

Precise Observation of Dynamic Structural Change of Pd Particles under CO/NO Catalytic Reaction Studied by Dispersive X-Ray Absorption Fine Structure

The metal particles used in the catalytic reaction are made fine in order to spread the surface area and increase the reaction space. However, it is expected that the nanometer-sized metal particles show the original catalytic reaction which is different from that for the larger particles. In recent studies, it has been revealed that the small particles show size dependent properties, that is, the lattice constant, oxidation process, shape of the particles, and so on. At this moment, we have to consider the fine particle itself as the independent research subject that includes the particle-support and particle-gas interactions, and the study of fine particles by the bulk and surface systems approach is insufficient.

Pd metal particles are used in automotive exhaust catalysts for the removal of CO, NO_x and hydrocarbons. Newton and coworkers pointed out that the Pd metal fine particles show a rapid change in the mean particle size during the catalytic reaction [1]. They used the X-ray absorption fine structure (XAFS) technique, which has the element-selective and local sensitive features, and therefore, has been frequently used for the study of the supported fine particles. In particular, the dispersive optical system that was used in the above study has some original features. The dispersive optical system enables us to observe XAFS spectra without mechanical movement [2]. Although this system has been mainly applied for the real-time-resolved observation of chemical reaction, the precise determination of XAFS parameters has also been accomplished. In this study, both advantages of dispersive XAFS, namely, fast and precise observations, were applied to the structure and shape changes of Pd metal fine particles [3]. *In situ* and real-time observations of the CO/NO catalytic reaction on the Pd/Al₂O₃ with 0.2 Hz rate resulted in the highly stable structural and electronic parameters.

The Pd *K*-edge XAFS spectra were measured at the bending magnet beamlines **BL14B1** and **BL28B2**. The main systems of optical equipment at both beamlines are similar and are displayed in Fig. 1. Dispersed X-rays were obtained from the curved crystal of the Si(422) reflection plane with the Laue configuration. From the curvature with a radius of 2000 mm, X-rays with an energy range of 800 eV were obtained. Gd₂O₂S(Tb) was exposed to dispersed X-rays from the sample, and emitted lights were collected using a charge-coupled device (CCD) camera (12 bits). Powdered γ-Al₂O₃ was used in the impregnation with dilute aqueous palladium nitric

acid, Pd(NO₃)₂. Following drying and calcination at 500°C, Pd(4 wt%)/Al₂O₃ sample was prepared. For the CO/NO catalytic reaction study, CO(9%)/He and NO(9%)/He were used. The gases were supplied at a flow rate of 50 cc/min. Spectra were measured at 0.2 Hz.

Figure 2 shows the extended X-ray absorption fine structure (EXAFS) functions of the Pd/Al₂O₃ during CO flow at 400°C for 1000 s. The gradual changes in the amplitude and wavelength are clearly recognized. A decrease in the amplitude means a decrease in the Pd-Pd coordination number (*CN*), and a shortening of the wavelength means an expansion of the Pd-Pd interatomic distance (*R*). It is noted that both changes in the amplitude and wavelength show very smooth shifts. Variations in the XAFS parameters during CO/NO successive flow for the Pd metal particles are shown in Fig. 3. From the analysis of Pd-Pd first shell in the metal state, *CN*, *R*, Debye-Waller factor (*C*₂) and edge shift were determined. It is understood that all the obtained XAFS parameters show high relative statistics, that is, 0.02 eV for the edge shift, 0.05 for the *CN* and 0.002 Å for the *R*.

For CO first flow, it is revealed that the enlargement of the *R* of 0.07 Å is brought about by CO. Some of the adsorbed CO are considered to dissociate on the surface of Pd particles, and the crystal lattice is expanded by atomic C that is absorbed into the interstitial position. The *CN* of the Pd-Pd shell gradually decreases at the same time scale as the increase in the *R*, which means that CO dissociative adsorption can induce the dispersion of Pd metal fine particles. After NO flow, the expanded lattice rapidly contracts with the recovery of the original values for the edge shift and *CN*, suggesting the removal of both the adsorbed CO and absorbed C. The edge shift denotes a gradual increase after CO removal by NO flow, which indicates that the surface of Pd particles is gradually oxidized by the dissociative

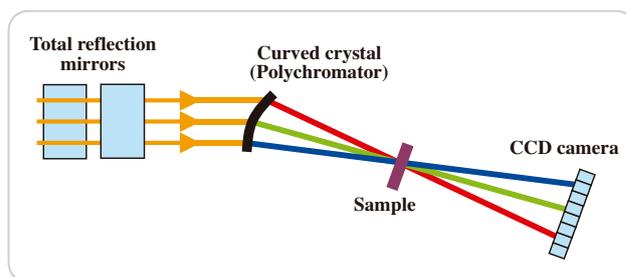


Fig. 1. Schematic of the dispersive XAFS observation.

