0.6–3.0 wt% of Vanadium on/in Titania Monitored by X-ray Absorption Fine Structure Combined with Fluorescence Spectrometry

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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 high-surface-area V-TiO_2 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,[1] the oxidation of naphthalene/*o*-xylene to phthalic anhydride, and the oxidation of butane to maleic anhydride.[2] The optimal catalytic performance in these applications has been reported to correspond to concentrations of V of less than a monolayer, dispersed on TiO_2. When the concentration of V corresponds to monolayer levels, major V species has been proposed to be a monomeric monooxo[3] or dioxo vanadate,[4] polyvanadates[3] such as decavanadate ($[V_{10}O_{28}]^{6-}$),[5] or to an epitaxial V_2O_5(010) layer over TiO_2[6] by Raman, ^{51}V NMR, UV-visible, etc.

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_2O_5) is mixed with TiO_2, the V K-edge jump is only 0.037 compared to a total absorption of 4 in transmission mode. The photon number ratio of V Kα_1/Ti Kα_1 is only 0.012 in fluorescence mode. When a solid-state detector (SSD; $\Delta E \approx 100$ eV) is used, the V Kα_1 (4952.2 eV) peak can be separated from the Ti Kα_1 (4510.8 eV) peak. However, the Ti K$\beta_{1,3}$ (4931.8 eV) still overlaps the V Kα_1. The ratio of V Kα_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. 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[7,8] was applied to selectively monitor low concentrations of V on/in TiO_2.

TiO_2 (P25, 60 m^2g^{-1}) was impregnated with V triisopropoxide oxide (**1**) in isopropanol solution (V/TiO_2). A high surface area (HSA; 1200 m^2g^{-1}) V-TiO_2 was prepared from compound **1**, Ti tetraisopropoxide (**2**), and dodecylamine.[9] 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 docecylamine 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.[7] The entire beam path was in helium, except for the I_0 ion chamber (N_2 : He = 3 : 7).

The V Kα_1 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 Kα_1 and V K rising edge energy of the V metal were calibrated to 4952.2 and 5463.9 eV, respectively.

The V Kα_1 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^{III}, V^{IV}, and V^V compounds, respectively.[10] Hence, the V sites in the catalysts are in the oxidation state of IV/V. The FWHM

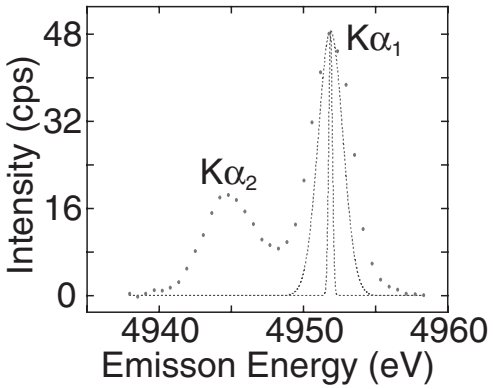

Figure 1. V Kα_1 and α_2 emission spectrum for V/TiO_2 of 3.0 wt%-V. Best energy resolution of the fluorescence spectrometer (narrower peak of dotted line) and of beamline (wider peak of dotted line) is also drawn.

