

# Enhancement of Catalytic Activity of Pt/Alumina by a Novel Pretreatment Method for the CO Oxidation for Fuel Cell Applications

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## Abstract

Hydrogen gas is used as a fuel for the proton exchange membrane fuel cell (PEMFC). Trace amount of carbon monoxide present in the reformat H<sub>2</sub> gas can poison the anode of the PEMFC. Therefore, preferential oxidation (PROX) of CO is essential for reducing the concentration of CO from a hydrogen-rich reformat gas. In this study, conventional Pt/Al<sub>2</sub>O<sub>3</sub> catalyst was prepared for the preferential oxidation of CO. The effects of catalyst preparation method, additive, and hydrogen on the performances of PROX reaction of CO were investigated. Water treatment and addition of Ce enhanced catalytic activity of the Pt/Al<sub>2</sub>O<sub>3</sub> catalyst at low temperature below 100°C.

**Key Words :** Fuel cell, Catalyst, Carbon monoxide, Preferential oxidation

## 1. Introduction

Fuel cells have been a major candidate for the efficient alternative energy source to fossil fuels. Among them, proton exchange membrane fuel cell (PEMFC) has received increasing attention because of their low operating temperature, high efficiency, and low environmental impact. Hydrogen is fed to the anode of the PEMFC as a fuel. However, trace amount of CO present in the hydrogen gas stream from reforming processor can poison the Pt catalyst in the anode. Therefore, preferential oxidation (PROX) of carbon monoxide is necessary to reduce the CO concentration to ~10 ppm level<sup>1,2)</sup>. There are two competing reactions in the PROX:



The catalyst in the PROX reactor must be highly active for the oxidation of CO while restraining the oxidation of H<sub>2</sub> to cause the loss of the fuel.

Noble metal catalysts supported over reducible oxide have been proposed for the PROX reaction<sup>3~7)</sup>. Highly dispersed Au nanoparticles are known to be active in CO oxidation<sup>4,5)</sup>. They are sensitive to the preparation method and deactivate rapidly by the produced CO<sub>2</sub>. Ru, Rh, and Pt supported over alumina were found to be the most efficient catalysts and CO was totally converted to CO<sub>2</sub><sup>6,7)</sup>. However, a noticeable amount of hydrogen was oxidized in the presence of excess oxygen at the same time. Pt/Al<sub>2</sub>O<sub>3</sub> has been widely used as an efficient PROX catalyst since it was first proposed by Los Alamos National Laboratory<sup>2)</sup>. It shows high CO conversion at high temperature ranges (150-250°C) and doesn't cause any methanation reaction. Therefore, enhancement of the catalytic activity at low temperatures below 100°C has been an issue for this catalyst. Highly dispersed small Pt particles are known to be effective in the PROX reaction especially at the low temperatures<sup>8~10)</sup>. Other investigators have sug-

gested that CeO<sub>2</sub> can promote the CO oxidation by supplying lattice oxygen<sup>11,12</sup>.

In this study, different kinds of water-treatment methods were applied to Pt/Al<sub>2</sub>O<sub>3</sub> catalyst and their performances on CO oxidation were compared with that of conventional Pt/Al<sub>2</sub>O<sub>3</sub> catalyst. In addition, Pt/CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst was prepared by impregnating Ceria to the conventional Pt/Al<sub>2</sub>O<sub>3</sub> catalyst and the effect of CeO<sub>2</sub> on the CO oxidation was investigated.

## 2. Materials and Methods

### 2.1. Catalyst preparation

The Pt/Al<sub>2</sub>O<sub>3</sub> catalyst was prepared using an incipient wetness method. Alumina (γ-Al<sub>2</sub>O<sub>3</sub>, 150 m<sup>2</sup>/g, acidic type, > 60 mesh, Alfa Aesar) was dried in an oven at 120°C for 24 h and was impregnated onto an aqueous solution of Pt precursor (H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O, Alfa Aesar). The catalyst was dried in an oven at 120°C for 24 h and was then calcined in air at 400°C for 2 h. After calcination, the catalyst was oxidized at 500°C for 2 h with pure O<sub>2</sub>, purged with He for 15 min, reduced at 500°C for 1 h with pure H<sub>2</sub>, and then cooled to room temperature. Pt content in the catalyst was 5%. This is the conventional Pt/Al<sub>2</sub>O<sub>3</sub> catalyst and is abbreviated as Pt-A. Pt/CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst was prepared by impregnating Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (Alfa Aesar) onto the aqueous solution of Pt precursor with the Alumina at the same time. The other procedures were the same as described above. Ce content in the catalyst was 5%. This Pt/CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst is abbreviated as Pt-Ce-A.

