Short communication

The study of the deactivation of water-pretreated Pt/γ-Al$_2$O$_3$ for low-temperature selective CO oxidation in hydrogen

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Abstract

The selective oxidation of carbon monoxide in a hydrogen-rich stream is an important reaction in fuel cell technology. Fuel cells that use hydrogen produced from a combustion source contain small amounts of CO that must be removed to extremely low levels (<10 ppm), otherwise, it will poison the anode of the polymer electrolyte fuel cells (PEFC). Our research group has developed an improved Pt catalyst on alumina using a water-pretreatment method. However, at temperatures below $100\,^\circ$C, water from the hydrogen-oxidation side reaction accumulates on the catalyst causing it to deactivate. To better understand the deactivation, the water-pretreated catalyst was characterized at room temperature ($28\,^\circ$C) and at $50\,^\circ$C with various reaction conditions (O$_2$ and H$_2$O concentration) by analyzing the activity of the catalyst and by measuring the reactor temperature profile using an infrared (IR) camera. The IR images clearly showed a decrease in the reactor temperature over time indicating the deactivation of the catalyst. As the catalyst became more deactivated, the reactor temperature decreased, the H$_2$ and CO conversions decreased, while the CO selectivity increased to nearly 100%.
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1. Introduction

The preferential oxidation (PROX) of CO in a hydrogen-rich environment is important for polymer electrolyte fuel cells (PEFC) because the Pt anodes of PEFC are easily poisoned by CO ($\sim$10 ppm) at low-temperatures. Because the PROX unit lies between the low-temperature shift reactor and the PEFC, the operating temperature range is restrained between 80 and 200 °C. Lower temperature (room temperature) activity is also important for start-up in transportation fuel cells [1].

Pt catalysts can be used for the PROX due to its higher activity around 200 °C with lower CH$_4$ formation rate. However, to satisfy start-up conditions in a transportation fuel cell, lower activity below 100 °C should be improved. The lower temperature activity and selectivity could be improved using smaller particles [1,2], promoters (Fe, Ce or Co) [3–6], formed alloys (PtSn) [7], sol–gel preparation [8], or acidic support [9,10] to overcome startup problems.

Our research group is currently developing improved Pt/γ-Al$_2$O$_3$ catalysts by using a water-pretreatment method to overcome startup problems. The pretreatment involves saturating the reduced catalyst with water and allowing it to vaporize during reduction [1]. The improved catalyst achieves higher CO conversion and selectivity for a wider reaction temperature range (27–200 °C). The water-pretreatment method generates stable, small, and metallic Pt particles ($\sim$2 nm) with a larger "strong metal–support interaction" (SMSI), causing higher H$_2$ spillover [1,2]. However, at temperatures below 100 °C, the CO conversion decreased with improving selectivity due to the accumulation of water from the hydrogen-oxidation side reaction [1]. Contrarily, over 100 °C the addition of H$_2$O enhanced the CO oxidation without an increase in the selectivity. This occurred for the Pt/γ-Al$_2$O$_3$ catalysts and the water-pretreated Pt/γ-Al$_2$O$_3$ [2,4,8,11–16]. The reason for positive water effects is unclear although several mechanisms were suggested.

This paper will study the deactivation of 5 wt.% Pt/γ-Al$_2$O$_3$ catalyst at low-temperatures (28 and 50 °C) with various reaction conditions (O$_2$ and H$_2$O concentration) using infrared (IR) thermography. Because the CO and H$_2$ oxidation reactions are highly exothermic, relatively large

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temperature gradients are present inside the reactor. These temperature gradients can be measured easily using an IR camera. The IR images give the temperature at each point along the tubular reactor. These temperature profiles were recorded at different times after the start of the reaction to quantitatively demonstrate the rate of deactivation of the catalyst.

2. Experimental

The deactivation tests were performed at room temperature ($\sim$28 °C) and at 50 °C. For both reactions, the concentration of CO and O_2 of the effluent gases were measured. At room temperature, an IR camera was used to measure the reactor temperatures. At 50 °C, a furnace was used to heat the reactor prohibiting the use of the IR camera. In both reactions, thermocouples measured the inlet and outlet flow rates.

The water-pretreated 5 wt.% Pt/γ-Al_2O_3 was prepared by the incipient wetness method using alumina (150 m^2/g, acidic type, >60 mesh, Alfa) and Pt ($H_2PtCl_6\cdot6H_2O$, Alfa). The 5 wt.% Pt/γ-Al_2O_3 was calcined in air at 400 °C. The water-pretreatment consists of heating the calcined catalyst in O_2 at 500 °C for 1 h, purging in He for 10 min, and

then reducing in H_2 at 500 °C for 1 h. The desired amount of water was then added to the catalyst. The catalyst was heated to evaporate the excess water and the reaction started [1]. We define the water-pretreated 5 wt.% Pt/γ-Al_2O_3 as water-pretreated 5Pt/Al.

