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V Kβ$_{2,5}$-detecting vanadium XAFS to select the valence and state

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Introduction

To understand molecular chemical reactions *e.g.* surface catalytic processes, monitoring the valence state and site structure changes of active sites is essential. VO_x supported on TiO_2 are practical catalysts and expected to be applicable to environmental use utilizing mesoporous organo/inorgano-synthetic technique [1]. Previously, low concentrations of V sites on/in TiO_2 matrix were studied using V Kα$_1$-detecting V K-edge XAFS [1]. In this proposal, greater chemical shifts of V Kβ$_{2,5}$ are applied to valence and state-selective XAFS for V species.
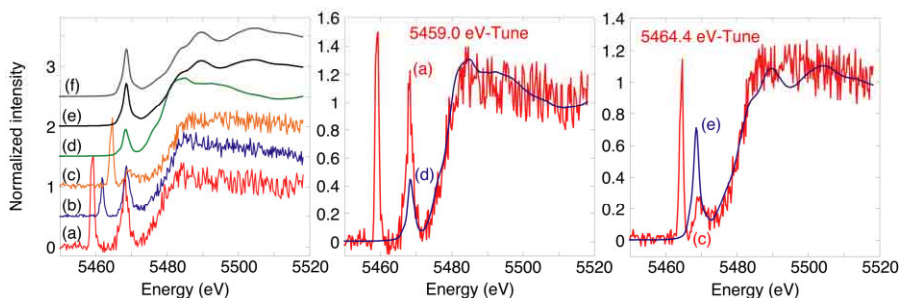
Experimental section
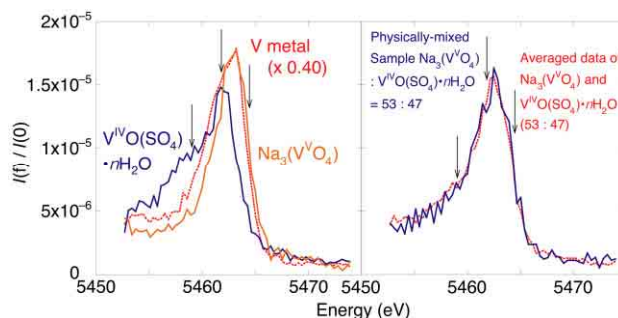
Measurements were performed at 290 K as in Figure1.
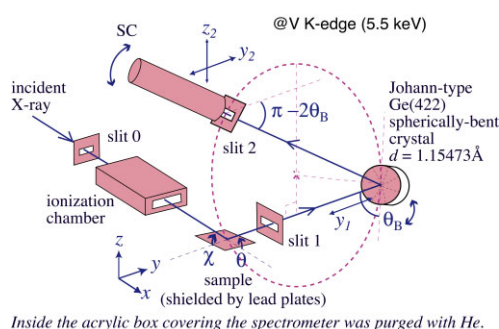
Figure1. The setup of V Kβ$_{2,5}$-detecting V K-edge XAFS.

Results and discussion

V Kβ$_{2,5}$ emission spectra for standard V compounds were summarized in Figure 2. Each spectrum consisted of main peak and weaker side-peak on lower energy side. The relative intensity ratio varied dependent on samples. Chemical shift for between V^{IV} and V^V was 0.9 eV. Spectrum for physical mixture of V^{IV} and V^V compounds well resembled average spectrum of ones for V^{IV} and V^V samples.

Figure2. V Kβ$_{2,5}$ emission spectra for V compounds (left panel) and physical mixture of $Na_3(V^VO_4)$ and $V^{IV}O(SO_4)•nH_2O$ (53 : 47 on V basis) (right panel, solid line). Arrows indicate tune energies for XANES measurements.

V K-edge XANES spectrum measured tuning the spectrometer to 5459.0 eV resembled one for V^{IV} (Figure 3a and d) except for 1s→3d pre-edge peak intensity (2.5 times), presumably due to resonance excitation effect to select side-peak V Kβ$_5$ (3d→1s).

When the tune energy was 5464.4 eV, obtained spectrum c was most similar to the average spectrum of ones for V^{IV} and V^V with the ratio 20:80. The discrepancies of pre-edge peak intensity (37%) and region between 5483.4 and 5500 eV may be because V Kβ$_2$ (4p→1s) was chosen at 5464.4 eV.

In next proposal 2006G097, this method will be applied to photo-dehydration of ethanol over mesoporous V-TiO$_2$ catalysts. By specifying both the red-ox V species and frontier V3d orbital symmetry and energy, the key role of doped V to trap electron/hole is elucidated.

References

[1] Y. Izumi, H. Yoshitake, Y. Iwasawa et al., *J. Phys. Chem. B*, **109(31),** 14884 – 14891 (2005).

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Figure3. V K-edge XANES. Fluorescence energy was tuned at 5459.0 (a), 5461.8 (b), and 5464.4 eV (c) for physical mixture of $Na_3(V^VO_4)$ and $V^{IV}O(SO_4)•nH_2O$ (53:47). Transmission measurements in spectra d – f for $V^{IV}O(SO_4)•nH_2O$ (d) and $Na_3(V^VO_4)$ (f). Spectrum e is the average of those d and f (20 : 80).