

CO Oxidation Catalyst | Very Important Paper |

VIP

Optimum Balance of Cu⁺ and Oxygen Vacancies of CuO_x-CeO₂ Composites for CO Oxidation Based on Thermal TreatmentBaolin Liu,^[a] Yizhao Li,^[a,b] Yali Cao,^{*[a]} Lei Wang,^[b] Shaojun Qing,^[c] Kun Wang,^[a] and Dianzeng Jia^{*[a]}

Abstract: It is important to exploit non-noble metal catalysts with excellent performance toward CO oxidation. Here, CuO_x-CeO₂ composites with a size of about 4 nm have been fabricated by a facile and mild in situ route without solvent or liquid reactant involved. The balance between Cu⁺ concentration and oxygen vacancy on the CeO₂ surface, which are beneficial for catalytic activity, can be tailored by the amount of Cu loading and the thermal treatment parameters of composites. The as-obtained CuO_x-CeO₂ (C-9-6-C) composites with lower Cu loading exhibited excellent CO reactivity and superior stability at

lower temperatures, which enable the total oxidation of CO at 110 °C. Appropriate heat treatment promoted the available migration of Cu species from the surface to the interior of the CeO₂ lattice, which guaranteed the existence of affluent oxygen vacancies. The enhanced activity of CuO_x-CeO₂ composites can be attributed to the preservation of highly dispersed Cu⁺ species and oxygen vacancies on the surface of CeO₂. Hopefully, the CuO_x-CeO₂ nanohybrids prepared by this facile and mild route can be used as a promising potential catalyst for CO oxidation with high efficiency and long life.

Introduction

Nowadays, an increasing amount of CO from industry waste gas, automobile exhaust, and incomplete combustion of fossil fuel is emitted into the atmosphere. As a kind of poisonous gas, CO can cause serious safety problems for human and environment.^[1–3] An effective and convenient strategy is transforming poisonous CO to nontoxic CO₂ with the appropriate catalyst, which has been given an increasing concern for researchers in automobile exhaust gas treatment, air purification and fuel cell technology.^[4–7] Up to now, noble metal-based catalysts with high activity for CO oxidation at lower temperature have been extensively studied.^[8–10] However, their extensive application are hindered due to high cost and shortage.^[12–15] Meanwhile, many elements on Earth are rare and unevenly distributed, and thus economically strategic and at potential supply risk.^[11] Therefore, it is necessary to exploit relatively cheap non-noble metal catalyst with high catalytic activity and decrease the metal loading for CO oxidation.

Among the various alternatives, CuO_x-CeO₂ catalysts has been extensively investigated as a result of their low-cost and environmentally friendly.^[16–20] CeO₂ exhibits the oxygen storage capacity (OSC) attributed to the rapidly reversible transformation between Ce³⁺ and Ce⁴⁺ can supply oxygen under the condition of oxygen deficit and reserve oxygen in the case of abundant oxygen.^[20–22] The oxygen vacancies that play important roles in catalytic reaction are created in the process of valence transition.^[19,21,23–26] The high activity of CuO_x-CeO₂ catalysts in CO oxidation is contributed by not only the active component (CuO_x) but also the strong CuO_x-CeO₂ interaction and the excellent oxygen supply capability of CeO₂. The metal oxide interaction can be enhanced by high heat treatment, but the catalytic activity may be limited by the sintering and growth of active component.^[27,28] Morphology adjusting of catalysts to preferential exposure active lattice planes and introducing foreign dopants into bulk phase are main routes for improving the performance of catalysts.^[3,5,29–31] In particular, the catalytic performance of catalyst with metals loading can be significantly modulated by the sizes or dispersions of metals on supports. Accordingly, although the catalytic activity of ceria-supported copper metal catalysts for CO oxidation can be greatly improved,^[13,32–35] a large amount of Cu loading was needed, which is not environment friendly and may cause a huge cost and resource waste. Meanwhile, the reported preparation methods for metal-doped CeO₂ catalysts are time-consuming and solvent-involved. These routes not only conflict with the meritorious fabrication but caused the serious contamination for environment. Therefore, it is imperative to explore an effective and green method for preparation of metal-doped CeO₂ catalyst.

In this paper, a facile and mild route is presented to in situ fabricate high dispersed CuO_x-CeO₂ nanohybrids with a size of

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about 4 nm. The configuration for the incorporating Cu into CeO₂ as catalysts toward CO oxidation was investigated in detail. The effects of the amount and distribution of Cu species on CeO₂ nanoparticles for the CO oxidation have been studied. The CuO_x-CeO₂ catalysts with lower Cu loading (Cu/Ce molar ratio = 0.09) exhibits excellent catalytic performance. The influences of thermal treatment on the structures of CuO_x-CeO₂ composite as well as the dependent relationship between of the constructions and performances of catalysts were also disclosed.

Results and Discussion

Influence of Cu Loading

The powder XRD patterns of various CuO_x-CeO₂ catalysts are showed in Figure 1a. It can be seen that all diffraction peaks correspond well to cubic fluorite phase of ceria (JCPDS NO. 34–0394). The characteristic diffraction peaks belonged to copper component cannot be observed, indicating the presence of highly dispersed CuO_x on the CeO₂ surface. No obvious change in the positions of diffraction peaks (Figure 1a) and lattice parameter with Cu species incorporation (Table 1) support the fact that Cu species are highly dispersed on the CeO₂ surface.^[36] The lower intensity and broader of diffraction peaks imply small size of the samples fabricated by solid-state method.

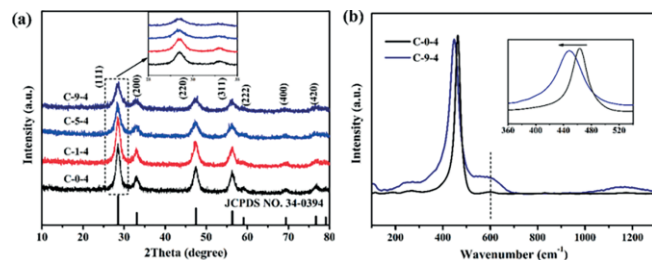


Figure 1. (a) The powder XRD patterns of samples calcined at 400 °C; (b) Raman spectra of C-0-4, C-9-4 samples.

Table 1. The average crystallite size, lattice parameter (LP) value, T₅₀ and T₁₀₀ of samples.

Sample	D [nm] ^[a]	LP [Å] ^[b]	A ₆₀₀ /A _{F2g} ^[c]	T ₅₀ (°C)	T ₁₀₀ (°C)
C-0-4	11.55	5.413	0.016	247	280
C-9-4	8.32	5.406	0.193	108	140
C-9-5	10.18	5.406	0.116	108	160
C-9-6	13.75	5.403	0.113	93	170
C-9-7	22.91	5.407	0.066	98	200
C-9-6-C	11.65	5.402	0.160	84	110

[a] Calculated from CeO₂ (111) lattice plane by the Scherrer equation. [b] Calculated from MDI jade software. [c] Integrated peak areas from the Raman spectra.

