RESEARCH NOTE

Promotion of Pt/γ-Al$_2$O$_3$ by New Pretreatment for Low-Temperature Preferential Oxidation of CO in H$_2$ for PEM Fuel Cells

I. H. Son,* M. Shamsuzzoha,† and A. M. Lane*,[1]

*Department of Chemical Engineering, University of Alabama, Tuscaloosa, Alabama 35487; and †School of Mines and Energy Development and Department of Metallurgical & Materials Engineering, University of Alabama, Tuscaloosa, Alabama 35487

The hydrogen-rich reformate used as a feed to polymer electrolyte fuel cells (PEFC) must contain less than 10 ppm CO since it poisons the Pt anode. The concentration of CO leaving the water–gas shift reactor is typically around 1 mol%, which is set by thermodynamic equilibrium. One method to remove the CO is by preferential oxidation (PROX) using O$_2$ over a (typically) Pt catalyst while minimizing the amount of H$_2$ oxidized. The activity and selectivity of this reaction were improved by a new pretreatment method for a 5 wt% Pt/γ-Al$_2$O$_3$ catalyst. The pretreatment involved saturating the reduced catalyst with water and allowing it to vaporize during reduction. The improvement is attributed to a reduction in size of the metallic Pt particles as measured by XRD and TEM. © 2002 Elsevier Science (USA)

Key Words: pretreatment; CO; selectivity; low temperature; preferential oxidation; Pt; γ-Al$_2$O$_3$; fuel cells; small Pt particles; deactivation.

I. 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: (a) hydrogen is produced by *autothermal reforming* of a hydrocarbon (fuel + O$_2$ + H$_2$O ↔ CO$_x$ + H$_2$), where without water it is *partial oxidation* and without oxygen it is *steam reforming*; (b) the water–gas shift reaction (CO + H$_2$O ↔ CO$_2$ + H$_2$) eliminates most of the CO, producing more hydrogen; and (c) any remaining CO is reduced to parts-per-million 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 U.S. 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 the state-of-the-art PROX catalyst and reaction system. It can achieve low concentrations of CO (10–20 ppm) in a multistage reactor over a Pt/Al$_2$O$_3$ or Ru/Al$_2$O$_3$ 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-temprature shift reactor (∼200°C) and the PEFC (∼80°C), it should operate between these temperatures.

PROX system operation at low temperature (room temperature) is also very important for start-up in transportation application fuel cells. Therefore, the PROX system must operate over a wide temperature range to be practical (3).

Supported noble metal catalysts, such as Pt, Ru, and Au, have been effective for the PROX reaction (4–7). For low temperatures, highly dispersed gold on an oxide support showed high activity and selectivity (maximized at 80°C) (5). However, the activity strongly depended on the preparation of the catalysts. The CO conversion and

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[1] To whom correspondence should be addressed.

selectivity were lower at higher temperatures (150–200°C) because of H$_2$ oxidation and the selectivity decreased at low CO concentrations. Supported Pt had a high conversion of CO at high temperatures (150–250°C) but the activity decreased at low temperatures. In addition, methanation did not occur even at high reaction temperatures (300°C) (4, 6). Therefore, supported Pt would be a practical PROX catalyst if the low-temperature activity (25–100°C) could be improved.

Altman and Gorte (8, 9) found that interactions between Pt particles and CO were affected by the size of the Pt particles; small Pt particles have a strong CO interaction, while bulk Pt has weak CO interaction. In addition, smaller Pt particles can show higher CO oxidation activity than can bulk Pt (10, 11).

The sol–gel method is effective for making very small particles of Pt but is very sensitive to preparation conditions. However, using this method, Seker and Gulari (12) were able to modify the dispersion of Pt and improve the activity of NO$_x$ reduction.

In this study, a new pretreatment method for Pt/γ-Al$_2$O$_3$ is described. The activity and selectivity for the PROX reaction are significantly higher than the same catalyst prepared with a conventional pretreatment, especially at low temperatures. Improvements are attributed to particle size as measured by XRD and TEM.