Water-treatment methods were applied to the conventional Pt/Al<sub>2</sub>O<sub>3</sub> catalyst in three different ways:

a). After cooling to room temperature, 5ml of water was added to the catalyst at a flowrate of 0.25 ml/min using a syringe pump in H<sub>2</sub> flow. After wetting, the catalyst was heated to 500°C at a ramping rate of 10°C/min, reduced at 500°C for 1 h with H<sub>2</sub>, and then cooled to room temperature. The Pt/Al<sub>2</sub>O<sub>3</sub> catalyst and Pt/CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst pretreated with this method are abbreviated as w-Pt-A and w-Pt-Ce-A, respectively.

b). While water was being added, 1% O<sub>2</sub> was started to flow at the same time. After the addition of water, the catalyst was then heated to 500°C at a ramping rate

of 10°C/min and maintained at 500°C for 1 h. When the water was not be seen in the reactor, O<sub>2</sub> flow was stopped. This catalyst is abbreviated as o-Pt-A.

c). The other catalyst was prepared using the preceding method described in b) with a modification. O<sub>2</sub> flow was maintained throughout process until the catalyst was cooled to room temperature. This catalyst is abbreviated as o1-Pt-A.

### 2.2. PROX reactor

Catalytic tests were carried out in an atmospheric continuous flow reactor system as seen in Fig. 1. Vertically equipped quartz tube (6 mm I.D.) was used as a reactor with an upward gas flow. 0.1 g of catalyst was loaded in the reactor and a total flowrate of reaction gases was 100 ml/min. The thermocouple located at the bottom of the reactor was used to control the reaction temperature in the range of 25-250°C with the temperature controller connected to the furnace. Analytical grade of gases (He, H<sub>2</sub>, air, CO, O<sub>2</sub>) were supplied by Airgas Co. and were further purified using 5 Å 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 a 6-way sampling valve (250 μL) and was vent to the atmosphere. In GC analysis, gas in the loop was swept by a carrier gas to the inlet of the GC. Each specific gas was calibrated with a known concentration of gas for analysis. the conversions of CO and O<sub>2</sub> and selectivity for the CO were calculated from the following formulas.

