

## Structures of Molybdenum Species in Silica-Supported Molybdenum Oxide and Alkali-Ion-Modified Silica-Supported Molybdenum Oxide

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Silica-supported molybdenum oxide ( $\text{MoO}_3/\text{SiO}_2$ ) and alkali-ion-modified  $\text{MoO}_3/\text{SiO}_2$  samples were characterized by Mo K-edge XAFS and Raman spectroscopies. The structure of the molybdenum species in  $\text{MoO}_3/\text{SiO}_2$  was confirmed to be monomeric and tetrahedral,  $(\text{O}=\text{Mo}=\text{O})\text{O}_2$ . In alkali-ion-modified  $\text{MoO}_3/\text{SiO}_2$ , the structure of the molybdenum species varied with the kinds and/or the amounts of added alkali ions. In  $\text{Na}^+$ -modified  $\text{MoO}_3/\text{SiO}_2$  with sodium ions of the molar ratio  $\text{Na}/\text{Mo} < 1.0$ , the molybdenum species were mainly  $\text{Na}_2\text{Mo}_2\text{O}_7$  besides  $(\text{O}=\text{Mo}=\text{O})\text{O}_2$  which was present in  $\text{MoO}_3/\text{SiO}_2$ , and the addition of sodium ions of molar ratio  $\text{Na}/\text{Mo} > 1.0$  caused the formation of  $\text{Na}_2\text{MoO}_4$  at the expense of  $\text{Na}_2\text{Mo}_2\text{O}_7$ . In the case of  $\text{K}^+$ - and  $\text{Rb}^+$ -modified  $\text{MoO}_3/\text{SiO}_2$ , the addition of alkali ions equimolar with the molybdenum atoms in the samples brought about the formation of  $\text{Mo}_2\text{O}_7$  species, and by the addition of alkali ions of molar ratio (alkali ion/ $\text{Mo}$ )  $> 1.0$ ,  $\text{MoO}_4$  species was formed on the silica support. In the molybdenum species in K-MS and Rb-MS with alkali ions of molar ratio (alkali ion/ $\text{Mo}$ )  $< 1.0$ , the proportion of an octahedral  $\text{MoO}_6$  unit to all the molybdenum species in the samples was higher than that in K-MS and Rb-MS with alkali ions of the molar ratio  $> 1.0$ .

### Introduction

Supported molybdenum oxide catalysts are excellent for the selective oxidation of hydrocarbons,<sup>1</sup> the oxidative dehydrogenation of alcohols,<sup>2</sup> and the metathesis of olefins.<sup>3</sup> The structure of the molybdenum species in supported molybdenum oxide catalysts is one of the factors controlling the catalytic performance and varies with the kinds of the support<sup>4</sup> and starting materials of supported molybdenum species,<sup>5</sup> preparation methods,<sup>5</sup> the loading amounts of molybdenum atom,<sup>6</sup> and so on. In the case of silica-supported molybdenum oxide ( $\text{MoO}_3/\text{SiO}_2$ ), crystalline  $\text{MoO}_3$  is liable to be formed on the silica support even at low loadings of molybdenum atoms, because the molybdenum species in  $\text{MoO}_3/\text{SiO}_2$  has weak interaction with the silica support, while in  $\text{MoO}_3/\text{TiO}_2$  and  $\text{MoO}_3/\text{Al}_2\text{O}_3$ , the formation of dispersed molybdenum species on the supports is preferable. Because the molybdenum species on the supports do not have a long-range structural ordering in general, the surface structure cannot be examined by X-ray diffraction. On the other hand, the characterization by X-ray absorption spectroscopy (XAFS) does not need a long-range structural ordering of the surface species in supported metal oxide catalysts and gives useful information about structural parameters such as coordination number, interatomic distance, and symmetry around the metal atom. In addition, Raman spectroscopy, which also does not require a long-range structural ordering of the surface species, is a very powerful technique for studying the surface structure of the supported catalysts. Raman spectroscopy allows the identification of the surface structure, composition, and relative quantity of the active species on the supported metal oxide catalysts. Recently, the surface structures of the supported metal oxide catalysts have been determined by using

the above spectroscopic methods, and the catalysis has become able to be clarified at a molecular level.

The catalytic performance of supported molybdenum oxide is also controlled by the addition of alkali ions, since the surface acidity can be considered as one of the main factors determining the catalytic properties. As is well-known, one of the distinct functions of alkali ions is their electron-donating ability leading to the enhancement of the basicity of the metal oxides, but either the exact nature or the role of alkali ions is still not well understood. The alkali ions act as both promoters and poisons. For example, the modification of bismuth- and molybdenum-containing systems by alkali ions improves the selectivity to partial oxidation products in the ammoxidation of olefins.<sup>7</sup> In the case of oxidation of methane by  $\text{N}_2\text{O}$  over silica-supported molybdenum oxide catalyst, the modification by sodium ion poisons the formation of formaldehyde at low loadings of molybdenum oxides, while the formation of formaldehyde is promoted by the addition of sodium ions at fairly high loadings of molybdenum oxides.<sup>8</sup>

Silica-supported molybdenum oxide exhibits photocatalytic activity under UV light irradiation and catalyzes the photooxidation of propane<sup>9</sup> and the photoassisted metathesis of propene.<sup>10</sup> We have investigated the effect of the addition of alkali ions to  $\text{MoO}_3/\text{SiO}_2$  on the photocatalysis.<sup>11</sup> In photooxidation of propane over alkali-ion-modified  $\text{MoO}_3/\text{SiO}_2$ , propanone was produced mainly, while over  $\text{MoO}_3/\text{SiO}_2$  a variety of products, such as propene, propanal, propanone, ethanal, and so on, were formed. In addition, alkali-ion-modified  $\text{MoO}_3/\text{SiO}_2$  converted propene to acraldehyde selectively under UV light irradiation, whereas selective oxidation of propene did not proceed over  $\text{MoO}_3/\text{SiO}_2$ , either. In photoassisted metathesis of propene, the addition of alkali ions to  $\text{MoO}_3/\text{SiO}_2$  caused a decrease in the activity. Photocatalytic performance of  $\text{MoO}_3/\text{SiO}_2$  is changed significantly by the addition of alkali ions. We expect that the

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addition of alkali ions to MoO<sub>3</sub>/SiO<sub>2</sub> brings about the structural change of the molybdenum species.

In the present study, we investigated the structure of the molybdenum species in MoO<sub>3</sub>/SiO<sub>2</sub> and alkali-ion-modified MoO<sub>3</sub>/SiO<sub>2</sub> under the dehydrated state by Mo K-edge XAFS (XANES and EXAFS) and Raman spectroscopies and described the structural change of the molybdenum species depending on the kinds of added alkali ions and the added amounts of alkali ions.

## Experimental Section

**Materials.** Tetraethyl orthosilicate (TEOS), ammonium heptamolybdate ((NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O), NaOH, KOH, and RbOH·H<sub>2</sub>O were commercially supplied.

**Preparation of Samples.** A silica support was prepared by the hydrolysis of the distilled TEOS and calcination at 773 K for 5 h in a dry air stream as described elsewhere.<sup>12</sup> Silica-supported molybdenum oxide (MS) was prepared by impregnating the silica with an aqueous solution of ammonium heptamolybdate ((NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O) at 353 K for 2 h and drying up the impregnated sample. The sample was dried at 363 K for 12 h and calcined in a dry air stream at 773 K for 5 h. The loading amount of molybdenum oxide was 4.0 wt % as MoO<sub>3</sub>. Alkali-ion-modified silica-supported molybdenum oxide samples (Na-MS, K-MS, and Rb-MS) were prepared by impregnating MS with aqueous solutions of NaOH, KOH, and RbOH·H<sub>2</sub>O, respectively, followed by calcination in a dry air stream at 773 K for 5 h, in the same manner as mentioned above. The molar ratio (alkali ion/Mo) is designated in parentheses following the sample name; for example, Na-MS with sodium ions equimolar with molybdenum atoms contained in sample is described as Na-MS(1.0).

**Pretreatment of the Samples.** The samples were pretreated by evacuation at 673 K for 1 h, treatment of gaseous oxygen (60 Torr) at 673 K for 2 h, and evacuation at 673 K for 10 min prior to spectral measurements.

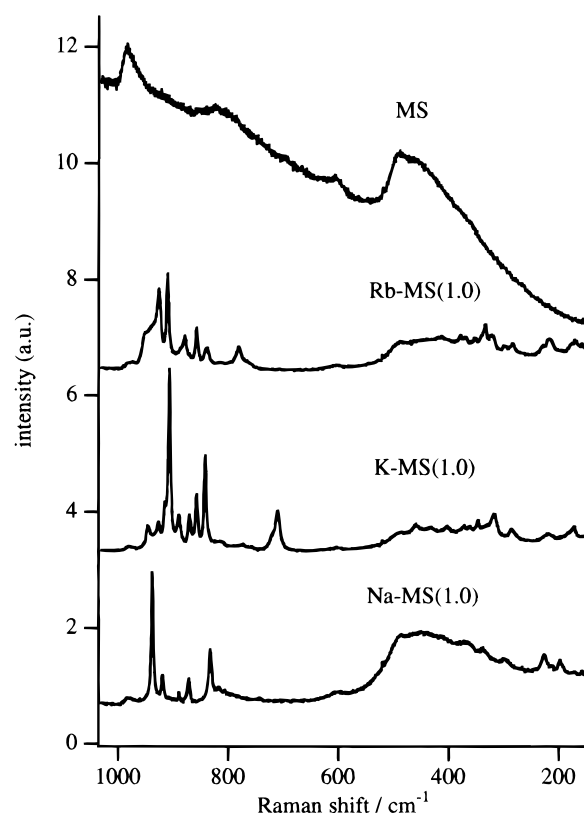
**Raman Spectra.** The laser Raman spectra were taken with the 514.5 nm line of an argon laser (JASCO NRS-2000) at room temperature. In the case of measurement of supported samples, the incident laser power at the samples was 30 mW, and spectra were recorded with a resolution of 4 cm<sup>-1</sup>. When the Raman spectra of reference samples were recorded, the incident laser power at the samples was 10 mW and the resolution of the spectra was 2 cm<sup>-1</sup>.

