

Effect of Reduction Treatment on CO Oxidation with CeO₂ Nanorod-Supported CuO_x Catalysts

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Understanding the correlation of thermal treatment with catalyst activity provides mechanistic information about how the catalysts can be activated or deactivated. In this paper, we report that a comparative study was conducted on CeO₂ nanorod-supported CuO_x catalysts before and after reduction treatment to gain insight on the effects of the copper oxidation state and catalyst–support interfacial interactions on CO oxidation. X-ray diffraction, Raman spectroscopy, hydrogen temperature-programmed reduction (H₂-TPR), and transmission electron microscopy (TEM) were used in a comprehensive way to study the effects of CuO_x (0 ≤ x ≤ 1) composition as well as their spatial distribution on CeO₂ nanorods on the H₂

consumption and CO oxidation of the catalysts. These techniques were then used to gain a better understanding of the correlation between the different copper species (α, β, and γ-type CuO_x) and the multiple reduction (H₂ consumption) peaks, found in the H₂-TPR data during the first run and during in situ reduction and redox cycling experiments. Also concluded from this study is that an abundance of surface defects are found on CeO₂ nanorods from high-resolution TEM, which consequently may be critical to strong CuO_x(0 ≤ x ≤ 1)–CeO_{2-x}(0 ≤ x ≤ 0.5) interactions, therefore resulting in the improved low-temperature catalytic activity.

Introduction

Both CuO–CeO₂ and Cu–CeO₂ have been reported to have high catalytic activity to promote carbon monoxide oxidation,^[1] the water–gas shift reaction,^[2,3] and methanol steam reforming.^[4–6] Catalytic activity similar to or even better than traditional noble metal catalysts has been achieved over copper-containing ceria catalysts, for example, in carbon monoxide oxidation,^[7] which promises an economical alternative catalyst system. Possible reaction pathways and active sites have been proposed recently. For instance, Tang et al.^[8] proposed a reaction pathway for CO oxidation over CuO–CeO₂ catalysts prepared by a deposition–precipitation method, in which CO adsorbs onto the copper and reacts with the adsorbed active oxygen on the CeO₂ support. Kundakovic et al.^[9] reported a lowered light-off temperature of methane oxidation in both Cu-modified Ce(La)O₂ and Zr(Y)O₂ catalysts, indicating the formation of new active sites owing to the addition copper. Gammarra et al.^[7] studied the selective CO oxidation in excess H₂ by operando diffuse reflectance infrared Fourier transform

spectroscopy (DRIFTS) and X-ray absorption near edge structure (XANES) over copper–ceria catalysts prepared by a microemulsion method and identified the active sites for CO oxidation located at interfacial areas of copper and ceria support. All these results sufficiently favor a conclusion that a synergistic effect of copper species and ceria support exists for CO oxidation.

However, much more information is required to evaluate the interface between copper species and the CeO₂ support. For the CuO–CeO₂ catalyst, the strong metal–support interactions (SMSI) between CuO species and CeO₂ support provide a synergistic effect that causes the reduction of both the CeO₂ support and CuO crystals to occur at lower temperatures, resulting in the enhanced activity.^[10] However, for Cu⁰–CeO₂ used as an oxidation catalyst, the improved low-temperature hydrogen consumption of CeO₂ in H₂ temperature-programmed reduction (TPR) experiments suggests that with the presence of copper there is an activation of lattice oxygen at CeO₂ at the interface. In other words, the high catalytic activity in CuO_x–CeO₂ is a result of the interplay between CeO_{2-x} (0 ≤ x ≤ 0.5) and CuO_x (0 ≤ x ≤ 1) at their interface. The redox functionality of both catalyst and support are vital components for gas adsorption, oxygen migration at the metal–support interface, and in the catalytic reactions mentioned above. At the interfacial areas, the formation of the active sites/phases can be attributed to the quick reversible Ce⁴⁺/Ce³⁺ redox couple,^[11] Cu²⁺/Cu⁺/Cu⁰ redox triple,^[7] and the CuO_x–CeO_{2-x} interactions during the redox processes.^[12] Recently, Elisa et al.^[13] reported that dispersed copper ions in the single phase Cu_yCe_{1-y}O_{2-x} are active sites for CO oxidation, instead of previously indicated bulk CuO, or the interfacial area between CuO with

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$\text{Cu}_y\text{Ce}_{1-y}\text{O}_{2-x}$, or Cu^+ . So, the active sites in $\text{CuO}_x\text{-CeO}_2$ catalysts still remain insufficiently understood.

In recent studies, CeO_2 nanorods showed superior low-temperature surface reducibility and high oxygen storage capacity owing to exposed $\{011\}$ and $\{001\}$ surfaces^[14,15] and/or rough $\{111\}$ surfaces with oxygen vacancy clusters and defects,^[16,17] compared with other morphologies, for example, nano-octahedra and nanocubes. A few studies were performed to elucidate the synergistic effect between CuO and CeO_2 nanorods.^[18] As the active sites (Cu , Cu^+ , Cu^{2+} , $\text{CuO}_x\text{-CeO}_2$) for CO adsorption and conversion in $\text{CuO}_x\text{-CeO}_2$ still remain obscure, to further understand the CuO/Cu-CeO_2 interfacial effect, a comparative study was conducted on CeO_2 nanorod-supported CuO and reduced CeO_2 nanorod-supported CuO_x catalysts for CO oxidation in this study.

Results and Discussion

Defect surfaces on CeO_2 nanorods

Following the previous report,^[17] CeO_2 nanorods were synthesized by using a hydrothermal reaction at 90°C with a dwell time of 24 h. Figure 1a and b show a low magnification TEM and a set of high-resolution TEM images of the as-synthesized CeO_2 nanorods, respectively. Notably, both $\{100\}$ and $\{111\}$ surfaces were observed in these nanorods. Among the more than 30 individual CeO_2 nanorods investigated by HR-TEM, the majority of termination surfaces are $\{111\}$, $\{100\}$, and $\{110\}$ crystal planes. This result is a little inconsistent with the earlier model of CeO_2 nanorods available in the literature prepared by using similar hydrothermal conditions,^[14,15] which claim two $\{100\}$ and two $\{110\}$ surfaces on the nanorods. The proposed explanation^[19–21] was that the oxygen vacancy formation energy on $\{100\}$ and $\{110\}$ surfaces (110 : 1.99 eV and 100 : 2.27 eV) is lower than that on the $\{111\}$ surface (111 : 2.60 eV), which

gives better low-temperature surface reducibility of CeO_2 nanorods. More recently, Ta et al.^[22] and Agarwal et al.^[23] reported the synthesis of CeO_2 nanorods with predominantly exposed $\{111\}$ surfaces with various surface defects.

