

Solid Solution Derived Cu Clusters on Partially Reduced CuCeO₂ with Abundant Oxygen Vacancies Enable Efficient Reverse Water Gas Reaction

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The reverse water gas shift (RWGS) reaction provides a convenient approach to convert CO₂ to CO, which facilitates to achieve the goals of carbon peaking and carbon neutrality. Herein, the Cu/CeO₂ catalyst prepared by a co-precipitation method using a mixture of Na₂CO₃ and NaOH at pH of 10 (sample Cu/CeO₂-10) achieved an intrinsic reaction rate of 428.4 mmol·g_{cat}⁻¹·h⁻¹ with 100% CO selectivity at 400 °C and CO₂/H₂ ratio of 1:4, which is much higher than Cu/CeO₂ prepared by impregnation and other methods. Various characterizations showed the highest fraction of CuCeO₂ solid solution

in the calcined Cu/CeO₂-10, and formed highly dispersed Cu clusters (~2.5 nm) on partially reduced CuCeO₂ solid solution with abundant of oxygen vacancies upon reduction. The Cu and oxygen vacancies facilitates the activation of H₂ and CO₂, respectively, resulting in lowered H₂ and CO₂ reaction orders. As a result, the synergy between the two components enhanced the overall RWGS activity with lowered activation energy. Moreover, the optimal catalyst is very stable in 24 h stability test without detectable agglomeration of Cu clusters.

Introduction

The continued rising CO₂ content in the atmosphere has brought sever environmental issues, such as global warming and ocean acidification.^[1–3] Therefore, the technologies of capture, storage, conversion and utilization of CO₂ have received extensive attentions. Compared with capture and storage, recycling waste CO₂ to value-added chemicals through advanced conversion technology is more favorable.^[4,5] Conversion of CO₂ with H₂ derived from renewable energy represents an appealing approach for CO₂ utilization.^[6,7] Among the likely C1 products (i.e., CH₄, CH₃OH and CO) that can be produced from CO₂ reduction, CO accompanied with H₂, i.e., syngas, can be used as a versatile feedstock to produce various industrial important products through the well-developed technologies, such as Fischer-Tropsch synthesis and methanol synthesis. Therefore, conversion of CO₂ to CO via the reverse water gas (RWGS) reaction is widely explored recently.^[8]

The RWGS reaction is mildly endothermic (41.3 kJ·mol⁻¹), and thus is favored at high reaction temperatures. However, the high temperature makes the process energy intensive and also favors the sintering the catalysts. On the contrary, when the reaction temperature is lowered, the activation of inert CO₂ becomes difficult. Moreover, the competition of exothermic methanation reaction (−164.7 kJ·mol⁻¹) may lower the selectivity toward CO. Hence, developing active and selective catalyst that can enable RWGS reaction at low temperature is challenging.

Despite noble metal based catalysts, such as Pt,^[9] Pd,^[10] Au,^[11] and Rh,^[12] showed good performance for RWGS, their high costs limit their application. Thus, the non-noble metal, such as Cu, Ni and Fe, based catalysts have also been widely explored.^[13] Compared with Ni that favors methanation, the weaker binding of CO on Cu results in high CO selectivity on Cu catalysts during the RWGS reaction. However, the bare Cu binds CO₂ weakly, which leads to low RWGS activity. To improve the activity of Cu based catalysts, the strategies of adding promotor to form bimetallic catalysts (such as NiCu, FeCu and MoCu)^[14–16] and tuning reducible metal oxide supports (such as TiO₂ and CeO₂)^[17–18] have been intensively investigated. The reducible metal oxides readily form oxygen vacancies, which absorb and activate CO₂. Thus, the Cu/CeO₂ catalysts, in combination of the advantages of high CO selectivity of Cu and facile activation of CO₂ on CeO₂, have been explored for the RWGS reaction.^[19] The preparation method plays a crucial on the final composition and structure of Cu/CeO₂, and thus significantly affects the catalyst performance.^[19–22] Zhang et al.^[23] prepared self-assembled 3-dimensional CeO₂ hollow nanospheres using a modified hydrothermal method and then loaded Cu by an impregnation method. The RWGS reaction test showed that the activity was significantly enhanced compared with the Cu on CeO₂ nanoparticles and nanocubes supports. Characterizations

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showed that surface oxygen vacancies were greatly increased on the CeO₂ hollow nanospheres support. Hsueh et al.^[24] prepared the Cu/CeO₂ by a spray method, which showed higher activity than that prepared by an impregnation method. Yang et al.^[19] used mesoporous SiO₂ as a template to limit the particle size of catalyst, which prevented the agglomeration of Cu and resulted in Cu/CeO₂ catalyst with high RWGS activity. Vovchok et al.^[25] mixed ZMS-5 and CeO₂ powder, and then loaded Cu by the impregnation method, which led to uniform distribution of Cu and Ce species in the catalyst. We noted that in these previous works, the Cu may enter the lattice of CeO₂ and form CuCeO₂ solid solution to different extents, which facilitates the formation of oxygen vacancies due to distortion of the lattice of CeO₂ upon Cu doping. However, few works have focused on the effect of extent of solid solution of CuCeO₂ on the RWGS performance.

The precipitation method is a traditional method to prepared metal oxide catalyst, and the properties of metal oxide are strongly dependent on the precipitation agent and pH values selected for precipitation.^[26–27] Recently, Wang et al.^[28] used a solution of sodium hydroxide and sodium carbonate as the precipitant to prepare Co/CeO₂ catalysts for the RWGS reaction. A 40% CO₂ conversion can be achieved on the optimal catalyst at 600 °C with a CO₂/H₂ ratio of 1:1. However, the selectivity of CO is <100%, due to Co catalyzes methanation reaction in the meantime. To best of our knowledge, there has no report on the high activity of RWGS reaction on Cu/CeO₂ prepared by the precipitation method.

In this work, we explored the Cu/CeO₂ catalysts by a co-precipitation method using a mixture of precipitants and tested the catalytic performance in the RWGS reaction. The results showed that the optimal preparation condition (NaOH/Na₂CO₃ = 1/1, and pH = 10) led to a Cu/CeO₂ catalyst with RWGS activity (intrinsic reaction rate of 428.4 mmol·g_{cat}^{−1}·h^{−1} at 400 °C) higher than those reported in the literature with a similar catalyst composition and under similar reaction conditions. Detailed characterizations indicated the reduction of CuCeO₂ solid solution led to the formation Cu clusters (~2.5 nm) on the partially reduced CuCeO₂ solid solution, which activated H₂ and CO₂, respectively, and synergistically improved the overall catalytic performance.

