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Control of the structure of niobium oxide species on silica by the equilibrium adsorption method

Hisao Yoshida [1], Tsunehiro Tanaka, Tomoko Yoshida, Takuzo Funabiki, Satohiro Yoshida *

Department of Molecular Engineering, Kyoto University, Kyoto 606-01, Japan

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Abstract

The loading amount and dispersion of tetrahedral species of niobium oxide in the NbO_x/SiO_2 catalysts could be controlled by adjusting the niobium and ammonia concentrations of impregnating oxalic acid solutions in the preparation by the equilibrium adsorption method. The structures in the solution and the adsorption state of the niobium oxalate complexes were the most important to control the structures of niobium oxide species on the silica surface. The addition of ammonia to the preparation solution affected not only the pH of the solution but also the states of the liquid–solid interface. The former influences the structure and adsorption equilibrium of niobium oxalate complex, while the latter changes the state of adsorption.

Keywords: Niobium oxide; Silica

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1. Introduction

Supported metal oxide often shows different catalytic activity from its bulk oxide, in this case niobium oxide. Therefore, recently, many studies on the nature of supported niobium species have been done.

Our previous studies have shown that niobium oxides supported on silica catalyze the photooxidation of propene to produce propanal or propene oxide and the selectivity is influenced by the local structure of niobium oxide species [1–3]. In this system, propene oxide was selectively produced over the highly dispersed monomeric NbO_4 species prepared by the equilibrium adsorption method, while propanal was formed over the oligomeric NbO_4 species. Polymeric NbO_6 octahedra directly produced ethanal, whereas oligomeric NbO_4 indirectly produced it via a propene oxide intermediate. This example makes it clear that the control of the local structure of niobium species is important and it is a key technique to obtain the desired performance of supported catalysts. From this view point, many investigations have been done to control the surface species by selecting suitable support materials (PVG [4], silica, alumina, magnesia, titania and zirconia [5–8]), niobium precursors (niobium oxalate, niobium ethoxide and niobium complexes with hydrocarbon ligands [9–15]) and preparation methods [16–19]. Among them, the equilibrium adsorption of

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* Corresponding author.

[1] Present address: Department of Applied Chemistry, School of Engineering, Nagoya University, Nagoya 464-01, Japan.

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metal complexes in aqueous solution is a simple and possible procedure for preparation of uniform species dispersed on supports [3,20]. Local structure and/or dispersion of metal oxide species prepared in this method was often controlled by the pH of solution. In the case of vanadium oxide catalysts supported on silica [20], the dispersion of vanadium oxide species on silica depended on the pH of the impregnating solution; some aggregates of octahedral species are formed from a low pH (3.3) solution, while tetrahedral species are dominant in the preparation from solutions of pH higher than 6.6, since, the structure of vanadate species in a solution were varied with the pH. In the case of the niobium oxalate solution, the niobium complexes were varied with the pH: monomer oxalate complexes existed in a low pH solution and a dimer complex existed in a high pH solution [21]. The catalytic activity of niobium oxide on silica was affected by the pH of the impregnating solution [3]. Therefore, it has been concluded that there were some types of local structure showing specific activity. There remain the following questions. Is there a correlation between the structure of the complexes in the impregnation solution and the structure of active species in the prepared catalysts and what is the important factor controlling the dispersion and local structure in this method?

In this study, we focus our attention on the structures of niobium species formed during the preparation procedure by the equilibrium adsorption method under several conditions to clarify the key factors controlling the structures of the niobium oxide species supported on silica. We measured the X-ray absorption fine structure (XAFS) for the structural analysis of niobium species in preparation [22].

2. Experimental

NbO_x/SiO_2 samples were prepared by the equilibrium adsorption method as follows. Niobic acid (CBMM) was dissolved in a 0.5 M oxalic acid solution ranging in niobium concentration from 8.4 to 134.4 mM. The pH of the solutions at this stage were ca. 0.8. The pH was controlled ranging in pH from 1 to 5 by addition of aqueous ammonia. A sample solution of the pH 1 was readjusted to pH 0.8 by addition of oxalic acid (referred to as '0.8 * '). Silica (1 g; BET surface area: 568 m^2 g^{-1}) was impregnated with the solutions (50 cm^3) in a stoppered flask and magnetically stirred for 24 h at room temperature, followed by filtration with suction. The silica adsorbing Nb ions was dried at 343 K for 24 h and calcined in a dry air stream at 773 K for 5 h. These were evacuated at 673 K for 2 h and sealed in polyethylene packs for the measurements of X-ray absorption spectra. Silica was prepared by a sol-gel method as described elsewhere [23]. Niobium oxalate complex in solid state as a reference sample was donated by Prof. Wachs. Niobium pentoxide was prepared from niobic acid by calcination at 773 K for 5 h.

