Promotion of Pt/γ-Al_2O_3 by Ce for preferential oxidation of CO in H_2

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Hydrogen for fuel cells can be produced by reforming hydrocarbons. The H_2-rich reformate typically contains about 1 mol% CO which will poison the anode of polymer electrolyte fuel cells. The CO concentration can be reduced by preferential oxidation (PROX) using near-stoichiometric amounts of O_2. The conversion of CO should be over 99% while minimizing oxidation of H_2. Supported Pt catalysts with and without promotion by Ce were compared for the catalytic oxidation of CO by O_2 in a H_2 stream. With unsupported Pt catalysts, selectivity (to CO_2 as opposed to H_2O) was highest at low temperatures and low O_2/CO ratios, however conversion was low. Addition of Ce significantly improved CO conversion under these conditions.

KEY WORDS: CO preferential oxidation; PROX; Pt; Ce; γ-Al_2O_3; fuel cells

1. Introduction

Hydrogen for automotive polymer electrolyte fuel cells (PEFC) can be produced in an onboard fuel processor. Although the term "reformer" is often used for the whole system, the production of hydrogen actually occurs in three processes: (1) hydrogen is produced by *autothermal reforming* of a hydrocarbon (fuel $+ O_2 + H_2O \rightleftharpoons CO_x + H_2$) where without water it is *partial oxidation* and without oxygen it is *steam reforming*; (2) the water–gas shift reaction ($CO + H_2O \rightleftharpoons CO_2 + H_2$) eliminates most of the CO, producing more hydrogen; and (3) any remaining CO is reduced to ppm levels by preferential oxidation (PROX) [1]. The PROX reaction is the selective catalytic oxidation of CO in the H_2-rich reformate using O_2. Many auxiliary processes such as fuel vaporization, sulfur removal, heat integration, and effluent gas combustion can make this a very complicated device.

The CO concentration from a reformer/water–gas shift unit is typically about 1 mol%, which is set by the thermodynamic equilibrium of the water–gas shift reaction. The PEFC anode uses a Pt catalyst that is very sensitive to CO poisoning at low temperatures. The partnership for a new generation of vehicles' (PNGV, a broad partnership between the US government, industry, universities and national labs) CO target concentration for the fuel processor is 10 ppm [2].

In order to achieve this low CO concentration, the PROX reactor is placed between the shift reactor and the fuel cell anode. Los Alamos National Laboratory (DOE's lead laboratory for PROX systems) has developed what many consider to be the state-of-the-art PROX catalyst and reaction system. It can achieve low concentrations of CO (10–20 ppm) in a multi-stage reactor over a Pt/Al_2O_3 or Ru/Al_2O_3 catalyst. The reaction chemistry is complicated, involving not only catalytic oxidation of both CO and H_2, but also methanation and water–gas shift.

As with many catalytic processes, the challenges here are activity and selectivity. The conversion of CO has to be 99.9% in order to achieve a concentration of 10 ppm. At the same time, the reformate is mostly hydrogen and its oxidation obviously decreases the overall fuel efficiency. Since the PROX unit is placed between the low-temperature shift reactor (~200 °C) and the PEFC (~80 °C), it should operate between these temperatures.

The extensive investigation of low-temperature CO oxidation catalysts has been reviewed [3]. However, less has been published specifically on CO oxidation in H_2-rich atmospheres. Catalysts investigated include Pt [4–7], Ru [5], and Au [8], and octahedral molecular sieves (OMS) [9]. Oh and Sinkevitch [5] reported that Pt catalysts supported on alumina could eliminate CO with less methanation. Igarashi *et al.* [4] reported that the selectivity is improved by changing supports. They also indicated that using a low O_2 concentration minimizes hydrogen oxidation [4]. These results lead to the hypothesis tested in this study that the selectivity for CO oxidation, compared to H_2 oxidation, of Pt catalysts supported on alumina can be improved at low oxygen concentrations if the oxygen supply to Pt is increased.

In automotive three-way catalysts (TWS), the activity of Pt catalysts was improved through oxygen storage components like CeO_2. Some have suggested that CeO_2 promotes CO oxidation by employing lattice oxygen. This fact implies that it may improve oxygen supply to Pt on CeO_2 in low-oxygen-concentration environments [10].

In this study, the selectivity and activity of Pt/Al_2O_3 and Pt/CeO/Al_2O_3 catalysts are examined as a function of oxygen concentration and residence time.

