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Preferential CO oxidation over Pt–SnO_2/Al_2O_3 in hydrogen rich streams containing CO_2 and H_2O (CO removal from H_2 with PROX)

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The effects of reaction gases including CO_2 and H_2O and temperature on the selective low-temperature oxidation of CO were studied in hydrogen rich streams using a flow micro-reactor packed with a Pt–SnO_2/Al_2O_3 sol–gel catalyst that was initially designed and optimized for operation in the absence of CO_2 and H_2O. 100% CO conversion was achieved over the 1 wt% Pt–3 wt% SnO_2/Al_2O_3 catalyst at 110 °C using a feed composition of 1.0% CO, 1.5% O_2, 25% CO_2, 10% H_2O, 58% H_2 and He as balance at a space velocity of 24,000 $cm^3/(g\ h)$. CO_2 in the feed was found to decrease CO conversion significantly while the presence of H_2O in the feed increased CO conversion, balancing the effect of CO_2.

KEY WORDS: Pt–SnO_2/Al_2O_3 sol–gel catalyst; selective CO oxidation; fuel processor; fuel cell.

1. Introduction

Fuel cells are considered to be one of the most attractive energy conversion devices of the future since they use hydrogen as fuel in an efficient manner and produce no pollution [1]. Considering that safe storage of hydrogen is not technologically possible yet, hydrogen production from a conventional fuel using a fuel processor seems to be the only feasible way of utilizing fuel cells in mobile or small to medium size stationary applications in the near future [1,2]. However, the hydrogen stream from a fuel processor is expected to contain 15–20% CO_2, about 10% H_2O and 0.5–1% CO. Since carbon monoxide poisons the anode catalyst of the fuel cell even at trace levels, effective catalyst(s) must be developed to remove CO selectively from the hydrogen rich streams at low temperatures and in the presence of carbon dioxide and water [3].

Various researchers have extensively investigated supported noble metal, especially platinum-based, catalysts for preferential CO oxidation over years [4–11]. Noble metal and reducible oxide catalysts are also considered 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 [6–10,12].

Although precipitation and impregnation are most widely used for catalyst preparation, the sol–gel method also presents a useful route for designing catalysts with well-defined micro-structural properties. However, there is a large number of parameters that affect the catalytic properties in the sol–gel process [13]. An effective experimental procedure should therefore be used to minimize the number of experiments without sacrificing valuable information.

We recently designed a 1.0 wt% Pt–3.0 wt% SnO_2/Al_2O_3 catalyst prepared by the sol–gel method for selective CO oxidation in hydrogen rich streams. Various sol–gel parameters were optimized using the Taguchi method of experimental design [9]. In order to evaluate the performance of this catalyst under realistic feed conditions, we have now investigated the effects of reaction temperature, presence of CO_2 and H_2O in the feed and feed concentration of O_2 on the CO conversion levels as well as on the selectivity for the CO oxidation reaction.

2. Experimental

2.1. Preparation of the catalyst

1 wt% Pt–3 wt% SnO_2/Al_2O_3 catalyst was prepared using the sol–gel method. $Pt(NH_3)_4(NO_3)_2$, $C_{16}H_{36}Sn$ and aluminum isopropoxide (AIP) were used as precursors. HNO_3, H_2O and aluminum nitrate (to enhance gel formation) concentrations, and the stirring speed were taken as the major parameters of the sol–gel process and were optimized using the Taguchi method. Details of experimental procedure have previously been reported [9].

2.2. Activity measurement

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 Brooks 5850E

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mass flow controllers. The water was injected into the preheated (150 °C) reactant gas mixture using a Jasko PU-2080-Plus HPLC pump and was evaporated in a glass wool bed before reaching the catalyst. 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 40×2.4 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 100 cm^3/min. 0.25 g catalyst samples were used in the experiments; all samples were calcined at 500 °C for 3 h and reduced *in situ* at 500 °C in a hydrogen environment for 5 h before each activity measurement [14].

3. Results and discussion

Percent conversion and selectivity for CO oxidation are defined and calculated as follows:

CO conversion (%) =

$$\frac{[CO]_{in} - [CO]_{out}}{[CO]_{in}} \times 100 \tag{1}$$

O_2 conversion (%) =

$$\frac{[O_2]_{in} - [O_2]_{out}}{[O_2]_{in}} \times 100 \tag{2}$$

Selectivity towards CO oxidation (%) =

$$\frac{0.5 \times ([CO]_{in} - [CO]_{out})}{[O_2]_{in} - [O_2]_{out}} \times 100 \tag{3}$$

3.1. *Effect of CO_2 in the feed*

Experiments were conducted in the absence and presence of 25% CO_2 in the feed at 110 °C and 24,000 cm^3/g h space velocity with the feed composition of 1% CO, 1% O_2, 58% H_2 and helium as balance. Although our previous work showed that CO can be completely removed at 100 °C in the absence of CO_2 and H_2O [9], the effects of CO_2 were investigated at 110 °C to be able to compare the results with those obtained in the presence of H_2O, which may condense at lower temperatures. The conversion and selectivity values obtained at 120 min time on stream are presented in figure 1.

Addition of 25% CO_2 caused a significant decrease in CO conversion from 100% to 47% at the end of 120 min on stream, which may mean that the reaction equilibrium for CO oxidation is shifted towards CO in the presence of CO_2 at high concentration, as would be indicated by thermodynamics. Considering that the O_2 conversion was also decreased significantly, another possible explanation is the formation carbonates over the reducible metal oxide, SnO_2, which would prevent the participation of oxygen in CO oxidation [3].

