

State-sensitive monitoring of vanadium catalyst sites excited under visible light by V $K\beta_{5,2}$ -selecting XAFS

Yasuo Izumi^{1,*}, Kazushi Konishi¹, Tomohisa Miyajima², and Hideaki Yoshitake²

¹Tokyo Institute of Technology, Nagatsuta 4259-G1-16, Midori-ku, Yokohama 226-8502

²Yokohama National University, Tokiwadai 79-5, Hodogaya-ku, Yokohama 240-8501

Introduction

State-sensitive XAFS technique is important for the understanding of catalysis because the system often consists of mixture of states. Based on high energy-resolution vanadium $K\beta_{5,2}$ spectra [1], the feasibility of state-sensitive V $K\beta_{5,2}$ -selecting XAFS is demonstrated for standard V compounds. Next, this new method is applied to mesoporous V-TiO₂ catalyst that catalytically dehydrates ethanol under visible light [2].

Experimental section

The detail for the setup of beamline, high energy-resolution fluorescence spectrometer, and visible light illumination was described in Ref. 1. V $K\beta_{5,2}$ -selecting V K-edge XAFS spectrum was measured by tuning the

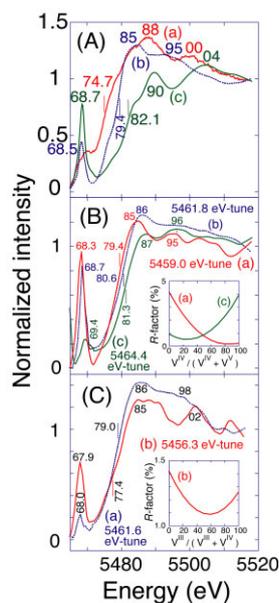


Figure 1. (A) V K-edge XANES spectra for (a) V₂O₅, (b) VO(SO₄)·nH₂O, and (c) Na₃VO₄ measured in transmission mode. (B) V $K\beta_{5,2}$ -detecting V K-edge XANES spectra for the 1:1 physical mixture of V^{IV}O(SO₄)·nH₂O and Na₃V^VO₄. The tune energy was 5459.0 (a), 5461.8 (b), and 5464.4 eV (c). (Inset) R-factor change of fit for spectra a and c with those for VO(SO₄)·nH₂O and Na₃VO₄ by changing mixing ratio. The fits were performed in energy range above 5474 eV. (C) V $K\beta_{5,2}$ -detecting V K-edge XANES spectra for mesoporous V-TiO₂ catalyst after visible light illumination in 2.1 kPa of ethanol. The tune energy was 5461.6 (a) and 5456.3 eV (b). (Inset) R-factor change of fit for spectrum b with those for V₂O₅ and VO(SO₄)·nH₂O. The fits were performed in energy range above 5473 eV.

fluorescence spectrometer at fixed emission energies around V $K\beta_{5,2}$ emission peak.

Results and discussion

For the physical mixture of V^{IV} and V^V compounds, the V $K\beta_{5,2}$ -selecting XAFS spectra by tuning the fluorescence spectrometer to 5459.0 and 5464.4 eV discriminated V^{IV} (100%) and V^V sites (80%), respectively (Figure 1B-a, c, inset).

The application to mesoporous V-TiO₂ catalyst was summarized in Figure 2 (tune energy: V $K\beta_{5,2}$ peak top). Native V^{IV} state was reduced to V^{III} state by photo-electrons in ethanol under the illumination of visible light. The population of V^{III} states was low during the study of Figure 2. The V^{III} site was extracted by tuning the fluorescence spectrometer to 5456.3 eV (Figure 1C-b). The V^{III} selection was 60% and the site structure was found to be similar to that of V₂O₃ [3].

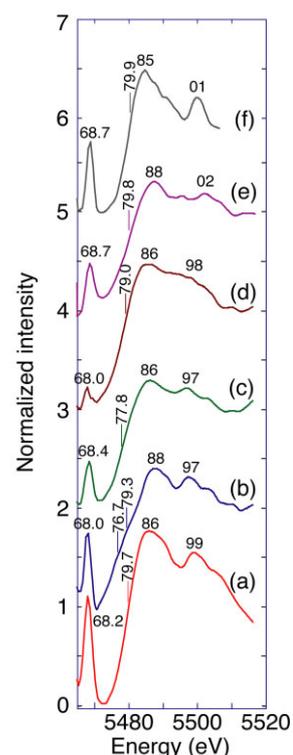


Figure 2. V $K\beta_{5,2}$ -detecting V K-edge XANES spectra for mesoporous V-TiO₂ catalyst. (a) Fresh sample in argon, (b) in 2.1 kPa of ethanol, (c) in ethanol with the illumination of visible light, (d) after the visible light was turned off, (e) in 101 kPa of O₂, and (f) in O₂ with the illumination of visible light. The tune energy was 5462.1, 5461.6, 5461.0, 5461.6, 5462.4, and 5462.4 eV, respectively.

References

- [1] Y. Izumi, K. Konishi, T. Miyajima, H. Yoshitake, *Photon Factory Activity Report* **24B**, 2005P014 (2007).
- [2] D. Masih, H. Yoshitake, Y. Izumi, *Applied Catalysis A*, in press (2007) (<http://dx.doi.org/10.1016/j.apcata.2007.02.037>).
- [3] Y. Izumi, K. Konishi, D. M. Obaid, T. Miyajima, H. Yoshitake, *Anal. Chem.*, in final reviewing process.

* izumi.y.ac@m.titech.ac.jp