Catalysis Letters Vol. 86, Nos. 1–3, March 2003 (© 2003) 107

A $CuO–CeO_2$ mixed-oxide catalyst for CO clean-up by selective oxidation in hydrogen-rich mixtures

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Received 13 August 2002; accepted 21 November 2002

A $CuO–CeO_2$ mixed-oxide catalyst was shown experimentally to be highly active and selective for the oxidation of CO in hydrogen-rich mixtures, and an attractive alternative to the noble metal catalysts presently used for CO clean-up in hydrogen mixtures for proton-exchange membrane fuel cells (PEMFC). Although the presence of H_2O and CO_2 in the feed decreased the activity and increased the reaction temperature considerably to achieve a given CO conversion with a reactor, the selectivity profile with respect to the conversion remained virtually the same. The effect of H_2O and CO_2 on the reaction was found to increase the required energy for reduction of the active copper species in the redox cycles undergone during the reaction. The catalyst showed a slow, reversible deactivation, but the activity was restored on heating the catalyst at 300 °C, even under an inert flow. At space velocities above $42\,g\,h\,m^{-3}$, the catalyst reduced the CO content to less than 10 ppm in the temperature range 166–176 °C for a feed of 1% CO, 1% O_2, 50% H_2, 20% H_2O, 13.5% CO_2 and balance He. Hence, with this catalyst it is feasible to clean up the CO in a single-stage reactor with relatively small excess oxygen, which is in contrast to the typical multistage reactor systems using noble metal catalysts.

KEY WORDS: CO clean-up; copper–ceria catalyst; hydrogen production; CO oxidation.

1. Introduction

Hydrogen mixtures for proton-exchange membrane fuel cells (PEMFC) should be essentially free of CO, as it strongly adsorbs on anode catalysts and substantially decreases the fuel cell performance. Hydrogen produced by hydrocarbon steam reforming contains typically 0.1–2% CO in the reforming mixture. Among other processes, selective CO oxidation is usually employed to reduce the CO content in the reformed gas to less than 10 ppm. Known catalysts for the selective oxidation of CO are predominantly supported noble metals. Ru on alumina [1], Pt on alumina [2,3], Pt–Ru on alumina [4], Pt–Ru impregnated on hopcalite [5], and a base-metal-promoted Pt on alumina [6] are reported to be active for the reaction.

For total oxidation of CO in the absence of hydrogen, $CuO–CeO_2$ catalysts have been shown to be very active for CO oxidation, exhibiting specific activities far superior to the conventional copper-based catalysts and comparable with or superior to platinum catalysts [7–9]. The mixed-oxide catalysts were applied to the selective oxidation in excess hydrogen and found to be also highly active and exceptionally selective [10,11]. Another similar catalyst, CuO/samaria-doped ceria, was also reported to be highly active in total CO oxidation [12], and active and selective in CO oxidation in the presence of hydrogen [13].

In the presence of hydrogen, hydrogen oxidation also occurs in the selective CO oxidation. Hence the amount of oxygen consumed in the reaction is usually in excess of the CO oxidation alone. This is denoted in terms of selectivity S, which is defined as the ratio of the amount of oxygen consumed for CO_2 formation divided by the total amount of oxygen consumed in the reaction:

$$S = \frac{1}{2}\,\frac{\text{moles of } CO_2 \text{ formed}}{\text{moles of } O_2 \text{ reacted}}. \qquad (1)$$

Pt/alumina catalysts showed a selectivity in the range 0.4–0.55 at around 200 °C [2,3]; a Pt/zeolite exhibited a selectivity of 0.6 at 200 °C [14]; an Au/Fe_2O_3 catalyst at 80 °C showed a decreasing selectivity from 0.75 to 0.2 with diminishing partial pressure of CO [15]; and a Fe-promoted Pt catalyst showed a selectivity of 0.5–0.8 in the range 90–150 °C [6]. On the other hand, $CuO–CeO_2$ exhibited a selectivity higher than 0.9 until the CO conversion reached ~0.8, indicating that hydrogen oxidation was virtually blocked on the catalyst in the presence of CO, and only after the CO concentration was substantially reduced in the hydrogen mixture did the hydrogen oxidation commence on the catalyst with the remaining oxygen [10,11].