Experimental

Preparation of Catalysts

For the Cu/CeO₂ catalysts prepared by the precipitation method, the aqueous solution B, containing NaOH and Na₂CO₃ with a molar ratio of 1:1, was added dropwise to solution A, containing Cu(NO₃)₂·3H₂O and Ce(NO₃)₃·6H₂O with a Cu/Ce molar ratio of 1:4, under stirring until the pH value reached 9, 10, and 11, respectively. Note that this Cu/Ce ratio has been reported to be the maximum amount of Cu that can participate in the CeO₂ lattice to form a solid solution.^[20,29] After stirring for 4 h, the slurry was left statically for 12 h, and then was filtered and washed with H₂O until the pH value of filtrate was <7.5. The resultant was dried at 80 °C for 12 h, and then calcined at 500 °C for 4 h with a ramping rate of 2 °C·min^{−1}. The catalysts were named Cu/CeO₂-x, where x is the value of

precipitation pH (x = 9, 10, and 11). A reference sample was prepared by the impregnation method. The bare CeO₂ support was also prepared by the precipitation method described above with a pH value of 10 without adding Cu precursor. The CeO₂ was impregnated with Cu(NO₃)₂·3H₂O (Cu/Ce molar ratio of 1/4) for 12 h, which was then dried and calcined in the same procedure described above. The resultant sample was named as Cu/CeO₂-i.

Characterization of Catalysts

Elemental analysis was performed on an inductive coupled plasma optical emission spectrometer (ICP-OES, Agilent 5110). N₂ adsorption was measured at −196 °C using a Tristar 3000 analyzer (Micrometrics). The sample of 350 mg was degassed at 300 °C for 3 h prior to N₂ adsorption. The specific surface area was calculated by the Brunauer-Emmett-Teller (BET) method. X-ray diffraction (XRD) patterns were recorded using a D8-Focus (Cu target) X-ray diffractometer (Bruker), operated at 40 kV and 200 mA.

Hydrogen temperature programmed reduction (H₂-TPR) was measured using a Chemisorb 2750 (Micrometrics) equipped with a thermal conductive detector (TCD). The sample of 100 mg was pretreated at 400 °C in flowing Ar for 1 h. Subsequently, the temperature was lowered to room temperature, and gas was switched to 10% H₂/Ar (25 mL·min^{−1}). When the baseline was stabilized, the temperature was ramped up to 800 °C at a rate of 10 °C·min^{−1}. Temperature programmed desorption of CO₂ (CO₂-TPD) was also performed on the Chemisorb 2750. The sample of 60 mg was pre-reduced at 400 °C for 1 h using in a stream of 10% H₂/Ar. Then, the gas was switched to He for 1 h to remove residual H₂O produced. When the temperature was lowered to room temperature, the gas was switched to a 5% CO₂/He stream for 1 h to adsorb CO₂, and then switched to He for another 1 h to remove the physically adsorbed CO₂. The sample was then ramped up to 800 °C in flowing He (25 mL·min^{−1}) at a rate of 10 °C·min^{−1}.

Raman spectra were recorded using a Confocal Raman microscope (Horiba) using a laser with a wavelength of 532 nm. X-ray photoelectron spectra (XPS) were acquired using a ThermoScientific Nexsa (ThermoFisher) equipped with an Al K α source (1485.6 eV) under vacuum of 5×10^{−9} mbar. The binding energy (BE) of C 1s at 284.4 eV was used as a reference for correction. Transmission electron microscopy (TEM) images were observed using a JEM-F200 field emission system operated at 200 kV.

Catalytic Tests

The catalytic evaluations were carried out using a fixed bed tubular quartz reactor at atmospheric pressure.^[30] For a typical run, sample of 10 mg (40–60 mesh) was charged into the reactor, and was reduced at 400 °C for 1 h using flowing H₂ (40 mL·min^{−1}). Next, the stream of CO₂ (10 mL·min^{−1}) and Ar (50 mL·min^{−1}) were introduced, resulting in a gas hourly space velocity (GHSV) of 600,000 mL·g_{cat}^{−1}·h^{−1}. The effluent of reaction was analyzed online by an Agilent 7890 gas chromatograph equipped with a TCD detector and two columns. For the experiments of kinetics, the conversion of CO₂ was adjusted to <10% by adjusting the GHSV. The CO₂ conversion (X_{CO₂}), CO selectivity (S_{CO}) and CH₄ selectivity (S_{CH₄}) were calculated according to the following equations:

$$X_{\text{CO}_2} = \frac{F_{\text{CO}_2,\text{in}} - F_{\text{CO}_2,\text{out}}}{F_{\text{CO}_2,\text{in}}} \times 100\% \quad (1)$$

$$S_{\text{CO}} = \frac{F_{\text{CO},\text{out}}}{F_{\text{CO}_2,\text{in}} - F_{\text{CO}_2,\text{out}}} \times 100\% \quad (2)$$

$$S_{CH_4} = \frac{F_{CH_4, out}}{F_{CO_2, in} - F_{CO_2, out}} \times 100 \% \quad (3)$$

where F represents the feed flow rate.

Results and Discussion

Catalyst Performance

The reduction temperature of catalysts was firstly optimized using the Cu/CeO₂-10 sample at the standard reaction conditions, i.e., 400 °C and GHSV of 600000 mL·g_{cat}⁻¹·h⁻¹. When no reduction was applied, i.e., the catalyst was heated up to 400 °C in flowing N₂ prior to reaction, the Cu/CeO₂-10 showed a low initial CO₂ conversion of 7.2% (Figure S1). This result indicated that pre-reduction of catalyst is required to achieve optimal active structure. Since the reaction was performed at 400 °C, the reduction temperature was varied from 400–500 °C. As shown in Figure S1, the CO₂ conversion dropped almost linearly from 14.8% to 5.0% with increase of reduction temperature from 400 to 500 °C. Hence, 400 °C was selected as the reduction temperature for all following tests.

The CO₂ conversion and CO selectivity on Cu/CeO₂ catalysts at 400 °C and GHSV of 600000 mL·g_{cat}⁻¹·h⁻¹ were compared in

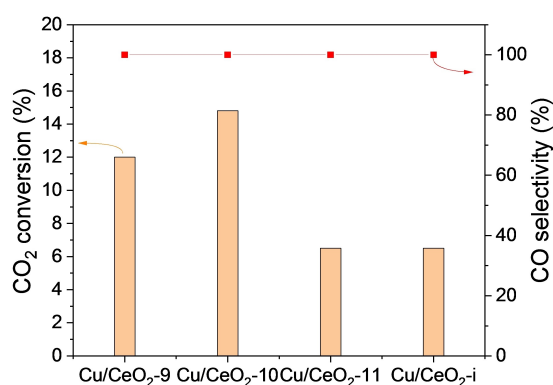


Figure 1. CO₂ conversion and CO selectivity during RWGS reaction on Cu/CeO₂ catalysts prepared by precipitation and impregnation methods. Reaction conditions: 400 °C, 1 atm, H₂:CO₂:Ar = 4:1:5, GHSV = 600000 mL·g_{cat}⁻¹·h⁻¹.