II. EXPERIMENTAL

The 5 wt% Pt/γ-Al$_2$O$_3$ (abbreviated 5Pt/Al) was prepared by the incipient wetness method. Alumina (150 m^2/g, acidic type, $\sim$0.25 mm, Alfa) was impregnated using an aqueous solution of H$_2$PtCl$_6 \cdot$6H$_2$O (Alfa). The catalyst was dried in an oven at 120°C for 24 h and calcined in air at 400°C for 2 h. Before the reaction, the catalyst ($\sim$0.25 mm) was heated again in O$_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. This is considered the standard pretreatment method and the reaction was started at 27°C.

In the water pretreatment method, the catalyst was pretreated as described above. However, after reduction in hydrogen for 1 h, the reactor was cooled to around 30°C and approximately 5 ml distilled water, enough to wet the catalyst, was added to the catalyst bed (13). The water was evaporated in the hydrogen atmosphere while the temperature was increased to 500°C at 10°C/min and then held at 500°C for 1 h. After cooling, the reaction was then started at 27°C.

Figure 1 is a diagram of the reactor. The reactor was a vertical quartz tube (6-mm I.D.) with the gas flow upward. The test conditions were 27–250°C, 1 atm, and a total flow rate of 100 ml/min (STP) using 0.1 g catalyst. The catalyst bed was held in place with glass-wool plugs. The reaction temperature was measured with two thermocouples, located
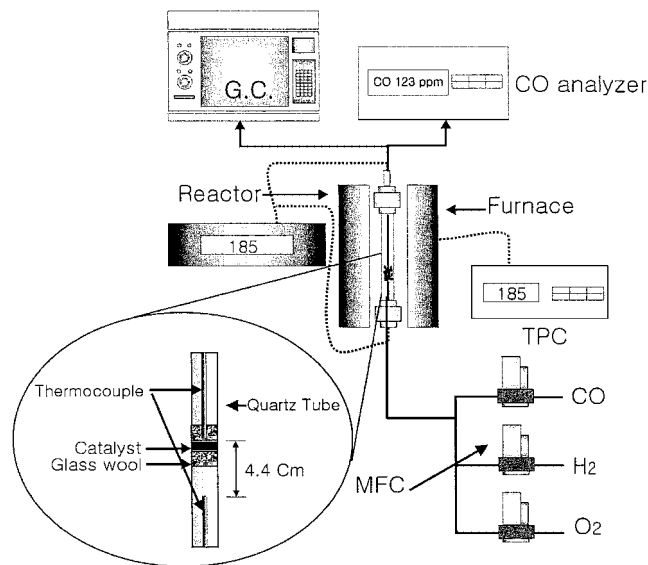

FIG. 1. Schematic of PROX reactor.

on both sides of the catalyst bed in the reactor. The distance between the two thermocouples was $\sim$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 maximum temperature difference was almost 20°C between the thermocouples because of the highly exothermic reactions. It is noted that to date most studies of the PROX reaction fail to report the temperature gradient (6).

Gas compositions (1% CO, 1% O$_2$, and balance H$_2$) were set by mass flow controllers (Tylan Co., U.S.). A gas chromatograph (HP 6890) with a HAYESEP DB column and TCD detector was used for measuring the concentrations of O$_2$, CH$_4$, and CO$_2$. An online CO analyzer (Thermo-Environmental Instrument, 48C, U.S.) sensitive to parts-per-million levels was used for measuring accurate CO concentrations. The conversions of CO and O$_2$ and the selectivity of CO were calculated using the following formulas:

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

X-ray diffraction (XRD) was performed with a Rigaku power diffractometer using nickel-filtered Cu$K\alpha$ radiation (40-kV tube voltage and 40-mA tube current). For crystal-phase identification, typical operating parameters were a 20–140°2θ scan range, a 2°/min scan rate, and a 0.02° data interval.

TEM (transmission electron microscope) specimens were obtained by crushing the catalyst powder and

preparing a colloidal suspension in ethanol. The suspended particles were scooped up with a carbon-coated Cu grid. The samples were sufficiently thin to be electron transparent and were investigated using a 200-keV Hitachi H-8000 TEM. Electron diffraction patterns taken from a thin foil specimen of a very-high-purity (99.999%) aluminum were used to determine an accurate calibration constant for the microscope parameters.