As shown from the HR-TEM images in Figure 1b, a variety of surface defects on CeO_2 nanorods were observed, including steps, lattice disorder, and dislocation. The gas adsorption step on the oxide surface is fundamentally important to many gas–solid reactions. Oxygen deficient surfaces or defected oxide surfaces contain oxygen vacancies and dangling bonds, which can contribute to some surface gas adsorption. This kind of gas molecular adsorption and continued interaction with lattice oxygen of the oxides are critical for many gas–solid catalytic cycles, for example, in the Mars–van Krevelen mechanism.^[24] Our HR-TEM analysis leads us to a conclusion that the origin of the superior surface reducibility of CeO_2 nanorods may also relate to these surface defects observed on the $\{111\}$ surface and demands much further research.

XRD and H_2 -TPR

CuO-CeO_2 nanorods (10 wt%) and reduced $\text{CuO}_x\text{-CeO}_2$ nanorods (10 wt%) catalysts were prepared by incipient wetness impregnation by using $\text{Cu}_2(\text{OH})_2\text{CO}_3\cdot\text{H}_2\text{O}$ (copper(II) carbonate) as the copper source followed by oxidation at 400°C in air and reduction treatment at 400°C in 5 vol% $\text{H}_2/95$ vol% He, respectively. The XRD patterns of the two samples are shown in Figure 2b and c, in which the labeled diffraction peaks corresponding to CuO (JCPDS 45-0937) and Cu (JCPDS 04-0836) are shown; each was identified after the oxidation and reduction treatments. From XRD analysis, after the reduced 10 wt% $\text{CuO}_x\text{-CeO}_2$ nanorods sample was exposed to air, no CuO was detected. However, it is still possible some small size copper oxides exist in the sample. The sharper metallic Cu peaks in Figure 2c indicates a larger particle size and a more crystalline nature of Cu compared with those of CuO particles before the reduction treatment. The XRD profile (Figure 2a) of CeO_2 nanorods was included as a reference, which revealed no noticeable change before and after copper loading and thermal treatments.

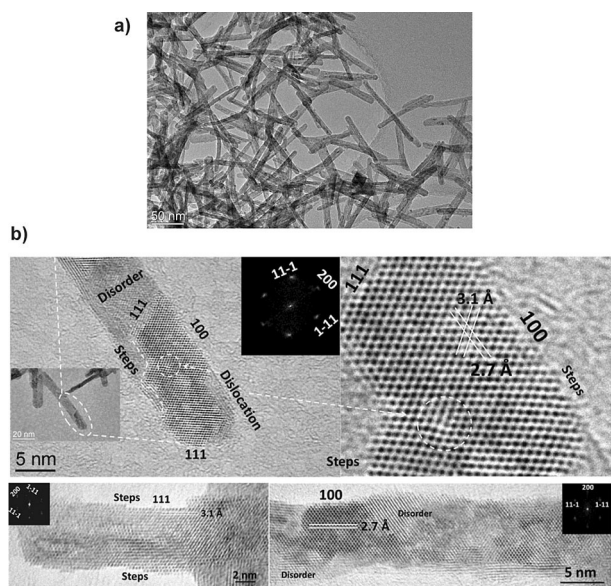


Figure 1. TEM (a) and HR-TEM images (b) of the as-synthesized CeO_2 nanorods (diffractogram inserted).

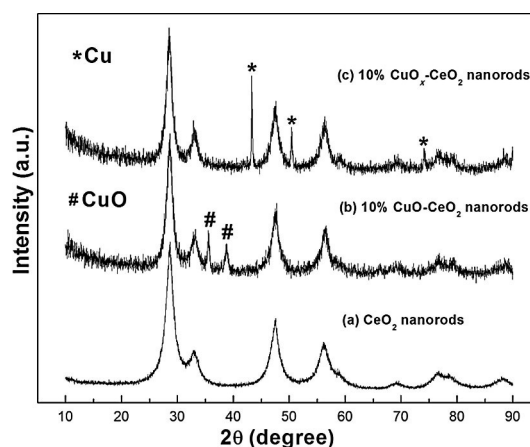


Figure 2. XRD patterns of CeO_2 nanorods, 10 wt% CuO-CeO_2 nanorods (oxidized), and 10 wt% $\text{CuO}_x\text{-CeO}_2$ nanorods (reduced) catalysts.

