

# Selective oxidation of carbon monoxide in hydrogen-rich stream over Cu-Ce/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts promoted with cobalt in a fuel processor for proton exchange membrane fuel cells

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## Abstract

Cu-Ce/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts promoted with cobalt are tested for the low-temperature selective oxidation of carbon monoxide (CO) in excess hydrogen, as produced by a fuel processor for proton exchange membrane fuel cells (PEMFCs). A small addition (0.2 wt.%) of Co to Cu-Ce/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> leads to a large increase in the activity for selective CO oxidation. When either CO<sub>2</sub> (13 vol.%) or H<sub>2</sub>O (10 vol.%) is present in the reformed gas feed, both Cu-Ce/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Cu-Ce-Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> show a decrease in CO oxidation activity at low temperatures, especially, under 200 °C. Compared with Cu-Ce/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, however, Cu-Ce-Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> gives higher resistance to CO<sub>2</sub> and H<sub>2</sub>O. There also exists a temperature window at 210–225 °C that corresponds to the conversion of 99.9% CO. From stability tests and temperature-programmed (TPD) desorption studies of CO<sub>2</sub>/H<sub>2</sub>O, it is concluded that the main cause for the decrease in catalytic activity with CO<sub>2</sub> and H<sub>2</sub>O in the feed is due to competitive adsorption of CO and CO<sub>2</sub> as well as to the blockage of the active sites by water vapor at low reaction temperatures.

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**Keywords:** Selective oxidation of carbon monoxide; Cu-Ce based catalyst; Effect of carbon dioxide and water; Cobalt dopant; Proton exchange membrane fuel cell; Fuel processor

## 1. Introduction

Various types of hydrocarbon fuel can be transformed into a hydrogen-rich fuel mixture, known as a 'reformat,' in a fuel processor. The fuel processor used to supply hydrogen to a proton exchange membrane fuel cell (PEMFC) for stationary distributed power purposes normally consists of several units: a desulfurizer, a catalytic steam reformer, and a two-stage water-gas shift (WGS) reactor. The gas at the outlet of the WGS reactor typically contains 53 vol.% H<sub>2</sub>, 13 vol.% CO<sub>2</sub>, 1.3 vol.% CH<sub>4</sub>, 0.5–1 vol.% carbon monoxide (CO), and 20–30 vol.% water [1]. The presence of more than 10 ppm (parts per million, ml/Nm<sup>3</sup>) of CO in the hydrogen-rich stream supplied to PEMFCs can lead to deterioration of the fuel cell via CO-induced poisoning of

the anode catalyst (Pt). Hence, it is important to keep the CO concentration below the permitted ppm level in the hydrogen stream. The available methods for CO removal are the use of a Pd or Pd-alloy membrane, methanation, and selective oxidation [2–5]. Of these methods, the selective oxidation of CO appears to be the most straightforward.

The most important requirements from a catalyst for the selective oxidation of CO are: (i) high CO oxidation activity at low temperatures; (ii) good selectivity with respect to the undesired oxidation of H<sub>2</sub>; (iii) a wide temperature window for a greater than 99% conversion of CO; (iv) tolerance towards the presence of CO<sub>2</sub> and H<sub>2</sub>O in the feed.

To date, most of the proposed catalysts are alumina-supported, platinum group metals (Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, Rh/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, and Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) [6–11], zeolite-supported platinum catalysts (Pt/A-zeolite [12] and Pt/mordenite [13]), or gold-based catalysts (Au/MnO<sub>x</sub> [14] and Au/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> [15]). The precious metals (Pt, Rh, Ru, Au, etc.) have an advantage of good activity for CO oxidation. On the other hand, these metals have the disadvantage of high cost, limited availability, decrease of selectivity at high temperature, and

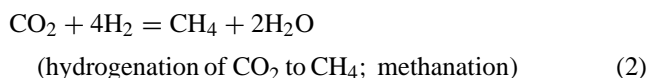
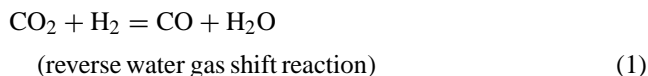
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the requirement for two-stage reactors to reduce CO levels to below 10 ppm. Since outlet gases from the water-gas shift reactor contain about 1% CO, a conversion of above 99.9% is required to reduce the CO concentration to several ppm in a single-stage reactor. These reasons have led to research being directed towards a low-cost catalyst that contains transition metals with good activities and selectivities [16–20]. Liu and Flytzani-Stefanopoulos [18,19] have reported that CuO-CeO<sub>2</sub> catalysts are very active for complete CO oxidation and exhibit good specific activity, i.e., several orders of magnitude higher than that of conventional Cu-based catalysts and comparable or superior to Pt-based catalysts. Kim and Cha [20] have reported that a 8 wt.% CuO-CeO<sub>2</sub> catalysts gave the highest CO conversion (>99%) and selectivity (50–90%) under experimental conditions ( $\lambda = 2$ ; 1 vol.% CO; 120–190 °C). It is well known that ceria as an oxygen-conducting oxide has unique properties as a thermally and chemically stable material with high capacity to store and release oxygen. It is usually employed in combination with other metal oxides or noble metals deposited on to thermally stable supports. This means that it may function as a structural/electronic promoter, but not act as a true active component with high redox properties and oxygen mobility. Hence, ceria can enhance the catalytic activity of CuO for complete oxidation due to the easy generation of oxygen vacancies to form interfacial active centers between the two metals. Also, cobalt oxides show very high activity for CO oxidation in CO/O<sub>2</sub> mixtures, even at ambient temperatures. For 50% conversion, a temperature ( $T_{50}$ ) of –54 °C has been reported for pure Co<sub>3</sub>O<sub>4</sub> [21] and –63 °C for Co<sub>3</sub>O<sub>4</sub> supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> [22]. Thus cobalt oxides may be possible dopants to enhance the activity of Cu-Ce based catalysts at low temperatures. In actual applications, however, selective oxidation catalysts are normally prepared by impregnating the active component on to a porous support such as  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

Also, it is found that the presence of CO<sub>2</sub> and H<sub>2</sub>O in the reformed gas may exert different effects on the performance of the catalyst. With a 2 wt.% Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst [23], for example, the presence of water in the feed dramatically enhances the CO oxidation reaction over the temperature range of 110–190 °C where the water vapor reduces the activation energy for CO oxidation to about 37 kJ compared with 74 kJ in the absence of water vapor. By contrast, it has been found that the presence of CO<sub>2</sub> in the feed decreases both CO oxidation reaction rate and oxygen consumption. This may be attributed to the fact that carbonates are formed over reducible metal oxide supports, and that these prevent the participation of support oxygen in the CO oxidation reaction [24]. Also, there may be a possibility that the interface between alumina and platinum crystallites containing mobile oxygen is blocked by CO<sub>2</sub> adsorption on the same sites [25]. When both CO<sub>2</sub> and H<sub>2</sub>O are present in the reactant feed, it is found that the rate of CO oxidation increases and that the maximum CO conversion temperature shifts down from 170 to 150 °C. This suggests that the positive effect of wa-

ter is more dominant than the negative effect of CO<sub>2</sub> in the feed.

For carbon-supported Ru and Pt catalysts [26], although a Ru/C catalyst is more active than a Pt/C catalyst in the absence of CO<sub>2</sub> and H<sub>2</sub>O in the reactant feed at low temperatures, the catalytic activities of both catalysts are observed to be decreased in the presence of CO<sub>2</sub> and H<sub>2</sub>O. In the case of Ru/C catalyst, the catalytic activity is decreased by CO<sub>2</sub> due to the enhancement of both the following reverse water-gas shift reaction and methanation, i.e.,



With the Pt/C catalyst, only the reverse water-gas shift reaction proceeds, and increases the CO concentration.

Also, the above mentioned increase in CO concentration in the presence of H<sub>2</sub>O with both catalysts may be linked to the blockage of catalyst active sites by adsorbed water, as well as to the formation of CO–H<sub>2</sub>O surface complexes which are less active than the adsorbed CO [26].

Research into finding alternative catalysts to those based on high-cost precious metals has focused on transition metals such as Cu-Ce based catalysts and has aimed to overcome the disadvantage of decreases in catalytic activity and selectivity in the presence of CO<sub>2</sub> and H<sub>2</sub>O in the reactant feed.

