Analysis of XANES for identification of highly dispersed transition metal oxides on supports

Satohiro Yoshida, Tsunehiro Tanaka, Tomoko Hanada, Takeshi Hiraiwa,
Hiroyoshi Kanai and Takuzo Funabiki

*Department of Hydrocarbon Chemistry and Division of Molecular Engineering, Kyoto University,
Sakyo-ku, Kyoto 606, Japan*

XANES of vanadium and niobium oxide on silica or alumina have been analyzed quantitatively by a deconvolution technique. Based on the results for reference compounds, local structures of supported vanadium and niobium species were identified. The composition was estimated from difference spectra for the samples which consisted of two kinds of species.

Keywords: XANES, vanadium oxocompounds; niobium oxocompounds; supported catalysts

1. Introduction

X-ray absorption near edge structure (XANES) can afford information on the local structure, coordination symmetry, oxidation states, and furthermore aggregated states of highly dispersed species on supports [1]. In the present letter, we will describe a quantitative analysis of XANES for identification of surface vanadium and niobium species on silica or alumina.

2. Experimental

SAMPLES AND XANES SPECTRA

Vanadium oxide or niobium oxide were dispersed on silica and/or alumina by an impregnation or CVD method as described elsewhere [2a,b,c]. Commercially available compounds for which the local symmetry around a metal atom is known were used as references. XANES spectra of samples were recorded with a facility of the BL-7C station for vanadium K-edge with a Si(111) double crystal monochromator or the BL-10B station for niobium K-edge with a Si(311) channel cut monochromator at the Photon Factory in the National Laboratory for High Energy Physics (KEK-PF) in a transmission mode. Higher harmonic components of the X-ray were removed by low angle reflection on a flat quartz plate for vanadium K-edge XANES. Energy resolution was about 0.5 eV at vanadium K-edge and about 4 eV at niobium K-edge. Energy calibration was done by using the pre-edge peak of V_2O_5 (5470.0 eV) [3] or the ionization threshold of niobium metal (18986.9 eV). Sample powders were sealed with polypropylene film in a dry box to keep a dry state after treatment with oxygen at 673 K for 2 h. For vanadyl(V) triisopropoxide ($VO(OiPr)_3$), a neat liquid was filled into a polyethylene cell.

ANALYSIS OF XANES

Back ground subtraction and normalization procedures of XANES were the same as those in a previous work [3]. The normalized XANES was deconvoluted to one arctangent curve (for continuum absorption) and several Lorentzian curves with a standard non-linear least square method using a FACOM M780 computer at The Data Processing Center of Kyoto University.

3. Results and discussion

3.1. VANADIUM REFERENCE COMPOUNDS

Fig. 1 shows XANES and deconvoluted curves of reference compounds of vanadium oxide and table 1 shows the peak energy position (relative to the absorption edge energy defined as the energy at half height of the continuum absorption curve), peak width (FWHM) and area (in eV unit) of each peak. Generally, the XANES are composed of a pre-edge peak, peaks around edge position (group A) and those of 5–10 eV higher than the edge position (group B) and others (group C). The pre-edge peak is caused by so-called 1s–3d transition and is sensitive to the symmetry around a vanadium atom [4]. From table 1, the following characteristics of the pre-edge peak can be deduced.

1) The relative peak position is lower for compounds of tetrahedral symmetry (Td) and higher for those of octahedral symmetry (Oh) than -12 eV.

2) The peak area is higher than 2 for Td compounds and lower than 1.8 for Oh compounds.

3) The FWHM is large for compounds with significant diversity in V–O bond length. For example, the bond lengths in V_2O_5 (FWHM $= 2.1$ eV) are diverse within 0.154 and 0.281 nm [5], while those in $VO(OiPr)_3$ (FWHM $= 1.7$ eV) are fairly close to each other (0.161×1 and 0.179×3 nm as determined by analysis of EXAFS).

The assignment of the group A peaks is still ambiguous. However, we notice that the peaks are clear in XANES of the Td compounds.