Figure 1. The CO selectivity was 100% without CH₄ being detected on all catalysts, which is as expected since Cu is not active for catalyzing methanation reaction. It is interesting to note that no methanol was detected on all samples, despite Cu is a well-known methanol synthesis catalyst. This is likely resulted from the reaction condition of atmospheric pressure in current work, which is much lower than the typical pressure 3 MPa of for methanol synthesis.^[31–36] The CO₂ conversion varied significantly over different samples, and showed a volcano dependence on the precipitation pH. That is, the conversions were 12.0%, 14.8%, and 6.5% for pH value of 9, 10, and 11, respectively. In comparison, the reference sample of Cu/CeO₂-i showed a low conversion of 6.5%. The reaction rate in terms of mass for the optimal sample of Cu/CeO₂-10 was 396 mmol·g_{cat}⁻¹·h⁻¹, and the intrinsic reaction rate measured under differential condition with a conversion of 4.8% was as high as 428.4 mmol·g_{cat}⁻¹·h⁻¹, which is much higher than other Cu/CeO₂ samples (Table 1). When the intrinsic rate was normalized by the surface area (Table 1), the Cu/CeO₂-10 still showed the highest rate (3.29 mmol·m⁻²·h⁻¹) among all Cu/CeO₂ samples. Note that rate on Cu/CeO₂-10 was much higher than the Cu based catalysts reported in literature under similar reaction conditions (Table S1), highlighting its superior performance.

The Cu/CeO₂-10 sample with the highest activity and the reference sample of Cu/CeO₂-i were selected for 24 h stability test at 400 °C. The GHSVs were adjusted to 375,000 and 200,000 mL·g_{cat}⁻¹·h⁻¹ for Cu/CeO₂-10 and Cu/CeO₂-i, respectively, to achieve a similar initial conversion of ~20%, which was away from the thermodynamic equilibrium conversion of 35% under current condition and thus allowed a better comparison of stability. As shown in Figure 2, the Cu/CeO₂-i deactivated apparently with the CO₂ conversion being dropped by 5.5% to 14.5% after 24 h reaction. In contrast, little deactivation was observed for Cu/CeO₂-10, with the CO₂ conversion being slightly decreased by 2.3% to 18.0%. Thus, the Cu/CeO₂-10 is much more stable than the Cu/CeO₂-i for RWGS reaction, which is likely originated from the stronger interaction between Cu and support to prevent the agglomeration of Cu for Cu/CeO₂-10.

The optimal sample of Cu/CeO₂-10 and reference sample of Cu/CeO₂-i were used to further investigate the activation energy (E_a) and reaction orders, which were measured under differ-

Table 1. Intrinsic reaction rate of RWGS reaction in terms of mass and area, specific surface area, the Cu/(Cu + Ce) molar ratio, the H₂/Cu ratio and the I_D/I_G ratio of Cu/CeO₂ catalysts.

Samples	Intrinsic reaction rate ^[a] (mmol·g _{cat} ⁻¹ ·h ⁻¹)	Specific surface area ^[b] (m ² ·g ⁻¹)	Intrinsic reaction rate ^[c] (mmol·m ⁻² ·h ⁻¹)	Cu/(Cu + Ce) molar ratio ^[d]	H ₂ /Cu ^[e]	I _D /I _G ^[f]
CeO ₂	–	109.2	–	–	–	0.040
Cu/CeO ₂ -9	342	127.7	2.67	0.194	1.0	0.050
Cu/CeO ₂ -10	428	130.1	3.29	0.190	1.7	0.132
Cu/CeO ₂ -11	174	80.0	2.18	0.192	1.5	0.121
Cu/CeO ₂ -i	174	77.5	2.24	0.184	1.4	0.090

^[a] Mass based intrinsic reaction rate, which was measured at 400 °C, 1 atm, H₂:CO₂:Ar = 4:1:5 with conversion < 10% by adjust the GHSV. ^[b] BET specific surface area.

^[c] Intrinsic reaction rate normalized by BET surface area. ^[d] Cu/(Cu + Ce) was obtained from ICP measurement. ^[e] Derived from H₂-TPR. ^[f] Derived from Raman, and the samples were pre-reduced at 400 °C.

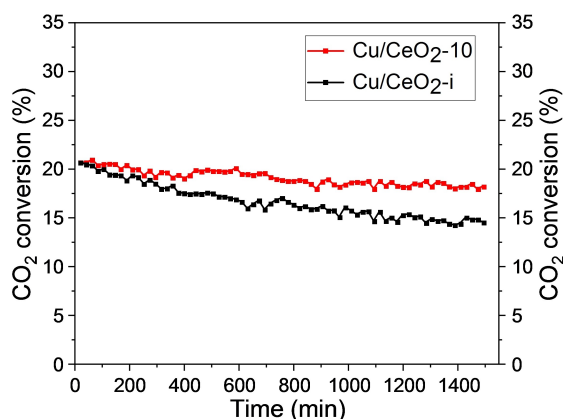


Figure 2. Effect of reaction time on CO₂ conversion over Cu/CeO₂-10 and Cu/CeO₂-i catalysts. Reaction conditions: 400 °C, 1 atm, H₂:CO₂:Ar = 4:1:5, GHSV: 375000 mL·g_{cat}⁻¹·h⁻¹ for Cu/CeO₂-10 and 200000 mL·g_{cat}⁻¹·h⁻¹ for Cu/CeO₂-i.

ential conditions with conversion < 10% by adjusting the GHSV. The Arrhenius plots of the dependence of intrinsic reaction rate on the reaction temperature (360–400 °C) was shown in Figure 3a. The derived E_a on Cu/CeO₂-10 (64.4 kJ·mol⁻¹) was significantly lower than that on Cu/CeO₂-i (108.7 kJ·mol⁻¹), which are in good agreement with their activities and likely reflecting different structure of major active centers.

The reaction rates showed 0.67 and 0.47 orders of dependence on H₂ partial pressure at 400 °C on Cu/CeO₂-i and Cu/CeO₂-10, respectively, and then turned to 0 orders when the H₂ partial pressure was increased > 20.3 and 40.5 kPa, respectively (Figure 3b). This trend indicates that increasing H₂ pressure gradually led H₂ and derived species to saturate the surface of active sites, and thus became having little influence the reaction rate. The relatively lower reaction order and lower critical H₂

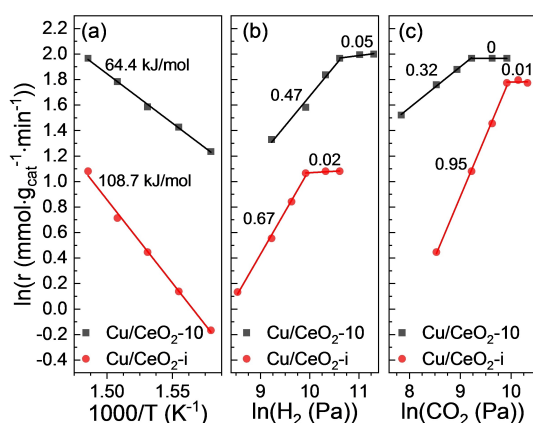


Figure 3. Kinetics of RWGS reaction on Cu/CeO₂-10 and Cu/CeO₂-i. (a) Arrhenius plots of intrinsic reaction rate, reaction conditions: T = 360–400 °C, 1 atm, H₂:CO₂:Ar = 4:1:5, GHSV = 600,000–2,000,000 mL·g⁻¹·h⁻¹; (b) Dependence of intrinsic reaction rate on H₂ partial pressure, 400 °C, 1 atm, CO₂ = 10 mL·min⁻¹, H₂ = 5–80 mL·min⁻¹, and total gas flow rate = 100 mL·min⁻¹; (c) Dependence of intrinsic reaction rate on CO₂ partial pressure, 400 °C, 1 atm, H₂ = 40 mL·min⁻¹, CO₂ = 2.5–30 mL·min⁻¹, and total gas flow rate = 100 mL·min⁻¹.

partial pressure for 0 order reaction on Cu/CeO₂-10 point to higher efficiency for adsorption and activation of H₂.