Besides the low selectivities of the noble metal catalysts, it has been shown that over a range of CO input concentrations of 500–10 000 ppm, a single-stage reactor packed with noble metal catalysts could not reduce the CO concentration to 20 ppm without considerable

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hydrogen consumption [4,5]. Large hydrogen consumption does not only decrease the system efficiency by reducing the hydrogen content in the mixture to the fuel cell, but also makes the reactor temperature difficult to control due to the large exothermic heat of hydrogen oxidation. To avoid this, CO clean-up units with noble metal catalysts typically consist of multi-staged reactors [4,5].

In this study we explored the potential of the CuO–CeO$_2$ catalyst for CO clean-up in hydrogen mixtures. For a realistic simulated reformed gas, we tested its activity, selectivity, and activity change with time on stream. We demonstrated that with the CuO–CeO$_2$ catalyst it is indeed feasible to clean up CO to less than 10 ppm in a single-stage reactor without substantial consumption of hydrogen.

2. Experimental

CuO–CeO$_2$ catalysts were prepared by coprecipitation. The precursor salts, $Cu(NO_3)_2{\cdot}3H_2O$ and $Ce(NO_3)_3{\cdot}6H_2O$, were dissolved in deionized water, mixed together and heated to 70 °C. NaOH solution was added dropwise to precipitate the metals as hydroxides under vigorous stirring and the precipitate was aged with stirring at 70 °C for 5 h. The pH of the mixed solution was kept at 10. The precipitate was filtered and washed with deionized water to remove the residual sodium, and then dried for 12 h at 90 °C. The dried precipitate was calcined at 500 °C for 5 h in air. The calcined catalyst was crushed and sieved to 0.15–0.18 mm. The BET surface area of the catalyst was 91 m^2/g. The Cu content in the catalyst was designated as Cu/(Cu + Ce) atom ratio × 100 (at%).

The reaction experiments were carried out in a quartz tube reactor (4 mm i.d.) at atmospheric pressure. Typically 50 mg of the catalyst was mixed with 250 mg of inert α-alumina particles of the same size to dissipate the reaction heat and to keep the catalyst bed isothermal. A thermocouple was placed at the center of the bed to monitor the reaction temperature. The temperature increase due to the heat of reaction in the bed was less than 5 °C. Also the pressure drop through the bed at a typical flow rate of 100 ml/min was less than 5 kPa.

The CO gas (99.95%) was passed through a hot quartz tube at 400 °C to decompose the likely impurity of iron carbonyl before entering the reactor [16]. The other gases, H$_2$, O$_2$, He (ultrahigh purity), and CO$_2$ (high purity), were used without further treatment. The gas flow rates were controlled by mass flow controllers. To add water into the feed stream, the dry gas mixture was bubbled through a saturator. The water vapor pressure in the feed was controlled by the saturator temperature. The oxygen content in the feed was denoted in terms of the parameter λ defined as $2 \times O_2/CO$ mole ratio. The reactor effluent was analyzed on-line by a gas chromatograph (GC) with a thermal conductivity detector (TCD). The column mounted on the GC to separate O$_2$, CO, and CO$_2$ was a Carboxen column (Supelco I-2390). As water could not be analyzed simultaneously due to too long a retention time with the column, the gas mixture was dehydrated in a cold trap before being put into the sample loop in the GC. Normally a 250 μl sample loop was used for analysis of CO concentrations greater than 1000 ppm. For measurement of extremely low CO concentrations, the highest TCD sensitivity setting (maximum allowable current) and a sample volume of 1 ml were employed to enhance the detection limit.