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

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

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

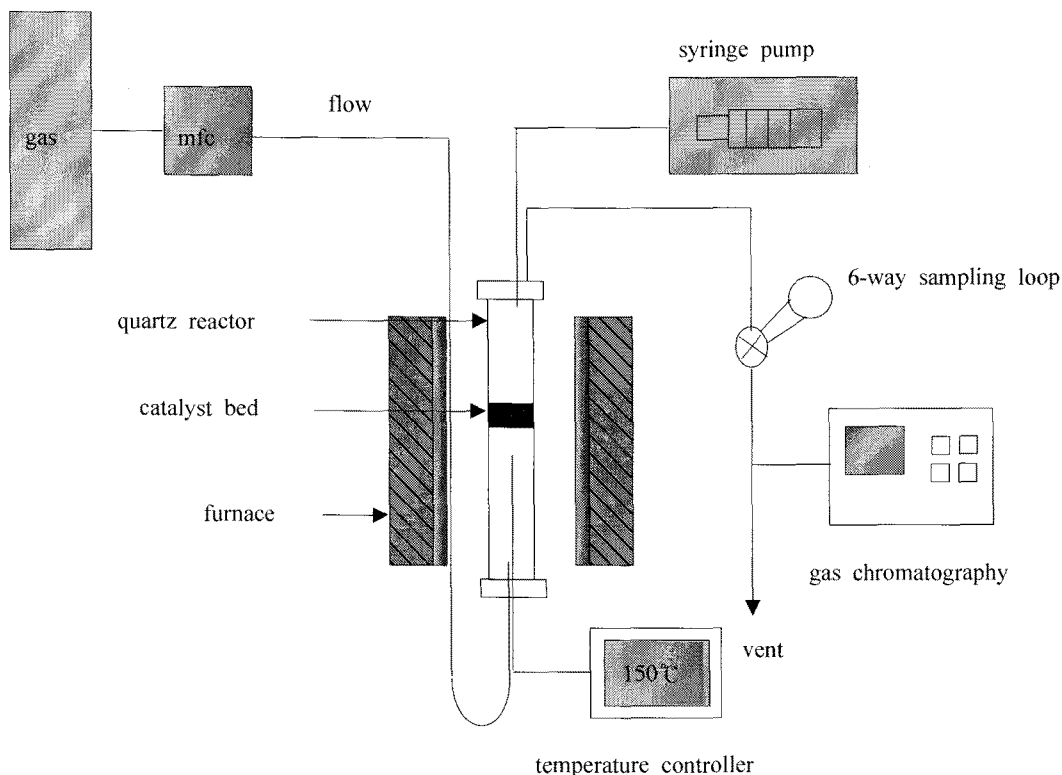


Fig. 1. Schematic of the PROX reactor system.

### 2.3. H<sub>2</sub> chemisorption

H<sub>2</sub> chemisorption was conducted using an excess pulse technique to determine the dispersion of Pt catalyst on the support. 0.05 g of the catalyst was loaded in an u-type quartz tube and reduced with pure H<sub>2</sub> at 500°C for 20 min. After the purge with pure N<sub>2</sub> for 10 min, the catalyst was cooled to room temperature. In pure N<sub>2</sub> flow at room temperature, 5% H<sub>2</sub> gas (95% N<sub>2</sub>) filled in a 1 ml loop was injected using a 6-way sampling valve until saturation of H<sub>2</sub> was observed. The gas was allowed to stabilize for 2 min before each injection. The concentration of the H<sub>2</sub> gas was monitored using a TCD detector. After the saturation, 1 ml and 5 ml of the 5% H<sub>2</sub> gas (95% N<sub>2</sub>) were injected and these two peaks were used for the calibration.

Dispersion is defined as the ratio of the adsorbed moles of H to total moles of Pt, referred to as H/Pt. It is assumed that H<sub>2</sub> dissociates on the surface of Pt and chemisorbs on the surface in a ratio of 1-H/1-Pt.

The adsorbed moles of H<sub>2</sub> were measured by the H<sub>2</sub> pulse method and used to calculate the dispersion of the Pt particles. The volume area mean diameter was estimated using the dispersion data by the following equation<sup>13)</sup>:

$$d_{vm} = \alpha \times \frac{M_w}{A_e \rho N} \times \left(\frac{H}{Pt}\right)^{-1}$$

where,  $\alpha$  is the geometrical parameter and 6 on the assumption of spherical particle,  $M_w$  is the atomic weight of Pt,  $A_e$  is the effective area occupied by Pt on the surface and is  $\frac{1}{12.5} \frac{nm^2}{Pt}$ ,  $\rho$  is the density of Pt, and  $N$  is the Avogadro's number.

### 3. Results and Discussion

In order to investigate the catalytic activity, CO oxidation reaction in hydrogen-rich condition was carried out in the PROX reactor. 0.1 g of 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. After the conditioning, the catalyst was cooled to 25°C. The reaction was started by flowing O<sub>2</sub> and CO of 1 ml/min, respectively at the same time and was allowed to stabilize for 1 h. Then, the exit gas from the reactor was sent to GC for analysis using the 6-way gas sampling valve. For the reactions at 50 and 75°C, the temperature was ramped to 125°C after each reaction 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 the conditioning.

