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Photo-oxidation over mesoporous V-TiO$_2$ catalyst under visible light monitored by vanadium Kβ$_{5,2}$-selecting XANES spectroscopy ☆

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Abstract

Visible light-excited ethanol dehydration reaction steps to adsorb ethanol and then to donate an electron to transform V(IV) to V(III) site exposed on mesoporous V(IV)-TiO$_2$ catalyst were successfully monitored by means of V Kβ$_{5,2}$-selecting XANES spectroscopy. Spherically-bent Ge(422) crystal was used for the X-ray fluorescence analyses and Xe arc lamp of 500 W was illuminated at 10 mm apart from catalyst samples under *on reaction* conditions. Specific redox reaction mechanism between V(IV) and V(III) states was proposed for dehydration reaction over the mesoporous V-TiO$_2$ catalyst based on the V Kβ$_{5,2}$-selecting XANES compared to general vanadium catalysts starting from V(V) state for dehydrogenation reaction.
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1. Introduction

Utilization of solar energy is expected to be clean energy source. One of the technological possibilities is photo-catalysis over TiO$_2$-based catalysts doped with V, Cr, Mn, Fe, Ni [1], C, N, or S atoms [2,3] under the illumination of visible light. Recently, we reported that the energy gap between conduction and valence bands became smaller for mesoporous TiO$_2$ doped with 1–3 wt.% of V [4] compared to conventional catalysts based on anatase-type TiO$_2$ [5].

Promoting effects of V doping on/in TiO$_2$ were reported for ethanol photo-oxidation [6], degradation of crystal violet and methylene blue [7,8], and nitric oxide [9]. Under the illumination of visible light (>420 nm), mesoporous TiO$_2$ exhibited poor activity [5]. The mesoporous V-TiO$_2$ catalyst with the specific surface area (SA) as much as 1000 m^{2}g^{-1} became active and proceeded dehydration of ethanol (1.0 kPa) to produce acetaldehyde, in clear contrast to the ethanol

dehydrogenation over [V-doped] anatase-type TiO$_2$ catalysts [5]. Because the V addition sometimes hampers photo-catalysis of TiO$_2$ [10], it is critical to understand the catalytic role of V under the illumination of visible light. The role must be complex [10] and still open for discussion, especially in the case of mesoporous V-TiO$_2$ catalysts [5].

The keys to understand the V catalytic role are (1) state-sensitive monitoring of V site structure transformation by X-ray absorption fine structure (XAFS) under *on-reaction* conditions [11–13] and (2) sample setting design to illuminate the catalyst very near the exit window of visible light lamp during the XAFS measurements under *on-reaction* conditions. To satisfy both requisites, we employed X-ray fluorescence-detecting XAFS to selectively detect V Kβ$_{5,2}$ fluorescence associated with the electronic transition from V 3d and oxo π levels to V K-level [14–16]. V Kβ$_{5,2}$ fluorescence (M$_{4,5}$→ K) was chosen for the first time in the state-sensitive XAFS measurements rather than V Kα$_1$ fluorescence (L$_3$→ K) [11–13] because the Kβ$_{5,2}$ is derived from the electronic transition from frontier levels *e.g.* V 3d to V 1s and thus the electronic state information of frontier levels will be emphasized in the V Kβ$_{5,2}$-selecting XAFS, closely correlated with the photo-catalysis originated from the
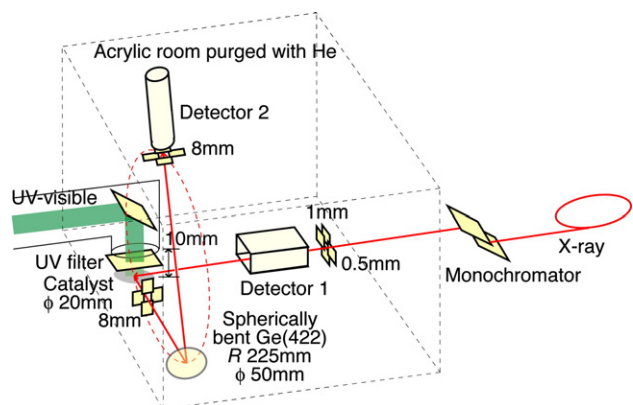
Fig. 1. The sample, UV-visible Xe arc lamp, UV-cut filter, analyzer crystal, and detectors set for vanadium $K\beta_{5,2}$-selecting XAFS measurements.

electron-hole pair formation at the frontier levels. Also, greater chemical shifts were expected for V $K\beta_{5,2}$ than for V $K\alpha_1$.

