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Preferential oxidation of CO in H_2 over CuO-CeO$_2$ catalysts

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Abstract

CuO-CeO$_2$ catalysts prepared by the urea gelation/co-precipitation (UGC) method were studied for the preferential oxidation of CO in H_2. The activity and selectivity of these catalysts are among the best reported to date for application to reformate-type gas mixtures. For a material calcined at 650 °C, ∼5 at.% Cu content is sufficient for maximum activity. Cu–O–Ce phases, comprising copper oxide clusters strongly associated with ceria, are proposed as the active sites for the reaction. No inhibition by CO_2 is observed at temperatures above 140 °C, but the combined effect of H_2O and CO_2 is stronger, requiring operation at 165 °C for 99% CO conversion and 65% selectivity.

Keywords: Preferential oxidation; Selective oxidation of carbon monoxide; Fuel cells; Cerium oxide; Copper; Redox; Hydrogen production

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1. Introduction

A promising fuel cell technology currently under rapid development for various applications is the polymer electrolyte membrane fuel cell (PEMFC) fueled with hydrogen [1]. Hydrogen can be produced through steam reforming or partial oxidation of liquid fuels or natural gas in combination with the water gas shift reaction. The reformate gases contain about 50% H_2, 20% CO_2, 0.5–1% CO, 10% H_2O and N_2. The PEMFC anode will be poisoned by CO at levels of 10–100 ppm. As a result, carbon monoxide must be reduced to below these levels. An effective route for the removal of CO is the preferential oxidation (PROX) of CO in H_2. PROX catalysts must meet the requirements of high CO oxidation activity, high selectivity (so that no valuable hydrogen fuel is consumed), and good resistance towards deactivation by H_2O and CO_2 [2–5].

The catalysts for PROX of CO in H_2 reported in the literature can be classified into three types: (1) noble metal catalysts (Pt, Pd, Rh or Ir supported on Al_2O_3, SiO_2 or zeolite) [6–13]. These catalysts exhibit very good activity in the temperature range of 150–250 °C, but their selectivity generally is not good enough to meet the practical requirement; (2) gold catalysts supported on one or two of the following oxides: MnO_x, FeO_x, TiO_2, Al_2O_3, NiO, MgO and SnO_2 are very active for PROX of CO in H_2 at temperatures under 100 °C and are resistant to water and CO_2 [14–17]. However, they are also active for the oxidation of H_2 at reaction temperatures higher than 80 °C; (3) several kinds of base metal oxide catalysts have also been studied, such as the oxides of Cu, Mn, Co, Ni, Fe alone or in combination; and CuO-CeO$_2$ [18–21]. Among these, the most promising is the system CuO-CeO$_2$. Issues for CuO-CeO$_2$ PROX catalysts reported in literature are their low activity and selectivity at high space velocities, and their poor resistance to deactivation by water. Further studies are needed to develop practical PROX catalysts.

In this work, a series of CuO-CeO$_2$ catalysts were prepared by the urea gelation co-precipitation method, and their catalytic performance was tested for PROX of CO in H_2-rich gas streams. These catalysts exhibited good catalytic activity and selectivity for the PROX reaction, even in the presence of water and carbon dioxide.

2. Experimental

CuO-CeO$_2$ and CuO-doped (Zr, La, Pr)CeO$_2$ were prepared by the urea gelation/co-precipitation (UGC) method,

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as described elsewhere [22–24]. The precursor salts were metal nitrates (Aldrich, ACS grade). The cerium salt was $(NH_4)_2Ce(NO_3)_6$ (Aldrich, 99.99% pure). The preparation procedure consists of mixing the aqueous metal nitrate solutions with urea (NH_2–CO–NH_2); heating the solution to 100 °C under vigorous stirring and addition of de-ionized water; boiling the resulting gel for 8 h at 100 °C; filtering and washing the precipitate twice with de-ionized water at 50–70 °C; drying the cake in a vacuum oven at 80–100 °C for 10–12 h; crushing the dried lump into smaller particles and calcining the powder in a muffle furnace in air at 650 °C for 4 h. A heating rate of 2 °C/min was used in the calcination step. The BET surface areas of the thus prepared catalysts were in the range of 90–100 m^2/g after calcination at 650 °C. The copper content in CuO-CeO_2 or in the doped catalysts is 10 at.%.

