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On-reaction, state-selective vanadium K$\beta_{5,2}$-selecting XAFS elucidated oxidative dehydrogenation reaction mechanism under visible light

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Introduction

The feasibility [1] and the application to each reaction step [2] of state-selective vanadium K$\beta_{5,2}$-selecting XAFS were reported. In this report, the monitoring was performed under *on-reaction* (*in situ*) condition over V-TiO_2 with uniform mesopores under visible light (> 420 nm).

Methods

The synthesis of sample and the measurements of state-selective V K$\beta_{5,2}$-selecting XAFS were described in recent papers [3,4]. V-TiO_2 with uniform mesopores (3 nm) was synthesized using dedecylamine as template. Homemade X-ray fluorescence analyzer equipped with Johann-type Ge(422) crystal was used to tune to fixed emission energies around V K$\beta_{5,2}$ emission peak.

Results and discussion

The V sites of mesoporous V-TiO_2 sample were gradually reduced from V^{IV} to V^{III} upon water adsorption or ethanol under visible light (Figure 1). The reduction rate (14 µmol-V h^{-1} g_{cat}^{-1}) corresponded to steady ethanol oxidative dehydrogenation to acetaldehyde (23 µmol h^{-1} g_{cat}^{-1}). V K$\beta_{5,2}$-selecting XAFS confirmed this correlation and the presence of 75% of V^{III} sites in mesoporous V-TiO_2 under visible light for 27.7 h. The V^{III} site geometry was found to resemble that of $V^{III}{}_2O_3$.

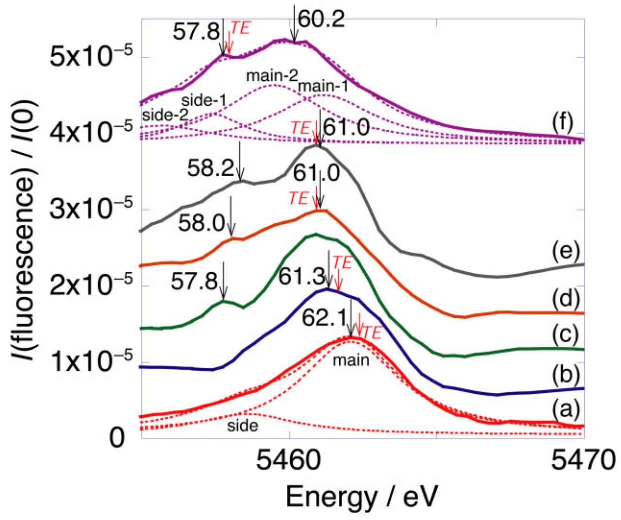

Figure 1. V K$\beta_{5,2}$ emission spectra for mesoporous V-TiO_2 as (a) fresh, (b) in 0.37 kPa of water, and (c – f) in 4.3 kPa of ethanol under visible light for 1.2 (c), 3.3 (d), 11.9 (e), and 22.4 h (f). The excitation energy was set to 5483.6 eV. Spectrum deconvolutions were depicted as dotted lines with Lorentz functions for spectra a and f. The longer/black and shorter/red arrows indicate peak top and tune energy for the measurements in Figure 2, respectively.

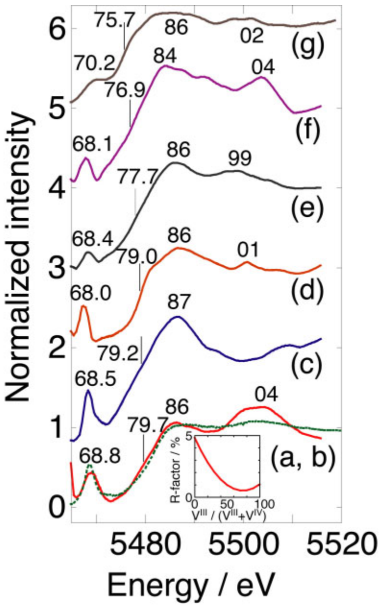

Figure 2. V K$\beta_{5,2}$-selecting V K-edge XANES spectra for mesoporous V-TiO_2 as (a, solid line) fresh, (c) in 0.37 kPa of water, and (d – f) in 4.3 kPa of ethanol under visible light for 7.0 (d), 17.3 (e), and 27.7 h (f) and for V_2O_3 diluted with boron nitride (3.0 wt% V; g). The tune energy values were 5462.4, 5461.7, 5460.9, 5460.9, 5458.0, and 5458.7 eV, respectively. Spectrum-b (dotted line) was corresponding data to spectrum-a, measured in transmission mode.

References

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