**XAFS.** X-ray absorption (XAS) experiments were carried out on the beam line BL 7C at the Photon Factory in National Laboratory for High Energy Physics, Tsukuba, Japan, with a ring energy of 2.5 GeV and stored current of 260–350 mA. XAS data of the samples were collected by the EXAFS facilities installed at BL7C in a transmission mode at room temperature with an Si(111) two-crystal monochromator.

Data reduction was performed using a FACOM M1800 computer of Kyoto University Data Processing Center. Normalization of XANES and data reduction on EXAFS were carried out as described elsewhere.<sup>13</sup> For curve-fitting analysis, the following EXAFS formula was applied.

$$k^3\chi = \sum_j (k^2 N_j / R_j^2) A_j(k) \exp(-2k^2 \sigma_j^2) \sin(2kR_j + \delta_j(k))$$

where  $k$  is the wavenumber of photoelectron,  $N_j$  the number of scattering atoms of the  $j$ th shell located at a distance of  $R_j$  from a molybdenum atom,  $A_j$  the envelope function which includes backscattering amplitude and damping factor caused by inelastic

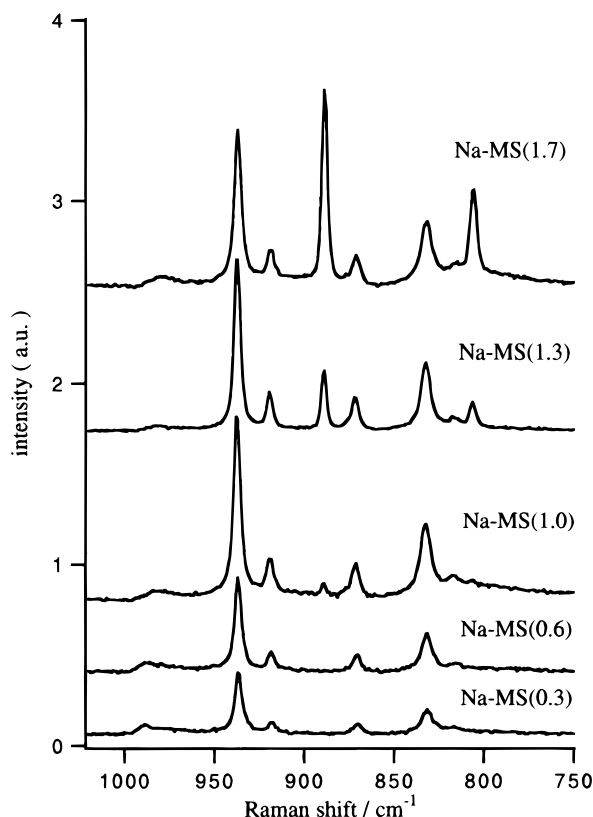


**Figure 1.** Raman spectra of MS and alkali-ion-modified MS samples.

loss during electron traveling,  $\sigma_j$  the Debye–Waller factor, and  $\delta_j$  the phase shift. For an oxygen atom scatterer,  $A_j$  and  $\delta_j$  were extracted from Na<sub>2</sub>MoO<sub>4</sub>, and hence  $\sigma_j$  corresponds to the relative Debye–Waller factor derived from that of the compound. For a molybdenum atom scatterer,  $A_j$  and  $\delta_j$  were estimated with FEFF(6.0).<sup>14</sup> The mathematical errors in  $N_j$ ,  $R_j$ , and  $\sigma_j$  can be obtained, but the values have no physical meaning because our system contains many species as a mixture and the information is not statistically sufficient to determine all the possible parameters, as mentioned below. Therefore, we do not tabulate the errors and the deviations.

## Results

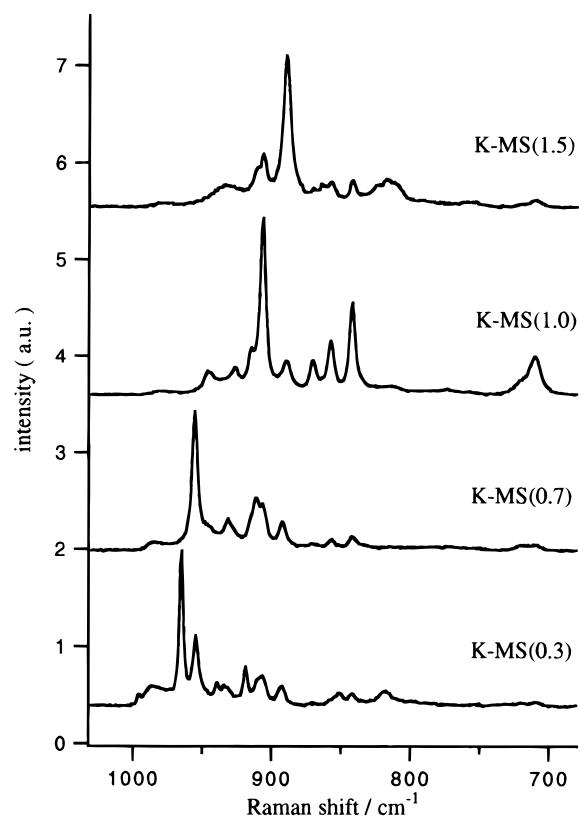
**Raman Spectra.** Figure 1 shows Raman spectra of MS and alkali-ion-modified MS samples. Alkali-ion-modified samples listed in Figure 1 contain alkali ions equimolar with molybdenum ions in the samples. In the Raman spectrum of MS, a band was observed at 986 cm<sup>-1</sup>. This band was assigned to the Mo=O stretching vibration of the surface molybdenum species in MoO<sub>3</sub>/SiO<sub>2</sub>.<sup>15</sup> In the Raman spectrum of MS, no band due to crystalline MoO<sub>3</sub> was found,<sup>16</sup> indicating that crystalline MoO<sub>3</sub> was absent in MS sample. In the X-ray diffraction pattern of MS, no peak corresponding to crystalline MoO<sub>3</sub> was observed either. In vibration modes due to the Mo–O–Mo bond in many molybdenum samples, the symmetric stretching, asymmetric stretching, and deformation vibrations are observed at 450–650, 700–900, and 170–230 cm<sup>-1</sup>, respectively.<sup>16</sup> In the Raman spectrum of MS, the band due to the Mo–O–Mo bond could not be confirmed. This result suggests that the molybdenum species in MS is isolated, i.e., a monomeric one. On the other hand, Raman spectra of alkali-ion-modified MS were significantly different from the Raman spectrum of MS. The results elucidate that new alkali-molybdate species were formed by the addition of alkali ions



**Figure 2.** Raman spectra of Na-MS samples with various amounts of sodium ions.

to MS. In addition, differences in the positions of Raman bands were found depending on the kinds of added alkali ions. Therefore, the structures of molybdenum species are different to some degree among all the alkali-ion-modified MS samples.

To further investigate the change of the structure of the molybdenum species by the addition of alkali ions, we prepared the alkali-ion-modified MS samples with different amounts of alkali ions and recorded Raman spectra of the samples. Figure 2 shows Raman spectra of Na-MS with various amounts of sodium ions. The molar ratios Na/Mo were changed from 0.3 to 1.7. In the Raman spectrum of Na-MS(0.3), four sharp bands were found at 937, 918, 870, and 831  $\text{cm}^{-1}$ , and the intensities of the four bands were enhanced with an increase in the added amounts of sodium ions up to the molar ratio Na/Mo = 1.0. The positions and relative intensities of four bands at 937, 918, 870, and 831  $\text{cm}^{-1}$  found in the Raman spectra of all the  $\text{Na}^+$ -modified MS are identical with those of  $\text{Na}_2\text{Mo}_2\text{O}_7$ .<sup>17</sup> In the Raman spectrum of  $\text{Na}_2\text{Mo}_2\text{O}_7$ , the bands at 940, 920, 875, and 830  $\text{cm}^{-1}$  were observed. As for the structure of the molybdenum species in  $\text{Na}_2\text{Mo}_2\text{O}_7$ , an equal number of a tetrahedral  $\text{MoO}_4$  unit and an octahedral  $\text{MoO}_6$  unit forms the chain structure.<sup>17</sup> Therefore, the addition of sodium ions up to the molar ratio Na/Mo = 1.0 would bring about the selective formation of  $\text{Na}_2\text{Mo}_2\text{O}_7$ -like molybdenum species. In addition, the small band at 986  $\text{cm}^{-1}$ , which was observed in the Raman spectrum of MS, was detected in the spectra of Na-MS(0.3) and Na-MS(0.6). This result indicates that some molybdenum species that do not interact with sodium ions are present in Na-MS samples containing sodium ions below the molar ratio Na/Mo = 1.0. In the Raman spectrum of Na-MS(1.0), small bands at 810 and 888  $\text{cm}^{-1}$  appeared besides the four bands due to  $\text{Na}_2\text{Mo}_2\text{O}_7$ . The intensities of the Raman bands at 810 and 888  $\text{cm}^{-1}$  became high with an increase in the added amounts of sodium ions, while the intensities of the bands due to  $\text{Na}_2\text{Mo}_2\text{O}_7$



**Figure 3.** Raman spectra of K-MS samples with various amounts of potassium ions.

became small to some degree. The two bands are identical with the Raman bands of  $\text{Na}_2\text{MoO}_4$ .<sup>18</sup>  $\text{Na}_2\text{MoO}_4$  which is composed of a tetrahedral  $\text{MoO}_4$  unit exhibits Raman bands at 892 and 808  $\text{cm}^{-1}$ . In Na-MS samples with sodium ions above molar ratio Na/Mo = 1.0, the molybdenum species exist as  $\text{Na}_2\text{MoO}_4$  and  $\text{Na}_2\text{Mo}_2\text{O}_7$  on the silica supports, and the formation of  $\text{Na}_2\text{MoO}_4$  becomes remarkable with an increase in added amounts of sodium ions.