A quartz tube reactor (6 mm i.d.) was used for testing the catalyst and an open type furnace was used to control the reaction temperatures for the reaction at 50 °C. Four mass flow controllers (Tylan Co.) were used to control the mixing of the reaction gases (1% CO, 0.5–1% O_2, 0–10.09% CO_2, 0–30% N_2, 0–2.3% H_2O, H_2 balance, total flow rate: 100 ml/min (STP) and with the 0.1 g catalyst, for more details, see [1]). The water ($\sim$2.3%, saturated water percentage in N_2 at room temperature) was supplied by a bubbler system. To avoid water condensation, heating tape was used to preheat the gas to around 100 °C.

Two thermocouples were used to measure reaction temperatures upstream (SP01) and downstream (SP02) from the catalyst bed (Fig. 1). The distance between the two thermocouples was 4.4 cm. The top thermocouple, which was placed directly on top of the catalyst bed, was used with the furnace to control the reaction temperature. The reacted gases were analyzed using a gas chromatograph (HP 6890) with a TCD detector and an on-line CO analyzer (Thermo-Environmental Instrument, 48C, USA) [1]. The
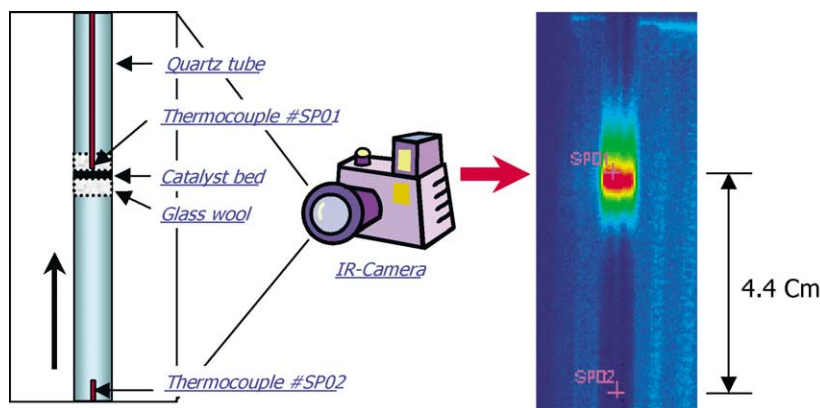

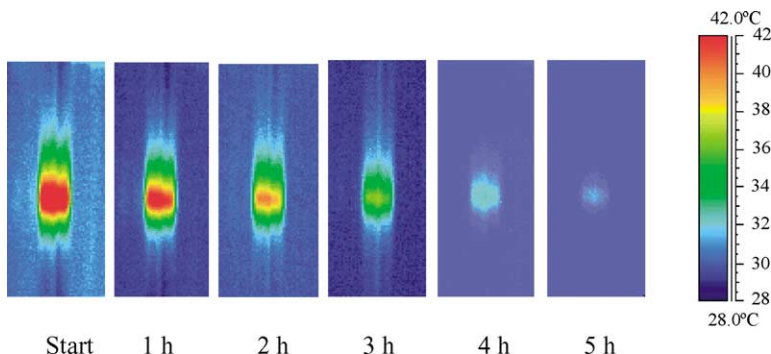Fig. 1. Sample infrared image of the water-pretreated 5Pt/Al catalyst bed in the PROX reaction.

Fig. 2. Infrared images of the water-pretreated 5Pt/Al catalyst bed over time. As the reaction proceeds, water accumulates on the catalyst and deactivates it.

following formulas were used for calculating the conversions of CO and O_2 and the selectivity of CO:

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

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

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

The IR images were recorded with a Flir model SC2000 IR camera. IR radiation was measured in the 7.5–13 μm wavelength range with an internal 7.5 μm cut-off filter. The temperature range of the camera was between −40 and 120 °C with a 14-bit resolution. This gives a relative temperature resolution of less than 0.1 °C and an absolute temperature accuracy of ±2%. The images were recorded with a 320 × 240 focal plane array and a 24° field of view. The reactor length (Fig. 3) was measured by placing an object of known dimension next to the reactor. An image was taken and the pixel/cm ratio was determined. A line was drawn axially through the center of the reactor to give the data seen in Fig. 3. The two thermocouples inserted inside the reactor were used to calibrate the temperature of the IR camera and correct for the effective emissivity of the reactor. The ambient temperature and the distance from the camera to the reactor were also recorded to correct for IR transmission loss. The IR pictures were imported into the software program for post analysis.