Bulk elemental composition was determined by inductively coupled plasma (ICP) atomic emission spectrometry (Perkin-Elmer, Plasma 40), and the BET surface area was measured on a Micromeritics Pulse Chemisorb 2705 instrument.

Activity tests were performed at atmospheric pressure with 100 mg catalyst sample with particle size of 50–150 μm and diluted with quartz sand loaded on a quartz frit at the center of a flow quartz-tube reactor (1.0 cm i.d.), which was heated inside an electric furnace. The contact time was 0.09 g s cm^{-3}, except as noted. All catalysts were used in the as prepared form without activation. For preferential oxidation, the reaction gas mixture consisted of 1 vol.% CO, 0.5–2.0 vol.% O_2, and 50 vol.% H_2 in He. The effect of CO_2 was examined in separate runs with the addition of 20 vol.% CO_2 in the feed gas. The effect of H_2O was investigated by the addition of 10 vol.% H_2O in the feed gas with a syringe pump, while heating the gas lines leading to the reactor at 120 °C in order to avoid condensation. The exit gas stream was continuously analyzed on-line by a gas chromatograph, HP-5880A, equipped with a thermal conductivity detector and a Carbosphere (Alltech) packed column.

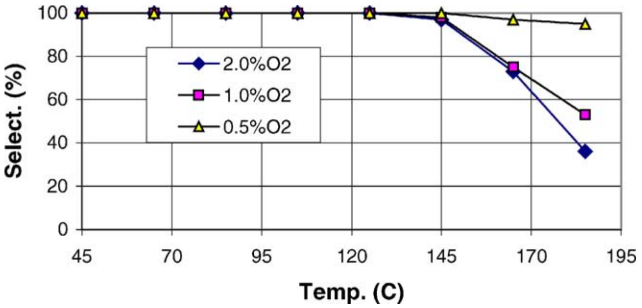

Fig. 2. Oxygen selectivity vs. temperature over CuO-CeO_2; reaction conditions are the same as in Fig. 1.

The percent fractional conversion of CO is expressed as $(CO^{in} - CO^{out})/CO^{in} \times 100\%$, and the percent oxygen selectivity is defined as $0.5 \times (CO^{in} - CO^{out})/(O_2{}^{in} - O_2{}^{out}) \times 100\%$.

3. Results and discussion

Figs. 1 and 2 show the conversion of CO and O_2 and the selectivity profiles with temperature over the CuO-CeO_2 catalyst. This catalyst exhibits very high activity and selectivity for PROX of CO in H_2. At a reaction temperature of 145 °C, the CO conversion is higher than 96% and the selectivity of O_2 for CO oxidation is 97%. The content of O_2 in the reaction mixture has little effect on CO conversion, while selectivity decreases with the O_2 content, but only above 145 °C, indicating that the H_2 oxidation reaction does not light off below this temperature on CuO-CeO_2.