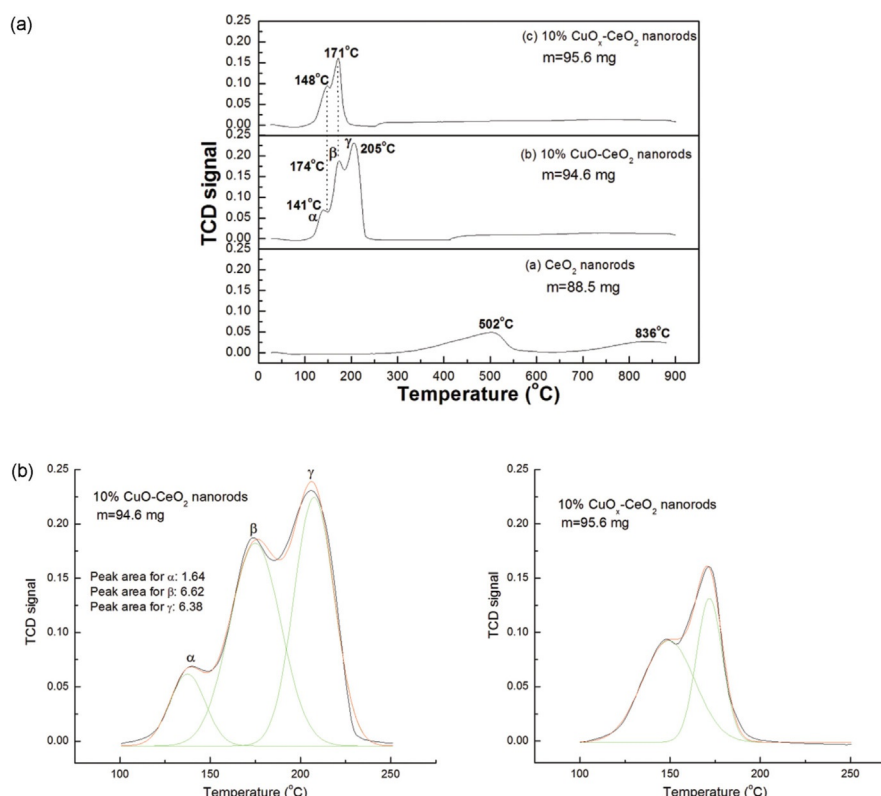


Figure 3. (a) H₂-TPR profiles of the CeO₂ nanorods, 10 wt% CuO–CeO₂ nanorods (oxidized), and 10 wt% CuO_x–CeO₂ nanorods (reduced) catalysts. (b) Peak area analysis (H₂ consumption) of the H₂-TPR profiles.

Figure 3 shows the H₂-TPR profiles and H₂ consumption analysis of CeO₂ nanorods, 10 wt% CuO–CeO₂ nanorods, and reduced 10 wt% CuO_x–CeO₂ nanorods using the same TCD signal scale and similar sample weight (≈ 90 mg). The H₂-TPR profile in Figure 3a(a) for CeO₂ nanorods illustrates two reduction peaks for the surface and bulk reductions, with a relatively higher surface reduction peak at 502 °C. The distribution between the surface and bulk reduction areas is a good indicator for the overall low-temperature performance of the material as an oxidation–reduction catalyst. It is clear that CeO₂ nanorods have a much higher surface reduction percentage (a larger percentage of the reduction takes place in the lower temperature area) than their conventional octahedrally shaped counterparts with {111} crystal planes^[25] and nanocubes with {001} surfaces.^[15]

Figure 3a(b) and Figure 3a(c) show the H₂-TPR profiles of the 10 wt% CuO–CeO₂ nanorods and reduced 10 wt% CuO_x–CeO₂ nanorods, correlated to three-step (Figure 3a(b)) and two-step (Figure 3a(c)) reduction profiles. Both two-step and three-step H₂-TPR reduction profiles have been reported for CuO–CeO₂ catalysts. Typically, the low-temperature peak from the two-step reduction profile is assigned to the smaller crystalline CuO, which is well-dispersed and strongly interacting with the CeO₂ support. The high-temperature peak is attributed to “bulk-like” larger CuO particles that interact weakly with the CeO₂ support.^[10,26] In contrast, the three-step reduction profiles are assigned from low to high temperature as follows: CuO strongly interacting with CeO₂ support; highly dispersed

CuO_x species on the CeO₂ support; “bulk-like” larger size CuO particles.^[27] Our results appear to agree with the three-step reduction assignment for the CuO–CeO₂ sample, which are labeled as α , β , and γ in Figure 3a(b). The larger size CuO particles is a result of the thermal decomposition of Cu₂(OH)₂CO₃·H₂O (copper(II) carbonate). The reduced 10 wt% CuO_x–CeO₂ nanorods sample with metallic Cu⁰ (Figure 2c) was prepared with a typical reduction treatment at 400 °C for 5 h in 5 vol% H₂/95 vol% He, by using the CuO–CeO₂ sample (Figure 2b). According to the H₂-TPR profile of the reduced 10 wt% CuO_x–CeO₂ nanorods sample, the two H₂ consumption or reduction peak positions are documented at 148 °C and 171 °C. These peak positions are very close to the α and β -type reduction peaks (141 °C and 174 °C in Figure 3a(b)) for the CuO–CeO₂ sample, in which the low-temperature peak is assigned to CuO strongly interacting with the CeO₂ support and the intermediate temperature peak is attributed to highly dispersed CuO_x weakly interacting with the CeO₂ support.

After the reduction treatment of the CuO–CeO₂, the reduced 10 wt% CuO_x–CeO₂ nanorods sample was not protected under inert gas. Before the H₂-TPR experiment of the reduced 10 wt% CuO_x–CeO₂ nanorods sample, XRD analysis was used to check and no visible CuO phase was observed (Figure 2c). This suggests that the large size (or bulk) metallic copper on CeO₂ was not oxidized if exposed to air. As no further H₂ consumption (TCD signal ≈ 0) was observed for pure CuO in our experiment above 400 °C during H₂-TPR (Figure 4), it is assumed that CuO in the CuO–CeO₂ was reduced to metallic

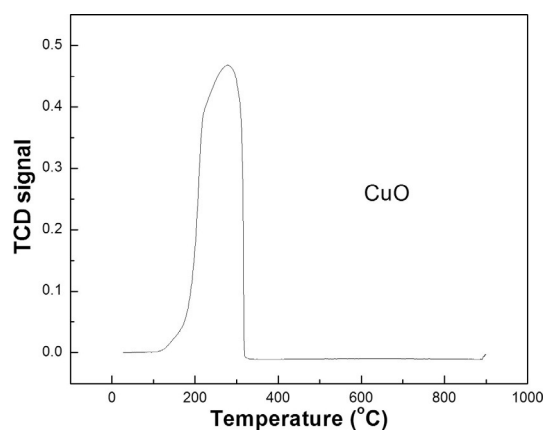


Figure 4. H₂-TPR profile of CuO.

