

Spontaneous Dispersion of PdO onto Acid Sites of Zeolites Studied by in situ DXAFS

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(Received April 15, 2003; CL-030323)

The generation of highly dispersed PdO over zeolite supports was studied using in situ energy-dispersive XAFS (DXAFS) technique. From the comparison with the Na-ZSM-5, it was found that the oxidation as well as the spontaneous dispersion of Pd was promoted through the interaction between PdO and acid sites of H-form zeolites.

Metal-support interaction in supported metal catalysts is important in understanding the structure and catalysis of supported metal. Previous studies concerning palladium catalysts revealed that the catalysis of Pd center was significantly affected by the acid property of support.¹ For instance, Brønsted acidity of zeolite is essential for selective reduction of NO by methane over Pd. In addition, methane combustion activity of Pd was affected by the support surface.² 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.^{3,4} This spontaneous dispersion of PdO was reversible upon repetition of reduction and oxidation treatment. The highly dispersed PdO was considered to be active center in the selective reduction of NO by methane in the presence of O₂.² These observations implied that the interaction between PdO and acid sites of zeolites played important role in the determination of dynamic behavior and structure of PdO. In this study, in order to elucidate the dispersion process of PdO onto acid sites of zeolites and to elucidate the nature of metal-support interaction of zeolites, Na-, H-ZSM-5 and H-mordenite were employed as supports for Pd. Although previous studies were primarily carried out under static conditions, the dynamic structural change could be directly observed using in situ and quick measurement of Pd structure. For this purpose, energy-dispersive EXAFS (DXAFS) technique was applied for the measurement of the local structure of Pd during oxidation of Pd.⁵

ZSM-5 (Si/Al₂ = 23.8) and mordenite (JRC-Z-HM15, Si/Al₂ = 15) were supplied from Tosoh Co. and Catalysis Society of Japan, respectively. Pd was loaded on these zeolites through an ion exchange method using Pd(NH₃)₄Cl₂ solution. The prepared samples were calcined in an N₂ flow at 773 K as a pretreatment. 0.4 wt% of Pd was loaded on each zeolite.

Pd K-edge DXAFS was measured at BL28B2 station of Japan Synchrotron Radiation Research Institute (SPring-8). The storage ring was operated at 8 GeV. Si polychromator crystal was switched to a Laue configuration with (422) net plane to obtain X-ray beam with dispersed energy region. The energy of X-ray was calibrated with Pd foil as a reference. A wafer from of sample was placed in a quartz in situ cell. The thickness of the sample was 2.5 cm. The sample was heated from room temperature to 773 K with ramping rate of 5 K min⁻¹ in an O₂ flow (50 mL min⁻¹) at atmospheric pressure. The spectra measured

for 0.3 sec were accumulated 10 times in every 10 K. An example of the raw spectra for Pd/HZSM-5 was given in Figure 1. For extended X-ray absorption fine structure (EXAFS) analysis, the oscillation was extracted from the EXAFS data by a spline smoothing method.⁶ The oscillation was normalized by edge height around 50 eV above the threshold. The Fourier transformation of the *k*³-weighted EXAFS oscillation from *k* space to *r* space was performed over the range 20–110 nm⁻¹ to obtain a radial distribution function. The inversely Fourier filtered data were analyzed with a usual curve fitting method. For the curve fitting analysis, the empirical phase shift and amplitude functions for Pd–O and Pd–Pd were extracted from the data for PdO and Pd foil, respectively. Debye–Waller factors of Pd–Pd (metal Pd) and Pd–O, Pd–(O)–Pd (Pd scattering in Pd oxide) were extracted from the spectra of Pd powder and PdO, respectively. In the analysis of spectra of samples, the Debye–Waller factors were fixed at those of the reference materials measured at the same temperatures.