The products of the reaction were CO$_2$ and H$_2$O, but a trace amount of CH$_4$ in the range 20–30 ppm was detected at reaction temperatures above 200 °C and hence not considered in the mass balance. When CO$_2$ was added to the feed stream, the CO conversion was estimated by comparing the CO peak areas of the chromatograms of the feed and the reactor effluent, since the amount of CO$_2$ generated in the reactor was usually much less than that of the input CO$_2$ and hence a small error in the CO$_2$ area in the GC analysis often caused large scatter in the data. Also the O$_2$ conversion was estimated from the O$_2$ peak areas of the two streams. The amount of water formed in the reactor was calculated from the O$_2$ balance. In the absence of CO$_2$ and H$_2$O in the feed, the reactor effluent was analyzed for CO$_2$ and H$_2$O to measure the selectivity directly.

Temperature programming with a rate of 30 °C/h was used to control the reactor temperature from 50 to 250 °C. Steady-state experiments at a few fixed temperatures verified that conversions and selectivities obtained with the programming were the same as the corresponding steady-state values. The catalyst showed slow but reversible deactivation with time on stream. Except in the long-term activity test, the catalyst was treated with 10% O$_2$/He flow at 300 °C for 3 h after 10 h in experiments to restore the activity.

H$_2$ temperature-programmed reduction (TPR) was carried out in a conventional TPR reactor with a TCD. An amount of 15 mg of the catalyst sample was pretreated in 10% O$_2$/N$_2$ flow at 300 °C for 1 h. After the catalyst sample was cooled to room temperature under nitrogen flow, TPR of the sample was started with a reducing gas mixture of 10% H$_2$/N$_2$ flowing at 50 ml/min through the sample tube. The temperature rate was 10 °C/min to 500 °C. The rate of hydrogen consumption was measured by the detector. In experiments to examine the effect of water vapor on the TPR of the catalyst, the hydrogen gas mixture was bubbled through a water saturator kept at 7.2 °C (water vapor pressure = 1.02 kPa) to produce a mixture with 1% water vapor. The effect of CO$_2$ on the TPR was also examined by adding 0.5 ml/min CO$_2$ to the hydrogen mixture.

3. Results and discussion

3.1. Activity and selectivity

Among the 10, 20, and 50% Cu loadings, 20% Cu showed a slightly better activity, about 5 °C lower in the isoconversion of CO, than the others, and 10 and 50% Cu were similar in performance. Liu and Flytzani-Stephanopoulos [9] reported that the catalytic activity was largely independent of the bulk copper content in the range 2–50%, and the bulk CuO on the catalyst surface, formed when the copper content exceeded 15%, contributed little to the catalyst activity. On the other hand, Avgouropolous *et al.* [10] found a 14.3% Cu catalyst performed significantly better than 7.3 and 20.9% Cu catalysts. We observed peaks due to crystalline CuO in the XRD of 50% Cu catalyst, and only peaks due to the characteristic fluorite structure of the ceria with 10 and 20% Cu catalysts (not shown), indicating the finely dispersed copper was XRD silent. All the data discussed below were obtained with the 20% Cu catalyst.

Figure 1 shows the CO conversion and the selectivity with respect to the reaction temperature for a feed without CO_2 and H_2O. When $\lambda = 1$, the stoichiometric oxygen input, the reaction was incomplete as the concomitant hydrogen oxidation consumed oxygen. The CO conversion passed through a maximum conversion of 92% at 115 °C with increasing temperature, which coincided with the complete conversion of the input oxygen. On the other hand, with $\lambda = 2$, a complete conversion of CO was obtained at 120 °C, while the oxygen conversion was 0.54, with 93% selectivity. Further increase in the temperature increased only the oxygen conversion and at 170 °C the input oxygen reacted completely inside the reactor, giving 50% selectivity. Above 170 °C, the CO conversion began to decrease due to early depletion of the oxygen by the increasingly avid hydrogen oxidation. This demonstrates that the catalyst is active and remarkably selective for the reaction in the presence of much excess hydrogen. Below 100 °C, hydrogen oxidation was virtually absent, and only CO oxidation consumed the oxygen, with 100% selectivity. Over a similar catalyst, samarium-doped CuO–CeO$_2$, the light-off of hydrogen oxidation was reported to occur above 130 °C and water formation was not detected below 100 °C, with or without the presence of CO [13]. Also in this temperature region, doubling the O_2 concentration in the feed little affected the CO conversion, indicating approximately a zero-order dependence of the CO oxidation rate on the oxygen partial pressure. In fact, a very low reaction order of 0.08 in the oxygen partial pressure was observed over a wide range of temperature in the absence of hydrogen [8,9].

