

Improvement of the Thermal Durability of an Exhaust Gas Purifying Catalyst Using Size-Controlled Pt-Hydroxide Clusters

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ABSTRACT

An exhaust gas purifying catalyst must be durable, i.e., it must maintain a sufficient catalytic performance even after thermal degradation. Therefore, large amounts of platinum group metals (PGMs), such as Pt, Pd, and Rh, should be loaded onto the catalyst substrate. Exhaust gas heat deteriorates the catalyst by sintering the PGM particles, which decreases the active surface area. It is important to reduce the PGM load and many researchers have therefore attempted to carry out PGM load reduction while maintaining sufficient durability.

We found that Pt ions could form Pt-hydroxide clusters in a hexahydroxyplatinate (IV) ($\text{Pt}(\text{OH})_6 \cdot \text{H}_2\text{O}$) nitric acid solution. The Pt-hydroxide cluster size could be controlled by varying the Pt and nitric acid concentrations and solution temperature. We expected that these "larger Pt-hydroxide clusters" would be efficient at improving the durability because a larger cluster size in the solution would equate to a greater distance between each Pt particle or uniform distribution of Pt particles on the support material. The greater distance or uniform distribution would lower the opportunity for Pt particle association at high temperatures. Therefore, we investigated the catalytic performance of a Pt catalyst containing larger Pt-hydroxide clusters.

The Pt catalyst containing larger Pt-hydroxide clusters exhibited an improved catalytic activity after thermal duration. Transmission electron microscopy (TEM) images revealed that the Pt particle distribution was more uniform on the Pt catalyst containing the larger Pt-hydroxide clusters than on the conventional catalyst. This uniformity is assumed to be the reason for the improved durability.

CITATION: Tsuda, T., Miura, K., Hikasa, A., Hosoi, K. et al., "Improvement of the Thermal Durability of an Exhaust Gas Purifying Catalyst Using Size-Controlled Pt-Hydroxide Clusters," *SAE Int. J. Engines* 9(4):2016, doi:10.4271/2016-32-0070.

INTRODUCTION

Exhaust purifying catalysts contain platinum group metals (PGMs), such as Pt, Pd, and Rh. These precious metals are unevenly distributed in South Africa and Russia. Therefore, the reduction of the PGM load in these catalysts is important to reduce the cost and to maintain PGM sustainability.

The catalyst performance is degraded by exposure to high temperature exhaust gas; this causes sintering of the PGM particles and decreases the active surface area. The initial active surface area should be large to maintain a sufficient catalyst performance even after thermal degradation, i.e., a large PGM load is essential for thermal durability. Many researchers have tried to satisfy the PGM load reduction and provide sufficient durability. The metal/support interaction was studied to prohibit the PGM particle emigration and sintering [1, 2], and the nano-structure control of PGM particles was studied to strengthen the catalytic activity [3, 4].

We found that Pt ions in the hexahydroxyplatinate(IV) ($\text{Pt}(\text{OH})_6 \cdot \text{H}_2\text{O}$) nitric acid solution had the form of 6-coordinate Pt-hydroxide ions that united and formed Pt-hydroxide clusters, as shown in Fig. 1. The Pt-hydroxide cluster size changed with respect

to the solution state. For example, a reduced nitric acid concentration or an increased Pt concentration provided larger Pt-hydroxide clusters. In addition, the Pt-hydroxide cluster size could be controlled between 1 to 6 nm by controlling the solution properties. We expected that these larger Pt-hydroxide clusters would be efficient to improve the durability because the larger cluster size (3-6 nm) in the solution would require a greater distance between each Pt particle or a uniform distribution of the Pt particles on the support material. A greater distance or a uniform distribution could lower the opportunity for Pt particle association at high temperatures. Therefore, we investigated the catalytic performance of Pt catalysts containing larger Pt-hydroxide clusters.

The Pt catalyst containing larger Pt-hydroxide clusters had a better durability than the conventional Pt catalyst. We noted that the larger Pt-hydroxide clusters were efficient for reducing the PGM load.

After the duration process, the Pt active surface area was larger on the Pt catalyst containing the larger Pt-hydroxide clusters than the conventional Pt catalyst, which implies that Pt particle sintering was inhibited. The TEM images of the Pt particles before the duration process revealed a more uniform distribution of Pt particles on the Pt

catalyst containing the larger Pt-hydroxide clusters than the conventional catalyst. This uniformity lowered the opportunity for association of each Pt particle; therefore, sintering was inhibited.

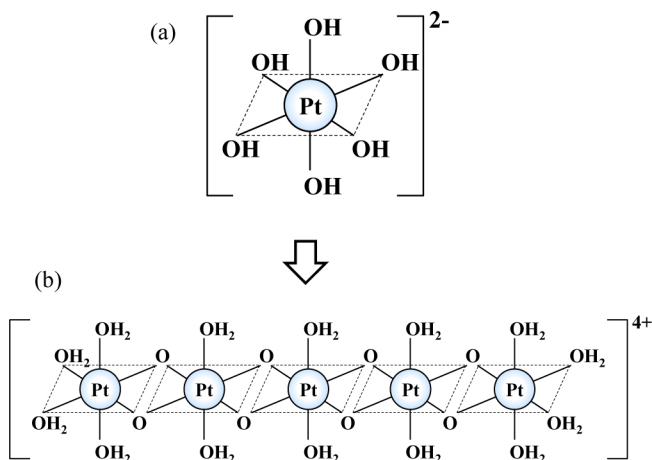


Figure 1. Schematics of (a) the Pt-hydroxide ion and (b) the Pt-hydroxide cluster.