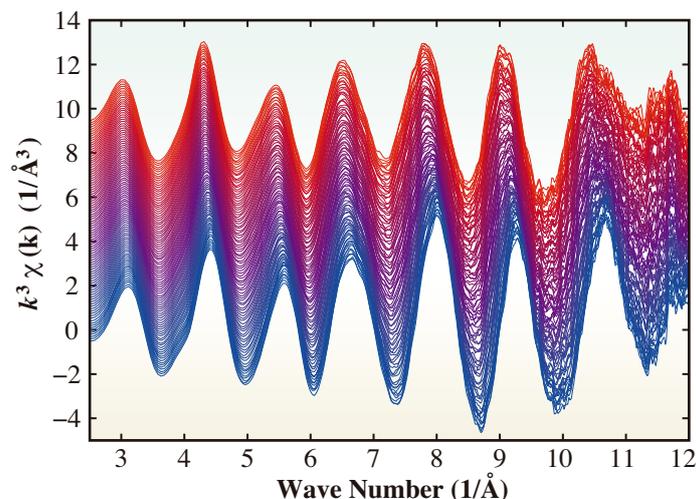


Fig. 2. 0.2 Hz observation of k^3 -weighted EXAFS functions of the Pd/Al₂O₃ at 400°C during CO flow from 0 s (bottom) to 1000 s (top).

adsorption of NO. This surface-oxidized layer is smoothly removed by the next CO flow, which is confirmed from the abrupt changes in the edge shift and CN. As for the edge shift, a slight positive shift is also observed just after second CO flow. CO adsorption on the Pd oxidized layer may induce the charge transfer from Pd to CO. After the removal of the surface-oxidized layer, a gradual increase in the R is observed again. CO adsorption on the Pd surface is normally considered as the molecular adsorption at

the C end. In this study, it has been revealed that the slow dissociative adsorption mode exists and causes the expansion of the Pd lattice and the dispersion of the Pd particles, which creates a new understanding of the CO/NO catalytic reaction. As for the surface-oxidized layer, the slow creation and rapid removal make the surface of the particles clean during the long catalytic reaction. The charge transfer just after the second CO flow implies the particular adsorption state and may be the key to the fast cleaning of the Pd surface oxide layer. It has been clearly demonstrated by *in situ* and real-time-resolved dispersive XAFS observation that several dynamic mechanisms such as contraction-expansion, aggregation-dispersion and oxidation-reduction changes are recognized in metal fine particles.

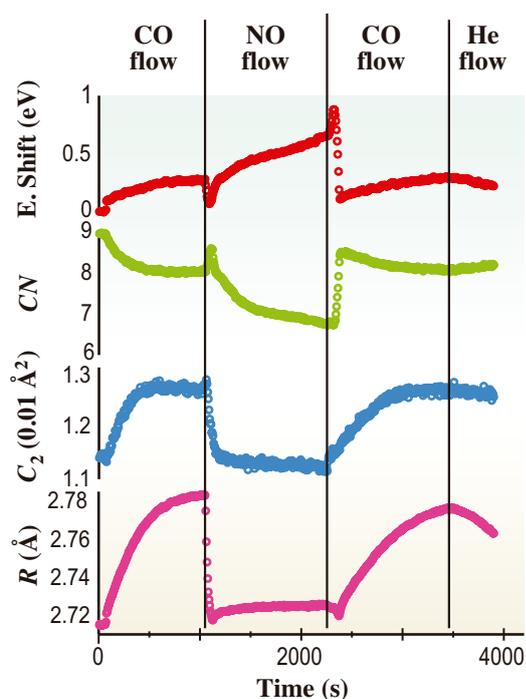


Fig. 3. Variations of XAFS parameters for the Pd-Pd shell of Pd/Al₂O₃ during CO/NO successive flow at 400°C.

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