copper during the H₂ reduction treatment at 400 °C for 5 h. The surface reduction temperature of the CeO₂ nanorods starts around 300 °C and is centered at 502 °C (Figure 3a(a)). Therefore, the two reduction peaks at 148 °C and 171 °C shown in Figure 3a(c) should originate from the CuO_x-CeO₂ interfacial areas (α and β -type copper species). To quantitatively compare the H₂ consumption of the samples, a peak fitting analysis was applied to the H₂-TPR profiles, shown in Figure 3b. Between 100 and 250 °C, 1293.3 $\mu\text{mol g}^{-1}$ and 3404.6 $\mu\text{mol g}^{-1}$ H₂ consumption (10.3 and 27.1 vol% of the theoretical H₂ consumption of CuO to Cu, respectively) were obtained for the reduced 10 wt% CuO_x-CeO₂ nanorods and 10 wt% CuO-CeO₂ samples, respectively. It is noticed that, in Figure 3b, right, or Figure 3a(c), the peak areas at 148 °C (peak area: 3.13 and H₂ consumption: 720.3 $\mu\text{mol g}^{-1}$) and 171 °C (peak area: 2.49 and H₂ consumption: 573.0 $\mu\text{mol g}^{-1}$) of the reduced 10 wt% CuO_x-CeO₂ nanorods catalyst are larger and smaller than those at 141 °C (peak area: 1.64 and H₂ consumption: 381.4 $\mu\text{mol g}^{-1}$) and at 174 °C (peak area: 6.62 and H₂ consumption: 1539.5 $\mu\text{mol g}^{-1}$) in Figure 3b, left, or Figure 3a(b) for the CuO-CeO₂ nanorods catalyst, respectively, with the similar sample weights (95.6 mg for CuO_x-CeO₂ and 94.6 mg for CuO-CeO₂). A possible explanation for this observation is that some well-dispersed β -type copper particles transform to α -type copper particles by forming stronger interactions with the CeO₂ support during the reduction treatment at 400 °C. Sun et al.^[28] reported that in a reducing environment, Pd and Ce_xZr_{1-x}O₂ form a strong metal/oxide interaction, involving complex mass and charge transportation around the metal/support interface area. As α -type copper strongly interacts with the support, it is possible copper and CeO₂ form Cu-O-Ce solid solutions at the interface during the reduction thermal treatment.

To further understand the thermal stability of the different types of copper species on CeO₂ nanorods and cyclic hydrogen consumption in the 10 wt% CuO-CeO₂ nanorods sample, a series of H₂-TPR and H₂-TPR/O₂-TPO cycling experiments were conducted. During the H₂-TPR cycling experiments, between the five TPR runs, the sample in the U-tube system was kept with no gas flow during cooling (and was not exposed to air).

For H₂-TPR/O₂-TPO cycling experiment, five H₂-TPR runs and four O₂-TPO runs were conducted. Between the TPR and TPO runs, the system was flushed by using 5% O₂/95% He or 5% H₂/95% Ar for 2 h at 50 °C to remove any residual gases from the previous run. To avoid thermal deactivation, each H₂-TPR or H₂-TPR/O₂-TPO was only run up to 350 °C. As shown in Figure 5a, with no oxidation treatment (O₂-TPO) in between, the second to fifth TPR cycling experiments show two reduction peaks similar to these assignments of α and β -type copper species in the reduced 10 wt% CuO_x-CeO₂ nanorods sample. As no γ -type ("bulk-like" larger size CuO particles) reduction peak was observed for the second to fifth TPR cycling experiments (Figure 5a), this suggests the larger size metallic copper (Cu) did not reoxidize during cooling, but the smaller size α and β -type copper species seemed to be reoxidized in the sample U-tube. As α and β -types of copper species are in good "contact" with the CeO₂ nanorod support, one possible origin of oxygen for the copper reoxidation may be from the interfacial area between copper and CeO₂. It is well-known that partially reduced CeO_{2-x} can be readily oxidized.^[12] The residual oxygen in the U-tube system could be the source for the oxidation of CeO_{2-x} during cooling. In other words, the

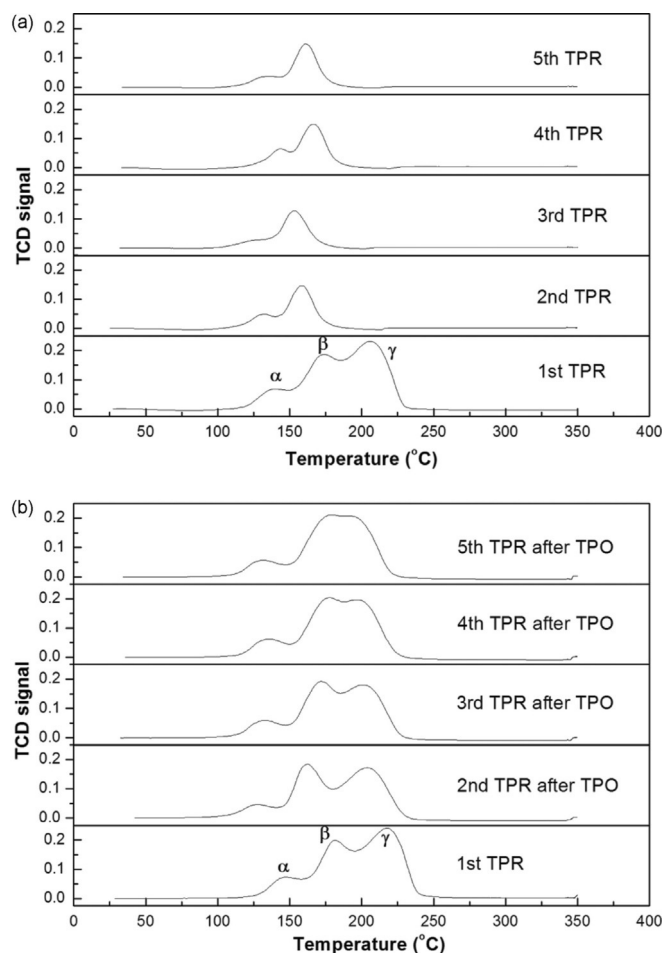


Figure 5. H₂-TPR cycling profiles for (a) five consecutive H₂-TPR runs and (b) five H₂-TPR runs with a TPO in between for CuO-CeO₂ nanorods (oxidized) sample.

redox behavior of CeO_2 was the key reason for the continuous H_2 consumption in the reduced 10 wt% $\text{CuO}_x\text{-CeO}_2$ nanorods samples during these H_2 -TPR cycling experiments. The role of copper species at the interfacial areas may be to trigger the lattice oxygen release of CeO_2 occur at a lower temperature. Wang et al.^[2] reported that the presence of Cu facilitates the formation of oxygen vacancies in CeO_2 if in situ techniques are used.