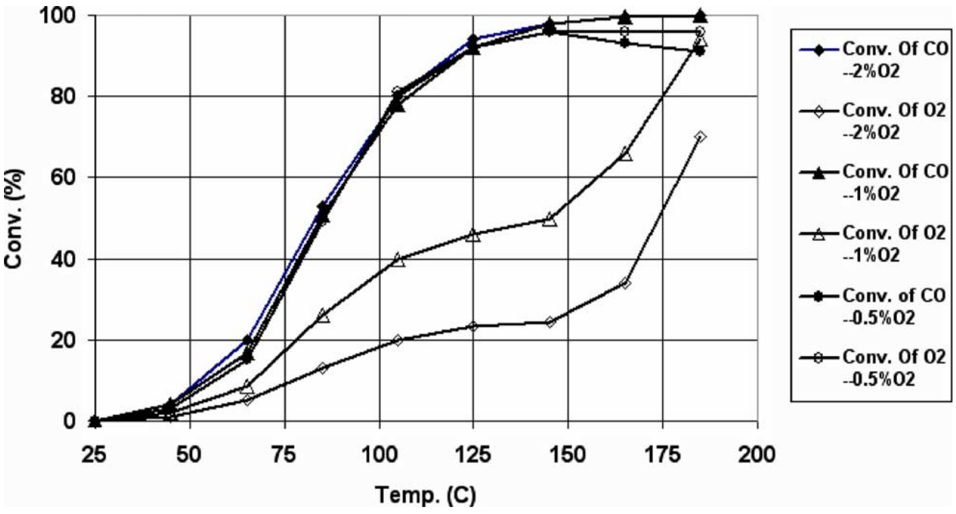

Fig. 1. Conversion of CO and O_2 vs. temperature over CuO-CeO_2. Contact time: 0.09 g s cm^{-3}; reaction gas mixture: 1 vol.% CO, 50 vol.% H_2 and O_2 in He; the content of O_2 is marked in the figure.

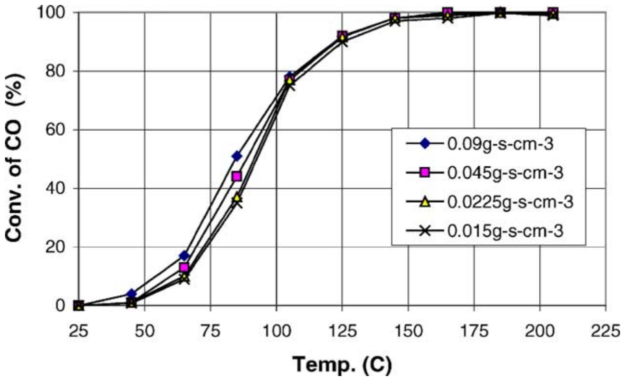

Fig. 3. Effect of contact time on the conversion of CO over CuO-CeO_2 under 1% CO, 1% O_2, 50% H_2 in He.

The effect of copper content and the calcination temperature of the catalyst on the catalytic performance were also investigated. Calcination temperature markedly influences the activity of CuO-CeO_2 catalysts, because it can change the copper state and dispersion [25–27]. We found that the highest activity was exhibited by catalysts calcined at 650 °C. We also found that there was no appreciable difference in the CO conversion and oxygen selectivity as the copper content of CuO-CeO_2 catalysts varied from 5 to 30 at.%, indicating that only a small amount of copper is adequate for the activity. A large excess of copper will form bulk CuO particles, which will have negligible interaction with ceria and negligible contribution to activity. This property has also been reported in the literature for CuO-CeO_2 catalysts used in CO oxidation and the water-gas shift reactions [22,25–27]. As stated in the experimental section, the data presented here are for a CuO-CeO_2 catalyst containing 10 at.% Cu after calcination at 650 °C.

The effect of contact time on CO conversion and selectivity are shown in Figs. 3–5. When contact time decreases from 0.09 to 0.015 g s cm^{-3}, the conversion and selectivity changed only slightly, showing that this catalyst is indeed very active for PROX of CO in H_2; a result of great practical significance.

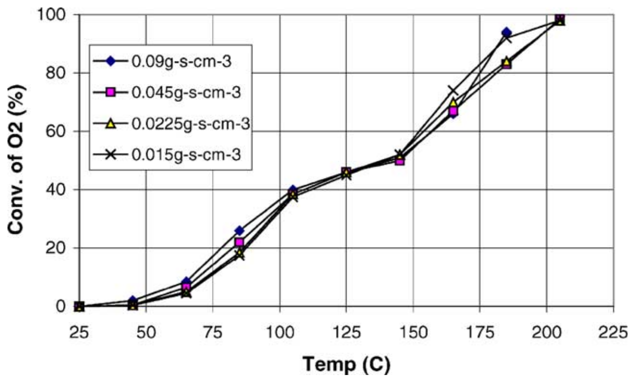

Fig. 4. Effect of contact time on the conversion of O_2 over CuO-CeO_2 under 1% CO, 1% O_2, 50% H_2 in He.