Figure 3 shows Raman spectra of K-MS samples with various amounts of potassium ions. In the case of K-MS samples, the change of the Raman spectra by the added amounts of potassium ions was different from that of Na-MS samples. The positions of main bands in Raman spectra of K-MS samples were changed significantly by the added amounts of potassium ions, while the Raman bands of Na-MS samples with sodium ions up to the molar ratio Na/Mo = 1.0 were found at the same positions. The Raman spectrum of  $\text{K}_2\text{Mo}_2\text{O}_7$  shows bands at 930, 910, 870, 860, 845, and 710  $\text{cm}^{-1}$ .<sup>17</sup> In the Raman spectrum of K-MS(1.0), bands at 927, 906, 870, 857, 842, and 710  $\text{cm}^{-1}$  were found, and the positions of the Raman bands coincided with those of  $\text{K}_2\text{Mo}_2\text{O}_7$ . This suggests that the molybdenum species in K-MS(1.0) is present as  $\text{K}_2\text{Mo}_2\text{O}_7$  mainly. In the Raman spectrum of K-MS(1.5), the intensities of bands due to  $\text{K}_2\text{Mo}_2\text{O}_7$  became significantly small, and the new bands appeared at 888, 856, and 820  $\text{cm}^{-1}$ . Figure 4 shows the Raman spectrum of  $\text{K}_2\text{MoO}_4$  composed of a tetrahedral  $\text{MoO}_4$  unit.  $\text{K}_2\text{MoO}_4$  exhibits Raman bands at 888, 852, and 823  $\text{cm}^{-1}$ , and the positions of the Raman bands coincide with those of K-MS(1.5). Hence, the addition of potassium ions beyond molar ratio K/Mo = 1.5 causes the formation of  $\text{K}_2\text{MoO}_4$  mainly at the expense of  $\text{K}_2\text{Mo}_2\text{O}_7$ . In the Raman spectrum of K-MS(0.7), Raman bands at 955 and 910  $\text{cm}^{-1}$  were observed besides the bands due to  $\text{K}_2\text{Mo}_2\text{O}_7$ . K-MS(0.3) exhibited the Raman bands at 965 and 918  $\text{cm}^{-1}$  in addition to the bands observed in the

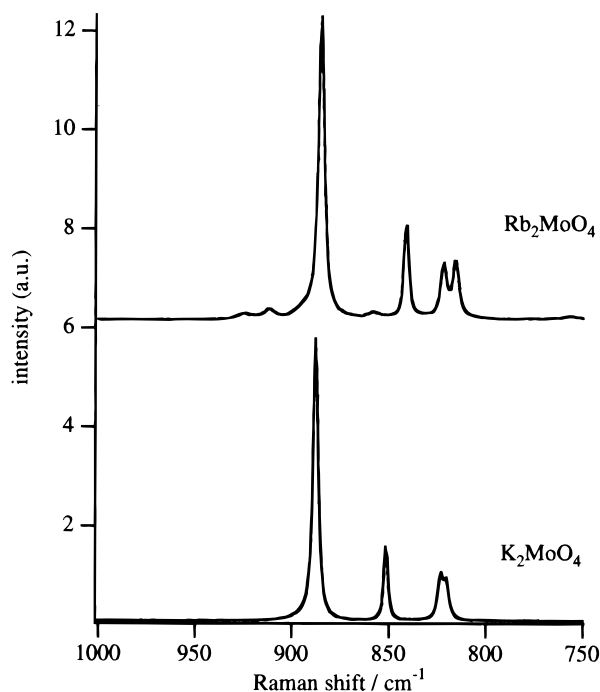


Figure 4. Raman spectra of K<sub>2</sub>MoO<sub>4</sub> and Rb<sub>2</sub>MoO<sub>4</sub>.

Raman spectrum of K-MS(0.7). In the case of Na-MS samples, Na<sub>2</sub>Mo<sub>2</sub>O<sub>7</sub> was formed selectively even when the small amounts of sodium ions were added to MS, and the addition of sodium ions up to the molar ratio Na/Mo = 1.0 brought about the selective formation of Na<sub>2</sub>Mo<sub>2</sub>O<sub>7</sub>. The structural change of the molybdenum species in Na-MS samples by the added amounts of sodium ions is not consistent with that in K-MS samples in the range of molar ratio K/Mo from 0 to 1.0. From the results that the molybdenum species exist as K<sub>2</sub>Mo<sub>2</sub>O<sub>7</sub> in K-MS(1.0) and K<sub>2</sub>MoO<sub>4</sub> is present mainly in K-MS(1.5), we consider that the proportion of the tetrahedral MoO<sub>4</sub> unit to all the molybdenum species in K-MS samples becomes high and that of the octahedral MoO<sub>6</sub> unit becomes low with an increase in the added amounts of potassium ions. Indeed, we cannot assign the Raman bands of K-MS(0.3) or K-MS(0.7), but it is likely that, in the range of molar ratio K/Mo from 0 to 1.0, the proportion of the octahedral MoO<sub>6</sub> unit to all the molybdenum species is high, compared to that in the range of molar ratio K/Mo > 1. In the Raman spectra of both K-MS(0.3) and K-MS(0.7), the band at 986 cm<sup>-1</sup>, which was found in the Raman spectrum of MS, could be seen, while the band was not able to be detected in the Raman spectra of K-MS(1.0) or K-MS(1.5), indicating that the molybdenum species which did not interact with potassium ions were present in K-MS samples with potassium ions up to the molar ratio K/Mo = 1.0.

Figure 5 shows Raman spectra of Rb-MS samples with various amounts of rubidium ions, and Figure 4 shows the Raman spectrum of Rb<sub>2</sub>MoO<sub>4</sub>. The Raman spectrum of Rb-MS(2.0) was identical with that of Rb<sub>2</sub>MoO<sub>4</sub>, indicating that most of the molybdenum species in Rb-MS(2.0) were Rb<sub>2</sub>MoO<sub>4</sub>. The Raman bands due to Rb<sub>2</sub>MoO<sub>4</sub> were also observed in the Raman spectrum of Rb-MS(1.5), suggesting that some molybdenum species in Rb-MS(1.5) existed as Rb<sub>2</sub>MoO<sub>4</sub>. The Raman spectrum of Rb-MS(1.5) is similar to that of Rb-MS(1.0), although the Raman bands due to Rb<sub>2</sub>MoO<sub>4</sub> are absent in the Raman spectrum of Rb-MS(1.0). In the range of molar ratio Rb/Mo < 1.0, Rb-MS samples exhibited the Raman bands at the same positions regardless of the added amounts of rubidium ions. Indeed, we cannot assign the Raman bands found in Rb-

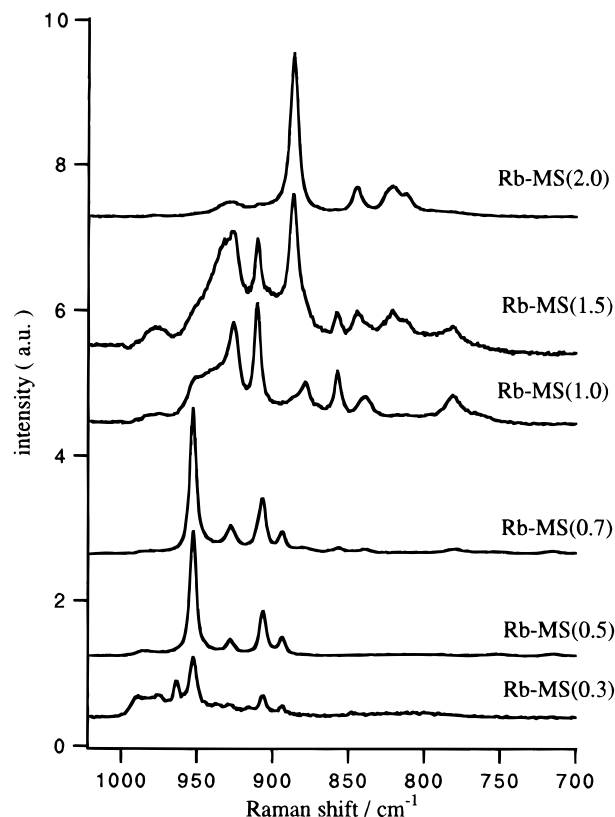
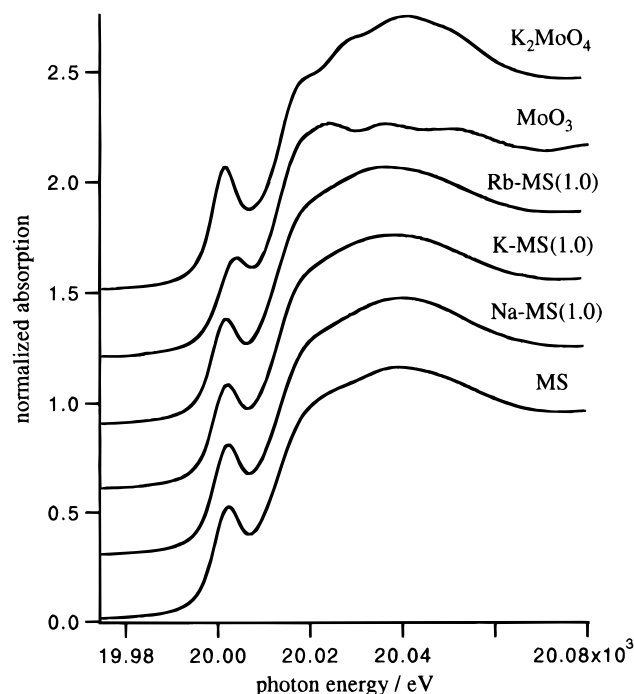


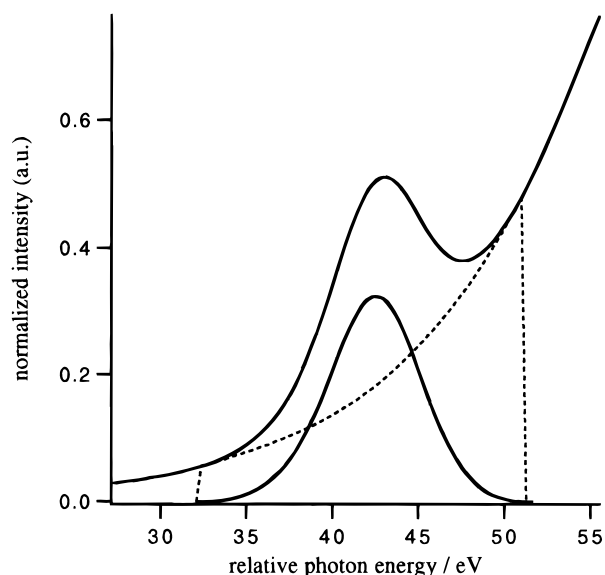
Figure 5. Raman spectra of Rb-MS samples with various amounts of rubidium ions.