The H_2 -TPR/ O_2 -TPO cycling experiments caused little change in the hydrogen consumption and reduction temperature of α -type copper species; however, the β and γ -type species seem to merge together with the increased cycling number, shown in Figure 5b. From the analysis and assignments above, β and γ -type species correspond to well-dispersed copper and "bulk-like" larger size copper species, respectively. The cycling results indicate a possible sintering process owing to the weak interaction of well-dispersed small β -type copper with the larger size CuO_x particles. Meanwhile, the α -type copper demonstrates good thermal stability on CeO_2 nanorods under reductive and oxidative conditions. With these findings, it suggests that maximizing the content of α -type copper species will provide a desired low-temperature hydrogen consumption profile and a thermally stable $\text{CuO}_x\text{-CeO}_2$ catalyst.

Raman analysis

Figure 6 shows the Raman spectra of CeO_2 nanorods, CuO-CeO_2 , $\text{CuO}_x\text{-CeO}_2$, and CuO . In Figure 6a, the CeO_2 nanorods exhibit the first-order F_{2g} peak near 461 cm^{-1} . The Raman bands at 262 and 602 cm^{-1} have been reported to be associated with oxygen vacancies in CeO_2 .^[29] The monoclinic CuO exhibits five major Raman bands at 275, 506, 622, 1086, and 1241 cm^{-1} in the range between 200 and 1300 cm^{-1} (Figure 6d). These five bands can also be observed in both 10 wt% CuO-CeO_2 and reduced 10 wt% $\text{CuO}_x\text{-CeO}_2$ samples with a relatively similar intensity. Metallic Cu is not Raman

active therefore all Raman bands are attributed to CeO_{2-x} ($0 \leq x \leq 0.5$) and CuO_x ($0 < x \leq 1$). From the H_2 -TPR experiments, α , β , and γ -type CuO are readily reduced at temperatures below 250°C (Figure 3a). Therefore, after a reduction treatment at 400°C for 5 h, all three types CuO (α , β , and γ) should be reduced to the metallic Cu phase, which was confirmed by X-ray diffraction analysis, as shown in Figure 2c, although it is not clear about the valence states of copper species at the $\text{CuO}_x/\text{CeO}_2$ interfacial area. Accordingly, no copper oxide species were detected from the X-ray diffraction in the reduced 10 wt% $\text{CuO}_x\text{-CeO}_2$ nanorods sample. However, the Raman analysis of the reduced 10 wt% $\text{CuO}_x\text{-CeO}_2$ nanorods sample, in Figure 6c, seems to point to a certain coexistence of CuO_x ($0 < x \leq 1$) (for the peaks at 622, 1086, 1241 cm^{-1}) with metallic Cu or a formation of Cu-O-Ce solid solutions. Compared with the pure CeO_2 sample (Figure 6a), an evident peak shifting for the F_{2g} band was observed for both the $\text{CuO}_x\text{-CeO}_2$ and CuO-CeO_2 samples, which is typically explained by the formation of solid solutions in cerium-based oxides or oxygen vacancy creation.^[30,31] In Au-CeO_2 , it was reported that this first-order CeO_2 F_{2g} peak shift correlates with the reactivity for CO oxidation.^[30] The most possible location of these oxygen-containing copper species should be at the $\text{CuO}_x\text{-CeO}_2$ interface for the reduced 10 wt% $\text{CuO}_x\text{-CeO}_2$ nanorods sample, probably owing to the abundance of surface oxygen and defects located on the CeO_2 nanorods. Ultimately, this demands a great deal of further investigation to understand the oxygen and copper distribution at the interface with high spatial resolution techniques, which are underway.

Catalytic activity

As shown in Figure 7, the catalytic activity of the 10 wt% CuO-CeO_2 nanorods and 10 wt% $\text{CuO}_x\text{-CeO}_2$ nanorods for CO oxidation were compared at varying temperatures up to 350°C . Results from a pure CeO_2 nanorods sample are included as a reference. The activities of the catalysts are compared as

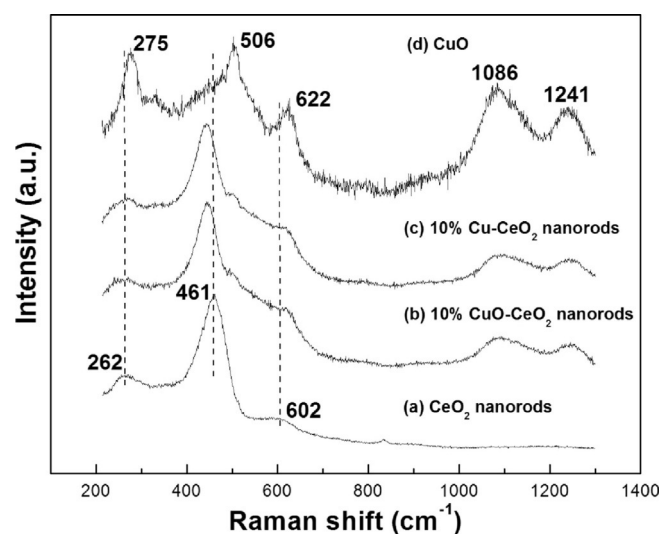


Figure 6. Raman spectra of CeO_2 nanorods (a), CuO-CeO_2 nanorods (oxidized) (b), $\text{CuO}_x\text{-CeO}_2$ nanorods (reduced) (c), and CuO (d).