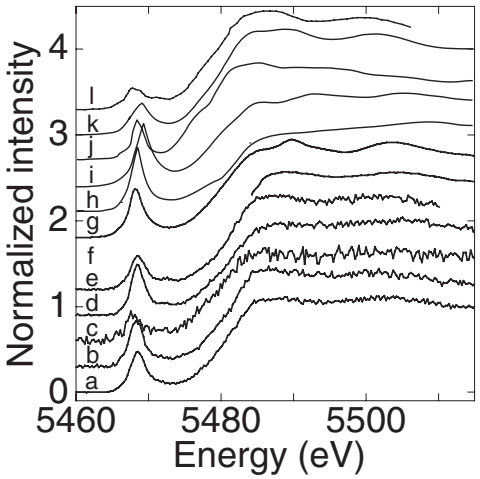

Figure 2. V K-edge XANES spectra for V+TiO_2 catalysts measured using a fluorescence spectrometer (a–c). V/TiO_2 of 3.0 (a) and 1.0 wt%-V (b). HSA V-TiO_2 (0.6 wt%-V, c). V/HSA-TiO_2 (1.0 wt%, d). V-TiO_2 (2.0 wt%, e). Reference V (f–k) and Ti K-edge (l) XANES measured in transmission mode for V/TiO_2 (3.9 wt%-V, f, above 5484 eV),[11] $Mn_{0.90}V^{V}_{1.80}Mo_{0.20}O_6$ (g), $CrV^{V}O_4$ (h),[12] $V^{V}{}_2O_5$ (i),[12] $V^{IV}OSO_4{\cdot}3H_2O$ (j),[12] $V^{IV}{}_2O_4$ (k),[12] and HSA-TiO_2 (l).[9]

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.[7]

Figure 2 shows the normalized V K-edge XANES spectra. In the case of V/TiO_2 (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_2 (3.9 wt%-V, f; 5489 and 5503 eV)[11] and $Mn_{0.90}V_{1.80}Mo_{0.20}O_6$ (**3**) (g; 5490 and 5504 eV). The V site in compound **3** is coordinated by two nearer O atoms (1.661–1.693 Å) and three farther O atoms (1.913–2.151 Å).[13] A weaker shoulder at 5486 eV appeared in (b) and (g). The post-edge pattern for $CrV^{V}O_4$ (h) and $V^{V}{}_2O_5$ (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_2 (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+M ($\approx$1.01 eV) and the ΔE of the beamline, whereas the emission peak width is related to the width of K+L_3 (1.26 eV) and the ΔE of the beamline+the fluorescence spectrometer. Therefore, the ΔE of the beamline was estimated to be 2.0 eV (Figure 1) and the ΔE of the fluorescence spectrometer 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 $K\beta_{1,3}$ appeared with these energy resolution values, demonstrating entirely no contribution of Ti in Figure 2a–e.

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

Entry	Sample	Intensity	Energy Position (eV)
a	V/TiO_2 (3.0 wt%)	0.47	5468.6
b	V/TiO_2 (1.0 wt%)	0.53	5468.3
c	HSA V-TiO_2	0.32	5467.9
d	V/HSA-TiO_2	0.59	5468.5
e	V-TiO_2	0.39	5468.5
g	$Mn_{0.90}V_{1.80}Mo_{0.20}O_6$	0.57	5468.2
h	$CrVO_4$	0.82	5468.7
i	V_2O_5	0.79	5469.5
j	$VOSO_4{\cdot}3H_2O$	0.48	5468.7
k	V_2O_4	0.35	5469.3
l	HSA-TiO_2	0.25	4967.7

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

The pre-edge peak in (a) and (b) appeared at a similar energy to the case of compound **3** (g) and $CrVO_4$ (h). The peak intensity for (a) and (b) was 57–65% of that for (h), suggesting that the V site symmetry of V/TiO_2 was higher than T_d.

For HSA V-TiO_2, the V $K\alpha_1$ emission peak position (4951.7 eV) corresponds to V^{IV}/V^{V} 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_2. Two broad peak features were observed at 5487 and 5505 eV in the post-edge region, shifted by $\pm$2 eV from the case of V/TiO_2 (a and b). The post-edge pattern of $VOSO_4{\cdot}3H_2O$ (j) was entirely different from (c). The post-edge pattern of V_2O_4 (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_2 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_2 (c) was 2.3 eV, a value smaller than the case of V/TiO_2 (2.5 eV, a and b). This implies that HSA V-TiO_2 primarily consists of V^{IV} sites rather than a mixture of V^{IV} and V^{V} sites. The V^{IV} site of V_2O_4 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_2 was 91% for the case of V_2O_4, suggesting a slightly higher symmetry than for the case of V_2O_4. 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_2.

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 V/HSA-TiO_2 (d) and V-TiO_2 (e), very similar to the case of V/TiO_2 (a and b).

The V^{IV} sites may be substituted on the Ti sites only in the case of HSA V-TiO_2, prepared from compounds **1** and **2** and dodecylamine. V^{V} 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 $[V_{10}O_{28}]^{6-}$ 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 V_2O_5. Relatively low calcination temperature (473 K) and ambient condition may be the reasons why monovanadate, decavanadate, and V_2O_5 were not observed.[3–6]

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