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Monitoring of Vanadium Site Transformations on Titania and in Mesoporous Titania by Selective Detection XAFS of the Vanadium Kα_1 Fluorescence

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Introduction

We reported vanadium Kα_1-selecting XAFS for various V+TiO_2 samples including mesoporous V-TiO_2 (Photon Factory Activity Report #19, 31; #20, 27) [1, 2]. Further, V site transformations on TiO_2 in *in-situ* conditions and in mesoporous TiO_2 were studied.

Results and Discussion

For 0.6 and 10.4 wt%-V samples, V K-edge spectra were similar to Ti K-edge one for mesoporous TiO_2 (Figure 1A). The V^{IV} sites should be substituted on the Ti sites. Based on the pre-edge peak change (a, b), major octahedral V sites in the case of 0.6 wt%-V may transform into tetrahedral for 10.4 wt%-V sample.

In-situ XANES spectra in 2-propanol and moisture are summarized in Figure 1B and C, respectively. In 2-propanol, both at 290 and 473 K (a, b), pre-edge peak became weaker and the post-edge peak at 5486 eV became prominent compared to the data of fresh sample (a). These data were similar to that for mesoporous V-TiO_2 (0.60 wt%-V; d). Thus, octahedral coordination was demonstrated by the dissociative adsorption of 2-propanol on vanadate.

In moisture, spectrum at 473 K (c) was similar to that for NH_4VO_3 (d). Distorted tetrahedral monooxo vanadate is proposed. Fresh (exposed) sample (a) corresponded to vanadate of 5-coordination. The hydration at 290 K thoroughly transformed the species into surface polymerized species (b). Further details of site transformations (some of the data were taken at undulator beamline 15XU of SPring-8) can be found in Ref.3.

References

[1] Y. Izumi et al., Chem. Lett. 1154 – 1155 (2002).
[2] Y. Izumi et al., Chem. Comm. 2402 – 2403 (2002).
[3] Y. Izumi et al., submitted to J. Phys. Chem.

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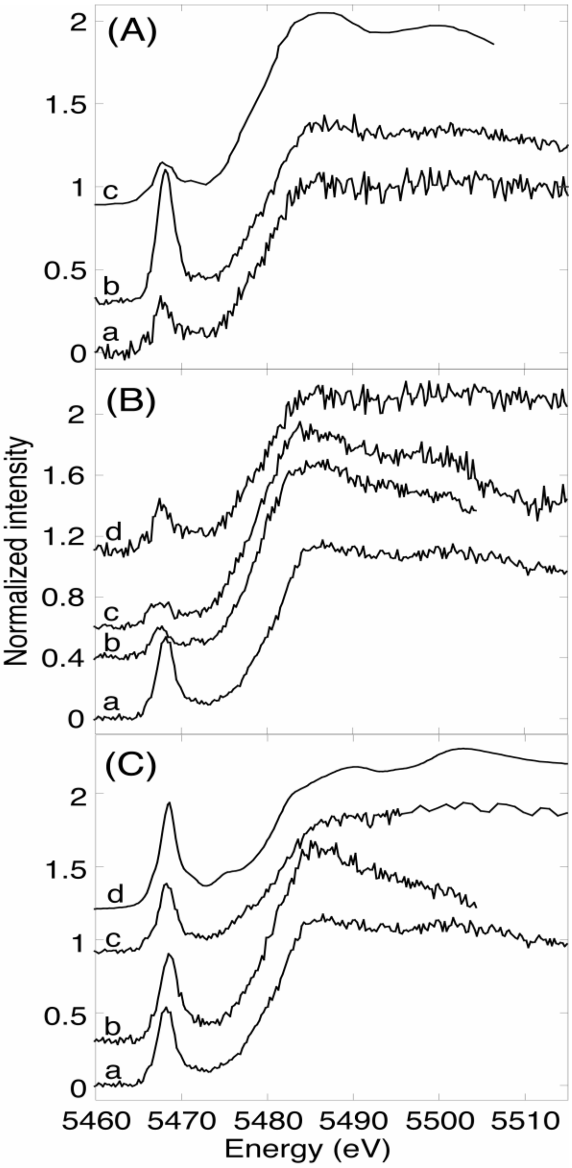

Figure 1. **(A)** V K-edge XANES spectra for mesoporous V-TiO_2 samples combined with high-energy-resolution XRF. 0.6 (a) and 10.4 wt%-V (b). Reference Ti K-edge XANES for mesoporous TiO_2 (c). The energy of spectrum c was shifted by +499.8 eV. **(B)** *In-situ* V K-edge XANES spectra for V/TiO_2 (1.0 wt%-V) combined with high-energy-resolution XRF. As prepared (a), in 3.2 kPa of 2-propanol at 290 (b) and 473 K (c), and mesoporous V-TiO_2 (0.6 wt%-V (d). **(C)** As prepared (a), in 0.85 kPa of water at 290 (b) and 473 K (c). Data for NH_4VO_3 (d).