The first stage of the study reported here determine both the optimum metal ratio and loading content on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> to maximize the catalytic activities for complete CO oxidation. Second, the enhancement effects of Co as a dopant to Ce-Ce/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> on selective CO oxidation are investigated. Third, the effects of CO<sub>2</sub> and H<sub>2</sub>O on the catalyst activity, O<sub>2</sub> consumption, and selective oxidation of CO are examined. Also, the results of characterization by CO<sub>2</sub>/H<sub>2</sub>O-temperature-programmed desorption (TPD) are presented.

## 2. Experimental

### 2.1. Catalysts

Cu-Ce/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts were prepared by the excess impregnation method. Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O (Junsei), Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (Aldrich) were used as metal precursors and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (Aldrich) as a support. A known amount of each metal salt was dissolved in de-ionized water in the presence of the dispersed support. The resulting mixture was evaporated in a rotary vacuum evaporator at 60 °C, followed by drying at 110 °C for 12 h and then calcination at 500 °C for 4 h in air. After calcination, the catalyst

was ground and sieved to obtain a 100–120 mesh powder. Also, to examine the promotional effect of including a small amount of Co ( $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , Junsei), the metal precursors were added simultaneously and the catalyst was prepared by the same procedure.

## 2.2. Activity

Catalytic tests were carried out in a conventional flow, micro fixed-bed reactor at atmospheric pressure. The reactor was pyrex tube (inner diameter, 4 mm; outer diameter, 6 mm) housed in an IR-furnace. A 100 mg of catalyst, diluted with 150 mg  $\gamma\text{-Al}_2\text{O}_3$  (in the form of a powder with a particle size in the region  $120 \mu\text{m} < d_p < 150 \mu\text{m}$ , Aldrich) in order to dissipate the reaction heat and to keep the catalyst bed isothermal, was used for each run and was examined in the temperature range of 100–300 °C. The feed gas was passed downward through the reactor that contained the catalyst bed, and its composition and flow rate were adjusted with electronic mass flow controllers (Alicat scientific). The total flow rate of the reaction mixture was equal to 100 ml/min. The reactant gas mixture consisted of 1 vol.%  $\text{CO}$ , 1 vol.%  $\text{O}_2$ , and 60 vol.%  $\text{H}_2$ , with  $\text{N}_2$  as the balance. The effect of  $\text{CO}_2$  was examined by adding 13 vol.%  $\text{CO}_2$  to the feed gases. Also, the effect of  $\text{H}_2\text{O}$  was investigated by the addition of 10 vol.%  $\text{H}_2\text{O}$  to the feed with a syringe pump (Cole-Parmer. 74900 S) with heating of the gas lines leading to the reactor to 100 °C in order to avoid condensation. The excess oxygen with respect to the minimum amount of oxygen required for  $\text{CO}$  oxidation to  $\text{CO}_2$  (in the absence of side reactions) was characterized by the stoichiometric parameter  $\lambda$  ( $=2[\text{O}_2]/[\text{CO}]$ ). Unless specifically noted, an excess of oxygen was used for the selective  $\text{CO}$  oxidation experiments ( $\lambda = 2$ ).

Product and reactant analyses were performed with a gas chromatograph (HP 6890N) equipped with a TCD detector, a methanizer, and a FID detector using 8%  $\text{H}_2/\text{He}$  as carrier gas. A HP-Molesiv column was used to separate  $\text{H}_2$ ,  $\text{O}_2$ , and  $\text{N}_2$  at the TCD detector. For the quantitative analysis of very small amounts of  $\text{CO}$ , methanation of  $\text{CO}$  was carried out by a Ni catalyst before passage to the FID detector. A Carboxen<sup>TM</sup> 1006 PLOT column was used to separate  $\text{CO}$ ,  $\text{CO}_2$ , and  $\text{CH}_4$  at the FID detector, but methane formation was not detected.

The conversion of  $\text{CO}$  ( $X_{\text{CO}}$ ) and consumption of  $\text{O}_2$  ( $X_{\text{O}_2}$ ) as well as the selectivity of  $\text{CO}$  oxidation ( $S_{\text{CO}}$ ) in excess hydrogen were calculated as follows:

$$X_{\text{CO}}(\%) = \frac{[\text{CO}]_{\text{in}} - [\text{CO}]_{\text{out}}}{[\text{CO}]_{\text{in}}} \times 100 \quad (3)$$

$$X_{\text{O}_2}(\%) = \frac{[\text{O}_2]_{\text{in}} - [\text{O}_2]_{\text{out}}}{[\text{O}_2]_{\text{in}}} \times 100 \quad (4)$$

$$S_{\text{CO}}(\%) = \frac{0.5[\text{CO}]_{\text{in}} - [\text{CO}]_{\text{out}}}{[\text{O}_2]_{\text{in}} - [\text{O}_2]_{\text{out}}} \times 100 \quad (5)$$

## 2.3. Temperature-programmed desorption ( $\text{CO}_2/\text{H}_2\text{O}$ -TPD)

Temperature-programmed desorption of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  was performed with a conventional temperature programming system (Autochem 2910, Micromeritics) equipped with a TCD for analysis. The catalyst sample (0.1 g) was pretreated in helium (99.999%) at 500 °C for 1 h. After cooling to room temperature in helium (99.999%), either  $\text{CO}_2$  or  $\text{H}_2\text{O}$  adsorption was conducted at 30 °C for 1 h. Following the adsorption of each gas, the He flow (30 ml/min) was maintained for 1 h to remove the physisorbed fraction of  $\text{CO}_2$  or  $\text{H}_2\text{O}$ . The temperature was increased at a rate of 20 °C/min from room temperature to 500 °C.

## 3. Results and discussion

### 3.1. Effect of Cu-Ce composition on selective $\text{CO}$ oxidation activity

In earlier work, it has been shown that a Cu/(Cu + Ce) atomic ratio of 2:8 [20] or 1.5:8.5 [27], prepared by coprecipitation, gave the best results for selective  $\text{CO}$  oxidation. In actual applications, however, selective oxidation catalysts are normally prepared by impregnating the active component on to a porous support such as  $\gamma\text{-Al}_2\text{O}_3$ , and thus it is necessary to determine the optimum metal content and weight ratio experimentally when these active metals are deposited on  $\gamma\text{-Al}_2\text{O}_3$ .

The effect of different Cu loadings on selective  $\text{CO}$  oxidation using synthetic reformat gas (1%  $\text{CO}$ , 1%  $\text{O}_2$ , 60%  $\text{H}_2$ , and  $\text{N}_2$  as balance) while maintaining a total metal content of 10 wt.% is shown in Table 1. For a metal loading of Cu-Ce (1:9 wt.%)/ $\gamma\text{-Al}_2\text{O}_3$ , the maximum  $\text{CO}$  conversion obtained is 93.5% at 250 °C. And for a metal loading of Cu-Ce (2:8 wt.%)/ $\gamma\text{-Al}_2\text{O}_3$ , it is 94.6% at 200 °C. Further increase in Cu content above 2 wt.% showed a decreasing trend in catalytic activity. This indicates that the maximum activity is obtained with a Cu:Ce weight ratio of 2:8 (i.e., atomic ratio of 3.5:6.5), which is somewhat higher than that of the unsupported catalysts.

The activity and selectivity changes with different metal loadings (10–25 wt.%) on to  $\gamma\text{-Al}_2\text{O}_3$ , where the Cu/(Cu + Ce) weight ratio is kept at a constant value of 0.2 are presented in Fig. 1. The data show that as the

Table 1  
Activity and temperature window for  $T_{>90}$  depending on Cu:Ce weight ratio

Catalyst	Maximum CO conversion (%)	Window for $T_{>90}$ (°C)
Cu-Ce [1:9 wt.%]/ $\gamma\text{-Al}_2\text{O}_3$	93.5 (at 250 °C)	220–260
Cu-Ce [2:8 wt.%]/ $\gamma\text{-Al}_2\text{O}_3$	94.6 (at 200 °C)	185–230
Cu-Ce [4:6 wt.%]/ $\gamma\text{-Al}_2\text{O}_3$	92.8 (at 200 °C)	190–210
Cu-Ce [8:2 wt.%]/ $\gamma\text{-Al}_2\text{O}_3$	53.5 (at 200 °C)	–

