Thermally stable Pt-Al₂O₃ cryogel with high platinum concentration for catalytic combustion

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The alumina cryogel with 5 mass% platinum was prepared from aluminum sec-butoxide and H₂PtCl₆ through the sol-gel processing and subsequent freeze drying. The cryogel showed higher thermal stability of platinum than the corresponding xerogel and impregnation catalysts at elevated temperatures. Also for the catalytic VOC combustion the cryogel exhibited higher activity than other catalysts. It was revealed that about half of the platinum surface was inside the alumina cryogel, and such encapsulation was considered the principal cause for the higher stability.

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1. Introduction

As growing the demands for global environmental protection, much attention has been paid to the performance of a catalyst for exhaust emission control.¹⁾ Platinum is one of the important elements used for purifying the harmful emissions.^{2),3)} However it is known that a precious metal agglomerates and sinters easily at high temperatures, decreasing the surface area of the metal, which results in catalyst deactivation.^{4),5)} It is also known that such agglomeration and sintering of a metal become pronounced with an increase in the concentration of the metal. In order to provide against such catalyst deactivation, excess precious metals have to be loaded despite the high cost. In our previous studies, the sol-gel processing and subsequent freeze drying, bringing about cryogel, successfully improved the stability of platinum (0.5 mass%) on alumina at elevated temperatures.^{6),7)} In the present studies, platinum-alumina cryogel with high platinum concentration (5 mass%) was prepared, and the thermal stability and catalytic combustion activity were examined in comparison to those of the corresponding xerogel and two impregnation catalysts using alumina cryogel and commercial alumina as the supports.

2. Experimental

A clear boehmite sol was prepared from 7.5 mL of aluminum sec-butoxide (Kanto Chemicals) by sol-gel processing according to the Yoldas's method.^{8),9)} 3.9 g of H₂PtCl₆ aqueous solution (2.0 mass%, Tanaka Precious Metals) was mixed with an aqueous solution (8.6 mL) containing oxalic acid (0.048 mol L⁻¹, Wako Pure Chemicals) and ammonia (3.4 mol L⁻¹, Wako Pure Chemicals), followed by keeping the temperature at 86°C for 30 min. The solution was introduced to the boehmite sol and refluxed at 86°C for several minutes. Then 0.5 g of urea (Wako Pure Chemicals) was added to the sol for gelation and the sol was allowed to stand for one night at the temperature without stirring. The freeze drying of wet gel was performed without solvent

exchange using a laboratory freeze-drier. After the drying the samples were calcined in air in the temperature range of 500–700°C. The corresponding xerogel and impregnation catalysts were also prepared for comparison according to the manner as previously reported.⁷⁾ Hereafter, the impregnation catalyst using alumina cryogel (287 m² g⁻¹) is described as Imp(cryo) whereas that using commercial alumina (Taimei Kagaku, TM-300D; 200 m² g⁻¹) as Imp(com).

The nitrogen adsorption at a liquid nitrogen temperature, X-ray powder diffraction analysis, transmission electron micrograph (TEM) image observation, CO chemisorption at room temperature, and the catalytic combustion of VOC containing acetaldehyde (67 ppm), methanol (33 ppm) and methyl formate (33 ppm) in air were carried out as previously reported.⁷⁾

3. Results

Figure 1 shows BET surface area, pore volume, and mean pore size of the catalysts after calcination. The cryogel showed almost the same surface area as that of Imp(cryo); the surface area was higher than that of Imp(com) but lower than that of xerogel. Between the sol-gel catalysts, the surface area, pore volume and mean pore size were lower on the cryogel than on the xerogel, whereas between the impregnation catalysts they were higher on Imp(cryo) than on Imp(com).

Figure 2 shows XRD profiles of the catalysts after calcination. At 500°C calcination, Pt diffraction peaks were observed on the impregnation catalysts, indicating the sintering of platinum, whereas on the sol-gel catalysts such peaks were not seen at the temperature. Also at 600°C the diffraction peaks were not observed on the sol-gel catalysts. The peaks were observed at 700°C on the xerogel but not on the cryogel at the temperature, indicating higher thermal stability of platinum on the latter.