Fourier transforms of the *k*³ $\chi(k)$ EXAFS for Pd loaded zeolites were given in Figure 2. Initially, the formation of Pd metal was confirmed from the appearance of an intense nearest-neighboring Pd–Pd peak situated at 0.25 nm in every sample. From the coordination number of the Pd–Pd peak, the diameter of metal Pd was estimated to be larger than 1 nm. The fact indicated the generation of agglomerated metal Pd after the calcination of ion-exchanged Pd complex in N₂. In the case of Pd/Na-ZSM-5 (Figure 2a), the Pd–Pd (metal) gradually reduced accompanied by raising the temperature in an oxygen flow. Alternatively, new peaks appeared at 0.25 and 0.32 nm. These peaks could be assigned to the Pd–O and Pd–(O)–Pd characteristic of bulk PdO from the comparison with the reference spectrum of bulk PdO, respectively. In the spectra of Pd/HZSM-5 (Figure 2b), the Pd–Pd peak steeply

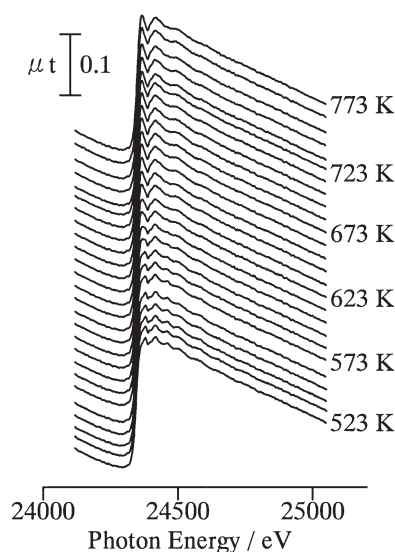


Figure 1. Pd K-edge XAFS spectra for Pd loaded on H-ZSM-5 (Si/Al₂ = 23.8) measured in an O₂ flow.

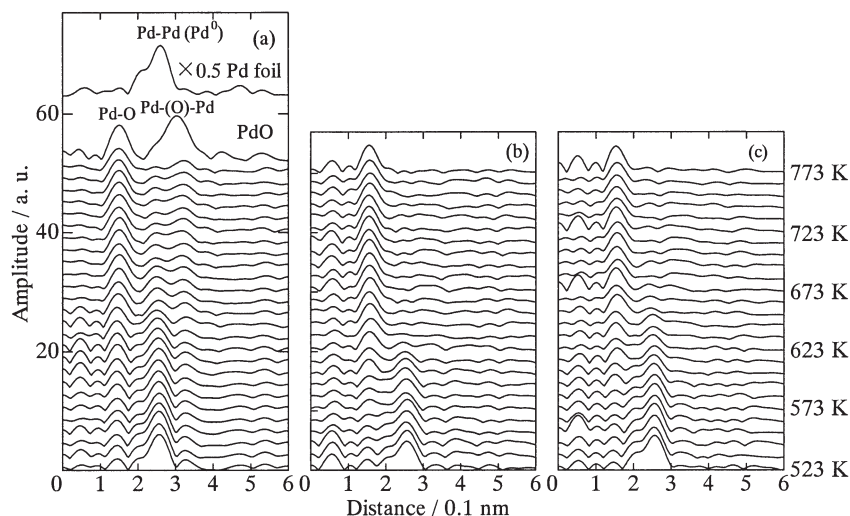


Figure 2. Pd K-edge EXAFS Fourier transforms for Pd loaded on (a) Na-ZSM-5 ($\text{Si}/\text{Al}_2 = 23.8$), (b) H-ZSM-5 ($\text{Si}/\text{Al}_2 = 23.8$), (c) H-Mordenite ($\text{Si}/\text{Al}_2 = 15$) measured in an O_2 flow; Pd loading, 0.4 wt%; Temperature ramping rate, 5 K min^{-1} ; The spectra of PdO and Pd foil were measured at room temperature.

