Structures of molybdenum silica catalysts reduced by ethanol, and their relations to catalytic oxidation reactions
I. Structure changes of Mo/SiO$_2$ with gradual reduction by ethanol

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Abstract

Structural changes of silica supported molybdenum catalysts accompanied with reduction by ethanol were investigated with EXAFS and UV–VIS spectroscopies. Catalysts made from four different precursors were investigated, and it was demonstrated that the dependence on preparation method was small. Catalysts prepared by the reaction between surface hydroxide groups and organometallic complexes are called 'fixed catalysts' and some researchers assert that fixed Mo/SiO$_2$ have uniform and specific molecular-like active sites, which remains controversial. It was found that what had been proposed as characteristics of the molecular-like active sites of the fixed catalysts were merely prejudiced interpretation of a few aspects in the structural changes common to Mo/SiO$_2$ in general. At least two distinctive states existed in the course of reduction. One has IVCT (intervalence charge transfer) absorption band and corresponds to shallow reductions. The other has 2.6 Å Mo–Mo bond and average oxidation state of it was estimated to be $+5$. Structure similar to the latter was found also on alumina supported Mo catalysts and can be considered thermodynamically stable. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Molybdenum; Fixed catalysts; EXAFS; UV–VIS; Ethanol; Intervalence charge transfer (IVCT) band

1. Introduction

Usually, heterogeneous solid catalysts are comprised of many atoms under many different situations. They are sticking to and correlating with each other. This ill-defined nature makes researches of heterogeneous catalyses difficult. Frequently, different researchers give contradictory results on the same heterogeneous system, and consensus can seldom be reached from the

discrepancy. Catalysts prepared utilizing reaction between surface hydroxide groups and organometallic compounds are called fixed (or immobilized, heterogenized homogeneous) catalysts. Researchers engaged in fixed catalysts has been thinking that they can avoid the problem of heterogeneous catalysts. Unlike many diverse reactions occurring in an ordinary impregnation process, they think, a selective and clean reaction in a fixing method will produce active sites

which are molecularly well-defined and reflect incipient structure of the precursor complexes [1–4].

Fixed molybdenum monomer and dimer catalysts proposed by Iwasawa et al. are most representative example of the fixed catalysts. These authors asserted that allyl molybdenum complexes, $Mo(C_3H_5)_4$ and $Mo_2(C_3H_5)_4$, react with OH groups on silica to give well-defined monomeric [5,6] and dimeric [7–9] molybdenum sites, respectively, reflecting initial nuclearity of the precursor complexes. They also asserted that the bonds anchoring Mo to the supports were so firm that the monomeric and pair-like structures were conserved even under treatments with oxygen or hydrogen at high temperatures like 773 K (Scheme 1). Iwasawa et al. investigated reactivities of the fixed monomer and dimer catalysts and concluded that uniform and unique monomer and dimer sites were really existing.

On the other hand, fixed molybdenum catalysts are sometimes regarded as questionable. As molybdenum is an important element in many mixed oxide catalysts, supported molybdenum oxides are frequently investigated, even though they are not practically in use by them-

selves [10–29]. For Mo/SiO_2 systems, catalysts of relatively low loadings are mainly studied, because interactions between silica and supported molybdenum oxide species are weak and microcrystals of MoO_3 are inevitably formed where the loadings are high. Some researchers who were investigating low loading Mo/SiO_2 catalysts tried to make the fixed catalysts for comparison. Kaliaguine and his coworkers applied the UV–VIS and other techniques to compare the fixed Mo monomer catalysts prepared with $Mo(C_3H_5)_4$ and conventional ammonium heptamolybdate (AHM) impregnated catalysts [10–14]. Contrary to the insistence of Iwasawa et al., they concluded that there were no large differences between them. Instead significant difference was observed between samples with different hydration states. They suggested that silicomolybdic acids (SMA) were formed by the extraction of Si from supports upon exposure to atmospheric conditions. They also showed that the fixed catalysts were not so strongly fixed that water easily removed most molybdenum from the support. Research groups of Koningsberger and Wachs used catalysts prepared by many different precursors and silica, and investigated them with Raman and EXAFS spectro-

