

Selective low-temperature removal of carbon monoxide from hydrogen-rich fuels over Cu–Ce–Al catalysts

Praveen K. Cheekatamarla*, William S. Epling¹, Alan M. Lane

Department of Chemical Engineering, Box 870203, The University of Alabama, Tuscaloosa, AL 35487, USA

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Abstract

The selective oxidation of CO in the presence of excess H₂ was investigated over a ceria-promoted Cu–alumina catalyst. This catalyst shows nearly exclusive oxidation of CO versus H₂ with an O₂ concentration in stoichiometric proportion to CO, making it possible to purify a fuel cell feed stream with a minimum loss of energy content associated with H₂. The effect of the presence of CO₂ and H₂O in the feed on the activity and selectivity of the catalyst, and the long-term stability were also investigated. The catalysts were characterized by X-ray diffraction (XRD), CO chemisorption and temperature-programmed reduction (TPR). Copper is better dispersed on the ceria-promoted alumina support in comparison to alumina alone. CuO is the active phase for selective CO oxidation. Oxygen vacancies supplied and enhanced by ceria are responsible for improved activity.

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1. Introduction

Polymer electrolyte fuel cells (PEFCs) show considerable promise for fuel-efficient vehicular applications and therefore a substantial amount of effort has recently been directed at their production and optimization. The PEFC fuel cell requires hydrogen as its fuel source and, in order to avoid storing high-pressure hydrogen in or on a vehicle, it has been proposed that the hydrogen be generated on board [1].

Although the term “reformer” is often used for the whole system, the production of hydrogen actually occurs in three processes: (a) hydrogen is produced by autothermal reforming (ATR) of a hydrocarbon ($\text{fuel} + \text{O}_2 + \text{H}_2\text{O} \leftrightarrow \text{CO}_x + \text{H}_2$), where without water it is partial oxidation (POX) and without oxygen it is steam reforming (SR) [2,3]; (b) the water–gas

shift (WGS) reaction ($\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2$) eliminates most of the CO, producing more hydrogen [4]; and (c) any remaining CO is reduced to parts per million levels by preferential oxidation (PROX) [2]. The PROX reaction is the selective catalytic oxidation of CO in the H₂-rich reformat using O₂. Many auxiliary processes, such as fuel vaporization, sulfur removal, heat integration and effluent gas combustion can make this a very complicated device.

The CO concentration from a reformer/water–gas shift unit is typically about 1 mol%, which is set by the thermodynamic equilibrium of the water–gas shift reaction. The PEFC anode uses a Pt catalyst that is very sensitive to CO poisoning at low temperatures [5,6]. DOE’s Hydrogen, Fuel Cells and Infrastructure Technologies Program recommends 10 ppm CO target concentration for the fuel processor [7]. The selective catalytic oxidation step therefore must achieve a 99.9% conversion. Other challenges in fuel processing exist, but the preferential oxidation step is highlighted since it is the focus of this study.

In order to achieve this low CO concentration, the PROX reactor is placed between the shift reactor and the fuel cell

* Corresponding author. Tel.: +1 303 949 1629; fax: +1 509 335 4806.

E-mail addresses: cheek004@bama.ua.edu (P.K. Cheekatamarla), bill.epling@cummins.com (W.S. Epling), alane@coe.eng.ua.edu (A.M. Lane).

¹ Present address: Cummins, Inc., Box 3005, Columbus, IN 47202-3005, USA.

anode. Los Alamos National Laboratory (DOE's lead laboratory for PROX systems) has developed what many consider the state-of-the-art PROX catalyst and reaction system. It can achieve low concentrations of CO (10–20 ppm) in a multistage reactor over a Pt/Al₂O₃ or Ru/Al₂O₃ catalyst [8]. The reaction chemistry is complicated, involving not only catalytic oxidation of both CO and H₂ but also methanation and water–gas shift.

