

Structure of low concentrations of vanadium on TiO₂ determined by XANES and *ab initio* calculations

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The major local structure of low concentrations (1–3 wt% V) of vanadium on TiO₂ was determined to have two terminal oxo groups and in total five oxygen coordination by means of vanadium K-edge XANES and *ab initio* calculations of XANES spectra.

The optimal catalytic performance of vanadium catalysts has been reported to correspond to low concentrations of V dispersed on TiO₂.^{1–3} X-Ray absorption fine structure (XAFS) directly determines the local structure of non-crystalline and heterogeneous materials. As V and Ti are neighboring in the periodic table, a high concentration of Ti interferes with the detection of relatively weak photon absorption of V and/or X-ray fluorescence derived from V.⁴ In the case of the V site, which has one/two terminal oxo group(s), precise determination of the coordination numbers of V=O and V–O is difficult from the curve fit analysis of EXAFS because the bond distances differ by only 0.1–0.3 Å.⁵ In this communication, X-ray absorption near-edge structure (XANES) was measured for low concentrations of V on TiO₂ by utilizing a high-energy-resolution fluorescence spectrometer.

TiO₂ (Aerosil P-25, BET surface area 60 m² g⁻¹) was impregnated with vanadium triisopropoxide oxide (**1**) in 2-propanol solution (V/TiO₂). An aqueous solution of **1** and titanium tetraisopropoxide was kept at 333 K for six days, following which the filtered powder was heated at 453 K for ten days (V-TiO₂). In both procedures, the dried powder was heated in air at 473 K.

XAFS spectra were measured at KEK-PF 7C. A Si(111) monochromator was used. The X-ray fluorescence from the sample was analyzed using a Rowland-type spectrometer.^{6,7} The V Kα₁ emission spectrum was measured and the fluorescence spectrometer was tuned to the peak. Next, the V K-edge XANES was measured. Normalized V K-edge XANES spectra for V/TiO₂ and V-TiO₂ are shown in Fig. 1a–c. The energy values of the pre-edge peak, absorption edge, and post-edge peaks are summarized in Table 1. These values were within the range of 0.3, 0.5, and 2 eV, respectively, suggesting that the V site structure was essentially identical whether supported on TiO₂ (anatase) or prepared by the sol–gel method, independent of the V loading ratio. The energy differences compared to the spectrum of V₂O₅ were –0.9 to –1.2, 1.8–2.3, and 2–9 eV, respectively. Thus, the V site in these samples was not an epitaxially-grown V₂O₅(010) layer.³

These experimental spectra were compared to XANES data theoretically generated by *ab initio* calculations. A code FEFF8.2 was applied to model clusters A–D based on anatase TiO₂⁸ (Fig. 2) up to fourth coordination (26–49 atoms) from the absorbing V atom and also to a model of V₂O₅ (Table 2)⁹ up to third coordination (39 atoms) both in self-consistent field and multiple scattering calculation modes.^{10,11} The calculated XANES spectra are shown in Fig. 1d–g. The spectrum pattern

significantly changed depending upon whether the V site had two (Fig. 1d–f) or one (Fig. 1g) oxo group(s). In the case of models which contained a single oxo group, the dominant single post-edge peak energy gradually shifted from 5497 to 5491 eV on going from total coordination number five (Fig. 1g) to three (model C'; Table 2), and then to six (model D; Table 2) (Table 1). A pre-edge peak was not resolved from the absorption edge for the calculated spectra of models C' and D (spectra not shown). As the pre-edge peak was well resolved and two broad peaks (5488 ± 1 and 5502 ± 1 eV) of nearly equivalent intensity were observed in the post-edge region for experimental spectra (Fig. 1a–c), single oxo models were rejected.

