Selective XAFS measurements of 0.6–3.0 wt% V sites on/in TiO$_2$ were enabled utilizing a fluorescence spectrometer. The V sites were V$^{IV}$ species in the case of conventional V-TiO$_2$ catalysts in contrast to V$^V$ species in the case of conventional V-TiO$_2$ catalysts, V supported on HSA-TiO$_2$, and V-TiO$_2$ prepared in the absence of dodecylamine (general sol-gel method).

Vanadium catalysts are used for the reduction of nitric oxide with ammonia, the oxidation of naphthalene/xylene to phthalic anhydride, and the oxidation of butane to maleic anhydride. However, exceptionally it is very difficult to measure XAFS directly determines the local structure of non-crystalline materials. However, exceptionally it is very difficult to measure XAFS data for low concentrations of V in the TiO$_2$ matrix. When 0.6 wt% of V (1.1 wt% V$_2$O$_5$) is mixed with TiO$_2$, the V K-edge jump is 0.037 compared to a total absorption of 4 in transmission mode. The photon number ratio of V K$_{\alpha}$/C$^{12}$ is 0.60. The selective detection of V K$_{\alpha}$/C$^{12}$ (4952.2 eV) still overlaps the V K$_{\alpha}$ peak. The ratio of V K$_{\alpha}$/Ti K$_{\alpha}$ is 0.058. The selective detection of V K$_{\beta}$/C$^{12}$ (5427.3 eV) is difficult using the SSD because scattered X-rays overlap. Auger or secondary photoelectrons derived from V are selectively monitored using an electron energy analyzer. However, these experiments need ultra-high vacuum, and in-situ measurements are impossible. In this Letter, XAFS combined with fluorescence spectrometry was applied to selectively monitor low concentrations of V on/in TiO$_2$.

TiO$_2$ (P25, 60 m$^2$ g$^{-1}$) was impregnated with Vtrisopropoxide oxide (1) in isopropanol solution (V/TiO$_2$). A high surface area (HSA: 1200 m$^2$ g$^{-1}$) V-TiO$_2$ was prepared from compound 1, Ti tetraisopropoxide (2), and dodecylamine. An aqueous solution was kept at 333 K for six days, and filtered. The obtained powder was heated at 453 K for ten days, and then washed by p-toluenesulfonic acid/ethanol. HSA-TiO$_2$ prepared in a similar procedure was impregnated with compound 1 (V/HSA-TiO$_2$). V-TiO$_2$ was prepared from compounds 1 and 2 in the absence of dodecylamine in a similar manner to the case of HSA V-TiO$_2$. In all cases, the dried powder was heated in air at 473 K and pressed into a disk in ambient air.

The XAFS spectra were measured at KEK-PF 7C. The storage ring energy was 2.5 GeV, and the current was 390–270 mA. A Si(111) double crystal monochromator was used. The beam was focused and fully tuned. 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 scintillation counter. The entire beam path was in helium, except for the $I_0$ ion chamber ($N_2$ : He = 3 : 7).

The V K$_{\alpha}$ emission spectrum was measured with the excitation energy set at 5484.1 eV. Next, the V K-edge XANES was measured. The fluorescence spectrometer was tuned to the emission peak energy ($\leq 1000$ cps). The Ge(331) crystal received a solid angle of 0.007 sr for the X-ray fluorescence from the sample. The step scan was $\approx 0.25$ eV. The dwell time of each data point was 60–200 s. The energy position was reproduced within $\pm 0.1$ eV. The V K$_{\alpha}$ and V K rising edge energy of the V metal were calibrated to 4952.2 and 5463.9 eV, respectively.

The V K$_{\alpha}$ emission spectra for the V/TiO$_2$ catalysts appeared at 4951.5–4952.0 eV (Figure 1). The chemical shifts with respect to V metal were reported to $-0.1, -0.3, -0.4$, and $-0.5$–$-0.6$ eV for V$^{IV}$, V$^V$, and V$^V$ compounds, respectively. Hence, the V sites in the catalysts are in the oxidation state of IV/V. The FWHM

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**Figure 1.** V K$_{\alpha}$$_1$ and $\alpha_2$ emission spectrum for V/TiO$_2$ of 3.0 wt% V. Best energy resolution of the fluorescence spectrometer (narrower peak of dotted line) and of beamline (wider peak of dotted line) is also drawn. 