Reformer effluent usually contains considerable amounts of water vapor and CO_2. For example, the reported reformed gas composition from a methanol processor for transport applications was 45.6% H_2, 2.6% CO, 16.6% CO_2, 18.2% N_2, 17% H_2O [17]. The composition may vary depending on the fuel for reforming and reformer operating conditions. We tested the catalyst performance for the feed with 20% H_2O and 13.5% CO_2. Figure 2 shows that addition of the two components substantially decreased the activity, and a given conversion can be achieved at a temperature higher by 60–70 °C when compared to figure 1. Avgouropolos *et al.* [10] also reported that the presence of 15% CO_2 in the feed raised the reaction temperature by about 15–35 °C and addition of 10% water vapor to the CO_2-containing feed further increased the temperature by about 20–40 °C for a given CO conversion. Among other catalysts for this reaction, Au/α-Fe_2O_3 was also strongly deactivated by the presence of water vapor and CO_2 [11], while the activity of Pt/γ-Al_2O_3 was little affected by the presence of the two components [2,3]. It is thus evident that the deactivation effect largely depends on the nature of the catalyst. The selectivity was also similarly shifted to high temperatures, indicating that hydrogen oxidation was also suppressed in parallel with CO oxidation in the presence of the two components.

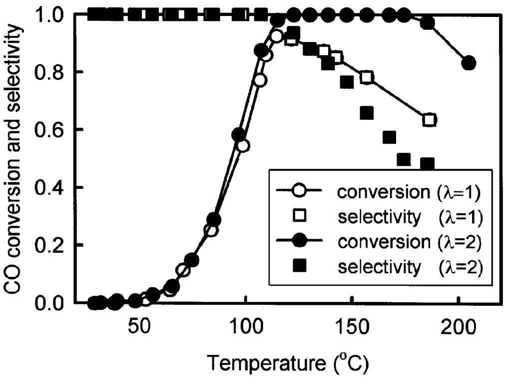

Figure 1. CO conversion and selectivity with respect to temperature. Catalyst: 50 mg CuO–CeO$_2$; feed: 100 ml/min, 1% CO, 0.5% ($\lambda = 1$) or 1% ($\lambda = 2$) O_2, 50% H_2, balance He.

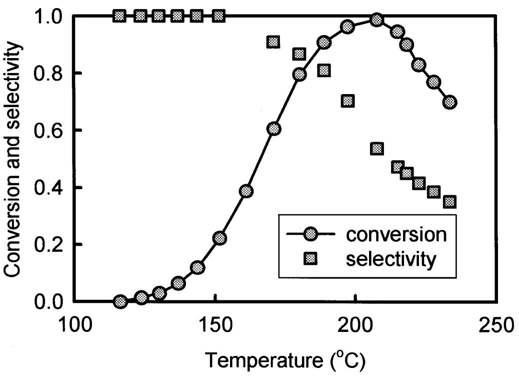

Figure 2. CO conversion and selectivity with respect to temperature in the presence of H_2O and CO_2. Feed: 1% CO, 1% O_2, 20% H_2O, 13.5% CO_2, 50% H_2, balance He.

