선택적인 일산화탄소 산화 반응용 백금 촉매계

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Pt-based catalysts for the preferential CO oxidation

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Introduction

The polymer electrolyte fuel cell (PEMFC) which has been attracting much attention in the application of electric vehicles or residential power generations produces heat and electricity with the hydrogen fuel generated via reforming of hydrocarbons followed by water-gas shift reaction [1]. However, 0.5~1vol% of carbon monoxide is usually contained in the hydrogen fuel from the water-gas shift reactor. This carbon monoxide should be removed to a trace-level because platinum, an anode of PEMFC, can be easily poisoned in the presence of small amounts of CO in hydrogen stream. The acceptable CO concentration is < 100 ppm even at CO-tolerant anodes [1]. The selective CO oxidation has been accepted as the most attractive way to decrease CO concentration. In this system, the following three reactions can occur.

$$CO + 1/2O_2 \rightarrow CO_2 \qquad (1)$$

$$H_2 + 1/2O_2 \rightarrow H_2O \qquad (2)$$

$$CO + 3H_2 \rightarrow CH_4 + H_2O \qquad (3)$$

The third reaction, which is called methanation, should be avoided except that CO concentration was quite low because it consumed relatively large amounts of hydrogen compared with the preferential CO oxidation (PROX). Although a number of catalysts more active for the first reaction than the second reaction have been reported, supported Pt-based catalysts have been reported to be most promising [1]. The monometallic Pt catalyst usually showed noticeable activities only above 423 K. Because PEMFC is operated below 423 K, catalysts operating at low temperatures can be more plausible. To increase catalytic activities at low temperatures, different methods have been tried for supported platinum catalysts. The pretreatment of Pt catalyst with water vapor was reported to enhance low-temperature catalytic activities for selective CO oxidation by increasing Pt dispersion [2]. Several groups have reported that the selective CO oxidation at low temperatures could be enhanced by the addition of 2nd metals such as Fe [3], Ce[4], Co[5], Ni[5], Mn[5], and alkali metals[6]. We also conducted comparative studies among promoted Pt catalysts at the same reaction condition and found that the addition of Ni was the most effective for the selective CO oxidation [7]. In this study, the effect of some preparation variables on the catalytic activity over Ni-promoted Pt/γ-Al_2O_3 was examined. Until now, most works have been conducted on Pt-based catalyst supported on γ-Al_2O_3. Recently, we found that Pt-Co/Y-ZrO_2 can be a promising PROX catalyst especially at low temperatures. The support effect on the catalytic activity over supported Pt-Co catalysts was also studied.

Experimental

All the catalysts were prepared by a wet impregnation method from an aqueous solution of Pt precursor, $Pt(NH_3)_4(NO_3)_2$, and transition metal precursors, metal nitrates. Different supports such as γ-alumina (Alfa), TiO_2 (P-25, Degussa), SiO_2 (Aldrich) and Y-ZrO_2 (TZ-8YS, Tosoh) were utilized. The content of Pt was 1 wt%. The molar ratio of Ni/Pt and Co/Pt was 5 and 10, respectively. All the catalysts were calcined at 573 K and reduced at different temperatures with hydrogen stream for 1 h before a reaction.

The CO chemisorption was conducted over 0.2 g sample in a He stream at 300 K by a pulsed injection of 50μl of CO after samples were pretreated at different conditions. The bright-field and dark-filed image of transmission electron microscopy (TEM) was obtained using a Technai G^2 TEM operated at 200 kV. Samples were finely ground in a mortar to fine particles and then dispersed ultrasonically in methanol. The sample was deposited on a Cu grid covered by a holey carbon film for measurements. Energy dispersive X-ray spectroscopy (EDX) was also conducted.