Much distinct difference was observed for CO₂ reaction orders (Figure 3c). The reaction rate showed a 0.95 order of dependence on CO₂ partial pressure on Cu/CeO₂-i, while the value decreased significantly to 0.32 on Cu/CeO₂-10. Similar to H₂ order, the CO₂ order also became 0, when the CO₂ partial pressure was > 20.3 and 10.1 kPa on Cu/CeO₂-i and Cu/CeO₂-10, respectively. Collectively, these results indicate that the Cu/CeO₂-10 is much more effective for CO₂ adsorption and activation.

Characterizations

A series of characterizations were carried out to elucidate the origin of difference in RWGS activity on different Cu/CeO₂ catalysts. The measured Cu/(Cu+Ce) ratios of all samples (Table 1) matched closely the target value of 0.2, indicating few Cu and Ce were lost during the precipitation or impregnation. This is not surprising since even the lowest pH of 9 was higher than the pH value that is required for complete precipitation of both Cu and Ce ions. The surface areas were high and similar for Cu/CeO₂-9 (127.7 m²·g⁻¹) and Cu/CeO₂-10 (130.1 m²·g⁻¹), which were higher than CuO–CeO₂ solid solution catalysts prepared by other methods, such as hydrothermal and impregnation methods (normally < 100 m²·g⁻¹).^[22,37–39] When the pH value increased to 11, the surface area decreased dramatically to 80.0 m²·g⁻¹, suggesting higher basicity may lead to higher precipitation and nucleation rates, resulting in larger particle sizes and lower surface areas. The reference sample of Cu/CeO₂-i showed a slightly lower surface area (77.5 m²·g⁻¹) relative to Cu/CeO₂-11.

The XRD patterns of all calcined samples (Figure 4a) showed a typical face-centered cubic fluorite structure of CeO₂ (PDF#34-0349), without CuO_x being detected. A close inspection of 2θ–32° region revealed a slight shift in diffractions of CeO₂ (111) (see inset in Figure 4a). The derived lattice parameters of Cu/CeO₂ (Table 2) showed a lattice shrink with respect to standard CeO₂. This result reflects the incorporation of Cu into the CeO₂ lattice to form a solid solution, due to the much smaller radius of Cu²⁺ (73 pm) than that of Ce⁴⁺ (97 pm).^[20,38] Compared with standard CeO₂, little cell parameter change was observed for Cu/CeO₂-9, pointing to few solid solution formation, which was likely resulted from very different precipitation rates of Cu and Ce species at a low pH of 9, resulting in separate phases. In contrast, Cu/CeO₂-10 showed the smallest cell parameter among other three Ce/CeO₂ samples, indicating the highest fraction of solid solution formation, which implied similar precipitation rates of Cu and Ce species to form a solid solution at pH of 10. When the precipitation pH increased to 11, the lattice parameter became larger, which indicated reduced fraction of solid solution, likely due to faster precipitation rates to form inhomogeneous mixing of Cu and Ce species. The lattice parameter became even larger for Cu/CeO₂-i, which indicated formation of limited solid solution in Cu/CeO₂-i. The estimated particle sizes from diffractions of CeO₂ (111) showed

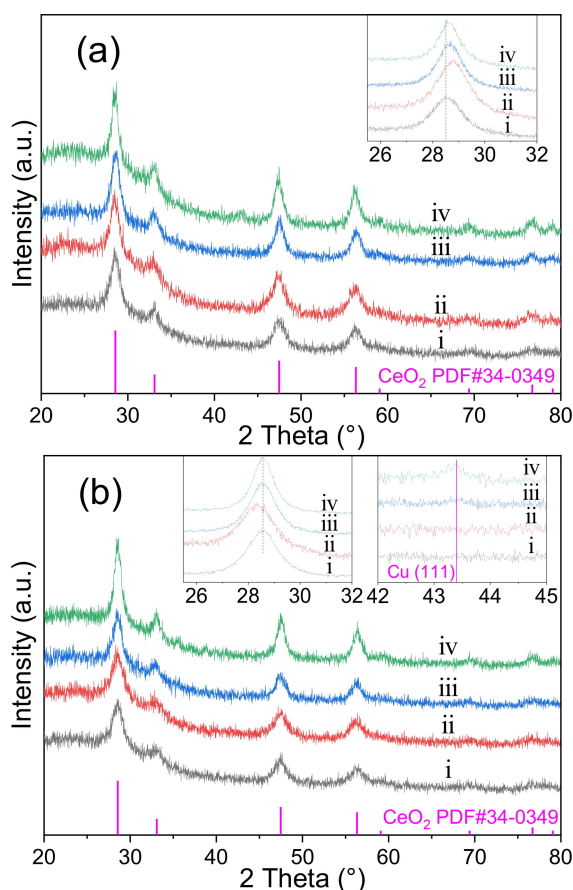


Figure 4. XRD patterns of (a) freshly calcined and (b) 400 °C pre-reduced Cu/CeO₂ samples. The labels of i, ii, iii and iv in the inset figures represent Cu/CeO₂-9, Cu/CeO₂-10, Cu/CeO₂-11, and Cu/CeO₂-i, respectively.

that the Cu/CeO₂-9 and Cu/CeO₂-10 displayed smaller particle sizes than the other two samples (Table 2), which are in good agreement with BET surface area. It is worth mentioning that the formation degree of solid solution of mixed metal oxides could be judged by the Vegard's law,^[40] i.e., the lattice parameter of CeO₂ decreases as the doping amount of Cu increases, and the lattice parameter will no longer decrease once the maximum amount of Cu in the lattice of CeO₂ is reached. Note that we chose the Cu/Ce molar ratio of 1/4, which is the maximum amount of Cu that can be doped into the lattice of CeO₂ to form a solid solution.^[20,29] The Cu/CeO₂-10

showed the lowest CeO₂ lattice parameter of 5.402 Å among all samples in this work, and this value is also among the lowest values for CuCeO₂ solid solution reported in the literature.^[29] Therefore, we concluded that the Cu/CeO₂-10 has the highest degree of CuCeO₂ solid solution, which is further supported by H₂-TPR, Raman and XPS results (see below).

When the samples were reduced at 400 °C for 1 h, no obvious change of CeO₂ structure was observed (Figure 4b). A close examination of diffraction in the range of 26–32° (see inset in Figure 4b) showed a lattice expansion of CeO₂ to different degrees relative to the respective calcined samples (Table 2), which was likely caused by the formation of larger radius Ce³⁺ (102 pm) upon reduction.^[38,41] The degree of change in cell parameter before and after reduction (Table 2) decreased following the order of Cu/CeO₂-10 > Cu/CeO₂-11 > Cu/CeO₂-i > Cu/CeO₂-9, which likely reflects the degree of Ce³⁺ formation in these samples. A close examination of the range of 42–45° region (see inset in Figure 4b) showed tiny diffractions of metallic Cu (111) for Cu/CeO₂-11 and Cu/CeO₂-i but not for Cu/CeO₂-9 and Cu/CeO₂-10, which indicate Cu was highly dispersed in the latter two samples with sizes smaller than the XRD detection limitation of 3 nm. The estimated Cu sizes using Scherrer equation were 14.8 nm and 16.9 nm for Cu/CeO₂-11 and Cu/CeO₂-i, respectively (Table 2).