MS samples with rubidium ions up to the molar ratio Rb/Mo = 1.0, but it seems that the change of the Raman spectra of Rb-MS samples by the added amounts of rubidium ions resembles that of K-MS samples. Therefore, the structure of molybdenum species may be changed by the added amounts of rubidium ions in the same way as in the case of K-MS samples; i.e., the proportion of the octahedral MoO<sub>6</sub> unit to all the molybdenum species in Rb-MS with rubidium ions up to the molar ratio Rb/Mo = 1.0 is higher than that in Rb-MS with rubidium ions of the molar ratio Rb/Mo > 1.0.

**XANES.** Mo K-edge XANES spectra are sensitive to the symmetry of the molybdenum species and useful in understanding the local structure of molybdenum oxide supported on the silica supports. Figure 6 shows Mo K-edge XANES spectra of MS, alkali-ion-modified MS, and reference samples. Alkali-ion-modified MS samples shown in Figure 6 contained the alkali ions equimolar with the molybdenum ions in the samples. All XANES spectra shown in Figure 6 have a preedge peak at around 20 002 eV. The peak is attributed to the 1s–4d transition in the molybdenum atom.<sup>19</sup> K<sub>2</sub>MoO<sub>4</sub> and MoO<sub>3</sub> are composed of a tetrahedral MoO<sub>4</sub> unit and a distorted octahedral MoO<sub>6</sub> unit, respectively. The intensity of the preedge peak in the XANES spectrum of K<sub>2</sub>MoO<sub>4</sub> is higher than that of MoO<sub>3</sub>, suggesting that when the structure of a molybdenum species is tetrahedral, a preedge peak is more intense than that in an octahedral one.<sup>13</sup> The XANES spectra of MS and alkali-ion-modified MS samples possessed a sharp preedge peak similar to that of K<sub>2</sub>MoO<sub>4</sub>, and significant differences of the XANES spectra were not observed among the four supported samples. It is likely that the addition of alkali ions to MS does not cause the pronounced change of the symmetry of molybdenum species, and the molybdenum species in both MS and alkali-ion-modified MS samples are mainly of tetrahedral MoO<sub>4</sub>. To further investigate the symmetry of the molybdenum species in MS

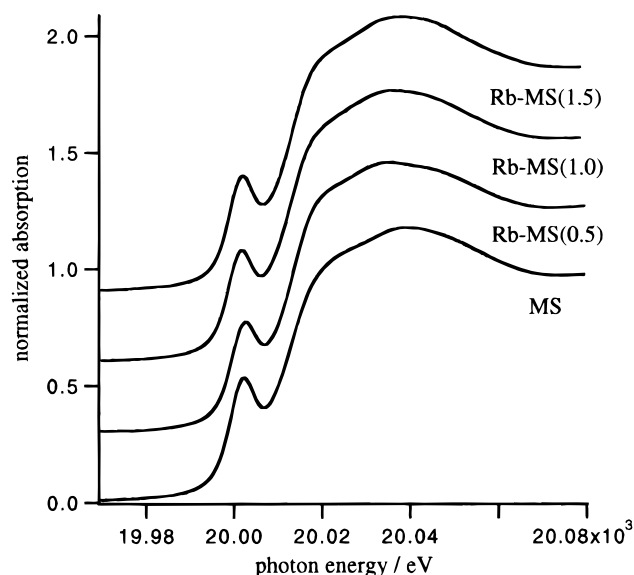


**Figure 6.** Mo K-edge XANES spectra of MS, alkali-ion-modified MS, and reference samples.



**Figure 7.** Estimation of the area and height of the pre-edge peak in XANES spectrum of Na-MS(1.0).

and alkali-ion-modified MS samples, we paid attention to the pre-edge peak in the XANES spectrum of each sample and estimated the area and height of the pre-edge peak by fitting an edge jump of the XANES spectrum with a polynomial function. As shown in Figure 7, a background of the pre-edge peak was estimated by fitting the regions before and after the pre-edge peak with a fourth-order polynomial function and followed by interpolation. The background was subtracted from the pre-edge peak region, and the pre-edge peak was extracted as shown in Figure 7. The peak was symmetric, and the area was evaluated simply by the Simpson method. The results are shown in Table 1. The area and height of the pre-edge peak of  $K_2MoO_4$ , which is composed of a tetrahedral  $MoO_4$  unit, were confirmed to be larger than those of  $MoO_3$ , which is composed of a distorted octahedral  $MoO_6$  unit, indicating that the area and height of the pre-edge peak were good indications of the symmetry of the



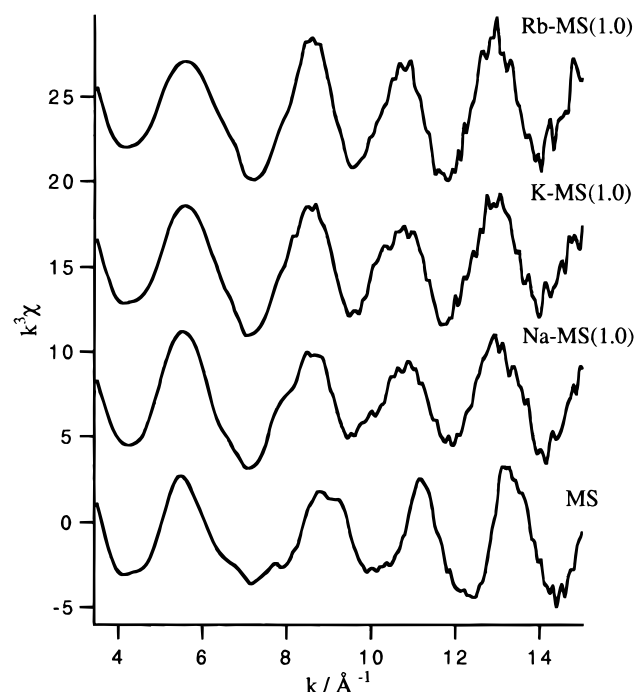
**Figure 8.** Mo K-edge XANES spectra of Rb-MS samples with various amounts of rubidium ions.

**TABLE 1: Area and Height of Preedge Peak of Mo K-Edge XANES of MS, Alkali-Ion-Modified MS, and Reference Samples**

sample	area/eV·unit	height/unit
$MoO_3$	1.74	0.249
$K_2MoO_4$	2.43	0.371
MS	2.26	0.328
Na-MS(1.0)	2.18	0.324
K-MS(1.0)	2.08	0.302
Rb-MS(0.5)	1.98	0.291
Rb-MS(1.0)	2.09	0.305
Rb-MS(1.5)	2.16	0.314

molybdenum species. MS possessed the largest area and height of the pre-edge peak of all the supported samples, and the height and area were decreased by the addition of alkali ions equimolar with molybdenum atoms in the samples. From the results, we expect that the proportion of a tetrahedral  $MoO_4$  unit to all the molybdenum species in the samples is the highest in MS, and the proportion becomes low by the addition of alkali ions to MS; i.e., an octahedral  $MoO_6$  is formed by the addition of alkali ions at the expense of a tetrahedral  $MoO_4$ .

XANES spectra of Rb-MS samples with various amounts of rubidium ions are depicted in Figure 8. All XANES spectra had almost the same characteristic peak, and pronounced differences of the spectra by the added amounts of rubidium ions were not found. We focused on the area and height of pre-edge peak in the XANES spectrum of each Rb-MS sample again. The results are found in Table 1. Of all Rb-MS samples, Rb-MS(0.5) possessed the smallest area and height of the pre-edge peak in the XANES spectrum. Although the addition of rubidium ions equal to half the amount of molybdenum atoms in the samples caused a marked decrease in the area and height of the pre-edge peak, the area and height of the pre-edge peaks were recovered gradually by the addition of more amounts of rubidium ions. Because MS possesses the largest area and height of the pre-edge peak, the molybdenum species in MS would be mainly a tetrahedral  $MoO_4$ . Although by the addition of small amounts of rubidium ions to MS some tetrahedral  $MoO_4$  species are changed to the octahedral  $MoO_6$  species, the proportion of the tetrahedral  $MoO_4$  unit to all the molybdenum species in the sample becomes higher with an increase in the added amounts of rubidium ions.