EXPERIMENTAL

Material Evaluation

Cluster Size Control and Exploring the Appropriate Conditions for Preparing the Pt-Hydroxide Cluster Solution

We expected that the Pt catalyst containing the larger Pt-hydroxide clusters would have a better durability than the conventional Pt catalyst; therefore, we initially explored the conditions in which the Pt-hydroxide clusters increased in size. A mixed solution of hexahydroxyplatinate(IV) (Pt(OH)₆·H₂O, Tanaka Kikinzoku Kogyo Co., Ltd.), nitric acid (60 wt% HNO₃), and ion-exchanged water was prepared. The following Pt and nitric acid concentrations were examined: 10, 12, and 14 g/L and 5.0, 5.5, 6.0, and 6.5 mol/L, respectively. After keeping the solutions at 70 °C for 22 h, the Pt-hydroxide cluster size was measured by dynamic light scattering (Zetasizer Nano ZS, Malvern Instruments, Ltd.).

Catalyst Samples

Catalyst Containing Larger Pt-Hydroxide Cluster

The methods to prepare the catalyst samples are shown in Fig. 2. The solution for Pt precipitation was prepared by adding zirconium oxynitrate to the Pt-hydroxide cluster solution, and then diluting by adding a 1 mol/L ammonium acetate solution. The final molar ratio of Pt to Zr was Pt/Zr=1/15, and the Pt concentration was 0.50 g/L.

The Pt-hydroxide clusters precipitated on a cerium-zirconium composite oxide support by maintaining a mixture of 10 g Ce-Zr composite oxide powder and a 200 mL solution for Pt precipitation at 60 °C for 6 h, and next at 70 °C for 18 h with agitation. The solid substance that was divided from the mixture was calcined at 500 °C for 1 h. The Pt catalyst containing the larger Pt-hydroxide clusters was obtained; the Pt load was 1 wt% Pt.

Conventional Catalyst

The solution for Pt precipitation was prepared by diluting a dinitrodiammine-Pt (Tanaka Kikinzoku Kogyo Co., Ltd.) solution with ion-exchanged water. The Pt concentration was 0.50 g/L. The dinitrodiammine-Pt precipitated on a cerium-zirconium composite oxide support by keeping a mixture of 10 g Ce-Zr composite oxide powder and a 200 mL solution for Pt precipitation at room temperature for 24 h with agitation. Then, the conventional Pt catalyst was obtained by calcining the solid substance in the solution according to the same procedure as for the catalyst containing the larger Pt-hydroxide clusters. The Pt load was 1 wt% Pt.

Thermal Duration

Thermal duration was processed by maintaining the catalyst containing the larger Pt-hydroxide clusters and the conventional catalyst at 900 °C for 10 min or 5 h (300 min) in an air atmosphere.

Nano-Structure Observation

The nano-structure of the catalyst containing the larger Pt-hydroxide clusters and the conventional catalyst before the thermal duration were observed by high angle annular dark field-scanning transmission electron microscopy (HAADF-STEM, JEM-ARM200F JEOL Co., Ltd.). The samples were pretreated with a H₂ flow at 500 °C for 60 min.

Pt Active Surface Area Measurement

The Pt active surface area was estimated for each Pt catalyst before and after the thermal duration by the CO chemisorption method (Quantachrome Instruments Autosorb-1). The amount of chemisorbed CO is proportional to the active Pt surface area, and was measured at 35 °C. The samples were pretreated with an O₂ flow at 400 °C for 120 min followed by a H₂ flow at 400 °C for 120 min.

Catalytic Activity Evaluation

Catalyst Samples for Simulant Gas Test

Catalyst Containing Larger Pt-Hydroxide Cluster

The solution for the Pt precipitation of the larger Pt-hydroxide clusters was prepared by the same method as described in the Material Evaluation section. The Pt-hydroxide cluster size was 6 nm, the molar ratio of Pt and Zr was Pt/Zr=1/15, and the Pt concentrations were 0.50 g/L and 0.17 g/L. The Pt-hydroxide clusters were precipitated on honeycomb substrates by keeping each honeycomb immersed in a 30 mL solution at 60 °C for 6 h then at 70 °C for 18 h. The honeycombs were then removed from each solution and calcined at 500 °C for 1 h. The Pt loads of the obtained catalysts were 1.0 g/L and 0.3 g/L. The honeycomb was made of cordierite and was coated with the Ce-Zr composite oxide and alumina (diameter = 25 mm, length = 30 mm, cell density = 900 cpsi (cells per square inch), and wall thickness = 63.5 μm).