The XRD patterns of spent Cu/CeO₂-10 and Cu/CeO₂-i samples after 24 h stability test (Figure 2) were also recorded to track the structure change in the RWGS reaction. The Cu(111) diffraction of Cu/CeO₂-i (Figure S2) became sharper after reaction, and the estimated Cu size increased significantly to 37.0 nm relative to the 16.9 nm for the fresh sample. In contrast, there was no Cu(111) peak observable for Cu/CeO₂-10 after reaction, indicating the Cu clusters were still well dispersed. Such significant difference indicates the higher extent of solid solution resulted in stronger interaction between the reduction formed Cu cluster and support, which stabilized the Cu clusters from agglomeration during RWGS reaction.

Figure 5 shows the H₂-TPR profiles of Cu/CeO₂ catalysts. Note that bare CeO₂ was reduced at temperatures > 400 °C,^[42] and CuO was reduced at 248 °C.^[43] In comparison, the reduction peaks shifted significantly to lower temperatures (< 200 °C) for all Cu/CeO₂ catalysts, which indicate the interaction between dispersed Cu species and CeO₂ support likely through the Cu–O–Ce bonds activates the O species and facilitates its reduction.^[37,44–46] The reference sample Cu/CeO₂-i displayed

Table 2. Average particle sizes of CeO₂ and Cu, and lattice parameters of CeO₂ obtained by XRD for Cu/CeO₂ catalysts.

Samples	CeO ₂ particle size ^[a] (nm)	CeO ₂ lattice parameters (Å)		Difference ^[b] (Å)	Cu particle size ^[a] (nm)
		Calcined	Reduced		
Cu/CeO ₂ -9	6.6	5.408	5.408	0.000	–
Cu/CeO ₂ -10	6.9	5.402	5.413	0.011	–
Cu/CeO ₂ -11	9.2	5.404	5.409	0.005	14.8
Cu/CeO ₂ -i	10.0	5.406	5.408	0.002	16.9

^[a] Estimated by Scherrer's equation, ^[b] Difference of CeO₂ lattice parameter before and after reduction.

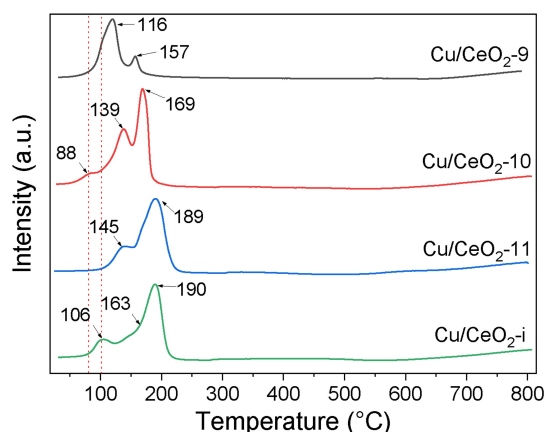


Figure 5. H₂-TPR profiles of Cu/CeO₂ catalysts.

three reduction peaks at 106, 163 and 190 °C. The former two peaks are likely associated with reduction of highly dispersed surface CuO clusters and Cu species in the solid solution, respectively.^[17] The latter peak is likely related with the reduction of larger CuO particles with weaker interaction with CeO₂ support,^[29,45] since the formation of large Cu particles after reduction were evidenced in XRD. For the samples prepared by precipitation, the reduction temperatures of various Cu related species shifted gradually to lower temperatures with decreasing pH values, indicating higher Cu dispersion and reducibility. Moreover, the highly dispersed surface CuO cluster (at 116 °C) appeared to be the dominant species for Cu/CeO₂-9, while the solid solution Cu species (at 169 °C) appeared to be major species for Cu/CeO₂-10. However, we point out that the exact assignment of these species is difficult due to very close reduction temperatures. The quantified H₂/Cu molar ratio (Table 1) was close to 1 for Cu/CeO₂-9, which implies few CeO₂ species was reduced and CuO and CeO₂ were likely in separate phases. Differently, the H₂/Cu was much higher than 1 for other three samples, indicating CeO₂ was partially reduced in addition to CuO. The H₂/Cu ratio decreased in the order of Cu/CeO₂-10 > Cu/CeO₂-11 > Cu/CeO₂-i. This trend suggests much higher fraction of solid solution in Cu/CeO₂-10 than Cu/CeO₂-i, in good agreement with XRD, and therefore facilitates the reduction of CeO₂ species in close proximity to CuO.

Raman spectra of the pre-reduced Cu/CeO₂ samples at 400 °C were displayed in Figure 6. A sharp peak at 464 cm⁻¹, accompanied with shoulder peaks at 536 and 596 cm⁻¹, was present for Cu/CeO₂-9. The former peak is related with F_{2g} mode of cubic CeO₂ structure, and the latter two peaks are related to the defect-induced modes due to different oxidation states (D1) and different ionic radius (D2), respectively.^[47–48] The peak of F_{2g} mode of Cu/CeO₂-9 is close to bare CeO₂,^[49] which indicates few solid solution in this sample. Interestingly, the F_{2g} peak shifted to 447 cm⁻¹ and became wider for other Cu/CeO₂ samples. As the CeO₂ particle sizes were similar for Cu/CeO₂-9 and Cu/CeO₂-10, these changes indicate the formation of more defects, i.e., oxygen vacancies, in the samples other than Cu/CeO₂-9.^[48] The density of oxygen vacancies can be semi-quantified by the integral band intensity ratio of D to F_{2g}, i.e., I_D/I_{F2g}.^[50] As listed in

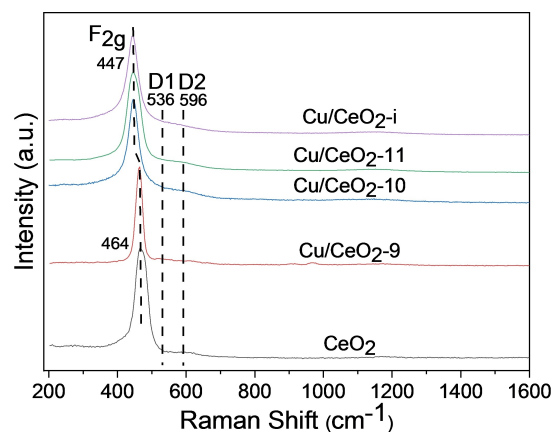


Figure 6. Raman spectra of Cu/CeO₂ catalysts pre-reduced at 400 °C.