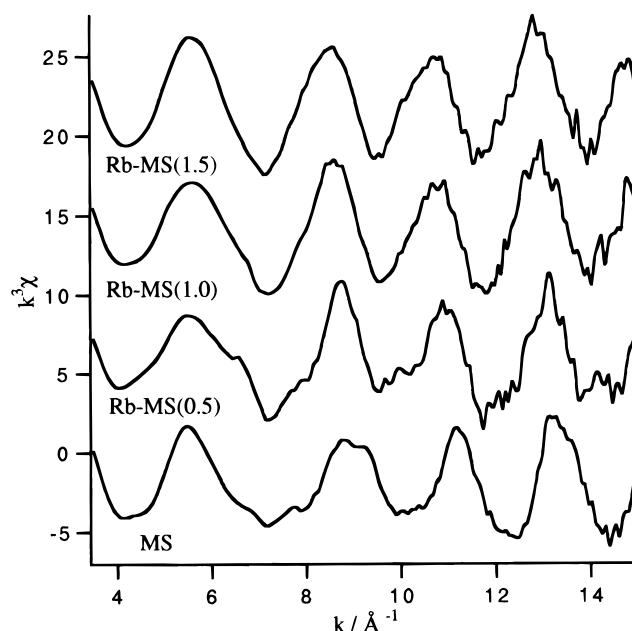


**Figure 9.**  $k^3$ -weighted Mo K-edge EXAFS spectra of MS and alkali-ion-modified MS.

**EXAFS.** Figure 9 shows  $k^3$ -weighted Mo K-edge EXAFS spectra of MS and alkali-ion-modified MS samples. Alkali-ion-modified MS samples shown in Figure 9 contained alkali ions equimolar with the molybdenum ions in the samples. The oscillation pattern of the EXAFS spectrum of MS was different from those of alkali-ion-modified MS samples, but EXAFS spectra of alkali-ion-modified MS samples exhibited almost the same patterns regardless of the kinds of added alkali ions. These results suggest that although the structure of molybdenum species in MS is distinct from that in alkali-ion-modified MS samples, the structure of the molybdenum species in alkali-ion-modified MS is similar to each other regardless of the kinds of added alkali ions.

We investigated the change of the structure of molybdenum species with the added amounts of alkali ions by Mo K-edge EXAFS spectra and depicted the results in Figure 10. The EXAFS spectrum of Rb-MS(1.5) possessed almost the same characteristic pattern as that of Rb-MS(1.0), suggesting that the structure of the molybdenum species in Rb-MS(1.0) resembles that in Rb-MS(1.5). On the other hand, the EXAFS spectrum of Rb-MS(0.5) was different from not only that of MS but also that of Rb-MS(1.0). The results indicate that the structure of molybdenum species is changed even by the addition of small amounts of alkali ions. The structure of the molybdenum species in Rb-MS(0.5) is also distinct from that in Rb-MS(1.0) and Rb-MS(1.5).

We performed a Fourier transform on the EXAFS in the 3.5–14 Å<sup>-1</sup> region to obtain the radial structure function (RSF). The RSFs of MS and alkali-ion-modified MS samples are shown in Figure 11. Alkali-ion-modified MS listed in Figure 11 contained alkali ions equimolar with molybdenum atoms in the samples. In RSF of MS, the peaks due to Mo–O bonds were found at around 0.8–2.0 Å. The peaks at around 3.0–3.5 Å in RSF of MS may suggest the presence of the neighboring molybdenum atoms. The RSF of MS was different from the RSFs of alkali-ion-modified MS samples, but the RSFs of alkali-ion-modified MS samples were similar to each other regardless of the kinds of added alkali ions. The height of peaks at around 0.9–2.0 Å

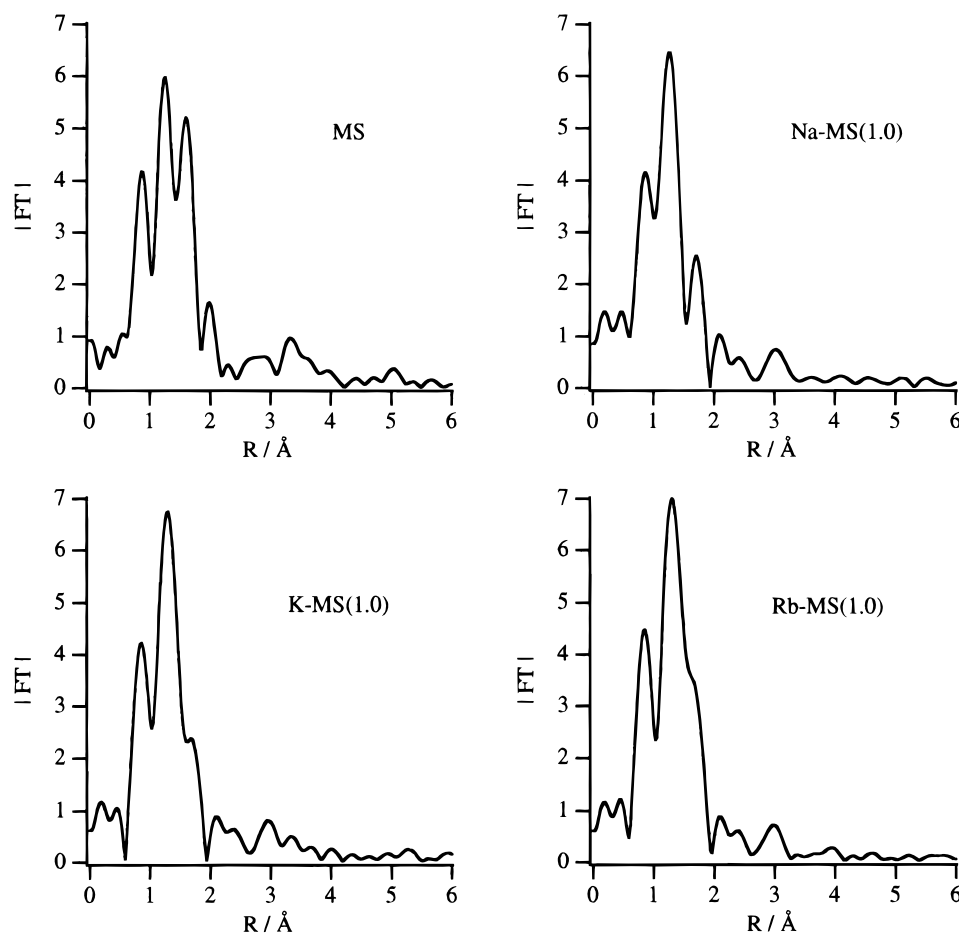


**Figure 10.**  $k^3$ -weighted Mo K-edge EXAFS spectra of Rb-MS samples with various amounts of rubidium ions.

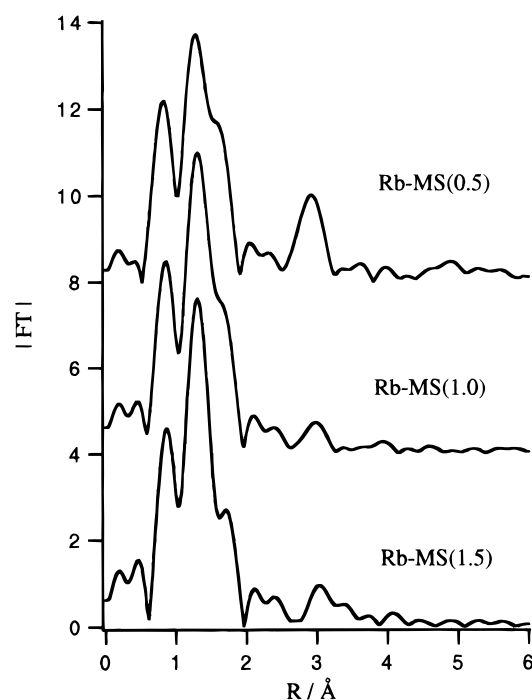
due to Mo–O bonds was higher in the RSFs of alkali-ion-modified MS samples than that in the RSF of MS. Since RSF is another expression in R space of the oscillation of EXAFS and the summation of sine curves with similar but different frequencies reduces the intensity, known as a beat phenomenon, it is likely that the molybdenum species in alkali-ion-modified MS samples possess the Mo–O bonds with uniform bond lengths, in contrast to those in MS. In addition, a small peak was observed at around 3.0 Å in the RSFs of all the alkali-ion-modified MS samples, and the position and intensity of the peak were almost the same regardless of the kinds of the added alkali ions. This indicates that the peaks were not due to the neighboring alkali atoms, but due to the neighboring molybdenum atom. This could be also elucidated by the shape of the envelope function of Fourier-filtered EXAFS of the peaks.

Figure 12 shows Fourier transforms of  $k^3$ -weighted Mo K-edge EXAFS spectra of Rb-MS samples with various amounts of rubidium ions. In the RSFs of all Rb-MS samples, the peaks due to Mo–O bonds were found at around 0.8–2.0 Å, and the intensities of the peaks were enhanced with an increase in the added amounts of rubidium ions. It may suggest that the molybdenum species that possess Mo–O bonds with more uniform lengths are formed with an increase in the added amounts of rubidium ions. In the RSFs of all the Rb-MS samples, the peaks were confirmed at around 3.0 Å. The intensity of the peak in RSF of Rb-MS(0.5) was the highest of all the Rb-MS samples, while the intensity of the peak of Rb-MS(1.0) was the same level as that of Rb-MS(1.5).

We carried out further analysis of the EXAFS oscillations employing nonlinear curve fitting against the Fourier-filtered EXAFS spectra of MS and alkali-ion-modified MS samples with alkali ions equimolar with molybdenum ions in the samples. The results are summarized in Table 2. The curve-fitting analysis for MS suggests that the molybdenum species in MS have four Mo–O bonds. The length of two shorter bonds is estimated to be 1.68 Å and that of the other bonds to be 1.88 Å. It is likely that the shorter Mo–O bonds have a double-bond character. In addition, the shorter Mo–O bonds would be terminal ones, and the longer bonds would be bound directly to the silica support. Although Mo–Mo scattering was sug-



**Figure 11.** Fourier transforms of  $k^3$ -weighted Mo K-edge EXAFS spectra of MS and alkali-ion-modified MS.



**Figure 12.** Fourier transforms of  $k^3$ -weighted Mo K-edge EXAFS spectra of Rb-MS samples with various amounts of rubidium ions.

gested by the peaks at 3.2 Å in RSF of MS, the envelope functions of the inversely transformed spectra of the corresponding peaks were monotonic, and the intercept of the function at  $k = 0 \text{ Å}^{-1}$  was far from zero. This indicates that

**TABLE 2: Curve-Fitting Results of MS and Alkali-Ion-Modified MS Samples**

sample	shell	CN <sup>a</sup>	$R/\text{Å}^b$	$\sigma^2/\text{Å}^2$
MS	Mo–O	1.9	1.68	–0.0003 <sup>c</sup>
	Mo–O	1.8	1.88	0.0003 <sup>c</sup>
Na-MS(1.0)	Mo–O	3.3	1.71	0.0032 <sup>c</sup>
	Mo–O	1.3	1.93	0.0010 <sup>c</sup>
K-MS(1.0)	Mo–Mo	0.5	3.32	0.0084 <sup>d</sup>
	Mo–O	2.8	1.72	0.0021 <sup>c</sup>
Rb-MS(1.0)	Mo–O	1.3	1.96	0.0020 <sup>c</sup>
	Mo–Mo	0.3	3.28	0.0043 <sup>d</sup>
	Mo–O	2.9	1.72	0.0022 <sup>c</sup>
	Mo–O	1.4	1.97	0.0004 <sup>c</sup>
	Mo–Mo	0.3	3.30	0.0055 <sup>d</sup>

<sup>a</sup> CN = coordination number. <sup>b</sup>  $R$  = interatomic distance. <sup>c</sup> Relative Debye–Waller factor against that of reference sample ( $\text{Na}_2\text{MoO}_4$ ). <sup>d</sup> Debye–Waller factor.

the peaks at around 3.2 Å in RSF of MS are mainly composed of the noisy oscillation. Therefore, we cannot conclude whether the peaks are due to the presence of neighboring molybdenum atoms or silicon atoms or due to the noise.