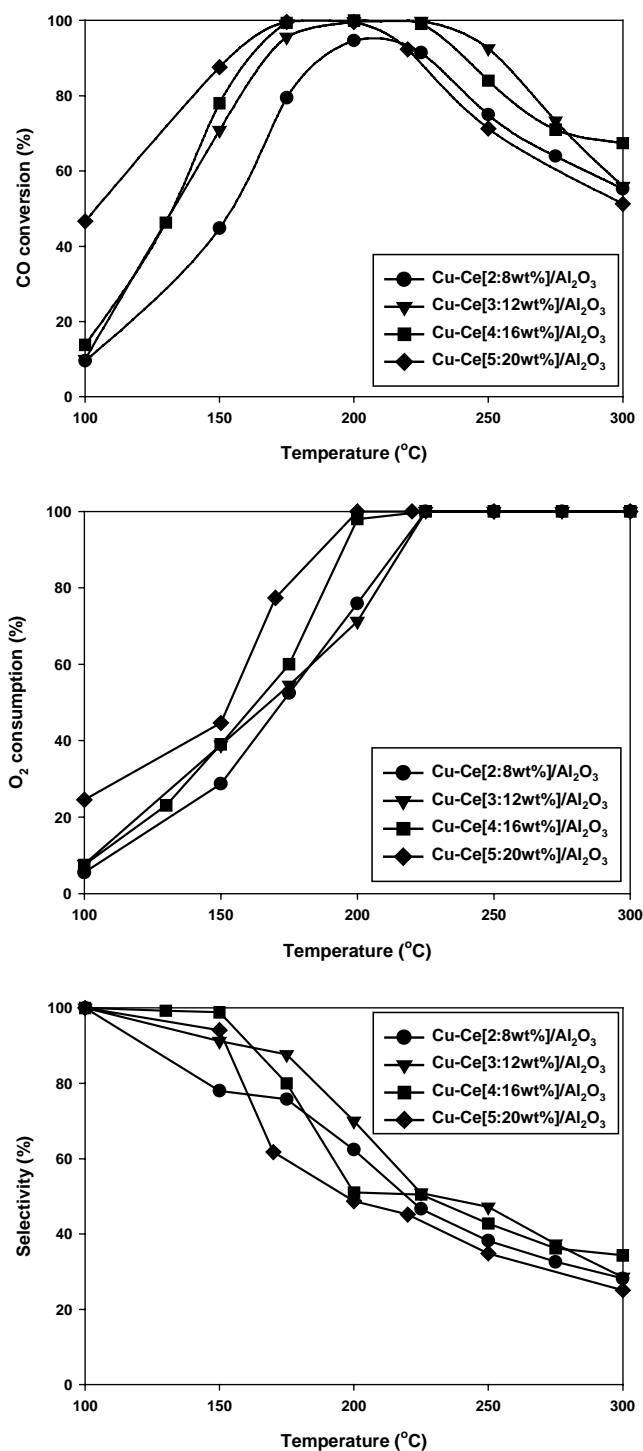


Fig. 1. Effect of amount of catalysts loaded over  $\gamma$ - $\text{Al}_2\text{O}_3$  on CO conversion,  $\text{O}_2$  consumption and selectivity. Reaction conditions: 1% CO, 1%  $\text{O}_2$ , 60%  $\text{H}_2$ , and balance  $\text{N}_2$ . Flow rate, 100 ml/min; GHSV, 60,000  $\text{h}^{-1}$ .

Cu-Ce loading increases, the CO conversion also increases. Actually, the temperature for 50% conversion is decreased from 160 to 100 °C, which reveals a significant increase in low-temperature activity below 200 °C. Apparently, this may be attributed to the fact that CO adsorption at low temperatures is likely to increase with increase in metal

loading. Although Cu-Ce (25 wt.%) shows the best characteristics at low temperatures, the temperature window for 99% conversion ( $T_{99}$ ) is very narrow (about 175–200 °C) compared with Cu-Ce (20 wt.%) with  $T_{99}$  at 175–220 °C and selectivities that range from 80 to 50%. In actual use as a selective oxidation catalyst, the window for  $T_{99}$  can be an important parameter in determining the effectiveness of the catalysts. For this reason, the Cu-Ce (4:16 wt.%) /  $\gamma$ - $\text{Al}_2\text{O}_3$  (hereinafter referred to as the CuCe/A catalyst) was selected as a reference for comparison purposes.

### 3.2. Effect of cobalt doping

To enhance the activity of the CuCe/A catalyst, the promotional effect of some of 3d-group transition metals (Co, Fe, Mn, Ni, and Zn) was investigated by adding small amounts (0.5 wt.%) of each metal to the reference catalyst. Although not shown in this study, it is demonstrated that cobalt-doped CuCe/A appears to be the most active and selective for CO oxidation. The effects of Co doping amount (namely 0, 0.2, 0.5 wt.%) as a secondary promoter on the selective oxidation of CO to  $\text{CO}_2$ ,  $\text{O}_2$  consumption and selectivity of  $\text{O}_2$  to CO oxidation as a function of temperature are shown in Fig. 2. A small addition of cobalt leads to a large increase in activity, and the extent of this promotion is higher for 0.2 wt.%; CO than for 0.5 wt.%. Little hydrogen is oxidized at temperatures below 150 °C, which indicates that the selectivity is nearly constant at 100%. Further increase to higher reaction temperatures results in a progressive decrease in selectivity from 100% at 150 °C to 50% at 210 °C. The  $\text{O}_2$  consumption simply increases with reaction temperature and is 100% at temperatures higher than 210 °C on all of the catalysts. These results suggest that although competitive oxidation of CO and  $\text{H}_2$  occurs in this temperature region, CO is more selectively oxidized and is bound in a preferentially higher concentration on the catalyst surface than  $\text{H}_2$ . For low reaction temperatures (<150 °C), where selectivity is higher than 90% for all samples, the catalytic activity is in the order: Cu-Ce-Co (4:15.8:0.2 wt.%) /  $\gamma$ - $\text{Al}_2\text{O}_3$  (hereinafter referred to as CuCeCo0.2/A catalyst) > Cu-Ce-Co (3.9:15.6:0.5 wt.%) /  $\gamma$ - $\text{Al}_2\text{O}_3$  (hereinafter referred to as CuCeCo0.5/A catalyst) > CuCe/A (as a reference catalyst) and the temperature where 50% conversion of CO is attained at 110, 125, and 138 °C, respectively, and the temperature window for 99% conversion is 150–220, 170–210, and 175–220 °C, respectively.

### 3.3. Effect of stoichiometric ratio ( $\lambda = 2\text{O}_2/\text{CO}$ )

Generally, the catalytic activity for CO conversion increases with the  $\text{O}_2$ :CO molar ratio. It is very important, however, to keep the  $\text{O}_2$ :CO ratio as low as possible to improve the fuel-processing efficiency. This means that there should be an adequate  $\text{O}_2$ :CO ratio for maximizing CO conversion. For example, at  $\lambda = 1$  (stoichiometric), the presence of CO may lead to blockage of active sites by CO