Raman spectroscopy was also employed to identify the detailed structural information of CuO_x-CeO₂ catalysts. As shown in Figure 1b, the evident peak at ca. 464 cm⁻¹ can be assigned to the triply degenerate F_{2g} active mode in the cubic fluorite structured ceria.^[26,29,37] Besides, a weaker peak was also observed at 600 cm⁻¹, which can be attributed to oxygen vacancies induced by the existence of trivalent cerium ion (Ce³⁺ cat-

ion).^[15,38,39] Raman peak around 1180 cm⁻¹ corresponds to second-order longitudinal optical (2LO) mode in the ceria lattice, which is related with the O–O stretching vibration mode of surface adsorbed superoxide species (O₂⁻).^[15,38,39] The F_{2g} peak of C-9-4 sample, compared to pure CeO₂, shifted significantly to lower wavenumber and broadened. These phenomenon are contacted with either the decrease of ceria crystallite size or more oxygen vacancies originated from Cu addition.^[40,41] Moreover, the peak intensity at about 600 cm⁻¹ and 1180 cm⁻¹ obviously increased in intensity of peak along with the increasing of Cu content in ceria. It suggests that the incorporation of Cu species induce the increase of oxygen vacancies benefited catalytic performance.

The micromorphology and sizes of samples were acquired by TEM and SEM. As shown in Figure 2, the morphology of pure CeO₂ (C-0-4) and CuO_x-CeO₂ (C-9-4) samples present irregular particles with the size about 4 nm and 3 nm, respectively on the basis of statistical analysis of more than 100 of CeO₂ particles. The grain diameters gradually diminish with the participation of Cu species (Figure 2c-d), which matches well with the results from XRD and Raman. Furthermore, the detailed Cu/Ce ratios of samples with different Cu contents was verified by SEM-EDS measurement and shown in Figure S2 and Table S1, which are consistent with theoretical addition. The low and similar K⁺ content for each samples analyzed by EDS (Table S1) may exhibited positive effect on the catalytic activity, which has been confirmed by previous work.^[42] EDS mapping elemental analysis of CuO_x-CeO₂ (C-9-4) samples were performed. As shown in Figure 2e-f, Cu element distributed homogeneously on CeO₂ surface. The morphology features of samples were acquired by SEM exhibited in Figure S3, which are similar to the TEM results.

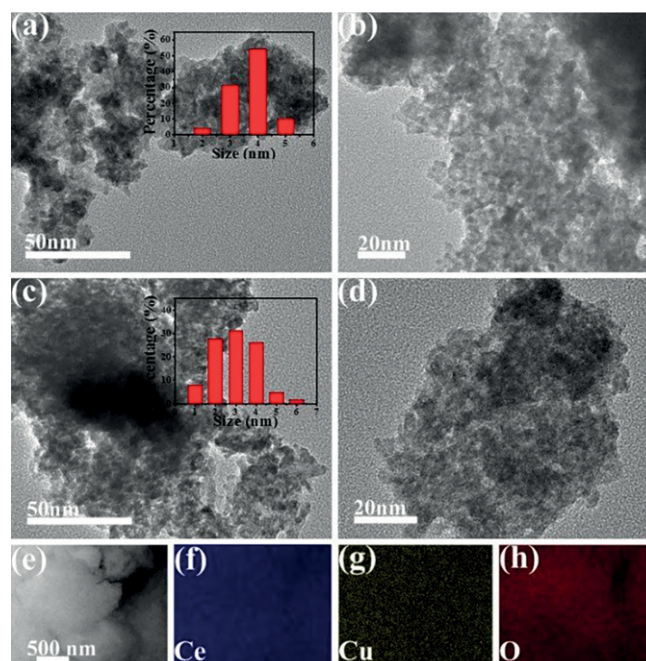


Figure 2. TEM images of samples: (a-b) C-0-4; (c-d) C-9-4; (e-h) mapping analysis of C-9-4 sample (the inset show CeO₂ particle size distribution).

The influence of Cu loading on catalytic performances of $\text{CuO}_x\text{-CeO}_2$ catalysts was investigated. As shown in Figure 3, these catalysts displayed different catalytic performance for CO conversion reaction. The activity enhanced significantly with increasing of Cu concentration. The CO total conversion was accomplished at 280 °C for pure CeO_2 sample. The C-9-4 sample exhibits the best catalytic performance, which could catalyze CO completely oxidation to CO_2 at 140 °C. However, C-15-4 samples obvious decrease in the conversion of CO resulting from the more Cu loading. Therefore, we choose the C-9 sample with the ratio value 0.09 of Cu/Ce to further research.

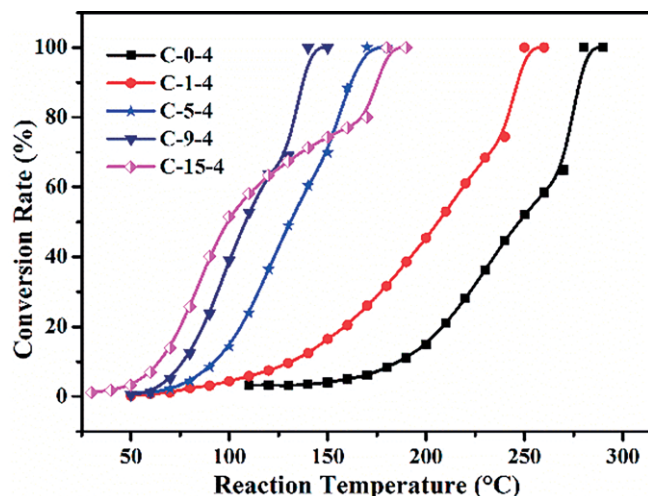


Figure 3. The activities of C-0-4, C-1-4, C-5-4, C-9-4 and C-15-4 samples for CO oxidation.

