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Mesoporous Cu-Ce-O_x Solid Solutions from Spray Pyrolysis for Superior Low-Temperature CO OxidationRengui Li, Yixuan Yang, Na Sun, and Long Kuai*^[a]

Abstract: Development of Pt group metal-free catalysts for low-temperature CO oxidation remains critical. In this work, active and stable mesoporous Cu-Ce-O_x solid solutions are prepared by using spray pyrolysis. The specific surface areas and pore volumes reach as high as 170 m² g⁻¹ and 0.24 cm³ g⁻¹, respectively. The results of CO oxidation study suggest that (1) the catalyst obtained by spray pyrolysis possesses much higher activity than those made by co-precipitation, sol-gel, and hydrothermal methods; (2) the optimal Cu_{0.2}-Ce_{0.8}-O_x solid solution presents a reactivity over 28 times that of both single-component CuO and CeO₂ at

70 °C. Based on the study of pure-phase Cu-Ce-O_x solid solutions by selective leaching of segregated CuO_x species, the active center for CO oxidation is confirmed as the bimetallic Cu-Ce-O site, whereas the individual CuO_x particles not only act as spectators but also block the active Cu-Ce-O sites. A low apparent activation energy of approximately 48 kJ mol⁻¹ is detected for CO oxidation at the Cu-Ce-O site, making Cu-Ce-O_x solid solutions able to present high activity at low temperature. Furthermore, the Cu-Ce-O_x catalysts exhibit excellent stability and thermal tolerance toward CO oxidation.

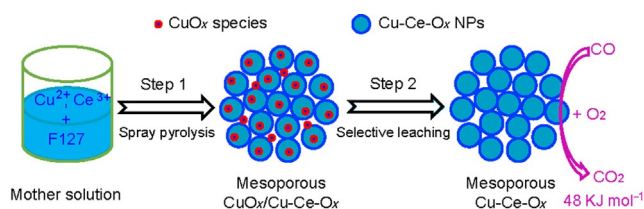
Introduction

Recently, the low-temperature CO catalytic oxidation reaction has aroused huge attention for its high importance in (1) the emission control of advanced engines with low-temperature exhausts (< 150 °C) and (2) the purification of H₂ for low-temperature (80–130 °C) proton exchange membrane fuel cells (PEMFCs).^[1–4] The existing catalysts for low-temperature CO oxidation primarily focus on the Pt-group noble metals and Au-based catalysts as well.^[5–9] Although the atomic dispersion technologies have been developed to enhance their atom efficiency,^[10–15] the rare earth abundance still limits their future commercial applications. Accordingly, it is a major direction and hotspot to develop low-cost catalysts with earth-abundant metals (e.g., Cu and Co).^[16]

Numerous Cu-based catalysts, covering single-component copper oxides (CuO_x, e.g., CuO and Cu₂O) and their composites, have been studied for low-temperature CO oxidation.^[17–20] On the whole, composites containing Cu-Ce-O_x solid solution exhibit notably superior activity than CeO₂-supported CuO_x, CuO-CeO₂ heterostructures, and pristine CuO_x.^[21,22] The conventional co-precipitation and combustion methods are

most frequently adopted for preparing Cu-Ce-O_x solid solution-based catalysts.^[21,23,24] In addition, the sol-gel method and hydro(solvo)thermal synthesis have also been experimentally explored.^[22,25,26] Nevertheless, these methods give insufficient control over the morphology, or the obtained catalysts display low surface areas, leading to an unpredictable reactivity. Moreover, the mentioned works suggest that the segregation of CuO_x species was nearly unavoidable, especially for Cu loadings over 10 at%.^[27] Large-sized CuO crystals even appear with the further rise in the Cu content or annealing temperature.^[28] However, doubts have been raised about the contribution of CuO_x species to the CO oxidation, especially for the easily ignored subnano CuO_x clusters as they are undetectable by X-ray diffraction and hardly distinguishable under routine electron microscopy. To improve both the understanding of this catalysis and its industrial applications, an ideal strategy should be capable of producing a well-shaped pure-phase Cu-Ce-O_x solid solution that displays high specific surface areas.

As shown in Scheme 1, this work presents a well-shaped mesoporous Cu-Ce-O_x solid solution by using a nitrate spray pyrolysis route (NSPR, Step 1),^[28,29] a continuous and easy



Scheme 1. The illustration of strategy and processes for obtaining pure-phase mesoporous Cu-Ce-O_x solid solution for CO oxidation.

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large-scale method that uses cheap nitrates for producing mesoporous metal oxides.^[30,31] The specific surface areas and pore volumes of the products were $170 \text{ m}^2 \text{ g}^{-1}$ and $0.24 \text{ cm}^3 \text{ g}^{-1}$, respectively. Moreover, the CO catalytic oxidation study demonstrates the advantages of the as-prepared mesoporous Cu-Ce-O_x solid solution in comparison with the samples obtained by co-precipitation, sol-gel, and hydrothermal methods. Subsequently, to fundamentally understand the role of segregated CuO_x species in CO oxidation, as shown in Step 2, pure-phase Cu-Ce-O_x solid solutions are further obtained by a selective leaching strategy that removes the CuO_x species from the surface and pore channel of the Cu-Ce-O_x framework. We demonstrated that the actual active center is the bimetallic Cu-Ce-O site with an apparent activation energy of approximately 48 kJ mol^{-1} , whereas the individually segregated CuO_x particles not only act as spectators, but also block the active Cu-Ce-O sites. Finally, this work investigates the stability and thermal tolerance of a typical mesoporous pure phase Cu_{0.2}-Ce_{0.8}-O_x solid solution catalyst from spray pyrolysis.

