

Structure of low concentrations of vanadium supported on titania determined by X-ray absorption fine structure combined with fluorescence spectrometry

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Introduction

It is very difficult to measure XAFS data for low concentrations of V in the TiO₂ matrix. When 0.6 wt% of V is supported on TiO₂, XAFS measurements in transmission mode are difficult because the V K-edge jump is only 0.037 compared to a total absorption of 4. Experiments carried out in conventional fluorescence mode are also difficult because the photon number ratio of V K α_1 /Ti K α_1 is only 0.012. When a solid-state detector (SSD; energy resolution \approx 100 eV) is used, the V K α_1 (4952.2 eV) peak can be separated from the Ti K α_1 (4510.8 eV) peak. However, the Ti K $\beta_{1,3}$ (4931.8 eV) still overlaps the V K α_1 peak. The ratio of V K α_1 /Ti K $\beta_{1,3}$ is 0.058. The selective detection of V K $\beta_{1,3}$ (5427.3 eV) is difficult using the SSD because scattered X-rays overlap. In this report, XAFS combined with a high-energy-resolution fluorescence spectrometer was applied to selectively monitor low concentrations of V on TiO₂.

Experimental section

The X-ray spectra were measured at 7C. A Si(111) monochromator was used and the beam was focused. The X-ray fluorescence from the sample was analyzed using a Rowland-type spectrometer ($R = 180$ mm) equipped with a Johansson-type Ge(331) crystal and a scintillation counter. The entire beam path was in helium, except for the I_0 ion chamber (N₂:He = 3:7). The V K α_1 emission spectrum was measured with the excitation energy set at 5484.1 eV. Next, the V K-edge XANES was measured. The step scan was \approx 0.25 eV. The dwell time of each data point was 60s, and two/three scans were measured for each sample. The energy position was reproduced within \pm 0.1 eV.

Results and discussion

Figure 1 shows the normalized V K-edge XANES spectra. In the case of conventional V/TiO₂, 3.0 (a) and 1.0 wt%-V (b), the rising edge appeared at 5480.8 – 5481.0 eV, corresponding to the valence state of +5. Two broad peak features were observed at 5489 and 5502 eV at nearly equivalent intensity. The two peak positions were similar to the case of Mn_{1-x}V_{2-2x}Mo_{2x}O₆ ($x = 0.10$)(1) (d; 5490 and 5503 eV). The V site in **1** is coordinated by two terminal oxo ($d_{V=O}$ 1.661 – 1.693 Å) and three farther

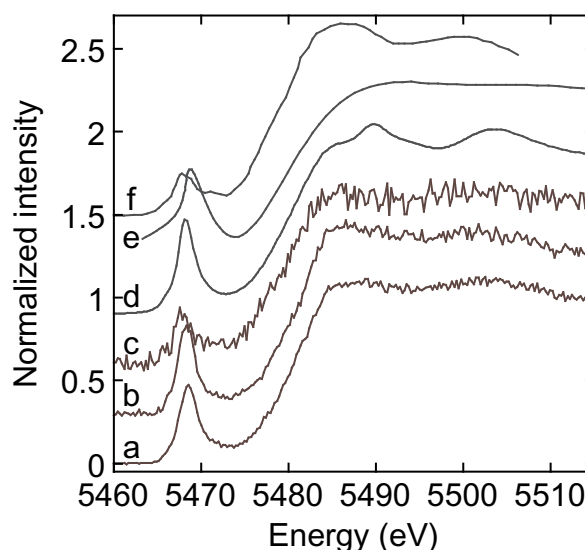


Figure 1. V K-edge XANES for V+TiO₂ catalysts measured using fluorescence spectrometry (a – c). V/TiO₂ of 3.0 (a) and 1.0 wt%-V (b). HSA V-TiO₂ (0.6 wt%-V, c). Reference XANES measured in transmission mode for Mn_{0.9}V_{1.8}Mo_{0.2}O₆ (d) and HSA TiO₂ (f). (e) was generated by FEFF 8.2 for vanadate model A on antase TiO₂(001).

oxygen atoms ($d_{V=O}$ 1.913 – 2.151 Å). The spectra (a) and (b) were also similar to XANES generated by FEFF 8.2 for a V site model A on anatase TiO₂(001) face ($d_{V=O}$ 1.620, 1.922, and 2.151 Å) (e).

For high-surface-area (HSA) V-TiO₂ prepared from V triisopropoxide oxide, Ti tetraisopropoxide, and dodecylamine, the rising edge position (5479.8 eV, c) was at lower energy than the case of V/TiO₂. Two broad peak features were observed at 5487 and 5505 eV. The post-edge pattern of V₂O₄ was relatively similar to (c), but the pre-edge position was at higher energy by 1.4 eV. The Ti K-edge data for HSA TiO₂ was compared to the V K-edge by shifting the energy by +499.8 eV (f). Both the post-edge pattern and pre-edge peaks were similar to the case of (c). A plausible structural model is that the V^{IV} sites are substituted on the Ti sites of HSA TiO₂.

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