The structural parameters for Mo–O bonds of the molybdenum species in alkali-ion-modified MS samples, which contained alkali ions equimolar with the molybdenum atoms in the samples, were similar to each other regardless of the kinds of added alkali ions. Roughly speaking, the bond lengths of Mo–O became longer, and the coordination numbers of the molybdenum atom became larger by the addition of alkali ions to MS. Because the results of Raman spectra suggested that the molybdenum species were composed of the tetrahedral  $\text{MoO}_4$  and octahedral  $\text{MoO}_6$  units in alkali-ion-modified MS

**TABLE 3: Curve-Fitting Results of Rb-MS Samples with Various Amounts of Rubidium Ions**

sample	shell	CN <sup>a</sup>	R/Å <sup>b</sup>	σ <sup>2</sup> /Å <sup>2</sup>
Rb-MS(0.5)	Mo—O	2.1	1.69	0.0032 <sup>c</sup>
	Mo—O	1.9	1.94	0.0010 <sup>c</sup>
	Mo—Mo	0.9	3.27	0.0058 <sup>d</sup>
Rb-MS(1.0)	Mo—O	2.9	1.72	0.0022 <sup>c</sup>
	Mo—O	1.4	1.97	0.0004 <sup>c</sup>
	Mo—Mo	0.3	3.30	0.0055 <sup>d</sup>
Rb-MS(1.5)	Mo—O	3.3	1.73	0.0027 <sup>c</sup>
	Mo—O	0.9	1.98	0.0010 <sup>c</sup>
	Mo—Mo	0.3	3.31	0.0038 <sup>d</sup>

<sup>a</sup> CN = coordination number. <sup>b</sup> R = interatomic distance. <sup>c</sup> Relative Debye—Waller factor against that of reference sample (Na<sub>2</sub>MoO<sub>4</sub>).

<sup>d</sup> Debye—Waller factor.

samples with alkali ions equimolar with molybdenum atoms in the samples, the structural parameters estimated by the curve fitting were the averages of lengths of Mo—O bonds in both tetrahedral MoO<sub>4</sub> and octahedral MoO<sub>6</sub> units. Therefore, it is difficult to elucidate the structure of the molybdenum species in alkali-ion-modified MS samples only from the structural parameters estimated by the curve fitting. In alkali-ion-modified MS samples, the presence of the neighboring molybdenum atom at ca. 3.3 Å was detected, and the coordination numbers were estimated to be 0.5 for Na-MS(1.0) and 0.3 for K-MS(1.0) and Rb-MS(1.0). From the results that the coordination numbers of Mo—Mo are low, we consider that the molybdenum species in alkali-ion-modified MS samples exist as small clusters.

Table 3 shows the results of curve fitting of Rb-MS samples with various amounts of rubidium ions. Because the molybdenum species in all Rb-MS samples with various amounts of rubidium ions are also expected to be composed of tetrahedral MoO<sub>4</sub> and octahedral MoO<sub>6</sub> units, the structural parameters estimated by the curve-fitting analysis of EXAFS represent the averages of several Mo—O bond lengths in both a tetrahedral MoO<sub>4</sub> and an octahedral MoO<sub>6</sub>. The trend of the structural change of the molybdenum species by the added amounts of rubidium ions can be found from the structural parameters listed in Table 3. The coordination numbers of Mo—O bonds with the length ca. 1.70 Å became large and those of Mo—O bonds with the length ca. 1.95 Å became small with the increase of the added amounts of rubidium ions. The longer Mo—O bonds possibly belong to an octahedral MoO<sub>6</sub> unit. Therefore, the proportion of the octahedral MoO<sub>6</sub> unit to all the molybdenum species in the sample decreases with the increase in the added amounts of rubidium ions; i.e., the proportion of the tetrahedral MoO<sub>4</sub> unit becomes higher. It was found that the coordination number of Mo—Mo in Rb-MS(0.5) was the largest of all the Rb-MS samples, and the coordination number of Mo—Mo in Rb-MS(1.0) was the same as that in Rb-MS(1.5). These results suggest that more molybdenum species in Rb-MS(0.5) are aggregated than those in Rb-MS(1.0) and Rb-MS(1.5) and that the degree of aggregation of the molybdenum species becomes low with the increase of added amounts of rubidium ions.

## Discussion

**Structure of the Molybdenum Species in MoO<sub>3</sub>/SiO<sub>2</sub>.** The structure of the molybdenum species in MS was investigated by Mo K-edge XAFS (XANES and EXAFS) and Raman spectroscopies. The XANES spectrum of MS exhibited the intense preedge peak as found in the case of K<sub>2</sub>MoO<sub>4</sub> which is composed of a tetrahedral MoO<sub>4</sub> unit only. This indicates that the proportion of the tetrahedral MoO<sub>4</sub> unit to all the molybdenum species in MS is remarkably high. The result of the

curve-fitting analysis against Mo K-edge EXAFS showed that the molybdenum species in MS was a tetrahedral MoO<sub>4</sub> and possessed two shorter Mo—O bonds (1.68 Å) and two longer ones (1.88 Å). The shorter Mo—O bonds possibly have a double-bond character. In addition, the presence of the neighboring Mo atom could not be identified in the curve fitting of MS, suggesting that the molybdenum species in MS was mainly monomeric. From the results mentioned above, we propose that the molybdenum species in MS is monomeric and tetrahedral, (O=Mo=O)O<sub>2</sub>. The proposed structure of the molybdenum species in MS is consistent with that proposed in many reports.<sup>20–23</sup>

In the Raman spectrum of MS, bands due to neither crystalline MoO<sub>3</sub> nor Mo—O—Mo bonds were observed, indicating that the molybdenum species in MS was monomeric. The result is compatible with that obtained by EXAFS analysis. In the Raman spectra of MS, a band was found at 986 cm<sup>−1</sup>. The band was assigned to the stretching vibration of a terminal Mo=O bond in the surface molybdenum species in MoO<sub>3</sub>/SiO<sub>2</sub>.<sup>15</sup> On the basis of the results obtained by EXAFS and XANES spectra of MS, we can assign the band at 986 cm<sup>−1</sup> to the stretching vibration of Mo=O in the tetrahedral species (O=Mo=O)O<sub>2</sub> in MS. However, different proposals have been made for the assignment of the Raman band. Zhang et al. stated that the Raman band at 984 cm<sup>−1</sup> is due to Mo=O stretching vibration in octahedrally coordinated monomeric molybdenum species.<sup>24</sup> In addition, Hu et al. investigated the structure of the molybdenum species in MoO<sub>3</sub>/SiO<sub>2</sub> by Raman spectroscopy and Mo L<sub>3</sub>-edge XANES.<sup>25</sup> In the report, they concluded that the surface molybdenum species in MoO<sub>3</sub>/SiO<sub>2</sub> are isolated and highly distorted at MoO<sub>3</sub> loadings from 1 to 5 wt % and possess a symmetry somewhat between octahedral and tetrahedral coordination. These conclusions are far from ours. In MoO<sub>3</sub>/SiO<sub>2</sub> under the dehydrated state, the surface molybdenum species have been reported to be either the octahedral MoO<sub>6</sub><sup>20–23</sup> or the tetrahedral MoO<sub>4</sub>,<sup>24,26–28</sup> and a consistent conclusion as for the structure has not been obtained. As for this point, we consider the following. As found in the present study, the structure of molybdenum species in MoO<sub>3</sub>/SiO<sub>2</sub> is changed sensitively by the presence of additives such as alkali ions in the silica support. The silica samples used widely are commercially supplied, and trace amounts of sodium, calcium, aluminum atoms, and so on are often contained in the silica samples. Williams et al. examined the effect of calcium and sodium ions contained in silica on the structure of the molybdenum species in MoO<sub>3</sub>/SiO<sub>2</sub>.<sup>29</sup> They found from the results of Raman spectra that the presence of sodium or calcium ion caused the formation of Na<sub>2</sub>MoO<sub>4</sub> or CaMoO<sub>4</sub> despite the trace amounts of sodium and calcium ions. On the other hand, the presence of aluminum ions in silica samples causes the enhancement of the acidic property of the silica samples and changes the point of zero surface charge of the silica samples. When the silica samples are impregnated with an aqueous solution containing molybdenum ions, the surface state of the silica samples in the solution would vary with the amounts of additives and/or the kinds of additives. Hence, the structure of the molybdenum species in MoO<sub>3</sub>/SiO<sub>2</sub> should be changed by the types of silica supports. We used a homemade silica sample prepared by a sol–gel method in the present study. The homemade silica contains less amounts of additives such as aluminum and sodium ions and has a larger specific surface area (ca. 600 m<sup>2</sup> g<sup>−1</sup>) than the commercial silica samples. MoO<sub>3</sub>/SiO<sub>2</sub> was prepared by using the homemade silica sample, and the loading amount of MoO<sub>3</sub> was 4 wt %. Many studies



