STUDIES ON THE FORMATION AND STRUCTURE OF HIGHLY DISPERSED PdO INTERACTING WITH ACIDS SITES OF ZEOLITE BY EXAFS

Recently, much attention has been given to metal-loaded zeolite catalysts that use hydrocarbons as reductants. Methane is the most widely-used reductant because it is the main component of natural gas. Palladium is one of the most active and durable catalysts for the NO-CH_4-O_2 reaction. Zeolite is an especially favorable support for palladium, containing micropore and acid sites that allow it to retain its active structure It is widely believed that the acid sites of zeolite house the Pd^{2+} cation, and thus these were considered the active centers for the NO-CH_4-O_2 reaction. However, the development and structure of the active Pd species and its precursor, as well as the role of the acid sites associated with Pd are not clearly understood. In this study, the H-form of ZSM-5 zeolites with different Al contents were employed as supports for Pd and the induced structural change in Pd was followed by Pd K-edge EXAFS measurement [1,2].

ZSM-5 materials with various Al contents were used as supports for Pd. Pd was loaded onto HZSM-5 by ion exchange with a $Pd(NH_3)_4Cl_2$ solution. The catalysts were pre-treated by calcination in N_2 at 773 K. The final concentration of loaded Pd was calculated to be 0.2 wt%. The sample was transferred anaerobically to aluminum cells with two Kapton windows connected to a flow reaction system. In spite of the low Pd concentration, fairly good spectra were obtained.

Pd K-edge EXAFS was measured at beamline **BL01B1** . The storage ring was operated at 8 GeV with a stored current of 44-65 mA. Si(311) double crystal monochromator was used to obtain monochromatic X-ray beam. EXAFS data were collected in a transmission mode at room temperature. Two ion chambers filled with Ar and Kr were used as detectors of I_0 and I, respectively.

Figure 1 shows the Fourier transforms (FT) of the $k^3\chi(k)$ EXAFS for Pd/HZSM-5 with different Al content. All samples were oxidized under a flow of O_2 at 773 K for 3 hours before the measurement. In the Pd/HSM-5 (Si/Al_2=75) spectrum, two intense Pd-Pd peaks appeared at 0.26 and 0.31 nm
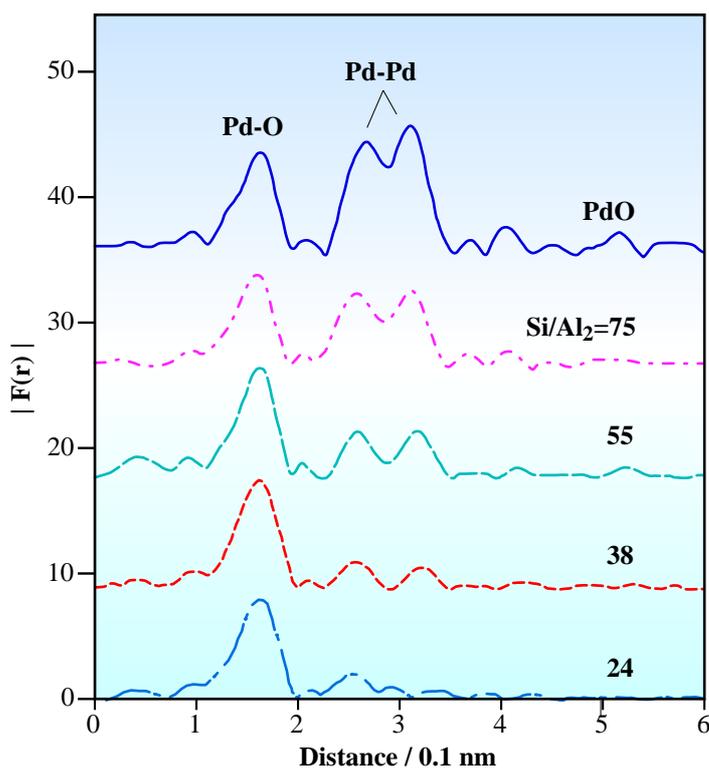
Fig. 1. Pd K-edge EXAFS Fourier transforms for PdO and Pd HZSM-5 oxidized at 773 K.