Table 1, the rather low I_D/I_{F2g} further confirms few oxygen vacancies in Cu/CeO₂-9. The highest value of I_D/I_{F2g} is achieved on Cu/CeO₂-10 among samples prepared by precipitation, and this value is much higher than that on Cu/CeO₂-i, which indicates formation of more oxygen vacancies due to formation of more solid solution in Cu/CeO₂-10 than in Cu/CeO₂-i. Interestingly, the I_D/I_{F2g} ratio can be positively correlated with the difference of lattice parameter before and after reaction (Figure S3), as well as the H₂/Cu ratio derived from H₂-TPR (Figure S4), which may indicate the density of oxygen vacancy (or Ce³⁺) is closely related with degree of solid solution in various samples.

CO₂-TPD profiles of Cu/CeO₂ catalysts are shown in Figure 7. Generally, the profile can be divided into three regions, i.e., 25–200, 200–400, and 400–800 °C, relating with CO₂ desorption from weak, moderate, and strong basic sites, respectively.^[42,51] The surface –OH groups are the weak base sites, which form bicarbonate (HCO₃^{*}) upon CO₂ adsorption.^[24,52] The Ce–O pair act as moderate base sites, which form bidentate carbonate.^[24,42,52] The coordinatively unsaturated Ce–O pair is closely related with the formation of oxygen vacancy in proximity.^[23,53] The strong base sites are associated with unsaturated O²⁻ anion,^[24,52] which form monodentate and

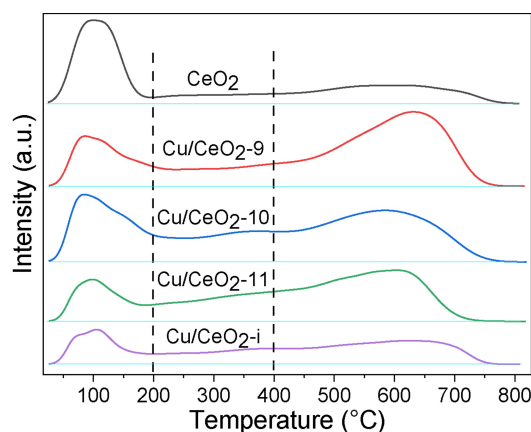


Figure 7. CO₂-TPD profiles of Cu/CeO₂ catalysts pre-reduced at 400 °C.

polydentate carbonates. These strong basic sites may not participate in the reaction, since CO₂ desorption occurs at > 400 °C, which is higher than the reaction temperature tested. As compared in Table 3, the presence of Cu clearly improved the densities of moderate and strong base sites of CeO₂, which was likely resulted from the presence of Cu facilitated the creation of oxygen vacancies upon reduction. The Cu/CeO₂-10 showed the highest density of moderate base site among all samples, in agreement with its highest density of oxygen vacancies.

The XPS of pre-reduced Cu/CeO₂-10 and Cu/CeO₂-i at 220 °C are compared in Figure 8. The selection of 220 °C was based on H₂-TPR results, which showed all species were reduced at this temperature. Despite the samples were measured ex situ and might lead to partial oxidation of the samples, the same measurement procedure ensured the valence states reflect the difference of intrinsic property between samples. The appearance of shake up peak at BE of 937–950 eV in Cu 2p region indicated the presence of Cu²⁺ species (Figure 8a). Hence, the Cu 2p spectrum was fitted with Cu²⁺ and low valence Cu⁰ and/or Cu¹⁺, by fixing the intensity ratio of 2p_{3/2} to 2p_{1/2} at 2:1 and the BE distance between 2p_{3/2} and 2p_{1/2} at 19.8 eV.^[43,54] As listed in Table 4, the higher Cu²⁺/(Cu²⁺ + Cu⁰) for Cu/CeO₂-10 relative to Cu/CeO₂-i suggests the highly dispersed Cu species with stronger interaction with support, which stabilized more Cu in higher oxidation state for the Cu/CeO₂-10. However, more Cu species aggregated into large particles on the surface for the Cu/CeO₂-i sample, which resulted in weaker interaction with support and thus fewer Cu was stabilized in higher oxidation state. The Ce 3d region can be fitted with 10 peaks, i.e., v, v', v'', v''', u, u', u'', u''', u'''' (Figure 8b), which are related with Ce³⁺ (v, v'', u, u''), Ce⁴⁺ (v', v''', u', u''', u'''), respectively.^[25,50] The integral band intensity ratio of Ce³⁺/(Ce³⁺ + Ce⁴⁺) reflects the fraction of Ce³⁺ in the sample. As listed in Table 4, the Ce³⁺ fraction in Cu/CeO₂-10 was much higher than that in Cu/CeO₂-i. The O 1s region can be fitted with two peaks at 529.3 and 531.4 eV (Figure 8c), which correspond to lattice O (O_L) of bulk CeO₂ and surface O close to the oxygen vacancies (O_V), respectively.^[55–56] The fraction of O_V of Cu/CeO₂-10 is higher than that in Cu/CeO₂-i (Table 4), in good agreement with the Ce³⁺ fraction, indicating the Cu/CeO₂-10 contains more oxygen vacancies.

Low resolution TEM images of pre-reduced Cu/CeO₂-10 and Cu/CeO₂-i (Figure S5) showed nanoparticles with sizes of 6.4 and 10.2 nm, respectively, which are in agreement with the XRD derived CeO₂ sizes. However, it is difficult to distinguish Cu from

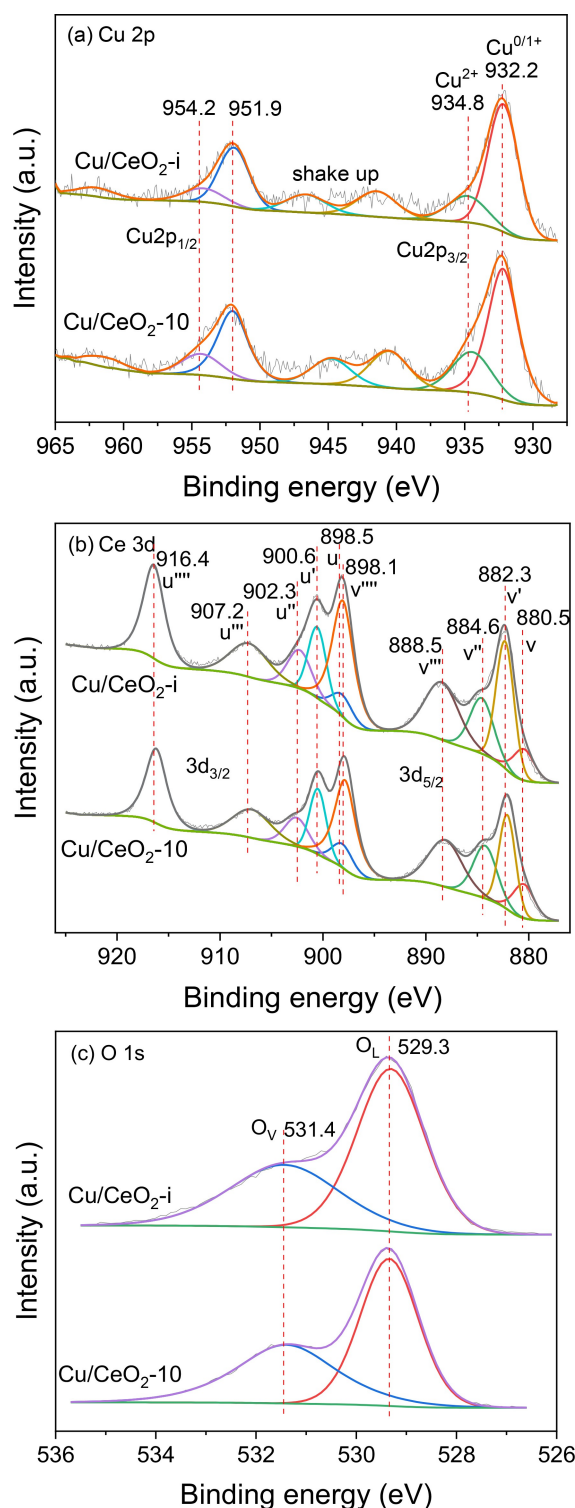


Figure 8. XPS of Cu/CeO₂ catalysts pre-reduced at 220 °C in the (a) Cu 2p, (b) Ce 3d, (c) O 1s region.

