

X-Ray Absorption Spectroscopy (EXAFS/XANES) Evidence for the Preferential Formation of Isolated VO_4 Species on Highly Photoactive $\text{V}_2\text{O}_5/\text{SiO}_2$ Catalysts

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Vanadium K-edge XANES and EXAFS studies revealed that the surface vanadium oxide species of $\text{V}_2\text{O}_5/\text{SiO}_2$ prepared by impregnating silica with a basic solution (NaOH) of ammonium metavanadate is dominantly an isolated tetrahedral VO_4 species, which brings about an enhanced photocatalytic activity.

$\text{V}_2\text{O}_5/\text{SiO}_2$ exhibits activity for photocatalytic oxidations^{1,2} and a V=O bond of surface VO_4 tetrahedral species has been proposed for the active site based on photoluminescence studies.³ Recently, we found that the addition of NaOH as an ingredient enhances the activity of the catalysts for selective photo-oxidation of propan-2-ol and propene to ketones and aldehydes.⁴ U.v. absorption spectra of both the sodium-ion-modified (VSS) and unmodified (VS) catalysts exhibited a band centred at 340 nm due to an oxygen-to-vanadium charge-transfer transition of VO_4 tetrahedra,⁵ suggesting the presence of similar active species. We report here the preferential formation of isolated VO_4 tetrahedra by the addition of sodium ions, clarified by means of extended X-ray absorption fine structure⁶ (EXAFS) and X-ray absorption near edge structure (XANES) spectroscopy.

The catalysts were prepared by impregnating silica with

aqueous solutions containing the desired amounts of vanadium and sodium and calcined as described elsewhere.⁷ The solutions were prepared by dissolving NH_4VO_3 in the correct amounts of 0.1 M NaOH solution. The V_2O_5 content was adjusted to 5% by weight for each catalyst. Contents of sodium ions were 0 wt% (VS), 1.9 wt% (VSS2), and 5 wt% (VSS5) as Na_2O . X-Ray absorption spectra were recorded by the EXAFS facilities installed at the beam line 7-c of the Photon Factory (ring energy: 2.5 GeV and ring current: 150–200 mA) in the National Laboratory for High Energy Physics (KEK-PF) in the transmission mode with an Si(111) two-crystal monochromator. Computational analyses were carried out with the FACOM M382 computer system at the Data Processing Centre of Kyoto University.

Figure 1 shows the normalised K-edge XANES spectra of the catalysts and related compounds. NH_4VO_3 and dodecahy-

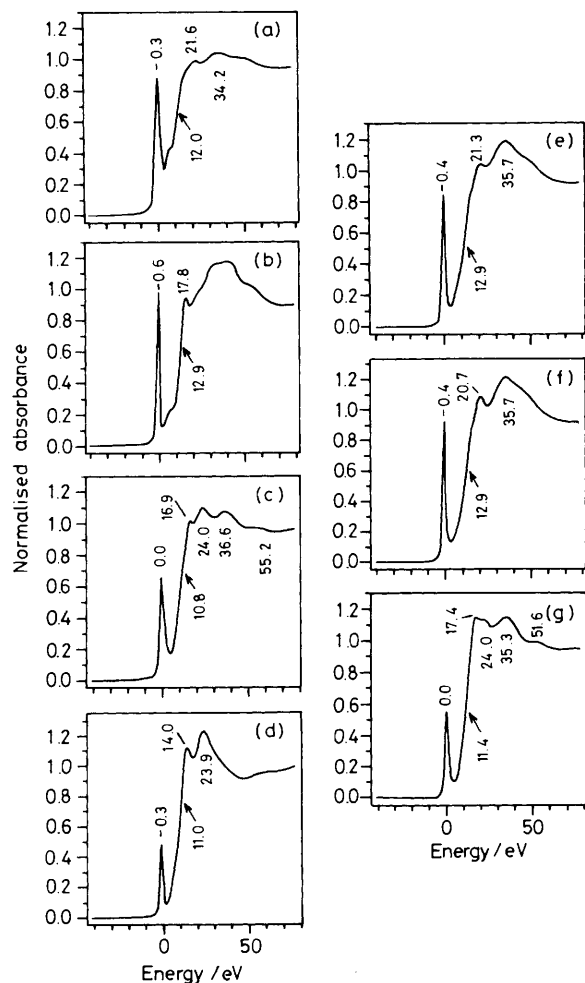


Figure 1. Vanadium K-edge XANES spectra of (a) NH_4VO_3 , (b) Na_3VO_4 , (c) V_2O_5 , (d) $\text{VO}(\text{acac})_2$, (e) VSS2, (f) VSS5, and (g) VS. Each spectrum was normalised to the height of the edge jump. Energy offset is taken to be the position of the pre-edge peak of the spectrum of V_2O_5 (5470.0 eV) and energy resolution is ± 0.5 eV. Each value indicated with an arrow is the position of the absorption edge determined from the position of the inflection point.