Results and Discussion

The mesoporous Cu-Ce-O_x solid solution was prepared by one-pot NSPR of Cu and Ce nitrates by evaporation-induced self-as-

sembly (EISA) of triblock copolymer Pluronic F127.^[28] The details are shown in the Experimental Section. According to the thermal decomposition temperature of Cu(NO₃)₂·3H₂O ($\approx 250^\circ \text{C}$) and Ce(NO₃)₃·6H₂O ($\approx 300^\circ \text{C}$) in air,^[32] the preparation can be under milder conditions (600°C , in air) than flame spray pyrolysis and other similar processes summarized by Sanchez et al.^[33,34] In addition, the mild conditions mean there is significantly less decomposition of F127 so that EISA of F127 can remain intact and acts as the pore template for mesoporous products. Herein, the solid solution proportion was controlled by regulating the Cu/Ce ratio in the mother solution. All the proportions in the following discussion are given as molar ratios. The X-ray diffraction (XRD) patterns (Figure 1a) suggest that the Cu atoms were almost fully incorporated into the CeO₂ lattice with low Cu loading. In particular, the XRD pattern of Cu_{0.2}-Ce_{0.8}-O_x (blue) was nearly the same as that of single-component CeO₂ (green) with a cubic crystal phase (PDF NO. 4-593), and no visible CuO or Cu₂O phase was detected. Gradually, owing to formation of the solid solution phase, the peak position of 2θ centered at approximately 28.6° was shifted higher by about 0.28° compared with the pure CeO₂ sample. Nevertheless, the further rise in Cu content, for example, Cu_{0.5}-Ce_{0.5}-O_x (red), caused a clear CuO segregation with reference to single-component CuO (black). In addition, it is

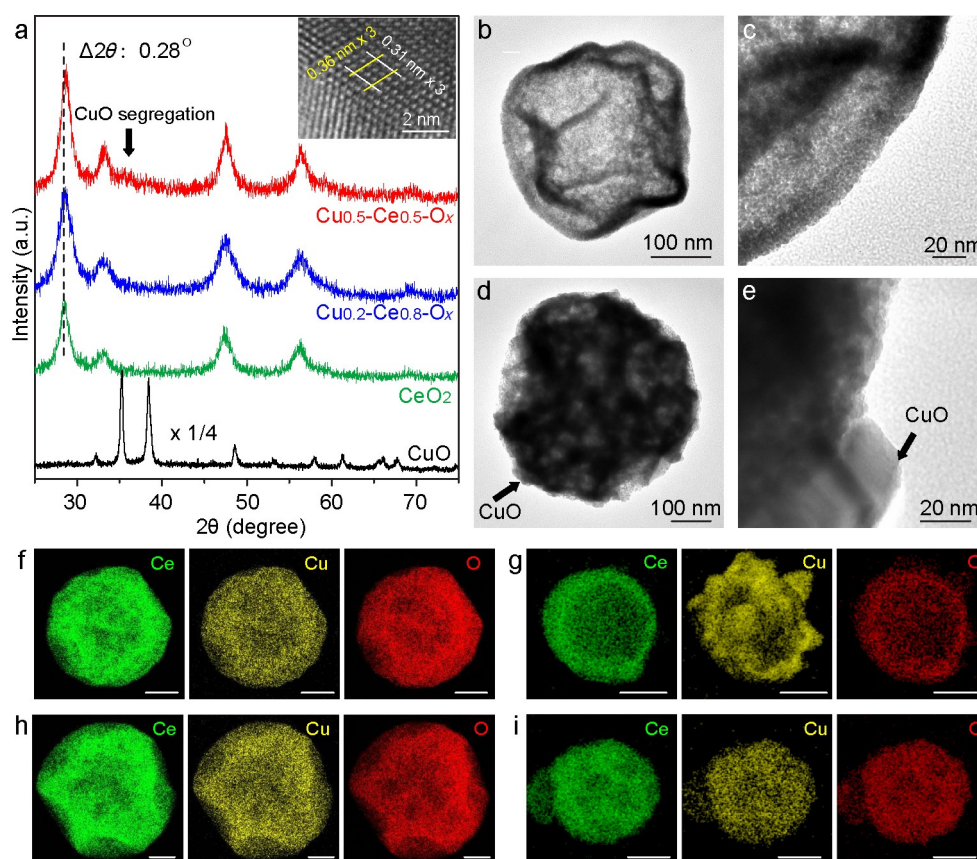


Figure 1. XRD patterns (a) of mesoporous CuO (black), CeO₂ (green), Cu_{0.2}-Ce_{0.8}-O_x (blue), and Cu_{0.5}-Ce_{0.5}-O_x (red). Low (b) and high (c) magnification TEM images of Cu_{0.2}-Ce_{0.8}-O_x. Low (d) and high (e) magnification transmission electron microscopy (TEM) images of Cu_{0.5}-Ce_{0.5}-O_x. The transmission electron microscopy (STEM)-EDS element mappings of Cu_{0.2}-Ce_{0.8}-O_x (f), Cu_{0.5}-Ce_{0.5}-O_x (g), Cu_{0.2}-Ce_{0.8}-O_x-NH₃ (h), and Cu_{0.5}-Ce_{0.5}-O_x-NH₃ (i). The scalebars of (f)–(i) are 200 nm. The top right inset in (a) is the HRTEM image of Cu_{0.5}-Ce_{0.5}-O_x.

well known that a peak width increase indicates that the crystallite size decreases. We observed that the peak width at half-height of $\text{Cu}_{0.2}\text{-Ce}_{0.8}\text{-O}_x$ (1.8°) is slightly larger than that of $\text{Cu}_{0.5}\text{-Ce}_{0.5}\text{-O}_x$ (1.4°), revealing an enlarged sized of the solid solution with more Cu loading. The top right inset in Figure 1a illustrates clear lattice fringes of $\text{Cu}_{0.5}\text{-Ce}_{0.5}\text{-O}_x$, where the distances of 0.36 nm and 0.31 nm matched well to the (110) and (111) planes of CeO_2 , respectively.