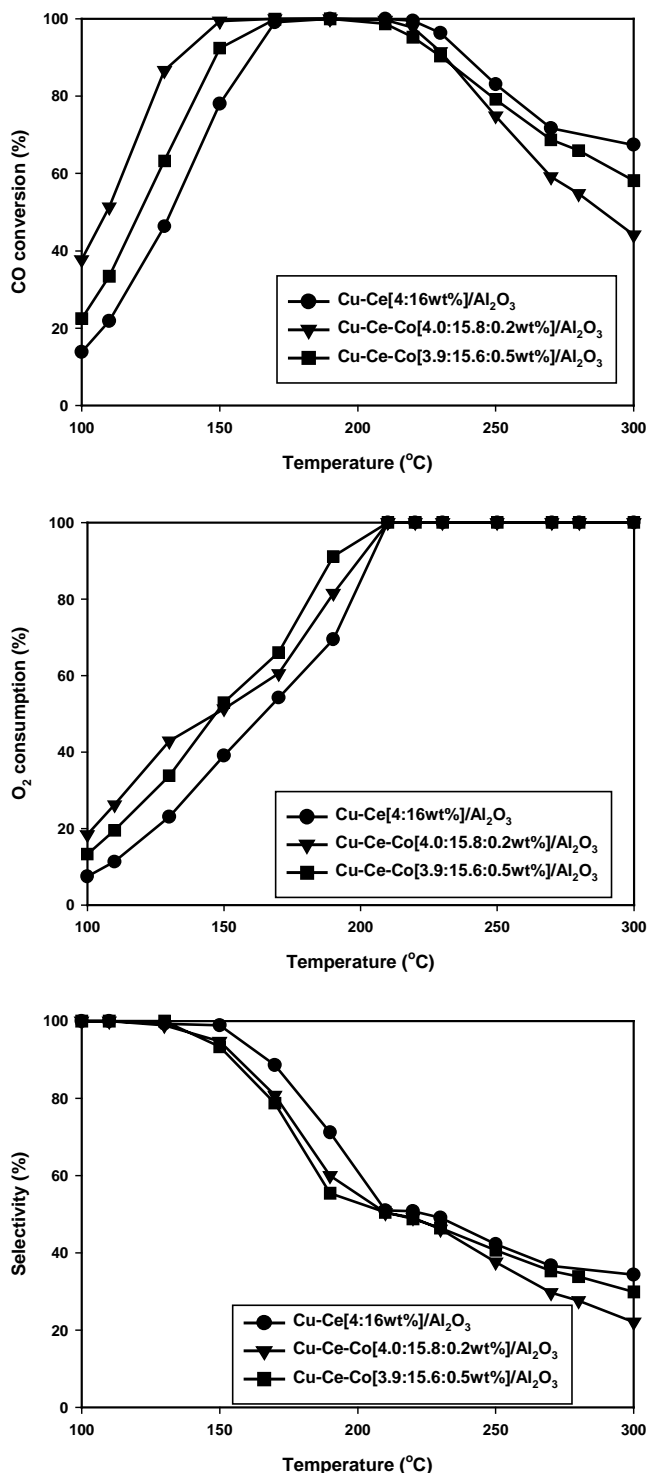


Fig. 2. Effect of Co addition to Cu-Ce catalyst on CO conversion,  $O_2$  consumption and selectivity. Reaction conditions: 1% CO, 1%  $O_2$ , 60%  $H_2$ , and balance  $N_2$ . Flow rate, 100 ml/min; GHSV, 60,000  $h^{-1}$ .

due to preferential binding, which decreases the adsorption probability of oxygen and lowers the CO conversion. The effect of stoichiometric ratio ( $\lambda = 2O_2/CO$ ) on the selective CO oxidation over the CuCeCo0.2/A catalyst is shown in Fig. 3. It is seen that CO conversion increases with in-

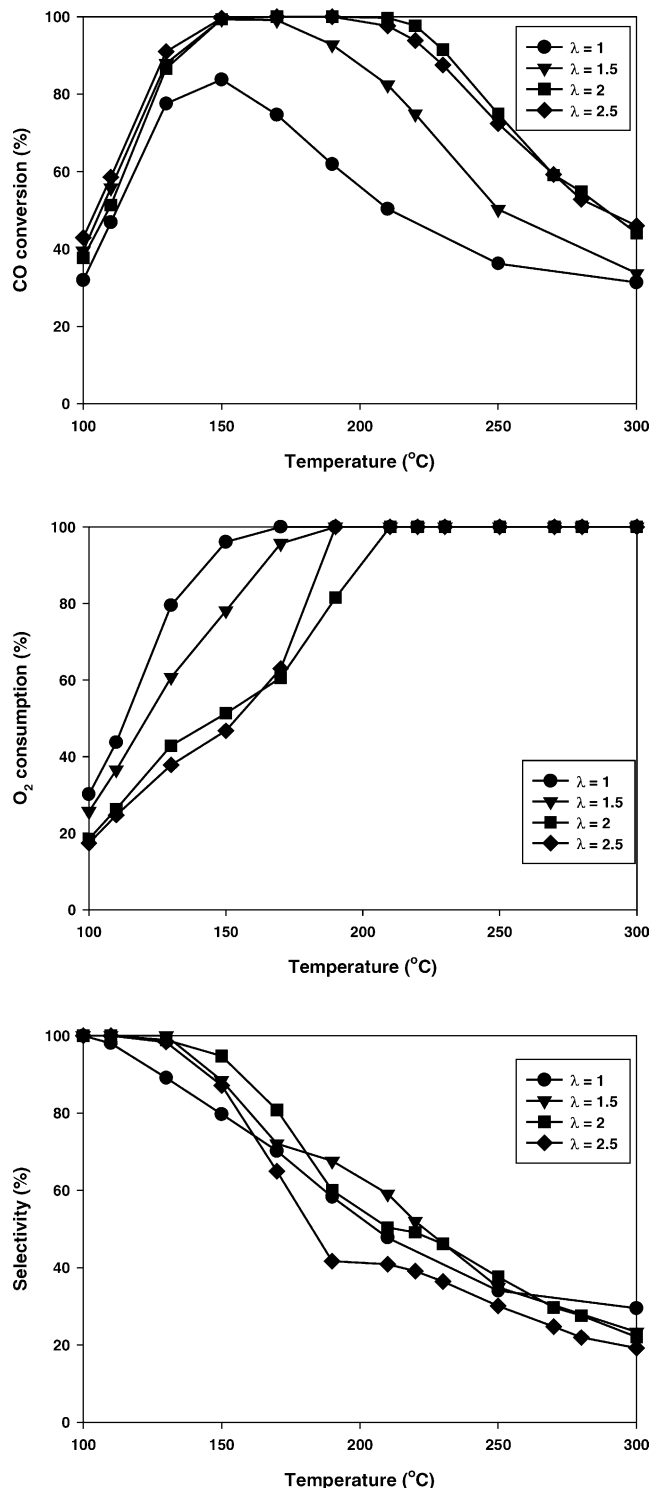


Fig. 3. Change in CO conversion,  $O_2$  consumption and selectivity with  $\lambda$  for reaction over Cu-Ce-Co (4.0:15.8:0.2 wt.%) catalyst. Reaction conditions: 1% CO, 0.5–1.25%  $O_2$ , 60%  $H_2$ , and  $N_2$  as balance. Flow rate, 100 ml/min; GHSV, 60,000  $h^{-1}$ .

creasing oxygen concentration. For  $\lambda = 1$ , the maximum CO conversion attainable is about 80% at 150 °C. Increase in  $O_2$  concentration to  $\lambda = 1.5$  increases the peak conversion to above 99% at the same temperature. Increasing the

O<sub>2</sub> concentration to twice the stoichiometric ratio ( $\lambda = 2$ ) gives a peak conversion of 99% at a temperature window between 150 and 220 °C. Further increase in O<sub>2</sub> concentration to  $\lambda = 2.5$  shows little change in the temperature window for 99% conversion and only a selectivity decreases of about 10% compared with  $\lambda = 2$ .

### 3.4. Effect of CO<sub>2</sub> on selective CO oxidation

The temperature dependency for selective CO oxidation over the reference catalyst (CuCe/A) and CuCeCo0.2/A catalyst with or without 13 vol.% CO<sub>2</sub> in the reactant feed is presented in Fig. 4. The presence of CO<sub>2</sub> in the reactant feed provokes a significant decrease in the performance of both catalysts. This may be due to competitive adsorption of CO and CO<sub>2</sub> on the catalyst surface [26], and to carbonate formation over reducible metal oxides [23,24] that prevents the participation of support oxygen in CO oxidation. The temperature at which 50% CO conversion is attained ( $T_{50}$ ) is shifted to a higher temperature by about 10 and 35 °C for CuCe/A and CuCeCo0.2/A catalysts, respectively. At low temperatures, especially under 150 °C, it is seen that the catalytic activity in the presence of CO<sub>2</sub> for CuCe/A and CuCeCo0.2/A catalysts is decreased by about 20 and 40% respectively, and the O<sub>2</sub> consumption also shows a decrease of about 10 and 20%, respectively. Apparently, the effect of CO<sub>2</sub> on the selectivity exhibits different behavior. With the CuCe/A catalyst, the selectivity remains nearly unchanged with temperature, either with or without CO<sub>2</sub> in the feed. Meanwhile, for the CuCeCo0.2/A catalyst, the selectivity is enhanced by the presence of CO<sub>2</sub>, which suggests that Co can modify the selectivity of CuCe/A for the effective use of oxygen. For actual use as a selective CO oxidation catalyst, temperature windows at which 99% CO conversion occurs are very important to keep the CO outlet concentration as low as possible. With the CuCe/A catalyst, addition of CO<sub>2</sub> shifts the onset of  $T_{99}$  to higher temperature by 15 °C and the window for  $T_{99}$  is decreased by 20 °C to 190–215 °C. Over the CuCeCo0.2/A catalyst, the onset of  $T_{99}$  shifts to a higher temperature by 40 °C and the window for  $T_{99}$  is narrowed by 30 °C to 190–230 °C. A negative effect of CO<sub>2</sub> on the selectivity for the same conversion is observed for both catalysts. For example, with the CuCe/A catalyst, at  $T_{99}$  the presence of CO<sub>2</sub> decreases the selectivity from 85% (175 °C) to 70% (190 °C). The CuCeCo0.2/A catalyst also exhibits a selectivity decrease from 94% (150 °C) to 83% (190 °C). Nevertheless, it is seen that the selectivity of CuCeCo0.2/A catalyst is higher than that of the CuCe/A catalyst in the presence of CO<sub>2</sub> which indicates that Co can promote oxygen transfer for selective CO oxidation.