The loading amount of niobium oxide as Nb_2O_5 in the samples were determined by X-ray fluorescence intensities. Nb K-edge XAFS were recorded at room temperature at BL-6B, 7C, 10B stations in KEK-PF with a Si(311) or Si(111) two crystal monochromator (ring energy 2.5–3.0 GeV and stored current 140–370 mA). XAFS measurements were carried out to the following samples: (1) niobium oxalic acid solutions, (2) niobium complexes adsorbed on the silica, which were filtered after achieving the adsorption equilibrium followed by drying at 343 K, (3) calcined niobium oxides on silica under ambient condition, (4) evacuated ones in situ and (5) reference compounds such as niobium pentoxide, niobium oxalate and so on. Low loading samples were measured in the fluorescence mode and others including reference samples were measured in the transmission mode.

XANES (X-ray absorption near edge structure) analyses were carried out as described elsewhere [2]. The normalized XANES spectrum was deconvoluted to a set of one pre-edge

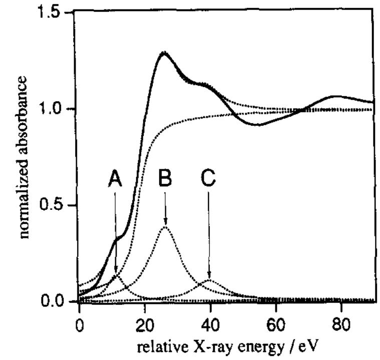


Fig. 1. The normalized Nb K-edge XANES and its deconvoluted spectra of niobium oxalate in solid state. A, B, C: see text.

peak (A) and two post-edge peaks (B, C) with a continuum absorption curve (Fig. 1). The peaks at higher energy than the three peaks were not considerate because the assignment is very difficult due to the influence by multiple scattering of photo-electrons.

Curve-fitting analysis of Fourier-filtered EXAFS was performed by using empirical parameters extracted from EXAFS of reference compounds. As there were no suitable niobium compounds to extract the parameters for Nb–O, Nb–Nb and Nb–C (of carboxyl group) shells, we adopted the parameters for a Mo–O shell extracted from K_2MoO_4, for a Zr–Zr shell from ZrC, for a Rh–C (of carboxyl group) shell from a Rh(I)Vasca complex [24] to fit the Nb–O, Nb–Nb and Nb–C (carbonyl) shells, respectively. As there were also no suitable compounds for the Nb–Si shell, the phase shift function for a Mo–Mg shell was calculated from Mo–O, Ni–O and Ni–Mg shells in K_2MoO_4, NiO and Ni–Mg–O solid solution [25], to fit the Nb–Si shell. The amplitude function for a Ni–Mg shell extracted from a Ni–Mg–O solid solution [25] was adopted to fit the function for the Nb–Si shell.

3. Results and discussion

3.1. Loading amount of niobium oxide on silica

When niobium acid was dissolved in an oxalic acid aqueous solution, it would exist as a niobium oxalate complex in the solution [21]. It precipitated in a solution of low niobium concentration at a pH above 5, while precipitation was observed in a lower pH value for a solution of high niobium concentration. The preparation of the samples was carried out under such conditions that the precipitation did not occur.

The adsorption equilibrium would control the loading amount; we can obtain the information of the equilibrium state from the loading amount of niobium oxide in the prepared samples. Fig. 2 shows a relationship between the loading amount of niobium oxide supported on silica and the niobium concentration of the prepared oxalic acid solution. The plots were divided into two groups: (a) pH 0.8 to 4 and (b) of pH 5. Both groups showed a good relationship in which the loading amount was proportional to the concentration of niobium, although only one point was out of line. This indicates that the loading amount could be controlled by the niobium concentrations at each pH. Fig. 3 shows the effect of pH of the impregnating solution on the loading amount. It was clear that the loading amounts were constant in the range of pH 0.8 to 4 for the solution of low niobium concentrations although the constant range was reduced in the case of high niobium concentration. The loading amounts in this range corresponded to 3%–4% of the dissolved niobium ions. In the case of the

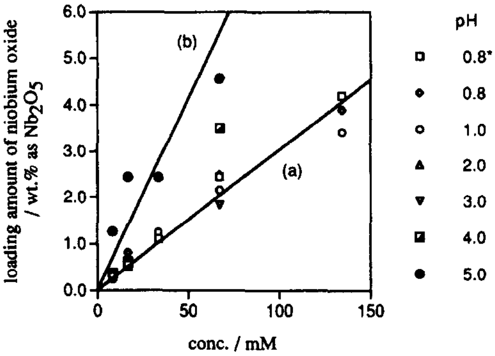


Fig. 2. Loading amount of niobium oxide as Nb_2O_5 vs. concentration of niobium ion in the impregnating solutions. The points along line (a) are those for samples prepared with pH 0.8–4 solutions and the points along line (b) are those with pH 5 solutions.