Experiments were carried out in a small fixed bed reactor with catalysts that had been retained between 45 and 80 mesh sieves. A standard gas of 1.0 vol% CO, 1.0 vol% O_2, 2 vol% H_2O and 80 vol% H_2 balanced with helium was fed to a reactor at an atmospheric pressure. The catalytic activity with increasing reaction temperature was measured from 313 K to 473 K at a heating rate 1 K/min. For all experiments, 0.10g of catalyst without diluents was contacted with a reactant gas at a flow rate of 100ml/min. The conversion of CO and O_2 and the yield of CH_4 were determined through gas chromatographic analysis (HP5890A, molecular sieve 5A column) of the effluent from the reactor. The detection limit of CO was 10 ppm. The CO conversion, O_2 conversion, CO_2 selectivity, and the CH_4 yield were calculated using the following formulas:

$$\text{CO conversion (\%)} = \{([CO]_{in}-[CO]_{out})/[CO]_{in}\} \times 100;$$

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

$$CO_2 \text{ selectivity (\%)} = \{0.5 \times ([CO]_{in}-[CO]_{out}-[CH_4]_{out})/([O_2]_{in}-[O_2]_{out})\} \times 100;$$

$$CH_4 \text{ yield (\%)} = ([CH_4]_{out})/[CO]_{in}) \times 100.$$

Results and Discussion

The pretreatment effect of this Pt-Ni/γ-Al_2O_3 catalyst on the catalytic activity was examined as shown in Fig. 1. The unreduced Pt-Ni/γ-Al_2O_3 catalyst showed the noticeable activity only when the reaction temperature was higher than 400 K. The CO conversion decreased but the O_2 conversion increased at the same reaction temperature with increasing reduction temperatures when the reduction temperature was higher than 423 K. The CO_2 selectivity also decreased with increasing reduction temperatures. Therefore, Pt-Ni/γ-Al_2O_3 catalyst calcined at 573 K and reduced at 423 K can be selected as the most active catalyst for the selective CO oxidation. The amount of chemisorbed CO on Pt/γ-Al_2O_3 calcined and reduced both at 573 K and Pt-Ni/γ-Al_2O_3 calcined at 573 K and reduced at 423 K was determined to be 34.8 mol/$g_{cat.}$ and 23.9 mol/$g_{cat.}$, respectively.

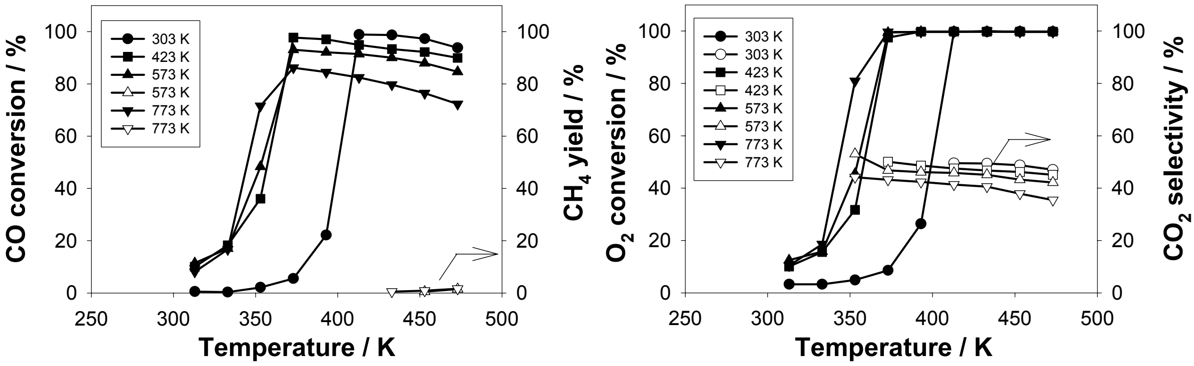

Figure 1. CO conversion, CH_4 yield, O_2 conversion, and CO_2 selectivity for the preferential CO oxidation over 1%Pt-1.5%Ni/γ-Al_2O_3 with increasing reaction temperatures. The catalyst was calcined in air at 573 K and reduced with hydrogen at different temperatures. F/W = 1000 ml/min/gcat.