Ceria was added to Pt/Al<sub>2</sub>O<sub>3</sub> catalyst to prepare for the Pt-Ce-A catalyst. Fig. 2 shows the conversions of CO and Fig. 3 shows the O<sub>2</sub> conversions and selectivities for CO of Pt-A and Pt-Ce-A catalysts. As can be seen in Fig. 2, The CO conversion of Pt-Ce-A was higher than that of Pt-A at low temperatures below 100°C. This result implies that Ceria can supply lattice oxygen to Pt in low oxygen concentration and thus improve the CO conversion of Pt catalyst. The CO conversion increased with temperature and was maximized at 150°C. However, the CO conversion at higher temperatures at or above 150°C was lower for Pt-Ce-A. This is due to the increased oxidation of hydrogen. This result was consistent with the results of other investigators<sup>11,12</sup>. They reported that too much loading of Ce can

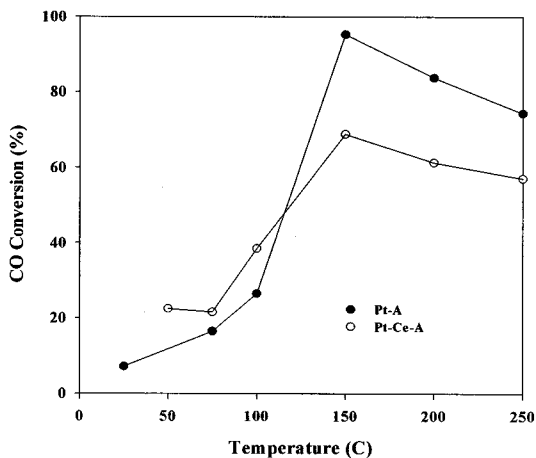


Fig. 2. CO conversions of Pt-A and Pt-Ce-A catalysts.

decrease the CO conversion by supplying excess oxygen to the catalyst to cause oxidation of hydrogen. Therefore, the selectivity of CO decreased at the high temperature ranges as can be seen in Fig. 3.

Effect of water treatment on the catalyst was investigated using w-Pt-A and w-Pt-Ce-A catalysts. As shown in Fig. 4, the CO conversion trend of the water-treated catalysts was similar to those of the Pt-A and Pt-Ce-A catalysts. The CO conversions of both water-treated catalysts increased at low temperatures below 100°C compared to Pt-A and Pt-Ce-A catalysts. Water treatment makes hydroxyl-rich condition on the catalyst surface. Hydroxyls are known to be a good ox-

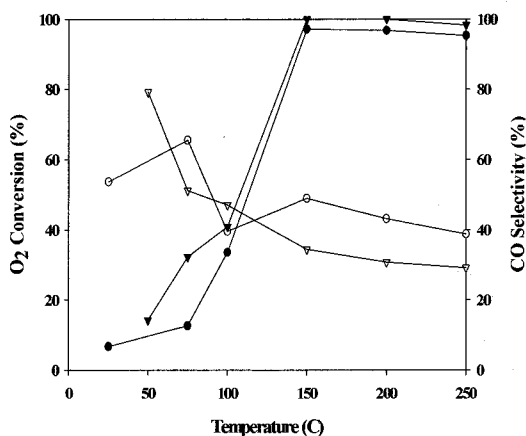


Fig. 3. O<sub>2</sub> conversions (filled symbol) and CO selectivities (open symbol) of Pt-A (● ○) and Pt-Ce-A (▼ ▽) catalysts.

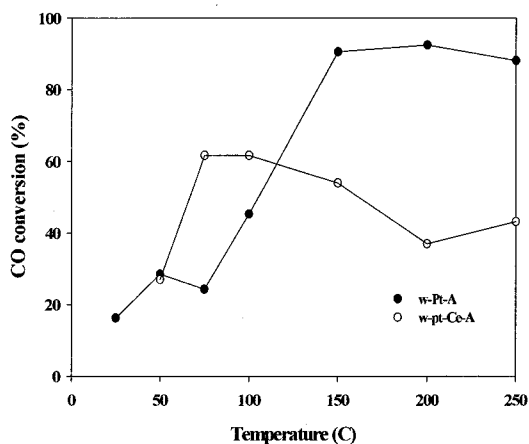


Fig. 4. CO conversions of w-Pt-A and w-Pt-Ce-A catalysts.

oxidant and thus, thought to increase CO oxidation activity at low temperatures<sup>1)</sup>. At higher temperatures, CO-Pt bond becomes weaker and more H<sub>2</sub> oxidation occurs. This fact implies that oxygen supplied from CeO<sub>2</sub> or oxygen in the reaction gas stream is used mainly for the oxidation of hydrogen at the higher temperatures. Therefore, selectivity of CO decreases at the high temperature ranges as shown in Fig. 5.