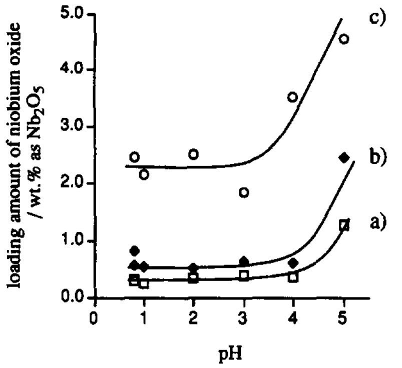


Fig. 3. Effect of pH and niobium concentration of the impregnating solutions on the loading amount of niobium oxides on silica. The niobium concentration of the solutions were (a) 8.4, (b) 16.8 and (c) 67.2 mM, respectively.

solution of pH 5, the adsorbed amount was 8%–13%. This difference of the loading amount indicates that the chemistry of adsorption depends on the pH. It is expected that the structures of niobium complexes or the surface condition of silica were affected by the pH of the solutions. It has been reported that a monomeric niobium oxalate complex changed to a dimeric niobium oxalate complex before precipitation [21]. Therefore, the niobium complex would be a dimeric one in the solution of pH 5, and it would be a monomeric one in the solution of pH 1–4 and the adsorption equilibrium of these complexes could be different from each other.

Assuming that all of the species in the solution of pH 5 exist as the dimer complex, the concentration of niobium complex should be a half in comparison with the case of all species being the monomer under the constant niobium concentration as shown in Eq. (1).

$$C_1 = 2C_2 \quad (1)$$

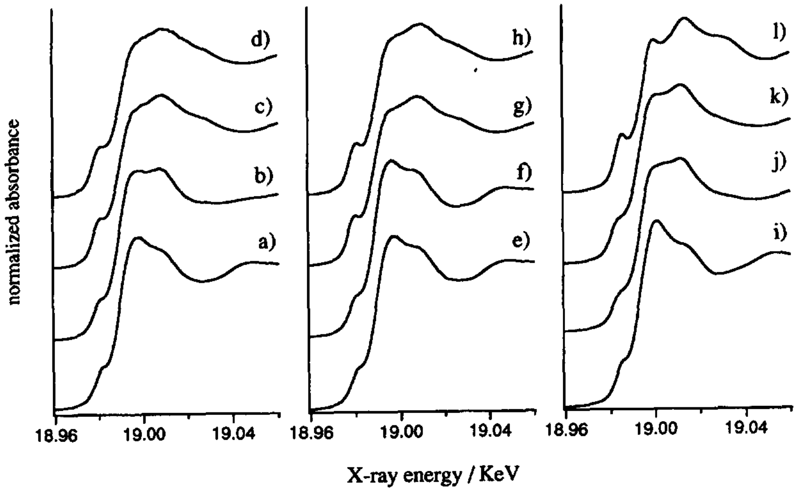
where, C_1: concentration of the monomer complex in the solution, C_2: that of the dimer complex.

The concentrations of adsorbed complexes and loading amount of niobium oxide were as follows:

$$C_{a1} = K_1C_1,\ C_{a2} = K_2C_2 \quad (2)$$

$$A_1 = aC_{a1},\ A_2 = 2aC_{a2} \quad (3)$$

where, C_{a1}: concentration of the adsorbed monomer complex, C_{a2}: that of the dimer complex, K_1: equilibrium constant of the monomer complex, K_2: that of the dimer complex, A_1:



(A) pH 0.8 (B) pH 4 (C) reference compounds

Fig. 4. Nb K-edge XANES spectra of samples during the preparation from the solution of pH 0.8 (A), 4 (B) and the spectra of reference compounds (C). (a), (e) Solution samples; (b), (f) dried samples; (c), (g) calcined samples (ambient); (d), (h) calcined sample (evacuated); (i) niobium oxalate in solid state; (j) niobium pentoxide; (k) niobic acid and (l) $YbNbO_4$. The niobium concentration of the impregnating solutions in (A) and (B) was 16.8 mM.

loading amount of niobium oxide prepared from the monomer, A_2: loading amount of niobium oxide prepared from the dimer, a: constant for the conversion of the concentration to the loading amount. Therefore,

$$A_2 = (K_2/K_1)A_1 \tag{4}$$

If the equilibrium constant of monomer complex K_2 is equal to K_1, the loading amount A_2 should be equal to A_1, as well. However, the slope of the line (b) of the solution of pH 5 in Fig. 2 was more than two times greater than that of line (a), indicating that the value of K_2 was more than two times greater than that of K_1. The equilibrium in the solution of pH 5 was obviously shifted to the adsorption side in comparison with the equilibrium of the solution of pH 0.8–4.