Considering the problems associated with other methods for CO removal (methanation and membrane-based processes [9]), the selective catalytic oxidation of CO seems to be the most straightforward and efficient method to reduce the residual CO in the reformat to desired levels. The crucial requirement for the PROX reactor is a high CO oxidation rate with a high selectivity. The selectivity in this study is defined as the ratio of O₂ consumption for the CO oxidation reaction (to CO₂) over the total O₂ consumption, which includes the oxygen loss due to H₂ oxidation (to H₂O). The formation of H₂O obviously reduces the amount of H₂, the input to the fuel cell. Similar losses of hydrogen can also be caused by other side reactions, e.g. the methanation of both CO and CO₂. It is desirable to keep up a high selectivity so that the fuel efficiency of the overall system remains high.

Since the PROX unit is placed between the low-temperature shift reactor (~200 °C) and the PEFC (~80 °C), it should operate between these temperatures. PROX system operation at low temperature (room temperature) is also very important for start-up in transportation application fuel cells. Therefore, the PROX system must operate over a wide temperature range to be practical [10].

A number of catalysts have been investigated for the PROX reaction. Some of the effective catalysts include supported zeolites [5], Pt [11,12], Au [13–16], Cu [14,17,18] and Ag [19]. The Pt-based and Cu-based catalysts tested thus far achieve maximum conversions at approximately 200 °C [17]. For low temperatures, highly dispersed gold on an oxide support showed high activity and selectivity (maximized at 80 °C) [16]. However, the activity strongly depended on the preparation method of the catalysts.

The objective of this study is to evaluate ceria-promoted Cu–alumina catalyst in improving the selective oxidation of CO in a stream rich in H₂ and determine the effects of CO₂ and H₂O on their performance. Copper was chosen as an alternative to the expensive precious metal group elements that have been tested before. Ceria was employed in the support to improve the metal–support interfacial active sites as reported in a previous study [20].

2. Experimental

A quartz tube with a diameter of 3/16 in. was used as the reactor, with an upward gas flow. A bypass flow system was also built to test the reactant stream composition intermit-

tently. The tube was placed in a tube furnace with digital control for heating. The catalysts tested were in powder form. A thermocouple was placed inside the reactor tube and the tip was typically located just above the powder during the reactions. Unit mass flow controllers were used to control flow rates entering the reactor. Pressures above 3 psig were not encountered. In each test, a GHSV of 22,000 h⁻¹ was used. The exit stream was attached to a drierite bed to remove H₂O.

The reactor effluent CO concentration was analyzed with a Thermo Environmental CO analyzer, capable of reading CO levels in the ranges of 0–1 through 0–8000 ppm. GC analysis was also performed with an HP 5890 using a Haysep DB column and thermal conductivity detector to monitor H₂, O₂, CO₂ and CH₄ levels. The conversion and the selectivity of CO were calculated using the following formulas:

$$\text{CO conversion (\%)} = ([\text{CO}_2]_{\text{out}}/[\text{CO}]_{\text{in}}) \times 100$$

$$\text{CO selectivity (\%)} = (0.5 \times [\text{CO}_2]_{\text{out}}/([\text{O}_2]_{\text{in}} - [\text{O}_2]_{\text{out}})) \times 100$$

Three model catalysts with different metal loadings were prepared: 4 wt.%Cu/11 wt.%Ce/Al₂O₃, 4 wt.%Cu/4 wt.%Ce/Al₂O₃, 9 wt.%Cu/11 wt.%Ce/Al₂O₃ and are denoted as 4Cu/11Ce/Al₂O₃, 4Cu/4Ce/Al₂O₃ and 9Cu/11Ce/Al₂O₃, respectively. The catalysts were prepared from precursor materials obtained from Johnson Matthey and Aldrich Chemical. The support was Al₂O₃ (basic, gamma). The precursor Cu material was Cu(NO₃)₂·6H₂O and the cerium precursor was Ce(NO₃)₃·6H₂O. The preparation technique adopted was a stepwise incipient wetness method using distilled water as the solvent for the precursor materials. The catalysts were prepared via depositing the Ce first, drying at 110 °C for 24 h and then depositing the Cu, with subsequent drying (110 °C) and calcination at 450 °C. The catalyst was then reduced in a mixture of 5% H₂ in N₂ for 1 h at 350 °C.