As described above, water treatment on the Pt-A catalyst could improve the catalytic activity for the CO oxidation. Therefore, three different kinds of water treatment methods were applied to the conventional Pt-A catalyst to prepare for the w-Pt-A, o-Pt-A, and oi-Pt-A catalysts. Their catalytic activities for the CO oxidation in H<sub>2</sub> were tested and compared with that of conventional Pt-A catalyst. Fig. 6 shows the CO conversion and Fig. 7 shows the O<sub>2</sub> conversion and CO selectivity for the catalysts. The CO conversions for all the water-treated catalysts were enhanced at the low temperatures below 150°C compared to that of the conventional Pt-A catalyst. In particular, the increase of the CO conversion of the oi-Pt-A was remarkable and the conversion was almost 75% or above at the temperature ranges. A slight decrease of the CO conversions for the water-treated catalysts below 100°C was probably due to the adsorption of water resulting from H<sub>2</sub> oxidation. Adsorption of water causes deacti-

vation of the Pt catalyst. As the temperature increased above 150°C, the CO conversion decreased because of the ignition of the H<sub>2</sub> oxidation due to the weakened CO-Pt bond. The O<sub>2</sub> conversions increased and reached the maximum of almost 100% at 150°C.

The order of the O<sub>2</sub> conversions were in the order of oi-Pt-A > o-Pt-A > w-Pt-A > Pt-A as shown in the Fig. 7. The CO selectivities decreased with temperature and reached constant of about 40%.

Among the water-treated catalysts, the CO conversions were in the following order at the low temper-

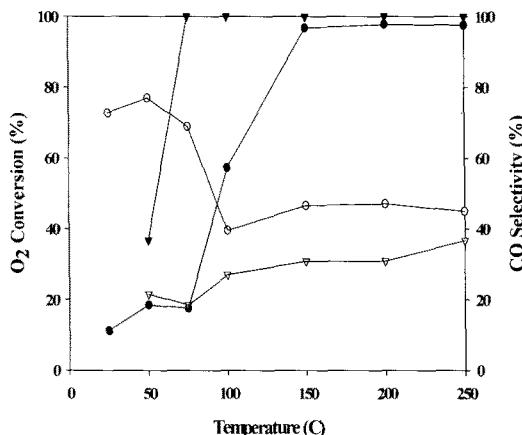


Fig. 5. O<sub>2</sub> conversion (filled symbol) and CO selectivity (open symbol) of w-Pt-A (● ○) and w-Pt-Ce-A (▼ ▽) catalysts.

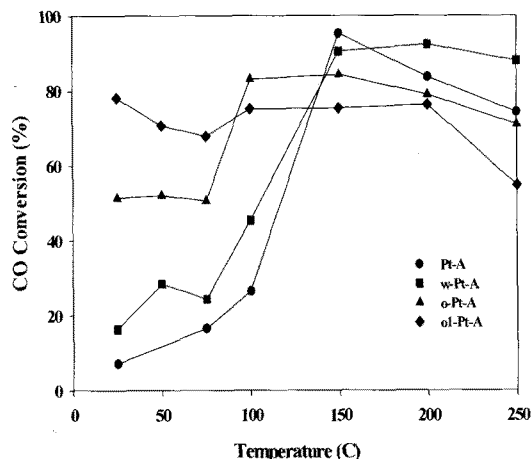


Fig. 6. CO conversions of Pt-A, w-Pt-A, o-Pt-A, and oi-Pt-A catalysts.