In addition, it is observed that CO conversion decreases sharply at higher temperature (>250 °C). This may be due to the fact that there may be reverse water-gas shift reaction that leads to the formation of CO by reacting CO<sub>2</sub> with H<sub>2</sub>. The reasons for this are discussed below.

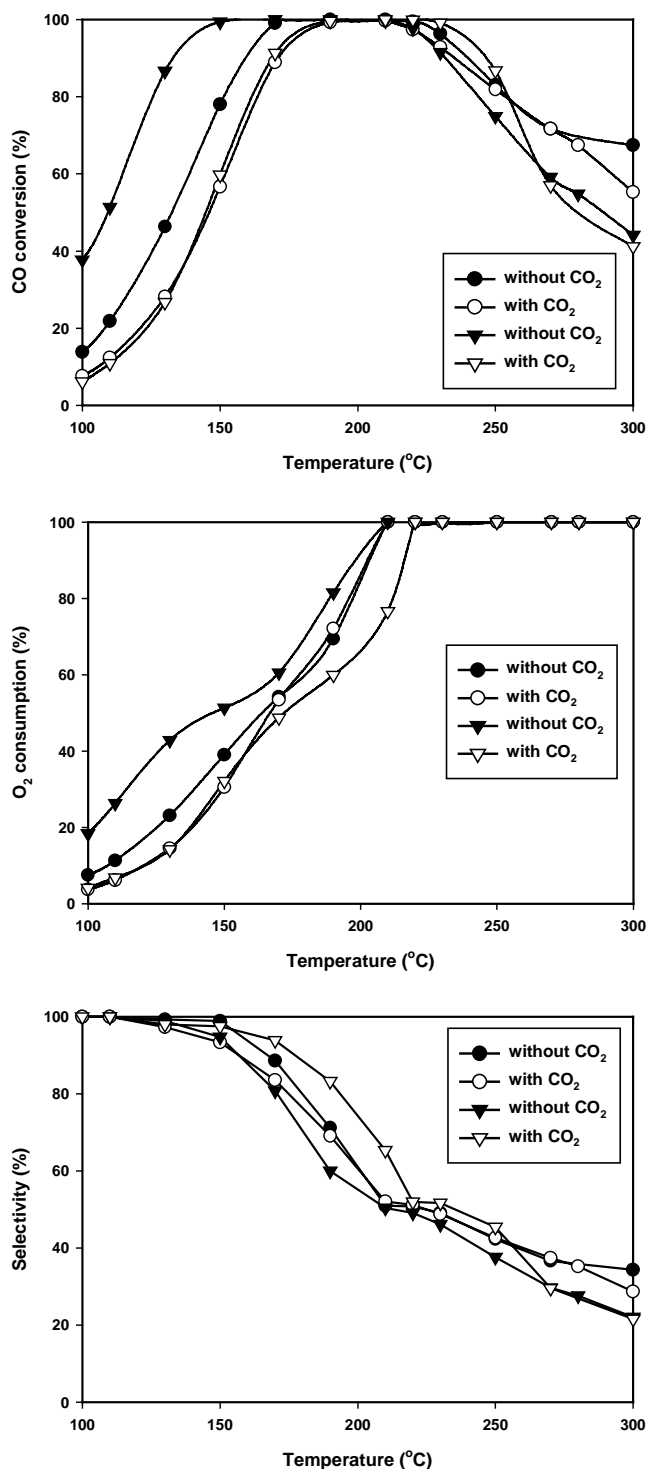


Fig. 4. Change in CO conversion, O<sub>2</sub> consumption and selectivity with reaction temperature for selective oxidation of CO over CuCe/A (circle) and CuCeCo0.2/A (triangle down) catalyst. Solid and open symbols denote, respectively, absence and presence of 13 vol.% CO<sub>2</sub> in reactant feed. Reaction conditions: 1% CO, 1% O<sub>2</sub>, 60% H<sub>2</sub>, and balance N<sub>2</sub>. Flow rate, 100 ml/min; GHSV, 60,000 h<sup>-1</sup>.

### 3.5. Effect of H<sub>2</sub>O on the selective CO oxidation

The results obtained for selective CO oxidation over the CuCe/A and CuCeCo0.2/A catalysts, with or without 10 vol.% H<sub>2</sub>O in the reactant feed, are given in Fig. 5. Addition of H<sub>2</sub>O to the hydrogen-rich feed stream decreases the catalytic activity for selective CO oxidation and the temperature at which 50% conversion of CO is obtained,  $T_{50}$ , shifts to a higher temperature by 15 and 40 °C for CuCe/A and CuCeCo0.2/A, respectively. At low temperatures (<190 °C), it is found that the catalytic activity decreases markedly. It is assumed that the decrease of CO conversion over Cu-Ce based catalysts in the presence of water vapor may be attributed to blockage of catalytic active sites by adsorbed water, as well as to the formation of CO–H<sub>2</sub>O surface complexes [26], which are less active than adsorbed CO. Compared with deactivation by CO<sub>2</sub>, however, it is seen that the degree of deactivation by water vapor for the CuCe/A is greater than that for the CuCeCo0.2/A catalyst. That is, CO conversion in the presence of CO<sub>2</sub> is nearly the same for CuCe/A and CuCeCo0.2/A catalysts, but CO conversion in the presence of H<sub>2</sub>O with the CuCe/A catalyst at a given temperature is lower than that with the CuCeCo0.2/A catalyst. This means that the presence of water vapor in the reactant feed has a higher negative effect with the CuCe/A catalyst.

Comparing the effect of H<sub>2</sub>O on O<sub>2</sub> consumption and selectivity at the same reaction temperature for both CuCe/A and CuCeCo0.2/A catalysts, it is seen that the selectivity increases while O<sub>2</sub> consumption decreases. Actually, both O<sub>2</sub> consumption and selectivity are largely dependent on CO conversion, and a decrease in CO conversion leads to decrease in O<sub>2</sub> consumption and an increase in selectivity. Therefore, careful analysis of the results based on the same reference conversion should be done to interpret correctly the changes in O<sub>2</sub> consumption and selectivity with H<sub>2</sub>O in the feed.

For the CuCe/A catalyst with or without H<sub>2</sub>O, the O<sub>2</sub> consumption is 50 and 48%, respectively, and the selectivity is nearly the same, viz., 92%, at the temperature where 90% of CO conversion is reached (i.e.,  $T_{90}$ ). Meanwhile, for the CuCeCo0.2/A catalyst, the O<sub>2</sub> consumption is 50 and 43% and the selectivity is 85 and 99% at  $T_{90}$ , respectively. Compared with the absence of H<sub>2</sub>O, it is found that the O<sub>2</sub> consumption increases, while selectivity decreases. These results indicate that the presence of H<sub>2</sub>O in the feed has a larger negative effect on the CuCeCo0.2/A catalyst than on the CuCe/A catalyst. The presence of H<sub>2</sub>O in the feed has a detrimental effect on both CuCe/A and CuCeCo0.2/A catalysts in that it leads to higher  $T_{99}$  and also the range of  $T_{99}$  is narrowed. For the CuCe/A catalyst, the  $T_{99}$  shifts to a higher temperature by 25 °C in the presence of H<sub>2</sub>O and the temperature window decreases by 10 °C to 200–235 °C. With the CuCeCo0.2/A catalyst, the  $T_{99}$  shifts to higher temperature by 35 °C and the  $T_{99}$  window decreases by 25 °C to 185–230 °C in comparison with the absence of H<sub>2</sub>O in the