3.2. Niobium complexes in the solution

The structure of the niobium complex in the oxalic acid solution was studied by X-ray absorption spectroscopy. XANES spectra of niobium complexes in the solution and niobium oxalate in solid state are shown in Fig. 4a, Fig. 4e and Fig. 4i. The line shape of each spectrum resembles each other as a whole: broad and small pre-edge and two peaks in the post-edge, indicating that the local structures of niobium complexes in the oxalic acid solution resemble that of the octahedral niobium oxalate complex $[NbO(C_2O_4)_2H_2O]^-$ in solid state [21].

To discuss in detail, a deconvolution analysis was carried out [2,22], as shown in Fig. 1 as an example. The areas and positions of the three peaks are given in Table 1. Those of the sample in the solution of pH 0.8 were similar to those of the solid niobium oxalate, although the area of peak A of solid niobium oxalate was slightly larger than that of the sample in the solution. The agreement of these values indicates that the complex at pH 0.8 has the same structure as the niobium oxalate complex $[NbO(C_2O_4)_2H_2O]^-$.

The peak positions of the pre-edge peak (A) and the post-edge peak (B or C) for the species in the solutions were also the same regardless of pH values, suggesting that the excited electrons from the 1s orbital in niobium were captured by the same empty bound states; the bonds of ligands–niobium ions in each pH solution are the same. On the other hand, the peak areas varies with pH in the range from 0.8 to 5. With an increase in the pH, the peak area of B decreased and that of C increased; the ratio of these areas (B/C) was reduced, indicating that the local structure was slightly changed by the pH. In the study of XANES of vanadium compounds, the B peak was concluded to be a characteristic peak of octahedra [2]. The reduction of the B peak area suggested that the octahedral symmetry was a little distorted. While the area and position of peak A was constant, therefore, the coordination structure around a niobium atom in the solution of pH 5 is described to be distorted octahedral.

The solution of pH 0.8* contained more oxalic acid than the solution of pH 1 and more oxalic acid and ammonia than the solution of pH 0.8. The A peak area of the complex in the solution of pH 0.8* was larger than that in the solution of pH 1 and 0.8; the B peak area was smaller, suggesting that the symmetry of complex was distorted. This would be caused by an increase in the concentration of oxalic anions which were further coordinated to the niobium atom.

Table 1
Areas and relative peak positions of pre-edge in Nb K-edge XANES spectra of niobium complexes in aqueous solution (67.2 mM) and niobium oxalate(solid)

pH	Peak position /eV [a]			Area /eV			
	A[b]	B	C	A	B	C	B/C
0.8	−7.0	7.8	18.5	1.0	6.8	1.9	3.6
1.0	−6.8	7.9	19.0	0.94	6.4	2.5	2.6
3.0	−6.9	7.5	18.5	0.94	6.5	2.5	2.6
5.0	−6.8	7.7	18.9	0.97	5.2	2.7	1.9
0.8*	−6.9	7.9	19.1	1.3	6.0	2.2	2.7
Oxalate	−6.9	8.2	20.2	1.4	6.7	1.9	3.5

[a] Relative energy to the ionization threshold determined as the position of the inflection point of the continuum curve.
[b] Consult Fig. 1 for the peak assignment.

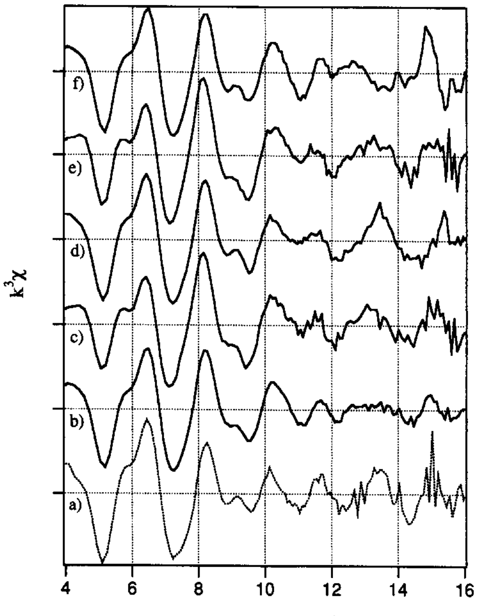


Fig. 5. The k^3 weighted EXAFS spectra of (a) the niobium oxalate in solid state and (b)–(f) the solution samples (67.2 mM) of various pH (b) 0.8, (c) 0.8*, (d) 1, (e) 3 and (f) 5.

EXAFS spectra (Fig. 5) also showed the structural variation of the niobium oxalate complexes. In the higher wavenumber region, 10–16 Å^{-1}, the oscillation was drastically varied with the pH of solution. This region of EXAFS oscillation was affected by the atoms which have a maximum of back scattering amplitude in this region, usually heavy atoms such as niobium atom in this case, and/or affected by 'focusing effects' [26–28], which was caused by a collinear arrangement of three (and more) atoms including a target atom; a carboxyl group is typical and the oxalic anion also shows the effect.

