**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. VOx supported on TiO2 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 TiO2 matrix were studied using V Ka1-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 Figure 1.

**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.

![Figure 1](image1.png)

**Figure 1.** The setup of V Kβ_{2,5}-detecting V K-edge XAFS.

![Figure 2](image2.png)

**Figure 2.** V Kβ_{2,5} emission spectra for V compounds (left panel) and physical mixture of Na3(V^V O4) and V^IV O(SO4)•nH2O (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_{2,5} (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_{2,5} (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-TiO2 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**


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