According to the scanning electron microscopy (SEM, Figure S1 in the Supporting Information) and TEM (Figure 1b–e) images, the incorporation of Cu induced loading-dependent morphology evolution and structural variation of the products. To be specific, $\text{Cu}_{0.2}\text{-Ce}_{0.8}\text{-O}_x$ solid solution with negligible CuO_x segregation exhibited concave hollow mesoporous microspheres with sizes of 0.5–1.5 μm (Figure 1b). The high-magnification TEM image suggests the mesoporous walls of the concave hollow microsphere were self-assembled by nanoparticles (Figure 1c). As shown in Figure S2a, c, and e (in the Supporting Information), the pore size distributions were highly uniform. The pore size was around 3.8 nm. However, the higher Cu loading led to a morphology of non-hollow mesoporous microspheres (Figure 1d). In addition, individual CuO nanocrystals were detected on the surface of a typical $\text{Cu}_{0.5}\text{-Ce}_{0.5}\text{-O}_x$ microsphere (Figure 1e). The STEM-energy-dispersive X-ray (EDX) elemental mappings clearly demonstrate the difference between the $\text{Cu}_{0.2}\text{-Ce}_{0.8}\text{-O}_x$ and $\text{Cu}_{0.5}\text{-Ce}_{0.5}\text{-O}_x$. The signals of Ce, Cu, and O elements in $\text{Cu}_{0.2}\text{-Ce}_{0.8}\text{-O}_x$ (Figure 1f) overlapped well with each other, revealing the uniform dispersion of Cu in the CeO_2 host lattice. For $\text{Cu}_{0.5}\text{-Ce}_{0.5}\text{-O}_x$ (Figure 1g), partially Cu overlapped with Ce and O elements, although significant segregated CuO crystals were present, in which the Ce element was not detected.

An existing study has presented that Cu segregation readily appeared for a Cu-based ternary oxide.^[27,28] For the subsequent study, selective leaching was developed to (1) verify the content of segregated CuO crystals and possible XRD-undetectable and/or TEM-undistinguishable CuO_x clusters and then to (2) fabricate phase-pure Cu-Ce- O_x solid solution catalysts. Based on the coordination chemistry of Cu^{2+} and NH_3 , concentrated ammonia ($\text{NH}_3\cdot\text{H}_2\text{O}$, 25–28%) was used to etch the CuO_x species (covering CuO nanocrystals and possible CuO_x clusters), whereas the Cu^+ or Cu^{2+} species were hardly removed from the Cu-Ce- O_x lattice. The availability from the leaching tests are shown in Figure S3 (in the Supporting Information). Three samples of $\text{Cu}_{0.05}\text{-Ce}_{0.95}\text{-O}_x$, $\text{Cu}_{0.2}\text{-Ce}_{0.8}\text{-O}_x$ and $\text{Cu}_{0.5}\text{-Ce}_{0.5}\text{-O}_x$ were selected for the case study. First, by inductively coupled plasma-atomic emission spectrometry (ICP-AES), the Cu contents before and after $\text{NH}_3\cdot\text{H}_2\text{O}$ leaching were analyzed. According to Tables S1 and S2 (in the Supporting Information), all the Cu/Ce ratios before leaching were significantly close to those in the mother solution. The samples after $\text{NH}_3\cdot\text{H}_2\text{O}$ leaching are labeled as $\text{Cu}_{0.05}\text{-Ce}_{0.95}\text{-O}_x\text{-NH}_3$, $\text{Cu}_{0.2}\text{-Ce}_{0.8}\text{-O}_x\text{-NH}_3$ and $\text{Cu}_{0.5}\text{-Ce}_{0.5}\text{-O}_x\text{-NH}_3$. It was found that the Cu/Ce ratio barely changed for $\text{Cu}_{0.05}\text{-Ce}_{0.95}\text{-O}_x$ revealing the Cu was fully involved in forming the solid solution. For $\text{Cu}_{0.2}\text{-Ce}_{0.8}\text{-O}_x$ a slight decrease in Cu ($\approx 12\%$) was presented, probably owing to the removal of small CuO_x clusters that cannot be observed by XRD (Fig-

ure 1a) and TEM (Figure 1c). Furthermore, the soluble CuO_x species rose to 55% for $\text{Cu}_{0.5}\text{-Ce}_{0.5}\text{-O}_x$, suggesting a high degree of segregation. The selective leaching results were consistent with those of the XRD analysis and TEM study.

