

# Characterization of Enhanced CO Oxidation Activity by Alumina Supported Platinum Catalyst

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## Abstract

A novel pretreatment technique was applied to the conventional Pt/alumina catalyst to prepare for the highly efficient catalyst for the preferential oxidation of carbon monoxide in hydrogen-rich condition. Their performance was investigated by selective CO oxidation reaction. CO conversion with the oxygen-treated Pt/Alumina catalyst increased remarkably especially at the low temperature below 100°C. This result is promising for the normal operation of the proton exchange membrane fuel cell (PEMFC) without CO poisoning of the anode catalyst. XRD analysis results showed that metallic Pt peaks were not observed for the oxygen-treated catalyst. This implies that well dispersed small Pt particles exist on the catalyst. This result was confirmed by high resolution transmission electron microscopy (HRTEM) analysis. Consequently, it can be concluded that highly dispersed Pt nanoparticles could be prepared by the novel pretreatment technique and thus, CO conversion could be increased considerably especially at the low temperatures below 100°C.

**Key Words :** Preferential oxidation of CO, PEMFC, Pt/Alumina catalyst, XRD

## 1. Introduction

As the depletion of fossil fuels increases, development of alternative energy source has been a critical issue of the world. Fuel cell has been considered as one of the major alternative energy source. Among them, the proton exchange membrane fuel cell (PEMFC) has been one of the most promising candidates for its low operation temperature, high efficiency, high power density, and possible substitution for automobile engines. The fuel for the PEMFC is hydrogen. Hydrogen is typically produced by reforming of hydrocarbons such as methanol and gasoline. After the reforming, the reformat hydrogen gas is purified by water-gas shift (WGS) reaction to reduce the CO concentration to ~1%<sup>1,2)</sup>. However, Pt anode catalysts are ex-

tremely intolerant to CO poisoning, the reformat hydrogen gas should be purified further to less than 10ppm level of CO concentration using the preferential oxidation (PROX) reaction of carbon monoxide<sup>1-4)</sup>. Because there are competing reactions of CO oxidation and hydrogen oxidation, the PROX catalyst should preferentially oxidize CO while restraining the hydrogen oxidation to minimize the loss of the fuel. In addition, the catalyst is demanded for 99% of the CO oxidation to prevent CO poisoning of the Pt anode of the fuel cell and for low temperature operation due to operation temperature limit between the final reforming processor (~200°C) and the PEMFC (~80°C).

Noble metal catalysts such as Pt, Ru, and Rh supported over reducible oxide has been proposed for the PROX reaction<sup>1-7)</sup>. They are known to be highly active in CO oxidation. However, they oxidize a noticeable hydrogen in the presence of excess oxygen leading to the loss of the hydrogen fuels. Highly dispersed Au catalysts over metal oxide also show high CO oxi-

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dation in wide temperature ranges, but are very sensitive to the preparation method and deactivate rapidly by the produced  $\text{CO}_2$ <sup>8,9</sup>. Recently, Cu-Ce type catalysts have been studied to replace the precious noble catalysts, but they also have disadvantages of losing catalytic activity and decreasing selectivity in the presence of  $\text{H}_2\text{O}$  and  $\text{CO}_2$ <sup>10,11</sup>.

Pt supported over  $\text{Al}_2\text{O}_3$  has been one of the most widely used catalysts for the PROX reaction since it was first proposed by Los Alamos National Laboratory<sup>1</sup>. This catalyst is effective for the selective CO oxidation at high temperature ranges of 150–250°C. Therefore, enhancement of selective oxidation at low temperatures below 100°C has been a challenge for this catalyst. The selective CO oxidation is known to be increased considerably even at the low temperatures below 100°C as the particle size of the Pt catalyst decreases<sup>12,13</sup>. Consequently, highly dispersed small Pt particles are expected to be a promising catalyst for the PROX reaction at the low temperatures.

In this study, pretreated Pt/ $\text{Al}_2\text{O}_3$  catalyst with water and oxygen was prepared. Catalytic activity of the catalyst was investigated in hydrogen-rich condition. The performance was characterized by high resolution transmission electron microscopy (HRTEM) and X-Ray diffraction (XRD) analysis in terms of the Pt particle size.