2. Experimental

The X-ray measurements were performed at beamline 7C or 9C in KEK-PF (Tsukuba) at 290 K. The storage ring energy was 2.5 GeV and the ring current was between 449 and 281 mA. Si (111) monochromator and focusing/higher-harmonics-rejection mirror were inserted. The beam was focused at sample position and fully tuned. In the setup (Fig. 1), catalyst disk positioned at 10 mm apart from the exit window of Xe arc lamp (500 W, UXL-500D, Ushio) and UV-cut filter L42 (cut-off energy 420 nm, Kenko) was set in between. The detectors 1 and 2 were ionization chamber purged with the mixture of helium and nitrogen gas (7:3) and scintillation counter, respectively. Sample, detector 2, and spherically-bent Johann-type Ge(422) crystal (Saint Gobain) were set in Rowland configuration of radius 225 mm. The curvature (radius) of the crystal was 450 mm. The inside of spectrometer was purged with helium and the spectrometer was set as close as possible to beam-duct connected to monochromator.

Energy resolution of the fluorescence spectrometer was 1.1–1.9 eV for the V $K\beta_{5,2}$ measurements [13]. The V $K\beta_{5,2}$ emission peak and V K absorption edge energy values were calibrated to 5462.9 ($\theta_{Bragg}=79.335°$) and 5463.9 eV, respectively [17]. Synthesis procedure of mesoporous V-TiO$_2$ catalyst was already described in Refs. [11,18]. The V content was fixed to 3.0 wt.%, corresponding to atomic ratio of V/Ti to be 1/21.

3. Results and discussion

V $K\beta_{5,2}$ emission spectra were measured for mesoporous V-TiO$_2$ samples in argon (fresh catalyst), after the introduction of ethanol (2.1 kPa), in the ethanol with illumination of visible light (>420 nm, illuminated for 7 h), and in ethanol after the arc lamp was turned off. The peak top for fresh sample at 5462.1 eV shifted progressively toward lower-energy side to 5461.6 eV in ethanol in dark, then to 5461.0 eV in ethanol under visible light. In ethanol after the visible light lamp was turned off, the peak top increased back to 5461.6 eV. The V $K\beta_{5,2}$ peak top was at 5458.5, 5462.0, and 5462.9 eV for

$V^{III}_2O_3$, $V^{IV}O(SO_4)\cdot nH_2O$ and $Na_3(V^VO_4)$, respectively. Thus, vanadium was valence state IV for fresh sample and was partially reduced toward III state in ethanol and/or with visible light illumination. The valence state IV for fresh sample was in agreement with conclusion based on V $K\alpha_1$ emission spectra and V $K\alpha_1$-detecting V K-edge XANES (X-ray absorption near-edge structure) [11,13].

The fluorescence spectrometer was set to each V $K\beta_{5,2}$ peak top under the four conditions, and V K-edge XANES spectra were measured for mesoporous V-TiO$_2$ sample (Fig. 2B). The data scan step was ≈0.25 eV and the accumulation time was 60–100 s for a point. The rising edge and pre-edge peak energy values were 5479.7 and 5468.2 eV, respectively, for fresh sample. These were very similar to corresponding values (5479.4–5479.8 and 5467.9–5468.5 eV, respectively) obtained for V^{IV} standard compound (Fig. 2A—b), V $K\alpha_1$-selecting XANES of mesoporous V-TiO$_2$ (0.6–10.4 wt.% V), and Ti K-edge XANES for mesoporous TiO$_2$ shifted by +499.8 eV [11]. Post-edge peak positions were also similar. Thus, V(IV) sites substituted on the Ti sites of amorphous TiO$_2$ matrix (Fig. 3a). This structure was supported by the curve fit analyses for V $K\alpha_1$-selecting V K-edge EXAFS (extended XAFS) [11].
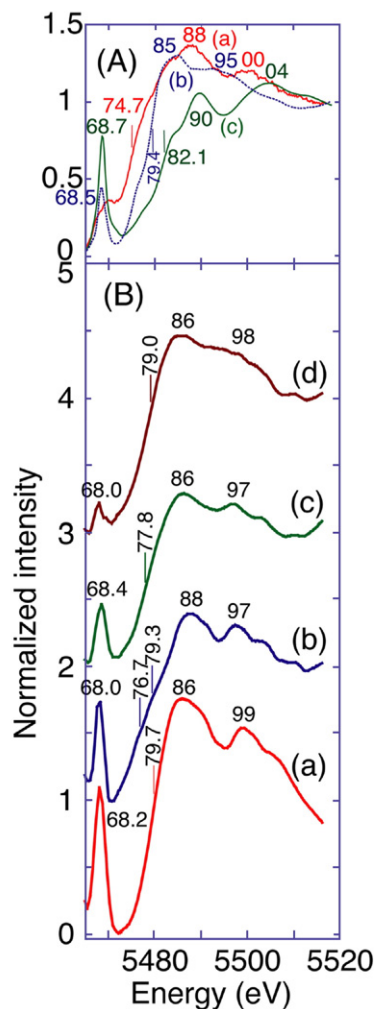