Monomer Catalysts
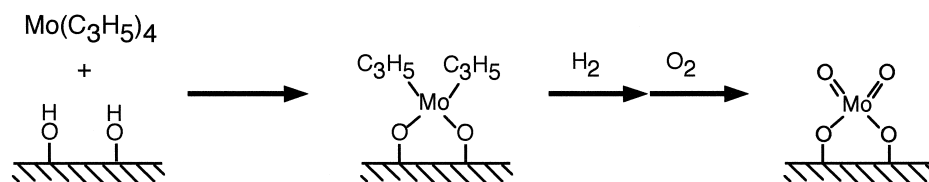
Dimer Catalysts
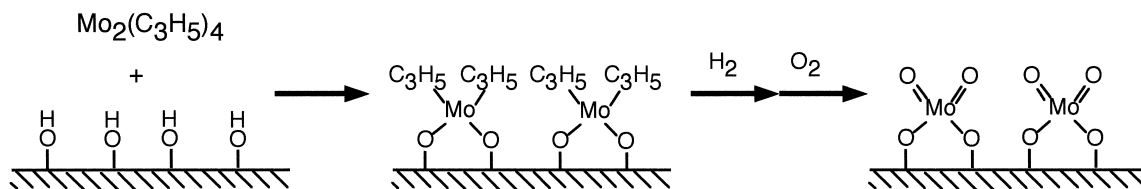
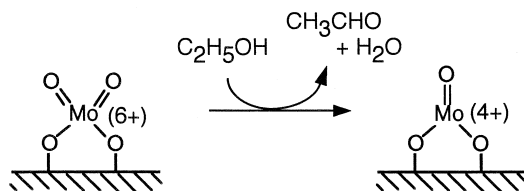Scheme 1. Schemes proposed by Iwasawa et al. for the preparation of the fixed molybdenum monomer and dimer catalysts.

scopies [15–18]. They insisted that after calcination, any molybdenum on SiO_2, including those prepared from $Mo_2(C_3H_5)_4$, would spread on the supports, and after hydration, polymolybdate-like structures were formed. They also compared the catalytic activity of these catalysts in methanol oxidation and found no significant difference. Based on these results, they claimed that the difference in catalysis of the Mo/SiO_2 with different preparation methods is not so drastic as has been imagined, and that structural changes of the catalysts under some conditions are much important.

Whether it was really possible to prepare well-defined molecular-like active sites or not is a critical problem, and thus more detailed inspection is needed. Pointing out that catalysts newly prepared by the fixing method are not special or showing that some reported properties of the fixed catalysts are not reproducible is not enough in itself, because from the view point of the fixed catalysts researchers, these refutations are resulting from insufficient skill in preparation of the catalysts [4]. It is necessary to pay more attention to evidence presented for the fixed catalysts. We have to reconsider whether the evidence really demonstrated that the active sites of the fixed catalysts were well-defined and molecular-like. And if it did not, we have to reconsider what it really was.

Structures of the fixed monomer and dimer molybdenum silica catalysts reduced by ethanol were first investigated by Iwasawa et al. [5,8,9]. They believed that reduction of both the monomer and dimer catalysts by ethanol were clean one-step reactions, in which exactly one ethanol molecule react with one active site. Oxidation state of a monomer site after calcination is $+6$ and it is reduced to $+4$ with formation of one acetaldehyde molecule per one molybdenum atom. Oxidation state of a dimer site after calcination is $+6$ and it is reduced to $+5$ with formation of 0.5 acetaldehyde molecule per one molybdenum atom (Scheme 2). To support the reaction scheme, EXAFS spectra were presented [9]. An EXAFS spectrum of the dimer
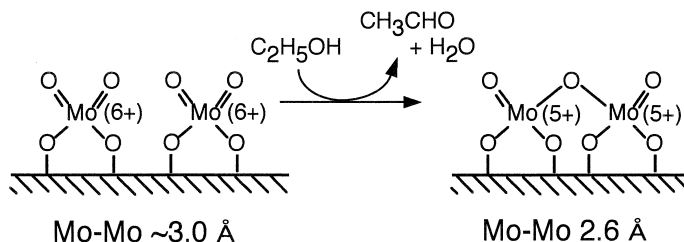
Scheme 2. Schemes proposed by Iwasawa et al. for the structural changes of the fixed molybdenum monomer and dimer catalysts with reduction by ethanol.

catalysts after calcination at 773 K was very similar to that of the monomer catalysts and it indicated no peak corresponding to Mo–Mo bonds. But when it was measured at 80 K, Mo–Mo peak was observed. From these results it was speculated that the disappearance of Mo–Mo features in the spectrum of the calcined catalysts at room temperature was thermal vibration and the molybdenum pairs remained intact though there was only a negligible peak for Mo–Mo in the spectrum. A spectrum of the catalysts reduced by ethanol at 433 K showed a peak corresponding to Mo–Mo distances about 0.26 nm. Although the coordination number was only 0.5, Iwasawa et al. assumed that this was an indication of the uniform dimer structure. EXAFS spectrum of the monomer catalysts reduced by ethanol was not issued.