## 2. Materials and Methods

### 2.1. Catalyst preparation

Three different types of the Pt catalyst supported over alumina were prepared in this experiment. Dried alumina ( $\gamma\text{-Al}_2\text{O}_3$ , 150  $\text{m}^2/\text{g}$ , acidic type, >60 mesh, Alfa Aesar) in an oven at 120°C for 24 h was impregnated on to an aqueous solution of Pt precursor ( $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ , Alfa Aesar) to prepare for the Pt/ $\text{Al}_2\text{O}_3$  catalyst. The catalyst was dried in an oven at 120°C for 24 h. The catalyst was calcined in air at 400°C for 2 h. After calcination, the catalyst was oxidized at 500°C for 2 h with pure  $\text{O}_2$ , purged with He for 15 min, and then reduced at 500°C for 1 h with pure  $\text{H}_2$ . This catalyst is the conventional Pt/ $\text{Al}_2\text{O}_3$  catalyst and is abbreviated as Pt-A.

After the Pt/ $\text{Al}_2\text{O}_3$  catalyst was cooled to room tem-

perature, 5 ml of water was added to the catalyst at a flow rate of 0.25 ml/min using a syringe pump in  $\text{H}_2$  flow. After wetting, the catalyst was heated to 500°C at a ramping rate of 10°C/min and was reduced at 500°C for 1 h with  $\text{H}_2$ . This water-treated catalyst is abbreviated as w-Pt-A.

A novel approach of pretreatment technique was applied to the conventional Pt/ $\text{Al}_2\text{O}_3$  catalyst. After cooling, 5 ml of water was added to the catalyst at a flow rate of 0.25 ml/min using a syringe pump in  $\text{H}_2$  flow while 1%  $\text{O}_2$  was allowed to flow at the same time. Then, the catalyst was heated to 500°C at a ramping rate of 10°C/min and was reduced at 500°C for 1 h under hydrogen atmosphere. This oxygen-treated catalyst is abbreviated as o-Pt-A.

### 2.2. PROX reaction experiment

The PROX reactions on the catalysts were performed in an atmospheric continuous flow reactor. Vertical quartz tube (6 mm I.D.) was used as the reactor and the catalyst was loaded in the reactor with glass wool plugs. The reaction was conducted in the temperature ranges of 25–250°C with atmospheric pressure. Total flow rate of the reaction gases was 100 ml/min and 0.1 g of the catalyst was used. Thermocouple located inside the reactor was used to control the reaction temperature by the temperature controller connected to the furnace.

All gases ( $\text{H}_2$ ,  $\text{O}_2$ , CO, He, air) with ultra-high purity were supplied by airgas Co. and were further purified using 5Å molecular sieve to remove traces of water and other impurities. Gas flowrates were controlled using mass flow controllers (8100 Celerity, Inc.). A Hewlett Packard gas chromatograph (HP 6890 GC) equipped with a ShinCarbon ST 100/120 micropacked column (Restek Corp., U.S.A.) and a thermal conductivity detector (TCD) was used to measure the concentrations of the reaction gases. Exit gas from the reactor flowed through the gas sampling loop (250  $\mu\text{L}$ ) and was vented to the atmosphere. Gases filled in the loop were swept by helium carrier gas for the GC analysis by turning the 6-way sampling valve lever. For the quantitative GC analysis, each specific gas was calibrated according to the concentrations.

### 2.3. X-Ray Diffraction (XRD) analysis

XRD analysis was performed using a Phillips PW3830 x-ray diffractometer operated at 40 kV and 35 mA. The scan range was 30–60°  $2\theta$  at a rate of 0.04°/min with a data interval of 0.2°. The x-ray source was Cu  $K\alpha$ .

### 2.4. High Resolution Transmission Electron Microscopy (HRTEM)

The particle size and dispersion of the Pt nanoparticles over alumina support was observed by an FEI Technai F20 super twin HRTEM. Fine powder was obtained by crushing the catalyst samples in a mortar with a pestle. The powder samples were transferred to a 5 ml ethanol solution and was sonicated to produce a suspension of the particles in the ethanol solution. A 1 ml solution was collected using a pipette and deposited onto a 3 mm C/Cu grid. The grid was placed onto a silicon wafer and was allowed to dry under atmospheric conditions. The samples were then analyzed by the HRTEM.