Fig. 2. (A) V K-edge XANES spectra for (a) $V^{III}_2O_3$, (b) $V^{IV}O(SO_4)\cdot nH_2O$, and (c) Na$_3$V^{V}O$_4$ measured in transmission mode. (B) V $K\beta_{5,2}$-detecting V K-edge XANES spectra for mesoporous V-TiO$_2$ catalyst (3 wt.% V). (a) Fresh sample in argon, (b) in 2.1 kPa of ethanol, (c) in ethanol with the illumination of visible light, and (d) in ethanol after the visible light was turned off.
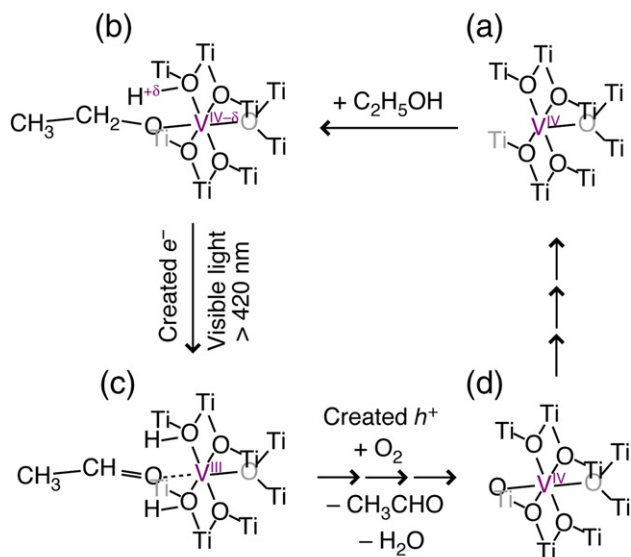
Fig. 3. Proposed reaction mechanism of ethanol dehydration over mesoporous V-TiO$_2$ based on V K$\beta_{5,2}$-selecting XANES.

With the introduction of 2.1 kPa of ethanol, rising edge shape for Fig. 2B—a split into two at 5476.7 and 5479.3 eV (Fig. 2B—b). This suggests two major vanadium states present. Because the rising edge positions were observed at 5471.0–5474.7, 5477.5–5479.8, and 5480.0–5482.2 eV for several V(III), V(IV), and V(V) standard inorganic compounds, respectively (Fig. 2A) [11,19], partially reduced V(IV-δ) states (Fig. 3b) should be formed due to the dissociative adsorption of ethanol on V(IV). The V(IV-δ) site was mixed with V(IV) site in this condition. Pre-edge and post-edge peak positions were relatively similar to those for fresh sample (Fig. 2B—a). Dissociative adsorption of 2-propanol was reported over mesoporous V-TiO$_2$ at 290 K [11].

Next, visible light was illuminated on the sample for Fig. 2B—b. The rising edge shape in the obtained data (Fig. 2B—c) was with inflection point at 5477.8 eV, shifted by −1.9 eV from native mesoporous V(IV)-TiO$_2$ catalyst. Hence, created electrons excited by visible light were distributed to the V(IV) to form V(III) (Fig. 3c). The ratio of V(III) state was quite small under the reaction equilibrium due to the fast electron excitation/distribution process [*i.e.* short lifetime of V(III) state], so that fully reduced state to V(III) may not be detected in comparison with data for standard V(III) compounds (Fig. 2A—a) [11,19].

