

XAFS study of niobium oxide on alumina

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Abstract

The structure of the niobium oxide on alumina surface was investigated for low loading (5 wt.-%) and high loading (19 wt.-%) samples. The TPD profile of water molecules showed the appearance of water adsorption sites other than those on alumina. The XANES and EXAFS spectra clearly showed that niobic acid-like species are formed on the surface of 19 wt.-% NbO_x/Al₂O₃. The XANES spectra of 5 wt.-% NbO_x/Al₂O₃ suggests that NbO₄ tetrahedra with two Nb=O bonds are present and one or two water molecules are adsorbed onto the species. On 5 wt.-% NbO_x/Al₂O₃, the presence of a mixture of the monomer NbO₄ and the dimer Nb₂O₇ are concluded from the EXAFS analysis.

Keywords: Niobium oxide; Alumina; X-ray absorption fine structure

1. Introduction

Vanadium oxides supported on metal oxide surfaces have been characterized extensively and it has been recognized that tetrahedrally coordinated vanadates are stabilized on silica and alumina [1] at a low level of vanadium loading. An orthovanadate-type species with a mono-oxo group and a metavanadate-type species with a di-oxo group were found to be present on silica and alumina [1–3], respectively, as being consistent with the prediction by ab initio molecular orbital calculations [4]. Water adsorption onto V₂O₅/SiO₂ brings about the change in coordination number of vanadium ions as well as the formation of linkage of adjacent vanadium ions

through bridged oxygen atoms of water molecules. On the other hand, water adsorption onto alumina does not cause the structural change of the vanadates. In this case, V=O bonds were found to be elongated by adsorption of water molecule(s) with hydrogen bonding on oxo-oxygen [1].

Although niobates belong to VA-group metal oxides as vanadates belong to, it seems that niobates exhibit a different character from vanadates. The niobates on alumina and silica have been confirmed to have oxo bonds by Raman spectroscopy [5–7] but their fundamental structures on these metal oxides have not been fully clarified. In EXAFS/XANES [3,8,9], UV/VIS and luminescence [10] studies, niobium ions on a silica surface were found to have a NbO₄ tetrahedral structure at an extremely low level of Nb₂O₅ loading (ca. 1 wt.-%). Adsorption of water molecules did not cause a significant

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change of the coordination state of niobium ions [8]. The presence of microcrystal of Nb_2O_5 have been suggested by in situ Raman spectroscopy [6] at 4 wt.-% Nb_2O_5 loading. On the other hand, niobium ions are dispersed on an Al_2O_3 surface more highly than on an SiO_2 surface and the niobium species is very sensitive to water adsorption [6]. The structure model of dehydrated niobium species has been predicted by Wachs and Jehng; distorted NbO_6 octahedral are plausible, possessing a $\text{Nb}=\text{O}$ bond with a bond length 1.76 Å [6]. These findings are in contrast with those for vanadium oxides. The present work is devoted to the elucidation of the structures of niobium oxides on alumina at different loadings by applying XAFS spectroscopy.

2. Experimental

2.1. Samples

$\text{NbO}_x/\text{Al}_2\text{O}_3$ samples were prepared by incipient-wetness impregnation method with an aqueous solution of niobium oxalate and oxalic acid, followed by calcination at 723 K in a dry air stream as described elsewhere [5].

The $\text{NbO}_x/\text{Al}_2\text{O}_3$ samples were evacuated (10^{-4} Torr) at 673 K for 2 h and these will be referred to as the dehydrated samples and the samples exposed to air will be referred to as the hydrated (water-adsorbing) samples.

Niobic acid ($\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$) was supplied by CBMM. The niobium pentoxide was prepared by calcination of niobic acid at 773 K for 1 h. The calcination lead to the formation of $\text{TT-Nb}_2\text{O}_5$ [11], confirmed by X-ray diffraction pattern.

2.2. Temperature programmed desorption (TPD)

The sample (100 mg) was placed in a vessel and heated at 673 K in vacuo for 2 h. After 15 μmol water molecules were admitted to the vessel at room temperature, the vessel was

evacuated (10^{-4} Torr). The sample was heated up at a rate of 10 K min^{-1} and desorbed water molecules were monitored by a quadrupole-type mass spectrometer [12].