## 3. Results and Discussion

### 3.1. CO oxidation activity

Catalytic CO oxidation was conducted in the PROX reactor described above using the three different catalysts of Pt-A, w-Pt-A, and o-Pt-A. The catalyst was loaded in the reactor and was conditioned at 125°C for 1 h under H<sub>2</sub> flow of 98 ml/min. The reactor was then cooled to room temperature under the H<sub>2</sub> flow. Reaction gases of O<sub>2</sub> and CO were started to flow at a flow rate of 1 ml/min, respectively and allowed to stabilize for 1 h before the sample of the exit gas was sent to GC for analysis. For the reactions at 25, 50, and 75°C, the temperature was ramped to 125°C after the reaction and allowed to stabilize for 30 min under pure H<sub>2</sub> flow of 98 ml/min to remove any water formed on the catalyst from previous experiments below 100°C. For the reactions at or above 100°C, the reaction was performed at the temperatures without conditioning at 125°C.

CO conversions of the catalysts are shown in Fig. 1. With increase in the reaction temperature, the CO conversion increased to reach a maximum at 150°C. A

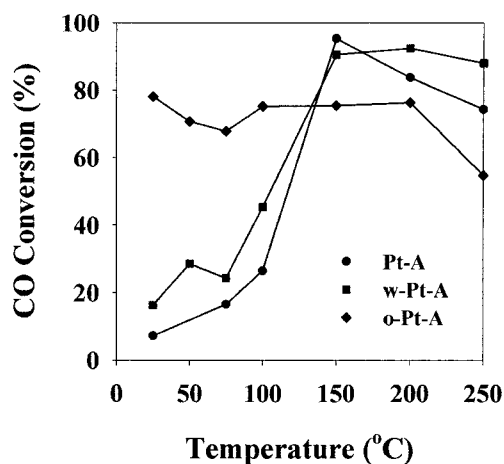


Fig. 1. CO conversion of the Pt-A, w-Pt-A, and o-Pt-A catalysts.

slight decrease of the CO conversions below 100°C for both the w-Pt-A and o-Pt-A catalysts were thought to be due to the formation of water resulting from the H<sub>2</sub> oxidation. Water can adsorb to the Pt surface to cause deactivation for the CO oxidation. At or above 100°C, the CO conversion increased again because of the desorption of the adsorbed water on the Pt surface. As shown in Fig. 2, O<sub>2</sub> conversion continuously increased with the reaction temperature to reach almost 100% at 150°C for all the catalysts. The O<sub>2</sub> conversions were in the order of o-Pt-A > w-Pt-A > Pt-A for all the reaction

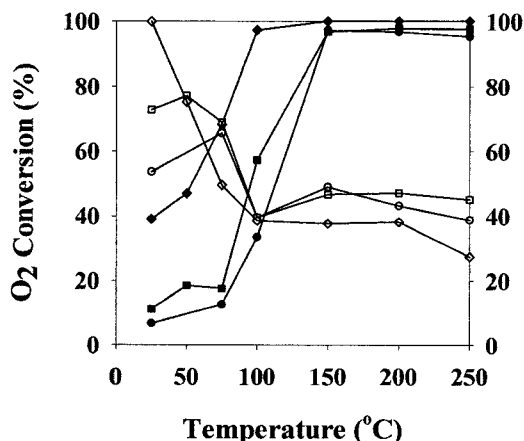


Fig. 2. O<sub>2</sub> conversion (filled symbol) and CO selectivity (open symbol) of Pt-A (●, ○), w-Pt-A (■, □), o-Pt-A (◆, ◇) catalysts.

temperature ranges. The CO selectivity decreased to around 40% with increase in the reaction temperature. This can be explained by the fact that the ignition of the H<sub>2</sub> oxidation started with increase in temperature. As the reaction temperature increased, CO-Pt bond becomes weaker and more H<sub>2</sub> oxidation occurs. In this study, no other side reactions such as formation of CH<sub>4</sub> and CH<sub>3</sub>OH were observed by GC peaks. This fact implies that the only side reaction was H<sub>2</sub> oxidation. This result agrees well with other investigators<sup>3,5</sup>.