BET surface area, chemisorption and temperature-programmed reduction (TPR) measurements were obtained using a Quantachrome CHEMBET 3000. BET surface area of the catalysts was analyzed by nitrogen adsorption–desorption technique. CO chemisorption at –80 °C was utilized to measure the dispersion of these catalysts using the pulse technique. The spillover of CO from metal on to the support gives higher dispersion values than the actual metal dispersion. It has been reported that the chemisorption of CO at –80 °C alleviates this phenomenon [21]. For TPR experiments, a temperature ramp rate of 10 °C min⁻¹ was used and the reductant gas was a 5% H₂/N₂ mixture. Powder X-ray diffraction (XRD) patterns were collected in air on a Philips Powder Diffractometer using Cu K α radiation with a nickel filter.

3. Results and discussion

3.1. Alumina-supported catalysts

The CO oxidation activity of 4Cu/Al₂O₃, 11Ce/Al₂O₃ and 4Cu/11Ce/Al₂O₃ catalysts is shown in Fig. 1. The inlet feed stream composition included 1% CO, 1% O₂, in H₂, with a total space velocity of 22,000 h⁻¹. This corresponds to 50% selectivity for a 100% CO and O₂ conversion. Before carrying out the activity tests, all the catalysts were reduced at 350 °C in a 5% H₂/N₂ mixture. The reactor temperature listed is that of the reactor furnace itself; the temperature read at the outlet of the catalyst bed was always higher (~20 °C) due to the exothermic oxidation reactions.

Each catalyst showed a similar trend in CO oxidation activity. A maximum occurred between 85 and 110 °C and then the activity decreased with a further increase in the temperature. This is due to the competitive hydrogen oxidation reaction occurring along with the CO oxidation. 4Cu/Al₂O₃ oxidized 75% of the entering CO and the 11Ce/Al₂O₃ oxidized approximately 30% of the CO at 100 °C. However, the most interesting results are obtained on the Cu-loaded Ce/Al₂O₃ catalyst. The 4Cu/11Ce/Al₂O₃ catalyst showed high activity converting >99% of CO at relatively lower temperature. The improved activity is probably due to a synergism between the catalyst components. This catalyst was further analyzed by modifying the metal loading on the support and the results are presented below.

3.2. Effect of metal loading

The dependence of CO conversion on the reaction temperature and on the amount of Cu or Ce, in a reactant gas of 1% CO and 1% O₂ in H₂ is shown in Fig. 2. The CO conversion simply decreased with an increase of temperature beyond 100 °C on all the catalysts; again due to a shift in the selectivity to H₂ oxidation as explained above. The CO conversion was in the order of 4Cu/11Ce/Al₂O₃ > 4Cu/4Ce/Al₂O₃ > 9Cu/11Ce/Al₂O₃,

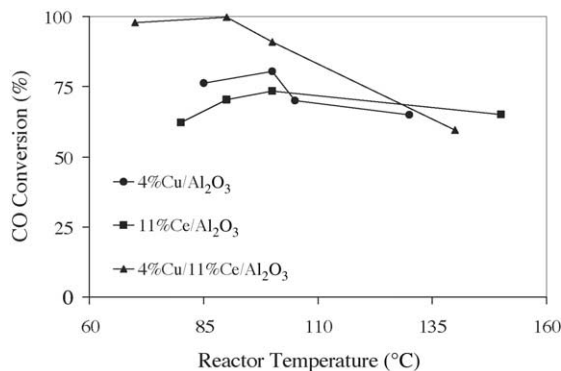


Fig. 1. CO conversion as a function of reactor temperature using 4Cu/Al₂O₃, 11Ce/Al₂O₃ and 4Cu/11Ce/Al₂O₃ with a feed stream consisting of 1% CO and 1% O₂ in the hydrogen at a GHSV of 22,000 h⁻¹.

