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Hydrogen clean-up by preferential CO oxidation over Pt–Co–Ce/MgO

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1.4 wt% Pt–1.25 wt% Co–1.25 wt% Ce catalyst on MgO support was prepared using incipient to wetness impregnation technique and tested in a micro-reactor flow system for the low temperature preferential oxidation of CO in hydrogen rich streams. 100% CO conversion was achieved at 130 °C with a feed composition of 1.0% CO, 1.0% O_2, 60% H_2 and He as balance at a space velocity of 24,000 cm^3/g-h. The addition of 25% CO_2 did not affect the performance of the catalyst significantly, while 10% H_2O in the feed decreased the activity. 100% CO conversion was obtained at 150 °C in the presence of 25% CO_2 and 10% H_2O in the feed.

KEY WORDS: Pt–Ce–Co/MgO catalyst; selective CO oxidation; fuel processor; fuel cell; hydrogen clean-up.

1. Introduction

Fuel cells operating on hydrogen are considered to be one of the most attractive energy conversion devices of the future due to their high conversion efficiency and low emission [1]. Since the safe storage of hydrogen has not been fully developed yet, on-site production of hydrogen from various hydrocarbons using a fuel processor seems to be the only feasible means of supplying hydrogen to fuel cells for small to medium size applications, and for transportation vehicles in the near future [1,2].

On the other hand, the hydrogen stream leaving the fuel processor typically contains 15–20% CO_2, 10% H_2O and 0.5–1% CO. Carbon monoxide is harmful for the anode catalyst of the fuel cell even at trace levels [3]. Therefore, effective catalyst(s) must be developed to eliminate CO selectively from the hydrogen rich streams at low temperatures and in the presence of carbon dioxide and water.

Supported noble metal, especially platinum-based, catalysts have been extensively studied for this purpose by various investigators [4–11]. Noble metal and reducible oxide catalysts seem to provide a promising choice [4]. For example, platinum based catalysts promoted by metals such as Co, Fe, Ce or Sn have been studied by various researchers and were found to be effective in eliminating CO [6–10]. Although the support most commonly used in these studies is Al_2O_3, some other support materials including MgO have also been investigated to improve the catalytic performance [4,12,13]. MgO is likely to be an effective support since it stabilizes the metals in unusual oxidation states and prevents sintering of metal atoms [14].

In this study, an MgO-supported Pt–Co–Ce catalyst was designed for the preferential oxidation of CO in hydrogen rich streams, and catalyst performance was studied under conditions that may exist in a fuel processor. The catalyst was prepared using the incipient to wetness co-impregnation technique and then tested in a flow micro-reactor system. The metal loadings were chosen as 1.4 wt% Pt, 1.25 wt% Co and 1.25 wt% Ce based on our previous work over Al_2O_3-supported Pt–Co–Ce catalysts [15]. The effects of reaction temperature and feed composition on CO conversion and selectivity were investigated.

2. Experimental

2.1. Catalyst preparation

Pt–Ce–Co/MgO catalysts were prepared using the incipient to wetness co-impregnation technique [16]. $Pt(NH_3)_4(NO_3)_2$, $Ce(NO_3)_3 \cdot 6H_2O$ and $Co(NO_3)_2 \cdot 6H_2O$ were used as metal precursors. 98% MgO (Aldrich) support was crushed and sieved to 45–60 mesh. The required volume of precursor solution was determined from the difference of dry and water saturated MgO. Five grams of support was placed in a vacuum flask and kept under vacuum for 30 min prior to impregnation. A Master-Flex computerized-drive peristaltic pump was used to feed the precursor solution to the vacuum flask at a rate of 5 cm^3/min through silicone tubing. The slurry was mixed in an ultrasonic mixer for 90 min during the impregnation and then dried in an electric oven at 115 °C for 16 h. The catalyst was not calcined since our initial work indicated that calcination has no significant effect on Pt–Co–Ce/MgO systems [17].