2. Experimental

Platinum ($H_2PtCl_6{\cdot}6H_2O$, Alfa) and ceria ($Ce(NO_3)_3{\cdot}6H_2O$, Alfa) were co-impregnated over γ-Al_2O_3 (150 m^2/g, basic type, >60 mesh, Alfa) using the incipient wetness method. All catalysts were dried in an oven at 120 °C for 24 h and calcined at 400 °C for 2 h. Before testing the catalysts, they were heated in O_2 at 500 °C for 1 h, purged in He for 10 min, and then reduced in H_2 at 500 °C for 1 h. The following notation identifies the catalysts: *X*Pt*Y*Ce/Al, where *X* and *Y* are wt% and Al is γ-Al_2O_3.

A continuous-flow reactor system consisting of a vertical quartz tube reactor (6 mm ID) in an oven was used to test the catalysts. The temperature was controlled from 100 to 250 °C in 50 °C steps. The tests were carried out under the following conditions: catalyst loading 0.3 g, total flow rate 300 ml/min (STP), and atmospheric pressure. These experimental conditions are similar to the expected operating conditions of a PROX reactor. The catalysts were held in place with glass-wool plugs. Reaction temperature was measured with two thermocouples, located on both sides of the catalyst bed. A thermocouple located at the top of the catalyst bed was used for controlling reaction temperature. The temperatures difference between the two thermocouples was 15–20 °C since the reactions are highly exothermic. All gas compositions (CO 1%, O_2 0.5–2% and balance H_2) were controlled using Tylan mass flow controllers.

The concentration of CO in the product was measured with an on-line CO analyzer (Thermo-Environmental Instrument, 48C, USA) after removing water using a drierite moisture trap. The concentrations of O_2, CH_4, and CO_2 were measured by a gas chromatograph (HP 6890) with a TCD detector and a Hayesep DB column. The concentrations of H_2O and H_2 were only measured approximately by GC. The data were collected over a period of 1–2 h in the steady state reaction. The conversions of CO and O_2 and the selectivity of CO were defined as follows:

$$\text{CO conversion (\%)} = \frac{[CO_2]_{out}}{[CO]_{in}} \times 100,$$

$$O_2 \text{ conversion (\%)} = \frac{[O_2]_{in} - [O_2]_{out}}{[O_2]_{in}} \times 100,$$

$$\text{CO selectivity (\%)} = \frac{0.5[CO_2]_{out}}{[O_2]_{in} - [O_2]_{out}} \times 100.$$

3. Results and discussion

Figure 1 shows CO conversion and figure 2 shows the O_2 conversion and CO selectivity with different ratios of O_2 to CO over 5Pt/Al. In all experiments, CO conversion increased with an increase in O_2 concentration, while the CO selectivity decreased. In addition, the O_2 conversion was almost 100% above 150 °C. The CO conversion was maximized at 200 °C with 0.5% O_2 and 1% O_2 and the CO conversion was almost 100% at 100 °C when 2% O_2 was used. The decrease in CO conversion at high temperature was caused by hydrogen oxidation: we found increasing GC water peaks without other peaks such as CH_4. Therefore, selectivity was improved at low O_2 concentrations and lower reaction temperatures because hydrogen oxidation was suppressed.

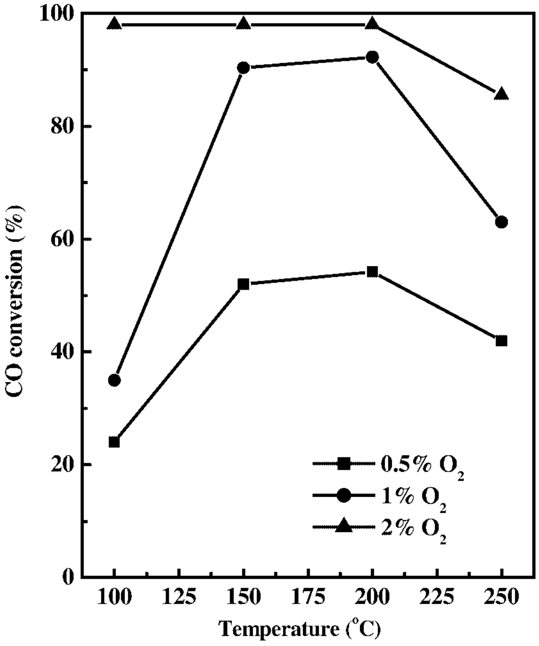

Figure 1. CO conversion with different ratios of O_2 to CO over 5Pt/Al (1% CO, 0.5–2% O_2, H_2 balance, total flow rate 300 ml/min, and $W/F = 0.06$ g s/cm^3).

