

In Situ Redispersion of Platinum Nanoparticles Supported on Ceria-Based Oxide for Autoexhaust Catalysts

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Introduction

Automotive three-way catalysts (TWCs) can purify harmful automobile emissions. When the autoexhaust catalyst is exposed to high temperatures (~800 °C and above), the metal nanoparticles agglomerate and sinter, decreasing the active surface area. Exhaust gases exiting from gasoline engines change quickly and dramatically, during operation. Hence, in situ dynamic observation on the sintering and redispersion phenomena of the precious metal in the automotive catalysts is very important indeed. In this report, we present the in situ observation of the nanoparticle behaviour of Pt supported on ceria-based oxide catalysts [1].

Materials and Methods

2 wt% Pt/Ce-Zr-Y-O₂ (referred to as CZY) catalysts were prepared by the conventional wet impregnation of CZY powders with Pt(NH₃)₂(NO₂)₂ aqueous solution. The impregnated powders were calcined at 500 °C for 3 h in air. The dynamic observation of Pt particle size was made by in-situ time-resolved Turbo-XAS in fluorescence mode at ID-24 of ESRF [2]. 3 % H₂ (He balance) and 4 or 20 % O₂ (He balance) gases were introduced to the in-situ cell cyclically every 60 seconds. Pt L_{III}-edge XANES spectra were collected every 6 seconds. Measurement of in situ TEM were was carried out at about 820 °C in 1.3 kPa of O₂.

Results and Discussion

Figure 1 shows the variation of the white line peak height of the normalized Pt L_{III} edge XANES for the fresh Pt/CZY catalysts under cyclical oxidizing/reducing condition at 400 ~ 800 °C. ΔI in Figure 1 denotes the difference between the white line peak height of the oxidized and reduced samples. From our experiment [1], we found that the ΔI increased with the decreasing particle size of Pt. Using the correlation between the Pt particle size and ΔI , we observed that the Pt particle size got bigger and smaller according to the temperature. It is interesting to note that the sintering/redispersion phenomena can be reversibly controlled using the sample temperature. Importantly, and in contrast, only facile sintering of Pt particles occurred is observed in the Pt/Al₂O₃ case, and Pt redispersion is not achieved at any temperature. As such, this kind of Pt redispersion on CZY is reasonably attributed to the strong Pt-ceria support interaction [3].

Figure 2 shows snapshots of the progression of structural changes as viewed by the in-situ TEM during the redispersion process. The Pt particles (1 and 2) decreased in size greatly, and Pt particle in the circle 3 disappeared completely. In the TEM movie, it should be noted that no crystallite migration and splitting were observed under these conditions.

Significance

Through in situ time-resolved spectroscopy and microscopy, an atomic migration mechanism is shown to account for the observed redispersion through the trapping of atomic Pt species at sites on the Ce support that exhibit a strong Pt-oxide-support interaction.

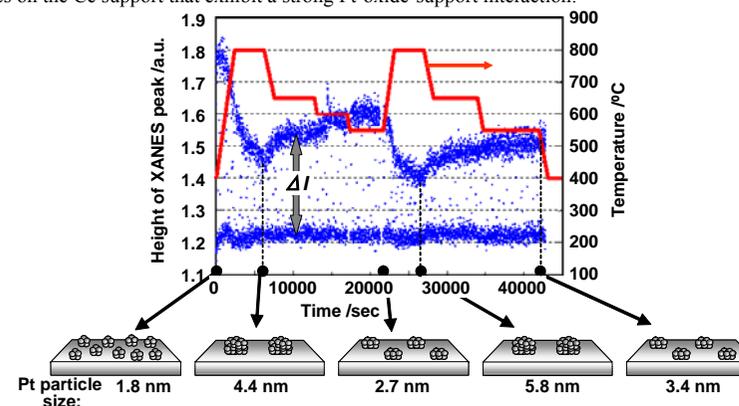


Figure 1. Temporal dependence of the white-line peak height of the Pt L_{III} edge XANES for fresh a) Pt/Al₂O₃ and b) Pt/CZY catalysts at 400–800 °C under redox cycling (4 or 20% O₂/He and 3% H₂/He gases, 60 sec each) and a schematic representation of the sintering/redispersion.

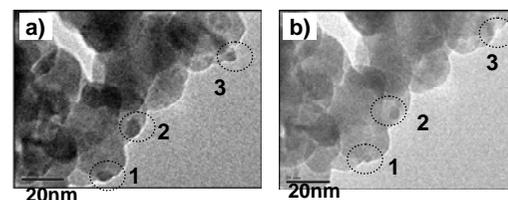


Figure 2. In situ TEM images of the Pt redispersion process for a preaged Pt/CZY sample (Pt particle size 6.7 nm). Images were recorded at a pressure of 1.3 kPa O₂ at 820 °C a) at the start of the experiment, and b) after 6 min.

References

1. Nagai Y., et al. *Angew. Chem. Int. Ed.*, 47, 9303 (2008).
2. Pascarelli, S., et al. *J. Synchrotron Rad.*, 6, 1044 (1999).
3. Nagai Y., et al. *J. Catal.*, 242, 103 (2006).