III. RESULTS AND DISCUSSION

Figure 2 shows the CO conversion and Fig. 3 shows the selectivity and O_2 conversion for the standard and water pretreatment catalysts. The reaction was started at room temperature and increased in 50°C increments. Measurements at each temperature were taken after 30 min to allow the reaction to stabilize. The initial conversion at each temperature was several percent higher than reported and fell quickly to a steady value (in the time scale of this experiment). This behaviour was probably due to the physical adsorption of water at the lower temperatures. A scan from high to low temperature did not follow the same path (activities were higher) and depended on the rate of descent. Equal concentrations of CO and O_2 were used.

After the standard pretreatment, the CO and O_2 conversion slowly increased with the reaction temperature and reached a maximum above 150°C. The selectivity at high temperatures improved to nearly the theoretical maximum of 50% at complete O_2 conversion. The CO and O_2 conversions correspond very well with the results of Watanabe
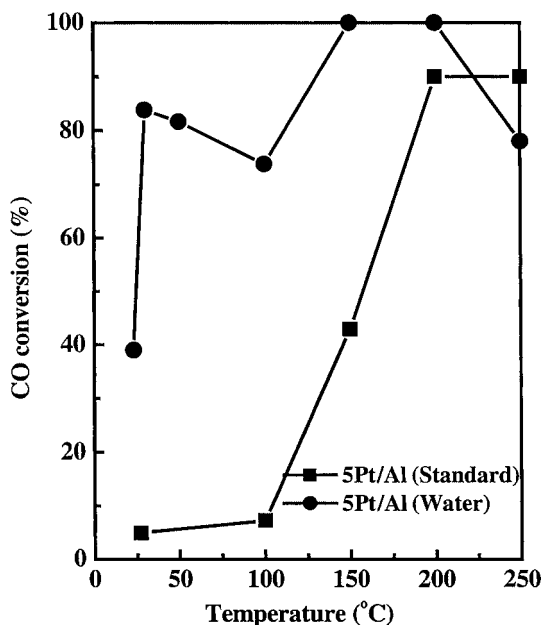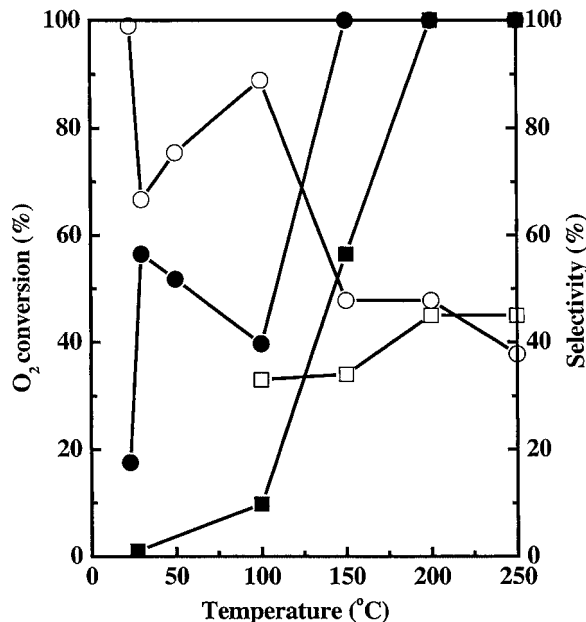

FIG. 3. O_2 conversion (filled symbol) and selectivity (open symbol) using standard pretreatment and water pretreatment 5Pt/Al catalysts (standard pretreated 5Pt/Al (■ □) and water pretreatment 5Pt/Al (● ○); 1% CO, 1% O_2, and H_2 balance; total flow rate, 100 ml/min).

and co-workers [7] using a similar catalyst and reaction conditions. GC peaks corresponding to side reactions, such as CH_4 or CH_3OH, were not observed. Therefore, in this temperature range the only side reaction was oxidation of H_2 to form H_2O.