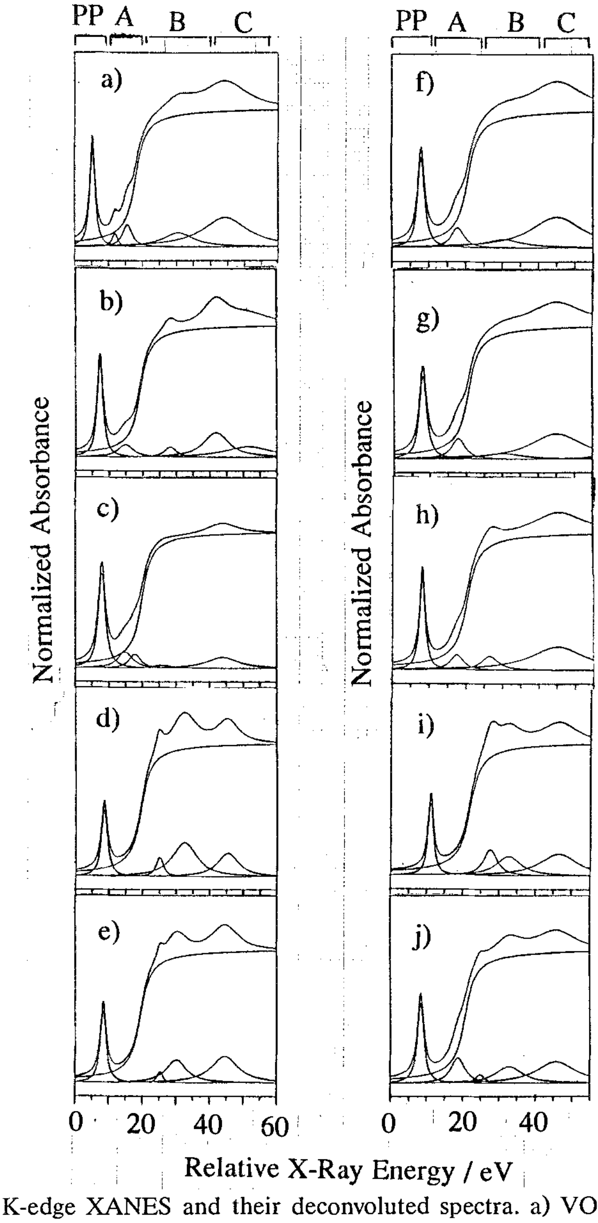

Fig. 1. Vanadium K-edge XANES and their deconvoluted spectra. a) $VO(OiPr)_3$, b) NH_4VO_3, c) $Ca_2V_2O_7$, d) V_2O_5, e) MgV_2O_6, f) 2.8VSCVD, g) 2.5VSIMP, h) 2.8VAIMP, i) 2.8VSCVD-H, and j) 11.6VSIMP. Energy offsets are 5465.0 eV for a), 5458.0 eV for b)–h) and j), and 5461.0 eV for i).

Group B peaks are assignable to 1s–4p or −5p transitions and are sensitive to the electronic state of V–O bonds. The peaks appear in both Td and Oh compounds, but FWHM is large in Td compounds (for NH_4VO_3: 4.4 and for

Table 1
Parameters of deconvoluted peaks in XANES spectra of vanadium compounds

Sample [a] (symmetry)	Peak [b]						E_0/eV [c]
	PP	A1	A2	B1	B2	C	
	−12.8	−6.1	−2.1		12.5	26.3	
VO(OiPr)$_3$	1.7	2.0	3.4		11.0	16.0	5481.9
(Td)	2.1	0.3	0.8		1.7	5.3	
	−12.1	−4.5			8.8	22.5	
NH$_4$VO$_3$	2.1	5.5			4.4	9.0	5481.0
(Td)	2.3	0.8			0.6	2.6	
	−12.0	−5.1	−2.2		6.0	23.9	
Ca$_2$V$_2$O$_7$	2.4	5.4	4.1		7.6	11.4	5481.6
(Td)	2.6	1.0	0.7		0.3	1.4	
	−11.1			5.4	12.8	25.8	
V$_2$O$_5$	2.1			2.5	8.6	7.9	5481.2
(Oh)	1.6			0.6	3.4	2.1	
	−11.1			5.8	10.7	25.1	
MgV$_2$O$_6$	2.0			2.0	7.4	9.7	5481.1
(Oh)	1.7			0.3	2.0	3.0	
	−12.7	−2.8			9.5	24.4	
2.8VSCVD	2.2	4.3			13.6	17.6	5482.2
	2.2	1.0			1.4	6.1	
	−12.7	−2.9			9.5	24.3	
2.5VSIMP	2.4	4.6			13.3	17.7	5482.3
	2.3	1.1			0.9	5.1	
	−12.2	−2.8			6.2	24.8	
2.8VAIMP	1.8	4.3			5.5	18.0	5482.1
	1.9	0.8			0.9	4.7	
	−11.1			5.6	10.6	24.4	
2.8VSCVD-H	1.8			4.4	8.1	12.4	5483.6
	1.5			1.3	1.8	3.1	
	−12.5	−2.0		4.0	12.0	2.50	
11.6VSIMP	2.1	4.6		3.0	9.0	13.1	5482.4
	2.0	1.4		0.3	1.8	3.3	

[a] See text.

[b] Consult fig. 1 for peak assignment. Three values for each peak show parameters in the order of peak position (eV), FWHM (eV) and area (eV unit).

[c] Energy offset (ionization threshold) determined as the position of the inflection point of the continuum curve.