Influence of Calcination Temperature

Structural and Textural Properties

$\text{CuO}_x\text{-CeO}_2$ (C-9) sample at different calcination temperature was carried out in order to studying the effect of calcination temperature on catalytic activity. With calcination temperature increasing from 400 to 700 °C (Figure 4), the diffraction peaks

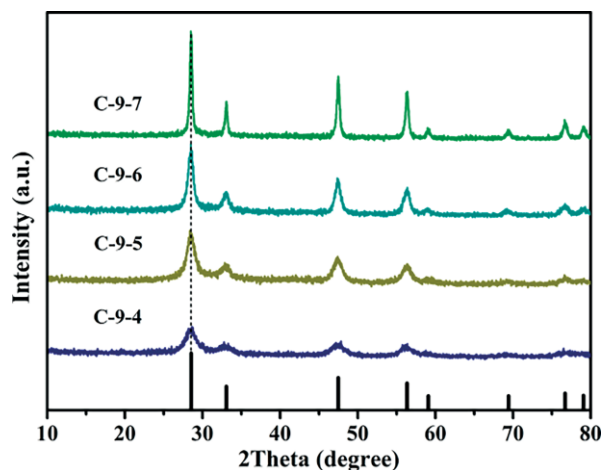


Figure 4. The powder XRD patterns: the C-9 sample with different calcination temperature.

of $\text{CuO}_x\text{-CeO}_2$ (C-9) obtained at different temperature become more sharp and narrow, indicating enhanced crystallization and increased crystalline grain. It's also well correspond to the results calculated by Scherrer equation applied for (111) (Table 1). Meanwhile, the characteristic diffraction peaks of copper compound cannot be observed in XRD pattern, which further demonstrated Cu species with good dispersion on the CeO_2 surface, even $\text{CuO}_x\text{-CeO}_2$ (C-9) calcined at 700 °C.

Furthermore, the changes of specific surface area, pore size and pore volume of $\text{CuO}_x\text{-CeO}_2$ (C-9) samples calcined at different temperature were investigated by N_2 adsorption-desorption isotherms. As shown in Table 2 and Figure S4, specific surface area and pore volume of C-9-4 sample are $91 \text{ m}^2 \text{ g}^{-1}$ and $0.079 \text{ m}^3 \text{ g}^{-1}$. Their pore size distribution curves (Figure S4) are distributed in a range of 2–50 nm, which are associated with the feature of mesoporous materials. The specific surface area of samples decreases drastically with increasing calcination temperature. This can be attributed to the aggregate and growth of CeO_2 nanoparticle.

Table 2. The BET surface area, pore volume, pore size over different catalysts.

Sample	S_{BET} ($\text{m}^2 \text{ g}^{-1}$)	Pore Volume ($\text{m}^3 \text{ g}^{-1}$)	Pore Size [nm]
C-9-4	91	0.079	3.418
C-9-5	54	0.072	3.411
C-9-6	39	0.063	3.415
C-9-7	21	0.043	3.825
C-9-6-C	40	0.056	3.417

Reduction Behavior of Catalysts Before/After N_2O Oxidation

As shown in Figure 5a, the H_2 -TPR technique further confirmed the reduction behavior of the $\text{CuO}_x\text{-CeO}_2$ catalysts. The reduction peaks of pure CeO_2 (C-0-4) at 300–600 °C (Figure S5) can be corresponded to the reduction on surface of CeO_2 .^[14,40] The reduction peaks of C-9-4 catalyst further changed compared to pure CeO_2 . It is obvious that two peaks can be observed at about 170 °C and 200 °C, ascribing to two kinds of copper species.^[39,43,44] No diffraction peaks can be assigned to bulk CuO of which reduction peaks are usually surpass 300 °C (Figure S6), revealing that the formation of the highly dispersed CuO_x species on CeO_2 surface and larger CuO_x species weakly interacted with the CeO_2 .^[39,45,46] As the calcination temperature increases from 400 °C to 700 °C, the intensity of the two reduction peaks both decreased and shifted to lower temperature range. This indicates the declined dispersion of CuO_x particles and stronger interaction between each other. The highly dispersed Cu species with lower reduction temperature would provide more active sites and improve the performance for CO oxidation.^[33] Meanwhile, the amount of total hydrogen uptake of all samples was calculated in Table S2. The amount of total hydrogen consumption of all C-9 samples calcined at different temperature are higher than the theoretical H_2 consumption of CuO ($12.17 \text{ mmol g}^{-1}$) (see Figure 5b), revealing that the CeO_2 can also be reduced as a result of the highly dispersed CuO_x species interacted with the CeO_2 . In addition, the intensity of reduction peaks among all tested samples were decreased, which can be

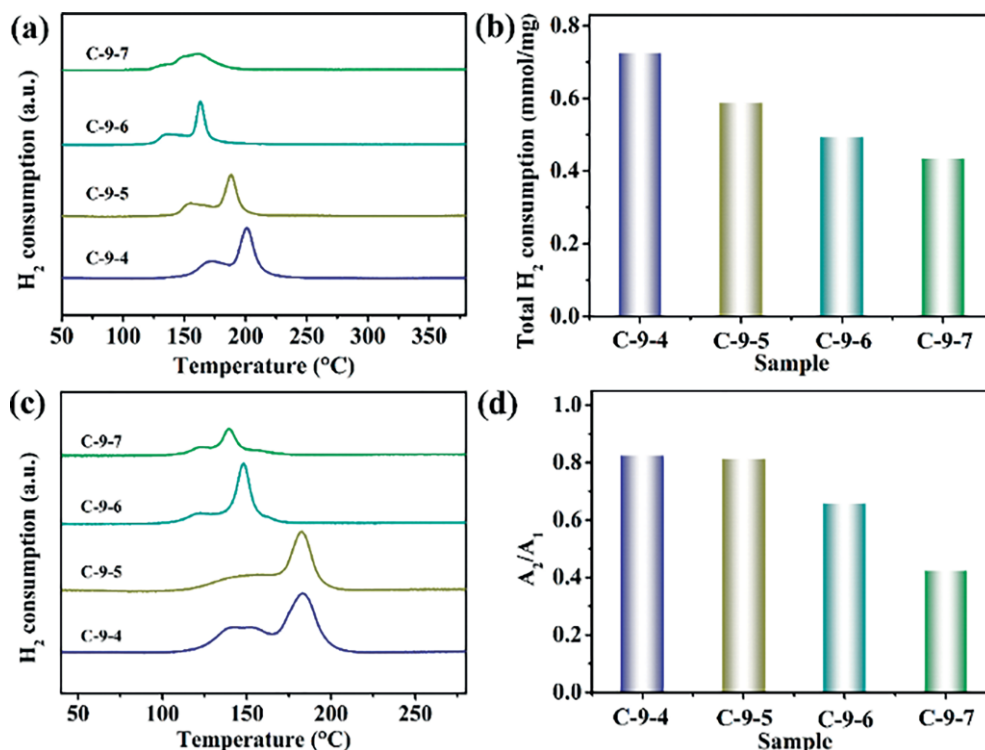


Figure 5. (a) H₂-TPR profile of C-9 sample with various calcination temperature before N₂O oxidizing; (b) The total values of H₂ consumption for different sample; (c) H₂-TPR profile of diverse sample after N₂O oxidizing; (d) the ratios (A₂/A₁) of the hydrogen consumption areas.

ascribed to the agglomeration of CuO_x species on CeO₂ surface, which is also consistent with the decrease of the consuming amount of H₂ in total (summarized in Table S2) for catalyst with increasing calcination temperature.