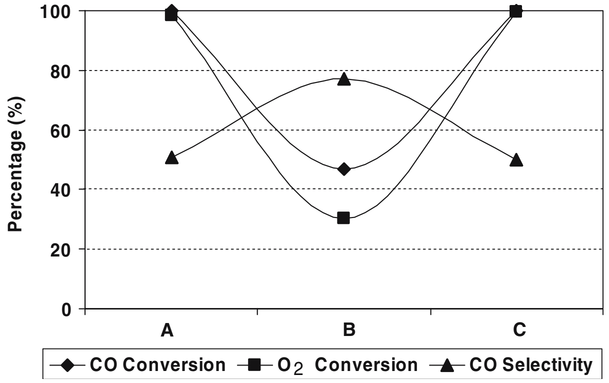

Figure 1. Effect of carbon dioxide and water in the feed containing 1.0% CO, 1.0% O_2, 58% H_2, balance He. T = 110 °C; F/W = 24,000 cm^3/g h. A: absence of CO_2 and H_2O, B: 25% CO_2 and C: 25% CO_2 + 10% H_2O; 120 min-on-stream.

3.2. *Effect of H_2O in the feed in the presence of CO_2*

On the other hand, the addition of 10% H_2O to the CO_2 containing feed stream increased CO conversion back to 100%, compensating the negative influence of CO_2 on the catalyst performance. The excess amount of water may result in some water gas shift (WGS) activity decreasing CO concentration while increasing H_2. It may be also possible that formation of OH groups on the surface contribute to the removal of CO [3].

3.3. *Effect of temperature in the presence of CO_2 and H_2O in the feed*

A slight loss in activity was observed in the presence of CO_2 and H_2O at 110 °C at extended time-on-stream values. In order to improve catalyst performance, the temperature was first increased to 120 °C and then to 130 °C. Catalyst activity and selectivity for CO oxidation were both measured at 240 min-on-stream (figure 2). Nevertheless, the activity loss increased further although the CO conversion was still higher than 95%. O_2 conversion also decreased first at 120 °C slightly and then increased to 100% at 130 °C. It is possible that the temperature increase may have favored reverse WGS reaction.

3.4. *Effect of O_2 concentration in the feed*

In order to prevent the activity loss observed after 180 min with 1% O_2 in the feed at 110 °C, the O_2 concentration in the feed was increased to 1.5%. The results obtained at 240 min on stream (given in table 1 for both 1% and 1.5% O_2 in the feed) indicate that the

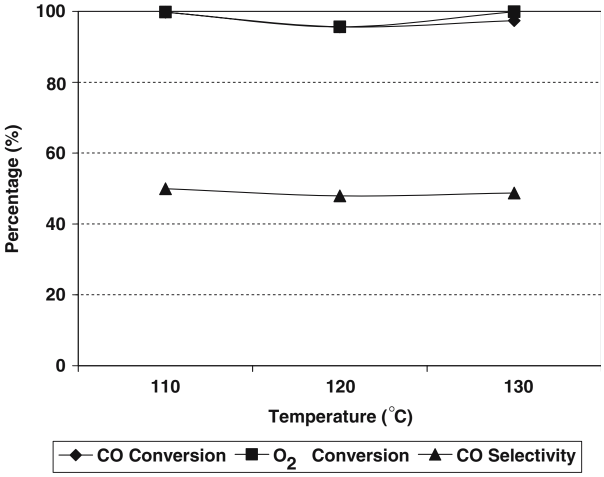

Figure 2. Effect of temperature on conversion and selectivity in the presence of CO_2 and H_2O. (Feed: 1.0% CO, 1.0% O_2, 58% H_2, 25% CO_2, 10% H_2O, balance He; F/W = 24,000 cm^3/g h; 240 min-on-stream).

increase in O_2 concentration did indeed prevent the slight activity loss observed. It should be noted that measuring a difference of 0.5% in CO conversion between the two cases above is actually in the limit of experimental accuracy, considering the fact that there is only 1% CO in the feed. However, a very small CO peak was continuously observed on the chromatogram after 180 min on stream with 1% O_2 concentration in the feed, and this peak totally disappeared when the O_2 concentration was increased to 1.5%.

Almost all O_2 in the feed was consumed in both cases indicating that excess oxygen oxidizes hydrogen in the feed although it prefers CO first. Although 1.5% O_2 in the feed results in 1–2% more hydrogen loss than in the case of 1% O_2, it is still tolerable considering that eliminating CO is the primary goal in fuel cell applications.

4. Conclusion

The following conclusions can be drawn from the present study:

- 100% CO conversion was obtained in the absence of CO_2 and H_2O at 110 °C and 24,000 cm^3/g h space velocity using a feed composition of 1% CO, 1% O_2, 58% H_2 and helium as balance. The addition of 25% CO_2 decreased CO conversion significantly (47%) while further addition of 10% H_2O to the CO_2 containing feed stream increased CO conversion back to 100%.
- The slight activity loss observed after 180 min on stream at 110 °C increased with temperature at 120 °C and 130 °C, although the conversion was still higher than 95%. Increasing the O_2 concentration in the feed to 1.5%, on the other hand, eliminated the activity loss completely.
- As a result, complete conversion of CO was achieved at 110 °C and 24,000 cm^3/g h space velocity using a feed composition of 1% CO, 1.5% O_2, 25% CO_2, 10% H_2O, 58% H_2 and helium as balance.

Table 1
Effect of O_2 concentration in feed on conversion and selectivity in the presence of CO_2 and H_2O

O_2 in feed (%)	CO conversion (%)	O_2 conversion (%)	Selectivity for CO oxidation (%)
1	99.5	99.5	50
1.5	100	99.5	33.4

(Feed: 1.0% CO, 1.0% O_2, 58% H_2, 25% CO_2, 10% H_2O, balance He; F/W = 24,000cm^3/g h; 240 min-on-stream, T = 110°C).

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