N_2 sorption isotherm plots (Figure 2 and Figure S4 in the Supporting Information) and Barrett–Joyner–Halenda (BJH) pore distribution analysis (Figure S2 in the Supporting Information) were conducted to investigate the pore structure of the solid solution before and after selective leaching. The N_2 adsorption volume of $\text{Cu}_{0.05}\text{-Ce}_{0.95}\text{-O}_x$ (Figure S4 in the Supporting Information) and $\text{Cu}_{0.2}\text{-Ce}_{0.8}\text{-O}_x$ (Figure 2a) remained almost unchanged after the selective leaching treatment, whereas that of $\text{Cu}_{0.5}\text{-Ce}_{0.5}\text{-O}_x\text{-NH}_3$ was nearly doubled (Figure 2b) because of the opening of pore channels. Table S2 (in the Supporting Information) reveals that the Brunauer–Emmett–Teller (BET) specific surface areas and pore volumes of both $\text{Cu}_{0.05}\text{-Ce}_{0.95}\text{-O}_x$ and $\text{Cu}_{0.2}\text{-Ce}_{0.8}\text{-O}_x$ were more than $170\text{ m}^2\text{g}^{-1}$ and $0.24\text{ cm}^3\text{g}^{-1}$, being barely affected by the selective leaching. The TEM image (Figure S5 in the Supporting Information) and EDS mapping (Figure 1h) of $\text{Cu}_{0.2}\text{-Ce}_{0.8}\text{-O}_x\text{-NH}_3$ also showed negligible difference from $\text{Cu}_{0.2}\text{-Ce}_{0.8}\text{-O}_x$. For $\text{Cu}_{0.5}\text{-Ce}_{0.5}\text{-O}_x$ half of the specific area and pore volume was lost compared with $\text{Cu}_{0.05}\text{-Ce}_{0.95}\text{-O}_x$ and $\text{Cu}_{0.2}\text{-Ce}_{0.8}\text{-O}_x$ because of (1) the increased sized of the particles and (2) the blocking of pores by the large amount of seg-

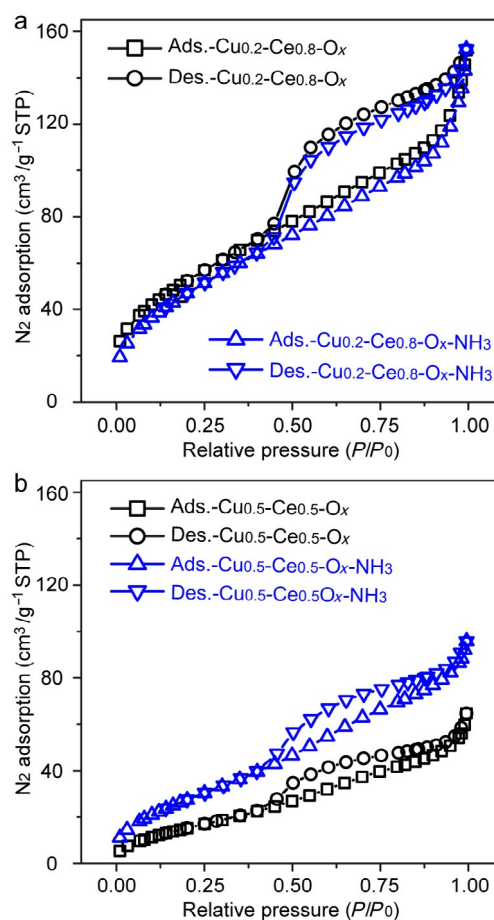


Figure 2. The N_2 isotherm adsorption/desorption plots of $\text{Cu}_{0.2}\text{-Ce}_{0.8}\text{-O}_x$, $\text{Cu}_{0.2}\text{-Ce}_{0.8}\text{-O}_x\text{-NH}_3$ (a) and $\text{Cu}_{0.5}\text{-Ce}_{0.5}\text{-O}_x$, $\text{Cu}_{0.5}\text{-Ce}_{0.5}\text{-O}_x\text{-NH}_3$ (b).

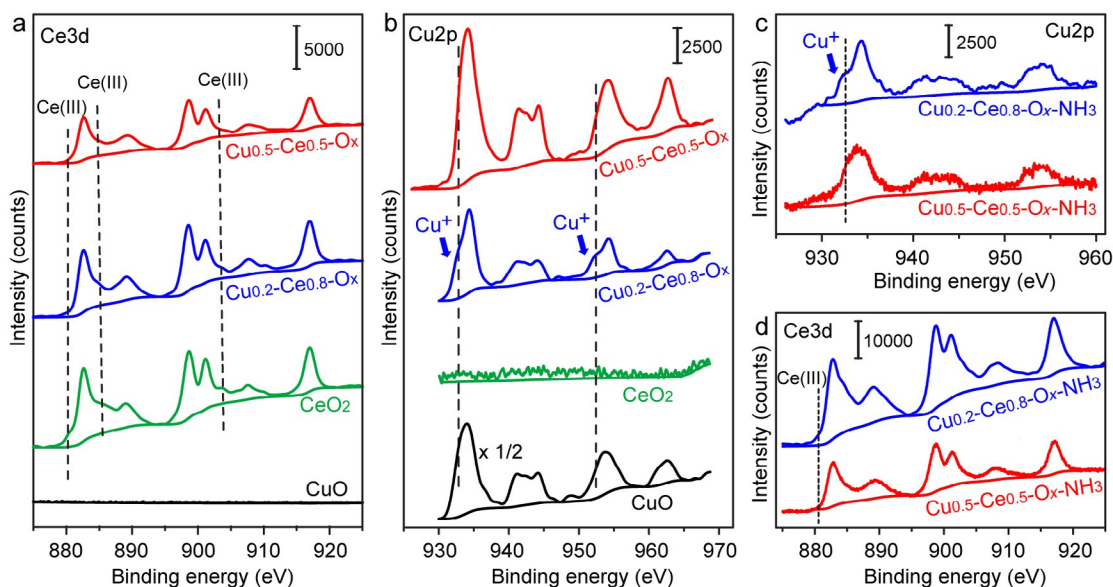


Figure 3. Ce3d (a) and Cu2p (b) XPS fine spectra of CuO (black), CeO₂ (green), Cu_{0.2}-Ce_{0.8}-O_x (blue), and Cu_{0.5}-Ce_{0.5}-O_x (red). Cu2p (c) and Ce3d (d) XPS spectra of Cu_{0.2}-Ce_{0.8}-O_x-NH₃ (blue) and Cu_{0.5}-Ce_{0.5}-O_x-NH₃ (red).