In order to investigate the surface dispersion of CuO_x on CeO₂ surface, N₂O decomposition analyses was performed. From Figure 5c, the intensity of two reduction peaks was greatly decreased after N₂O oxidizing, which is similar to the variation of the intensity of peaks in Figure 5a. The value of A₂/A₁ decreases with further increase of calcination temperature (Figure 5d and Table S2), which are related to relatively poor distribution of CuO_x as a result of the relative higher calcination temperature.

Oxygen Vacancies and Chemical States

Raman spectra was performed to investigate the structural change of CuO_x-CeO₂ (C-9) samples at different calcination temperature. As shown in Figure 6, the intensity of characteristic F_{2g} peak of CuO_x-CeO₂ (C-9) was enhanced with increasing calcination temperature from 400 to 700 °C. The phenomenon could be related to the increase of ceria crystallite size with further increasing calcination temperature,^[36] which is in line with the XRD results. Moreover, the decreased shoulder peak of oxygen vacancies at 600 cm⁻¹ can be attributed to reduced oxygen vacancies as result of agglomeration and sintering of CuO_x species on CeO₂ surface at higher calcination temperature. Previous literatures also reported that more Cu particle agglomeration on the stoichiometric CeO₂ (111) surface may

suppress the oxygen vacancy formation.^[45,47] On the other hand, partial Cu species would be separated from CeO₂ lattice and agglomerated continuously with increasing calcination temperature,^[48] which result in the reduction of oxygen vacancies. The relative content of oxygen vacancies can be expressed by the peaks area ratio of two bands (A₆₀₀/A_{F2g}) (Table 1). Clearly, the A₆₀₀/A_{F2g} ratios of C-9-4 samples is 0.193, large than other C-9 samples, indicating that C-9-4 samples has more oxygen vacancies, which exhibited better performance for CO oxidation.

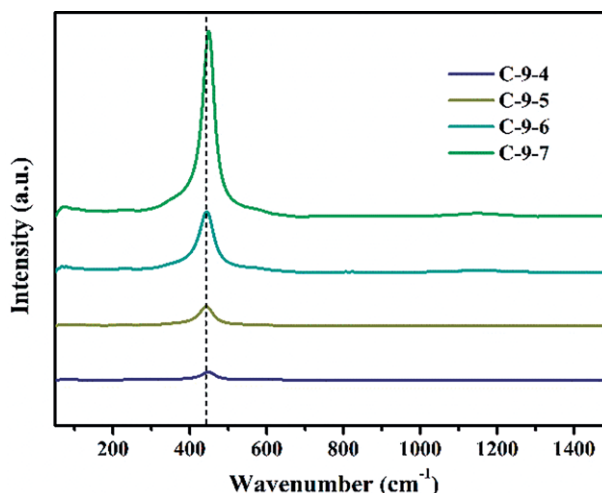


Figure 6. Raman spectra of C-9 samples treated with different calcination temperature.

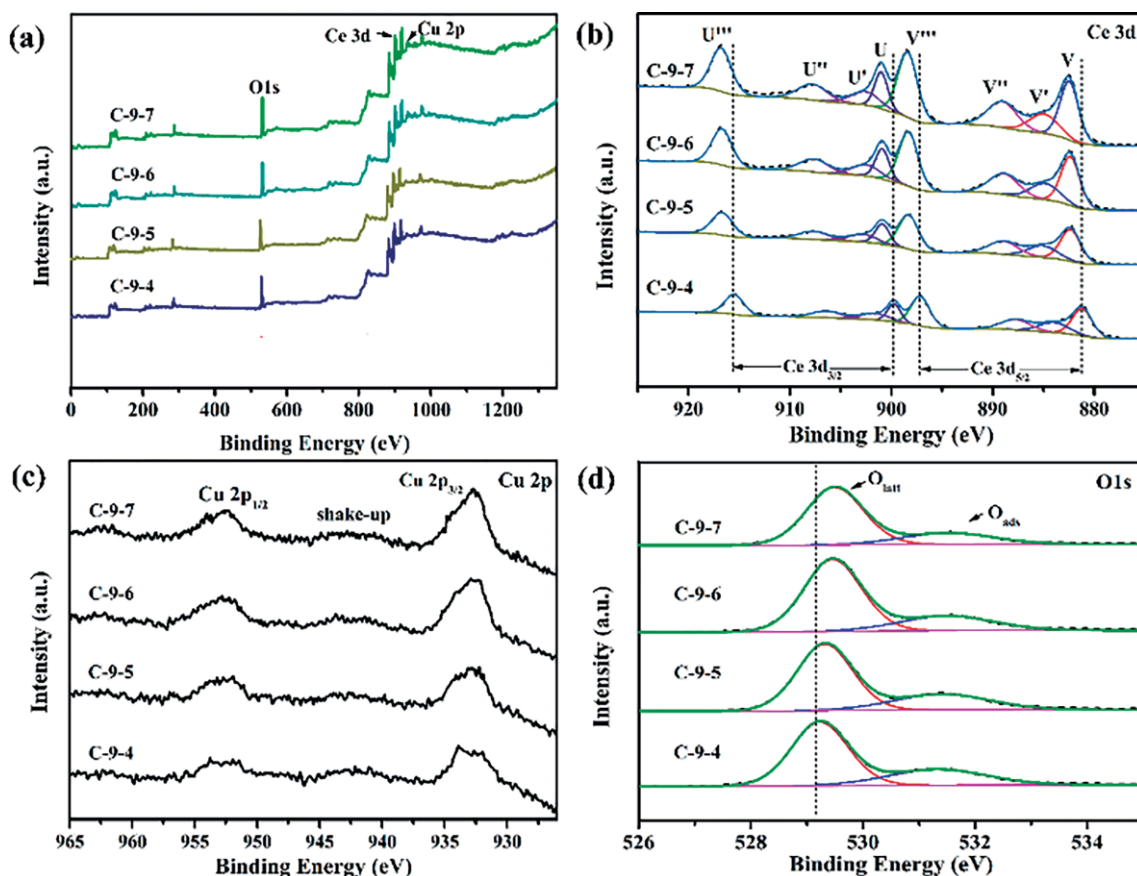


Figure 7. XPS spectra of catalysts with various calcination temperature: (a) survey spectrum; (b) Ce 3d; (c) Cu 2p; (d) O 1s.

XPS spectra of the Ce 3d, Cu 2p and O 1s of samples were measured to analyze the surface elementary compositions and chemical states, and the results are summarized in Figure 7 and Table 3.

Table 3. The Ce^{3+} %, $I_{\text{sat}}/I_{\text{mp}}$, Cu/Ce, O_A/O_L of samples based on XPS spectra.