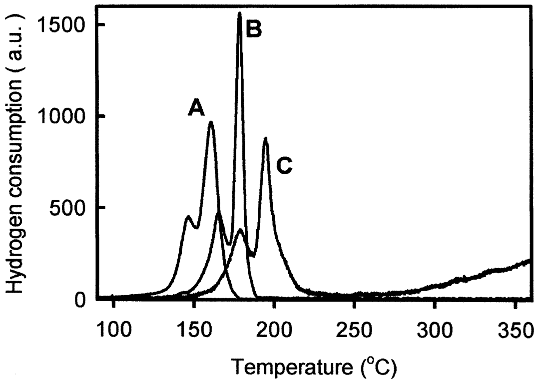

Figure 3. Temperature-programmed reduction profiles for various reducing mixtures: (A) 10% H_2; (B) 1% H_2O, 10% H_2; (C) 1% H_2O, 1% CO_2, 10% H_2.

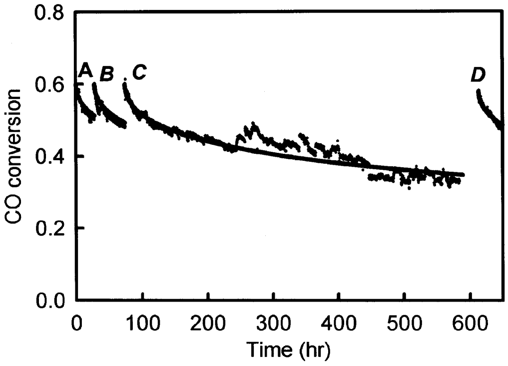

Figure 4. Variation of CO conversion with reaction time after various activations: (A) fresh catalyst; (B) 10% O_2; (C) 50% H_2; (D) 100% He at 300 °C, 1 h. Feed: 1% CO, 1% O_2, 20% H_2O, 13.5% CO_2, 50% H_2, balance He.

3.2. Temperature-programmed reduction

TPR profiles obtained for three different gas mixtures (10% H_2/N_2; 1% H_2O, 10% H_2/N_2; and 1% H_2O, 1% CO_2, 10% H_2/N_2) are shown in figure 3. Two reduction peaks were observed for all the mixtures. The low-temperature peak was assigned to the reduction of Cu clusters closely interacting with CeO_2 and the high-temperature peak to the reduction of segregated CuO [9,12,13,18,19]. Compared with the TPR of pure CuO, characterized by a single peak at around 360–380 °C [18,19], both copper species were reduced at significantly lower temperatures, indicating even the segregated CuO was not free from the influence of the neighboring CeO_2. Oxidation and reduction potentials of the copper species in CeO_2 were measured to be lower than the potentials of CuO [20]. Thus less energy is required to reduce the copper species in CuO–CeO_2 than in the case of CuO. With the addition of 1% H_2O in the flow, the low-temperature peak shifted from 146 to 165 °C, and with further addition of 1% CO_2, it shifted to 180 °C. The high-temperature peak showed similar shifts, from 160 to 179 °C and finally to 195 °C. The continuous upward drift of the TPR profile obtained in the presence of 1% H_2O and 1% CO_2 at temperatures above 250 °C was due to the increasing hydrogen consumption by the reverse water–gas shift reaction between CO_2 and H_2.

The shift of the TPR peaks indicates apparently that H_2O and CO_2 considerably stabilize the oxidized Cu species in CeO_2 against reduction by H_2. On fully reduced copper surfaces, both water and CO_2 have been reported to decompose and oxidize a small fraction (<20%) of the surface [21–24], and also to have inhibitory effects on methanol synthesis by keeping the copper surface partially oxidized [25,26]. These studies in fact suggest that H_2O and CO_2 can oxidize a part of the copper surface only after a significant fraction of the surface has been reduced. Since the copper species was fully oxidized before TPR, it is unlikely that the oxidizing effects of H_2O and CO_2 caused such a shift in the TPR profiles. In the present experiment, the nature of the apparent stabilization is not clear, but we can note that the presence of the two components in the reactant mixture increases the energy required for the reduction of the oxidized copper.

The high catalytic activity of the catalyst has been attributed to the synergy between the copper species and CeO_2 in the reduction–oxidation during the CO–O_2 reaction [27,28]. Reduced redox potentials of the copper species [20] and facile Cu^{2+}/Cu^{+} redox couple [29] in CeO_2 were deduced as the synergy effect, based on instrumental analysis. Thus an increase in the energy of reduction would result in the impediment of the redox cycles, which in turn reduces the reaction rate or increases the reaction temperature for a given conversion.