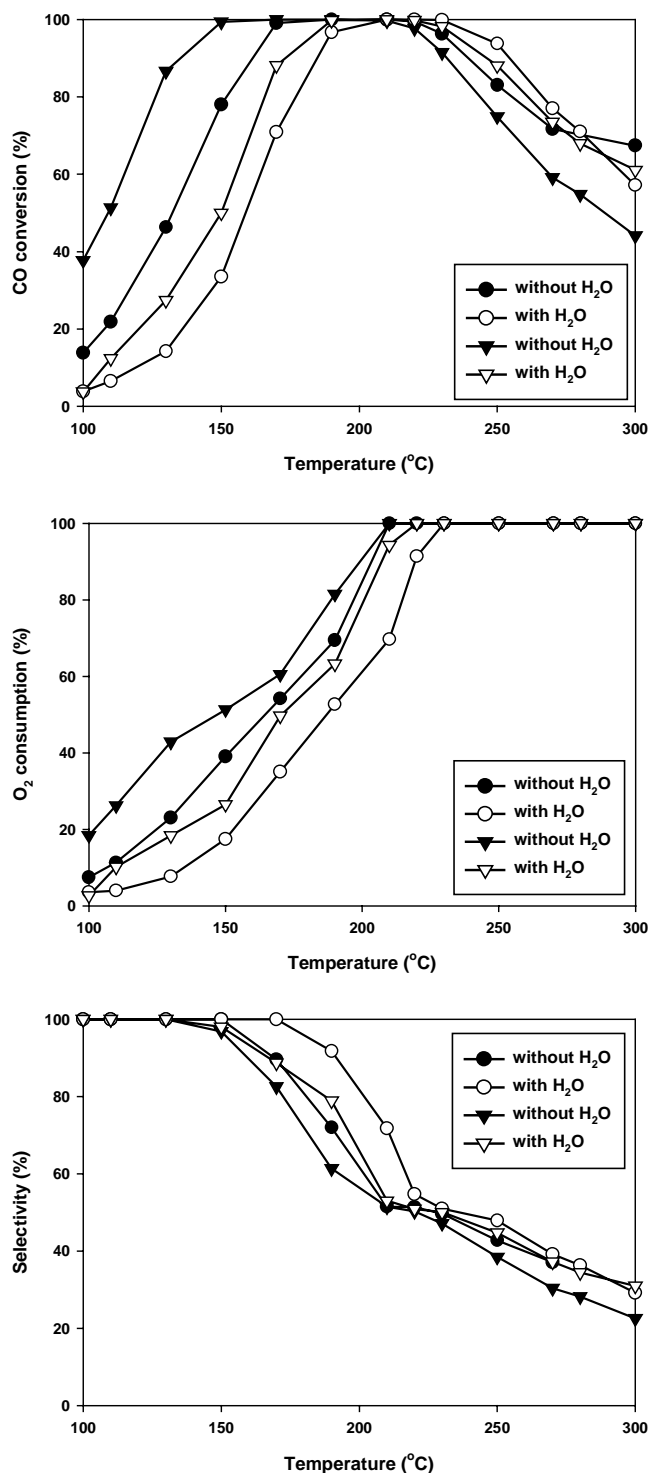


Fig. 5. Change in CO conversion, O<sub>2</sub> consumption and selectivity with reaction temperature for selective oxidation of CO over CuCe/A (circle) and CuCeCo0.2/A (triangle down) catalyst. Solid and open symbols denote, respectively, absence and presence of 10 vol.% H<sub>2</sub>O in reactant feed. Reaction conditions: 1% CO, 1% O<sub>2</sub>, 60% H<sub>2</sub>, and balance N<sub>2</sub>. Flow rate, 100 ml/min; GHSV, 60,000 h<sup>-1</sup>.

feed. That is, the CuCeCo0.2/A catalyst shows both a lower start temperature of  $T_{99}$  and wide temperature window compared with the CuCe/A catalyst.

In the presence of  $H_2O$ , the selectivity and  $T_{99}$  windows for both CuCe/A and CuCeCo0.2/A catalysts are 71 and 51% at 200–215 °C, and 78 and 50% at 185–230 °C, respectively.

### 3.6. Effect of both $H_2O$ and $CO_2$ on selective CO oxidation

A comparison of the experimental results obtained for the selective CO oxidation with the CuCe/A and CuCeCo0.2/A catalysts in the presence of both 10 vol.%  $H_2O$  and 13 vol.%  $CO_2$  in the reactant feed is shown in Fig. 6. Although each compound retards the CO oxidation activity, the combination of  $CO_2$  and water together gives a more significant decrease in CO conversion and selectivity with reaction temperature. As seen from the temperature at which 99% conversion of CO is obtained, it is obvious that when both  $CO_2$  and  $H_2O$  are present in the feed, the catalysts are much less active. For the CuCe/A catalyst, the onset temperature ( $T_{99}$ ) shifts to a higher temperature by 35 °C and the window for  $T_{99}$  decreases by 20 °C to 210–230 °C in the presence of both  $H_2O$  and  $CO_2$ . With the CuCeCo0.2/A catalyst,  $T_{99}$  shifts to a higher temperature by 55 °C and the  $T_{99}$  window decreases by 45 °C to 205–230 °C. Consequently, it can be said that the presence of either  $CO_2$  or  $H_2O$  may lead to a temperature increase for  $T_{99}$  and also narrows the range of the  $T_{99}$  window relative to the absence of these compounds in the feed.

The temperature windows for  $T_{99}$  and  $T_{99.9}$  over the CuCe/A and CuCeCo0.2/A catalysts with or without  $CO_2$  and  $H_2O$  are summarized in Table 2. As shown, the presence of both  $CO_2$  and  $H_2O$  provokes a larger decrease in both CO conversion and the range of the  $T_{99}$  window. In the presence of both  $CO_2$  and  $H_2O$ , however the results are quite similar for both CO conversion and the range of  $T_{99}$  windows compared with the presence of each component,  $CO_2$  or  $H_2O$ , alone. In particular, the window for  $T_{99.9}$  can serve as a guide for the oxidation of CO to reduce the CO concentration in the reformat gases from 1% down to the 10 ppm level in a single stage reactor.

In the presence of either  $CO_2$  or  $H_2O$  or  $CO_2$  and  $H_2O$ , both CuCe/A and CuCeCo0.2/A catalysts give a very markedly different  $T_{99.9}$  window. The CuCe/A catalyst exhibits its best catalytic activity in  $T_{99}$  window of 210–230 °C (selectivity, 75–50%) but does not show a  $T_{99.9}$  window. By contrast, the CuCeCo0.2/A catalyst gives the highest activity in the  $T_{99}$  window of 205–230 °C (selectivity, 80–50%) and exhibits a  $T_{99.9}$  window of 210–225 °C. Therefore, it can be said that the increase of CO conversion is due to the small addition of Co (0.2 wt.%) which is known for its higher oxidation activity at low temperatures.

### 3.7. Catalyst stability

To check the stability of the catalyst and to find out whether the inhibition effects of  $CO_2$  and  $H_2O$  are reversible