The peaks at 2–4 Å in Fourier-transform of EXAFS (Fig. 6) indicates the contribution from oxalate anions. The curve-fitting analysis of Fourier-filtered EXAFS revealed that the niobium complexes in the solution have five Nb–O bonds (2.11 Å) and one Nb=O bond (1.70 Å). A fairly strong scattering by the second (2.8, 3.2 Å) and third (3.8, 4.25 Å) neighboring oxygen and/or carbon was observed by the focusing effect, indicating that oxalate ions are coordinated to the niobium atom. Two coordination distances observed at each second and third shells would mean that each oxalate anion binds to the niobium atom asymmetrically.

Jehng and Wachs had studied niobium complexes in the solutions by Raman spectroscopy [21]. On the basis of their conclusion and our results, the major complexes in the solution is suggested as follows (Scheme 1): $[NbO(C_2O_4)_2H_2O]^-$ in the range of pH 0.8–4, a dimeric complex such as $[Nb_2O_4(C_2O_4)_2(H_2O)_2]^{2-}$ at pH 5 before precipitation, and $[NbO(C_2O_4)_3]^{3-}$ at pH 0.8*. The feature of EXAFS at pH 1 (Fig. 5d) was slightly different from other samples. This may

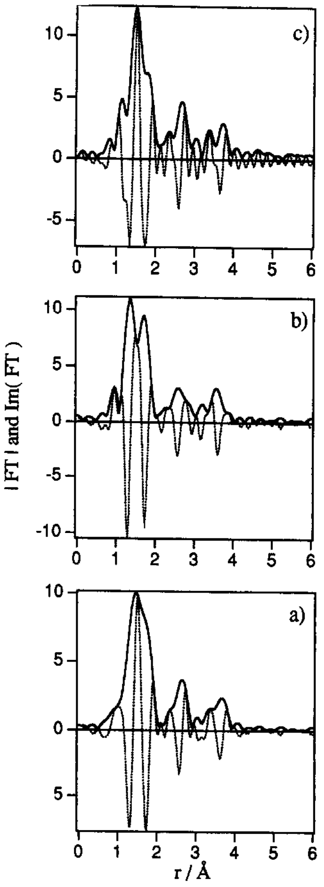
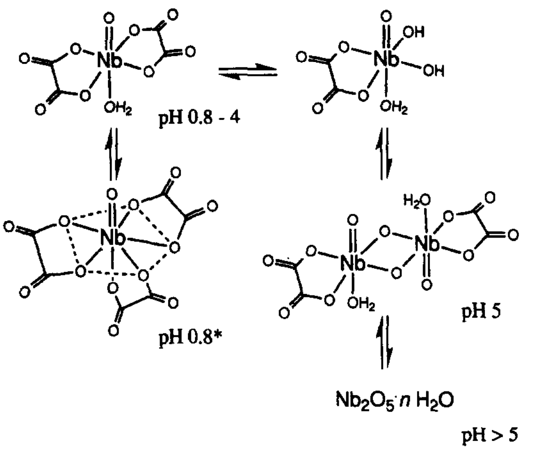


Fig. 6. The absolute of FT (|FT|) and the imaginary part of FT (Im(FT)) of the EXAFS of the solution samples of (a) pH 0.8, (b) pH 1 and (c) pH 5. The niobium concentration was 67.2 mM.



Scheme 1. Proposed structures of niobium complexes in oxalic acid solutions.

result from the existence of other complexes such as $[NbO(C_2O_4)(OH)_2H_2O]^-$ or $[NbO(C_2O_4)_2(OH)_2]^{3-}$ as proposed by Jehng and Wachs [21].

3.3. Dried samples (before calcination)

The adsorbed niobium species on silica which were obtained by filtration followed by drying at 343 K are discussed in this section. XANES spectra of adsorbed niobium species on silica clearly showed the structural difference caused by different pH of impregnating solutions (Fig. 4b and Fig. 4f). The adsorbed species prepared from the solution of pH 4 exhibited the same XANES spectrum (Fig. 4f) as that of the complex in the solution (Fig. 4e). The samples prepared from the solutions of pH 1–4 and 0.8 * also exhibited the same spectra. In these cases, ammonia existed in the solutions. On the other hand, the spectrum of adsorbed species prepared from the pH 0.8 solution (Fig. 4b), which was free from ammonia, was different from that in the solution, or rather, resembled that of niobium pentoxide (Fig. 4j) or niobic acid (Fig. 4k).