2.3. X-Ray absorption

The Nb K-edge X-ray absorption (XA) experiment was carried out at BL6B and BL7C, Photon Factory, National Laboratory for High Energy Physics, Tsukuba in a X-ray fluorescence mode for samples of low loading and in a transmission mode for other samples. The K-edge XANES spectra were recorded at BL6B facilitating a Si(311) two-crystal monochromator when a SR ring was operated at a 2.5 GeV energy and the K-edge EXAFS spectra at BL7C facilitating Si(111) two-crystal monochromator when a SR ring was operated at 2.8 GeV energy. The analysis of the spectra was performed by a KABO program [13] at Kyoto University Data Processing Center.

3. Results

3.1. Temperature-programmed desorption (TPD)

Fig. 1 shows the TPD profiles of water molecules adsorbed on the samples and some reference compounds. The experimental conditions for all the samples were the same except for that for niobic acid, for which the TPD profile was recorded without adsorption of water.

In the case of alumina, the desorption peak was found at 380 K with a long tailing part. The loading of niobates (5 wt.-% Nb_2O_5) on alumina shifts the desorption peak to 405 K without reducing the amount of the desorbed water, suggesting the presence of water adsorption sites other than those on alumina, Nb_2O_5 and niobic acid. An increase in Nb_2O_5 loading resulted in a split of the desorption peak at 395 and 415 K. The lower temperature corresponds to the des-

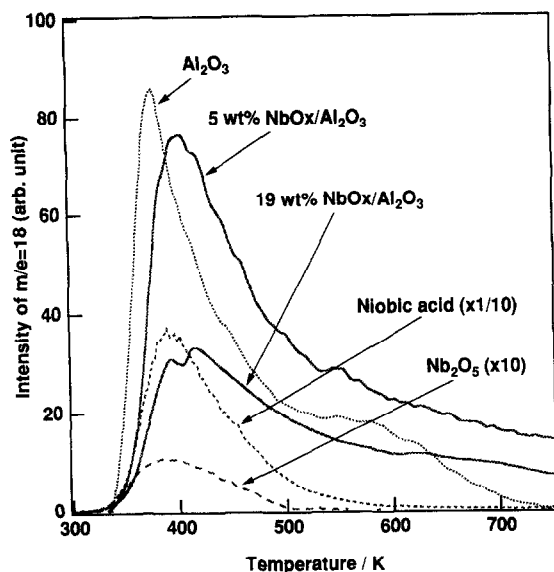


Fig. 1. TPD profiles of water adsorbed on $\text{NbO}_x/\text{Al}_2\text{O}_3$ samples, Al_2O_3 , niobic acid and niobium pentoxide.

orption temperature for Nb_2O_5 and niobic acid and the peak at the higher temperature may suggest the presence of the other adsorption sites as found in the case of 5 wt.-% $\text{NbO}_x/\text{Al}_2\text{O}_3$. Thus, polymeric niobates species and another type of niobates are possibly present as a mixture on alumina surface at Nb_2O_5 19 wt.-% loading.

3.2. Nb K-edge XANES

Normalized XANES spectra of niobic acid, niobium pentoxide and alumina-supported samples are shown in Fig. 2. It is generally accepted that the pre-edge peak found at low energy side of the edge absorption reveals the coordination state of a niobium complex [3,9]. The higher the intensity of the pre-edge peak, the more distorted is the coordination symmetry around a niobium ion. In the case of 5 wt.-% $\text{NbO}_x/\text{Al}_2\text{O}_3$, the pre-edge peak for the dehydrated sample is clearly observed whereas the peak appears only as a shoulder for the hydrated sample. This implies that the coordination state of niobium ions changes by adsorption of water molecules. The integrated areas (IA) for the peaks can be evaluated by deconvolution method [9] and one can estimate the coordination numbers. In the present case, the IAs were evaluated to be 3.36 and 2.46 for the dehydrated and the hydrated samples, respectively. The former IA value corresponds to that for a NbO_4 tetrahedron and the latter to that for a NbO_6 distorted octahedron or NbO_5 . Evidently, the NbO_4 tetrahedra on the dehydrated sample change to NbO_6 distorted octahedral or NbO_5 by adsorption of water molecules similar to the case of highly