Sample	Ce^{3+} [%]	$I_{\text{sat}}/I_{\text{mp}}^{[a]}$	Cu/Ce (atomic) ^[b]	$O_A/O_L^{[c]}$
C-9-4	18.1	0.43	0.28	0.4306
C-9-5	17.5	0.35	0.37	0.4138
C-9-6	16.2	0.32	0.45	0.3352
C-9-7	16.1	0.29	0.47	0.3230
C-9-6-C	16.6	0.27	0.35	0.3405

[a] $I_{\text{sat}}/I_{\text{mp}}$ was calculated from the ratio of the intensity of shake-up satellite peak to the intensity of the Cu $2p_{3/2}$ peak. [b] Cu/Ce atom ratio was evaluated from the results of XPS. [c] O_A , surface adsorbed oxygen; O_L , lattice oxygen.

The Ce 3d spectra of catalysts are showed in Figure 7b, which can be deconvoluted to two main peaks labeled as V and U, respectively. The Ce 3d spectra consists of V and U, which are responded to $3d_{5/2}$ and $3d_{3/2}$ deriving from the spin-orbit coupling, respectively.^[15,24,38,51] The main peaks of sample were further fitted into eight peaks, which marks as V, V', V'', V''', U, U', U'' and U''', respectively. The peaks of V' and U' are corresponded to Ce^{3+} related to oxygen defects, and the other peaks of V, V'', V''', U, U'' and U''' are assigned to Ce^{4+} chemical state^[4,27] Moreover, the relative content of Ce^{3+} cation related to oxygen vacancies on CeO_2 surface of all C-9 samples was calculated through the ratio of peaks area $[\text{Ce}^{3+}/(\text{Ce}^{3+} + \text{Ce}^{4+})]$.

Obviously, the relative content of Ce^{3+} of C-9-4 sample is 18.1 %, higher than other C-9 samples (Table 3), which agree well with the results of H_2 -TPR and Raman. The XPS spectra of Cu 2p are shown in Figure 7c, two peaks at ca. 933 eV and ca. 953 eV together with a shake-up satellite in ca. 940–946 eV region was observed, which was assigned to Cu $2p_{3/2}$ and Cu $2p_{1/2}$.^[35] Generally, the ratio of the intensity of shake-up satellite to the intensity of the main Cu $2p_{3/2}$ peak (assigned to $I_{\text{sat}}/I_{\text{mp}}$) was used to estimate the chemical states for Cu species. The ratio of $I_{\text{sat}}/I_{\text{mp}}$ is 0.55, indicating that only Cu^{2+} species was existed.^[48] As shown in Table 3, the $I_{\text{sat}}/I_{\text{mp}}$ ratio of all samples are lower than 0.55, which suggest the existence of reductive Cu species (Cu^+) within all samples.^[45,48,49] The presence of reductive Cu species may be corresponding to the strong interaction between highly dispersed Cu species and CeO_2 , which is favorable for CO catalytic reaction.^[45,50] Moreover, the atom ratio of Cu/Ce (Table 3) on the surface of the catalyst gradually increases with the calcination temperature elevating from 400 °C to 700 °C, which implies that the enrichment of Cu species on CeO_2 surface, as a result of CuO_x species sintering and particle agglomeration. Figure 7d exhibits the O 1s spectra of different samples. The two peaks with the bind energy of ca. 529.23 eV and ca. 531.34 eV are corresponded to lattice oxygen (O_L) and surface adsorbed oxygen (O_A), respectively.^[39] The ratio of O_A/O_L further were analyzed from O 1s spectra, The surface adsorbed oxygen decreased with the increase of calcination temperature are corresponding to the decrease of

oxygen vacancy concentration, which further imply that the surface adsorbed oxygen can be influenced by the dispersion of Cu species on CeO₂ surface.

Catalytic Performance

The performance of C-9 samples calcined at different temperature was evaluated by CO oxidation reaction. The catalytic activity of catalysts can be reflected by T₅₀ (the temperature of 50 % CO conversion) and T₁₀₀ (the temperature of 100 % CO conversion). The results were summarized in Table 1. As shown in Figure 8, C-9-4 sample exhibits the lowest temperature for total CO conversion and shows exponential increase in conversion with an increase of reaction temperature among all C-9 samples. However, the catalytic activity of 50 % CO conversion of C-9-4 sample is lower than other samples calcined at 500–700 °C that show “S” shaped behaviors with an increase of reaction temperature due to the reaction equilibrium. This phenomenon, showing “S” shaped behavior, was attributed to stronger interaction of CuO_x species with CeO₂ induced by calcination temperature. The stronger interaction the more unsaturated Cu species,^[45] which are favorable for the adsorption and activation of CO molecules. However, the decrease of oxygen vacancies concentration at higher calcination temperature, confirmed by Raman and XPS, are adverse to the adsorption, activation and migration of oxygen. Namely, samples obtained at higher calcination temperature are adverse to Langmuir-Hinshelwood (L-H) mechanism that the CO molecules adsorbed on the catalyst surface react with the adsorbed oxygen to forming CO₂ reported in the literature.^[40,52] Therefore, the best catalytic performance should be the balance of interaction and oxygen vacancies concentration.

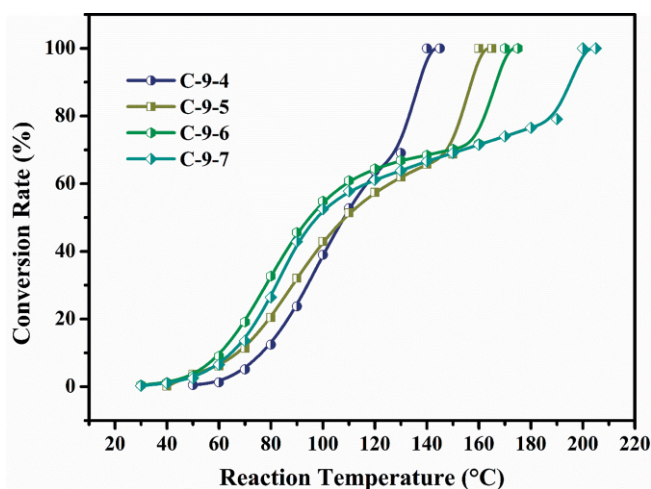


Figure 8. The catalytic performances of C-9 samples calcined at diverse temperature.