(phase shift uncorrected). These peaks decreased in magnitude with increasing Al content, disappearing completely in the spectrum for the Pd/HZSM-5 with highest Al content (Si/Al$_2$=24), the combination in which the NO-CH$_4$-O$_2$ reaction was most active. These results indicate that the size of PdO is inversely related to the acidity of HZSM-5, since the intensity of Pd-Pd shell seems to reflect the size of PdO.

To confirm the ability of zeolite acid sites to anchor PdO, the regeneration of dispersed PdO upon repetition of reduction and oxidation treatments was analyzed by EXAFS. The experiment was conducted using Pd/HZSM-5 (Si/Al$_2$=24), in which highly dispersed PdO was observed in the aforementioned oxidation experiment. Figure 2(b) shows the EXAFS FT spectrum measured after the reduction of previously oxidized Pd/HZSM-5 (Si/Al$_2$=24). The formation of metal Pd was confirmed by the appearance of an intense peak at 0.24 nm. The particle size of the metal Pd calculated from the Pd-Pd coordination number (CN=10.6) was estimated to be >3 nm, which is far larger than the zeolite pore diameter. This result indicates that treatment with H$_2$ reduced the highly dispersed PdO, which then migrated to form Pd metal aggregates on the external surface of ZSM-5. The reduced sample was successively re-oxidized under O$_2$ at 773 K for 3 hours. The spectrum measured after the reoxidation was identical to that measured after initial oxidation treatment (Fig. 2(c)). This result indicates that the Pd aggregates were disrupted upon oxidation and returned to the HZSM-5 pores as highly-dispersed PdO. This behavior illustrates the high mobility of PdO and the presence of strong interactions between PdO and acid sites of HZSM-5. Based on these analyses, the local structure of Pd in oxidized Pd/HZSM-5 (Si/Al$_2$=24) is proposed to be as shown in Fig. 3, where Pd was surrounded by four oxygen atoms, some of which are derived from the zeolite structure.

The disruption of Pd metal aggregates and reformation of the oxidized conjugates was driven by strong acid-base interactions between the acidic zeolite sites and the basic dispersed PdO. It is appropriate, then, to categorize PdO as a basic oxide.
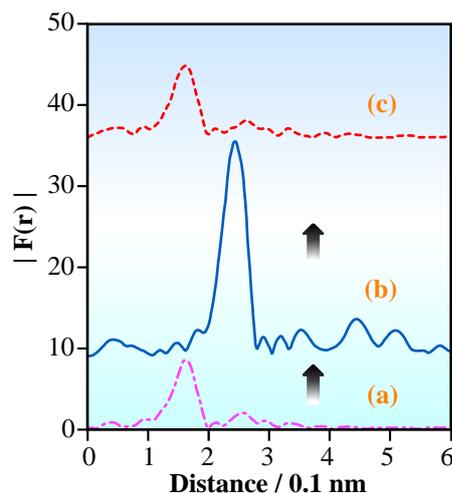
Fig. 2. Pd K-edge EXAFS Fourier transforms for Pd/HZSM-5 (Si/Al$_2$=24); (a) oxidized, (b) reduced by H$_2$, and (c) successively oxidized; treatments were conducted at 773 K.
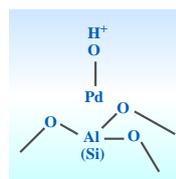
Fig. 3. Local structure of Pd in Pd/HZSM-5 (Si/Al$_2$=24) oxidized at 773 K.

Kazu Okumura, Jiro Amano and Miki Niwa

Tottori University

E-mail: mikiniwa@chem.tottori-u.ac.jp

References

[1] K. Okumura et al., Chem. Lett. (1999) 997.

[2] K. Okumura, J. Amano, N. Yasunobu and M. Niwa, J. Phys. Chem. B **104** (2000) 1050.