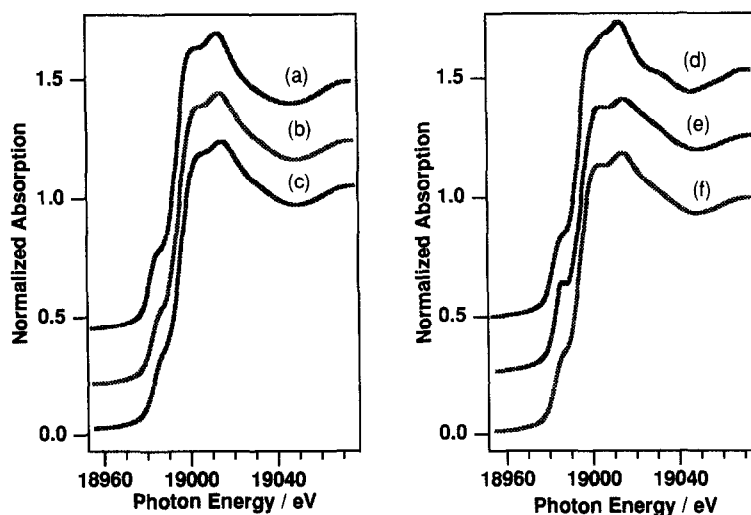


Fig. 2. Normalized Nb K-edge XANES spectra of (a) niobic acid, (b) dehydrated 19 wt.-% $\text{NbO}_x/\text{Al}_2\text{O}_3$, (c) hydrated 19 wt.-% $\text{NbO}_x/\text{Al}_2\text{O}_3$, (d) niobium pentoxide, (e) dehydrated 5 wt.-% $\text{NbO}_x/\text{Al}_2\text{O}_3$ and (f) hydrated 5 wt.-% $\text{NbO}_x/\text{Al}_2\text{O}_3$.

dispersed vanadium oxide supported on silica [1]. On the other hand, in the case of 19 wt.-% $\text{NbO}_x/\text{Al}_2\text{O}_3$, the difference of the pre-edge peak intensities between the dehydrated and the hydrated states is almost invisible. The IAs were evaluated to be 2.66 and 2.48 for dehydrated and hydrated states, respectively. This subtle difference indicates that the coordination states of the niobium ions did not change by adsorption of water molecules. It is likely that the niobium species on alumina at high Nb_2O_5 loading is a mixture of polyniobates and low-coordinated niobium species of a small amount. The latter may change the coordination state to a saturated one by adsorption of water molecules.

In Fig. 2, the XANES spectrum for niobic acid is also shown. The total feature of the spectrum is almost identical with those for 19 wt.-% $\text{NbO}_x/\text{Al}_2\text{O}_3$. This strongly indicates that polynuclear Nb species on alumina has the similar structure like niobic acid and it is the dominant species on alumina. This is consistent with the Raman result [5]. However, it is intriguing that the spectrum of niobium pentoxide (TT- Nb_2O_5) has a different line shape from that of dehydrated 19 wt.-% $\text{NbO}_x/\text{Al}_2\text{O}_3$. The calcination of niobic acid at 573–773 K brings about the phase transition to TT- Nb_2O_5 [11] and this was confirmed by Raman spectroscopy [14]. Although 19 wt.-% $\text{NbO}_x/\text{Al}_2\text{O}_3$ was evacuated at 673 K for 2 h and this procedure is sufficient to transform niobic acid to TT- Nb_2O_5 , the spectral feature for niobium pentoxide was missing in the spectrum of dehydrated 19 wt.-% $\text{NbO}_x/\text{Al}_2\text{O}_3$. TT- Nb_2O_5 would be the minor species, if any. Niobic acid-like species is stable on alumina surface.

The characteristic feature of XANES spectra of $\text{NbO}_x/\text{Al}_2\text{O}_3$ at low Nb_2O_5 loading is a well-resolved two maxima beyond the edge. In the case of the XANES spectra of $\text{NbO}_x/\text{SiO}_2$ [3,8], these two maxima are not clearly split. This fact would represent the difference in the structure of NbO_4 on alumina and silica as found in the case of vanadium oxide tetrahedra

[3]; an NbO_4 tetrahedron on alumina possesses two Nb=O bonds and a NbO_4 tetrahedron on silica has one Nb=O bond. At high level of loading, the XANES spectrum of alumina-supported sample also exhibits well-resolved two maxima and is similar to that of niobic acid whilst the spectrum of silica-supported sample exhibits poor-resolved two maxima and becomes similar to that of Nb_2O_5 [10].