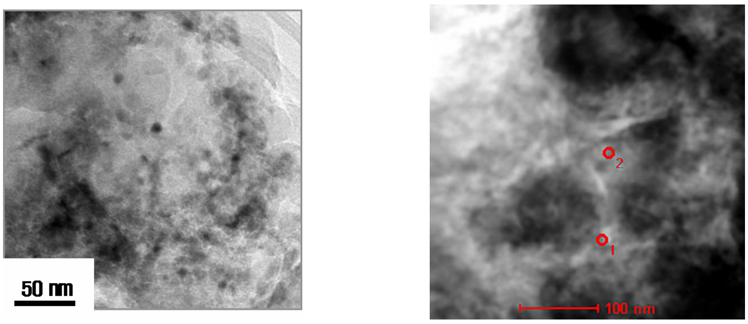

Figure 2. The bright-field and dark-field TEM images of Pt-Ni/γ-Al_2O_3 catalysts.

This shows that the addition of nickel decreased the amount of surface active site for CO chemisorption. This indicated that Pt-Ni/γ-Al_2O_3 showed much higher catalytic activities than Pt/γ-Al_2O_3 based on the active site. The increasing catalytic activity for O_2 oxidation with increasing reduction temperature for Pt-Ni/γ-Al_2O_3 catalyst can be explained by the increasing active sites because Pt-Ni/γ-Al_2O_3 calcined and reduced both at 573 K was determined to be 40.4 mol/$g_{cat.}$. To observe the bimetallic phase of Pt-Ni, the TEM image was obtained for Pt-Ni/γ-Al_2O_3 catalyst calcined in air at 573 K and reduced with H_2 at 423 K as shown in Fig. 2. The different sizes of metal particles from 3.5 nm to 10 nm were observed. The EDX analysis was conducted to find out the composition of the metallic particles. Two different points were selected as shown in Fig. 2. Pt and Ni were found to be present and the atomic ratio of Ni/Pt was determined to be 1.1 in point 1. However, only Ni was present and the atomic ratio of Ni/Al was analyzed to be 0.6 in point 2. Therefore, this result supports that some Ni are present as the bimetallic phase with Pt and the remaining nickel species exist as surface nickel aluminate ($NiAl_2O_4$).

The BET surface area of γ-Al_2O_3, SiO_2, TiO_2, and Y-ZrO_2 was determined to be 170 m^2/g, 350 m^2/g, 55 m^2/g, and 9 m^2/g, respectively. The preferential CO oxidation in H_2-rich gas mixture was conducted over Pt-Co catalyst supported on various supports as shown in Fig. 3. Pt-Co/TiO_2 appeared to be most active for complete oxidation. However, it showed the lowest CO_2 selectivity at all reaction temperatures. The methanation was observed over this catalyst above 393 K. Pt-Co/Y-ZrO_2 showed the highest CO conversion at low temperatures. This catalyst was also quite active for CO methanation. Pt-Co/SiO_2 exhibited slightly higher CO and O_2 conversion than Pt-Co/γ-Al_2O_3 at low temperatures. Pt-Co/γ-Al_2O_3 appeared to be the least active for CO methanation. From this screening test, it can be found that Pt-Co/Y-ZrO_2 is a quite promising candidate for the selective CO oxidation in an excess hydrogen stream especially at low temperatures.