Balance of Interaction and Oxygen Vacancies

In order to clarify the relationship of interaction and oxygen vacancies, the heat treatment condition of C-9-6 sample was further optimized by adjusting heating rate and preservation

period at 600 °C. As shown in Figure 9, the sample calcined at 600 °C for 1 h by heating rate of 10 °C min⁻¹ exhibits best catalytic activity. CO thorough conversion can be achieved at 110 °C for the C-9-6-C catalyst. CO conversion show exponential increase in conversion with reaction temperature which is very different from C-9-6 samples. The catalytic activity of other C-9 samples calcined at different temperature for 1 h by heating rate of 10 °C min⁻¹ were also evaluated. As shown in Figure S7, the catalytic activity enhanced as the increase temperature from 400–600 °C. The enhanced activity of the catalyst may be the result of the strong CuO_x-CeO₂ interaction and the abundant oxygen vacancies of CeO₂ created by Cu doping. What's more, the apparent activation energy of C-9-6-C sample was desirably decreased (Figure 9b), as a result of adjusting the thermal treatment parameter. The CO molecules more easily adsorbed on Cu⁺ and cooperates with the activated oxygen to complete the catalytic reaction, which are profitable to accelerate CO oxidation. In addition, in order to compare the catalytic performance between CuO_x species and CuO_x-CeO₂ nanocomposites. We fabricated the Cu₂O-CuO nanocomposites by simple solid-state chemical approach. The SEM, XRD pattern and catalytic activity of Cu₂O-CuO nanocomposites are shown in Figure S8 and Figure S9, the morphology of Cu₂O-CuO nanocomposites present irregular particles with the size about 30–50 nm, all diffraction peaks are corresponding to Cu₂O-CuO nanocomposites. CO thorough conversion can be achieved at 170 °C for Cu₂O-CuO nanocomposites, which higher than CuO_x-CeO₂ nanocomposites (110 °C). Here, the catalytic performance of C-9-6-C sample with lower Cu loading (without pretreatment) produced by solid-state synthesis strategy was comparable, even better than that of ceria-based catalysts obtained by other methods (Table S3).

Figure 9c presents the result of C-9-6-C sample for CO conversion when 5 vol.-% H₂O was involved in gas stream. The consequence suggests that the CO full conversion temperature shifts to higher temperature. The existence of moisture impeded the activity of sample due to the blockage of the active sites by water vapor.^[2] Cycling stability, as another significant evaluate indicator for performance of catalyst, was measured for C-9-6-C sample. The best sample performed quite stable for five light-off cycles (Figure 9d), and almost no degradation of catalytic activity was observed during the test. The long-term stability of CO oxidation at 100 % and 50 % CO conversion rate was performed in feed gas. As shown in Figure 9e, no deactivation can be observed during the process of 85 h of oxidation reaction, demonstrating superior stability and water tolerance in CO oxidation reaction. In addition, in order to investigate the deposition of inactive carbon over these catalysts, TGA (Figure 9f) was performed over the used catalysts after long-term stability test from room temperature to 800 °C with a heating rate of 10 °C/min in air. For the sample after deactivation tests almost no weight loss was observed in comparison with fresh sample. The negligible weight loss of CuO_x-CeO₂ composites catalysts at low temperatures (<100 °C) correspond to a partial dehydroxylation of support and not to coke oxidation. Thus, all catalysts are resistant toward coke formation and exhibited excellent stabilities under reaction conditions.

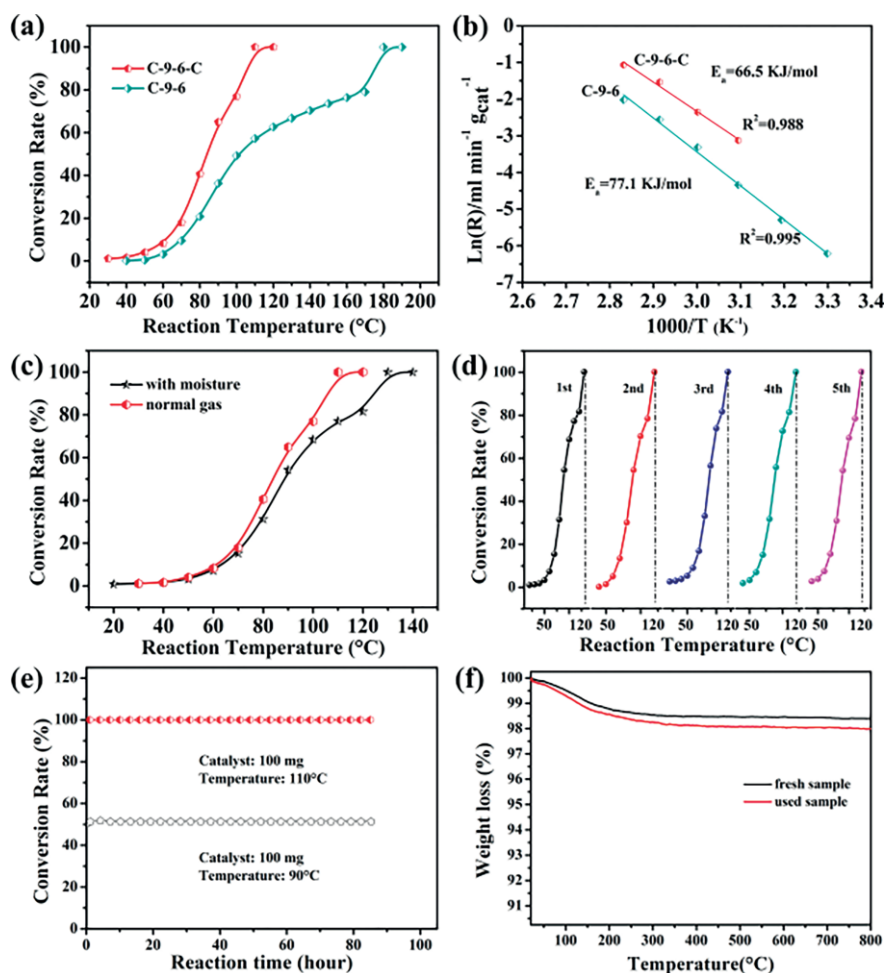


Figure 9. (a) the activities for CO oxidation; (b) the activation energy of C-9-6 and C-9-6-C samples; (c) the catalytic activities with 5 vol.-% H_2O treatment in gas stream for C-9-6-C sample; (d) the catalytic cycling curves of C-9-6-C sample with 5 vol.-% H_2O was involved in gas stream. (e) the stability test of C-9-6-C sample for CO oxidation at 100 % and 50 % conversion rate; (f) TGA of C-9-6-C sample before and after deactivation tests.

The XRD pattern and N_2 adsorption-desorption isotherms of C-9-6-C sample are shown in Figure S10a-b, all diffraction peaks are corresponding to cubic fluorite phase of ceria. Specific surface area and pore volume of C-9-6-C sample are $40 \text{ m}^2 \text{ g}^{-1}$ and $0.056 \text{ m}^3 \text{ g}^{-1}$ (Table 2), which are not much different from that of C-9-6 sample. The morphology and sizes of C-9-6-C sample were identified by TEM. The TEM images and corresponding FFT patterns are demonstrated in Figure 10, the nanoparticles consisted of ca. 6 nm were formed for C-9-6-C sample due to the roles of heat driving. From the HRTEM images, the lattice spacing of 0.3038 nm, 0.2642 nm, 0.1628 nm correspond well to the characteristic (111), (200), and (311) lattice plane of CeO_2 equipped fluorite type structure (Figure 10b), the lattice fringes of other substances are not discovered, confirming the XRD results that the formation of Ce-O-Cu solid solutions and/or CuO highly dispersed on the surface of CeO_2 . H_2 -TPR for CeO_2 (Figure 11a, inset total H_2 consumption) confirm it relatively weak interaction compared to C-9-6 sample, hinting lesser extent in CuO_x species sintering and particle agglomeration. These increase the number of CuO_x - CeO_2 contact points, resulting in more reduction for CeO_2 .