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2.2. *Activity measurements*

The activity of the catalyst was measured using a micro-reactor flow system. Research grade CO, O_2, H_2, CO_2 and He were used, and their flowrates were controlled using Aalborg DFC2600 and/or Brooks 5850E mass flow controllers. The water was pumped into the preheated (150 °C) reactant gas mixture using a Jasko PU-2080-Plus HPLC pump, and it was evaporated in a glass wool bed before the feed mixture was allowed to flow through the 4-mm ID stainless-steel fixed-bed micro-reactor. The temperature was controlled by a Shimaden FP-21 programmable controller in a 40 cm × 2.4 cm ID tube furnace. Product streams were analyzed using a Shimadzu CR-8APT gas chromatograph equipped with a Shimadzu CR-4A integrator. A Molecular Sieve 5A (60–80 mesh) column and a TCD were used for CO and O_2 analysis. CO_2 concentration was calculated using the carbon balance, assuming all the carbon reacted was converted into CO_2. The feed flowrate was kept constant at about 100 cm^3/min. 0.25 g catalyst used in the experiments, and samples were reduced *in situ* at 300 °C in a hydrogen environment for 3 h before each activity measurement.

3. Results and discussion

The conversion and selectivity were defined and calculated as follows:

$$\text{CO conversion }(\%) = \frac{[\text{CO}]_{\text{in}} - [\text{CO}]_{\text{out}}}{[\text{CO}]_{\text{in}}} \times 100 \tag{1}$$

$$\text{O}_2\text{ conversion }(\%) = \frac{[\text{O2}]_{\text{in}} - [\text{O2}]_{\text{out}}}{[\text{O2}]_{\text{in}}} \times 100 \tag{2}$$

$$\begin{array}{l}\text{Selectivity toward}\\ \text{CO oxidation}(\%)\end{array} = \frac{0.5 \times \left([\text{CO}]_{\text{in}} - [\text{CO}]_{\text{out}}\right)}{[\text{O2}]_{\text{in}} - [\text{O2}]_{\text{out}}} \times 100. \tag{3}$$

3.1. *Effect of temperature in the absence of carbon dioxide and water*

The dependence of CO conversion and selectivity on the reaction temperature was first investigated in the absence of carbon dioxide and water, in order to compare the results with those reported in the literature under similar conditions. The product mixture was analyzed every 30 min up to 120 min time-on-stream, and the data at 120 min are presented in figure 1. The catalytic activity measurements were started with 90 °C and continued with two subsequent experiments conducted at 20 °C intervals until 130 °C, at which 100% CO conversion was achieved up to 120 min time-on-stream, indicating that the lowest operating temperature of the catalyst should be 130 °C. This temperature is lower than or comparable with the results reported in the literature for Pt-based catalysts [6,9–11] as well as those obtained over a monometallic Pt/MgO catalyst [13]. Cobalt and cerium, when used together, promote Pt significantly, as was also observed by various investigators [6,10,15,18]. The MgO support, on the other hand, seems to be less effective than Al_2O_3 support, over which 100% CO conversion can be obtained at 90 °C with the same metal loadings and reaction conditions [15]. The lower surface area of MgO leading to lower metal dispersion [13] compared to Al_2O_3, as well as some differences in other characteristics, may be contributing to these results. Although Marino *et al.* [13] reported higher CO conversion over Pt/MgO than Pt/Al_2O_3, the presence of cobalt and cerium seems to change the order despite the positive impact produced in both cases.