3.3. Nb K-edge EXAFS

3.3.1. 19 wt.-% $\text{NbO}_x/\text{Al}_2\text{O}_3$

Fig. 3 shows the Fourier transformed (FT) spectra of k^3 -weighted EXAFS of 19 wt.-% $\text{NbO}_x/\text{Al}_2\text{O}_3$ in the dehydrated and the hydrated states together with the spectra of niobic acid and niobium pentoxide. As expected from the results of the XANES analysis, the spectra of 19 wt.-% $\text{NbO}_x/\text{Al}_2\text{O}_3$ resemble that of niobic acid as a whole. The positions of the principal peaks are the same for each spectrum, suggesting that the EXAFS signal for each sample comprises of the same kinds of sine wave components. The EXAFS spectrum has a very complex structure so that the FT spectrum may not correctly represent the radial distribution around niobium ions. However, the important feature of the FT spectra is the following:

(1) The peaks found in the region 0.6–2 Å for the dehydrated sample are sharper and higher than those for the hydrated sample and niobic acid. Since the peaks in this region are due to backscattering by the nearest oxygen atoms, uniformity of NbO_x is high in the dehydrated sample.

(2) The peaks in the region 2.8–4 Å found in all the spectra are mainly due to the backscattering by neighboring Nb ions. The line shape of the peaks for both the dehydrated and hydrated 19 wt.-% $\text{NbO}_x/\text{Al}_2\text{O}_3$ samples are similar to niobic acid but the height is only 65% of that for niobic acid, indicating that the size of niobic acid-like species on alumina is very small. Raman shows that Nb_6O_{19} clusters exists on hydrated 19 wt.-% $\text{NbO}_x/\text{Al}_2\text{O}_3$.

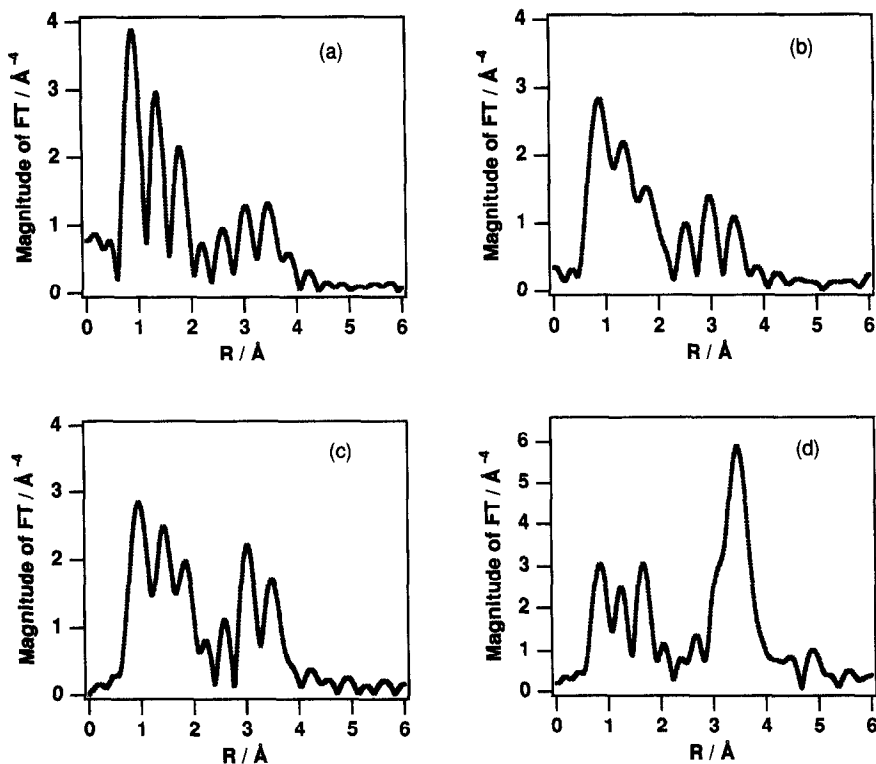


Fig. 3. Fourier transforms of Nb K-edge EXAFS spectra of (a) dehydrated 19 wt.-% $\text{NbO}_x/\text{Al}_2\text{O}_3$, (b) hydrated 19 wt.-% $\text{NbO}_x/\text{Al}_2\text{O}_3$, (c) niobic acid and (d) niobium pentoxide.

(3) As concluded by XANES analysis, niobium pentoxide was not formed on alumina. This is consistent with Raman studies [5–7] which demonstrated that crystalline Nb_2O_5 particles were only formed above monolayer coverage (> 19 wt.-% $\text{NbO}_x/\text{Al}_2\text{O}_3$).