Ca$_2$V$_2$O$_7$: 7.6 eV) compared with Oh compounds (for MgV$_2$O$_6$: 2.0 and V$_2$O$_5$: 2.5 eV). A noteworthy fact is the observation of only double peaks in the region of B and C in XANES of NH$_4$VO$_3$. The compound has two V–O bonds of double bond character (V=O). The double peaks appear to be useful for the identification of a dioxo structure.

Group C peaks are broad and of complicated nature because of the influence by multiple scattering of photo-electrons and can not be used for identification of the local structure.

3.2. VANADIUM OXIDE ON SUPPORTS

XANES of vanadium oxide on supports and the parameters of deconvoluted peaks are also shown in fig. 1 and table 1. XANES of 2.8VSCVD (vanadium oxide supported on silica by a CVD method; V content: 2.8 wt%;) and 2.5VSIMP (prepared by an impregnation method; V content: 2.5 wt%) are almost identical and closely resemble that of $VO(OiPR)_3$, indicating that the local structure is of Td symmetry and vanadium species are highly dispersed. The CVD method is expected to be a better method to prepare highly dispersed catalysts than the impregnation method. However the present results show that highly dispersed catalysts can be obtained by the impregnation method, if the loading of vanadium oxide is low. XANES does not show clear double peaks as observed with NH_4VO_3, indicating that the major species is not of a dioxo structure or pyrovanadate. The position of pre-edge peak is 1.3 eV higher than that of $VO(OiPR)_3$. This may reflect the difference of electronic interaction with alkoxide and silica; in other words, there may be some chemical interaction between VO_4 units and silicon atoms to stabilize the vanadium oxide species in a highly dispersed state.

When 2.8VSCVD was exposed to water vapor, the XANES changed significantly as shown in fig. 1(i) (2.8VSCVD-H) [6]. The XANES is different from those of reference compounds, but we can conclude that the structure is not of Td symmetry as pre-edge position (-11.1 eV) is higher than -12 eV and the peak area is low (1.5). The group A peak is also not observable. A clear peak is observed at the group B region, suggesting an Oh structure.

XANES of 2.8VAIMP (vanadium oxide supported on alumina by an impregnation method; V content: 2.8 wt%) is significantly different from that of 2.5VSIMP as shown in fig. 1(h). The spectrum is rather similar to that of NH_4VO_3. The pre-edge peak position and area show that the structure is of tetrahedral symmetry and, furthermore, clear double peaks suggest the presence of dioxo structure [7].

When the loading of vanadium is high, XANES is significantly different from that of samples of low loading as shown in fig. 1(j). The sample, 11.6VSIMP, contains 11.6 wt% vanadium. The general features are similar to that of V_2O_5 (an Oh compound). However, the pre-edge peak position and area suggest Td symmetry. Thus, both Td and Oh species should coexist. To determine the Oh/Td ratio, a difference spectrum was constructed. Subtraction of the 0.5 weighted 2.5VSIMP spectrum from 11.6VSIMP gave a spectrum almost identical to that of V_2O_5, indicating that about half of the species is still Td species. This information is useful for assignment of the B1 peak. The B1 peak is observed in both spectra of 11.6VSIMP and V_2O_5 and the areas are 0.31 and 0.56, respectively (table 1). The ratio, 0.31/0.56 = 0.55, is in good agreement

