Zhang, J. Xu, Y. Han, *Front. Chem. Sci. Eng.*, **2017**, 11, 603–612.
- [31] L. Qi, Q. Yu, Y. Dai, C. Tang, L. Liu, H. Zhang, F. Gao, L. Dong, Y. Chen, *Appl. Catal. B*, **2012**, 119–120, 308–320.
- [32] W. Huang, Y. Gao, *Catal. Sci. Technol.*, **2014**, 4, 3772–3784.
- [33] W. Huang, *Acc. Chem. Res.*, **2016**, 49, 520–527.
- [34] S. Chen, F. Xiong, W. Huang, *Surf. Sci. Rep.*, **2019**, 74, 100471.
- [35] F. Polo-Garzon, Z. Bao, X. Zhang, W. Huang, Z. Wu, *ACS Catal.*, **2019**, 9, 5692–5707.
- [36] G. Wulff, On the Question of Speed of Growth and Dissolution of Crystal Surfaces, *Z. Kristallogr.*, **1901**, 34, 449–530.
- [37] H.-X. Mai, L.-D. Sun, Y.-W. Zhang, R. Si, W. Feng, H.-P. Zhang, H.-C. Liu, C.-H. Yan, *J. Phys. Chem. B*, **2005**, 109, 24380–24385.
- [38] L. Yan, R. Yu, J. Chen, X. Xing, *Cryst. Growth Des.*, **2008**, 8, 1474–1477.
- [39] T.-D. Nguyen, C.-T. Dinh, D. Mrabet, M.-N. Tran-Thi, T.-O. Do, *J. Colloid Interfaces Sci.*, **2013**, 394, 100–107.
- [40] Z. L. Wang, X. Feng, *J. Phys. Chem. B*, **2003**, 107, 13563–13566.
- [41] J. Zhang, S. Ohara, M. Umetsu, T. Naka, Y. Hatakeyama, T. Adschiri, *Adv. Mater.*, **2007**, 19, 203–206.
- [42] Tana, M. Zhang, J. Li, H. Li, Y. Li, W. Shen, *Catal. Today*, **2009**, 148, 179–183.
- [43] S. Chang, M. Li, Q. Hua, L. Zhang, Y. Ma, B. Ye, W. Huang, *J. Catal.*, **2012**, 293, 195–204.
- [44] Y. Gao, W. Wang, S. Chang, W. Huang, *ChemCatChem*, **2013**, 5, 3610–3620.
- [45] Y. Liu, L. Luo, Y. Gao, W. Huang, *Appl. Catal. B*, **2016**, 197, 214–221.
- [46] R. You, X. Zhang, L. Luo, Y. Pan, H. Pan, J. Yang, L. Wu, X. Zheng, Y. Jin, W. Huang, *J. Catal.*, **2017**, 348, 189–199.
- [47] X. Zhang, R. You, D. Li, T. Cao, W. Huang, *ACS Appl. Mater. Interfaces*, **2017**, 9, 35897–35907.
- [48] R. You, Z. Li, T. Cao, B. Nan, R. Si, W. Huang, *ACS Appl. Nano Mater.*, **2018**, 1, 4988–4997.
- [49] W. Liu, M. Flytzani-Stephanopoulos, *J. Catal.*, **1995**, 153, 317–332.
- [50] A. Martinez-Arias, M. Fernandez-Garcia, J. Soria, J. C. Conesa, *J. Catal.*, **1999**, 182, 367–377.
- [51] X. Li, X.-Y. Quek, D. A. J. Michel Lighthart, M. Guo, Y. Zhang, C. Li, Q. Yang, E. J. M. Hensen, *Appl. Catal. B: Environ.*, **2012**, 123–124, 424–32.
- [52] W. H. Weber, K. C. Hass, J. R. McBride, *Phys. Rev. B*, **1993**, 48, 178–185.
- [53] A. Nakajima, A. Yoshihara, M. Ishigame, *Phys. Rev. B*, **1994**, 50, 13297–13307.
- [54] T. Taniguchi, T. Watanabe, N. Sugiyama, A. K. Subramani, H. Wagata, N. Matsushita, M. Yoshimura, *J. Phys. Chem. C*, **2009**, 113, 19789–19793.
- [55] M.-F. Luo, Y.-J. Zhong, X.-X. Yuan, X.-M. Zheng, *Appl Catal A: Gen.*, **1997**, 162, 121–131.
- [56] M. Meng, Y. Liu, Z. Sun, L. Zhang, X. Wang, *Int. J. Hydrogen Energy*, **2012**, 37, 14133–14142.
- [57] Z. Wu, H. Zhu, Z. Qing, H. Wang, L. Huang, J. Wang, *Appl. Catal. B: Environ.*, **2010**, 98, 204–12.
- [58] L. Kundakovic, M. Flytzani-Stephanopoulos, *J. Catal.*, **1998**, 179, 203–221.
- [59] R. Si, J. Raitano, N. Yi, L. Zhang, S.-W. Chan, M. Flytzani-Stephanopoulos, *Catal. Today*, **2012**, 180, 68–80.
- [60] Y. Gao, R. Li, S. Chen, L. Luo, T. Cao, W. Huang, *Phys. Chem. Chem. Phys.*, **2015**, 17, 31862–31871.
- [61] Z. Wu, M. Li, S. H. Overbury, *J. Catal.*, **2012**, 285, 61–73.
- [62] M.-F. Luo, J.-M. Ma, J.-Q. Lu, Y.-P. Song, Y.-J. Wang, *J. Catal.*, **2007**, 246, 52–59.
- [63] T. Caputo, L. Lisi, R. Pirone, G. Russo, *Appl. Catal. A: Gen.*, **2008**, 348, 42–53.
- [64] O. Dulaurent, X. Courtois, V. Perrichon, D. Bianchi, *J. Phys. Chem. B*, **2000**, 104, 6001–6011.
- [65] S. F. Tikhov, V. A. Sadykov, G. N. Kryukova, E. A. Paukshtis, V. V. Popovskii, T. G. Starostina, G. V. Kharlamov, V. F. Anufrienko, V. F. Poluboyarov, V. A. Razdobarov, N. N. Bulgakov, A. V. Kalinkin, *J. Catal.*, **1992**, 134, 506–524.
- [66] R. Kydd, D. Ferri, P. Hug, J. Scott, W. Y. Teoh, R. Amal, *J. Catal.*, **2011**, 277, 64–71.
- [67] K. Zhou, R. Xu, X. Sun, H. Chen, Q. Tian, D. Shen, Y. Li, *Catal. Lett.*, **2005**, 101, 169–173.