The difference was clearly demonstrated in the position and area of pre-edge listed in Table 2. Although the peak position and peak area did not change by adsorption on silica in the case of the pH 0.8 * and 4, those values changed in the case of pH 0.8. These results suggest that the complex in the pH 0.8 solution, which did not contain ammonia, reacted with the silica surface and the coordination geometry around the niobium atom was changed from that in the solution. On the contrary, the coordination states of the complexes in the solution containing ammonia did not change in contact with the silica surface.

The EXAFS oscillations (Fig. 7) of the dried samples became unclear above the 10 Å region. This could be caused by the interactions of complexes with silica surface. The structural parameters obtained by the curve-fitting analyses of Fourier-filtered EXAFS of the adsorbed species were the same as those of the complexes in the solution for all samples, except the sample of pH 0.8. On the other hand, the adsorbed species from the pH 0.8 solution exhibited a weak EXAFS oscillation and the results of curve-fitting analysis showed that the species had four Nb–O (2.07 Å), one Nb=O (1.71 Å) and another Nb–O bond (1.86 Å) whose distance was similar to a Nb–O (1.91 Å) bond found for the niobium oxide dispersed on silica and also the contribution of the second and third oxygen or carbon was observed. This suggests that the niobium oxalate complex in the solution of pH 0.8 reacted with the silica surface and

Table 2
Areas and relative peak positions of pre-edge peaks in Nb K-edge XANES of samples

Sample [a]	Peak position /eV [b]			Area /eV		
	pH 0.8	0.8 *	4	pH 0.8	0.8 *	4
Solution	−6.7	−6.7	−6.6	1.04	1.11	1.04
Dried	−7.2	−6.7	−6.7	1.12	1.12	1.04
Calcined (ambient)	−7.4		−7.4	2.21		2.15
Calcined (evac.)	−8.0		−7.9	2.83		2.51
Nb_2O_5		−7.3			1.88	
Oxalate		−7.1			1.43	

[a] The concentration of the impregnating niobium solution was 16.8 mM.

[b] Relative energy to the ionization threshold determined as the position of the inflection point of the continuum curve.

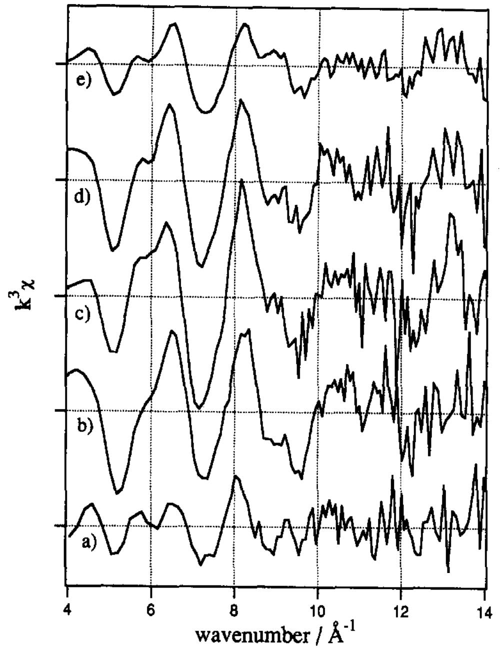


Fig. 7. The EXAFS spectra of the dried samples prepared from the solutions of pH (a) 0.8, (b) 0.8*, (c) 1, (d) 4 and (e) 5. The niobium concentration of the impregnating solution was 16.8 mM.

formed a Nb–O–Si bond, releasing the oxalate ligand(s) in part.

The effect of ammonia on the adsorption of complexes could result from the modification of the silica surface. As the silica surface is weekly acidic, ammonia is adsorbed on the surface preferentially to prevent direct fixation of the niobium complexes on the silica surface. Eventually, the complexes are in a physical adsorption state on the surface. While, on the surface free from ammonia, the complex can be fixed by reacting with the surface Si–OHs.

The dimer complex adsorbed from the solution of pH 5 exhibited a little smaller amplitude in EXAFS (Fig. 7e), although the feature of EXAFS oscillation is similar to that of the complex in the solution. The smaller amplitude would indicate that the adsorbed state of the dimer complex was not uniform because the dimer would have two or more coordination sites.

3.4. Calcined niobium oxide on silica

The adsorbed niobium species on silica were converted to niobium oxide species by calcination at 773 K. The obtained NbO_x/SiO_2 catalysts were evacuated at 673 K and the XAFS spectra were recorded. XANES spectra of the evacuated samples are shown in Fig. 8 (also Fig. 4d and Fig. 4h). Regardless of the loading amount of niobium oxide and pH of the impregnating solution, the shapes of the spectra are identical. The pre-edge peak is clearly observed in each spectra of the NbO_x/SiO_2 samples. The positions are lower and the areas are larger than those of the octahedra (Table 2), indicating that the niobium oxides on silica surface prepared in this method were tetrahedral species [1,2,29]. The pre-edge peak of the spectra of the 4.6 wt.-% NbO_x/SiO_2 catalysts prepared in the equilibrium adsorption method was obviously clearer than that of the 4.6 wt.-% NbO_x/SiO_2