3.3.2. 5 wt.-% $\text{NbO}_x/\text{Al}_2\text{O}_3$

FT spectra of k^3 -weighted EXAFS of 5 wt.-% $\text{NbO}_x/\text{Al}_2\text{O}_3$ in dehydrated and hydrated states are shown in Fig. 4. The sharp single peak centered at 1.3 Å is clearly visible, due to the backscattering by the neighboring oxygen atoms.

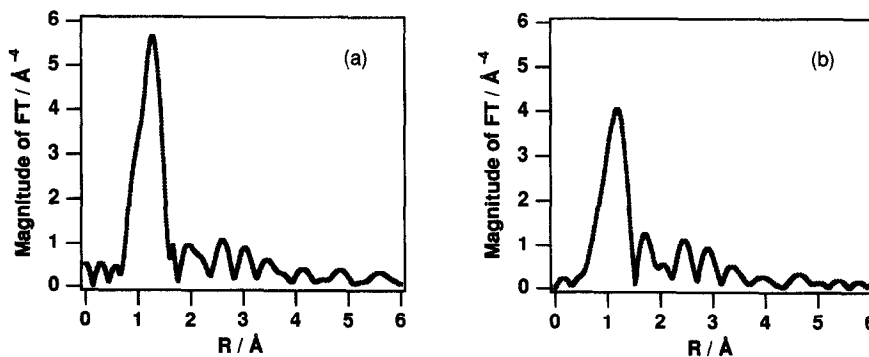


Fig. 4. Fourier transforms of Nb K-edge EXAFS spectra of (a) dehydrated 5 wt.-% $\text{NbO}_x/\text{Al}_2\text{O}_3$ and (b) hydrated 5 wt.-% $\text{NbO}_x/\text{Al}_2\text{O}_3$.

The variance of Nb–O bondlengths in NbO_x species is presumably small in comparison with that of 19 wt.-% $\text{NbO}_x/\text{Al}_2\text{O}_3$. The peakheight becomes smaller by adsorption of water. Taking the results of TPD and XANES analysis into account, the water adsorption onto niobium ions may increase the variance of Nb–O bondlength, which have an effect upon the enlargement of the Debye–Waller factor. The curve fitting analysis was performed with the empirical parameters [8] for Nb–O shells. The EXAFS oscillation for the Nb–O peaks was fitted with two sine waves for both the dehydrated and hydrated samples. The result is shown in Table 1. The niobate on alumina in dehydrated state is possibly a NbO_4 consisting of two terminal Nb=O bonds and two bridging Nb–O bonds. One water molecule is adsorbed onto the niobate resulting in the formation of a NbO_5 . In Fig. 4, small but unnegligible two peaks are seen in the region 2.3–3.3 Å for the both spectra. The spectra in these region were inversely transformed and the EXAFS oscillations were analyzed. Fig. 5 shows the inversely transformed spectrum for the dehydrated sample and the best fits performed with Nb–Nb and Nb–Al parameters. The trials using two sets of a Nb–Nb parameter did not give a satisfactory results. The results are given in Table 1. The adjacent Nb atom is evidently present and this strongly suggests that

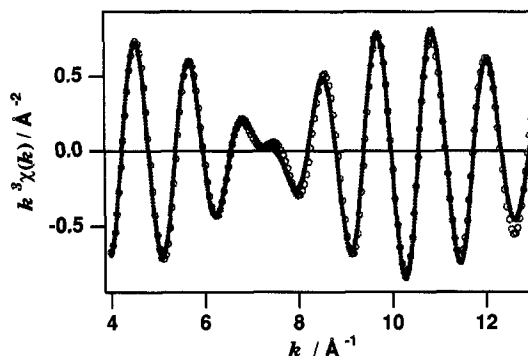


Fig. 5. The inversely transformed spectrum (solid curve) and the best fit (circle) for 5 wt.-% $\text{NbO}_x/\text{Al}_2\text{O}_3$.

a fair amount of niobium ions is present as a dimer species (Nb_2O_7). The two Nb ions should be bridged with at least one oxygen atom because the relative thermal displacement of niobium ions would disturb the backscattering of photoelectrons resulting in disappearance of Nb–Nb oscillation if they were not linked.