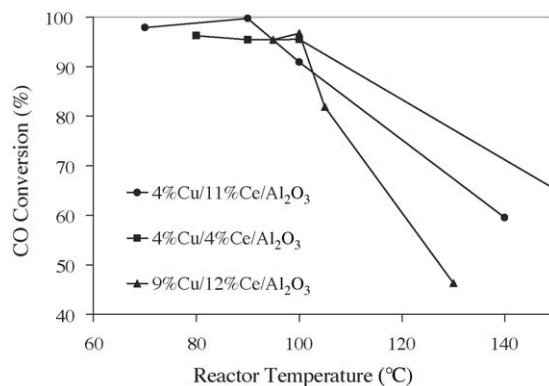


Fig. 2. CO conversion as a function of reactor temperature using 4Cu/11Ce/Al₂O₃, 4Cu/4Ce/Al₂O₃ and 9Cu/12Ce/Al₂O₃ with a feed stream consisting of 1% CO and 1% O₂ in the hydrogen at a GHSV of 22,000 h⁻¹.

with the 4Cu/11Ce/Al₂O₃ catalyst showing 99.9% CO conversion at 90 °C due to its high selectivity for the CO oxidation reaction. This catalyst was chosen for further study by varying the oxygen content in the feed stream.

3.3. Oxidation of CO in the presence of excess O₂

The effect of oxygen concentration on the CO oxidation activity was studied by changing the oxygen concentration from 1% (twice the stoichiometric concentration) to 0.5% (stoichiometric amount). Fig. 3 shows that the CO conversion decreases with a decrease in the oxygen content. At an oxygen concentration of 0.5%, the highest CO conversion noted is 93% corresponding to a selectivity of 93%. However, by increasing the oxygen concentration to 1%, the CO conversion reached 99.9% with a selectivity of 49.98%. The CO conversion corresponds very well with the results of Jordano and co-workers [8]. This catalyst shows the high activity needed to be an effective PROX catalyst.

Fig. 4 shows the CO conversion and CO selectivity on the 4Cu/11Ce/Al₂O₃ catalyst. These results correspond to the experiment described above and the CO selectivity and CO conversion were calculated as the oxygen concentration was increased from 0.5 to 1%. The data were taken at 90 °C,

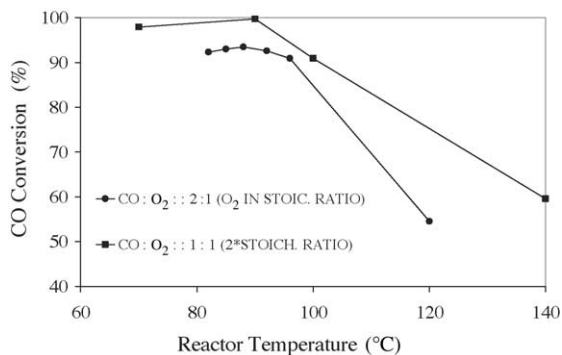


Fig. 3. CO conversion as a function of oxygen concentration on the 4Cu/11Ce/Al₂O₃ catalyst with an inlet composition consisting of 1% CO, 0.5%–1% O₂ and a H₂ balance inlet stream.