regulated CuO_x species. Note that the specific area and pore volume of Cu_{0.5}-Ce_{0.5}-O_x-NH₃ notably increased upon CuO_x removal (Table S2 in the Supporting Information) whereas the pore diameter (Figure S2 c and f in the Supporting Information) did not evolve, revealing the opening of pore channels. The STEM images (Figure S6 in the Supporting Information) and EDS mapping (Figure 1 i) of Cu_{0.5}-Ce_{0.5}-O_x-NH₃ also demonstrate the removal of segregated CuO_x species.

X-ray photoelectron spectroscopy (XPS, Figures S7 and S8 in the Supporting Information) was performed to study the surface chemical environment of the Cu-Ce-O_x solid solutions. The products of Cu_{0.2}-Ce_{0.8}-O_x and Cu_{0.5}-Ce_{0.5}-O_x were studied with references of pristine CuO and CeO₂. Their Ce3d spectra are shown in Figure 3a. It is known that Ce^{III} generally appears in CeO₂ samples.^[35] It is noteworthy that the amount of Ce^{III} decreased with the loading of Cu, and it even became nearly undetectable for Cu_{0.5}-Ce_{0.5}-O_x, revealing an electron-withdrawing effect of Cu. Accordingly, notable Cu^I appeared in the sample of Cu_{0.2}-Ce_{0.8}-O_x (blue, Figure 3b) compared with CuO (black). Owing to the CuO segregation of Cu_{0.5}-Ce_{0.5}-O_x (red), the relative content of Cu^I was lower after the selective leaching of soluble CuO_x. As shown in Figure 3c, the signal of Cu^I became dominant for both Cu_{0.2}-Ce_{0.8}-O_x-NH₃ (blue) and Cu_{0.5}-Ce_{0.5}-O_x-NH₃ (red). In addition, the selective leaching barely affected the state of Ce (Figure 3d). Thus, the Cu-Ce-O_x solid solution exhibited a strong electronic interaction between Ce and Cu.

The catalytic performance of the Cu-Ce-O_x solid solutions in low-temperature CO oxidation was investigated at temperatures ranging from 50 to 140 °C under ambient pressure. The feed gases included 1.0% CO, 1.0% O₂, and 98% He at a flow rate of 22 mL min⁻¹. First, the samples without selective leaching of CuO_x were studied. As shown in Figure 4a and Table S3 (in the Supporting Information), the Cu-Ce-O_x solid solution exhibited superior reactivity towards low-temperature CO oxida-

tion compared with both single-component CuO and CeO₂. The reactivity of the optimal Cu_{0.2}-Ce_{0.8}-O_x solid solution exhibited over 28 times that of both the single-component CuO and

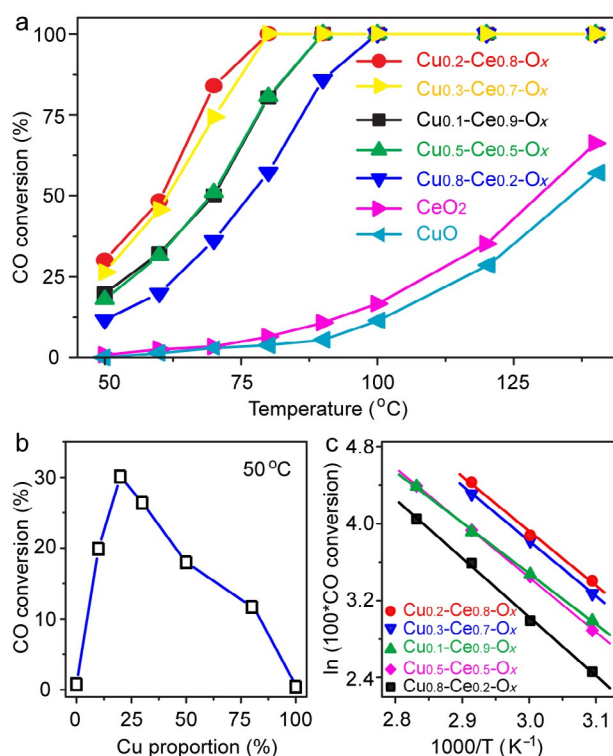


Figure 4. Temperature-dependent CO conversion plots (a) of the as-prepared Cu-Ce-O_x solid solution with reference to single-component CuO and CeO₂. Cu proportion-dependent CO conversions (b) at 50 °C. Arrhenius plot fittings (c) of Cu_{0.1}-Ce_{0.9}-O_x (green), Cu_{0.2}-Ce_{0.8}-O_x (red), Cu_{0.3}-Ce_{0.7}-O_x (blue), Cu_{0.5}-Ce_{0.5}-O_x (pink), and Cu_{0.8}-Ce_{0.2}-O_x (black).