4. Discussion

As mentioned above, three kinds of surface niobates are stabilized; NbO_4 monomer, Nb_2O_7 dimer and niobic acid-like polymer on alumina surface. The monomer and the dimer possess two Nb=O bonds with a bondlength of 1.77 Å. The value is well consistent with those reported in the EXAFS works on silica-supported niobium oxide [8,9,15] and with the values predicted by ab initio molecular orbital calculations [4] and a Raman study [6].

In the sample of low Nb_2O_5 loading, the number of the adjacent of Nb ions were estimated to be 0.6, suggesting the presence of a mixture of a monomer and a dimer. The model structure of these species on an alumina surface are illustrated in Fig. 6. The dimer species is possibly stabilized on $\gamma\text{-Al}_2\text{O}_3$ (100) face on which linear Al arrays exist. Lippens and Steggerde postulated that the $\gamma\text{-Al}_2\text{O}_3$ (100) face is selectively exposed [16]. The curve-fitting result suggests that one water molecule is presumably coordinated to a niobium ion. In the

Table 1
Curve fitting results for 5 wt.-% $\text{NbO}_x/\text{Al}_2\text{O}_3$ samples in hydrated and dehydrated states

State	Scatterer	CN ^a	Distance (Å)	$\Delta\sigma^2$ (Å ²) ^b
Dehydrated	O	1.8	1.77	-0.0010
	O	2.2	1.87	0.0042
	Nb	0.7	3.02	0.0026
	Al	1.4	3.27	0.0074
Hydrated	O	2.3	1.82	0.0032
	O	3.2	1.92	0.0052
	Nb	0.6	2.95	0.0016
	Nb	0.8	3.15	0.0083

^a Coordination number.

^b Relative Debye–Waller factor.

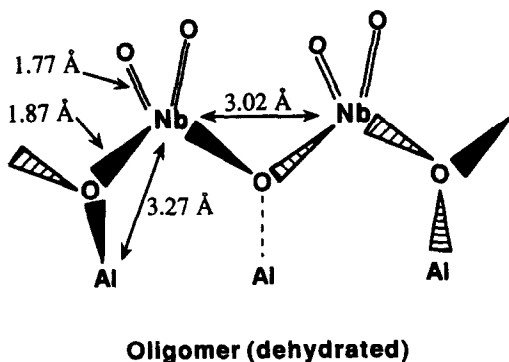
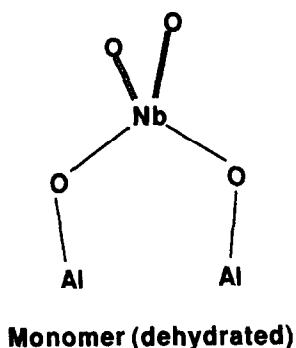


Fig. 6. Model structures of surface niobates on alumina.

case of $\text{NbO}_x/\text{SiO}_2$, an orthoniobate, NbO_4 possessing one $\text{Nb}=\text{O}$ bond or an oligomer consisting of NbO_4 orthoniobate unit are postulated [8]. The difference of these structures have been predicted by molecular orbital calculation [4]. Principally, the species of low coverage surface of silica and alumina are realized both for niobium and vanadium. The water adsorption on VO_x/SiO_2 is strong enough to change the V–V array on the surface [1] whereas Nb–Nb array is not much disturbed by water adsorption [8]. $\text{NbO}_x/\text{SiO}_2$ has been found to work as a photocatalyst suspended in ethanol [17] but VO_x/SiO_2 was hardly a stable catalyst because vanadium ions are leached out of the silica surface in ethanol. The disturbance by OH groups is serious for VO_x/SiO_2 .

In the sample of high Nb_2O_5 loading, the main surface species is niobic acid-like compound, which may be identical with hexaniobate

on alumina postulated in a Raman study [5]. The TPD profile of the $\text{NbO}_x/\text{Al}_2\text{O}_3$ was completely different from that of alumina may reveal that all the water adsorption sites on alumina surface are disturbed by the presence of niobates. This suggests that niobate compounds cover the alumina surface, i.e., niobic acid compounds are spread over alumina surface two-dimensionally [5].

Although the heat treatment of niobic acid brings about the phase transition to form niobium pentoxide, the niobic acid-like compound on alumina is stable against 773 K calcination. The $\text{NbO}_x/\text{Al}_2\text{O}_3$ is expected to be a stable solid acid. Oppositely, high loading of Nb_2O_5 brings about the formation of Nb_2O_5 microcrystal [10,18]. The difference might arise from the surface charge of the metal oxide surface [19].

Acknowledgements

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