3. Results and discussion

The reaction started after flowing the mixed gas of 1% CO and 10.09% CO_2 into the reactor and then suddenly adding 1% oxygen in a well mixed feed gas (30% N_2 and H_2 balance). The reaction temperature reached a maximum after approximately 20 min. The IR images showed that the maximum temperature in the reactor was located in the cat-
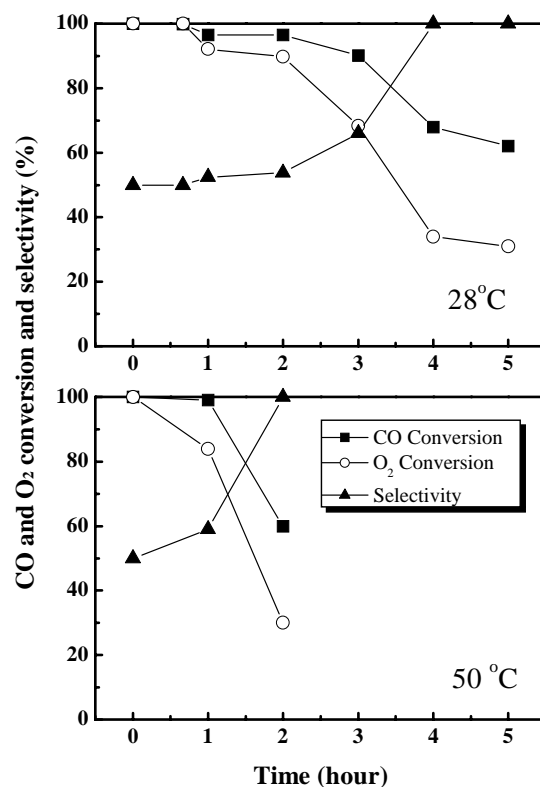

Fig. 4. CO conversion, O_2 conversion, and selectivity vs. time over the water-pretreated 5Pt/Al at room temperature (28 °C) and 50 °C (1% CO, 1% O_2, 10.09% CO_2, 30% N_2, H_2 balance, total flow rate: 100 ml/min, and water/feed gas: 0.06 g S/cm³).

alyst bed and the overall temperature decreased as the water deactivation increased (Figs. 2 and 3). The gray box in Fig. 3 indicates the position of the catalyst. The asymmetry of the temperature shows the amount of heat that is convected downstream by the flowing gases.

The CO conversion, O_2 conversion and selectivity were analyzed with increasing deactivation (Fig. 4a). The CO conversion and the O_2 conversion decreased, while the selectivity increased with time. The selectivity was seen to increase
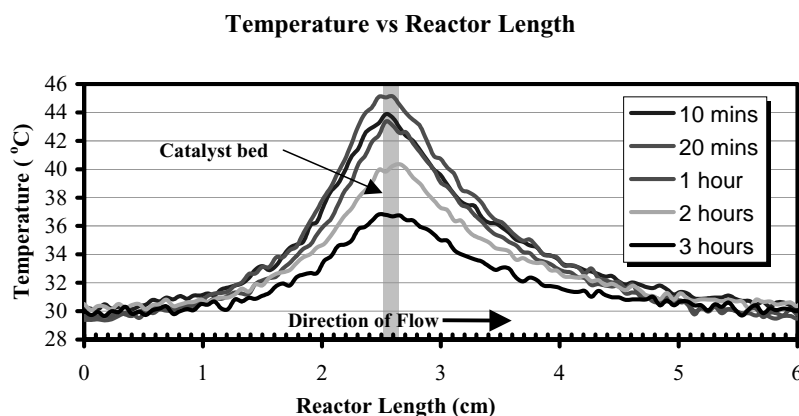
Temperature vs Reactor Length

Fig. 3. Temperature profiles taken from the IR images showing the deactivation of 5Pt/Al.

Table 1
Temperature of the two thermocouples for the reaction at room temperature and 50 °C

Time (h)	Room temperature (28 °C)			50 °C		
	SP01	SP02	ΔT	SP01	SP02	ΔT
Start	46	28	18	50	33	17
1	43	28	15	50	43	7
2	40	29	11	50	45	5
3	37	28	9	–	–	–
4	33	25	8	–	–	–
5	32	24	8	–	–	–

because the H_2 oxidation side reaction decreased. After 4 h, the reactions stayed relatively constant and showed very high selectivity (nearly 100%). The deactivation was caused by the accumulation of water as noted previously [1]. We note that the decrease in O_2 conversion always preceded the decline in CO conversion.