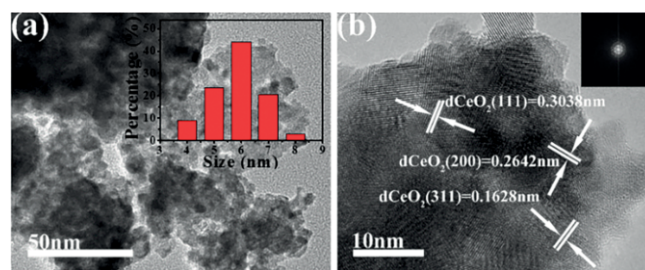


Figure 10. (a) TEM (the inset shows CeO_2 particle size distribution), (b) HRTEM images of C-9-6-C (inset: corresponding fast-Fourier-transform patterns).

Raman results (Figure 11b) also reveal the existence of abundant oxygen vacancies compared to C-9-6 sample, implying that the concentration of oxygen vacancies can be available manipulated by the means of adjusting calcination temperature and method. XPS results (Figure 11c-d and Table 3) confirm that the value of $I_{\text{sat}}/I_{\text{mp}}$ is 0.27, demonstrating the abundant content of Cu^+ species on CeO_2 surface. For C-9-6-C sample, the value of Ce^{3+} and O_A/O_L is higher in comparison with C-9-6

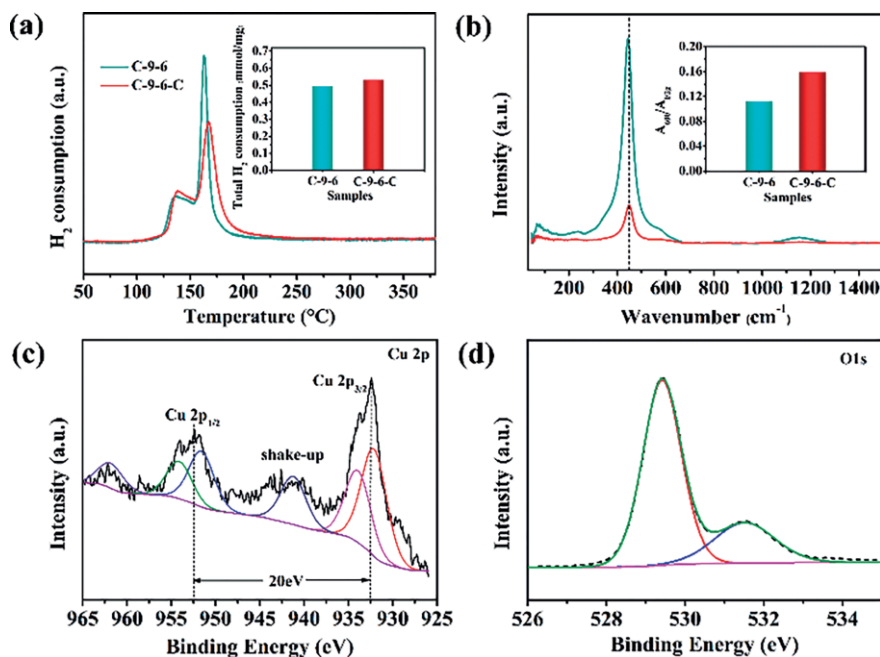


Figure 11. (a) H₂-TPR profile; (b) Raman spectra of C-9-6 and C-9-6-C samples. (c-d) XPS Spectra of C-9-6-C sample.

sample (Table 3), implying that the more oxygen vacancies which is favorable for catalytic performance are created by calcination. The ratio of Cu/Ce (0.35) is relatively lower than that of C-9-6 (0.45), suggesting that the aggregation extent of CuO_x species, or the improving amount of CuO_x species doped into CeO₂ lattice were manipulated by changing the temperature parameter. The abundant Cu⁺ and oxygen vacancies should be responsible for superbly catalytic activity.

Combining with previous literatures^[33,39,52] and the current conclusion of our study, the effect of thermal treatment for the Cu species on CeO₂ surface was speculated (Figure 12). When Cu species was incorporated into ceria, some Cu species was doped into its lattice, which create more oxygen vacancies. The presence of oxygen vacancies provides active sites for the adsorption of O₂, and form surface active oxygen species.^[13,30,37,44] Excessive amounts of Cu species highly dispersed on the surface of ceria, which supplied chemical adsorption sites for CO. Chemisorbed CO react with absorbed oxygen on the interface of CuO-CeO₂. Subsequently, the oxygen vacancies were refilled by external gas oxygen. Although the enhanced interaction between CuO_x and CeO₂, calcining at higher temperature is not conducive to the incorporation of Cu species

into CeO₂ lattice and induce the gather of Cu species on CeO₂ surface (Figure 12 route I). The decrease of oxygen vacancies, and the agglomeration of CuO_x species are negative aspects to effective conversion of CO. Appropriate heat treatment (Figure 12 route II) controlled the agglomeration of Cu species and the amount of CuO_x species doped into CeO₂ lattice, which guaranteed the existence of oxygen vacancies. These factors are profitable to accelerate CO oxidation, thus the sample show more excellent catalytic performance.

Conclusions

In summary, we reported CuO_x-CeO₂ catalysts with high activity and stability for CO oxidation prepared by a facile and mild strategy. The optimal catalytic activity was achieved as a result of the balance between of Cu⁺ concentration and oxygen vacancy on CeO₂ surface adjusted by the amount of Cu loading and thermal treatment parameters of composites. The C-9-6-C sample with lower Cu loading significantly enhanced the catalytic activity compared to pure CeO₂, which enabled CO total oxidation at a low temperature of 110 °C. In addition, CuO_x-CeO₂ catalysts exhibited superior long-term stability at 110 °C during the process of 85 h oxidation reaction. As CuO_x-CeO₂ catalysts were subjected to appropriate heat treatment, Cu species migrated from the surface to the lattice of CeO₂, which created more oxygen vacancies. The abundant oxygen vacancies and the state of highly dispersed Cu⁺ species tailored by appropriate heat treatment improve the absorption and activation of oxygen from the external environment and provide more active sites for the chemisorption and transform of CO, which contribute to the excellent catalytic performance. The work presented here exhibits the new insights obtained from the effect of heat treatment for catalysts with metal loading.