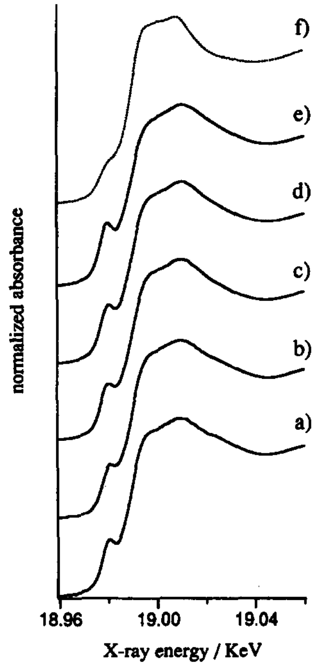


Fig. 8. Nb K-edge XANES spectra of the evacuated niobium oxide on silica (a)–(e) and niobium pentoxide (f). The loading amounts (wt.-% as Nb_2O_5) and the pH of impregnating solutions for the samples are (a) 0.29, 0.8; (b) 0.37, 4; (c) 3.9, 0.8; (d) 4.2, 0.8*; and (e) 4.6, 5, respectively.

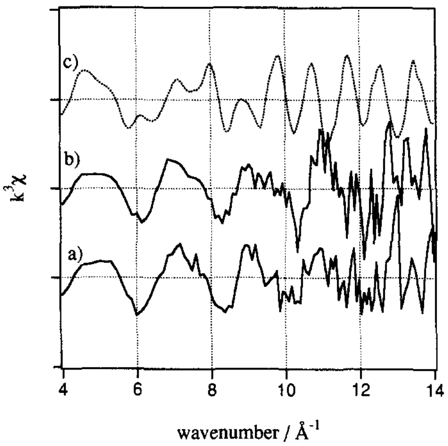


Fig. 9. The k^3 weighted EXAFS spectra of the evacuated niobium oxide on silica prepared from the solution (16.8 mM) of (a) pH 0.8, (b) pH 4 and that of (c) niobium pentoxide.

catalysts prepared in a conventional evaporation to dryness method [1]. This shows the advantage of the equilibrium adsorption method for the preparation of silica supported niobium oxide catalysts comprised of tetrahedral niobium oxide species even in the high loading, such as 4.6 wt.-%.

EXAFS spectra of the evacuated NbO_x/SiO_2 samples are shown in Fig. 9. The spectra (Fig. 9a and Fig. 9b) are also clearly different from those of niobium pentoxide. Asakura and Iwasawa [18] proposed that the shoulder at around 5.5 Å^{-1} resulted from the scattering by the neighboring Si atom. In our result, the same shoulder was also observed, indicating that niobium oxide species were fixed on the silica surface and did not aggregated much.

In the Fourier-transforms of the EXAFS (Fig. 10), the twin peaks observed at 2.9–3.4 Å can be assigned to the secondary neighboring Si and/or Nb, and this is confirmed by the curve-fitting analysis of Fourier-filtered EXAFS. The peaks for the sample prepared from pH 0.8 solution were smaller than that from pH 4 solution. The structural parameters were evaluated by the curve-fitting analysis and the results are given in Table 3. The amplitude and phase shift functions are empirical ones estimated by extraction of a combination of reference compounds, as described in the experimental section. Therefore, the absolute values of the results are not highly reliable, especially in the numbers of coordination at secondary neighboring atoms. Thus, we discuss the results qualitatively.

The parameters associated with the first neighboring oxygen atoms and of the secondary neighboring silicon atom were not affected by the pH of impregnating solutions. The number of the coordination of the Nb–Nb shell varied apparently with the pH; the lowest coordination of the Nb–Nb shell was exhibited by the sample prepared from the pH 0.8 solution. It indicates that the niobium oxide species on the sample prepared from the pH 0.8 solution was the most highly dispersed. In this case, the niobium complex under the adsorption equilibrium is sup-

Table 3
Curve-fitting results of the evacuated niobium oxides on silica [a] and niobium pentoxide

pH	Nb–O			Nb=O			Nb–Si			Nb–Nb		
	N	*r*/Å	$\Delta\sigma^2$	*N*	*r*/Å	$\Delta\sigma^2$	*N*	*r*/Å	$\Delta\sigma^2$	*N*	*r*/Å	$\Delta\sigma^2$
0.8	2.4	1.93	−0.001	1.2	1.69	0.003	0.9	3.23	−0.005	0.2	3.35	−0.006
0.8*	3.0	1.90	0.003	0.9	1.64	0.001	0.9	3.24	−0.005	0.5	3.34	−0.001
1	2.6	1.91	0.001	1.0	1.67	0.001	1.0	3.26	−0.004	0.6	3.35	0.005
4	2.6	1.91	0.000	0.8	1.65	−0.003	0.9	3.24	−0.002	0.7	3.33	−0.002
5	2.8	1.89	0.002	1.1	1.66	−0.004	1.0	3.23	0.005	0.4	3.30	−0.003
Nb_2O_5	3.7	2.02	0.007	1.3	1.76	0.006				1.1	3.33	0.009
(X-ray) [b]	(4)	(2.06)		(1)	(1.78)					(1.6)	(3.32)	
										2.5	3.70	0.002
										(3)	(3.86)	