In this paper, structural changes of Mo/SiO_2 catalysts accompanied with reduction by ethanol were investigated more thoroughly, aiming to give rational explanation for both the old data of the fixed catalysts and for the refutation against it.

2. Experimental

2.1. Preparation of catalysts

2.1.1. Catalysts prepared from $MoO_2(acac)_2 \cdot 2 H_2O$

$MoO_2(acac)_2 \cdot 2H_2O$ was commercial reagent (Wako–Dojindo) and was not purified further. SiO_2 (Fuji-Davison's #952 silica: 250 m^2/g) and Al_2O_3 (Nishio γ-alumina A-11: 120 m^2/g) were used as supports, and they were impregnated with methanol solution containing appropriate amount of $MoO_2(acac)_2 \cdot 2 H_2O$. Then the solvent was removed by heating in a water-bath, and dried at 373 K.

2.1.2. Catalysts prepared from $Mo_2(C_3H_5)_4$

Fuji-Davison #952 silica were used as supports. Otherwise the catalysts were prepared by the same method as the literature [7].

$Mo_2(C_3H_5)_4$ was synthesized under high purity Ar (99.9999%) and recrystallized in pentane at 193 K. SiO_2, which was pretreated by evacuation at 473 K, was mixed with pentane solution of $Mo_2(C_3H_5)_4$ at 273 K. Unreacted $Mo_2(C_3H_5)_4$ was removed by washing repeatedly with pentane, and the loadings of the catalysts were estimated from the amount of $Mo_2(C_3H_5)_4$ in the initial solution and in the wash liquid. The catalysts were dried by evacuation and sealed in U-shaped Pyrex-glass tubes. All the processes in the catalyst preparation were performed in a flow of high purity Ar or under vacuum.

2.1.3. Catalysts prepared from $[Mo_3O_2(OAc)_6(H_2O)(OH)_2] \cdot xH_2O$

$[Mo_3O_2(OAc)_6(H_2O)(OH)_2] \cdot xH_2O$ was made by literature method [30,31] with a slight modification, namely, the amount of Zn metal added as a reducing agent was decreased from 3–7 times excess to the stoichiometric value. NMR measurements in CD_3OD confirmed that there only bridging acetate ligands existed, and estimate value of hydrating water was determined with peaks in the spectra. Methanol solution of $[Mo_3O_2(OAc)_6(H_2O)(OH)_2] \cdot xH_2O$ was impregnated on #952 silica or Nishio γ-alumina. The solvent was removed by evacuation.

2.1.4. Catalysts prepared from AHM

They were prepared by impregnation of SiO_2 (Davison #952) with AHM in water solution.

The catalysts were calcined at 773 K for 1 h. In the following, these catalysts are denoted as Mo1/support, Mo2/support, Mo3/support and Mo7/support, respectively, referring to their precursors' nuclearity.

2.2. EXAFS spectroscopy [32]

Mo K-edge EXAFS spectra were measured with a Si(111) double crystal monochromator at the BL-7C station and with a Si(311) channel-cut monochromator at the BL-10B station of the

Photon Factory in the National Laboratory for High Energy Physics. Synchrotron ring energy was 2.5 GeV and the ring current was about 200–350 mA.

Samples were sealed in glass cells with Kapton (Toray–Dupont) windows without contacting air. Spectra were taken at room temperature unless otherwise mentioned. For low temperature measurement, a cryostat was used to cool samples.

Obtained spectra were analyzed by curve-fitting method with a program 'REX' provided by RIGAKU. Spectra of Mo foil (for Mo–Mo) and K_2MoO_4 (Mo–O) were used as references (of phase and amplitude functions). Fourier Transformations were performed within the range of 3.5–16 Å^{-1}, unless otherwise mentioned.