As shown in Fig. 1, o-Pt-A catalyst showed much higher CO conversion than those of other catalysts at low temperatures below 100°C. The CO conversion of the w-Pt-A catalyst was higher than that of the conventional Pt-A. In the preparation of the water-treated catalyst, addition of water makes the hydroxyl-rich condition on the catalyst surface. This can cause an enhancement of the hydrogen spillover to increase strong metal support interaction (SMSI)<sup>5,14</sup>. As a result, Pt particles become well dispersed and smaller. Small Pt particles are known to interact more strongly with CO and have higher CO oxidation activity than large Pt particles or bulk Pt<sup>15</sup>. This can explain the higher CO conversions with both o-Pt-A and w-Pt-A at the low temperatures.

The o-Pt-A catalyst is prepared with oxygen flow in hydrogen atmosphere during and after the water treatment process. It can oxidize the hydrogen to form water. It has advantages over the water treatment in terms of supplying water continuously to make more hydroxyl-rich condition on the catalyst surface throughout the reduction process. Increase in hydrogen spillover can enhance SMSI. Therefore, dispersion of the Pt particles can be increased to produce smaller Pt particles.

The effect of the flowrate ratio of O<sub>2</sub> to CO on the CO oxidation reaction was investigated using the o-Pt-A catalyst. With 1% of CO and H<sub>2</sub> balance, the O<sub>2</sub> concentration was varied with 0.5, 1, and 2%. With increase in the O<sub>2</sub> concentration, the CO conversion increased remarkably as can be seen in Fig. 3. The CO conversion with 1% O<sub>2</sub> was almost twice that with 0.5% O<sub>2</sub>. When 2% O<sub>2</sub> was used, the CO conversion was 100% in all the reaction temperature ranges. Even

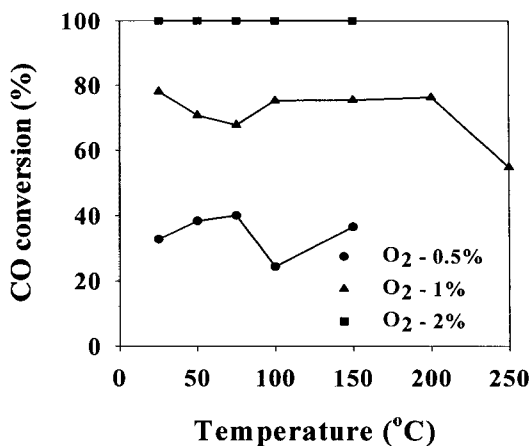


Fig. 3. Effect of O<sub>2</sub> concentration on the CO conversion with o-Pt-A catalyst.

though 2% O<sub>2</sub> is more than the stoichiometric concentration of 0.5%, 100% CO conversion result is much higher than those of other investigators<sup>3,5</sup>. The difference can be attributed to the novel pretreatment method for the catalyst described above.

### 3.2. XRD Analysis

XRD analysis was performed to determine the crystalline structure of the Pt nanoparticles on the three catalysts of Pt-A, w-Pt-A, and o-Pt-A before and after reaction. As can be seen in Fig. 4-6, XRD spectra for all the catalysts before the reaction did not show significant metallic Pt peaks. However, metallic Pt peaks

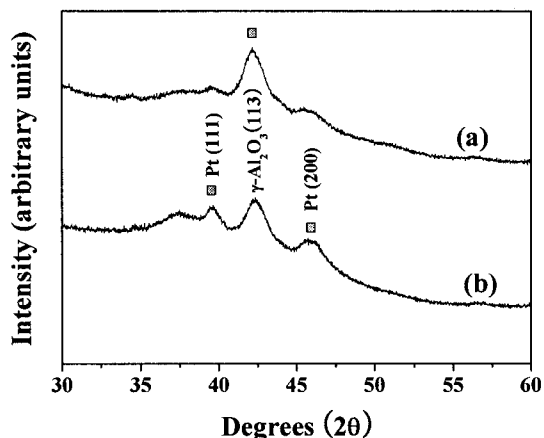


Fig. 4. XRD spectra of Pt-A catalysts before (a) and after (b) reaction.