3.3. Deactivation

The catalyst showed a slow deactivation under reaction. Figure 4 shows the activity change with time on stream, a total of 700 h for a feed with 20% H_2O and 13.5% CO_2. The activity test was started with fresh catalyst (point A) and in 24 h the CO conversion decreased from 0.6 to 0.5. Activation with 10% oxygen at 300 °C for 3 h restored the CO conversion to 0.6 (point B) and in two days on stream the conversion continuously decreased to 0.48. Then the catalyst was treated with 50% hydrogen flow at 300 °C for 3 h to determine whether reducing conditions also activated the catalyst (point C). Restoration to the initial activity can be seen in the figure after this treatment. Following the activation with hydrogen, the activity experiment was continued for three weeks. Intermittent shutdown to replenish water to the water vapor saturator and some instability in the temperature control caused scatter in the results after about a week. During this period the CO conversion decreased from 0.6 to 0.33. Finally the catalyst was treated with an inert helium flow at 300 °C for 3 h, and again the activity was restored to the initial activity (point D). Restoration of the activity after the three different treatments indicates that a complete drying of the catalyst at a high temperature is sufficient for catalyst activation. Wang *et al.* [30] reported that accumulation of a carbonate-like species was observed during CO oxidation with Au/ZnO, and this species was implicated in the deactivation of the catalyst by covering the available active sites. In their experiments, calcination at 240 °C for 2 h removed the accumulated species and restored the activity. In view of this, the deactivation of CuO–CeO$_2$ during reaction is thought to be caused by the accumulation of a similar carbonate species, which can be easily removed by heating the catalyst.

If we define the deactivation function as $a(t) = X_{\mathrm{CO}}(t)/X_{\mathrm{CO}}(t=0)$, where X_{CO} is the CO conversion and t is the time (h) after activation, the data in figure 4 are well described by

$$a(t) = \frac{1}{1 + 0.032\sqrt{t}} \qquad (2)$$

which is shown by the solid curve in figure 4. Among various deactivation equations in the literature [31,32], the form has fitted the data best with only one fitting parameter, in the present case 0.032 $\mathrm{h}^{-1/2}$. It is unclear whether the deactivation equation can be applied to operating conditions other than those shown in figure 4, but, in the absence of information in the literature for the reaction with the catalyst, the equation is thought to provide useful estimates for the deactivation. For a case of different feed composition and catalyst, Avgouropoulos *et al.* [10] reported 49% CO conversion after a week-long deactivation starting from an initial conversion of 60%, while equation (2) predicted 42.4% CO conversion.

3.4. Complete clean-up of CO in a single stage

Current CO clean-up units consist of more than one reactor, typically two or three reactors. Dudfield *et al.* [4] showed experimentally that, for a feed of hydrogen mixture with 0.7% CO, single reactors packed with various catalysts could not reduce the CO concentration to less than 20 ppm. In the multistage reactor configuration, the first reactor receives the reformer effluent stream containing CO in the range 0.5–2% and reduces the CO content to 0.1% or less with oxygen excess, typically $\lambda = 2$–3. The second stage with additional oxygen then reduces the CO content to less than 10 ppm with higher λ, typically 3 or higher. The overall selectivity of the clean-up units is considerably less than 50%, in the range 20–33% [4,5,17]. Moreover instrumentation and control of a multistage reactor system is much more complicated than a single-stage reactor system. Here it is demonstrated that with the present catalyst the CO content can be reduced to less than 10 ppm in a single stage for a realistic feed with CO content of 1%. Figure 5 shows the exit CO concentration lower than 10 ppm in the temperature range 165–175 °C with $\lambda = 2$ in the feed. The high selectivity of the catalyst enabled this remarkable performance. The overall selectivity of the reactor was 50%, significantly higher than current CO clean-up systems with noble metal catalysts. Figure 6 shows the increasing CO exit concentration with increasing feed rate at a reactor temperature of 170 °C. Up to a feed flow rate of 80 ml/min, 200 mg of the catalyst reduced the CO content from 1% to less than 10 ppm. If we assume 800 l/h hydrogen for 1 kW, the required amount of catalyst would be around 67 g/kW, which can be favorably compared with 100 g/kW with a noble metal catalyst [4].