Then, the visible light was turned off after 7 h illumination. Obtained data (Fig. 2B—d) was most similar to Fig. 2B—b except that the pre-edge peak intensity at 5468.0 eV became fairly weak.

The trend of valence state change in four sample conditions above was consistent in the V K$\beta_{5,2}$ emission spectra and V K absorption edge shifts: progressive shift from V(IV) (fresh) to partially reduced V(IV-δ) state in argon, ethanol, and then under the illumination of visible light. A shift back toward V(IV) was detected after the visible light off. The energy shifts were reproduced in repeated tests both for V K$\beta_{5,2}$ emission and V K-edge XANES spectra measurements. However, the final V(IV)-like state for Fig. 2B—d was not identical with native V(IV) state. The pre-edge peak remained essentially at the same position: 5468.0–5468.4 eV (Fig. 2B—a–d), but the intensity progressively decreased to 26%. Among mesoporous V-TiO$_2$ samples, systematic increase of the pre-edge peak was observed as the V content increased from 0.6 to 10.4 wt.% V due to the drop of site symmetry, while keeping the rising edge and post-edge feature unchanged [11]. Thus, V site symmetry was distorted as in Fig. 3a in fresh sample and became

higher due to ethoxyl group adsorption. The pre-edge peak intensity was still smaller in the presence of O$_2$ and subsequent visible light illumination [20].

Based on above spectroscopic observation, dehydration reaction mechanism was proposed in Fig. 3 in the presence of ethanol. The redox pair of V(IV) and V(III) is reasonable because the redox energy level near the conduction band was proposed for the V(IV)-substituting model in TiO$_2$ matrix to easily receive excited electron to form V(III) [10]. V(V) species were reported for the majority of impregnated catalysts over TiO$_2$. The difference of vanadium valence states may be primary reason of different catalysis: dehydration [V(IV)⇌V(III)] and dehydrogenation [native V(V)] of ethanol under visible light. The V(IV) sites were effectively exposed to surface in our mesoporous samples due to the high specific SA compared to V(IV)-TiO$_2$ samples prepared via sol–gel method [7,8,20,21].

The advantage of V K$\beta_{5,2}$-selecting XANES spectra should be mentioned compared to conventional XANES taken in transmission mode [18] or V Kα_1-selecting XANES [11–13]. The pre-edge peak intensity gradually increased from 0.32, to 0.46, and then to 0.80 for mesoporous V-TiO$_2$ samples with 0.6 [11], 5.0 [18], and 10.4 wt.% V [11], respectively. The peak intensity was 0.92 for mesoporous V-TiO$_2$ samples with 3.0 wt.% V in this work selecting V K$\beta_{5,2}$. Thus, the pre-edge peak was enhanced due to resonance excitation effect similar to reports for Fe K$\beta_{1,3}$-selecting [21,22], Cu Kα_1-selecting [22,23], and Sn Kα_1-selecting XANES [22,23]. In this work, the enhanced peak was derived from levels of V 3d character. Thus, responsible valence V sites excited by visible light illumination should be emphasized and the quantitative discussion of 1s→ 3d pre-edge peak was enabled by selecting V K$\beta_{5,2}$ fluorescence peak. Another advantage of V K$\beta_{5,2}$-selecting XANES was greater chemical shifts between V(V) and V(IV) and between V(IV) and V(III) states (1.0–3.2 eV) compared to corresponding values (0.2–0.5 eV) for V Kα_1 emission spectra [11] for state-sensitive XAFS measurements of V(III), V(IV), and V(V).

4. Conclusions

Vanadium K$\beta_{5,2}$-selecting XANES spectroscopy was successfully applied to mesoporous V-TiO$_2$ catalyst under *on-reaction* conditions of ethanol dehydration under the illumination of visible light. The pre-edge peak due to electronic transition K→ M$_{4,5}$ was enhanced and the chemical shifts were greater compared V Kα_1 emission. The initial state was V(IV) and ethanol dissociatively adsorbed to partially reduce the V(IV) site. When visible light was illuminated, electron should be excited and distributed to the V(IV) sites associated with ethoxyl group. However, fully reduced V(III) state was not detected probably because the reaction equilibrium due to electron excitation/distribution process was fast and the lifetime of V(III) state was short. The partially reduced V(IV-δ) sites oxidized back to V(IV) after the visible arc lamp was turned off.

Acknowledgements

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