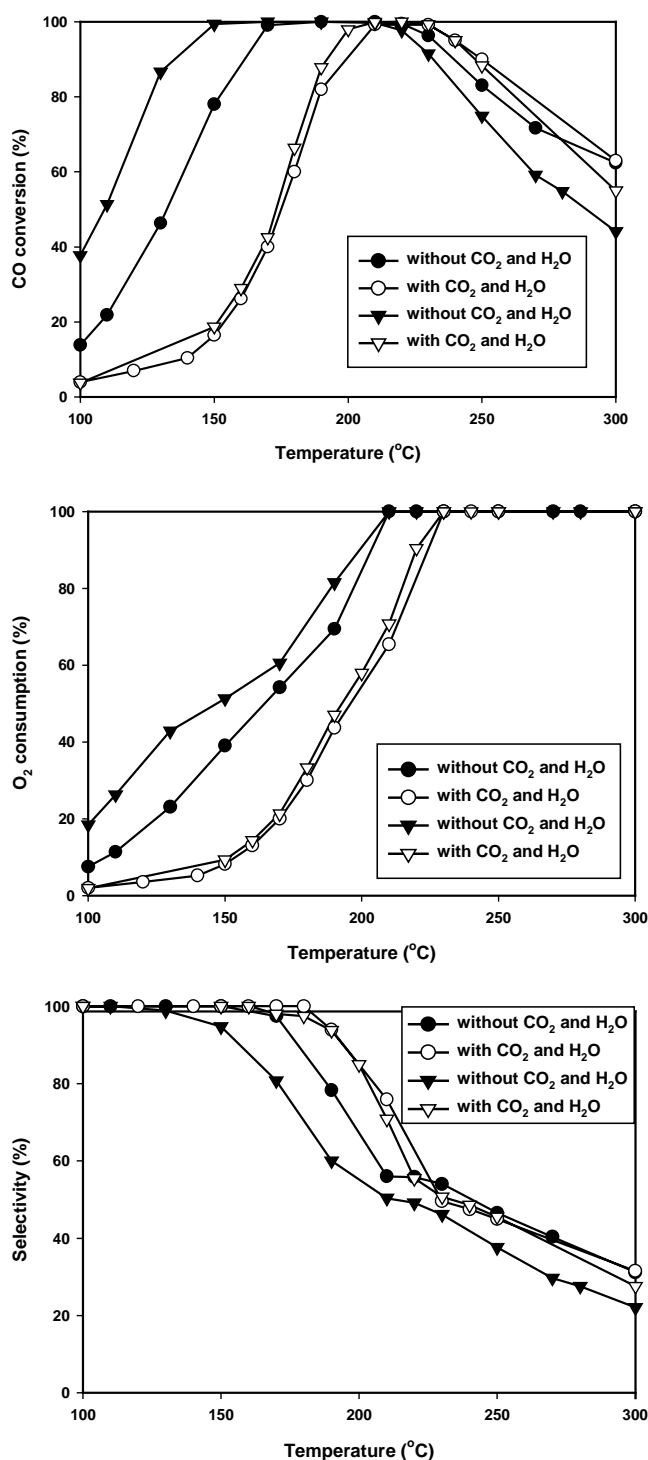


Fig. 6. Change in CO conversion and selectivity with reaction temperature for selective oxidation of CO over CuCe/A (circle) and CuCeCo0.2/A (triangle down) catalyst. Solid and open symbols denote, respectively, absence and presence of 10 vol.%  $H_2O$  and 13 vol.%  $CO_2$  in reactant feed. Reaction conditions: 1% CO, 1%  $O_2$ , 60%  $H_2$ , and balance  $N_2$ . Flow rate, 100 ml/min; GHSV, 60,000  $h^{-1}$ .



Table 2

Temperature windows for  $T_{>99}$  and  $T_{>99,9}$  over CuCe/A and CuCeCo0.2/A with or without CO<sub>2</sub> and H<sub>2</sub>O inhibition

Condition	Catalyst	$T_{99,S}^a$	$T_{99,E}^b$	$T_{99,(S)}^c$	$T_{99,9,S}^a$	$T_{99,9,E}^b$	$T_{99,9}$
Without CO <sub>2</sub> and H <sub>2</sub> O	CuCe/A <sup>d</sup>	175	220	45 (80–50%)	190	215	25
	CuCeCo0.2/A <sup>e</sup>	150	220	70 (94–50%)	160	210	50
With CO <sub>2</sub>	CuCe/A	190	215	25 (70–51%)	–	–	–
	CuCeCo0.2/A	190	230	40 (83–51%)	195	220	25
With H <sub>2</sub> O	CuCe/A	200	235	35 (71–51%)	210	230	20
	CuCeCo0.2/A	185	230	45 (78–50%)	190	220	30
With CO <sub>2</sub> and H <sub>2</sub> O	CuCe/A	210	230	20 (75–50%)	–	–	–
	CuCeCo0.2/A	205	230	25 (80–50%)	210	225	15

<sup>a</sup> S: start temperature.<sup>b</sup> E: end temperature.<sup>c</sup> (S): selectivity.<sup>d</sup> CuCe/A: Cu-Ce [4:16 wt.%]/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.<sup>e</sup> CuCeCo0.2/A: Cu-Ce-Co [4.0:15.8:0.2 wt.%]/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

or not, CO oxidation tests were performed at a temperature of 160 °C and a GHSV of 60,000 h<sup>-1</sup>. To determine whether initial activities could be reclaimed after stopping the introduction of CO<sub>2</sub> and H<sub>2</sub>O, the catalyst sample was treated in helium (99.999%) at 300 °C for 0.5 h after the reactant feed was stopped, and then the reactor was cooled to 160 °C in helium (99.999%). The test results shown in Fig. 7 present the temperature dependencies of CO conversion, O<sub>2</sub> consumption, selectivity, and CH<sub>4</sub> formation at selective CO oxidation in excess hydrogen with or without CO<sub>2</sub> and H<sub>2</sub>O.

In the first reaction step, in the absence of both CO<sub>2</sub> and H<sub>2</sub>O, CO conversion and the selectivity are both 100%, and O<sub>2</sub> consumption is about 50%. After the introduction of either CO<sub>2</sub> or H<sub>2</sub>O or both CO<sub>2</sub> and H<sub>2</sub>O, the catalyst activity decreases drastically. It is found that CO conversion decreases to 80, 55, and 30% and also O<sub>2</sub> consumption decreases to 25 and 18% in the presence of CO<sub>2</sub>, H<sub>2</sub>O and CO<sub>2</sub> and H<sub>2</sub>O, respectively. With stoppage of both H<sub>2</sub>O and

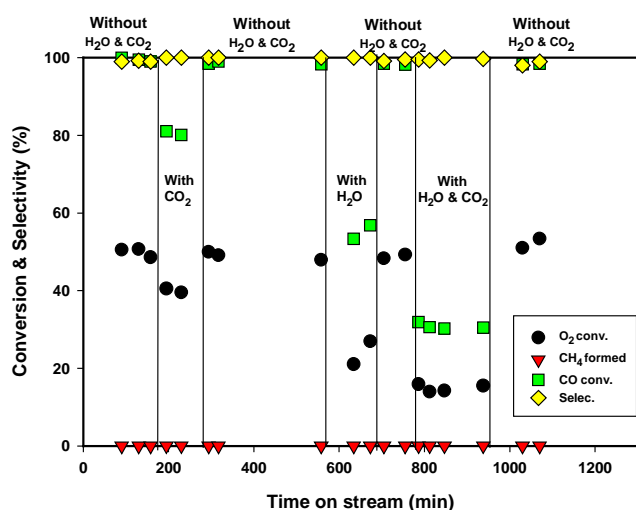


Fig. 7. Reversible test over CuCeCo0.2/A catalyst with or without CO<sub>2</sub> and H<sub>2</sub>O. Reaction conditions: 1% CO, 1% O<sub>2</sub>, 60% H<sub>2</sub>, 0–13% CO<sub>2</sub>, and 0–10% H<sub>2</sub>O. Flow rate, 100 ml/min; reaction temperature, 160 °C; GHSV, 60,000 h<sup>-1</sup>.

CO<sub>2</sub> into the reactant feed, however, the initial activity of CuCeCo0.2/A can be recovered. This means that deactivation by these components is reversible.

### 3.8. Reverse water-gas shift reaction

To study the reverse water-gas shift reaction (Eq. (1)) and methanation (Eq. (2)) on both CuCe/A and CuCeCo0.2/A catalysts, experiments are carried out with 1% CO<sub>2</sub> 60% H<sub>2</sub>, and balance N<sub>2</sub> as feed. The results are shown in Fig. 8. For the reference catalyst (CuCe/A), the reverse water-gas shift reaction forms CO by reacting CO<sub>2</sub> with H<sub>2</sub> at 240 °C, but the Co-doped catalyst forms CO at 170 °C. With increasing reaction temperature, the formation of CO over both catalysts is accelerated, which demonstrates the progress of the reverse water-gas shift reaction. It is clear that the activity for the reverse water-gas shift reaction over the CuCeCo0.2/A catalyst is higher than that over CuCe/A. No production of methane over both catalysts is detected until a temperature of 300 °C.

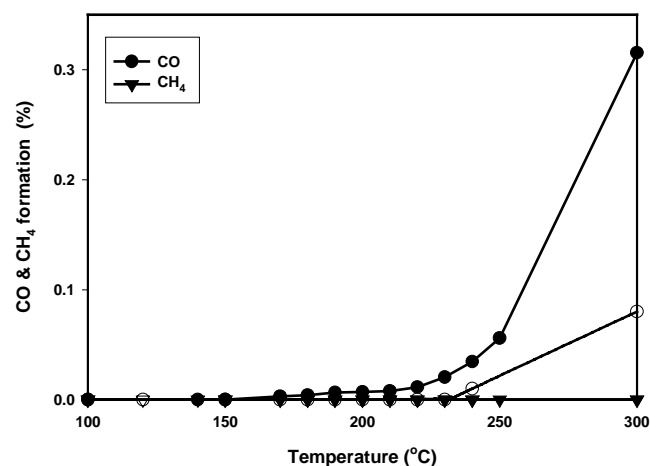


Fig. 8. Reverse water-gas shift and methanation activity of CuCe/A (open) and CuCeCo0.2/A (solid) catalyst. Reaction conditions: 1% CO<sub>2</sub>, 60% H<sub>2</sub> and balance N<sub>2</sub>. Flow rate, 100 ml/min.

