

DXAFS Studies on the Spontaneous Dispersion of PdO Interacted with Zeolites

Metal-support interaction in supported metal catalysts is important in understanding the structure and catalysis of supported metal. Previous studies concerning palladium catalysis, such as selective reduction of NO and total oxidation of methane, revealed that the catalysis of the Pd center was significantly affected by the acid property of the support. One of the reasons for these effects could be attributed to the strong interaction between PdO and acid sites of supports. Indeed, we have observed spontaneous migration of agglomerated metal Pd into the highly dispersed PdO on acid sites under O₂ atmosphere at elevated temperature. In addition it was found that the spontaneous dispersion of PdO upon repetition of reduction and oxidation treatment was reversible. The phenomena implied that the interaction between PdO and acid sites of zeolites plays an important role in the determination of dynamic behavior and structure of PdO. In this study, we tried to directly observe the dispersion process of PdO onto acid sites of zeolites. Although previous studies were primarily carried out under static conditions, the dynamic structural change of Pd could be directly observed using *in situ* and quick measurement of Pd structure. For this purpose, energy-dispersive EXAFS (DXAFS) technique newly equipped in SPring-8 was applied for the measurement of the local structure of Pd during Pd oxidation.

Pd *K*-edge DXAFS was measured at beamline BL28B2. An Si polychromator crystal was used in a Laue configuration with (422) net plane to obtain an X-ray beam with a dispersed energy region. The schematic configuration of DXAFS measurement is shown in Fig. 1. A waferlike sample was placed in a quartz *in situ* cell. The sample was heated from room temperature to 773 K with ramping rate of 5 K min⁻¹ in

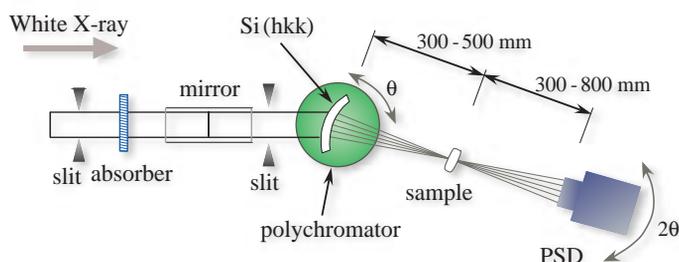


Fig. 1. Schematic view of DXAFS spectrometer with Laue configuration.

an O₂ flow at atmospheric pressure. The spectra measured for 0.3 sec were accumulated 10 times in every 10 K. An example of raw spectra for Pd/H-ZSM-5 (Si/Al₂ = 23.8) is shown in Fig. 2. It was confirmed that data with a high S/N ratio could be obtained despite the low concentration of Pd (0.4 wt%). Fourier transforms of the $k^3\chi(k)$ EXAFS for Pd loaded Na- and H-ZSM-5 were shown in Fig. 3. The coordination numbers of Pd-O, Pd-Pd (metal) and Pd-(O)-Pd (oxide) calculated based on the curve fitting analysis were given in Fig. 4. Initially, the formation of metal Pd was observed from the appearance of an intense nearest-neighboring Pd-Pd peak situated at 0.25 nm on both Pd/H-ZSM-5 and Na-ZSM-5. From the coordination number of the Pd-Pd peak, the Pd particle was supposed to locate on the external surface of zeolites. In the case of Pd/Na-ZSM-5 (Fig. 3(a)), the Pd-Pd (metal) gradually reduced accompanied by increasing the temperature in an oxygen flow. Alternatively, new peaks appeared at 0.15 and 0.32 nm. These peaks could be assigned to the Pd-O and Pd-(O)-Pd characteristic of bulk PdO that is apparent from the comparison with the

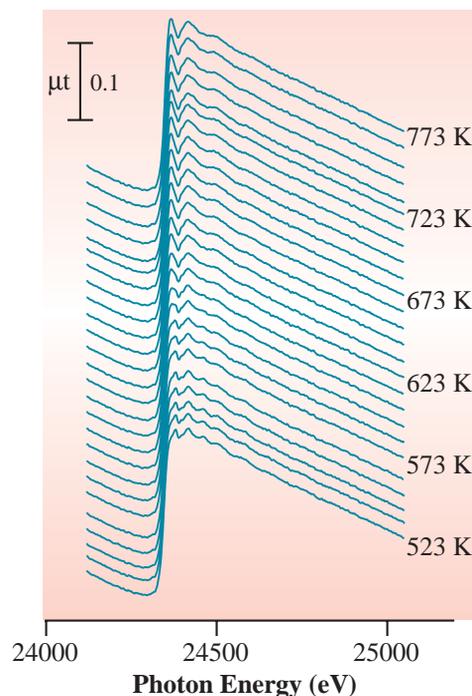


Fig. 2. Pd *K*-edge XAFS spectra for Pd (0.4 wt%) loaded on H-ZSM-5 (Si/Al₂ = 23.8) measured in an O₂ flow.