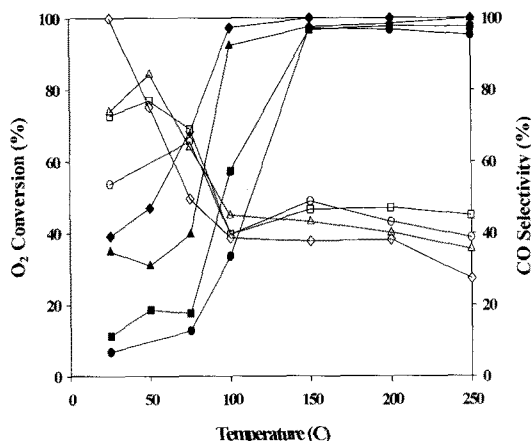


Fig. 7. O<sub>2</sub> conversion (filled symbol) and CO selectivity (open symbol) of Pt-A (● ○), w-Pt-A (■ □), o-Pt-A (▲ △), and oi-Pt-A (◆ ◇) catalysts.

ature below 100°C: o1-Pt-A > o-Pt-A > w-Pt-A. During the preparation of the catalysts, addition of water makes hydroxyl-rich condition on the catalyst surface. The w-Pt-A catalyst is prepared by adding water at the room temperature. On the other hand, o1-Pt-A and o-Pt-A are prepared with oxygen flow in hydrogen atmosphere as well as addition of water. Hydrogen is oxidized by the oxygen to form water. This process has advantages over the w-Pt-A in terms of supplying water continuously to make more hydroxyl-rich condition on the catalyst surface during the reduction step. The higher conversion of the CO of the o1-Pt-A catalyst than that of the o-Pt-A catalyst can be attributed to the fact that longer time of exposure to the oxygen flow condition for the preparation of the o1-Pt-A make more hydroxyls on the catalyst surface. That is, the hydroxyls on the catalyst surface are the key factor for the increase in the catalytic activity for the CO oxidation. Hydroxyls are known to be a good oxidant and thus, more hydroxyls on the catalyst can increase the CO oxidation.

To investigate the dispersion of the Pt particles on the catalyst, H<sub>2</sub> chemisorption experiment was conducted using the o1-Pt-A and Pt-A catalysts. 1 ml volume of the 5% H<sub>2</sub> gas (95% N<sub>2</sub>) was injected until saturation of the H<sub>2</sub> was observed. Each peak area was subtracted from the area of 1 ml calibration. The total areas resulting from the H<sub>2</sub> chemisorption was obtained by summing up the areas after the subtraction. Total moles of H<sub>2</sub> chemisorbed on the Pt surface were calculated using the measured total areas. Fig. 8 and 9 show the TCD spectrum from the H<sub>2</sub> chemisorption over the Pt-A and o1-Pt-A catalysts, respectively. Dispersion and mean particle diameter of the Pt on the o1-Pt-A and Pt-A catalysts were calculated using the adsorbed moles of H<sub>2</sub>. The results are summarized in Table 1.

The results showed that the dispersion of Pt over the o1-Pt-A catalyst was higher than that over the Pt-A catalyst. This means that more number of Pt sites are available for the CO oxidation. Also higher dispersion leads to the decrease in the particle size as shown in Table 1. Hydroxyls are known to enhance hydrogen spillover<sup>2)</sup>. The increase in the rate of hydrogen spillover is expected to enhance the strong metal support

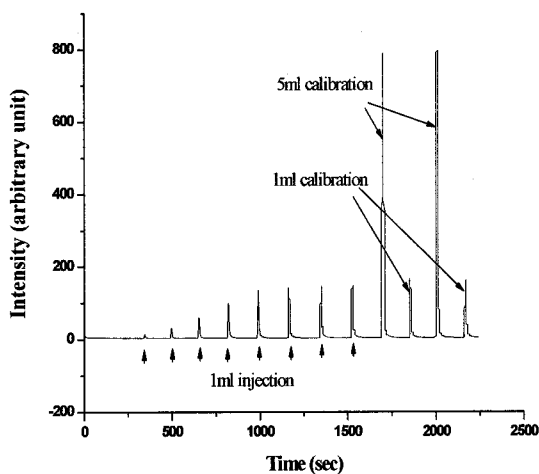


Fig. 8. TCD spectra from H<sub>2</sub> chemisorption over Pt-A catalyst.