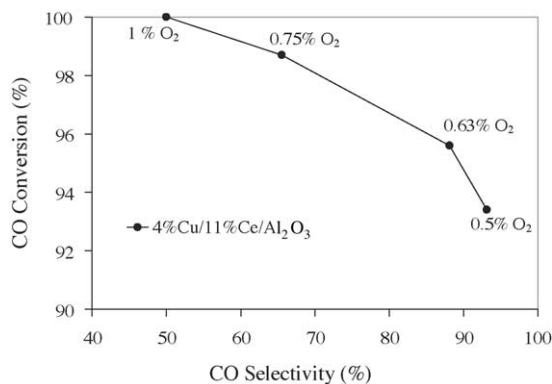


Fig. 4. CO conversion and CO selectivity as a function of oxygen concentration on the 4Cu/11Ce/Al₂O₃ catalyst; feed composition: 1% CO, 0.5–1% O₂ and a H₂ balance, GHSV = 22,000 h⁻¹.

the temperature at which highest CO conversion was noted. The selectivity increased from 49.98% at [O₂]_{in} = 0.5 to 93% at [O₂]_{in} = 1% associated with a drop in the CO conversion from 99.9 to 93%. The selectivity decreased simply as the oxygen addition increased. However, these results show that most of the oxygen added after the stoichiometric proportion (theoretical molar concentration of oxygen needed for 100% CO conversion) is utilized for the oxidation of CO and that hydrogen oxidation rarely occurs in spite of the presence of 98% hydrogen.

3.4. Catalytic performance with time

The 4Cu/11Ce/Al₂O₃ catalyst was tested for its performance with time (at 90 °C, the temperature for highest conversion). As shown in Fig. 5, the catalyst was stable for 80 h of operation, with the CO conversions still above 99%. Gas chromatography was frequently used during the experiments to monitor any undesired product formation. No byproducts (such as methane) were observed in the effluent during any of the experiments at any of the temperatures tested. This is true of all catalysts tested during this study. Typical PROX catalysts such as Pt/Al₂O₃ and Ru/Al₂O₃ achieve such low

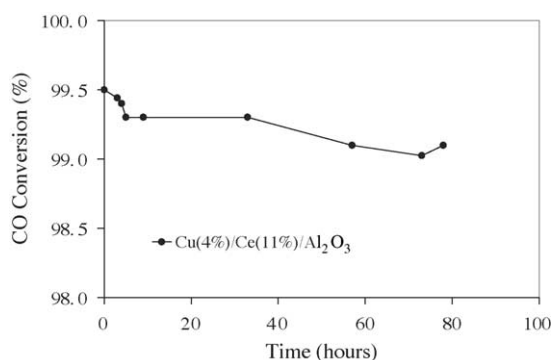


Fig. 5. CO conversion as a function of time on stream using the 4Cu/11Ce/Al₂O₃ catalyst with a feed stream consisting of 1% CO and 1% O₂ in the hydrogen at a GHSV of 22,000 h⁻¹.

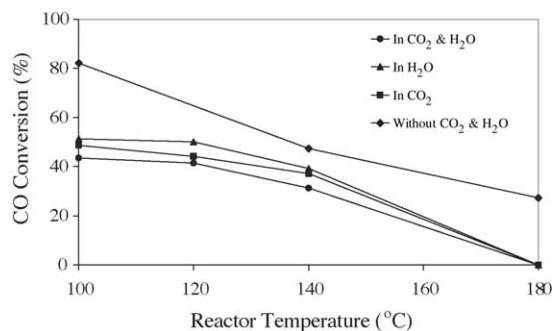


Fig. 6. CO conversion as a function of reactor temperature using the 4Cu/11Ce/Al₂O₃ catalyst with an inlet composition consisting of 1% CO, 1% O₂, 18% CO₂ and/or 7% H₂O and a H₂ balance inlet stream at a GHSV of 22,000 h⁻¹.

CO concentrations (10–20 ppm); however, the reaction chemistry involves not only oxidation of both CO and H₂, but also methanation and water–gas shift [8,14]. In view of the above results, the 4Cu/11Ce/Al₂O₃ catalyst seems to be the most suitable catalyst for the preferential oxidation of CO in excess hydrogen, considering its high activity and selectivity.