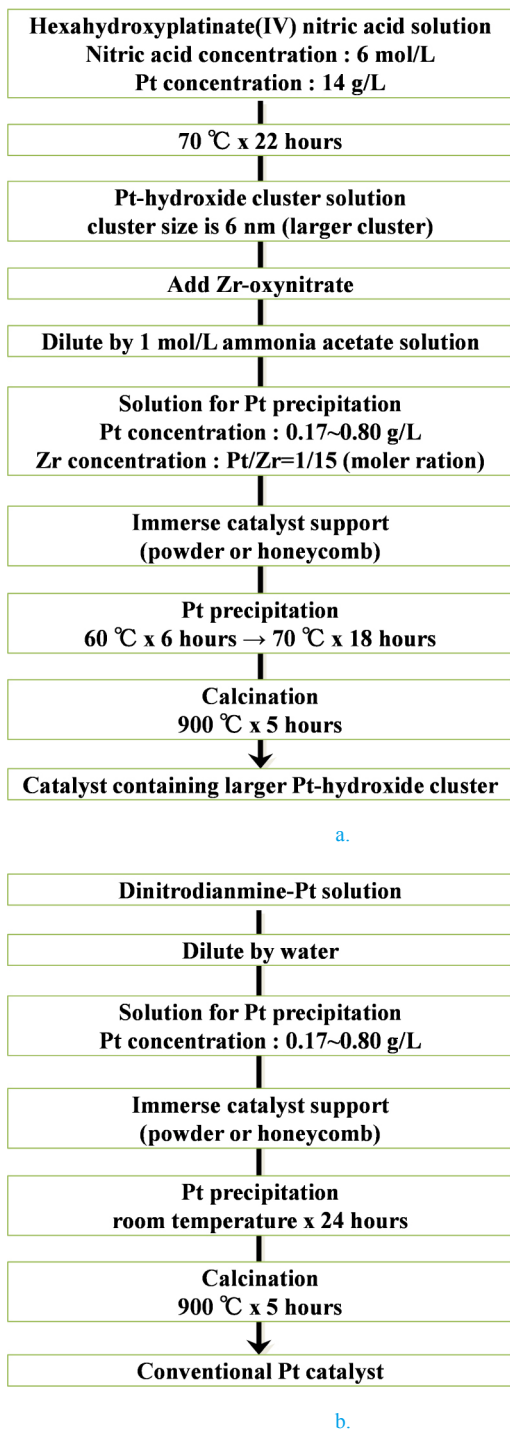


Figure 2. Methods for preparing each catalyst sample: (a) the catalyst containing the larger Pt-hydroxide clusters and (b) the conventional catalyst.

Conventional Catalyst

The solution for Pt precipitation was prepared by the same method as outlined in the Material Evaluation section. The Pt concentration was 0.50 g/L.

Pt was precipitated on honeycomb substrates by keeping the honeycomb immersed in the 30 mL solution for Pt precipitation at room temperature for 24 h. Then, the salvaged honeycomb was calcined at 500 °C for 1 h. The Pt load was 1.0 g/L. The honeycomb was the same as that used for making the Pt catalyst containing the Pt-hydroxide clusters.

Thermal Duration

Thermal duration was processed by keeping each Pt catalyst at 900 °C for 5 h in an air atmosphere.

Simulant Gas Test

The Pt catalyst sample (25.4 mm (diameter) × 30 mm (length)) was set in a gas flow reactor and the simulant stoichiometric exhaust gas was supplied at 25 L/min, i.e., the space velocity was 90 000 h⁻¹. The composition of the simulant gas is shown in Table 1. The inlet gas temperature was elevated from 150 °C to 500 °C at a ramp rate of 30 °C/min. The simulant gas was sampled at the inlet or outlet of the catalyst, and the concentrations of CO, HC, and NO_x were measured. The conversion was calculated according to the following formula:

$$\text{Conversion [\%]} = 100 * \left(1 - \frac{\text{outlet gas concentration}}{\text{inlet gas concentration}}\right)$$

Table 1. Composition of the simulant stoichiometric exhaust gas.

Component	Concentration
N ₂	Balance
CO ₂ [%]	13.9
O ₂ [ppm]	7 600
NO [ppm]	3 400
CO [ppm]	13 900
C ₃ H ₆ [ppm]	530
C ₃ H ₈ [ppm]	260
H ₂ O [%]	10

Catalyst Sample for Vehicle Test

Catalyst Containing Larger Pt-Hydroxide Cluster / Conventional Catalyst

The catalyst containing the larger Pt-hydroxide clusters and the conventional catalyst (93 mm (diameter) × 95 mm (length)) were obtained by the same method as described in the Simulant Gas Test section. The Rh catalyst was coated with an additional top layer for the vehicle test only. The Pt and Rh loadings were 1.0 and 0.1 g/L, respectively.

Thermal Duration

Thermal duration was processed by keeping each Pt catalyst at 950 °C for 50 h under the exhaust gas flow of a gasoline engine.