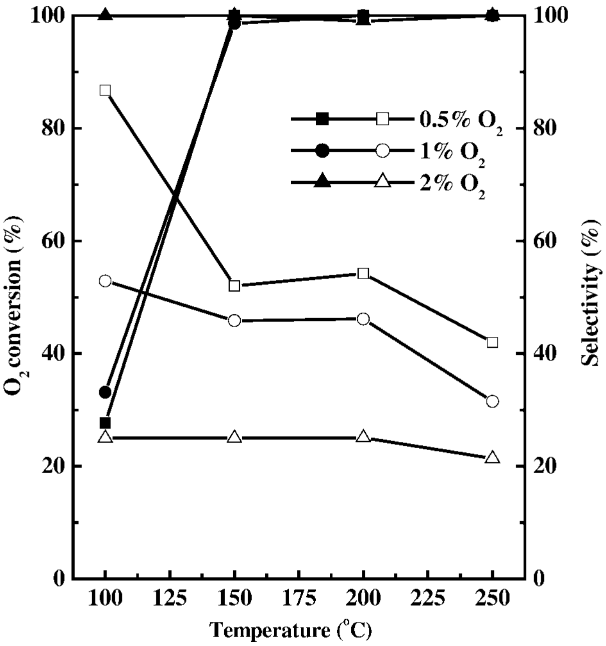

Figure 2. O_2 conversion (filled symbols) and selectivity (open symbols) with different ratios of O_2 to CO over 5Pt/Al (1% CO, 0.5–2% O_2, H_2 balance, total flow rate 300 ml/min, and $W/F = 0.06$ g s/cm^3.

In order to understand the effect of contact time over 5Pt/Al, the *W*/*F* (ratio of the catalyst weight to feed rate) was varied by changing the loading weight of catalyst. Fig-

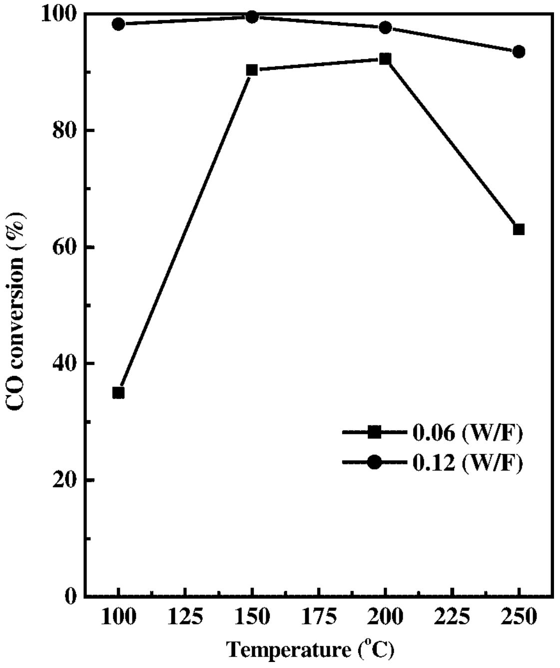

Figure 3. CO conversion with changing ratios of W/F over 5Pt/Al (1% CO, 1% O_2, H_2 balance, and total flow rate 300 ml/min).

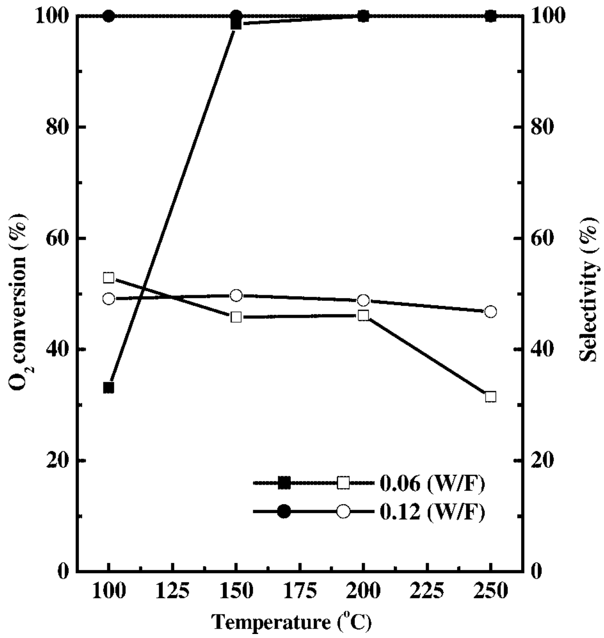

Figure 4. O_2 conversion (filled symbols) and selectivity (open symbols) with changing ratios of W/F over 5Pt/Al (1% CO, 1% O_2, H_2 balance, and total flow rate 300 ml/min).