The conversion and selectivity of water-pretreated 5Pt/Al were much greater, especially at lower temperatures. Oxidation of both CO and H_2 increased dramatically between 27 and 30°C due to ignition of the reaction: the actual temperature of the catalyst bed should be higher due to the exothermic reactions. The CO conversion generally increased with temperature and peaked between 150 and 200°C. The curious but repeatable dip in conversion between 30 and 100°C will be discussed later. However, since the O_2 conversion decreased more than the CO conversion in this temperature range, the selectivity improved.

In some ways, these results are typical of low-temperature PROX catalysts (5). The CO conversion generally goes through a maximum as temperature is varied. Some H_2 oxidizes at low temperatures, which increases the actual catalyst bed temperature as opposed to the furnace, or inlet, temperature usually reported. Thus, CO oxidation begins at a lower apparent temperature than might be expected. At higher temperatures, the CO bond becomes weaker and more H_2 oxidation occurs (4, 5). On some catalysts, methanation has been observed at higher temperatures (6).

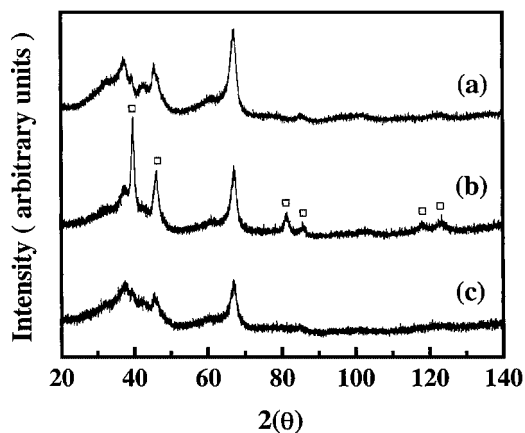X-ray diffraction (XRD) was applied to determine the structure of the Pt particles present in different pretreated

FIG. 2. CO conversion using standard pretreatment and water pretreatment 5Pt/Al catalysts (1% CO, 1% O_2, and H_2 balance; total flow rate, 100 ml/min).

FIG. 4. XRD spectra after reaction of (a) γ-Al$_2$O$_3$, (b) standard pretreatment 5Pt/Al, and (c) water pretreatment 5Pt/Al (metallic Pt peaks ($\square$)).

catalysts after reaction. The XRD patterns of all catalysts in Fig. 4 contain broad diffraction peaks due to poorly crystalline grains of alumina. The pattern for the standard pretreatment catalyst contains additional diffraction peaks due to metallic Pt crystals. The absence of Pt peaks for the water pretreatment catalyst could result from Pt particles that are either amorphous or too small to be detected by X-ray diffraction methods. The lower intensity of the alumina peaks for the water-pretreatment catalyst may be a consequence of greater surface coverage by the smaller Pt particles.

Seker and Gulari (12) reported similar absences of diffraction peaks due to Pt particles in the XRD pattern of a sol–gel 2% Pt/alumina catalyst containing Pt particles of size ranging between 2 and 5 nm. They also found larger Pt particles and a similar diffraction pattern for a 2% Pt/alumina catalyst prepared by conventional methods.