showed that crystalline  $\text{MoO}_3$  was present in  $\text{MoO}_3/\text{SiO}_2$  despite low loadings of  $\text{MoO}_3$ .<sup>20,21,30</sup> In our  $\text{MoO}_3/\text{SiO}_2$  sample, we could not detect the presence of crystalline  $\text{MoO}_3$  despite the loading amounts of 4 wt % as  $\text{MoO}_3$ . Because we used the homemade silica, which contained little additive, the molybdenum species would be supported mainly as a highly dispersed tetrahedral one,  $(\text{O}=\text{Mo}=\text{O})\text{O}_2$ . In addition, the surface structure of supported metal oxides is sensitive to the condition of pretreatment, i.e., the state of the samples prior to spectroscopic measurements. We have found that the structure of the vanadium species is of a tetrahedron,  $\text{VO}_4$ , in silica-supported vanadium oxide after evacuation at 673 K, while the structure of vanadium species is of an octahedron under the hydrated state.<sup>31</sup> It was also reported that in  $\text{MoO}_3/\text{SiO}_2$  samples the structure of the molybdenum species was changed by the condition of the samples. Stencel et al. described that silicomolybdic acid was present in  $\text{MoO}_3/\text{SiO}_2$  under the hydrated condition, while silicomolybdic acid collapsed upon calcination at 773 K.<sup>33</sup> Williams et al. found that octahedrally coordinated polymolybdate,  $\text{Mo}_7\text{O}_{24}^{6-}$  and  $\text{Mo}_8\text{O}_{26}^{4-}$ , was the only surface molybdate species observed in hydrated  $\text{MoO}_3/\text{SiO}_2$ .<sup>29</sup> Heating of the  $\text{MoO}_3/\text{SiO}_2$  destroyed the polymolybdate cluster and led to the formation of isolated molybdenum species. Therefore, the condition of  $\text{MoO}_3/\text{SiO}_2$  samples prior to a spectroscopic measurement is one of the factors determining the structure of the molybdenum species. It is quite natural that the consistent conclusion has not been obtained as for the structure of the molybdenum species in  $\text{MoO}_3/\text{SiO}_2$  because the factors determining the structure mentioned above, i.e., the types of silica supports and the condition of samples, were different in each study.

**Structure of Molybdenum Species in Alkali-Ion-Modified  $\text{MoO}_3/\text{SiO}_2$ .** The change of the structure of the molybdenum species by addition of alkali ions to MS was observed by Raman, XANES, and EXAFS spectroscopies. The XANES spectrum of Na-MS(1.0) showed that the proportion of a tetrahedral  $\text{MoO}_4$  unit to all the molybdenum species contained in Na-MS(1.0) was lower than that in MS. From the curve-fitting results of the EXAFS for Na-MS(1.0), it was confirmed that, by the addition of sodium ions to MS, the coordination number of the molybdenum atom increased and the bond lengths of Mo–O became long, suggesting that the proportion of an octahedral  $\text{MoO}_6$  unit to all the molybdenum species in the sample became high by the addition of sodium ions. In addition, the neighboring molybdenum atom was found to be present at 3.3 Å from a molybdenum atom in Na-MS(1.0), while the neighboring molybdenum atom was not detected in MS. From the results mentioned above, we expect that the molybdenum species in Na-MS(1.0) is composed of a small cluster that contains the octahedral  $\text{MoO}_6$  and tetrahedral  $\text{MoO}_4$  units. The idea is supported by the results of the Raman spectra of  $\text{Na}^+$ -modified MS samples. In the Raman spectra of Na-MS samples with sodium ions of molar ratio Na/Mo from 0.3 to 1.0, the bands assignable to  $\text{Na}_2\text{Mo}_2\text{O}_7$ , which is made up of the tetrahedral  $\text{MoO}_4$  and octahedral  $\text{MoO}_6$  units, were observed in addition to the band due to a monomeric tetrahedral species,  $\text{MoO}_4$ , observed in MS. By the addition of sodium ions more than the molar ratio Na/Mo = 1.0, the bands due to  $\text{Na}_2\text{MoO}_4$ , which is composed of a tetrahedral  $\text{MoO}_4$  unit, appeared in the Raman spectra, and the intensity of the bands became higher with the increase in the added amounts of sodium ions. Hence, in Na-MS with sodium ions up to the molar ratio Na/Mo = 1.0,  $\text{Na}_2\text{Mo}_2\text{O}_7$  is present mainly on the silica support besides tetrahedral  $(\text{O}=\text{Mo}=\text{O})\text{O}_2$  which also exists in the MS sample.

The addition of sodium ions more than the molar ratio Na/Mo = 1.0 causes the formation of  $\text{Na}_2\text{MoO}_4$  at the expense of  $\text{Na}_2\text{Mo}_2\text{O}_7$ .  $\text{Na}_2\text{Mo}_2\text{O}_7$  has an equal number of  $\text{MoO}_4$  and  $\text{MoO}_6$  units sharing the vertex to form a chain. Because the coordination number of Mo–Mo was estimated to be 0.5 in the curve fitting on EXAFS of Na-MS(1.0), the degree of the oligomerization of the molybdenum species would be very low. Martin et al. investigated the effect of sodium ion addition to  $\text{MoO}_3/\text{TiO}_2$  on the structure of the molybdenum species.<sup>33</sup> They concluded that the addition of sodium ions to  $\text{MoO}_3/\text{TiO}_2$  caused the formation of a  $\text{Mo}_2\text{O}_7^{2-}$  chain on the titania support. Their conclusion is consistent with ours, suggesting that the addition of sodium ions gives the above effect on the structure of supported molybdenum species regardless of the kinds of support materials.

The structure of the molybdenum species in K-MS(1.0) seems to be similar to that in Na-MS(1.0). The features of XANES and EXAFS of K-MS(1.0) were almost the same as those of Na-MS(1.0), and the structural parameters of molybdenum species in K-MS(1.0) estimated by EXAFS analysis were also compatible with those in Na-MS(1.0), suggesting that the molybdenum species in K-MS(1.0) was mainly  $\text{Mo}_2\text{O}_7^{2-}$ . In the Raman spectrum of K-MS(1.0), the bands due to  $\text{K}_2\text{Mo}_2\text{O}_7$  were confirmed, which was consistent with the results of XANES and EXAFS spectra. Therefore, the molybdenum species in K-MS(1.0) mainly exists as  $\text{K}_2\text{Mo}_2\text{O}_7$ . On the other hand, the Raman bands due to  $\text{K}_2\text{MoO}_4$  were found in the Raman spectrum of K-MS(1.5) besides the small bands due to  $\text{K}_2\text{Mo}_2\text{O}_7$ , indicating that the molybdenum species in K-MS(1.5) is mainly  $\text{K}_2\text{MoO}_4$ . When the alkali ions of the amount of molar ratio (alkali ion/Mo) = 1.0 are added to MS, a  $\text{Mo}_2\text{O}_7$  unit is formed predominantly in both Na-MS and K-MS. As the added amount of alkali ion exceeds 1.0 in the molar ratio (alkali ion/Mo),  $\text{MoO}_4^{2-}$  is formed preferentially in both Na-MS and K-MS at the expense of  $\text{Mo}_2\text{O}_7^{2-}$ . This trend seems to be the same for the case of Rb-MS samples. In the Raman spectrum of Rb-MS(1.5), the bands due to  $\text{Rb}_2\text{MoO}_4$  were observed, and only the bands were found in the spectrum of Rb-MS(2.0). Hence, the addition of rubidium ions of the amounts beyond molar ratio Rb/Mo = 1.0 brings about the formation of  $\text{Rb}_2\text{MoO}_4$ . In the Raman spectra of Rb-MS(1.0) and Rb-MS(1.5), bands different from those due to  $\text{Rb}_2\text{MoO}_4$  were detected, and the Raman bands in Rb-MS(1.0) were compatible with the bands except those due to  $\text{Rb}_2\text{MoO}_4$  in Rb-MS(1.5). We could not assign the Raman bands. However, because XANES and EXAFS spectra of Rb-MS(1.0) exhibited the same feature as those of K-MS(1.0) and Na-MS(1.0), the structure of the molybdenum species in Rb-MS(1.0) is possibly the same as that in K-MS(1.0) and Na-MS(1.0), i.e.,  $\text{Rb}_2\text{Mo}_2\text{O}_7$ , and the molybdenum species in Rb-MS(1.5) possibly are  $\text{Rb}_2\text{Mo}_2\text{O}_7$  and  $\text{Rb}_2\text{MoO}_4$ . This idea is supported by the results of the XANES analysis of Rb-MS samples. The preedge peak in the XANES spectrum of Rb-MS(1.5) was more intense than that of Rb-MS(1.0), as seen in Table 1. The results indicate that the proportion of a tetrahedral  $\text{MoO}_4$  to all the molybdenum species in Rb-MS(1.5) is higher than that in Rb-MS(1.0); i.e., the proportion of an octahedral  $\text{MoO}_6$  unit in Rb-MS(1.0) is higher than that in Rb-MS(1.5). As suggested by the results of Raman spectroscopy, by the addition of rubidium ions of molar ratio Rb/Mo > 1.0,  $\text{Rb}_2\text{MoO}_4$ , which is made up of a tetrahedral  $\text{MoO}_4$  unit, is formed, while the molybdenum species in Rb-MS(1.0) is mainly  $\text{Rb}_2\text{Mo}_2\text{O}_7$ , which is composed of a tetrahedral  $\text{MoO}_4$  and an octahedral  $\text{MoO}_6$ . Because  $\text{Rb}_2\text{MoO}_4$  is formed by the addition of rubidium ions of molar ratio Rb/Mo > 1.0, the intensity of

the preedge peak in the XANES spectrum of Rb-MS(1.5) is higher than that in Rb-MS(1.0).