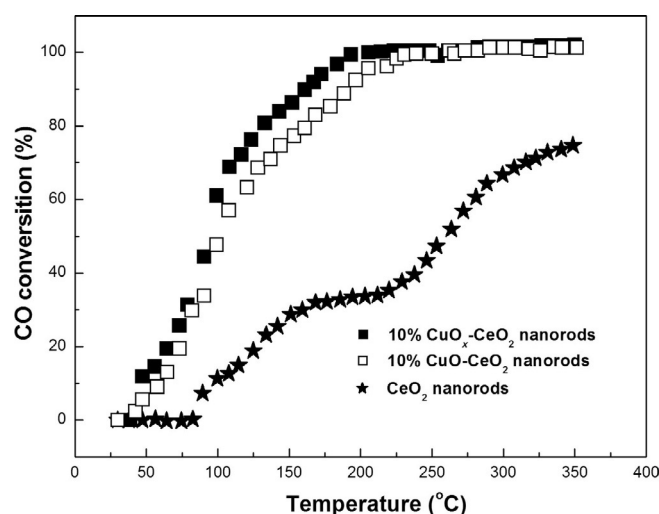


Figure 7. CO conversion by using CeO_2 nanorods, 10 wt% CuO-CeO_2 nanorods (oxidized), and 10 wt% $\text{CuO}_x\text{-CeO}_2$ nanorods (reduced).

follows based on the T_{50} and T_{100} (temperatures under which 50% CO and 100% conversion are achieved): T_{50} : $\text{CuO}_x\text{-CeO}_2$ (92°C) < CuO-CeO_2 (100°C) < CeO_2 (258°C) and T_{100} : $\text{CuO}_x\text{-CeO}_2$ (201°C) < CuO-CeO_2 (231°C) < CeO_2 (N/A), denoted in Table 1. Both the CuO-CeO_2 and $\text{CuO}_x\text{-CeO}_2$ samples have very

	Sample mass [mg]	BET surface area [m^2g^{-1}]	T_{50} [$^\circ\text{C}$]	T_{100} [$^\circ\text{C}$]
CeO_2 nanorods	29.1	46.4	258	–
10 wt% CuO-CeO_2 nanorods	24.4	41.5	100	231
10 wt% $\text{CuO}_x\text{-CeO}_2$ nanorods	24.5	38.8	92	201

similar activity; however, they are more effective catalysts for CO oxidation compared with pure CeO_2 , which was expected. The CeO_2 nanorods also show an enhanced catalytic activity for CO oxidation compared with previously reported CeO_2 octahedral nanoparticles,^[14,15] which is consistent with H_2 consumption during the H_2 -TPR experiment. Octahedral or truncated octahedral shape CeO_2 possesses eight {111} planes with less surface defect density, shown in Figure 8. With a higher defect density on {111} planes and exposing more reactive {011} and {001} surfaces, this result suggests a stronger

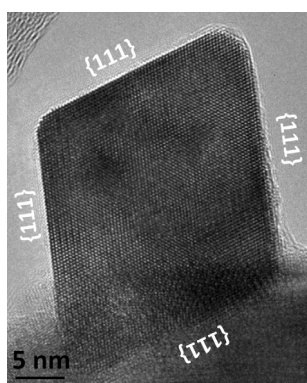


Figure 8. HR-TEM image of individual octahedral shape CeO_2 .

metal–oxide interaction at the interface for the CeO_2 nanorod-supported CuO_x catalysts.

TEM analysis

A detailed TEM analysis was performed to provide information about the spatial distribution and interaction of CuO_x ($0 \leq x \leq 1$) species with the CeO_2 nanorod support. Figure 9 shows the TEM images of the CuO-CeO_2 nanorod and $\text{CuO}_x\text{-CeO}_2$ nanorod catalysts. The evidence obtained from TEM analysis confirms the previous assignments about three-type CuO , and two-type Cu supported on CeO_2 nanorods. To distinguish α and β -type copper species on CeO_2 nanorods, tilting experiments were carefully conducted for these clusters presented in Figure 9 to confirm there is an epitaxial-like relationship between α -type copper and the CeO_2 support, whereas β -type copper is just loosely dispersed over the CeO_2 nanorods. HR-TEM imaging was used to identify the atomic-level structure and defects and as indicated in Figure 10 and a relatively large amount of defects on the CeO_2 nanorods was observed, including voids, lattice distortion, and steps. For the individual nanorods along a specific zone axis (projection), direct spacing measurements on the HR-TEM images was used to determine the plane distance among those surface lattice fringes. In most cases, those lattice fringes correspond to the {111} and {100} family, with a d -spacing at about $3.12\text{--}3.16\text{ \AA}$ and $2.7\text{ \AA}$, respectively. In some cases, in addition to {111} and {100} planes,

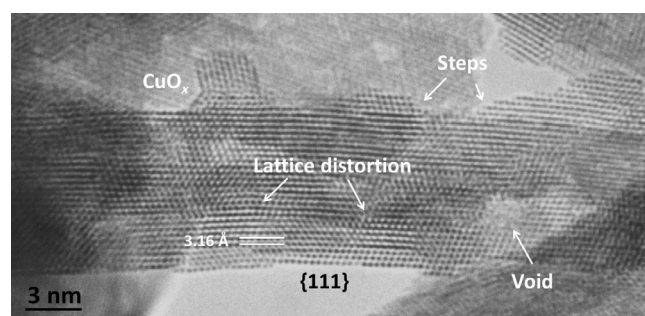


Figure 10. High-resolution TEM analysis of $\text{CuO}_x\text{-CeO}_2$ nanorods (reduced).