CeO₂ at 70 °C. The temperature of 100% CO conversion on the Cu_{0.2}-Ce_{0.8}-O_x and Cu_{0.3}-Ce_{0.7}-O_x catalysts was 80 °C lower than those of CuO and CeO₂, which are comparable to numerous Pt-based catalysts.^[1,2,10,36–38] To position the relative performance of the samples from spray pyrolysis, Cu_{0.2}-Ce_{0.8}-O_x samples (Figure S9 in the Supporting Information) from co-precipitation, sol-gel, and hydrothermal methods were studied for meaningful comparison. As shown in Figure S10 (in the Supporting Information), the catalyst from spray pyrolysis exhibited notably higher performance. The temperature of 100% CO conversion was about 40 and 60 °C lower than that with samples from co-precipitation and sol-gel methods, respectively.

The CO conversion at 50 °C (Figure 4b) was employed to investigate the Cu proportion-dependent performance of the Cu-Ce-O_x solid solutions. Figure 4b presents a typical “volcano”-shaped relationship between the reactivity and Cu proportion. The optimum Cu proportion was about 20 at%. Arrhenius plot fittings were carried out to estimate the apparent activation energy (E_a) values.^[39] As shown in Figure 4c, the E_a values were independent of Cu content, revealing the active center was the same for all the Cu-Ce-O_x solid solutions. Thus, the bi-metallic Cu-Ce-O centers acted as active sites, and the segregated CuO_x species were spectators. Thus, the reactivity was determined by the number of surface Cu-Ce-O sites. As shown in Table S3 (in the Supporting Information), the E_a value of CO oxidation on the Cu-Ce-O_x solid solution was around 48 kJ mol⁻¹, very close to that in the work by Qin et al. (53 kJ mol⁻¹), determined by the density function theory (DFT) study of CO oxidation on CeO₂-supported single-atom Cu catalysts.^[40] The DFT study revealed that the CO oxidation complied with the Mars van Krevelen mechanism, in which the Cu site facilitates the activation of the CO molecule. With low Cu content (e.g., Cu_{0.1}-Ce_{0.9}-O_x), the insufficient Cu-Ce-O sites for CO adsorption led to an inferior reactivity. Nevertheless, for the cases with Cu loadings higher than 20 at%, especially for Cu_{0.5}-Ce_{0.5}-O_x, the drop in reactivity was because (1) most of the Cu sites were segregated out from the solid solution to form individual CuO_x species, leading to a limited rise in Cu-Ce-O_x active sites; (2) the segregated CuO_x species partially covered the active sites and seriously blocked the pore channels, causing a decrease in the efficient active sites; (3) the specific surface area of Cu-Ce-O_x solid solutions becomes lower with increasing of Cu, thus the specific active sites also decreased.

To delve into the active sites of the Cu-Ce-O_x solid solution, the CO oxidation reactions on Cu_{0.2}-Ce_{0.8}-O_x-NH₃ (Figure S11 in the Supporting Information) and Cu_{0.5}-Ce_{0.5}-O_x-NH₃ (Figure S12 in the Supporting Information) were studied to confirm the spectator role of single-component CuO_x. As shown in Figure 5 and Table S3 (in the Supporting Information), Cu_{0.2}-Ce_{0.8}-O_x-NH₃ (black) sample exhibited nearly the same performance as Cu_{0.2}-Ce_{0.8}-O_x (red). The results of ICP-AES (Table S2 in the Supporting Information) suggest that the Cu content in Cu_{0.2}-Ce_{0.8}-O_x-NH₃ was 12% lower than that in Cu_{0.2}-Ce_{0.8}-O_x, demonstrating that the segregated CuO_x species contributed little to the CO oxidation reaction. More interestingly, the performance of Cu_{0.5}-Ce_{0.5}-O_x-NH₃ (blue) was even enhanced after the removal of segregated CuO_x species. However, all of their E_a values were about

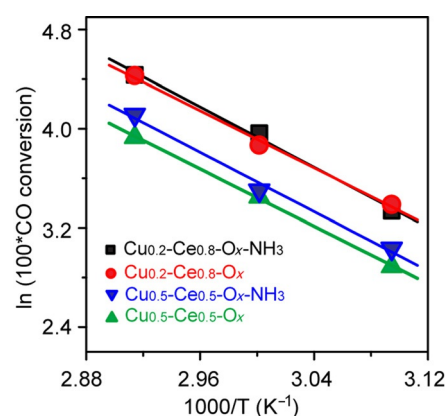


Figure 5. Arrhenius plot fittings of Cu_{0.2}-Ce_{0.8}-O_x-NH₃ (red), Cu_{0.2}-Ce_{0.8}-O_x (black), Cu_{0.5}-Ce_{0.5}-O_x-NH₃ (green), and Cu_{0.5}-Ce_{0.5}-O_x (blue).

48 kJ mol⁻¹, revealing the reactivity difference originated from the number of active sites. Note that the Cu loading decreased by 55% after selective leaching of CuO_x species. Thus, the segregated CuO_x species even adversely affected the performance because they partially blocked the Cu-Ce-O active sites.