In K-MS and Rb-MS samples, the change of the Raman bands by the addition of alkali ions is complex in the range of molar ratio (alkali ion/Mo) from 0 to 1.0. In the case of Na-MS samples, Na<sub>2</sub>Mo<sub>2</sub>O<sub>7</sub> is formed even by the addition of sodium ions of molar ratio Na/Mo = 0.3, while the Raman bands of K-MS(0.3) and Rb-MS(0.3) are different from those due to K<sub>2</sub>Mo<sub>2</sub>O<sub>7</sub> and Rb<sub>2</sub>Mo<sub>2</sub>O<sub>7</sub>, respectively. We expect that the structural change of the molybdenum species in Rb-MS samples by the added amounts of rubidium ions in the range of molar ratio Rb/Mo < 1.0 is similar to that in K-MS in the range of molar ratio K/Mo < 1.0, because the change in Raman bands by the added amounts of rubidium ions in Rb-MS samples resembles that in K-MS samples. Bañares et al. examined the effect of alkali ion addition to MoO<sub>3</sub>/SiO<sub>2</sub> on the structure of the molybdenum species by Raman spectroscopy.<sup>34</sup> They reported that the new compounds similar to Na<sub>2</sub>Mo<sub>2</sub>O<sub>7</sub> or K<sub>2</sub>Mo<sub>2</sub>O<sub>7</sub> were formed by the addition of alkali ions (sodium or potassium ions) of molar ratio (alkali ion/Mo) = 0.3 to MoO<sub>3</sub>/SiO<sub>2</sub>. Although their result of Na<sup>+</sup>-modified MoO<sub>3</sub>/SiO<sub>2</sub> is consistent with our result, in the case of K<sup>+</sup>-modified MoO<sub>3</sub>/SiO<sub>2</sub> samples, their result is different from ours. They prepared K<sup>+</sup>-modified MoO<sub>3</sub>/SiO<sub>2</sub> by impregnating the silica, which had been impregnated with an aqueous solution of KNO<sub>3</sub> and calcined at 873 K, with a solution of ammonium paramolybdate. This preparation method is different from ours. The difference in the preparation method of K<sup>+</sup>-modified MoO<sub>3</sub>/SiO<sub>2</sub> samples may cause the inconsistent results as for the structure of the molybdenum species. XANES spectra of Rb-MS samples showed that the proportion of a tetrahedral MoO<sub>4</sub> unit to all the molybdenum species in Rb-MS(0.5) was lower than that in Rb-MS(1.0) and Rb-MS(1.5); i.e., the proportion of an octahedral MoO<sub>6</sub> unit in Rb-MS(0.5) was higher. Therefore, the proportion of an octahedral MoO<sub>6</sub> unit in K-MS and Rb-MS in the range of molar ratio (alkali ion/Mo) < 1.0 is higher than that in K-MS and Rb-MS in the range of molar ratio (alkali ion/Mo) > 1.0. Martin et al. reported the effect of alkali ion addition to MoO<sub>3</sub>/TiO<sub>2</sub> on the surface structure.<sup>35</sup> They confirmed the presence of Rb<sub>2</sub>Mo<sub>3</sub>O<sub>10</sub>·H<sub>2</sub>O and Rb<sub>2</sub>Mo<sub>4</sub>O<sub>13</sub> in MoO<sub>3</sub>/TiO<sub>2</sub> with rubidium ions of molar ratio Rb/Mo = 0.2. The molybdenum species of both Rb<sub>2</sub>Mo<sub>3</sub>O<sub>10</sub>·H<sub>2</sub>O and Rb<sub>2</sub>Mo<sub>4</sub>O<sub>13</sub> are made up of an octahedral MoO<sub>6</sub> unit. This report is compatible with our result that the proportion of an octahedral MoO<sub>6</sub> unit in Rb-MS(0.5) is high. In K-MS and Rb-MS in the range of molar ratio (alkali ion/Mo) < 1.0, the molybdenum species such as Mo<sub>3</sub>O<sub>10</sub><sup>2-</sup> and Mo<sub>4</sub>O<sub>13</sub><sup>2-</sup> may be present on the silica support besides the (O=Mo=O)<sub>2</sub> species that is present in MS. In addition, by the curve fitting against the EXAFS of Rb-MS samples, the coordination number of Mo–Mo in Rb-MS(0.5) was estimated to be higher than that in Rb-MS(1.0) and Rb-MS(1.5). Therefore, the molybdenum species in Rb-MS and K-MS with small amounts of alkali ions is more aggregated than that in Rb-MS and K-MS with alkali ions equimolar with molybdenum ions in the samples.

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## References and Notes

- (1) Liu, H. F.; Liu, R. S.; Liew, K. Y.; Johnson, R. E.; Lunsford, J. H. *J. Am. Chem. Soc.* **1984**, *106*, 4117.
- (2) Iwasawa, Y.; Tanaka, H. *Proc. 8th Int. Congr. Catal. Berlin* **1984**, *4*, 381.
- (3) Yermakov, Y. I. *Catal. Rev.* **1976**, *14*, 78.
- (4) Cáceres, C. V.; Fierro, J. L. G.; Lázaro, J.; Agudo, A. L.; Soria, J. *J. Catal.* **1990**, *122*, 113. Rajagopal, S.; Marzari, J. A.; Miranda, R. *J. Catal.* **1995**, *151*, 192.
- (5) Iwasawa, Y. *Adv. Catal.* **1987**, *35*, 187.
- (6) Kisfaludi, G.; Leyrer, J.; Knözinger, H.; Prins, R. *J. Catal.* **1991**, *130*, 192.
- (7) Grasselli, R. K.; Suresh, D. D.; Hardman, H. F. U.S. Pat. 4778930, 1988.
- (8) MacGiolla, C. E.; Mulhall, E.; Van Hoek, R.; Hodnett, B. K. *Catal. Today* **1989**, *4*, 383.
- (9) Marcinkowska, K.; Rodrigo, L.; Kaliaguine, S.; Roberge, P. C. *Proc. 9th Int. Congr. Catal.* **1988**, *4*, 1521.
- (10) Anpo, M.; Tanahashi, I.; Kubokawa, Y. *J. Chem. Soc., Faraday Trans. 1* **1982**, *78*, 2121.
- (11) Takenaka, S.; Tanaka, T.; Funabiki, T.; Yoshida, S. *J. Chem. Soc., Faraday Trans.*, in press.
- (12) Yoshida, S.; Matsugasaki, T.; Kashiwazaki, T.; Mori, K.; Tarama, K. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 1564.
- (13) Tanaka, T.; Yamashita, H.; Tsuchitani, R.; Funabiki, T.; Yoshida, S. *J. Chem. Soc., Faraday Trans. 1* **1988**, *84*, 2987.
- (14) Rehr, J. J.; de Mustre, L.; Zabinsky, S. I.; Albers, R. C. *J. Am. Chem. Soc.* **1991**, *113*, 5135.
- (15) Jeziorowski, H.; Knözinger, H.; Grange, P.; Gajardo, P. *J. Phys. Chem.* **1980**, *84*, 1825.
- (16) Desikan, A. N.; Huang, L.; Oyama, S. T. *J. Phys. Chem.* **1991**, *95*, 10050.
- (17) Becher, H. J. Z. *Anorg. Allg. Chem.* **1981**, *474*, 63.
- (18) Buey, R. H.; Keller, O. L., Jr. *J. Chem. Phys.* **1964**, *41*, 215.
- (19) Cramer, S. P.; Hodgson, K. O.; Gillum, W. O.; Mortenson, L. E. *J. Am. Chem. Soc.* **1978**, *100*, 3398.
- (20) Desikan, A. N.; Huang, L.; Oyama, S. T. *J. Phys. Chem.* **1991**, *95*, 10050.
- (21) Liu, T.; Forissier, M.; Coudurier, G.; Védren, J. C. *J. Chem. Soc., Faraday Trans. 1* **1989**, *85*, 1607.
- (22) Iwasawa, Y.; Ogasawara, S. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 3709.
- (23) Louis, C.; Che, M.; Anpo, M. *J. Catal.* **1993**, *141*, 453.
- (24) Zhang, W.; Desikan, A.; Oyama, S. T. *J. Phys. Chem.* **1995**, *99*, 14486.
- (25) Hu, H.; Wachs, I. E.; Bare, S. R. *J. Phys. Chem.* **1995**, *99*, 10897.
- (26) Smith, M. R.; Zhang, L.; Driscoll, S. A.; Ozkan, U. S. *Catal. Lett.* **1993**, *19*, 1.
- (27) de Boer, M.; van Dillen, A.; Koningsberger, D. C.; Geus, J. W.; Vuurman, M. A.; Wachs, I. E. *J. Phys. Chem.* **1991**, *95*, 8781.
- (28) Seyedmonir, S. R.; Howe, R. F. *J. Catal.* **1988**, *110*, 216.
- (29) Williams, C. C.; Ekerdt, J. G.; Jehng, J. M.; Hardcastle, F. D.; Turek, A. M.; Wachs, I. E. *J. Phys. Chem.* **1991**, *95*, 8781.
- (30) Datta, A. K.; Ha, J. W.; Regalbutto, J. R. *J. Catal.* **1992**, *133*, 55.
- (31) Yoshida, S.; Tanaka, T.; Nishimura, Y.; Mizutani, H.; Funabiki, T. *Proc. 9th Int. Congr. Catal.* **1988**, *3*, 1473.
- (32) Stencel, J. M.; Diehl, J. R.; D'Este, L. E.; Makovsky, L. E.; Rodrigo, L.; Marcinkowska, K.; Adnot, A.; Roberge, P. C.; Kaliaguine, S. *J. Phys. Chem.* **1986**, *90*, 4739.
- (33) Martin, C.; Martin, I.; Rives, V.; Malet, P. *J. Catal.* **1994**, *147*, 465.
- (34) Bañares, M. A.; Spencer, N. D.; Jones, M. D.; Wachs, I. E. *J. Catal.* **1994**, *146*, 204.
- (35) Martin, C.; Martin, I.; Rives, V.; Malet, P. *J. Catal.* **1996**, *161*, 87.