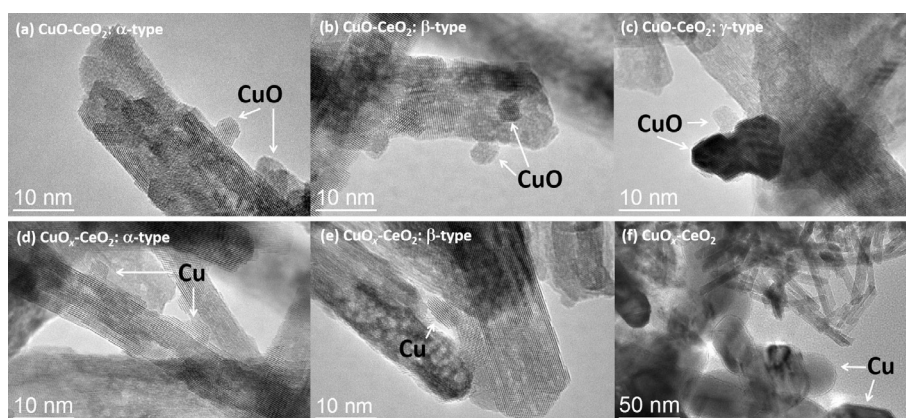


Figure 9. TEM analysis of CuO-CeO_2 nanorods (oxidized) and $\text{CuO}_x\text{-CeO}_2$ nanorods (reduced) catalysts to identify various CuO_x ($0 \leq x \leq 1$) species assigned in the H_2 -TPR profiles.

some rods exhibit {011}-type surfaces, with a *d*-spacing at approximately 1.9 Å. HR-TEM analysis provides a two-dimensional (2D) projection of the object along a certain direction, which can tell us about the surface structure and defect distribution of the three-dimensional (3D) CeO₂ nanorods, it was then postulated that the surface defects extend uniformly along the total surface of the rods. Importantly, these CeO₂ nanorods with dominant {111} and {100} surfaces show significantly improved surface reduction, which was inconsistent with the reduction behavior of octahedral shape CeO₂ with predominantly exposed {111} surfaces, which are less reactive (higher percentage of bulk reduction in H₂-TPR). These results suggest that the surface defects might be responsible for the strong interactions of CuO_x and CeO₂ and result in the improved low-temperature reducibility and catalytic activity.

Several reaction mechanisms have been proposed to understand the CO oxidation on CeO₂-supported metal catalysts, including the Langmuir–Hinshelwood mechanism,^[32] Mars–van Krevelen mechanism,^[33] and Eley–Rideal mechanism.^[34,35] These mechanisms all point out the importance of oxygen vacancies and surface defects on the CeO₂ support. For example, for the Langmuir–Hinshelwood mechanism,^[32] CO is adsorbed on the metal/metal oxide catalyst, oxygen is adsorbed on the CeO₂ support, and the reaction takes place at the perimeter at the catalyst/support interface. Therefore, owing to the superior surface oxygen storage capacity (OSC), the CeO₂ nanorods with significant surface defects certainly provide gas sorption sites and anchoring sites for metal/metal oxide catalysts to form a stronger bonding and interface. If crystalline migration is the sintering mechanism, this SMSI would immobilize the copper species and thereby decrease the rate of sintering, leading to a better thermal stability of the catalysts.

Structural models of CuO_x–CeO_{2–x} interfaces

As shown in Figure 11, based on the TEM analysis as well as the H₂-TPR results, possible structural models are proposed to elucidate the interfacial structures in CuO–CeO₂ and CuO_x–CeO₂ and the reduction processes from CuO–CeO₂ to CuO_x–CeO₂. In the CuO–CeO₂ sample, three copper species co-exist: α–CuO_x strongly interacting with CeO₂ nanorods; β–highly dispersed CuO_x species with CeO₂ nanorods; γ–“bulk-like” larger CuO particles mixed with CeO₂ nanorods. For

the first two copper species, it is likely to form a mixture of Cu⁺ and Cu²⁺ or Cu–O–Ce solid solutions, particularly at the CuO–CeO₂ and CuO_x–CeO₂ interfaces owing to incomplete oxidation/reduction or charge/oxygen interaction with the CeO₂ support. It has been reported that a high ratio of Ce³⁺ on the surface was observed on CeO₂ nanorods.^[36] The oxygen transfer could lead to oxidation of Ce³⁺ to Ce⁴⁺ and reduction of Cu²⁺ to Cu⁺ at the interface. After the reduction treatment at 400 °C for 5 h, the α and β-type CuO_x are reduced to α and β-type metallic Cu, although the oxidation state of copper and structure at the interface is not clear. Owing to the surface defects on CeO₂ nanorods, a strong interaction between CuO_x and CeO₂ is formed. α-Type CuO_x is highly dispersed and strongly bonded on the CeO₂ nanorods support and do not undergo significant growth or sintering, as indicated from TPR and TPR/TPO cycling experiments. β-Type CuO_x is loosely bonded on the CeO₂ nanorods support, so it merged with γ-type larger size CuO owing to the sintering effect. The γ-type CuO_x is not only reduced to metallic Cu, but also sinters significantly based on the crystalline migration mechanism (XRD pattern in Figure 2c and TEM image in Figure 9f). This explains the transition from three reduction peaks to two reduction peaks in the H₂-TPR experiments (Figure 3).

Conclusions

The high activity of CeO₂ nanorod-supported CuO_x (0 ≤ *x* ≤ 1) for CO oxidation reaction at low temperature is primarily attributed to the synergistic effect of CuO_x (α and β) species and the superior oxygen storage/release capability of the CeO₂ nanorods support. Several surface defects on the CeO₂ nanorods were observed by using HR-TEM, including voids, lattice distortion, and steps. These defects induce a strong interaction between the CuO_x (0 ≤ *x* ≤ 1) and CeO_x (1.5 ≤ *x* ≤ 2) nanorods. The reduction treatment further accelerates the formation of active states or sites and mass transfer/interaction between CuO_x and CeO_{2–x} support. This creates not only sites for gas molecule sorption and metal catalyst anchoring, but also immobilizes the migration of the copper species during the thermal cycling. This then provides a way to make desirable low-temperature active and thermally stable catalysts.

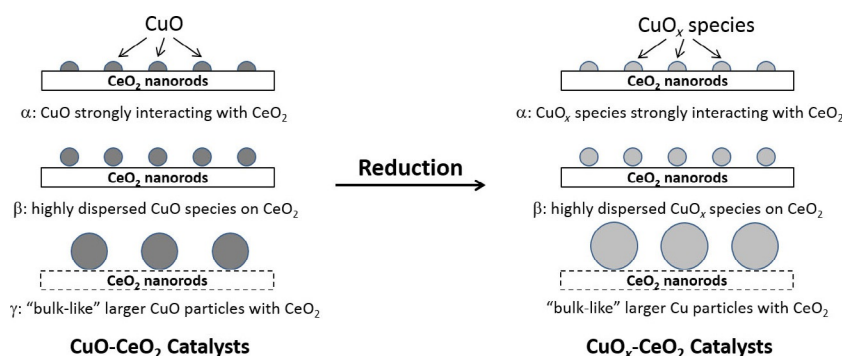


Figure 11. Proposed mechanism for CuO/CuO_x-CeO₂ nanorod catalysts to explain the H₂-TPR results.