从头开始理解形貌依赖的CuO_x-CeO₂相互作用

高玉仙^{a,†}, 张振华^{b,†}, 李兆瑞^a, 黄伟新^{a,*}

^a中国科学技术大学化学物理系, 中国科学院能量转换材料重点实验室, 安徽省教育厅表界面化学与能源催化重点实验室, 合肥微尺度物质科学国家研究中心, 安徽合肥 230026

^b浙江师范大学物理化学研究所, 先进催化材料教育部重点实验室, 浙江金华 321004

摘要: CuO_x/CeO₂催化剂在CO氧化反应中表现出高催化活性和显著结构敏感性。文献报道中CuO_x/CeO₂催化剂体系的合成条件差异较大, 从而导致观察到的CuO_x-CeO₂相互作用存在较大争议。因此, 系统研究并阐明CuO_x/CeO₂催化剂中CuO_x-CeO₂相互作用对于理解复杂的CuO_x-CeO₂界面催化作用具有重要的研究意义。近期发现, 氧化物纳米晶的形貌可作为一种新的结构参数, 在不改变氧化物催化剂组成的条件下实现其结构和性能的调控。本文以不同形貌CeO₂纳米晶为载体, 包括优先暴露{110}+{100}晶面的CeO₂纳米棒、优先暴露{100}晶面的CeO₂纳米立方体和优先暴露{111}晶面的CeO₂纳米多面体, 采用等体积浸渍方法合成了Cu担载量为0.025%~5%的CuO_x/CeO₂纳米晶催化剂, 结合谱学和电镜表征方法, 以及CO吸附原位红外光谱, 系统研究了CuO_x物种在不同形貌CeO₂纳米晶上的结构演化及其催化CO氧化的构-效关系。

结构表征结果表明, CuO_x物种结构不仅依赖于Cu的担载量, 也依赖于载体CeO₂的形貌。随着Cu担载量的增加, CuO_x物种优先沉积在CeO₂的表面缺陷位, 然后聚集和长大; 同时伴随着CuO_x物种从孤立Cu离子到与载体强/弱相互作用的CuO_x团

簇, 高分散CuO颗粒和大尺寸CuO颗粒. 孤立Cu⁺离子和与载体弱相互作用CuO_x团簇主要形成于CeO₂纳米立方体的表面, 这可能与CeO₂纳米立方体暴露的氧终止CeO₂ {100}晶面相关. CO吸附原位红外结果表明, CuO_x团簇与不同CeO₂表面相互作用的强度顺序为: CeO₂纳米棒暴露的{110}面 > CeO₂纳米多面体暴露的{111}面 > CeO₂纳米立方体暴露的{100}面. CeO₂纳米立方体与Cu²⁺离子间相互作用弱于与Cu⁺之间的, 因此CeO₂纳米立方体负载的CuO_x物种在CO还原过程中容易停留在稳定的Cu⁺中间物种; 而CeO₂纳米棒与Cu²⁺离子之间的相互作用强于与Cu⁺之间的相互作用, 因此CeO₂纳米棒负载的CuO_x物种在CO还原过程中容易形成金属铜. 因此CO吸附原位红外光谱观察到CeO₂纳米立方体负载CuO_x催化剂中吸附在Cu⁺的CO物种远远多于CeO₂纳米棒负载CuO_x催化剂.

CO氧化反应结果表明, CuO_x/CeO₂催化剂表现出同时依赖于CuO_x物种结构和CeO₂形貌的结构敏感性. CuO_x/CeO₂催化剂活性表现出与CuO_x/CeO₂催化剂的CO还原性能的正相关性, 说明中CuO_x/CeO₂催化CO氧化反应遵循MvK反应机理. 这些结果系统地关联了CeO₂形貌, CuO_x-CeO₂相互作用, CuO_x物种结构和CeO₂还原性能, CuO_x/CeO₂催化CO氧化反应活性.

关键词: CeO₂纳米晶; CuO_x/CeO₂催化剂; 金属-载体相互作用; CO氧化反应; 形貌效应

收稿日期: 2019-10-20. 接受日期: 2019-11-29. 出版日期: 2020-06-05.

*通讯联系人. 电话/传真: (0551)63600435; 电子信箱: huangwx@ustc.edu.cn

基金来源: 国家自然科学基金(21525313, 21761132005); 中国科学院和教育部长江学者奖励计划.

本文的电子版全文由Elsevier出版社在ScienceDirect上出版(<http://www.sciencedirect.com/science/journal/18722067>).