2.3. Diffuse reflectance (DR) UV–VIS spectroscopy

Samples were transferred to flat quartz cells without air exposure, and the spectra were recorded by HITACHI U3500 spectrometer
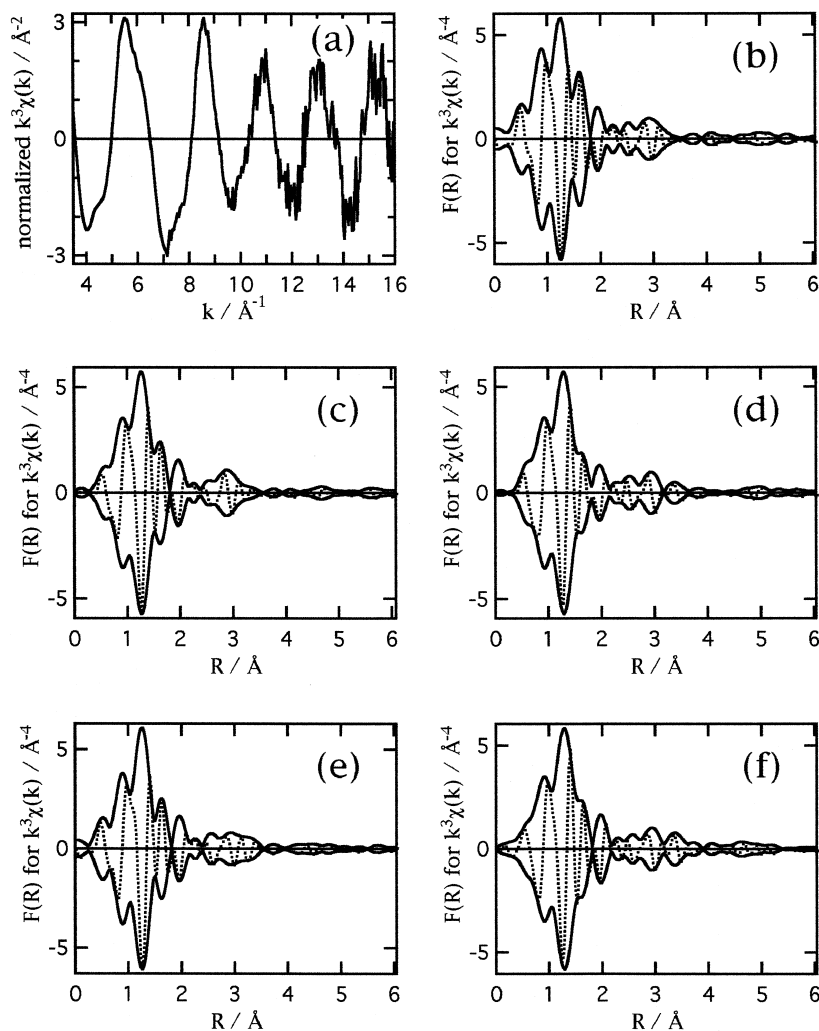
Fig. 1. Mo K-edge EXAFS of calcined molybdenum silica catalysts derived from various precursors. (a) k^3-weighted EXAFS spectrum of calcined 2.5 wt.% Mo3/SiO$_2$. Fourier transforms of k^3-weighted Mo K-edge EXAFS for calcined Mo/SiO$_2$: (b) 2.0 wt.% Mo1/SiO$_2$; (c) 2.1 wt.% Mo2/SiO$_2$; (d) 2.5 wt.% Mo3/SiO$_2$; (e) 2.0 wt.% Mo7/SiO$_2$; (f) 2.5 wt.% Mo3/SiO$_2$ measured at low temperature (ca. 100 K) (Fuji-Davison #952 silica was used as supports).

equipped with a integrating sphere. Reflection from MgO (Wako, 0.1 mm) in the same cell was used as a reference with 100% reflection. Ordinates of the graphs were logarithms of Kubelka–Munk remission function $F(R)$ [33].

3. Results

3.1. Calcined Mo / SiO$_2$

It is not necessary to comment much about calcined Mo/SiO$_2$, because the results obtained

here were basically the same as those presented by de Boer et al. [15]. Fig. 1 shows EXAFS spectra of the calcined Mo/SiO$_2$. Backscattering from Mo can be detected only in a noise level, and no significant variations can be seen among those spectra with different precursors. A spectrum obtained at lower temperature (100 K) was not so different from the one obtained at room temperature (Fig. 1(f)).