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progressively decreased (3.7–2.4 eV) as the length of two slits in the Rowland circle changed from 8.0 to 2.0 mm.  

Figure 2 shows the normalized V K-edge XANES spectra. In the case of V/HSA-TiO (a and b), the rising edge appeared at 5480.8–5481.1 eV. Two broad post-edge peak features were observed at 5489 and 5502 eV at nearly equivalent intensity. The two peak positions were similar to the cases of V/TiO (3.9 wt%–V, f; above 5484 eV)11, Mn/HSA V1.10Mo0.2O6 (g), CrV2O4 (h),12 V1.2O7 (i),12 V3O4 (h),12 and HSA-TiO (l).6

The FWHM values of the pre-edge peaks were 2.5 eV, independent of the V loadings (3–1 wt%) and of the ΔE of the fluorescence spectrometer. The pre-edge peak width is related to the core-hole lifetime width of K+L(C1/25) and Ti K-edge (E of the fluorescence spectrometer. Therefore, the pre-edge peak width is related to the core-hole lifetime width of K+L(C1/25) and Ti K-edge (E of the fluorescence spectrometer. Therefore, the pre-edge peak width is related to the core-hole lifetime width of K+L(C1/25) and Ti K-edge (E of the fluorescence spectrometer. Therefore, the pre-edge peak width is related to the core-hole lifetime width of K+L(C1/25) and Ti K-edge (E of the fluorescence spectrometer. Therefore, the pre-edge peak width is related to the core-hole lifetime width of K+L(C1/25) and Ti K-edge (E of the fluorescence spectrometer. Therefore, the pre-edge peak width is related to the core-hole lifetime width of K+L(C1/25) and Ti K-edge (E of the fluorescence spectrometer. Therefore, the pre-edge peak width is related to the core-hole lifetime width of K+L(C1/25) and Ti K-edge (E of the fluorescence spectrometer. Therefore, the pre-edge peak width is related to the core-hole lifetime width of K+L(C1/25) and Ti K-edge (E of the fluorescence spectrometer. Therefore, the pre-edge peak width is related to the core-hole lifetime width of K+L(C1/25) and Ti K-edge (E of the fluorescence spectrometer. Therefore, the pre-edge peak width is related to the core-hole lifetime width of K+L(C1/25) and Ti K-edge (E of the fluorescence spectrometer. Therefore, the pre-edge peak width is related to the core-hole lifetime width of K+L(C1/25) and Ti K-edge (E of the fluorescence spectrometer.

A weaker shoulder at 5486 eV appeared in (b) and (g). The post-edge pattern for CrV2O4 (h) and V1.2O7 (i) was entirely different from that of (a) and (b).  

A 1s–3d pre-edge peak appeared at 5468.3–5468.6 eV for V/TiO (a and b, Table 1). The FWHM values of the pre-edge peaks were 2.5 eV, independent of the V loadings (3–1 wt%) and of the ΔE of the fluorescence spectrometer. The pre-edge peak width is related to the core-hole lifetime width of K+L(C1/25) and Ti K-edge (E of the fluorescence spectrometer. Therefore, the pre-edge peak was estimated to be 2.0 eV (Figure 1) and the ΔE of the fluorescence spectrum decreased from 2.8 to 0.3 eV (Figure 1) as the slit width was decreased from 8.0 to 2.0 mm.7 No contribution of Ti Kβ1,2 was observed with these energy resolution values, demonstrating entirely no contribution of Ti in Figure 2a–e.  

The pre-edge peak in (a) and (b) appeared at a similar energy to the case of compound (3) and CrV2O4 (b). The peak intensity for (a) and (b) was 57–65% of that for (h), suggesting that the V site symmetry of V/TiO was higher than TiO.