drated Na_3VO_4 have four-co-ordinate vanadium ions, while V_2O_5 and $\text{VO}(\text{acac})_2$ (Hacac = $\text{MeCOCH}_2\text{COMe}$) have five-co-ordinate vanadium ions.⁸ Characteristic of the XANES spectra is the pre-edge peak attributed to the so-called 1s–3d transition caused mainly by mixing of the 2p orbitals of oxygen with the 3d orbital of vanadium in the terminal oxo group ($\text{V}=\text{O}$).⁹ The pre-edge peak becomes more intense when a vanadium atom is in tetrahedral co-ordination, as in NH_4VO_3 and Na_3VO_4 . In the spectrum of VS, the absorption edge and peaks are found in similar positions to those for V_2O_5 and the height of the pre-edge peak is smaller than those for NH_4VO_3 and Na_3VO_4 . On the other hand, the pre-edge features of the spectra of both VSS catalysts are similar to those of NH_4VO_3 and Na_3VO_4 . It is noteworthy that the spectrum of VSS5 in the post-edge region is different from that of Na_3VO_4 in spite of the similar atomic ratio of Na to V. According to the classification of the XANES feature of vanadium by symmetry,¹⁰ it is suggested that a vanadium atom in VS is surrounded by five or more oxygen atoms, whereas a vanadium atom in VSS is in tetrahedral co-ordination. A VO_4

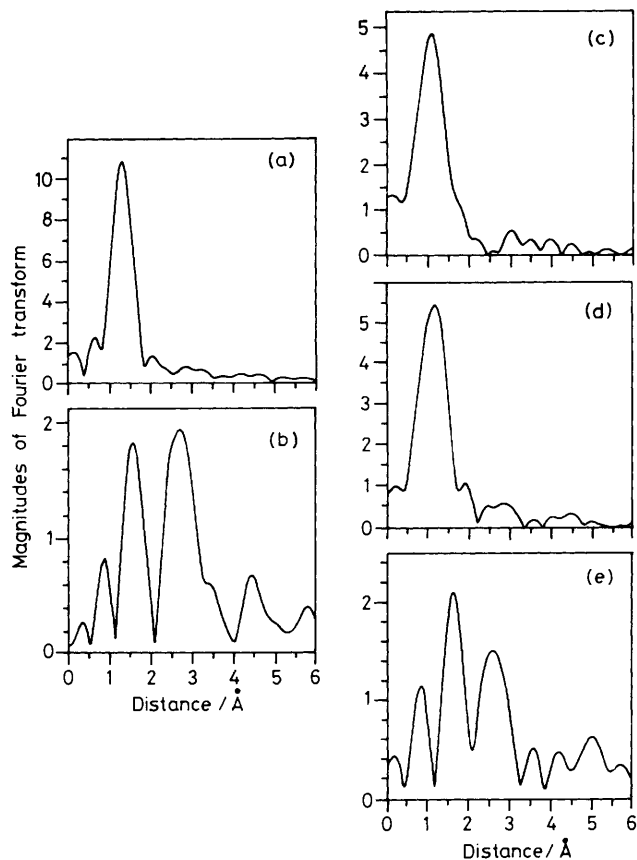


Figure 2. Magnitudes of Fourier transforms of normalised k^3 -weighted EXAFS of (a) Na_3VO_4 , (b) V_2O_5 , (c) VSS2, (d) VSS5, and (e) VS. EXAFS were transformed in the range of 3.5 – 11.0 \AA^{-1} .

unit in Na_3VO_4 is considered to be very close to a regular tetrahedron because its XANES feature is similar to that of a regular tetrahedron VO_4 in $\text{Pb}_5(\text{VO}_4)_3\text{Cl}$ ¹⁰ rather than that of the distorted VO_4 units in NH_4VO_3 .⁷ The XANES spectra of VSS catalysts are more like that of NH_4VO_3 than Na_3VO_4 , suggesting that the VO_4 tetrahedra in VSS are distorted from a regular tetrahedron.

Figure 2 shows the Fourier transforms (F.t.s) of k^3 -weighted EXAFS obtained by standard analysis,¹¹ which reflect the radial distribution around a V atom of the catalysts. F.t.s of V_2O_5 and dodecahydrated Na_3VO_4 are also shown. The peak appearing at 1 – 2 \AA in each F.t. is due to V–O bonds and the peak appearing at the long distance (2 – 4 \AA) shows the presence of neighbouring vanadium atoms. The V–V peaks can be seen in the F.t. of VS as in the case of V_2O_5 , suggesting that dominant surface vanadates are polymeric. However, the height of the V–V peak at 2.6 \AA is lower in VS than that in V_2O_5 showing that the number of neighbouring vanadium ions in VS is smaller than that in the V_2O_5 crystal. A detailed discussion on the structure of surface vanadate on VS will appear elsewhere.¹² On the other hand, in the F.t. of VSS there are no peaks above noise levels at long distances (>2 \AA) as in the case of Na_3VO_4 , in which discrete VO_4^{3-} ions exist.⁸ This result clearly suggests that vanadium ions in VSS catalysts are isolated from other vanadium ions. The peak due to the V–O shell of each VSS catalyst is lower and broader than that

of Na_3VO_4 , resulting from a beat phenomenon together with disorder.¹² This proves the variance in the V–O distances within the VO_4 units of VSS catalysts. The analysis by a curve-fitting technique indicated that the vanadate in each VSS catalyst has one short and three long bonds (1.61, 1.78 Å for VSS2 and 1.62, 1.77 Å for VSS5). The shorter bond may correspond to the V=O bond. It seems reasonable to attribute the enhanced activity of VSS to the preferential formation of isolated tetrahedral VO_4 species by the effect of sodium ions since bulk V_2O_5 is photoinactive.^{2,13}

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