CeO₂ species in these images due to low contrast between Cu and Ce species. The elemental mapping images of the two samples are shown in Figure S6 and S7. Despite Cu appeared to be highly dispersed in both samples, the Cu/CeO₂-10 showed better Cu dispersion. High resolution (HR) TEM image of Cu/

Samples	Density of base site (mmol·g ⁻¹)			
	Weak	Moderate	Strong	Total
CeO ₂	1.15	0.44	0.67	2.26
Cu/CeO ₂ -9	0.79	0.68	2.43	3.90
Cu/CeO ₂ -10	1.01	1.35	1.71	4.07
Cu/CeO ₂ -11	0.66	0.72	1.83	3.21
Cu/CeO ₂ -i	0.52	0.63	0.79	1.94

Table 4. The percentage of Cu^{2+} , Ce^{3+} and O_v for $\text{Cu}/\text{CeO}_2\text{-10}$ and $\text{Cu}/\text{CeO}_2\text{-i}$ derived from XPS.

Samples	$\text{Cu}^{2+}/(\text{Cu}^{2+} + \text{Cu}^0)$ (%)	$\text{Ce}^{3+}/(\text{Ce}^{3+} + \text{Ce}^{4+})$ (%)	$\text{O}_v/(\text{O}_v + \text{O}_i)$ (%)
$\text{Cu}/\text{CeO}_2\text{-10}$	27.9	25.7	39.9
$\text{Cu}/\text{CeO}_2\text{-i}$	22.1	22.5	32.2

$\text{CeO}_2\text{-10}$ (Figure 9a) showed Cu particles of ~ 2.5 nm with a d-spacing of 0.208 nm that can be assigned to Cu (111). In close proximity to the Cu, lattice fringe of 0.310 nm is related with CeO_2 (111) surface. More HR-TEM images are provided in Figure S8, which also show Cu clusters of ~ 2.5 nm dispersed on the CeO_2 surface. Considering the highly dispersed Cu species in elemental mapping (Figure S6), one may conclude $\text{Cu}/\text{CeO}_2\text{-10}$ contain both high dispersed Cu clusters and CuCeO_2 solid

solution. In contrast, large Cu particle of ~ 17.0 nm was observed for the $\text{Cu}/\text{CeO}_2\text{-i}$ (Figure 9b, circled, see more examples in Figure S8). In direct contacting this Cu particle, the lattice fringe of 0.311 nm is related with the CeO_2 (111) surface. In combination of dispersed Cu species in elemental mapping and Cu (111) peak in XRD, one may expect that $\text{Cu}/\text{CeO}_2\text{-i}$ contains both large and small Cu particles while $\text{Cu}/\text{CeO}_2\text{-10}$ contains highly dispersion Cu clusters and Cu species in CuCeO_2 solid solution.

Discussion

The XRD results of freshly calcined samples clearly indicated that the $\text{Cu}/\text{CeO}_2\text{-10}$ sample formed the highest fraction of CuCeO_2 solution among all Cu/CeO_2 samples. According to the characterization results, the representative dominant structure models of reduced $\text{Cu}/\text{CeO}_2\text{-10}$ and $\text{Cu}/\text{CeO}_2\text{-i}$ were proposed and schematically shown in Figure 10. Due to the limited fraction of CuCeO_2 solution in freshly calcined $\text{Cu}/\text{CeO}_2\text{-i}$, the reduction at 400°C resulted in formation of large Cu particles (~ 17.0 nm) and partially reduced CeO_2 support (Figure 10a), with limited density of oxygen vacancies. In contrast, due to the highest fraction of CuCeO_2 solution in freshly calcined $\text{Cu}/\text{CeO}_2\text{-10}$, the reduction resulted in Cu clusters of ~ 2.5 nm, which are highly dispersed on partially reduced CuCeO_2 solution with abundant oxygen vacancies (Figure 10b). The $\text{H}_2\text{-TPR}$ results clearly indicated that the $\text{Cu}/\text{CeO}_2\text{-10}$ has much higher reducibility than $\text{Cu}/\text{CeO}_2\text{-i}$, which may facilitate the formation and refilling the oxygen vacancies during the RWGS reaction. Despite the H_2/Cu ratio of $\text{Cu}/\text{CeO}_2\text{-10}$ is higher that required

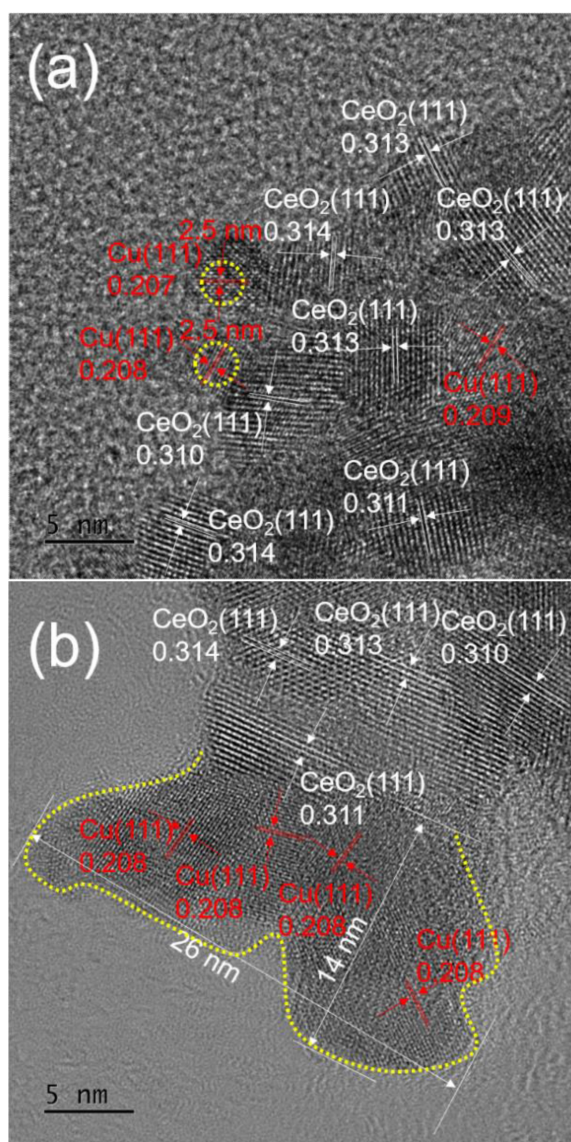


Figure 9. High resolution TEM images of (a) $\text{Cu}/\text{CeO}_2\text{-10}$ and (b) $\text{Cu}/\text{CeO}_2\text{-i}$ pre-reduced at 400°C .