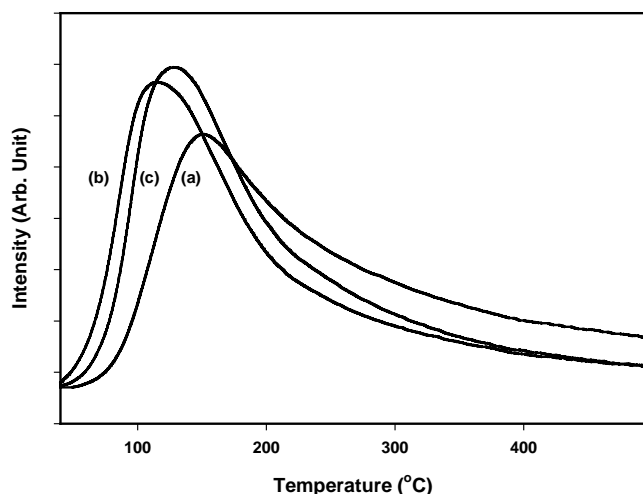


Fig. 9. H<sub>2</sub>O-TPD profiles for various  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> supported catalysts. (a) Cu-Ce [4:16 wt.%], (b) Cu-Ce-Co [4.0:15.8:0.2 wt.%], and (c) Cu-Ce-Co [3.9:15.6:0.5 wt.%].

### 3.9. Temperature-programmed desorption (H<sub>2</sub>O-/CO<sub>2</sub>-TPD)

To elucidate the influence of both CO<sub>2</sub> and H<sub>2</sub>O in the H<sub>2</sub>-rich feed stream on the selective oxidation of CO, CO<sub>2</sub>-TPD, and H<sub>2</sub>O-TPD measurements were made with the Cu-Ce catalysts with different Co loadings (0.2 and 0.5 wt.%).

The H<sub>2</sub>O TPD profile (Fig. 9) for the CuCe/A catalyst shows a single desorption peak at around 150 °C. For the two catalysts modified with different Co loadings of 0.2 and 0.5 wt.%, the  $T_{max}$  (temperature at peak maximum) in the H<sub>2</sub>O-TPD profile shifts towards lower values of 115 and 130 °C, respectively. Also, the peak intensity is increased by the addition of a small amount of Co. When the reaction temperature is lower than the desorption temperature of water, the catalytic activity with H<sub>2</sub>O in reactant feed decreases due to the blockage by adsorption of H<sub>2</sub>O on the active sites. In the CuCeCo0.2/A catalyst, adsorbed water is found to be desorbed almost completely at 115 °C, and thereby has less influence on the activity in the  $T_{>99}$  window of 185–230 °C. In the CuCe/A catalyst, however, water is desorbed by about 130 °C (15 °C higher than in the CuCeCo0.2/A catalyst) and the onset of  $T_{99}$  is also increased by 15 °C compared with the CuCeCo0.2/A catalyst, at 200–235 °C.

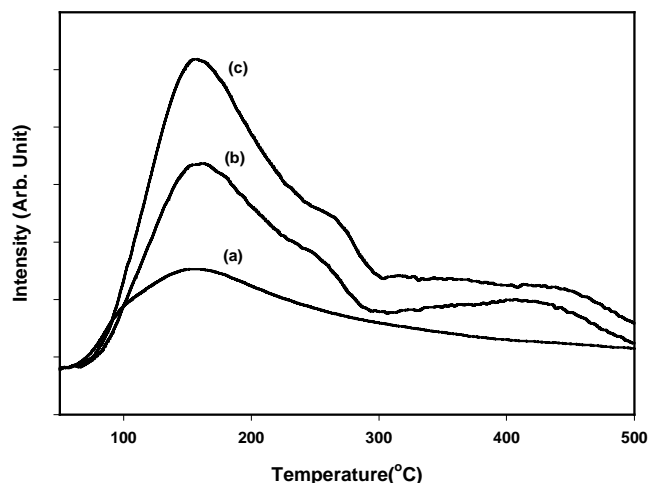


Fig. 10. CO<sub>2</sub>-TPD profiles for various  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> supported catalysts. (a) Cu-Ce [4:16 wt.%], (b) Cu-Ce-Co [4.0:15.8:0.2 wt.%], and (c) Cu-Ce-Co [3.9:15.6:0.5 wt.%].

The CO<sub>2</sub>-TPD results for the addition of Co (0.2, 0.5 wt.%) to the CuCe/A reference catalyst are given in Fig. 10. In the CuCe/A catalyst, the CO<sub>2</sub>-TPD gives one desorption peak at about 155 °C. By contrast, in catalysts modified with Co, the  $T_{max}$  shifts towards higher values. Upon a small addition of Co, the CO<sub>2</sub>-TPD profile gives three distinct desorption peaks at 160, 250, and 410 °C. The peak intensity increases with increasing addition of Co (namely from 0.2 to 0.5 wt.%). For the CuCeCo0.2/A catalyst, the catalytic activity shows a remarkable decrease because the catalytic surface sites are occupied by strongly adsorbed CO<sub>2</sub>. From CO<sub>2</sub>/H<sub>2</sub>O-TPD results, it is concluded that the main cause for the decrease in catalytic activity is the competitive adsorption of CO and CO<sub>2</sub> as well as blockage of catalyst active sites by adsorbed water at low reaction temperatures.

## 4. Conclusions

From the activity tests and characterization studies for the CuCe/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst promoted with Co as a dopant, the following conclusions can be drawn:

- (i) Temperature windows for  $T_{>99}$  and  $T_{>99,9}$  over CuCe/A and CuCeCo0.2/A catalysts are listed as follows:

Catalyst	$T_{99, S}^a$	$T_{99, E}^b$	$\Delta T_{99, (S)}^c$	$\Delta T_{99,9, S}^a$	$T_{99,9, E}^b$	$\Delta T_{99,9}$
CuCe/A <sup>d</sup>	175	220	45 (80–50%)	190	215	25
CuCeCo0.2/A <sup>e</sup>	150	220	70 (94–50%)	160	210	50

<sup>a</sup> S: start temperature (°C).

<sup>b</sup> E: end temperature (°C).

<sup>c</sup> (S): selectivity.

<sup>d</sup> CuCe/A: Cu-Ce [4:16 wt.%]/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

<sup>e</sup> CuCeCo0.2/A: Cu-Ce-Co [4:15.8:0.2 wt.%]/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

- (ii) Under stoichiometric O<sub>2</sub> concentration, i.e.,  $\lambda = 1$ , the maximum conversion attainable is  $\sim 80\%$  at 150 °C. Increasing the O<sub>2</sub> concentration to twice the stoichiometric ratio ( $\lambda = 2$ ) results in a peak conversion of 99% at temperature windows between 150 and 220 °C. Further increase in O<sub>2</sub> concentration to  $\lambda = 2.5$  shows little change in the temperature window for 99% conversion and gives a selectivity decrease of only about 10% compared with  $\lambda = 2$ .
- (iii) With H<sub>2</sub>O and CO<sub>2</sub> in the reactant feed, although the Cu-Ce/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst promoted with Co gives higher activity than the Cu-Ce/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> reference catalyst, both catalysts experience a drastic decrease in activity by the action of these compounds. On the other hand, the catalytic deactivation by CO<sub>2</sub> and H<sub>2</sub>O is shown to be reversible, i.e., the catalytic activity is completely recovered in the absence of CO<sub>2</sub> and H<sub>2</sub>O. This means competitive adsorption of CO and CO<sub>2</sub>, as well as blockage of catalyst active sites by adsorbed water, may be the main causes of the decrease in activity.
- (iv) From CO<sub>2</sub>-/H<sub>2</sub>O-TPD results, it is found that the CO oxidation activity of the catalyst is closely related to the desorption temperature of CO<sub>2</sub> and H<sub>2</sub>O.

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