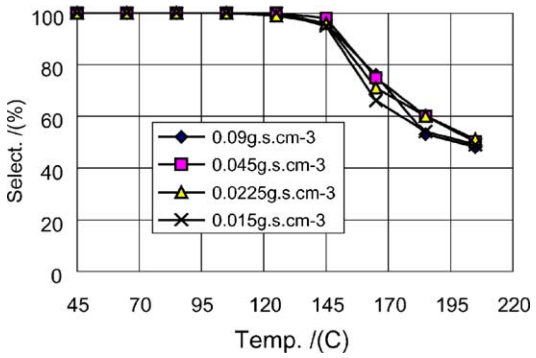

Fig. 5. Effect of contact time on the selectivity of CuO-CeO_2 under 1% CO, 1% O_2, 50% H_2 in He.

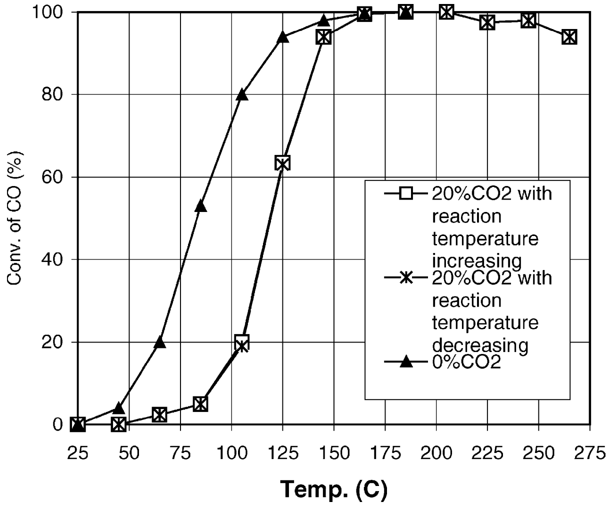

Fig. 6. Effect of adding 20% CO_2 in the reaction gas mixture of 1% CO, 2% O_2, 50% H_2–He on the CO conversion; contact time: 0.045 s g cm^{-3}.

The effects of CO_2 on CO conversion and selectivity are shown in Figs. 6–8. When 20 vol.% of CO_2 is added into the reaction mixture, CO conversion decreases, while the selectivity increases a little. The conversion of CO reaches nearly

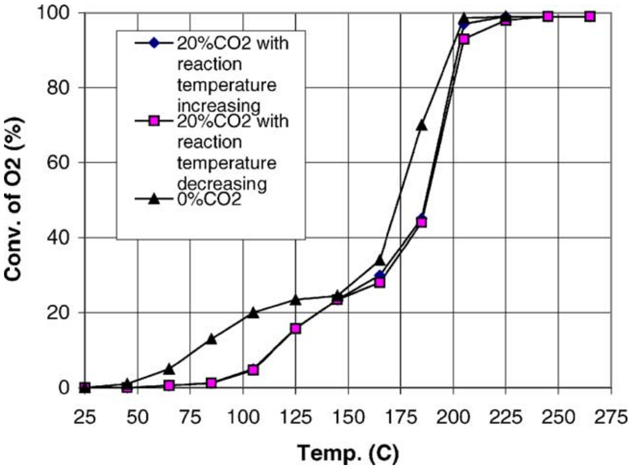

Fig. 7. CO_2 effect on the O_2 conversion over CuO-CeO_2; reaction conditions are the same as in Fig. 6.

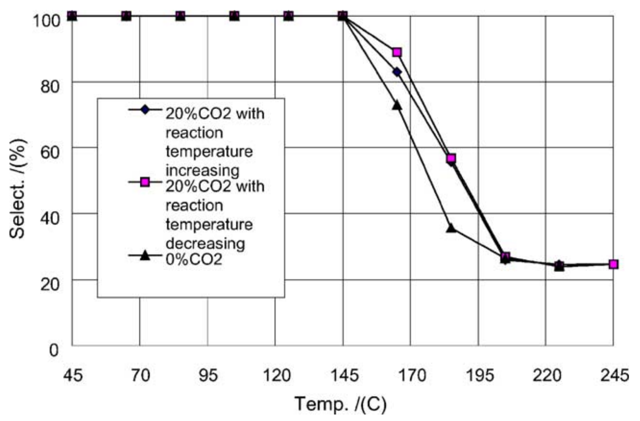

Fig. 8. Effect of CO_2 on the selectivity of CuO-CeO_2; reaction conditions are the same as in Fig. 6.