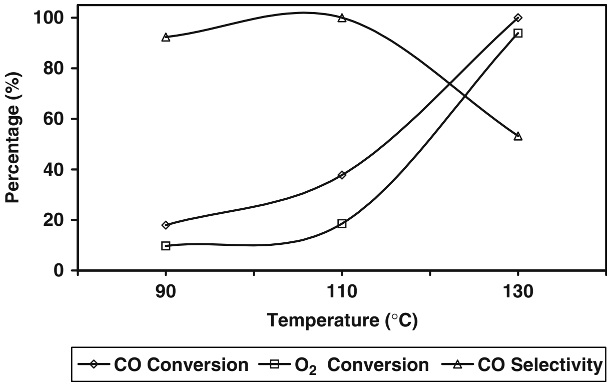

Figure 1. Effect of temperature on conversion and selectivity in the absence of CO_2 and H_2O. Feed: 1.0% CO, 1.0% O_2, 60.0% H_2, balance He; F/W = 24,000 cm^3/g-h, 120 min time-on-stream.

O_2 conversion followed a similar trend, reaching almost 100% at 130 °C for all time-on-streams up to 120 min leading to a selectivity value of 40% for CO oxidation. Considering that the H_2/CO ratio in the feed was 60, it seems that some hydrogen was also oxidized although the catalyst was more selective for CO oxidation.

3.2. *Effect of carbon dioxide and water in the feed*

25% CO_2 was introduced into the feed containing 1% CO, 1% O_2 and 60% H_2, at the expense of balance He. At a reaction temperature of 130 °C, the addition of 25% CO_2 did not affect activity of the catalyst significantly. 100% CO conversion was reached during 120 min accompanied by a small increase in the selectivity (figure 2). The addition of 10% H_2O at the expense of He, on the other hand, decreased CO conversion down to 58% at 30 min time-on-stream. The conversion continued to decrease with time and reached 44% at 120 min as seen in figure 2. The negative effect of water on conversion was also observed by Snytnikov *et al.* [19] over Pt/C and by Park *et al.* [20] over Cu–Ce/

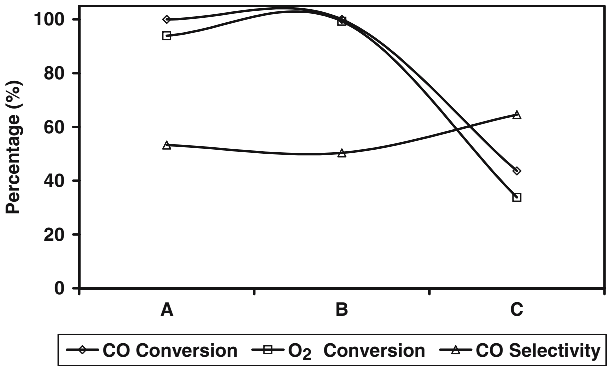

Figure 2. Effect of carbon dioxide and water in the feed containing 1.0% CO, 1.0% O_2, 60% H_2, balance He. T = 130 °C; F/W = 24,000 cm^3/g-h. (a) absence of CO_2 and H_2O, (b) 25% CO_2 and (c) 25% CO_2 + 10% H_2O, 120 min time-on-stream.

Al_2O_3, and it was attributed to the blockage of active sites of the catalyst by adsorbed H_2O and the formation of CO–H_2O surface complexes, which are less active than adsorbed CO. On the other hand, we have observed a positive effect of water and no significant effect of CO_2 when we used Al_2O_3 as support with the same Pt–Co–Ce loadings under similar reaction conditions [15], which provides additional evidence indicating that support-metal interaction plays a crucial role and leads to different results even for relatively inert supports such as MgO and Al_2O_3. A similar trend was also observed in O_2 conversion over Pt–Co–Ce/MgO while there was no considerable difference in the selectivity for CO oxidation.

3.3. *Effect of temperature in the presence of carbon dioxide and water*

The temperature was then increased from 130 to 140 °C and then to 150 °C in the presence of 25% CO_2 and 10% H_2O, which is the typical composition in the hydrogen stream from a fuel processor [3]. The results showed that the negative effect of 10% H_2O on CO conversion was compensated by the temperature increase. 100% conversion was achieved at 150 °C for both CO and O_2 up to 240 min time-on-stream, and the conversion and selectivity values are presented in figure 3. Over the MgO-supported catalyst, complete removal of CO in the presence of H_2O can be achieved at a higher temperature than in its absence, which is similar to some reports on other catalysts [20]. However, this was not the case when Al_2O_3 was used as support with the same Pt–Co–Ce loadings [15], indicating the effect of the nature of support on catalyst performance. The reaction temperature of 150 °C is still within the range of 80–200 °C corresponding to the operating temperatures of PEM fuel cells, and it is comparable to the temperatures reported for Pt based catalysts in the literature [3,10,11].