ure 3 shows that the CO conversion improved with increasing contact time over the entire temperature range and especially at the extremes. Moreover, figure 4 shows that the O_2 conversion was significantly improved at 100 °C and the selectivity was only slightly affected up to 250 °C. These CO conversions are much higher than reported by Watanabe *et al.* [6]. The differences may be due to the pretreatment methods.

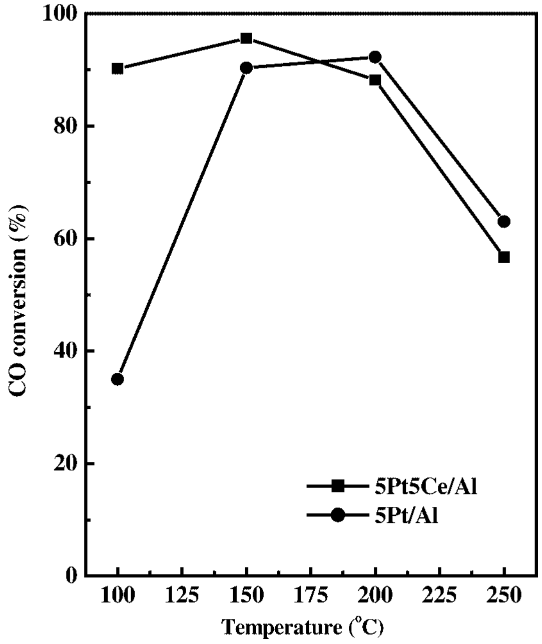

Figure 5. CO conversion over 5Pt/Al and 5Pt5Ce/Al (1% CO, 1% O_2, H_2 balance, total flow rate 300 ml/min, and $W/F = 0.06$ g s/cm^3).

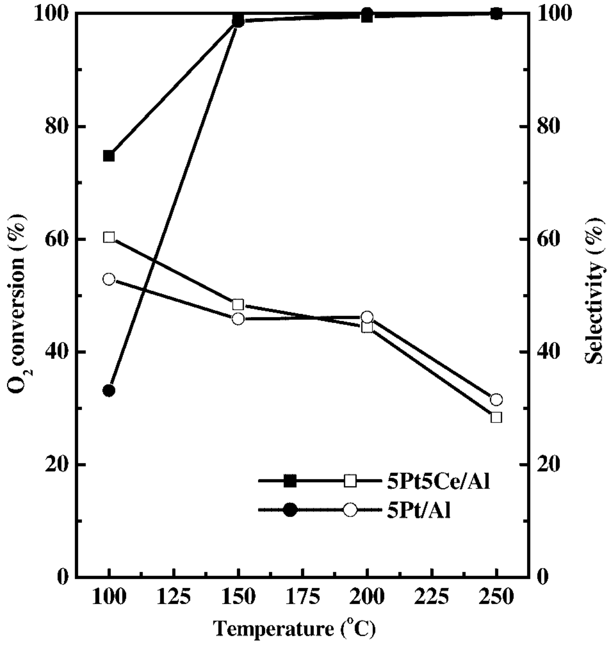

Figure 6. O_2 conversion (filled symbols) and selectivity (open symbols) over 5Pt/Al and 5Pt5Ce/Al (1% CO, 1% O_2, H_2 balance, total flow rate 300 ml/min, and $W/F = 0.06$ g s/cm^3).

Figures 5 and 6 show the effect of adding ceria to 5Pt/Al. 5Pt5Ce/Al showed much higher CO conversion, O_2 conversion and selectivity at 100 °C than 5Pt/Al. At higher temperatures the differences were smaller.

The ratio of O_2 and CO was varied from 0.5 (stoichiometric) to 2.0 (large excess) over 5Pt5Ce/Al and 5Pt/Al at 150 °C (figures 7 and 8). 5Pt5Ce/Al showed much higher CO conversion and selectivity at the stoichiometric ratio. The effect of ceria is small at higher O_2 to CO ratios.