For HSA V/TiO, the V Kα1,2 emission peak position (4951.7 eV) corresponds to VIVIV state. The rising edge position of the XANES (5479.8 eV, c) shifted by 1.0–1.3 eV toward lower energy compared to the case of V/TiO. Two broad peak features were observed at 5487 and 5505 eV in the post-edge region, shifted by ±2 eV from the case of V/TiO (a and b). The post-edge pattern of VOSO3·3H2O (i) was entirely different from (c). The post-edge pattern of V2O4 (k) was relatively similar to (c), but the pre-edge peak position was at higher energy by 1.4 eV. The Ti K-edge data for HSA-TiO was compared to the V K-edge by shifting the energy by +499.8 eV (l), since the phase parameters are similar between Ti and V. Both the post-edge pattern and pre-edge peak were similar to the case of (c).

The FWHM value of the pre-edge peak at 5467.9 eV (Table 1) for HSA V/TiO (c) was 2.3 eV, a value smaller than the case of V/TiO (2.5 eV, a and b). This implies that HSA V/TiO primarily consists of VIV sites rather than a mixture of VIV and VV sites. The VV site of V2O4 is coordinated by three nearer O atoms (1.76–1.87 Å) and three farther O atoms (2.01–2.05 Å). The pre-edge peak intensity of HSA V/TiO was 91% for the case of V2O4, suggesting a slightly higher symmetry than for the case of V2O4. EXAFS combined with fluorescence spectrometry until the wavenumber of 11 Å−1 gave an average V-O distance of 1.74 Å in the case of HSA V/TiO.

The pre-edge, rising edge, and two post-edge peaks appeared at 5468.5, 5481.1–5481.3, 5487–5488, and 5501–5504 eV and the FWHM of pre-edge peak was 2.4–2.5 eV for HSA-V/TiO (d) and V/TiO (e), very similar to the case of V/TiO (a and b).

The pre-edge peak from the V2+ sites may be substituted on the Ti sites only in the case of HSA V/TiO, prepared from compounds 1 and 2 and dodecylamine. VV species were dominant for the other samples and major V site structure may be common due to the similarity of spectrum. Eight of ten V atoms of [V2O12]6− are coordinated by one nearer O atom (1.61 Å) and four farther O atoms (1.83–2.05 Å),14 similar to the case of V site in V2O5. Relatively low calcination temperature (473 K) and ambient condition may be the reasons why monovanadate, decavanadate, and V2O5 were not observed.5,6

Table 1. The Intensity and Energy Position of Pre-edge Peaks

<table>
<thead>
<tr>
<th>Entry</th>
<th>Sample</th>
<th>Intensity</th>
<th>Energy Position (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>V/TiO (3.0 wt%)</td>
<td>0.47</td>
<td>5468.6</td>
</tr>
<tr>
<td>b</td>
<td>V/TiO (1.0 wt%)</td>
<td>0.53</td>
<td>5468.3</td>
</tr>
<tr>
<td>c</td>
<td>HSA V-TiO</td>
<td>0.32</td>
<td>5467.9</td>
</tr>
<tr>
<td>d</td>
<td>V/HSA-TiO</td>
<td>0.59</td>
<td>5468.5</td>
</tr>
<tr>
<td>e</td>
<td>V-TiO</td>
<td>0.39</td>
<td>5468.5</td>
</tr>
<tr>
<td>g</td>
<td>Mn0.8V1.2O6</td>
<td>0.57</td>
<td>5468.2</td>
</tr>
<tr>
<td>h</td>
<td>CrV2O4</td>
<td>0.82</td>
<td>5467.8</td>
</tr>
<tr>
<td>i</td>
<td>V2O4</td>
<td>0.79</td>
<td>5469.5</td>
</tr>
<tr>
<td>j</td>
<td>VOSO3·3H2O</td>
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<td>5468.7</td>
</tr>
<tr>
<td>k</td>
<td>V2O4</td>
<td>0.35</td>
<td>5469.3</td>
</tr>
<tr>
<td>l</td>
<td>HSA-TiO</td>
<td>0.25</td>
<td>4967.7</td>
</tr>
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</table>

Only the post-edge region was reported for Fig. 2f,11

References