TEM images of the catalysts after calcination at 500°C were compared in **Fig. 3**. The sintered platinum particles with diameter of ca. 60–120 nm were observed on the impregnation catalysts, whereas very fine particles with ca. 1 nm diameter were seen on the sol-gel catalysts. After the

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Fig. 1. (a) BET surface area, (b) pore volume (BJH), and (c) mean pore size (BJH) of the catalysts after the calcination for 1 h; ○: cryogel, □: xerogel, △: Imp(cryo), and ◇: Imp(com).

Fig. 2. XRD patterns of the catalysts after the calcination for 1 h (500 °C for 5 h); (a) cryogel and xerogel, (b) Imp(cryo) and Imp(com).

calcination at 700 °C, the fine particles disappeared completely on the xerogel, giving sintered large particles over 50 nm (Fig. 4). Whereas such nanoparticles still remained on the cryogel even after the calcination, indicating higher thermal stability of platinum on the cryogel, the results of which were

in agreement with those of XRD shown in Fig. 2.

Figure 5 shows CO chemisorption and (apparent) Pt dispersion on the catalysts; the chemisorption decreased significantly with calcination temperature on the impregnation catalysts; between the impregnation catalysts the decrease

Fig. 3. TEM images of the catalysts after the calcination at 500°C for 5 h; (a) cryogel, (b) xerogel, (c) Imp(cryo), and (d) Imp(com).

Fig. 4. TEM images of the catalysts after the calcination at 700°C for 1 h; (a) cryogel, (b) xerogel, (c) Imp(cryo), and (d) Imp(com).

was more marked on Imp(cryo) than on Imp(com). Whereas such significant decrease was not observed on the sol-gel catalysts; on the xerogel a gentle decrease was seen whereas on the cryogel the decrease was not observed, suggesting again higher stability of platinum on the cryogel.

The catalytic combustion of VOC on the catalysts was shown in Fig. 6. The cryogel showed higher combustion activity than other catalysts for all the VOC, although activi-

Fig. 5. CO adsorption and (apparent) platinum dispersion after the calcination for 1 h followed by reduction at 500°C for 1 h; ○: cryogel, □: xerogel, △: Imp(cryo), and ◇: Imp(com).

ty difference was small among the catalysts except for xerogel for methanol combustion. Between the impregnation catalysts, marked activity difference was not observed for all the VOC combustion.

4. Discussions

In our previous paper, platinum-alumina cryogel with 0.5 mass% platinum was prepared and the thermal stability of platinum and catalysis were investigated by comparison to those of the corresponding xerogel and impregnation catalysts.⁷⁾ It was found that the cryogel exhibited higher platinum stability and catalytic combustion activity than other catalysts. In the present paper alumina cryogel loading 5 mass% platinum was prepared, and the stability and catalysis were examined in the similar manner.

A key point for the preparation of wet gel was to mix a platinum solution with a chelating one. When the latter was added to the former at a burst, an orange precipitate least soluble in water was observed despite the absence of such precipitation in the case of 0.5 mass% platinum. So that the chelation of platinum ion proceeded without precipitation, the chelating solution was added little by little, soon after which the mixed solution was warmed in an oil bath at 86°C for 5 min at each time. The color of the solution was changed from brownish yellow to lemon yellow. By such procedure, the precipitation was successfully prevented and consequently, the uncontrolled reduction to metallic platinum was also prevented during the addition of the platinum solution to the boehmite sol. This may be owing to the chelating agents of ammonium oxalate and ammonia.