4. Conclusions

CuO–CeO$_2$ catalysts, prepared by coprecipitation, were very active and selective in the selective CO oxidation in hydrogen mixtures. Although the presence of H$_2$O and CO$_2$ increased the reaction temperature for a given conversion of CO, the catalyst retained a

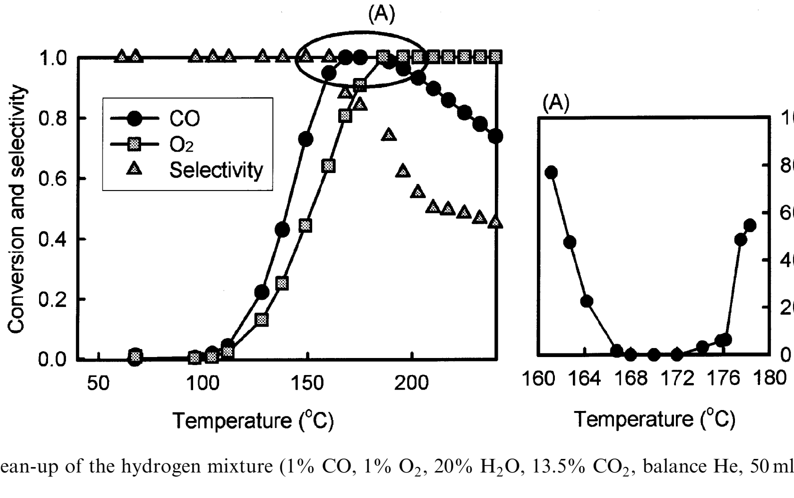

Figure 5. CO clean-up of the hydrogen mixture (1% CO, 1% O$_2$, 20% H$_2$O, 13.5% CO$_2$, balance He, 50 ml/min; Catalyst: 0.2 g).

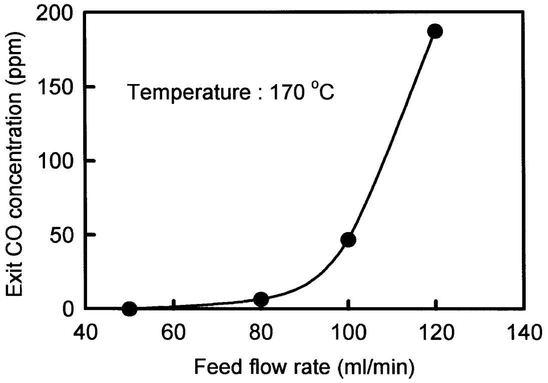

Figure 6. Variation of exit CO concentration with feed flow rate. Feed composition: 1% CO, 1% O_2, 20% H_2O, 13.5% CO_2, balance He, 50 ml/min; catalyst: 0.2 g.

remarkable selectivity in the CO oxidation, and at space velocities above 42 g h m^{-3} the catalyst completely oxidized CO to less than 10 ppm at 165–175 °C for a realistic simulated reformed gas of 1% CO, 1% O_2, 50% H_2, 20% H_2O, 13.5% CO_2 and balance He. The negative effects of H_2O and CO_2 on the reaction were to impede the redox steps in the catalysis by stabilizing oxidized copper species in the catalysts. The catalysts exhibited a slow, reversible deactivation with time on stream, but heating the catalysts to 300 °C, even under an inert flow, completely restored the activity. The catalyst shows a promising potential as an attractive alternative to the noble metal catalysts used in CO clean-up systems.

Acknowledgment

The authors are grateful for the financial support of the Kyungpook National University Research Fund, 2002.

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