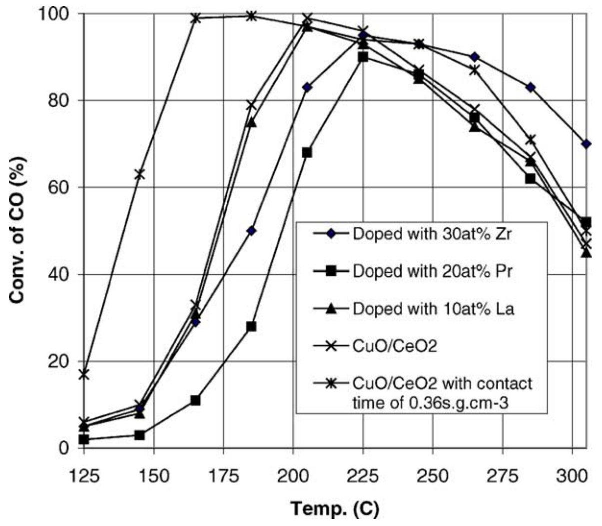

Fig. 9. Conversion of CO vs. temperature over CuO-CeO_2 and doped CuO-CeO_2 in a reformate gas mixture: 1% CO–1% O_2–10% H_2O–20% CO_2–50% H_2–He; contact time: 0.045 g s cm^{-3}.

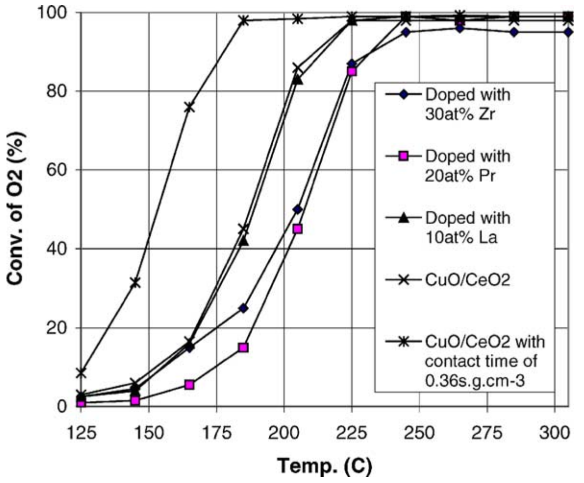

Fig. 10. Conversion of O_2 vs. temperature over CuO-CeO_2 and doped CuO-CeO_2; reaction conditions are the same as in Fig. 9.

100% and the selectivity is about 90% over the CuO-CeO_2 catalysts in a feed gas containing 1% CO, 20% CO_2, 1–2% O_2 and 50% H_2 in He at 165 °C. An adverse effect of CO_2 on CO oxidation is observed only at temperatures below 140 °C (compare Figs. 3 and 6). We attribute this to strong binding of CO_2 on the ceria surface at these temperatures [26,27].

When both 20% CO_2 and 10% H_2O are added into the reaction gas mixture, to reach the same conversion of CO, the reaction temperature must increase by about 60 °C, as shown in Fig. 9 (compare with Fig. 3). Thus, the presence of water lowers the CO oxidation activity of CuO-CeO_2 appreciably. This is not due to the onset of the water-gas shift reaction, as this would have boosted the CO conversion. However, high CO conversion and good selectivity are reported here for this catalyst at the higher contact time of 0.36 g s cm^{-3}. The conversion of CO and selectivity are 99% and 65%, respectively, at a reaction temperature of 165 °C in 1% CO, 1% O_2, 10% H_2O, 20% CO_2 and 50% H_2 in He (Figs. 9 and 11). The corresponding higher conversion of oxygen under