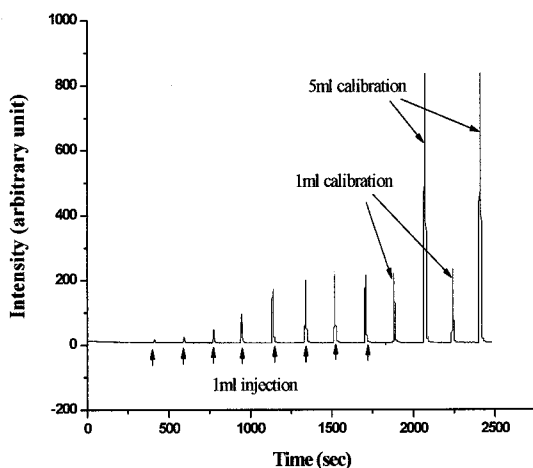


Fig. 9. TCD spectra from H<sub>2</sub> chemisorption over o1-Pt-A catalyst.

Table 1. Dispersion and mean particle diameter of the Pt

Catalyst	Dispersion (%)	Mean Particle Diameter (nm)
Pt-A	60.8	1.86
o1-Pt-A	45.7	2.48

interaction (SMSI). As a result, Pt particles are well dispersed and smaller. Well dispersed smaller Pt particles are known to interact more strongly with CO and thus, higher CO oxidation activity than larger or bulk Pt particles<sup>2)</sup>.

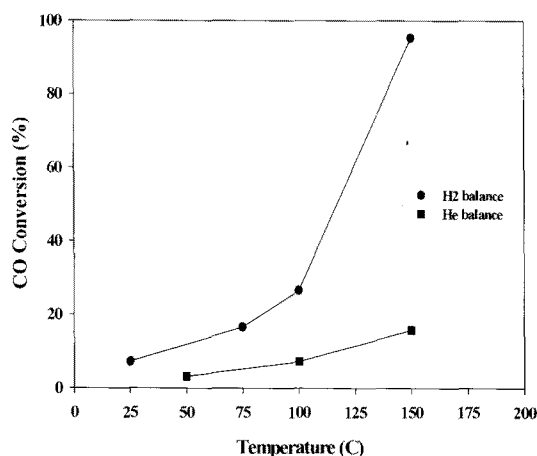


Fig. 10. CO conversion with H<sub>2</sub> and He as a balance gas.

To confirm the effect of the hydrogen spillover, CO oxidation reaction was carried out with and without H<sub>2</sub> in the reaction gas stream. For the reaction without H<sub>2</sub>, He was used as the balance gas. Flowrates of the CO and O<sub>2</sub> were 1ml/min, respectively and the flowrate of the balance gas was 98 ml/min. Fig. 10 shows the CO conversion with H<sub>2</sub> and He as a balance gas. The CO conversion with H<sub>2</sub> gas was much higher than that with He gas. This result suggests that hydrogen spillover enhances the CO oxidation with higher SMSI. With increased SMSI, Pt particles become smaller and well dispersed and thus, provide more active sites for the CO oxidation.

#### 4. Conclusions

Ceria addition could enhance CO oxidation activity of the Pt-A catalyst at low temperature below 100°C. This result implies that Ceria can supply lattice oxygen to Pt in low oxygen concentration and thus improve the CO conversion of Pt catalyst. However, the CO conversion of the Pt-Ce-A catalyst at higher temperatures at or above 150°C was lower than that of the Pt-A. This is due to the increased oxidation of hydrogen. Too much loading of Ce can decrease the CO conversion by supplying excess oxygen to the catalyst to cause oxidation of hydrogen.

Water treatment on the Pt-A catalyst enhanced CO conversion at the low temperature below 100°C. In

particular, oxygen-treated o-Pt-A and ol-Pt-A catalysts showed remarkable increase in the CO conversion at the low temperature. This can be attributed to the fact that oxygen treatment and water treatment can make hydroxyl-rich condition on the catalyst surface and the hydroxyls can oxidize CO effectively. In addition, increase in hydrogen spillover by the hydroxyl groups enhance the SMSI to cause well dispersed smaller Pt particles as confirmed by the H<sub>2</sub> chemisorption results. As a result, more active sites are available for the CO oxidation.

Water treatment is promising as a method to improve the catalytic activity of the conventional Pt-A catalyst for the preferential oxidation of the carbon monoxide from reformed gas.

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