The stability of the Cu-Ce-O_x solid solutions was evaluated with Cu_{0.2}-Ce_{0.8}-O_x-NH₃ as an example at 70 °C with continuous feeding of reactants. Figure 6a suggests that an approximately 30% decrease in CO conversion during the initial 25 h was observed, whereas the activity barely varied afterward, even with the reaction time prolonged to over 80 h. More importantly, the activity could be fully recovered by regenerating the catalyst in situ by thermal treatment at 400 °C for 1 h, and then a new round of decay started. Thus, the catalysts were considered stable during long-term continuous usage. As shown in Figure 6b, the morphology and structure of the used catalyst presented no visible evolution, further revealing the good stability of Cu-Ce-O_x solid solution. According to the experimental results and existing works,^[41–44] the deactivation was likely caused by the surface carbonate accumulation, a common phenomenon in CO oxidation and water-gas shift reactions catalyzed by metal oxides or supported metals. The possible monodentate or other carbonate species partially blocked the active Cu-Ce-O sites and led to the reactivity drop.^[43,44] The activity was easy to recover by thermal treatment because we found the carbonates can be completely decomposed at about 350 °C.^[13] Furthermore, the Cu-Ce-O_x solid solution exhibited prominent thermal tolerance. Figure 6c shows that the performance of Cu_{0.2}-Ce_{0.8}-O_x-NH₃ dropped < 15% even when the catalysts were further annealed at 600 °C. The TEM image (Figure 6d) suggests the structure was not destroyed after the treatment at 600 °C. Gradually, a certain degree of sintering was observed (as shown in the red circle). According to the XRD pattern (Figure 6e), the crystal phase was also maintained well. Nevertheless, a peak width at half-height (1.2°) at 2θ ≈ 28.6° grows after the treatment at 600 °C, suggesting that the crystal size increased. The size evolution was likely responsible for the small activity loss.

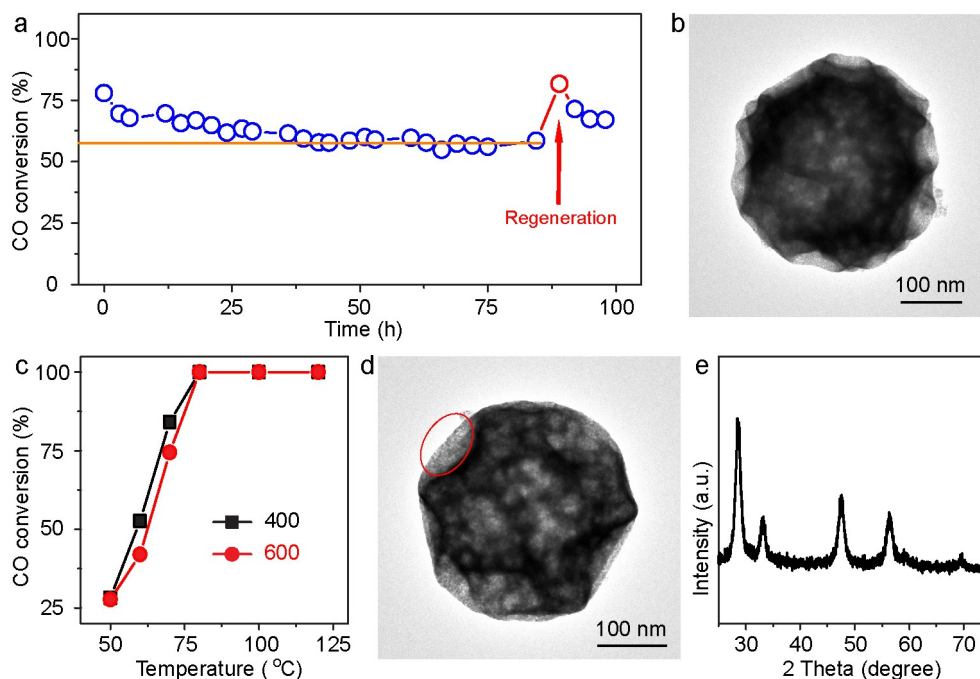


Figure 6. Time-dependent CO conversions of $\text{Cu}_{0.2}\text{-Ce}_{0.8}\text{-O}_x\text{-NH}_3$ catalyst (a) with continuous feeding reaction gas at 70 °C, and the data points after the red circle are the CO conversions after regeneration of catalysts by in situ thermal treatment at 400 °C. The TEM image (b) of the used catalyst after stability test. CO conversion plots (c) of $\text{Cu}_{0.2}\text{-Ce}_{0.8}\text{-O}_x\text{-NH}_3$ treated at 400 (black) and 600 °C (red). The TEM image (d) and XRD pattern (e) of the $\text{Cu}_{0.2}\text{-Ce}_{0.8}\text{-O}_x\text{-NH}_3$ treated at 600 °C (red).

Conclusion

A well-shaped mesoporous Cu-Ce- O_x solid solution was produced for low-temperature CO oxidation by using a nitrate spray pyrolysis route, and a selective leaching strategy was adopted to remove the surface segregated CuO_x species. The bimetallic Cu-Ce-O site was confirmed as the active center for CO oxidation, whereas the individually segregated CuO_x species not only acted as spectators, but also blocked the active Cu-Ce-O sites. The apparent activation energy was approximately 48 kJ mol⁻¹ for CO oxidation at the Cu-Ce-O site, which is sufficiently low to make Cu-Ce- O_x solid solutions work at low temperature. This work not only provides an efficient Pt group metal-free catalyst but also elucidates the CO oxidation on the Cu-Ce- O_x solid solution.