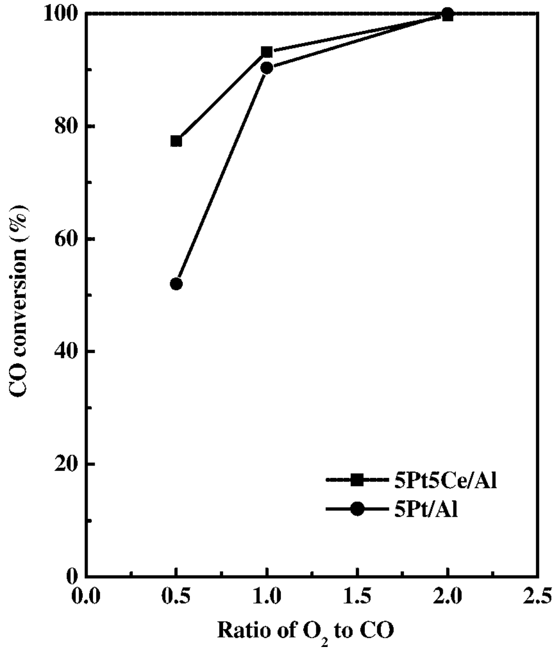

Figure 7. CO conversion with different ratios of O_2 to CO over 5Pt/Al and 5Pt5Ce/Al at 150 °C (1% CO, 0.5–2% O_2, H_2 balance, total flow rate 300 ml/min, and $W/F = 0.06$ g s/cm^3).

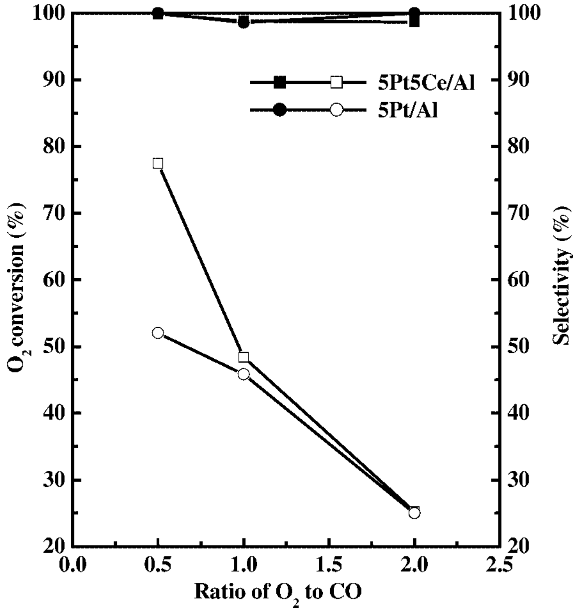

Figure 8. O_2 conversion (filled symbols) and selectivity (open symbols) with different ratios of O_2 to CO over 5Pt/Al and 5Pt5Ce/Al at 150 °C (1% CO, 0.5–2% O_2, H_2 balance, total flow rate 300 ml/min, and $W/F = 0.06$ g s/cm^3).

In summary, a 5Pt/Al catalyst showed high selectivity but low CO conversion at low temperatures (100 °C). Increasing the temperature improved the CO conversion but decreased the selectivity because of the competing H_2 oxidation. The low-temperature conversion could be improved without significant loss of selectivity by increasing the residence time. A less-expensive alternative would be to improve the efficiency of the Pt catalyst. Ceria was added to enhance the oxygen supply to Pt under conditions of low oxygen concentration. 5Pt5Ce/Al significantly improved CO conversion and selectivity at low temperatures (100 °C) and low oxygen concentrations (stoichiometric).

The stability of 5Pt5Ce/Al was tested by monitoring the CO conversion for 15 h and 4 days. The temperature was kept at 200 °C to enhance any deactivation. The CO conversion was stable and even improved slightly (~5%) over this time.

4. Conclusions

The selectivity of CO over H_2 oxidation on a 5 wt% Pt/γ-Al_2O_3 was highest at low temperatures (100 °C) and low O_2/CO ratios (stoichiometric). However, the conversion was rather low and could be improved only by increasing the contact time. Ceria was added by co-impregnation to enhance oxygen supply to the Pt under these conditions. CO conversion and selectivity were significantly improved because the side reaction, hydrogen oxidation, was depressed. Moreover, the catalyst activity for CO conversion was very stable during continuous operation over 4 days at 200 °C.

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