Experimental Section

Catalyst preparation

CeO₂ nanorods were prepared by a hydrothermal method at 90 °C for 24 h, by using 0.1 M Ce(NO₃)₃·6H₂O as the cerium source and 6 M NaOH. Typically, 0.1 M Ce(NO₃)₃·6H₂O and 6 M NaOH mixtures were heated to 90 °C and held for 24 h in a sealed 23 mL Teflon-lined autoclave (≈50% fill). Then, the autoclave was cooled to room temperature before the solid products were recovered by suction or vacuum filtration. The materials were washed thoroughly with distilled water to remove any co-precipitated salts, then washed with ethanol to avoid hard agglomeration of the nanoparticles, and dried in air at 50 °C for 12 h. No further calcination was done on the CeO₂ nanorods. The CeO₂ powders were not calcined before metal loading. CuO (10 wt%) was loaded onto the CeO₂ nanorod supports by using an incipient wetness technique (impregnation method) by using Cu₂(OH)₂CO₃·H₂O (copper(II) carbonate) as the copper source. The filtered sample was dried at 100 °C for 12 h. The 10 wt% CuO–CeO₂ catalyst was obtained by calcination in air at 400 °C for 5 h. The reduced 10 wt% CuO_x–CeO₂ catalyst was then obtained by a reduction treatment in a tube furnace under 5 vol% H₂/95 vol% He atmosphere at 400 °C for 5 h. The reduced 10 wt% CuO_x–CeO₂ catalyst was exposed to air and stored in a glass vial before characterization, and no detectable oxidation was observed based on XRD analysis.

Catalyst characterization

Powder X-ray diffraction (XRD) analysis was performed with a Rigaku Miniflex II diffractometer using CuK_α radiation with a wavelength of 1.5408 Å. The sample was loaded on an aluminum plate and the data was collected over a 2θ range of 5–90° with a step size of 0.5° min^{−1}. The recorded patterns were analyzed by using JADE software to determine peak positions, lattice constants, and average crystalline sizes by use of Scherer's formula.

Raman scattering was performed with a Horiba iHR 320 Raman Spectrometer with a 532 nm laser module and 10–40 s exposure time. All peak intensities and positions were obtained with Lorentzian fitting. The Raman scattering in the 100–3200 cm^{−1} region was collected. Single-point BET surface area analysis of the catalysts was determined by N₂ adsorption/desorption isotherms at liquid nitrogen temperature. Hydrogen temperature-programmed reduction (H₂-TPR) study of the as-prepared catalysts was examined by using hydrogen chemisorption with a Micromeritics AutoChem™ II 2920 chemisorption analyzer instrument to explore how much hydrogen adsorbs and is consumed by the catalyst as a function of temperature. No pretreatment was performed before each H₂-TPR run unless otherwise indicated. The powder samples were heated at a rate of 10 °C min^{−1} from room temperature to 900 °C. The gas mixture (5 vol% H₂ and 95 vol% Ar with oxygen trace less than 10 ppm) was passed through the catalyst sample (80–100 mg) at a rate of 50 mL min^{−1}. A cold trap filled with a mixture of isopropanol, KCl, and ice was placed in the gas line upstream of the thermal conductivity detector (TCD) to remove any water moisture. A thermal conductivity detector continuously monitored the H₂ concentration. A cuprous oxide sample (Cu₂O) was used to calibrate the TPR profile peak area allowing the consumption of H₂ to be calculated. Temperature-programmed reduction and temperature-programmed oxidation (TPR/TPO) cycling experiments, including five TPR and four TPO, were carried out from room temperature to 350 °C under 5 vol% H₂/95 vol% Ar and 5 vol% O₂/95 vol% He atmosphere, respectively. Between TPR and TPO or TPO and TPR, the

system was flushed with 5 vol% O₂/95 vol% He or 5 vol% H₂/95 vol% Ar for 2 h at 50 °C, respectively.

A JEOL 2100 transmission electron microscope (TEM) was used for structural and chemical analysis of the nanocrystals at the atomic level. The JOEL 2100 equipped with an EDAX detector for chemical composition analysis and an annular dark-field detector was operated at 200 kV. High-resolution transmission electron microscopy (HR-TEM) was used to determine the exposed crystal facets in individual CeO₂ nanocrystals. Samples for the TEM were prepared by using dilute suspensions of the nanopowder samples. These solutions were obtained by sonication of particles in ethanol for 5 min then dropping the suspension of the sample powders onto an ultrathin carbon film/holey carbon, 400 mesh copper grid (from Ted Pella) and air drying for several hours.

Measurement of catalytic activity for CO oxidation

The catalytic oxidation of CO was conducted by using a fixed-bed plug flow reactor system. 1 vol% CO/20 vol% O₂/79 vol% He with a 70 mL min^{−1} flow rate was supplied by a mass flow controller and passed through the catalyst bed. The catalyst (≈30 mg) was mixed with quartz wool (coarse, 9 μm) and filled in the quartz tube reactor. The reaction temperature was programmed between 30 °C and 350 °C and monitored by a thermocouple. The reactant CO and product CO₂ were analyzed by using an on-line gas chromatograph (SRI multiple gas analyzer GC, 8610C chassis) system. The catalytic activity or CO conversion was calculated with Equation (1):

$$\% \text{CO conversion} = \left[\frac{P_{\text{CO}_2}}{P_{\text{CO}} + P_{\text{CO}_2}} \right] \times 100 \quad (1)$$

where P_{CO} and P_{CO_2} are the partial pressure of CO and CO₂, respectively, which are determined from the relative peak areas of the CO and CO₂ peaks normalized to the He standard.

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