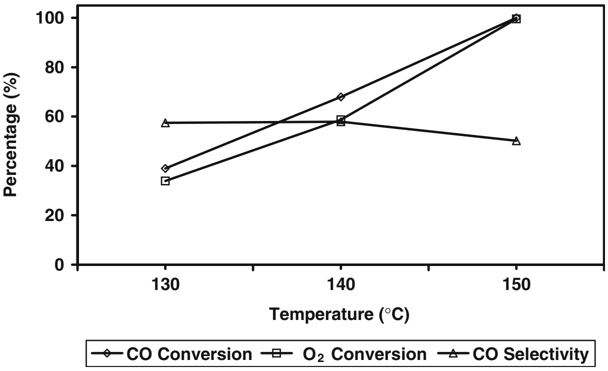

Figure 3. Effect of temperature on conversion and selectivity in the presence of carbon dioxide and water. 1.0% CO, 1.0% O_2, 60% H_2, balance He; F/W = 24,000 cm^3/g-h, 240 min time-on-stream.

3.4. *Effect of O_2 concentration in the presence of carbon dioxide and water*

The effect of O_2 concentration in the feed on conversion and selectivity for CO_2 formation was also studied at a fixed CO concentration of 1% at 150 °C (table 1). The CO conversion dropped to about 50% when O_2 concentration in the feed was decreased from 1.0% to 0.5% for all time-on-stream values up to 240 min. O_2 conversion, on the other hand, was almost 100% in both cases leading to the same level of selectivity (about 50%). However, 1.0% O_2 in the feed, which is twice the stoichiometric O_2/CO ratio, is still reasonably low and comparable to the values reported in the literature [6,9–11].

4. Conclusion

The following conclusions can be drawn from the present study:

- 100% CO conversion is obtained over Pt–Co–Ce/MgO at 130 °C and 24,000 cm^3/g-h space velocity with a feed composition of 1% CO, 1% O_2, 60% H_2 and He as balance.
- The addition of 25% CO_2 does not significantly affect catalyst activity at 130 °C, other reaction conditions being constant. Further addition of 10% H_2O into the CO_2 containing mixture, on the other hand, decreases CO conversion from 100% to about 44% at 120 min time-on-stream, which is in contrast to the positive effect of water observed for Al_2O_3-supported Pt–Co–Ce catalyst of similar composition. However, increasing the reaction temperature from 130 to 150 °C balances the negative effect of H_2O leading to 100% CO conversion.
- To sum up, 100% CO conversion is obtained up to 240 min time-on-stream for a realistic gas mixture of 1% CO, 1% O_2, 25% CO_2, 10% H_2O, 60% H_2 and He as balance at 150 °C, which is within the desired

Table 1

Effect of O_2 concentration in feed on conversion and selectivity in the presence of carbon dioxide and water at 240 min time-on-stream

O_2 in feed (%)	CO conversion (%)	O_2 conversion (%)	Selectivity (%)
0.5	54.1	99.7	54.3
1.0	100	99.6	50.2

1.0% CO, 60% H_2, balance He; F/W = 24,000 cm^3/g-h; T = 150 °C.

range of 80–200 °C required for the fuel cell applications. It can be concluded that the 1.4 wt% Pt–1.25 wt% Co–1.25 wt% Ce/MgO catalyst should be considered as a promising catalyst alternative for CO removal in hydrogen-rich streams, since both the operating temperature and the O_2/CO ratio in the feed are reasonably low or comparable to other catalysts reported in the literature.

Acknowledgments

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