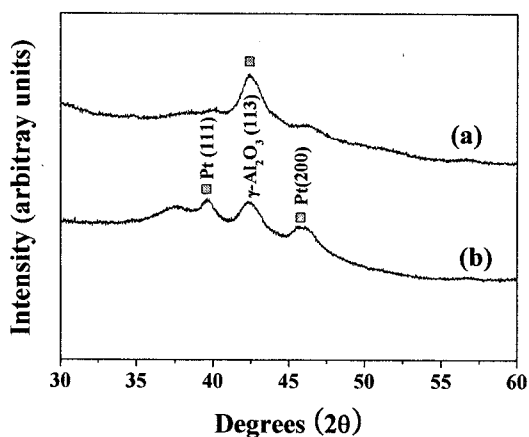


Fig. 5. XRD spectra of w-Pt-A catalysts before (a) and after (b) reaction.

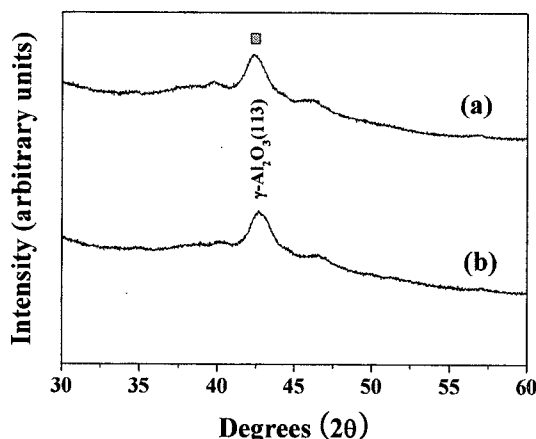


Fig. 6. XRD spectra of o-Pt-A catalysts before (a) and after (b) reaction.

were observed for both the Pt-A and w-Pt-A catalysts after reaction. The absence of the Pt peaks for the o-Pt-A catalyst after the reaction implies that Pt particles are too small to be detected by X-ray diffraction. The broad diffraction patterns are due to poor crystalline grains of alumina. The decreased intensity of the alumina peaks after reaction in Fig. 4 and 5 may be due to a consequence of the surface coverage by the Pt particles.

The Seker and Gulari reported the similar phenomena to this result<sup>16</sup>. They could not observe the metallic Pt peaks with a sol-gel 2% Pt/alumina catalyst containing particles less than 2-5 nm, but could identify

Pt peaks after reaction with the catalysts containing sintered larger particles of size ranging from 10 to 15 nm. This would suggest that Pt particles could sinter to the larger particles over 5 nm and thus, lose their catalytic activity during the reaction. This could also suggest that Pt particles over the o-Pt-A catalyst are well dispersed with small size and maintain their catalytic activity throughout the reaction. This result was consistent with CO oxidation result as shown in Fig. 1. That is, considerably increased CO conversion with o-Pt-A catalyst can be ascribed by the fact that well dispersed small Pt particles can effectively oxidize CO during the reaction.

### 3.3. HRTEM analysis

HRTEM was used to observe the dispersion as well as the size of the Pt particles on the catalyst surface. Pt particles show a highly contrasted images compared to the faintly contrasted images of the poorly crystalline grains of the alumina. Fig. 7 shows the HRTEM images of the Pt-A, w-Pt-A, and o-Pt-A catalysts. As shown in Fig. 7(a), some large particles of about 10 nm size are seen on the conventional Pt-A catalysts. As shown in Fig. 7(b) and 7(c), Pt particles on the o-Pt-A catalyst are well dispersed and smaller than those of the Pt-A and w-Pt-A catalysts.

From the HRTEM images of each sample catalysts, 150 sample particles were selected and their particle sizes were measured. Most of the Pt particle sizes of the catalysts ranged from 0.5 to 6 nm. From the particle size distribution, average particle size was calculated. As can be seen in Table 1, average particle sizes of the Pt-A, w-Pt-A, and o-Pt-A catalysts were 3.00, 2.89, and 2.24 nm. However, there were numerous larger Pt particles on the Pt-A catalysts. This could result from the sintering of the Pt particles during the reaction. This HRTEM analysis result was also consistent with the XRD analysis results and CO oxidation activity results.