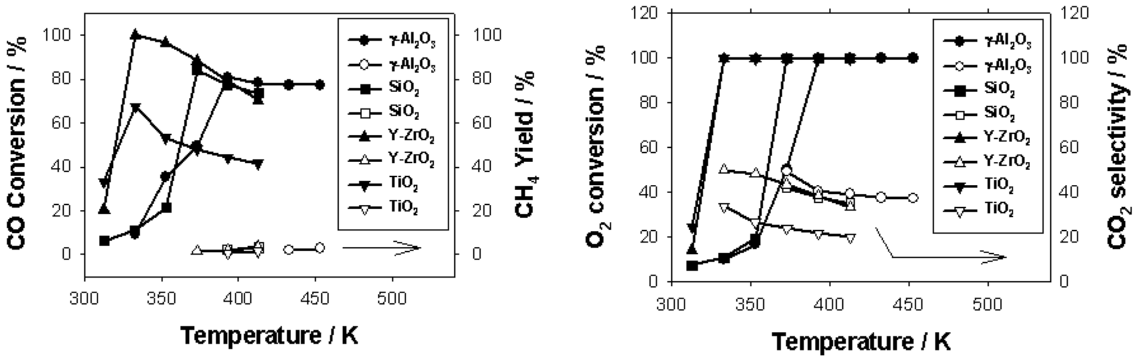

Figure 3. CO conversion, CH_4 yield, O_2 conversion, and CO_2 selectivity for the preferential CO oxidation over Pt-Co catalysts supported on different supports with increasing reaction temperatures. The catalyst was calcined in air at 573 K and reduced with hydrogen at 573 K. F/W = 1000 ml/min/gcat.

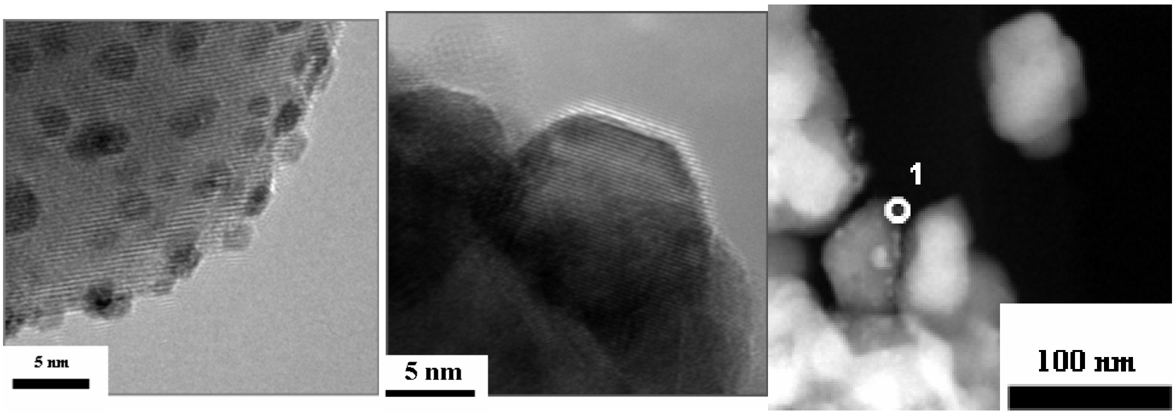

Figure 4. The bright-field and dark-field TEM images of Pt-Co/Y-ZrO_2 catalysts.

To observe the bimetallic phase of Pt-Co, the TEM image was obtained for Pt-Co/Y-ZrO_2 catalyst as shown in Fig. 4. The different sizes of metal particles from 2 nm to 10 nm were observed. Most metal particles showed homogeneous crystalline nature. The EDX analysis was conducted to find out the composition of the metallic particles as shown in Fig. 4. Pt and Co were found to be present and the atomic ratio of Co/Pt was determined to be 0.75 in point 1.

Conclusion

Pt-Ni/γ-Al_2O_3 calcined in air at 573 K and reduced at 423 K showed the high CO conversion for the preferential CO oxidation over a wide reaction temperature. Pt-Co/Y-ZrO_2 exhibited the high catalytic activity for the selective CO oxidation in the presence of hydrogen especially at low temperatures. The bimetallic phase of Pt-Ni and Pt-Co was observed for both catalysts. Therefore, it can be concluded that this bimetallic phase is responsible for enhanced catalytic activity for PROX.

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