

Feasibility of vanadium $K\beta_{5,2}$ -selecting XAFS for the application to vanadium catalysts excited under visible light

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Introduction

State-sensitive XAFS technique is important for the understanding of catalysis because the system often consists of mixture of states [1]. This work, X-ray fluorescence V $K\beta_{5,2}$ originated from valence state(s) of doped vanadium was chosen in relation to the photocatalytic role to create electron and hole pair between the band gap of TiO_2 . In the V $K\beta_{5,2}$ -selecting XAFS, better site selection is expected based on greater chemical shifts of V $K\beta_{5,2}$ compared to V $K\alpha_1$ emission [1]. In this report, V $K\beta_{5,2}$ emission spectra were measured for standard V compounds and mesoporous V- TiO_2 catalyst to demonstrate the feasibility of state-sensitive V $K\beta_{5,2}$ -selecting XAFS.

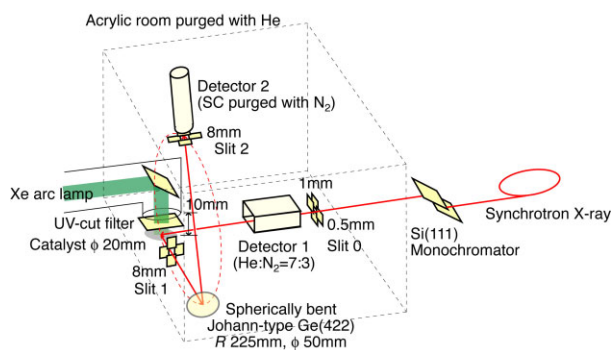


Figure 1. Schematic View of Fluorescence Spectrometer Combined with XAFS Beamline for V $K\beta_{5,2}$ -selecting XAFS Measurements under the Illumination of Visible Light.

Experimental section

The X-ray measurements were performed at beamline 9C for standard V compounds and at 7C for mesoporous V- TiO_2 catalyst. Si(111) double crystal monochromator and focusing/higher harmonics-rejection mirror were inserted. The X-ray beam was focused at sample position and fully tuned.

The X-ray fluorescence from sample was analyzed as in Figure 1 [2]. The catalyst sample was set in on-reaction cell equipped with polyethylene naphthalate window of 16 μm thickness. The exit of Xe arc lamp and UV-cut filter were set at 10 mm apart from sample.

Results and discussion

The V $K\beta_{5,2}$ emission spectra for standard V compounds were depicted in Figure 2A. The intense peak appeared at each energy with arrow accompanied with weaker shoulder on lower-energy side. The chemical shifts of

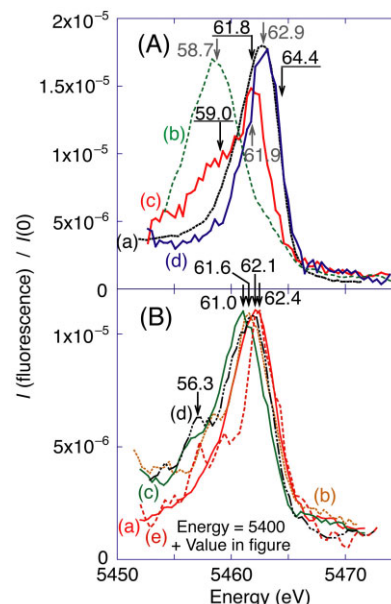


Figure 2. V $K\beta_{5,2}$ emission spectra (A) for V metal (a), V_2O_3 (b), $\text{VO}(\text{SO}_4)\cdot n\text{H}_2\text{O}$ (c), and Na_3VO_4 (d) and (B) mesoporous V- TiO_2 catalyst as fresh in argon (a), in 2.1 kPa of ethanol (b), in ethanol under the illumination of visible light (c), after the visible light was turned off (d), and in 101 kPa of O_2 under the illumination of visible light (e). The peak intensity was reduced to 1/20 and 1/4 for spectra A-a and A-b, respectively.

main peak were confirmed to +3.2 and +1.0 eV between standard V^{III} and V^{IV} and between V^{IV} and V^{V} sites, respectively, in consistent with literature [3].

The V $K\beta_{5,2}$ emission spectra for mesoporous V- TiO_2 catalyst under each catalytic condition were depicted in Figure 2B. The peak top position basically corresponded to V^{IV} state, however, it shifted toward the energy of V^{III} state in ethanol under the illumination of visible light and shifted back to initial state in air and/or under visible light. The catalytic site transformation was discussed in combination with associated V $K\beta_{5,2}$ -selecting XAFS in this CD-ROM for proposal 2006G097 and in Refs. 2, 3.

References

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