

## Sintering Inhibition Mechanism of Platinum Supported on Ceria-Based Oxide for Automotive Catalysts

Three-way catalysts (TWCs) can efficiently purify harmful automobile emissions. Since being commercialized in the USA and Japan in 1977 [1], TWCs have played an important role in environmental protection. Recently, due to the increasing demand for global environmental protection, more stringent regulations have been imposed on the automobile industry. As a result, automobile companies are striving to purify automobile exhaust emissions. Consequently, there is a strong demand for the development of more advanced TWCs through technical innovations. **Figure 1** shows a brief overview of the TWC. An automotive TWC is placed under the floor or beside the engine of a vehicle. TWCs are composed of three components, namely, a precious metal such as Pt or Rh, a support such as  $\text{Al}_2\text{O}_3$ , and an oxygen storage/release component. The precious metal functions as a source of active sites that extract harmful components from automotive exhausts such as nitrogen oxides ( $\text{NO}_x$ ), carbon monoxide (CO) and unburned hydrocarbons (HC). The precious-metal particles are a few nanometers in diameter and are dispersed on a support oxide. When a TWC is exposed to a high temperature of about  $800\text{ }^\circ\text{C}$  or greater, the precious-metal agglomerates and is sintered, reducing the active surface area of the catalyst. Generally, the sintering of precious-metal particles during operation is considered to reduce the catalytic activity, that is, it degrades the catalyst. In addition, the exhaust from an automotive gasoline engine fluctuates between an oxidizing and a reducing atmosphere during vehicle operation. Specifically, the

activity of Pt-supported catalysts decreases to a considerably lower extent during high-temperature ageing in an oxidizing atmosphere than in a reducing atmosphere due to the sintering of the Pt particles [2]. Thus, the development of highly durable catalysts that do not undergo Pt sintering in an oxidizing atmosphere is a current goal of automotive industrial research. Although it is known that ceria-based oxides stabilize precious-metal dispersion [3], the interaction between Pt and ceria is very complicated and is still not fully understood. Here, we present the sintering inhibition mechanism of Pt particles on a ceria-based oxide at the atomic level based on the results of X-ray absorption spectroscopy at **BL01B1** and **BL16B2** [4].

In this work, we prepared  $\text{Pt}/\text{Al}_2\text{O}_3$  and  $\text{Pt}/\text{Ce-Zr-Y}$  mixed oxide (referred to as CZY).  $\text{Pt}/\text{Al}_2\text{O}_3$  and  $\text{Pt}/\text{CZY}$  samples are considered as models of conventional and newly developed catalysts, respectively. The samples were aged in air for 5 h at  $800\text{ }^\circ\text{C}$ . This ageing treatment involved to an accelerated test for durability in an oxidizing atmosphere. **Figure 2** shows the Fourier transforms (FTs) of Pt  $L_3$ -edge EXAFS spectra for the aged catalysts and reference samples. The FT spectrum of  $\text{Pt}/\text{Al}_2\text{O}_3$  after ageing is clearly different from that of  $\text{Pt}/\text{CZY}$ . For the aged  $\text{Pt}/\text{Al}_2\text{O}_3$ , only an intense peak at  $2.76\text{ \AA}$ , which corresponds to the Pt-Pt bond, was observed. The FT spectrum of  $\text{Pt}/\text{Al}_2\text{O}_3$  was similar to that of Pt foil. The coordination number of the Pt-Pt shell in the aged  $\text{Pt}/\text{Al}_2\text{O}_3$  was 11.5. This indicates that the Pt metal particles on  $\text{Al}_2\text{O}_3$  after ageing are at

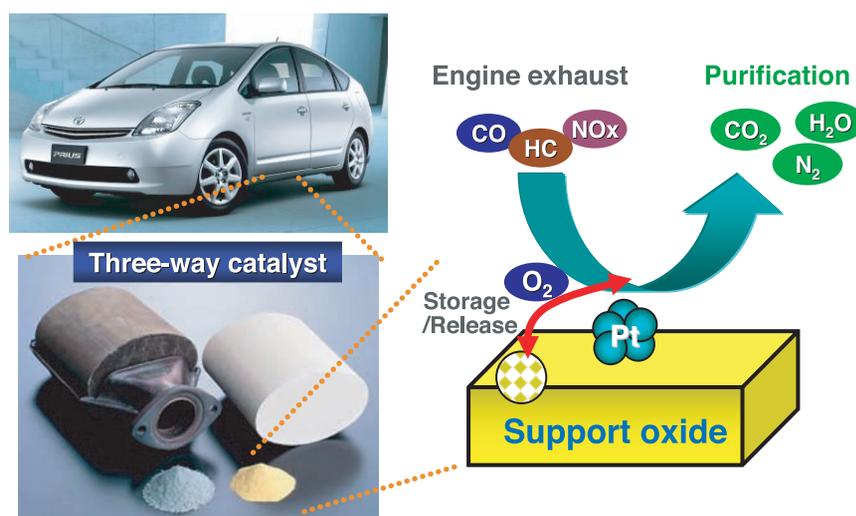


Fig. 1. Automotive three-way catalyst used for emission control.

