

## Ti K-edge XAFS measurements by a conversion electron yield method of nickel ion-doped titanium dioxide thin film coating glass substrate

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A thin film of TiO<sub>2</sub> is an important technological material in the fields of photocatalysts and photochemistry. Nakano et al. reported to indicate highly photocatalytic activity by doping metal ion in the TiO<sub>2</sub> thin film[1]. However, it is not clear how the local structure of Ti ion on the surface of the thin film depends upon the photocatalytic activity, though the chemical state of the thin film surface influences the photocatalytic activity. In order to examine the correlation between the local structure of Ti ion on the surface of the thin film and photocatalytic activity, we measured Ti K-edge XAFS of Ni ion-doped TiO<sub>2</sub> thin films coating glass substrate, Ni/TiO<sub>2</sub>/glass, in Conversion Electron Yield mode.

The TiO<sub>2</sub>/glass was prepared by the following method. Amorphous titanium dioxide was dissolved in hydrogen peroxide to form an orange-colored gel. And, the hydrogen peroxide was further added to the gel[2], then a transparent solution was obtained. Glass plates were dip-coated by the solution and dried. Ni/TiO<sub>2</sub>/glass was prepared by a similar method except that an aqueous solution of nickel acetate was added to the sol. These thin films were not heat-treated.

The data were collected with two flat Si(111) crystals as a monochromator and with double mirrors (5mrad). X-ray incident angle is approximately 1°. Ti foil was used as a reference.

Ti K-edge XANES spectra of TiO<sub>2</sub>/glass and Ni/TiO<sub>2</sub>/glass are shown in Fig. 1. The feature of the spectrum of Ni/TiO<sub>2</sub>/glass is mostly corresponding to that of TiO<sub>2</sub>/glass except for the feature of preedge peaks in the

region of 4965 – 4975 eV. Matsuo et al. have reported from the XANES analysis by a molecular orbital calculation that the change in the feature of the preedge peaks is important to show the change of the charge density and chemical bonding state of the Ti atom and its surrounding atoms[2]. Therefore, it is considered that the local structure around the titanium ion on Ni/TiO<sub>2</sub>/glass is similar to TiO<sub>2</sub>/glass, but the doped nickel ion affects the electronic state around the titanium ion on Ni/TiO<sub>2</sub>/glass.

More detailed analyses of XANES and EXAFS are now going on with appropriate methods.

[1] K. Nakano, S. Shizuru, K. Yamamoto, *Japan Patent*, **1999**, 2913257.

[2] S. Matsuo et al., *Anal. Sci.*, **2001**, 17, 149.

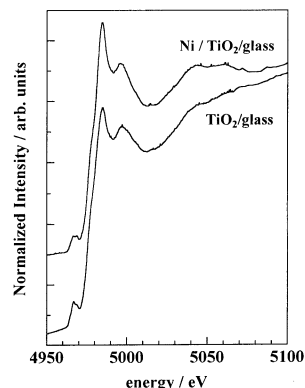


Fig.1 Ti K-edge XAFS spectra for Ni/TiO<sub>2</sub>/glass and TiO<sub>2</sub>/glass

## Structural analysis of fine metal and alloy particles created in pore of inorganic porous materials by XAFS

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Palladium has been known to be active for decomposition of methanol. We previously found that the catalytic activity of Pd catalysts is highly depended on the dispersion of Pd metal particles. In this report, the structural analysis of Pd metal particles (and Pd cations) on K-L zeolite was performed by means of the Pd K-edge XAFS technique. Furthermore, the effects the addition of Cu and Zn cations and preparation methods were also investigated. Pd/K-L zeolite was prepared by an ion-exchange method from Pd amine complex and K-form L zeolite (Si/Al=6). In the case of Pd-Cu/K-L and Pd-Zn/K-L, Cu or Zn was added by ion exchange or impregnation methods. The loading of Pd was 1.0 wt%. Pd K-edge XAFS spectra were measured at room temperature in a transmission mode at the beam line BL01B1 of SPring-8. Si(311) single crystal was used to obtain monochromatic X-ray beam.

Figure 1 shows the Fourier transforms of  $k^3$ -weighted EXAFS of the samples. In the case of both calcined Pd/K-L and Pd/K-X, a peak appeared at 0.16 Å due to Pd-O. In the case of Pd/K-L reduced at 623K, an intense peak appeared at 2.5 Å, indicating the formation of Pd metal, which was evident from the similarity with the spectrum for Pd foil. The CN of the nearest neighbor Pd atoms was 8.6 and the particle size was estimated to 12 Å. This value exceeded the pore size of K-L, suggesting that Pd metal particle formed on outer surface. Three peaks were observed at 1.6, 2.5 and 3.1 Å due to Pd-O, Pd-Pd (metal), Pd-Pd (Pd-O-Pd) in the spectra of the reduced Pd-M/K-L,

suggesting that both Pd<sup>0</sup> and Pd cations were present even after the reduction at 623 K. This is independent on both the preparation method and the kind of M species (Cu or Zn). The analysis of the small peak at 2.5 Å was not successful, when the curve fitting was conducted with parameters of Pd-Pd (metal), suggesting that this peak may be assign to the contributions of Pd-Pd, Pd-Cu and Pd-Al/Si.

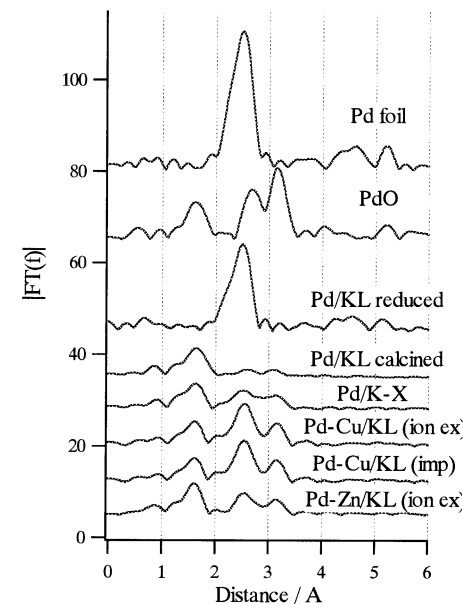


Fig.1 Fourier transformed  $k^3$ -weighted Pd K-edge EXAFS