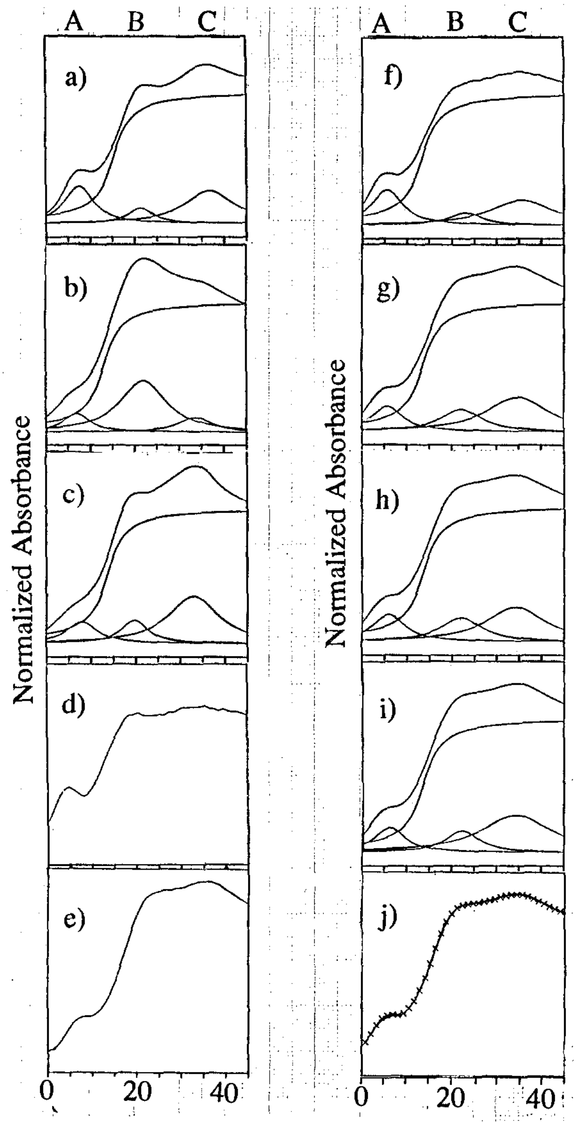

Fig. 2. Niobium K-edge XANES and their deconvoluted spectra. a) $YbNbO_4$, b) Niobium oxalate, c) $KCa_2Nb_3O_{10}$, d) tetr, e) oct, f) 0.66NbSIMP, g) 4.6NbSIMP, h) 10NbSIMP, i) 4.6NbSIMP-H, and j) 4.6NbSIMP (———) and 0.33×ter+0.67×oct (×———×). Energy offsets are 18976 eV for a), d)–i), and 18975 eV for b) and c).

Table 2
Parameters of deconvoluted peaks in XANES spectra of niobium compounds

Sample ^{a} (Symmetry)	Peak ^{b}			E_0/eV ^{c}
	A	B	C	
	−7.9	6.0	21.4	
$YbNbO_4$	8.0	7.2	13.6	18993.8
(Td)	3.5	1.3	5.2	
	−6.1	8.9	20.6	
Niobium oxalate	7.5	12.5	9.4	18993.1
(Oh)	1.6	7.7	1.6	
	−5.7	6.1	19.2	
$KCa_2Nb_3O_{10}$	8.1	7.2	13.1	18993.8
(Oh)	2.0	1.9	7.2	
	−7.9	9.6	22.2	
0.66NbSIMP	8.6	9.0	17.4	18993.8
	3.5	1.3	5.0	
	−7.9	8.5	21.1	
4.6NbSIMP	8.8	11.5	16.9	18994.0
	2.6	3.0	7.0	
	−7.8	8.4	20.6	
10NbSIMP	8.6	11.0	15.5	18994.0
	2.6	3.0	5.8	
	−7.6	8.5	20.6	
4.6NbSIMP-H	8.3	9.0	19.0	18994.2
	2.4	2.2	8.1	

^{a,b,c} See text. Consult fig. 2 for peak assignment.

with the estimate from spectrum subtraction mentioned above. (Note that all spectra were normalized.) Thus, the B1 peak is assignable to V_2O_5 phase.

3.3. NIOBIUM REFERENCE COMPOUNDS

Niobium K-edge is at 18986.9 eV and energy resolution at the XANES region is unfortunately poor (ca. 4 eV) compared with that of the vanadium K-edge region. Thus, deconvolution results are not as precise as those for vanadium compounds and our discussion is limited to the pre-edge peak. Fig. 2 shows XANES of some niobium compounds and parameters for the pre-edge peak are shown in table 2. Again, the general correlation between the parameters and the local structure can be observed; lower energy position and higher area for Td compounds than those for Oh compounds.

3.4. NIOBIUM OXIDE ON SUPPORTS

Three samples of niobium oxide on silica with different loading were investigated. As shown in fig. 2, all XANES spectra are different from those of the reference compounds; the intensity of the pre-edge peak is in the middle of that of Td and Oh compounds and the line shape as a whole does not resemble any reference compound. We assume that both Td and Oh species coexist and we attempted to estimate the Td : Oh ratio. From the results of vanadium oxide on silica, adsorption of water vapor will cause a change in the local structure from Td to Oh symmetry. On the other hand, a sample of low content of niobium oxide, 0.66NbSIMP (niobium oxide supported on silica by impregnation method; Nb content: 0.66 wt%), is expected to be composed of Td species with a high ratio. Thus, a difference spectrum constructed from XANES data for these samples can be assumed to be the XANES of pure Td species. It was found that a combination of the XANES of 0.66NbSIMP and 0.4 weighted 4.6NbSIMP-H (hydrated) gave a reasonable spectrum (TETR) (fig. 2(d)). Then, a difference spectrum was constructed by subtraction of 0.3 weighted TETR from 4.6NbSIMP. The spectrum (OCT) (fig. 2(e)) was almost identical to XANES of 4.6NbSIMP-H. We succeeded in simulating the original spectra of three Nb/silica samples by superposition of TETR and OCT spectra. An example is shown in fig. 2(j). As expected, the relative concentration of Oh species increased with Nb loading from about 23% with 0.66% Nb to 70% with 10% Nb sample. This analysis is semiquantitative, but is believed to be useful for the estimation of the relative composition in a sample which contains two kinds of species different in the local structure.

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