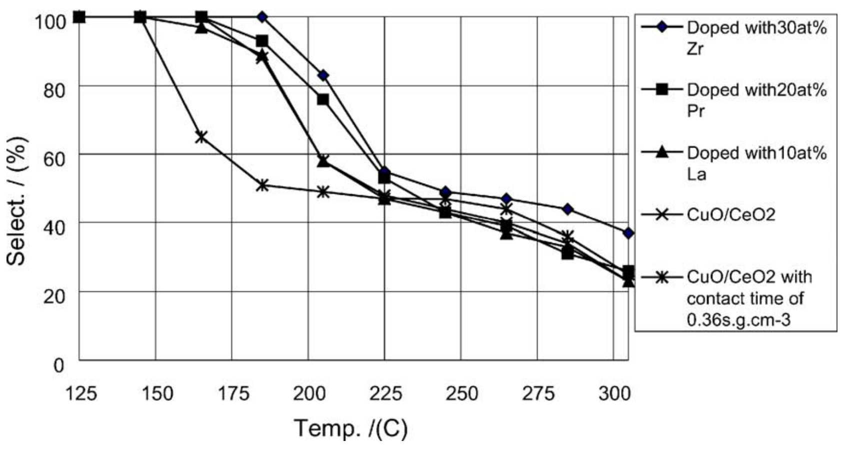

Fig. 11. Selectivity vs. temperature over CuO-CeO_2 and doped CuO-CeO_2; reaction conditions are the same as in Fig. 9.

these conditions (Fig. 10), shows that indeed the activity for the PROX reaction is decreased by the presence of water.

It has been reported that the introduction of Zr, Pr or La into the CeO_2 lattice improves its bulk and surface oxygen vacancies [27–30], which in turn improves the redox properties of ceria-based catalysts. Here, we checked whether the observed inhibition of the PROX reaction by water could be suppressed if a dopant from the above list was added to the CuO-CeO_2 material. However, we found that La doping had no effect, while doping with Zr or Pr reduced the conversion of CO, as can be seen in Figs. 9 and 10. A more detailed study of these effects was outside the scope of the present work (Fig. 11).

Table 1 lists the catalytic performance of the CuO-CeO_2 catalyst prepared in this work and of other PROX catalysts reported in the literature. As stated in the introduction, while noble metals have higher activity, their selectivity (for the same CO conversion) is inferior to the CuO-CeO_2 catalysts. This is because the noble metals have a much narrower temperature window for PROX. Among the oxides and mixed oxide catalysts, CuO-CeO_2 is a better choice, in terms of activity. As shown in Table 1, while CO can be nearly completely removed over some Co-based catalysts at 145 °C, the contact time was much higher. Also, the effect of water and carbon dioxide on the Co- and Fe-based catalysts can be detrimental to their activity.

Avgouropoulos et al. [18] recently reported on the catalytic performance of CuO-CeO_2 for PROX of CO in H_2. Their catalysts were prepared by co-precipitation and exhibited high activity and selectivity. As can be seen in Table 1, the CuO-CeO_2 prepared by UGC is more active in a gas mixture free of H_2O and CO_2. For example, the conversion of CO and selectivity are 96 and 97%, respectively, over the catalyst prepared by UGC in 1% CO, 1% O_2 and 50% H_2 in He, at a contact time of 0.015 g s cm^{-3} and a reaction temperature of 145 °C; while over the co-precipitated catalyst [18], the highest conversion of CO is 96% and the corresponding selectivity 50%, obtained at the much higher reaction temperature of 210 °C in 1% CO, 1.25% O_2 and 50% H_2 in He at a contact time of 0.03 g s cm^{-3}. The advantage of the preparation method is lost, however, in the presence of CO_2 and H_2O, as shown in Table 1. Inhibition of the CO oxidation reaction on CuO-CeO_2 by water and CO_2 has been reported also in H_2-free gases [26,27].

The data shown in Fig. 1 suggest that the partial pressure of oxygen has little effect on the CO conversion. Zeroth order kinetics in oxygen has been reported by Liu and Flytzani-Stephanopoulos [27] for the CO oxidation on CuO-CeO_2 in H_2-free gases. The PROX reaction is carried out in excess hydrogen, which should affect the redox state of the ceria surface. Yet, it appears that the oxygen dependence of CO oxidation is similar in the two reaction gas mixtures.