3.5. Effect of CO₂ and H₂O

Under realistic conditions, the product gas from a methanol or hydrocarbon reformer also contains CO₂ and H₂O along with H₂ and CO. Therefore experiments were performed to study the effects of the presence of these components on the stability and activity of the 4Cu/11Ce/Al₂O₃ catalyst. Fig. 6 shows the dependence of CO conversion on reaction temperature and the presence of these two components. The inlet feed stream composition included 1% CO, 1% oxygen, 7% H₂O and/or 18% CO₂ in hydrogen. The presence of H₂O and/or CO₂ caused a decrease in the CO oxidation activity of the catalyst. Maximum conversion occurred at 100 °C for all the feed conditions. The effect of CO₂ on catalytic activity was greater than that of H₂O. The combined effect of CO₂ and H₂O was even worse, although not additive, with the CO conversion dropping to around 45% compared to 82% at the dry conditions (without CO₂ and H₂O). The observed decrease in activity in the presence of H₂O and/or CO₂ is probably a kinetic rather than an equilibrium effect of water–gas shift reaction owing to the low operating temperatures (<180 °C) [22].

3.6. Catalyst characterization

The best performance was obtained using the ceria-promoted Cu–alumina catalyst. Although identical reaction conditions were used in each experiment, the CO oxidation activity of Ce–alumina and Cu–alumina was very low compared to the Cu–Ce–alumina catalyst. Therefore, some synergistic effect must be present. Exploring this possibility was accomplished using XRD, CO chemisorption and TPR analysis.

Table 1
Compositions, BET areas and dispersions of oxide catalysts

Catalyst	BET area ($\text{m}^2 \text{g}^{-1}$)	Dispersion (%)
4Cu/alumina	198	35
11Ce/alumina	165	–
4Cu/11Ce/alumina	103	58

BET surface area and dispersion values of the catalysts used in the experiments described in Fig. 1 are listed in Table 1. The decrease in BET surface areas of the ceria-promoted catalyst is presumably a result of micropore plugging by CuO_x . However, the most interesting results are obtained in the dispersion values of these catalysts. Cu is better dispersed in the ceria-promoted catalyst than in the alumina catalyst suggesting that the ceria-promoted alumina support improves the metal dispersion. Previous experiments conducted at lower space velocities and higher metal loadings did not effectively improve the CO conversion, hence, improved dispersion alone cannot be attributed to the superior performance of the Cu–Ce–Al catalyst. Additional studies were conducted on these catalysts to examine the synergistic effect between the active Cu metal and the Ce–Al phase, if any.

Fig. 7 shows the XRD patterns obtained for Ce–Al and supported Cu and Cu–Ce catalysts. Fig. 7(A) represents XRD peaks corresponding to the Ce–Al support consisting of ceria and alumina alone. The 4Cu/Al₂O₃ catalyst showed only line characteristic of the alumina support (Fig. 7(B)). The absence of XRD peaks characteristic of crystalline CuO suggests that copper exists as a well-dispersed copper surface phase (probably as small particles not detectable by XRD). These results are consistent with previous work done by Friedman et al. [23]. The 4Cu/11Ce/Al₂O₃ catalyst in Fig. 7(C) clearly shows the signals corresponding to all the components and particularly that of crystalline CuO. The significant increase in the selective CO oxidation activity of this catalyst suggests that crystalline CuO is the active phase for CO oxidation. We speculate that when alumina alone acts as the support, the surface becomes saturated with a copper surface phase, whereas on the Ce–Al catalyst, the metal forms fine CuO crystallites due to some interaction between the Ce–Al and the metal phase.