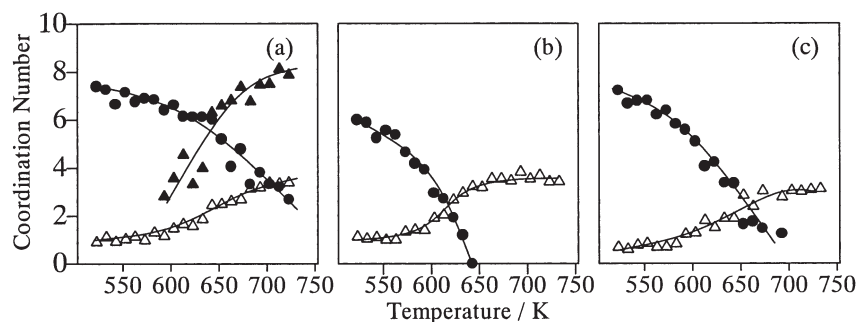


Figure 3. Dependence of coordination number on temperature for Pd loaded on (a) Na-ZSM-5 ($\text{Si}/\text{Al}_2 = 23.8$), (b) H-ZSM-5 ($\text{Si}/\text{Al}_2 = 23.8$), (c) H-Mordenite ($\text{Si}/\text{Al}_2 = 15$). Δ Pd-O, \bullet Pd-Pd (metal), \blacktriangle Pd-(O)-Pd (oxide).

disappeared at 643 K. At the same time, the intensity of the Pd-O peak increased, indicating the oxidation of metal Pd progressed with raising the temperature. However, Pd-(O)-Pd peak due to the agglomerated PdO did not appear. Although similar feature was observed in Pd/H-Mordenite (Figure 2c), the temperature for disappearance of Pd-Pd and the growth of Pd-O was higher than that of Pd/H-ZSM-5.

Figure 3 shows the coordination numbers (CN) of Pd-O, nearest-neighbor metal Pd-Pd, Pd-(O)-Pd of Pd oxide plotted as a function of oxidation temperature. The CN values were calculated based on the curve fitting analysis. As shown in Figure 3a, Pd-O and Pd-(O)-Pd peaks appeared in place of decrease in Pd-Pd due to metal on Na-ZSM-5 accompanied by increase in the temperature. The generation of the Pd-(O)-Pd meant that the metal Pd was simply transformed into the agglomerated PdO on the external surface of Na-ZSM-5 at elevated temperature. On H-ZSM-5 ($\text{Si}/\text{Al}_2 = 23.8$), the disappearance of Pd-Pd peak and the growth of Pd-O was observed at 643 K. However, in contrast to the Na-form of zeolites, Pd-(O)-Pd peak did not appear even after the disappearance of metal Pd, which was characteristic of the agglomerated PdO. The fact meant 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 seemed to reflect the size of PdO. In addition, the data suggested that the migration of Pd occurred immediately after the oxidation of metal Pd particle, since the oxidation and the dispersion of Pd took place at the same time. Another dispersion process of PdO

was revealed from the comparison with H-ZSM-5 and Na-ZSM-5. Namely, 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 the fact into account, it could be supposed 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. The disappearance of metal Pd-Pd and the alternative growth of the Pd-O were steep over H-ZSM-5 with respect to H-mordenite. Thus it could be noted that the dispersion of Pd on ZSM-5 was easier than that of Pd/H-mordenite. Probably, the pore structure of zeolite or character of acid center affected the oxidation and migration process of Pd.

The spontaneous dispersion process of PdO onto acid sites of zeolite was successfully measured using in situ DXAFS method. From the comparison with the Na-type zeolite, it was clarified that the strong interaction between PdO and H-form zeolites assisted the oxidation and migration of metal Pd.

References

- 1 K. Okumura and M. Niwa, *Catal. Surv. Jap.*, **5**, 121 (2002).
- 2 Y. H. Chin and D. E. Resasco, in "Catalysis," Vol. 14, Royal Society of Chemistry, London (1998).
- 3 K. Okumura, J. Amano, and M. Niwa, *J. Phys. Chem.*, **104**, 1050 (2000).
- 4 K. Okumura, J. Amano, and M. Niwa, *J. Phys. Chem.*, **104**, 9670 (2000).
- 5 M. K. Neylon, C. L. Marshall, and A. J. Kropf, *J. Am. Chem. Soc.*, **124**, 5457 (2002).
- 6 J. B. Van Zon, D. C. Koningsberger, H. F. J. Van Blik, and D. E. Sayers, *J. Phys. Chem.*, **82**, 5742 (1985).