The state of copper in CuO-CeO_2 catalysts has been extensively examined in the literature [26–28,30,31]. H_2-TPR studies [23,30,32,33], and XPS and STEM/EDX analyses [26,27] show that there are three kinds of copper in

Table 1
Comparison of catalyst performance for the preferential oxidation of CO in H_2-rich gas mixtures

Catalyst	Conversion of CO (%)	Selectivity (%)	Reaction mixture (vol.)	Reaction temperature (°C)	Contact time (g s cm^{-3})	Reference
CuO-CeO_2 prepared by UGC	96	97	1% CO, 1% O_2, 50% H_2 in He	145	0.015	This work
	99	65	1% CO, 1% O_2, 20% CO_2, 10% H_2O, 50% H_2, He	165	0.36	
CuO-CeO_2 prepared by co-precipitation	96	50	1% CO, 1.25% O_2, 50% H_2 in He	210	0.03	[18]
	99	63	1% CO, 1.25% O_2, 50% H_2, 15% CO_2, 10% H_2O in He	170	0.36	
Ru/C	99.9	50	0.6% CO, 0.6% O_2, 98.8% H_2	105	0.3	[9]
Pt/C	99.9	50		135	0.3	
Pt/CeO_2-Al_2O_3	∼95	∼50	1% CO, 1% O_2, 98% H_2	150	0.06	[10]
Au-base metal oxide	100	33	0.5% CO, 0.8% O_2, 20% CO_2	100	0.06	[14]
	100	45	0.5% CO, 0.8% O_2, 20% CO_2, moisture	100	0.06	
Pt/Al_2O_3	84	43	1% CO, 1% O_2, 98% H_2	200	0.06	[8]
Pt/Al_2O_3—base metal oxide	75	80	1000 ppm CO, 500 ppm O_2, 20% H_2 in N_2	90	0.03	[11]
CoO	∼100	90	1% CO, 1.86% O_2, 90% H_2	100	0.3	[19]
$CoFeO_4$	∼100	∼100	1% CO, 1.86% O_2, 90% H_2	147	0.3	
Co octahedral molecular sieve	98	98	1% CO, 0.5% O_2, 30% H_2 in He	100	1.0	[20]

$CuO-CeO_2$, namely; bulk CuO particles that do not contribute to the activity; well dispersed Cu_xO clusters; and isolated ions strongly associated with ceria. Bulk CuO particles are reduced to metallic copper at temperatures higher than ~180 °C; copper oxide clusters are quite reducible, at temperatures about 100 °C; and ions have higher stability, beginning to reduce at ~160 °C, for a $CuO-CeO_2$ material calcined at 650 °C [30]. The interaction of copper oxide clusters with the surface oxygen of ceria is strong, and the latter is reduced at ~100 °C along with the copper oxide clusters [30,34]. A good correlation was found between surface reducibility and activity of $CuO-CeO_2$ for the CO oxidation reaction [27,34]. The similarity of CO conversion (lightoff) curves in Figs. 1 and 3 to those in H_2-free gas streams [26], indicate that the same Cu–O–Ce sites are the active sites for the PROX reaction. Interestingly, the adverse effect of water is moderated here by the presence of excess hydrogen. Again, this points out to the importance of the redox state of Cu–O–Ce for the CO oxidation reaction [28].

Similar to the H_2-free CO oxidation study on $CuO-CeO_2$ [26,27], and to the water-gas shift reaction on $CuO-CeO_2$ [22,35], we found here that the conversion of CO is nearly the same for samples with varying copper loading in the range of 5% to 30 at.%. Thus, there is a limit in the amount of copper that can be associated with ceria in an active form for all these reactions. Most likely this is dictated by the number of surface oxygen defects of ceria. For ceria-supported Au and Pt catalysts, Fu et al. recently reported [36] that metal nano-particles do not participate in the water gas shift reaction, while nonmetallic gold or platinum species strongly associated with surface cerium oxygen groups are responsible for the activity. The same may be true for $CuO-CeO_2$ catalysts for the CO oxidation in various gas streams. The oxidation state of copper in the active Cu–O–Ce phases may be +1, as has been shown both in O_2 [27,28] and in H_2 [31] gas mixtures.

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