

Real-time Observation of Platinum Redispersion on Ceria-based oxide by In-situ Turbo-XAS

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Introduction

Automotive three-way catalysts (TWCs) can efficiently purify harmful automobile emissions [1]. When the TWC is exposed to high temperatures (~800 °C and above), the precious metal (Pt, Rh, Pd) agglomerates and sinters, decreasing the active surface area (i.e., degradation). Moreover, exhaust conditions from an automotive gasoline engine fluctuate between oxidative and reductive atmospheres during vehicle operation. Therefore, in-situ dynamic observation on the sintering and redispersion phenomena of the precious metal in the automotive catalysts is important. In this report, we present the real-time observation of the redispersion of Pt supported on ceria-based oxide catalysts.

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. Catalyst powders were treated under various aging conditions to obtain the specific particle size of sintered Pt. The particle size of Pt metal was measured using a CO pulse adsorption method. The real-time observation of redispersion behavior of sintered Pt was made by in-situ time-resolved Turbo-XAS in fluorescence mode at ID-24 of ESRF [2]. 3% H₂ (He balance) and 20% O₂ (He balance) gases were introduced to the in-situ cell cyclically every 60 seconds. Pt L₃-edge XANES spectra were collected every 1.1 seconds.

Results and Discussion

Fig. 1-a) shows Pt L₃-edge XANES spectra of Pt/CZY catalyst under oxidizing (20% O₂) / reducing (3% H₂) atmosphere at 400 °C. The ΔI denotes the difference between the white-line peak height of the oxidized and reduced samples. The ΔI did not change under the repetition of oxidizing/reducing conditions at 400 °C. The relationship between the various Pt particle size determined by the CO pulse method and the ΔI is presented in Fig. 1-b). The ΔI increases with the decreasing particle size of Pt. This indicates that the portion of surface oxidation on the Pt particles enlarges as the particle size gets smaller. Therefore, time-resolved measurement of XAFS spectra under in-situ condition enables “in-situ real-time measurement of Pt particle size”

Real-time observation of Pt redispersion on CZY support is presented in Fig. 2. The preliminarily sintered Pt/CZY catalyst with the Pt particle size of 7 nm determined by the CO

pulse adsorption method was used for the redispersion experiment. In this figure, the changing of the white-line peak height of the normalized Pt L₃-edge XANES spectra under cyclical oxidizing/reducing condition at 600 °C is shown as a function of time. While the white-line peak height of the reduced catalyst is constant, the height of the oxidized catalyst corresponds to ΔI . The ΔI gradually increased with time. Using the correlation between the Pt particle size and ΔI in Fig. 1-b), this redispersion phenomenon is interpreted as follows. The Pt particle size of the aged catalyst decreases from 7 to 5 nm after 60 seconds, and then to 3 nm after 1000 seconds. This kind of Pt redispersion was not observed in a conventional Pt/Al₂O₃ catalyst. It is reasonable that the strong Pt-ceria support interaction [3] caused this Pt redispersion.

Significance

Using the in-situ T-XAS in fluoro-mode, we discovered a in-situ dynamic redispersion behavior for sintered Pt supported ceria-based oxide catalyst.

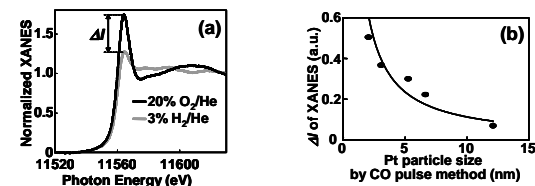


Figure 1. (a) Pt L₃-edge XANES of a Pt/CZY catalyst under oxidizing/reducing atmosphere at 400°C. (b) Relationship between ΔI and Pt particle size estimated by CO pulse method for pre-aged Pt/CZY catalysts with the specific particle size of sintered Pt.

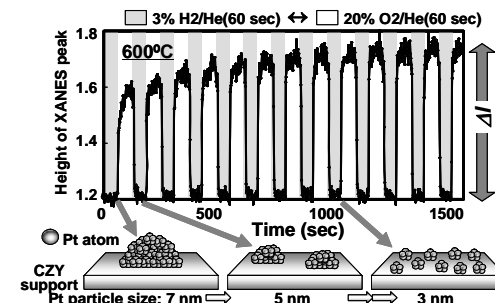


Figure 2. Time course of the height of XANES peak for the sintered Pt/CZY catalyst (Pt particle size; 7nm) and the schematic representation of the redispersion behavior.

References

1. Matsumoto, S. *Catal. Today*, 90, 183 (2004).
2. Pascarelli, S., et al. *J. Synchrotron Rad.*, 6, 1044 (1999).
3. Nagai Y., et al. *J. Catal.*, 242, 103 (2006).