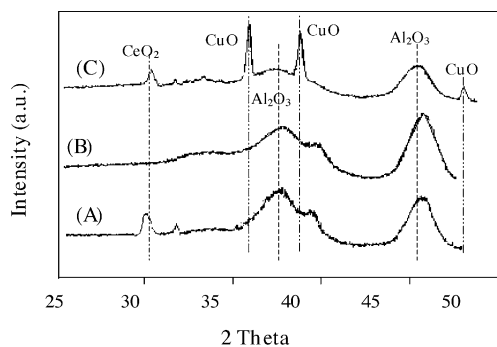


Fig. 7. XRD patterns measured for (A) 11Ce/Al₂O₃, (B) 4Cu/Al₂O₃ and (C) 4Cu/11Ce/Al₂O₃.

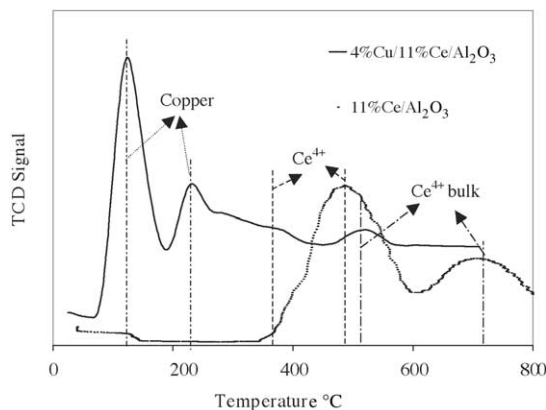


Fig. 8. TPR patterns of (a) 4Cu/11Ce/Al₂O₃ and (b) 11Ce/Al₂O₃, operating conditions: 10 °C min⁻¹, 5% H₂ in N₂.

The data from TPR experiments over these catalysts are shown in Fig. 8. Two reduction peaks can be observed on the 11Ce/Al₂O₃ catalyst, one at 520 °C and another at 730 °C. From Yao et al. [24], the surface capping oxygen anion which attaches to a surface Ce⁴⁺ is reducible at 500 °C, and the bulk oxygen anion that is bonded to Ce⁴⁺ in bulk ceria is reducible at 750 °C. The peaks at 520 and 730 °C on the 11Ce/Al₂O₃ catalyst can thus be attributed to the reduction of surface oxygen anion (Ce⁴⁺ → Ce³⁺) and the bulk ceria, respectively. It has been reported that the TPR peak temperature of surface oxygen ions of ceria shifts downward in the presence of a precious metal [25,26]. An explanation for the peak shift to lower temperature after copper had been loaded on YSZ was also proposed by Dow et al. [27]. The same reasoning is applicable to the TPR patterns of Fig. 8 as it is clear that the peak at 500 °C shifts to 350 °C in the presence of Cu. No significant differences were found between the reduction profiles of 4Cu/Al₂O₃ and Cu–Ce–Al catalysts, and hence not represented.

For CO oxidation over alumina-supported copper oxide catalysts, it is generally considered that the reaction involves a redox mechanism on the CuO surface. Jernigan et al. [28] proposed that CO oxidation proceeds by a redox mechanism involving CuO and Cu₂O and that the reduction of CuO by CO is the reaction's rate-determining step. Since the selective oxidation reaction may require adsorption of CO at oxygen vacancies, the availability of these vacancies is important for Cu-based catalysts. On the basis of TPR results, it may be concluded that the oxygen vacancies are supplied and enhanced in the presence of ceria.

4. Conclusions

The selective or preferential oxidation of CO in a H₂ stream using a ceria-promoted Cu–alumina catalyst was investigated for potential application downstream from a fuel cell reformer. These catalysts are quite effective as PROX catalysts due to their high activity and high selectivity for

CO oxidation. Also, these catalysts were observed to be very stable with time. However, the performance is decreased to some extent in the presence of H₂O and CO₂. Characterization techniques on these catalysts suggest that the increase in selectivity and activity for CO oxidation is possibly due to the formation of crystalline CuO and that the presence of an oxygen-ion conducting support such as ceria leads to the supported copper exhibiting a precious metal-like catalytic behavior.

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