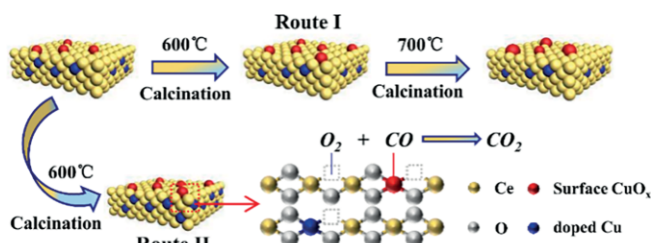
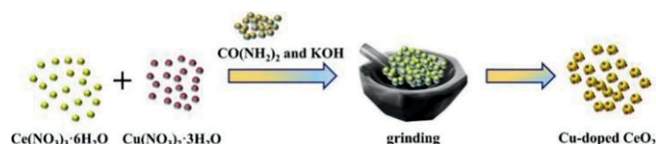


Figure 12. A schematic diagram of mechanism toward CO oxidation reaction on the surface of catalysts.

Experimental Section

Preparation of Catalysts

The $\text{CuO}_x\text{-CeO}_2$ nanohybrids with different ratio of reactants were fabricated through a facile and mild route. No any solvents were involved in preparation process. Typically, 3 mmol of cerium nitrate hexahydrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, AR) was firstly ground into powder in a agate mortar, then 0.27 mmol of cupric nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, AR) (Cu/Ce molar ratio = 0.09), 12 mmol of urea ($\text{CO}(\text{NH}_2)_2$, AR) and 12 mmol of potassium hydroxide (KOH, AR) were put into the agate mortar. After grinding about 40 min, the mixture was washed and filtered with distilled water to eliminate impurities (K^+) until the pH value of the filtrate reached 7.0. The obtained sample was dried at ambient temperature overnight and calcined at different temperature (400–700 °C) for 2 h (2 °C min^{-1}) in air. The obtained samples were named as C-X-T, where X represents the Cu/Ce molar ratio (e.g. Cu/Ce = 0.09, X = 9), T indicates the calcination temperature (e.g. 400 °C, T = 4). Therefore, the obtained metal oxides were named as C-9-4, C-9-5, C-9-6, and C-9-7, respectively. The lowest calcination temperature of 400 °C was determined in this study based on (Scheme 1).



Scheme 1. Schematic illustration of the preparation process.

thermogravimetric analyses (TGA) experiments (Figure S1). In addition, C-0-4, C-1-4, C-5-4 and C-15-4 nanoparticles with different Cu/Ce molar ratio (Cu/Ce = 0.00, 0.01, 0.05, 0.15) were also prepared by the similar method with the calcination temperature of 400 °C. In order to insights the effect of thermal treatment, the heat treatment at 600 °C with 10 °C min^{-1} heating rate for 1 h were also applied to C-9, and the obtained Cu doped CeO_2 nanoparticles were named C-9-6-C.

In order to compare the catalytic performance between CuO_x species and $\text{CuO}_x\text{-CeO}_2$ nanocomposites. We fabricated the $\text{Cu}_2\text{O-CuO}$ nanocomposites by simple solid-state chemical approach. Typically, 10 mmol of cuprous chloride (CuCl , AR) was sufficiently grinded to powder in agate mortar, respectively, and then of potassium hydroxide (KOH, AR) was added into the agate mortar. The mixture was continuous grinded about 40 min; the obtained product was washed and filtered with distilled water to eliminate impurities. Finally, these samples were dried overnight at room temperature.

Characterizations

The X-ray powder diffraction (XRD) were performed to acquire the structure information of samples on Bruker D8 employing $\text{Cu-K}\alpha$ radiation (1.54056 Å) equipped an operating voltage of 40 kV and a beam current of 40 mA. The morphologies of samples were observed by field emission scanning electron microscope (FESEM) and high-resolution transmission electron microscope (HRTEM). FESEM images were obtained on Hitachi S-4800H field emission scanning electron microscope with an accelerating voltage of 5 kV. HRTEM images were obtained from a JEOL JEM-2010F electron microscope with an accelerating voltage of 200 kV. TGA were recorded by NETZ SCH-STA449F3 instrument from room temperature to 800 °C with a heating rate of 10 °C/min in air. The element component of catalysts were measured by energy disperse X-ray spectrum (EDS, EDAXTLS). Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH)

methods were used to determine the specific surface area, pore size and pore volume of the samples on a surface area and porosity analyzer (Quantachrome, Autosorb-iQ2). In order to remove the moisture and physical adsorbed gases, all samples were degassed at 300 °C for 6 h before N_2 adsorption-desorption. Raman spectra of all samples were recorded to determine the structural properties of samples at the condition of ambient temperature on a Bruker Senterra. The surface components and structure of samples were characterized by X-ray photoelectron spectra (XPS) (Thermo Fisher Scientific ESCALAB250Xi) employing $\text{Al K}\alpha$ (1486.6 eV).

Determination of the Redox Properties of $\text{CuO}_x\text{-CeO}_2$ before/after N_2O Oxidation

The reducibility of Cu-doped CeO_2 nanoparticles was investigated by H_2 temperature-programmed reduction ($\text{H}_2\text{-TPR}$) (Thermo TPDRO 1100 series) measured in a quartz reactor. Typically, 30 mg of samples was pretreated in He stream at 100 °C with a flow rate of 40 mL min^{-1} for 30 min before testing, and then they were cooled to room temperature. After that a flow of 5 % H_2/Ar (40 mL min^{-1}) was employed and tested from room temperature to 400 °C with a heating rate of 10 °C min^{-1} . The amount of H_2 consumption (A_1) and the TPR profile was monitored and recorded by a thermal conductivity (TCD) detector. Afterward, the reduced sample was cooled to 90 °C in He (40 mL min^{-1}) and was purging for 1 h. Secondly, the samples was oxidized by 5 vol % N_2O (99.995 % purity) in N_2 (99.999 % purity) balance at this temperature with the flow rate of 40 mL min^{-1} for 1 h. Lastly, the sample was purged again with He using same condition and then to start a $\text{H}_2\text{-TPR}$ run. The amount of H_2 consumption (A_2) was also recorded by a TCD detector.

The Test of Catalytic Performance

The activity and stability of catalysts toward to CO oxidation was evaluated in a fixed bed quartz reactor at atmospheric pressure. Typically, 100 mg of catalyst without any pretreatment was loaded. The mixed feed gas contained with 1 vol.-% CO and 20 vol.-% O_2 in N_2 balance at 50 mL min^{-1} of flow rate (space velocity = 30000 $\text{mL gcat}^{-1} \text{h}^{-1}$) was applied to the reactor. The change of gas concentration was monitored with an online gas chromatography system (Agilent 7890B) equipped with a TCD. The CO conversion was calculated based on the following formula, where $[\text{CO}]_{\text{in}}$ and $[\text{CO}]_{\text{out}}$ are the CO concentration in the inlet and outlet gas, respectively.

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

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