Transmission electron microscopy (TEM) was applied to ascertain the crystallinity as well as the size of the Pt particles in these catalysts. Crystals of Pt are expected to yield a highly contrasted and morphologically resolved image compared to the faintly contrasted image of the poorly crystalline grains of the alumina. Figure 5 shows TEM bright-field micrographs of the catalysts. The micrographs exhibit well-contrasted particles, presumably of Pt, scattered on the surface of the lightly contrasted matrix. The size of the contrasted particles measured from a number of such TEM micrographs ranged between 10 and 30 nm (average particle size: ~16 nm) for the standard pretreatment catalyst and between 1 and 5 nm (average particle size: ~2 nm) for the water pretreatment catalyst. The contrasted particles of both catalysts were also subjected to crystallographic identification. In this process microdiffraction patterns (one such pattern is shown in Fig. 5c) were taken by irradiating a 5-nm electron beam solely on the particles. Analyses of the
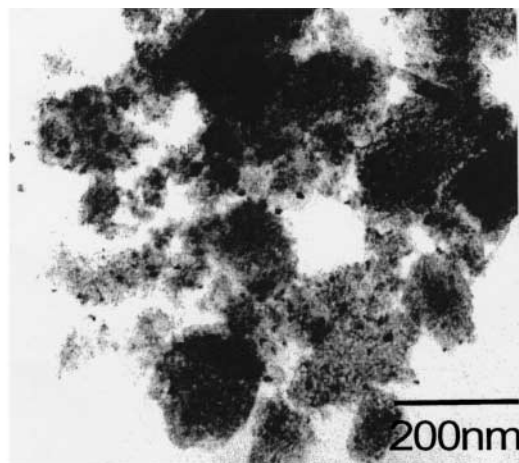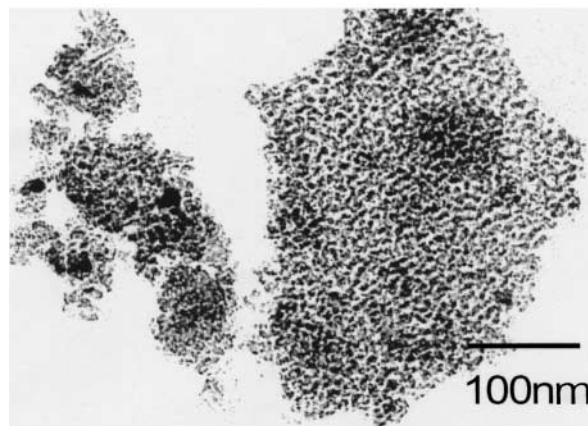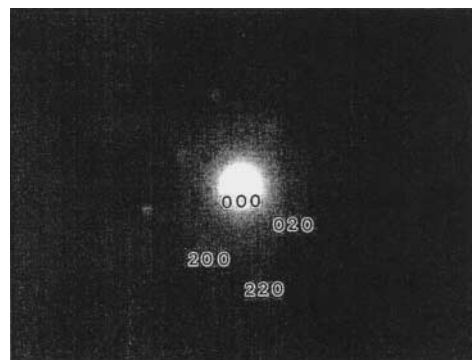
FIG. 5. TEM images of (a) standard pretreatment 5Pt/Al, (b) water pretreatment 5Pt/Al, and (c) the microdiffraction pattern of water pretreatment 5Pt/Al after reaction.

microdiffraction patterns taken along various major zone axes of the particles yielded a face-centered cubic lattice with a cell parameter of 3.97 Å, which agrees well with that of Pt. These structural investigations revealed that both
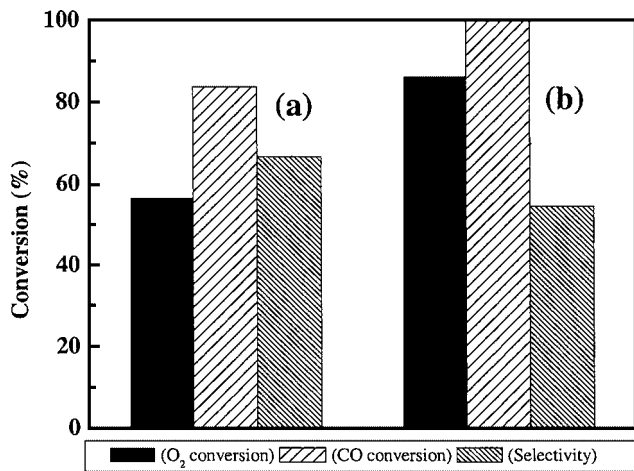
FIG. 6. O_2 conversion, CO conversion, and selectivity of water pretreatment 5Pt/Al at 30°C ((a) before increasing temperature and (b) after increasing temperature; 1% CO, 1% O_2, and H_2 balance; total flow rate, 100 ml/min).

catalysts have particles of crystalline Pt affixed on the surface of the alumina matrix.

Figure 2 showed that the conversion of CO decreased with temperature in the range 30–100°C while the selectivity increased. The following experiment was conducted to gain insight into this behavior. The water pretreatment catalyst was gradually deactivated at 30°C by running the reaction with 1% O_2, 1% CO, and balance H_2 in the feed gas for 2 h. It was then heated at 250°C under reaction conditions for 1 h and then quickly cooled again to 30°C by opening the furnace. Figure 6 shows that the CO conversion and O_2 conversion increased (in fact, the CO was less than 10 ppm) while the selectivity decreased. Moreover, the CO conversion decreased and the selectivity increased over time as the reaction continued.