least 20 nm in size. Actually, the average particle size in the aged Pt/Al<sub>2</sub>O<sub>3</sub>, determined by the CO pulse method, was 24 nm. The FT spectrum of Pt/CZY after ageing was different from the spectra of both Pt foil and PtO<sub>2</sub> powder. The position of the first peak at 2.02 Å in Pt/CZY was close to that of PtO<sub>2</sub>, and this peak was fitted with the Pt-O bond. It should be noted that the second peak in the spectrum, which was absent in the spectra of both Pt foil and PtO<sub>2</sub> powder, was at 3.01 Å. A curve-fitting simulation of this second peak was carefully performed. An excellent fitting result for the simulation of a Ce atom could be obtained. This result leads to the conclusion that Pt atoms strongly interact with the CZY support during ageing and form Pt-O-Ce bonds. The value of the coordination number of the Pt-Ce shell in the aged Pt/CZY was 3.5. This is lower than 12, which is the saturated coordination number for the cubic fluorite structure. This indicates that Pt ions exist on the surface of the CZY support.

On the basis of the above observation, we propose the sintering inhibition mechanism of Pt supported on CZY shown in Fig. 3. In the case of Pt/Al<sub>2</sub>O<sub>3</sub>, since the interaction between Pt and Al<sub>2</sub>O<sub>3</sub> is weak, Pt particles migrate across the surface of the Al<sub>2</sub>O<sub>3</sub> support and are sintered during 800 °C ageing treatment in an oxidizing atmosphere. In contrast, Pt supported on CZY strongly interacts with the CZY support. Therefore the CZY support stabilizes the high-oxidation state of Pt, and the formation of a rigid Pt-O-Ce bond acts as an anchor. The formation of Pt-O-Ce bonds on CZY suppresses the sintering of Pt. Generally, Pt<sup>0</sup> (metal) is considered to be the active

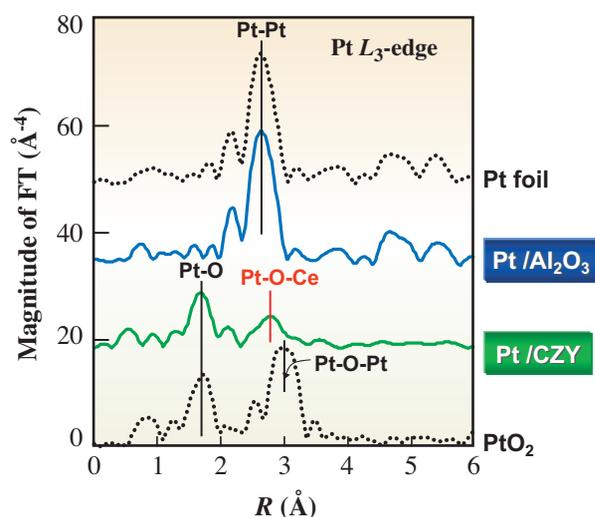


Fig. 2. Fourier-transformed  $k^3\chi$  data of Pt L<sub>3</sub>-edge EXAFS for supported Pt catalysts after 800 °C ageing in air and the standard samples of Pt foil and PtO<sub>2</sub> powder.

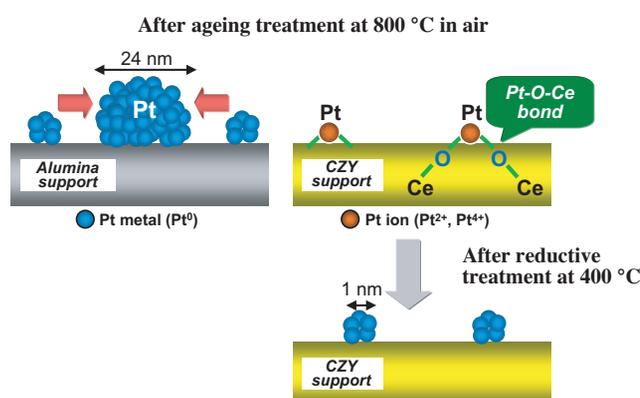


Fig. 3. Schematic illustration of the Pt sintering inhibition mechanism for a Pt/ceria-based catalyst and a conventional Pt/Al<sub>2</sub>O<sub>3</sub> catalyst.

site for the catalytic reaction in automotive exhaust conditions. The CZY support can stabilize a high-oxidation state of Pt after aging. Therefore, Pt on the CZY support must be reducible during the catalytic reaction. In another experiment, we confirmed that the Pt-O-Ce bond easily breaks by reductive treatment and that Pt metal particles are highly dispersed on the CZY support. According to the results from the CO pulse method, the estimated average size of Pt metal particles in the reduced Pt/CZY after the aging is ca. 1 nm. The Pt particle size is the same as that in the fresh catalyst. This indicates that Pt in the Pt/CZY catalyst did not sinter at all during the ageing treatment.

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