Experimental Section

Materials preparation

Mesoporous Cu-Ce- O_x solid solution catalysts: Spray pyrolysis was carried out to obtain the precursors of solid solutions. Generally, F127 (0.5 g, $\text{PEO}_{106}\text{PPO}_{70}\text{PEO}_{106}$, Sigma) and a total of 4 mmol of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (AC, Aladdin) and $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (AC, Aladdin) were dissolved in deionized water (30 mL). The solution was sprayed by using a household ultrasonic humidifier. The mist was drawn into a quartz tube embedded in a tube furnace (30 cm) by a vacuum pump. The temperature of the tube furnace was pre-heated to 600 °C. The precursor powders were collected with a filter paper. The solid solutions were obtained after calcination of precursors in air at 400 °C for 2 h at a heating rate of 5 °C min⁻¹.

The solid solution proportion was controlled by regulating the ratio of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ in the mother solution.

The single-component mesoporous CuO and CeO_2 were prepared the as same as Cu-Ce- O_x solid solution catalysts except that only $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ or $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was added.

Cu-Ce- $\text{O}_x\text{-NH}_3$ solid solution catalysts: A selective leaching strategy with concentrated $\text{NH}_3 \cdot 6\text{H}_2\text{O}$ (25–28 %) was used to obtain pure-phase Cu-Ce- $\text{O}_x\text{-NH}_3$ solid solution catalysts. In detail, the catalyst powders (0.3 g) were dispersed in concentrated $\text{NH}_3 \cdot 6\text{H}_2\text{O}$ (6 mL). The mixture was vigorously stirred at 50 °C for 1 h. The catalysts were separated by centrifugation and a blue filtrate could be obtained if there were CuO_x species in the catalysts. The leaching was repeated 2–5 times until the filtrate was colorless. Typically, 3 and 5 repeated leaching processes were generally needed for $\text{Cu}_{0.2}\text{-Ce}_{0.8}\text{-O}_x$ and $\text{Cu}_{0.5}\text{-Ce}_{0.5}\text{-O}_x$, respectively.

The leached catalysts were dried at 60 °C overnight for subsequent use.

The Cu/Ce ratios in the solid solutions before and after leaching were measured by inductively coupled plasma-atomic emission spectrometry (ICP-AES). The data are shown in Table S1 (in the Supporting Information).

$\text{Cu}_{0.2}\text{-Ce}_{0.8}\text{-O}_x$ sample by co-precipitation method: $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (0.8 mmol) and $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (3.2 mmol) were dissolved in deionized water (30 mL). Na_2CO_3 solution (12 mL, 0.5 mol L⁻¹) was added into the above solution drop by drop. After aging for 4 h, the precipitation was washed with deionized water two times and dried at 100 °C. The products were obtained after calcination of precipitation in air at 400 °C for 2 h at a heating rate of 5 °C min⁻¹.

$\text{Cu}_{0.2}\text{-Ce}_{0.8}\text{-O}_x$ sample by sol-gel method: $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (0.8 mmol), $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (3.2 mmol), and F127 (0.5 g) were dissolved in absolute ethanol (30 mL). The mixture was treated at 60 °C for 4 h and subsequently at 100 °C for 4 h. The products were

obtained after calcination of the gels in air at 400 °C for 2 h at a heating rate of 5 °C min⁻¹.

Cu_{0.2}-Ce_{0.8}-O_x sample by hydrothermal method: Cu(NO₃)₂·3H₂O (0.8 mmol), Ce(NO₃)₃·6H₂O (3.2 mmol), F127 (0.5 g), and urea (1.2 g) were dissolved in deionized water (30 mL). Then, 15 mL of the mixture was transferred into a 25 mL autoclave. The reaction was kept for 12 h at 180 °C. After cooling to room temperature, the product was separated by centrifugation and washed with water and ethanol two and three times, respectively.

Characterizations

The samples were characterized by SEM (Hitachi, S-4800) with 5 kV accelerating voltage and TEM (Technai G20 S-TWIN, FEI) with 200 kV accelerating voltage, HAADF-STEM-EDX elements mapping (JEOL, JEM 2100), X-ray diffraction (D8, Brook) with Cu_{Kα} radiation ($\lambda = 0.15418$ nm), and X-ray photoelectron spectroscopy (XPS, ESCALAB 250, America). The N₂ isotherm sorption measurements (77 K) with TriStar II 3020 V1.03 (Micromeritics, America) was used to obtain the Brunauer–Emmett–Teller (BET) specific surface area and Barrett–Joyner–Halenda (BJH) pore distribution.

Catalytic tests for CO oxidation

Evaluation of activity: A fixed-bed tube reactor (WFSM-3060, Tianjin) was used to evaluate the performance of the catalysts toward CO oxidation at atmospheric pressure. Typically, catalyst (0.10 g) and quartz sands (3 mL) were mixed and filled into a stainless-steel reaction tube with 8 mm diameter and 30 cm length. The feed gas was a mixture of 1.0% CO, 1.0% O₂, and 98% balance He at a flow of 22 mL min⁻¹, which was controlled by a mass flowmeter. An in situ pretreatment was carried out at 400 °C to remove the possible adsorbates. The conversion of CO was measured by on-line gas chromatography (GC, Fuli Instruments, China) equipped with a TDX-01 column (2.0 m in length and 3 mm in diameter) and thermal conductor detector (TCD). He (99.99%) was used as the carrier gas. The working temperature for the column was set at 100 °C. The working temperature and current of TCD were 150 °C and 140 mA, respectively.

Evaluation of stability: The stability was evaluated with the Cu_{0.2}-Ce_{0.8}-O_x-NH₃ solid solution catalyst. After in situ activation at 400 °C, the exhaust was monitored with the continuous feed of reaction gas. The reaction temperature was 70 °C.

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Conflict of interest

The authors declare no conflict of interest.

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