In the case of models which contained two terminal oxo groups, the post-edge peak position of XANES for model A of five coordination (Table 2) was most similar to Fig. 1a–c within the range of 1–5 eV (Table 1) and the two peak intensity was nearly equivalent (Fig. 1d). The XANES for four coordination models B and C (Fig. 1e and f) were similar to each other despite the difference of the distance to fifth and sixth oxygen atoms (2.791 and 2.875 Å, respectively). Therefore, bonding distance and coordination number of the first shell primarily determine the V K-edge XANES pattern. The intensity of the second post-edge peak at 5500–5501 eV was stronger than that of the first peak at 5487–5488 eV in Fig. 1(e) and (f). A six coordination V site which has two terminal oxo groups is not plausible.⁵

The typical errors in the estimate of density of state of V 3d (pre-edge peak) and Fermi level (absorption edge) by FEFF are 1 eV.¹⁰ In this work, energy values of pre-edge peak and absorption edge for V₂O₅ were reproduced within the range of 0.2–0.6 eV (Table 1). The differences of these values between

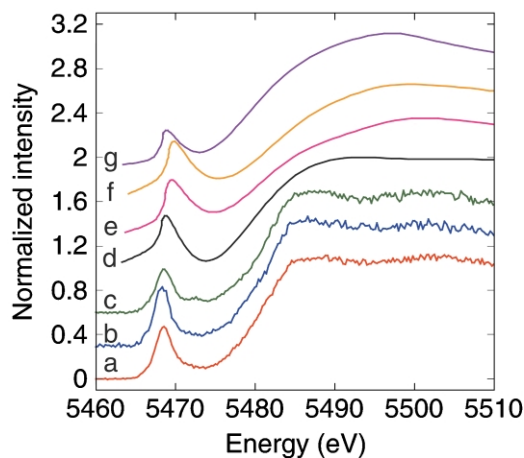


Fig. 1 Normalized V K-edge XANES for V/TiO₂, 3.0 (a) and 1.0 wt% (b) and V-TiO₂, 2.0 wt% (c). V K-edge XANES generated by FEFF for model A on anatase TiO₂(001) (d), model B on (110) (e), model C on (011) (f), and model of V₂O₅ (g).

Table 1 Energy values (eV) of the pre-edge peak, absorption edge, and post-edge peaks of V K-edge XANES for V/TiO₂ and V-TiO₂

Sample V	wt%	Pre-edge peak	Absorption edge	Post-edge peaks	
V/TiO ₂	3.0	5468.6	5480.8	5489	5502
	1.0	5468.3	5481.1	5487	5502
V-TiO ₂	2.0	5468.5	5481.3	5487	5501
V ₂ O ₅		5469.5	5479.0	5485	5493
Model	No. of oxo groups				
A	2	5468.8	5479.6	5492	5503
B	2	5469.5	5479.9	5487sh	5501
C	2	5469.8	5481.6	5488sh	5500
C'	1	5471.2 ^a	5483.6	5496	
D	1	5468.8 ^a	5478.6	5491	
V ₂ O ₅	1	5468.9	5478.8	5488sh	5497

sh: unresolved shoulder peak.^a Peak was not well resolved from the absorption edge.