Another deactivation test was performed at a higher temperature of 50 °C to further understand the deactivation and the reaction mechanisms (Fig. 4b). The deactivation was faster as the hydrogen-oxidation occurred more easily at the higher temperature. In addition, the CO conversion and selectivity after 2 h at 50 °C (Fig 4a) were very similar to those after 5 h at 28 °C (Fig. 4b). Table 1 shows the thermocouple readings of the water-pretreated catalyst bed at 28 and 50 °C. The temperature differences (ΔT) at start and after 2 h at 50 °C were very similar to the temperature differences at start and after 5 h at 28 °C.

Fig. 5 shows the effects of O_2 and H_2O concentration in the feed gas on the deactivation of water-pretreated 5Pt/Al at 50 °C as a function of time. With lower O_2 concentration (Fig. 5a), the deactivation was much slower due to slower H_2 oxidation, which causes accumulation of water on the catalyst. When H_2O was added to the feed gas, the deactivation rate was much faster due to faster water accumulation on the catalyst (Fig. 5b). To regenerate the deactivated catalyst by evaporating the water, the reaction temperature was gradually increased to 200 °C in H_2 and then held for 1 h. The activity was again measured after cooling the reactor to 50 °C. After desorbing the water, the deactivated catalyst was regenerated and the CO selectivity and conversion were similar to previous results [1,2].

We propose a deactivation mechanism using the IR images and the reaction activity. The temperature of the catalyst bed increased due to the exothermic CO and H_2 oxidation reactions, which then increased the rate of the hydrogen-oxidation. However, the overall temperature was too low to evaporate the water, causing water to accumulate on the catalyst. As the water accumulated, the CO and H_2 oxidation rates decreased and the overall reaction temperature decreased. When the alumina and Pt saturated with H_2O, the H_2 oxidation reaction on the Pt decreased significantly and the selectivity reached nearly 100%.
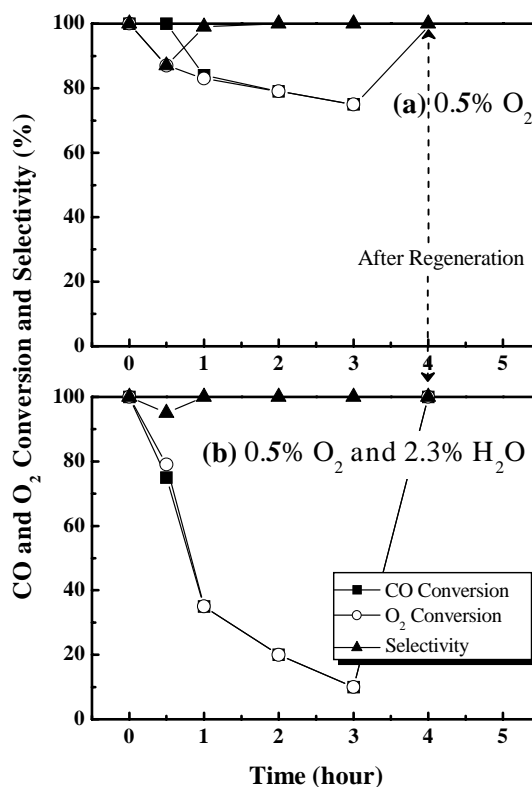

Fig. 5. CO conversion, O_2 conversion, and selectivity vs. time over the water-pretreated 5Pt/Al at 50 °C (1% CO, 0.5% O_2, 0–2.3% H_2O, H_2 balance, total flow rate: 100 ml/min, and water/feed gas: 0.06 g S/cm^3). The catalyst was regenerated by increasing the reaction temperature to 200 °C in H_2 for 1 h.

4. Conclusion

The deactivation of water-pretreated Pt catalyst on alumina was characterized by detailed temperature measurements using an IR camera and thermocouples, and by measuring the outlet gas concentrations. The reaction temperatures decreased over time as water, generated by the hydrogen-oxidation side reaction and water in the feed gas, accumulated on the catalyst. After the catalyst became deactivated, it was heated above 100 °C for several minutes and the catalyst was regenerated. The role of the hydrogen-oxidation side reaction at lower temperatures is just the opposite of that at higher temperatures where hydroxyl groups increase the CO oxidation. It helped, however, the selectivity at lower temperatures.

Acknowledgements

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