Small Pt particles are known to interact more strongly with CO and have higher CO oxidation activity than large Pt particles or bulk Pt (8–10). This suggests an explanation of the low-temperature reaction behavior of these catalysts. For simplicity, imagine that only small and large sizes of Pt particles exist with the following hypothetical properties. The small particles strongly react with CO, even at low temperatures, to the exclusion of H_2. They cannot adsorb much heat so the microscopic temperature rise due to exothermic reactions may be quite large. This contributes to the high activity and keeps water from physically adsorbing on the surface. The large particles are not so active or selective and oxidize both CO and H_2, with the selectivity for CO oxidation increasing with temperature. The large particles can adsorb more heat, so the microscopic temperature rise may not be high enough to desorb the water. The buildup of water slowly deactivates the large particles.

The water pretreatment catalyst contains primarily small Pt particles. CO conversion on the small particles is very

high at low temperatures. As the temperature increases, more H_2 oxidation occurs on the large particles, with cumulative deactivation by water adsorption. This causes a net decrease of CO conversion but also eliminates H_2 oxidation, so the selectivity increases. At 100°C, the water desorbs from the catalyst, so all particles are active for CO and H_2 oxidation. The CO conversion increases again but the selectivity decreases. If water is completely removed from the surface by heating to 250°C, when returned to 30°C all sites will be momentarily active, resulting in a high conversion and low selectivity (Fig. 6).

The standard pretreatment catalyst contains primarily large Pt particles. At low temperature, these are more active for H_2 oxidation and the active sites are quickly deactivated by water adsorption. The activity remains low until 100°C, where the water desorbs and CO oxidation can occur. The selectivity for CO oxidation is large at the higher temperatures.

This explanation qualitatively describes the observed behavior of the water and standard pretreatment catalysts. In fact, the XRD and TEM analyses showed that particle size was a major difference between the catalysts.

The water pretreatment catalyst offers some advantages over the standard pretreatment catalyst. It is more active and selective over a very broad range of temperatures. For the PROX reactor's typical operating temperatures of 100–200°C the conversion and selectivity are substantially higher. In addition, at low temperatures, which could be encountered during start-up of the car, the catalyst also has a very high conversion and selectivity.

We could not measure the dispersion successfully over the water-pretreated 5Pt/Al since the various CO and H_2 chemisorption experiments were complicated by H_2 spillover. However, we could indirectly estimate the dispersion by calculating composition from the XPS peak area: the dispersion of standard and water-pretreated 5Pt/Al were 33 and 41% after reaction, respectively. Although this is too low to reflect the small particles observed by TEM, it does demonstrate a trend.

We believe that the water pretreatment effects were not caused by Cl impurities from the precursor of Pt since we obtained similar results with 5 wt% of a nitrate-type Pt ($(NH_3)_2Pt(NO_2)_2$, Alfa) loaded on γ-Al_2O_3.

A topic of current research is the mechanism by which this pretreatment method decreases the Pt particle size. Also being explored is the range of operating parameters, including tolerance to the other reformate gases, such as H_2O, CO_2, and N_2.

IV. CONCLUSION

In order to avoid deactivation of the PEFC anode by CO from the reforming gas, preferential oxidation (PROX) of CO was used for supplying pure hydrogen.

Low-temperature preferential oxidation of CO is very important for start-up. In order to satisfy this condition, a Pt/γ-Al$_2$O$_3$ catalyst was improved by a new method of pretreatment, involving saturation with water during reduction. After reaction, XRD and TEM analyses showed that small metallic Pt particles ($\sim$2 nm) exist on the water pretreatment catalyst, while larger metallic Pt particles ($\sim$16 nm) exist on the standard pretreatment catalyst. The small metallic Pt particles showed higher activity and selectivity over a broad temperature range: 27–200°C. Below 100°C, water adsorption caused a reversible deactivation.

ACKNOWLEDGMENT

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