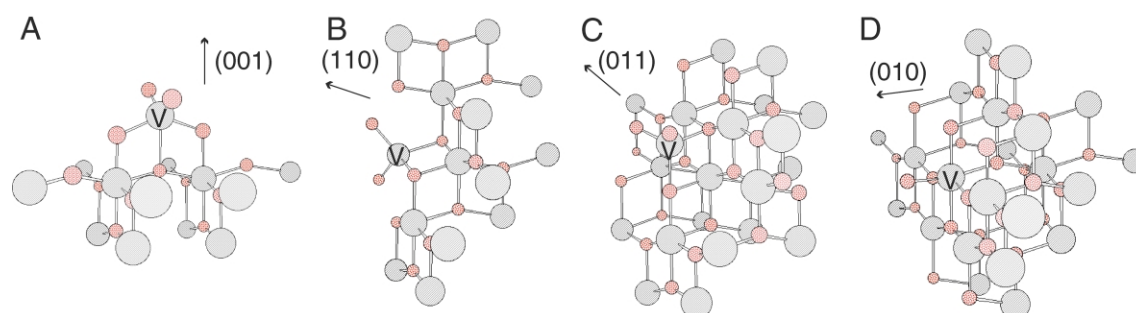


Fig. 2 V site models supported on TiO₂ (anatase) on (001) (A), (110) (B), (011) (C), and (010) face (D). Vanadate in models A–C and D has the coordination of two and one terminal oxo group(s), respectively. Model C that has one terminal oxo group was also considered (C'). All the smaller balls are oxygen atoms and all the larger balls without the notation are titanium atoms.

experimental data of Fig. 1a–c and calculated data for models A–C (Fig. 1d–f), were in the range of 0.2–1.7 eV. Taking the typical estimate errors of FEFF and data variation among the V/TiO₂ and V-TiO₂ samples (0.2–0.5 eV, Table 1) into account, models A–C are acceptable with respect to the pre-edge and absorption edge energies.

In summary, the calculated XANES spectrum for model A reasonably reproduced the XANES for V/TiO₂ and V-TiO₂ (Fig. 1a–c) in terms of the energy values of the pre-edge peak, absorption edge, and post-edge peaks and also the relative intensity ratio of post-edge peaks.

The effects of the bonding distance of first coordination were further evaluated for model A. The distance between V and two terminal oxo groups was elongated on going from 1.620 (Table 2) to 1.650, and then to 1.680 Å. The post-edge peak at 5492 eV grew stronger whereas the peak at 5503 eV remained unchanged. The *R* factor ($(|k_{\text{exp}} - k_{\text{fit}}|^2 dE / |k_{\text{exp}}|^2 dE)$ value of the fit to Fig. 1a increased from 2.3 to 2.5, then to 2.9%. Then, the V–O distance of 1.922 Å was elongated to 1.937 Å (shorter bonding distance of Ti–O in anatase). The post-edge two peaks merged into a single peak at 5494 eV. The *R* factor value of the fit to Fig. 1a increased from 2.3 to 3.5%. As the oxidation state of V supported on TiO₂ is +5, a longer V^V–O distance than the Ti^{IV}–O distance is unrealistic. The V site model for V/TiO₂ was proposed^{1,2} based on the V site structure of brannerite-type Mn_{1-x}V_{2-2x}Mo_{2x}O₆ (*x* < 0.36).¹² The V–O distances are 1.661, 1.693, 1.913, 1.939 and 2.151 Å. The V=O distance in model A may be shortened because two terminal oxo groups are

exposed to the surface. EXAFS analysis gave an average V–O distance of 1.74 Å in the case of a sample prepared using a similar procedure to V-TiO₂, which is consistent with the average values of 1.620 and 1.922 Å obtained by XANES or of 1.65 and 1.90 Å given in ref. 2.

The above calculated data considered only dipole electronic transition from V 1s to 3d. Calculations which consider both dipole and quadrupole transitions were also performed for each model. The pre-edge peak energy position was unchanged and the intensity increased only by 0–2.3%.

The models which contain a single oxo group *e.g.* epitaxial V₂O₅(010) layer were found to be not plausible both in the cases of V/TiO₂ and V-TiO₂. The possibility of hydrated monomeric monovanadate or 2-dimensional polyvanadate cannot be excluded compared to Raman studies¹³ dependent upon ambient gas and calcination temperature.

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Table 2 Values of V–O distances and O=V=O angles used for XANES calculations by FEFF8.2

	V–O distance/Å	O=V=O angle/deg
A	1.620 × 2, 1.922 × 2, 2.151	105.8
B	1.620 × 2, 1.922 × 2	105.8
C	1.620 × 2, 1.922 × 2	105.8
C'	1.620, 1.922 × 2	—
D	1.800, 1.937 × 3, 1.964 × 2	—
V ₂ O ₅	1.54, 1.77, 1.88 × 2, 2.02	—