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

Yasuo Izumi*,1, Fumitaka Kiyotaki1, Ken-ichi Aika1, Hideaki Yoshitake2, Tae Sugihara2, Takashi Tatsumi1, Yasuhiro Tanizawa1, Takafumi Shido1, Yasuhiro Iwasawa3
1 Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8502
2 Graduate School of Environment and Information Sciences and Graduate School of Engineering, Yokohama National University, Tokiwadai, Hodogaya, Yokohama 240-8501
3 Graduate School of Science, The University of Tokyo, Bunkyo-ku, Hongo 113-0033

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 Kα/Ti Kα is only 0.012. When a solid-state detector (SSD; energy resolution = 100 eV) is used, the V Kα (4952.2 eV) peak can be separated from the Ti Kα (4510.8 eV) peak. However, the Ti Kβ1 (4931.8 eV) still overlaps the V Kα peak. The ratio of V Kα/Ti Kβ1 is 0.058. The selective detection of V Kβ1 (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 I3 ion chamber (N2:He = 3:7). The V Kα 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 0.25 eV. The dwell time of each data point was 60 s, and two/three scans were measured for each sample. The energy position was reproduced within ±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 Mn3+ V2+ O4(α = 0.10) (d; 5490 and 5503 eV). The V site in I is coordinated by two terminal oxo (dν = 1.661 – 1.693 Å) and three farther oxygen atoms (dν = 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 (dν = 1.620 2, 1.922 2, 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 V2O5 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 V2O5 sites are substituted on the Ti sites of HSA TiO2.

izumi@chemenv.titech.ac.jp