[a] The concentration of the impregnating niobium solution was 16.8 mM.
[b] Ref. [18].

posed to be fixed on the silica surface, as mentioned above. Since, the complex is fixed by a Nb–O–Si bond, the complex could not migrate easily on the surface by calcination in air. On the other hand, the complexes physically adsorbed from the ammoniacal solution could migrate easily and aggregate under calcination.

Although the present results did not clarify the state of aggregation, we could propose that niobium pentoxide was not produced and only the tetrahedral niobium oxide species were obtained on silica surface. We propose the local structure of the species fixed on the silica tetrahedral network, shown in Fig. 11.

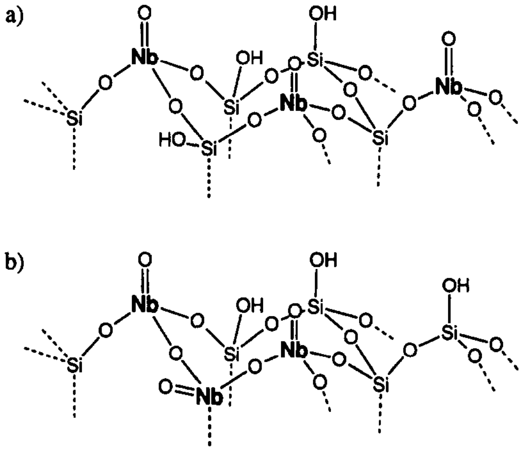


Fig. 11. Proposed models for the surface structure of (a) niobium monomer species and (b) niobium oligomer species attached on silica.

The calcined samples before evacuation could be regarded as hydrated samples in ambient condition. The samples exhibited the same XAFS spectra regardless of the condition of the impregnating solutions. As shown in Table 2, the areas of the pre-edge peak of the samples were larger than that of the complexes in the solution and smaller than that of the following evacuated samples. The positions of the pre-edge were in a lower energy side than that of complexes in the solution and in a higher energy side than that of evacuated samples. The results indicate that the niobium oxide species has lower symmetry than the oxalate complexes and higher symmetry than the evacuated oxide species. Although the evacuated niobium oxide species were tetrahedral as described above, the species on the calcined samples under ambient condition would be a distorted octahedral, because of the adsorption of water molecules [2,30].

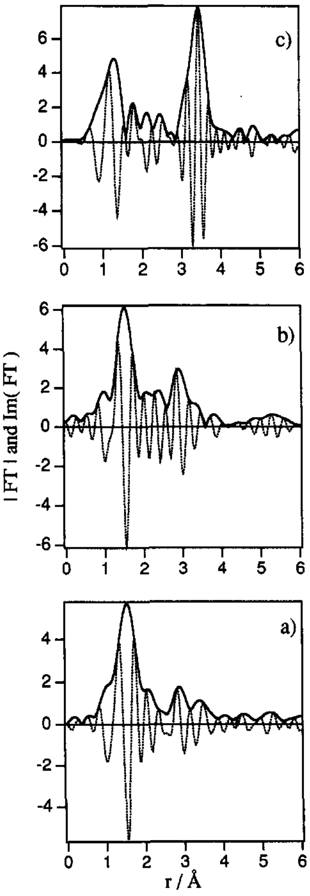


Fig. 10. The absolute of FT (|FT|) and the imaginary part of FT (Im(FT)) of the EXAFS of the evacuated niobium oxide on silica prepared from the solutions (16.8 mM) of (a) pH 0.8, (b) pH 4 and that of (c) niobium pentoxide.

4. Conclusion

The present study reveals that the dispersion of tetrahedral niobium oxide species supported on the silica surface can be controlled by changing the conditions of the equilibrium adsorption method as follows: (1) the loading amount of niobium oxide species on silica is proportionally controlled by adjusting the niobium concentration of the impregnating solution, (2) when the solution is adjusted at pH 5 by the addition of ammonia, the loading amount increases more than two times on keeping a highly dispersion, where the tetrahedra species exist as small oligomers without much aggregation, (3) the most dispersed monomeric tetrahedron of niobium oxide is obtained from the solution of pH 0.8 which does not contain ammonia, while a small oligomer comprised of the tetrahedral species on silica is prepared from the solution of pH 0.8–4 in the presence of ammonia.

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