Increase of CO conversions with o-Pt-A catalyst can be attributed to the well dispersed small Pt particles on the alumina surface because small Pt particles are more active for the selective CO oxidation especially at the low temperature ranges. Even though water

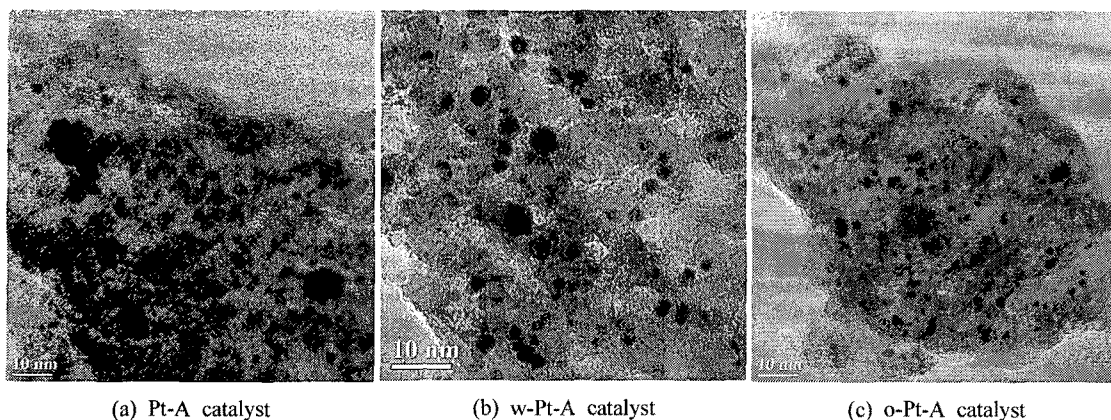


Fig. 7. HRTEM images of (a) Pt-A, (b) w-Pt-A, and (c) o-Pt-A catalysts after reaction.

Table 1. Average particle size of the catalysts after reaction

Catalyst	Pt-A	w-Pt-A	o-P-A
Average particle size (nm)	3.00	2.89	2.24

treatment was applied to both the w-Pt-A and o-Pt-A catalysts, o-Pt-A catalyst showed much higher CO oxidation conversion and formed smaller Pt particle size. This could be due to the increase in the number of hydroxyl groups on the alumina support in the preparation of the o-Pt-A catalyst. The o-Pt-A catalyst is prepared by supplying oxygen under hydrogen atmosphere while water is being added. Oxidation of hydrogen can produce more hydroxyl groups on the catalyst surface. Therefore, enhanced hydrogen spillover through the hydroxyl groups can increase SMSI to produce highly dispersed small Pt particles. In addition, hydroxyls are known to be a good oxidant and thus, thought to increase the CO oxidation activity of the catalyst at the low temperatures<sup>14)</sup>.

#### 4. Conclusions

Water treatment technique could enhance the CO oxidation activity of the conventional Pt catalyst supported over alumina. Especially, oxygen treated o-Pt-A catalyst increased CO conversion remarkably at the low temperatures below 100°C. When 2% O<sub>2</sub> was used, CO conversions with the o-Pt-A catalyst were

100% in all the low temperature ranges from 25 to 125°C. This result is promising for the desirable operation of PEMFC without CO poisoning.

It is evident that the novel water and oxygen treatment technique could reduce the size and dispersion of the Pt nanoparticles. Hydroxyl groups formed in the preparation of the catalyst are thought to cause continuous hydrogen spill over to increase SMSI. Due to the increased SMSI, well dispersed small Pt nanoparticles could be produced. This was confirmed by the XRD and HRTEM analysis. Highly dispersed small Pt particles are known to interact more strongly with CO and have higher CO oxidation activity than large Pt particles or bulk Pt. This can explain the high CO conversions with o-Pt-A catalyst. In addition, hydroxyl groups on the catalyst are thought to participate in the CO oxidation to increase the CO conversion at the low temperature below 100°C.

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