spectrum of bulk PdO. The generation of the Pd-(O)-Pd indicated that the metal Pd was simply transformed into the agglomerated PdO on the external surface of Na-ZSM-5 at elevated temperature. On the other hand, the metal Pd-Pd peak steeply disappeared at 643 K in the spectra of Pd/H-ZSM-5 (Fig. 3(b)). At the same time, the intensity of the Pd-O peak increased, indicating that the oxidation of metal Pd progressed with increasing the temperature. However, in contrast to the Na form of zeolites, the Pd-(O)-Pd peak due to the agglomerated PdO did not appear. The fact indicated that the agglomerated metal Pd was migrated on the acid sites of zeolites to generate highly dispersed PdO, because the intensity of Pd-(O)-Pd shell reflected the size of PdO. In addition, the data suggested that the migration of Pd occurred immediately after the oxidation of the metal Pd particle since the oxidation and the dispersion of Pd took place at the same time, which was confirmed from the data given in Fig. 4(b). Another dispersion process of PdO was revealed from the comparison with H-ZSM-5 and Na-ZSM-5. That is to say, the transformation of the metal Pd-Pd into Pd-O was steep and occurred at lower temperature over H-ZSM-5 with respect to Na-ZSM-5. Taking this into consideration, it could be assumed that, in addition to spontaneous dispersion of PdO, the oxidation of metal Pd was promoted through the strong metal-support interaction between acid sites of H-ZSM-5 and PdO which possessed basic character.

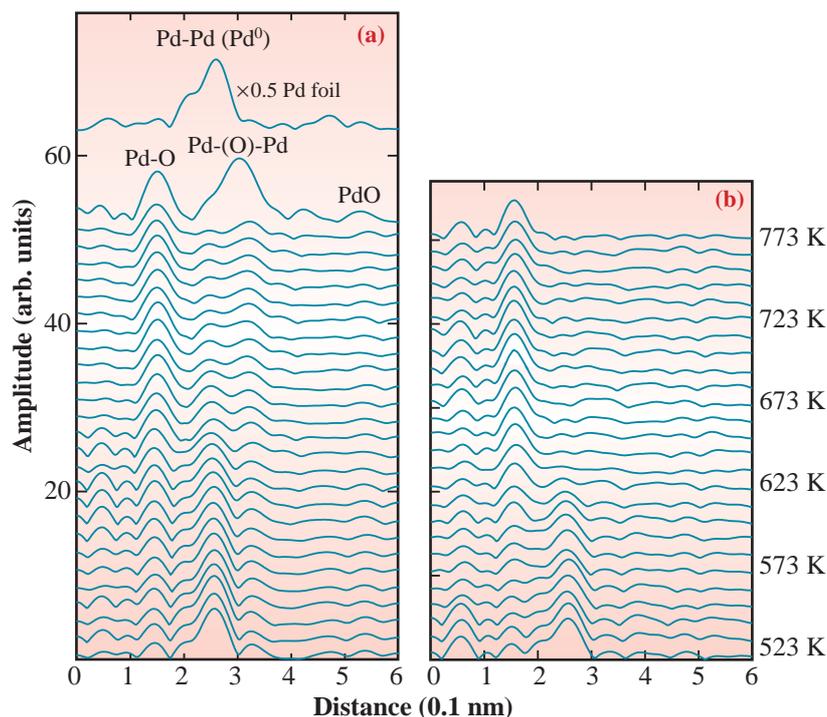


Fig. 3. Pd K-edge EXAFS Fourier transforms for Pd loaded on (a) Na-ZSM-5 ($\text{Si}/\text{Al}_2 = 23.8$) and (b) H-ZSM-5 ($\text{Si}/\text{Al}_2 = 23.8$) measured in an O_2 flow; Pd loading, 0.4 wt%; temperature ramping rate, 5 K min^{-1} . The spectra of PdO and Pd foil were collected at room temperature.

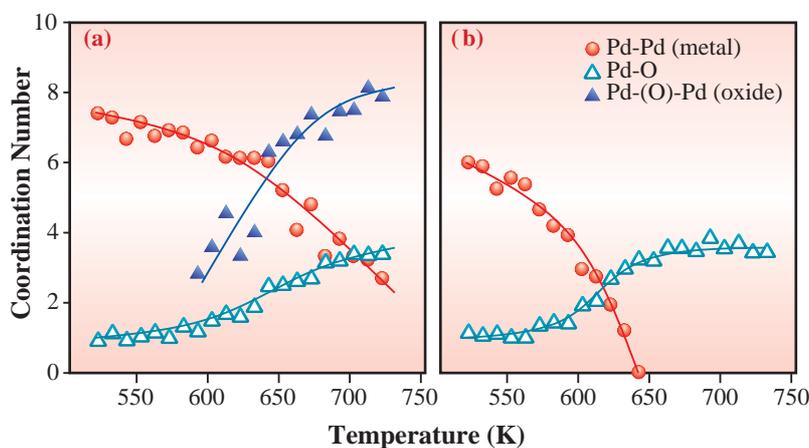


Fig. 4. Relationship between the coordination numbers of Pd loaded on (a) Na-ZSM-5 and (b) H-ZSM-5 and the temperature measured in an O_2 flow.

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References

- [1] K. Okumura, R. Yoshimoto, T. Uruga, H. Tanida, K. Kato, S. Yokota and M. Niwa: *J. Phys. Chem. B* **108** (2004) 6250.
- [2] K. Okumura *et al.*: *Phys. Scripta* - in press.
- [3] K. Okumura *et al.*: *Chem. Lett.* **32** (2003) 636.
- [4] K. Okumura and M. Niwa: *Catal. Surv. Jpn.* **5** (2002) 121.