From the results of XRD, TEM and CO chemisorption shown in Figs. 2-5, it can be summarized that the stability of platinum was in the order of: cryogel > xerogel > Imp(com) ≈ Imp(cryo), the pattern of which agreed well with that of the 0.5 mass% Pt catalysts, though Imp(com) seemed to form the exception.⁷⁾ The higher stability of platinum on the cryogel should be ascribed to the more-intimately developed metal-support interaction accompanied by the encapsulation

Fig. 6. The conversion of (a) acetaldehyde, (b) methyl formate, and (c) methanol; ○: cryogel, □: xerogel, △: Imp(cryo), and ◇: Imp(com). The catalysts were calcined at 500°C for 1 h followed by reduction at 500°C for 1 h.

of the metal into the alumina cryogel.⁷⁾

It is interesting to notice that apparent Pt dispersion on the cryogel was ca. 35–36% (Fig. 5), in good agreement with that on the cryogel with 0.5 mass% platinum, ca. 30–40%.⁷⁾ The platinum particle size was ca. 1 nm (Figs. 3 and 4), which also agreed well with that of the 0.5 mass% Pt catalyst.⁷⁾ Assuming that the mean diameter of platinum particles is 1 nm, the theoretical Pt dispersion is calculated to be ca. 73% from the Anderson's equation.^{10),11)} However, the observed dispersion was ca. 35–36% as described above. By comparison with these theoretically calculated and observed values, it can roughly be deduced that ca. 51–52% of platinum surface was inside the cryogel; i.e., about half of the platinum surface was buried in the alumina gel. Such encapsulation should be the principal cause for the higher thermal stability of platinum on the cryogel. On the xerogel, on the other hand, the apparent dispersion at 500°C was ca. 38% whereas the particle size was ca. 1 nm at the temperature, which indicates that ca. 48% of platinum surface was considered to be inside the alumina gel. However high thermal stability of platinum could not be obtained for 700°C calcination in contrast to the case of the cryogel despite the similar embedding percentage. This might be due to the less strong interaction between platinum and alumina xerogel support, owing to the movement of platinum ions in the wet gel during the evaporation of water in the normal drying. Further investigations are required to reveal the true factors.

It should also be noted that platinum nanoparticles shown in Figs. 3 and 4 appeared after the calcination whereas such fine particles were observed after the subsequent reduction in the case of 0.5 mass% platinum.⁷⁾ It is generally known that platinum can disperse as oxide on alumina surface at temper-

atures below the decomposition temperatures of the oxide.¹²⁾

It is also known that the sintering of platinum is followed by the decomposition of platinum oxide to metallic platinum.^{12),13)} In the present cryogel loading higher concentration of Pt, the decomposition of platinum oxide might proceed more easily due to the less strong interaction between platinum oxide and alumina cryogel support.

As shown in Fig. 6, the VOC combustion was higher on the cryogel than on the xerogel and Imp(cryo) despite the similar metal accessibility (Fig. 5). This might be due to the contribution of active sites such as kink or step. Or alumina cryogel support and/or the metal-support boundary might also contribute to the higher activity. Further studies are still necessary for unambiguous discussions.

In spite of the higher platinum stability and catalytic activity on the cryogel, the BET surface area and pore volume decreased with platinum concentration. The BET surface area of the cryogel after the 500°C calcination was 278, 274, 260 and 225 m² g⁻¹ for 0.5, 1, 2.5 and 5 mass% platinum, respectively, whereas the pore volume was 438, 386, 297 and 158 mm³ g⁻¹, respectively. In order to design a high-performance cryogel catalyst having longer lifetime, such decline should be suppressed by an appropriate technique, which is left to future studies.

5. Conclusions

The catalyst of alumina cryogel loading 5 mass% platinum showed higher stability of platinum and catalytic combustion activity than other catalysts. It was revealed that about half of the platinum surface was buried in the alumina cryogel in the Pt concentration range of 0.5–5 mass% and thereby, such higher thermal stability should be derived. The

cryogel seems fascinating also for use at elevated temperatures because of the high resistance to heat compared to the conventional impregnation catalysts.

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