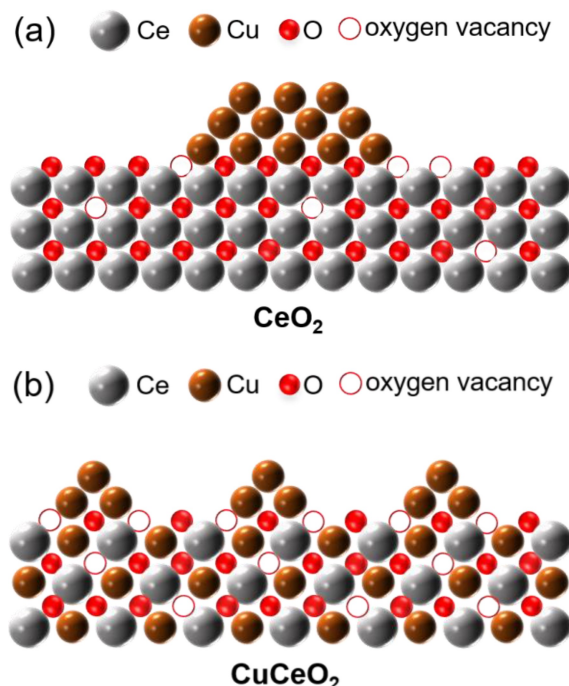


Figure 10. Schematic representation of the structure of reduced (a) $\text{Cu}/\text{CeO}_2\text{-i}$ and (b) $\text{Cu}/\text{CeO}_2\text{-10}$.

for complete reduction of CuO, the solid solution of CuCeO₂ may still present, as supported by XRD and XPS results.

It is widely known that the RWGS reaction may follow either redox or associative mechanism, depending on the catalysts and reaction conditions.^[15,19] In both mechanisms on metal/reducible metal oxide catalyst, the activation of H₂ is achieved on the metal, and activation of CO₂ is facilitated on the metal oxide with vacancies,^[53,57–58] and reaction likely takes place at the interfacial perimeter sites of metal/oxide.^[30] On one hand, the Cu clusters with more defect sites in Cu/CeO₂-10 facilitate the more efficient dissociation of H₂ than the large Cu particles in Cu/CeO₂-i. As a result, the lower H₂ reaction order and lower critical H₂ pressure were achieved on Cu/CeO₂-10 relative to Cu/CeO₂-i. On the other hand, the CuCeO₂ solid solution support in Cu/CeO₂-10 facilitates the formation oxygen vacancies vicinal to Cu clusters, which is much more effective than the dominant CeO₂ support in Cu/CeO₂-i. Consequently, the adsorption and activation of CO₂ is more readily to achieve on Cu/CeO₂-10 than Cu/CeO₂-i, as evident in the density of moderate base sites derived from CO₂-TPD. Hence, a much lower CO₂ reaction order was achieved on Cu/CeO₂-10 than Cu/CeO₂-i. The synergy of Cu cluster and CuCeO₂ solid solution support with oxygen vacancies at the interface of Cu/CuCeO₂ enables both H₂ and CO₂ activation and thus enhance the overall RWGS, resulting in much a lower E_a on Cu/CeO₂-10 (64.4 kJ·mol⁻¹) than Cu/CeO₂-i (108.7 kJ·mol⁻¹). As a result, the intrinsic RWGS reaction rate on the optimal Cu/CeO₂-10 (428.4 mmol·g_{cat}⁻¹·h⁻¹) is much higher than the Cu based catalysts reported in literature under similar reaction conditions (Table S1), likely due to limited CuCeO₂ solid solution and larger Cu particle sizes in these catalysts. It is also worth mentioning that the strong interaction between Cu clusters and partially reduced CuCeO₂ solid solution stabilizes Cu clusters from agglomeration during the reaction, resulting in remarkable stability.

It is evident the precipitation method with an optimal pH of 10 facilitated the formation of CuCeO₂ solid solution, and thus showed superior RWGS activity than the Cu/CeO₂-i due to the formation of limited solid solution in the latter sample. It is worth mentioning that the precipitation pH value plays a crucial role on the formation of CuCeO₂ solid solution. Despite the low pH of 9 led to high dispersion of Cu and high surface area due to low precipitation rate, few CuCeO₂ solid solution was formed, which resulted in slightly lower activity for RWGS reaction than Cu/CeO₂-10. In contrast, the high pH value of 11 led to low surface area due to high precipitation rates of both Cu and Ce species, and hence limited fraction of CuCeO₂ solid solution, resulting in similar low activity for RWGS reaction as the Cu/CeO₂-i. In summary, the optimal co-precipitation condition developed in this work allows efficient mixing of Cu and Ce ions during precipitation, and therefore results in higher fraction of CuCeO₂ solid solution with smaller crystallite size and larger surface area, leading to superior RWGS performances than the Cu/CeO₂ catalysts prepared by conventional methods (e.g., hydrothermal, template, impregnation, etc.).

Conclusions

In this work, CuCeO₂ solid solution catalysts were prepared using a co-precipitation method and applied in RWGS reaction. The optimal catalyst of Cu/CeO₂-10 (prepared using Na₂CO₃/NaOH of 1 and pH of 10) showed an intrinsic reaction rate of 428.4 mmol·g_{cat}⁻¹·h⁻¹ at 400 °C, H₂:CO₂:Ar = 4:1:5, and GHSV = 2,000,000 mL·g_{cat}⁻¹·h⁻¹, which was much higher than that prepared by impregnation method and Cu/CeO₂ catalysts prepared by other methods with similar composition at similar reaction conditions. Characterizations of XRD, TPR, XPS, Raman and CO₂-TPD showed that the highest fraction of CuCeO₂ solid solution was achieved on the Cu/CeO₂-10 relative to impregnation method and precipitation method under other pH values. As a result, the highest redox property, density of oxygen vacancies, and density of moderate base sites were achieved on Cu/CeO₂-10. Moreover, the Cu clusters of ~2.5 nm was highly dispersed on partially reduced CuCeO₂ solid solution, which efficiently enable H₂ activation and CO₂ activation, respectively. Consequently, the reaction orders of both H₂ and CO₂ were much lower on Cu/CeO₂-10 than impregnation prepared Cu/CeO₂-i. The cooperation of highly dispersed Cu clusters and CuCeO₂ solid solution with abundant oxygen vacancies synergistically lowered the activation energy and enhanced the activity for RWGS. Moreover, the strong interaction between Cu clusters and partially reduced CuCeO₂ solid solution stabilizes Cu clusters from agglomeration during the reaction, resulting in remarkable stability. Our results demonstrated that the strategy of using CuCeO₂ solid solution to derive highly dispersed Cu clusters on partially reduced CuCeO₂ solid solution to achieve high RWGS activity and stability.

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: CO₂ reduction · reverse water gas shift reaction · oxygen vacancy · Cu/CeO₂ catalysts · solid solution

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