Fig. 2 shows structural change of calcined Mo/SiO$_2$ when they were exposed to air humidity. As de Boer and coworkers have pointed out, a Mo–Mo peak appeared. The Mo–Mo
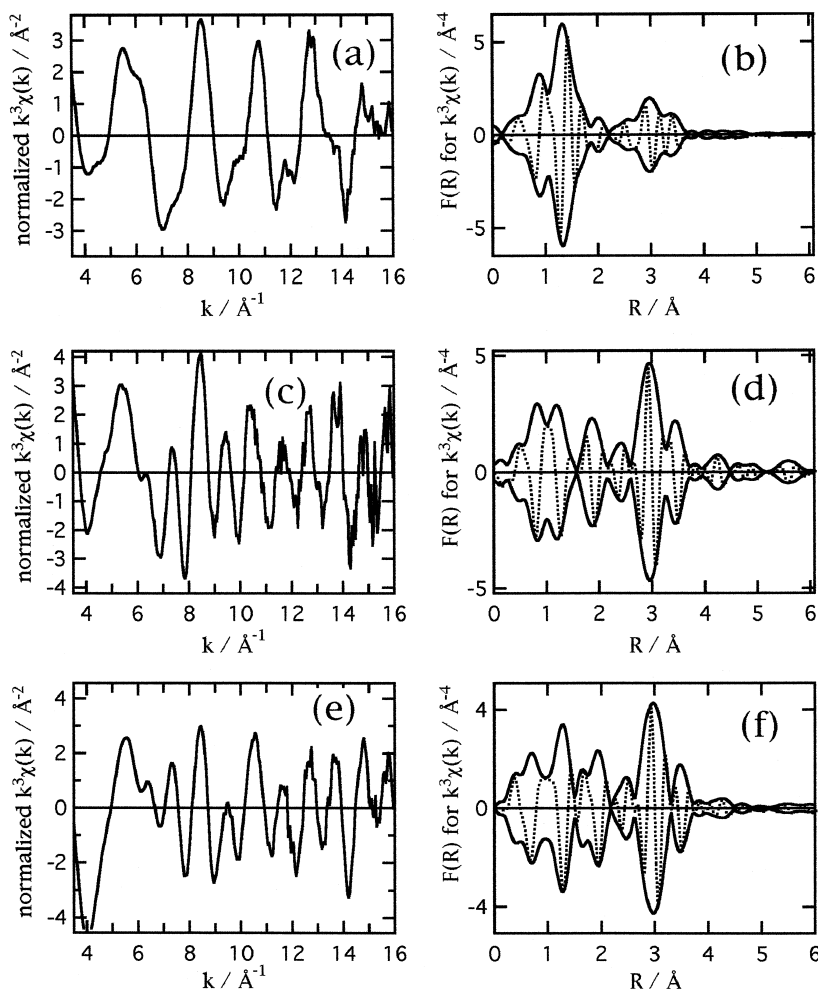
Fig. 2. Effect of hydration on Mo K-edge EXAFS of calcined Mo/SiO$_2$. k^3-weighted EXAFS spectra and their Fourier transforms for 2.1 wt.% Mo2/SiO$_2$: (a), (b) exposed over night to water vapor in a closed circulating system; (c), (d) after 5-day exposure to moist air. k^3-weighted Mo K-edge EXAFS oscillations (e), and their Fourier transform spectrum (f) of silicomolybdic acid, which were obtained with a BN diluted disk, are presented as a reference.

peak for the sample exposed to moist air for a longer time was larger than that of the one exposed for a shorter time. The position of the second shells in the spectra is similar to that of Keggin type heteropolyanion $[SiMo_{12}O_{40}]^{4-}$. The first shell in the spectrum of the more highly hydrated sample is significantly smaller than that of less hydrated samples or that of samples just after calcination.

3.2. Mo / SiO$_2$ reduced by ethanol

When calcined Mo/SiO$_2$ were exposed to ethanol at 433 K without oxygen, the molybdenum species were reduced and acetaldehyde was formed. Ethene and diethyl ether were also detected but they were formed by the dehydration of ethanol and were not related to the reduction of the catalysts (water must be also
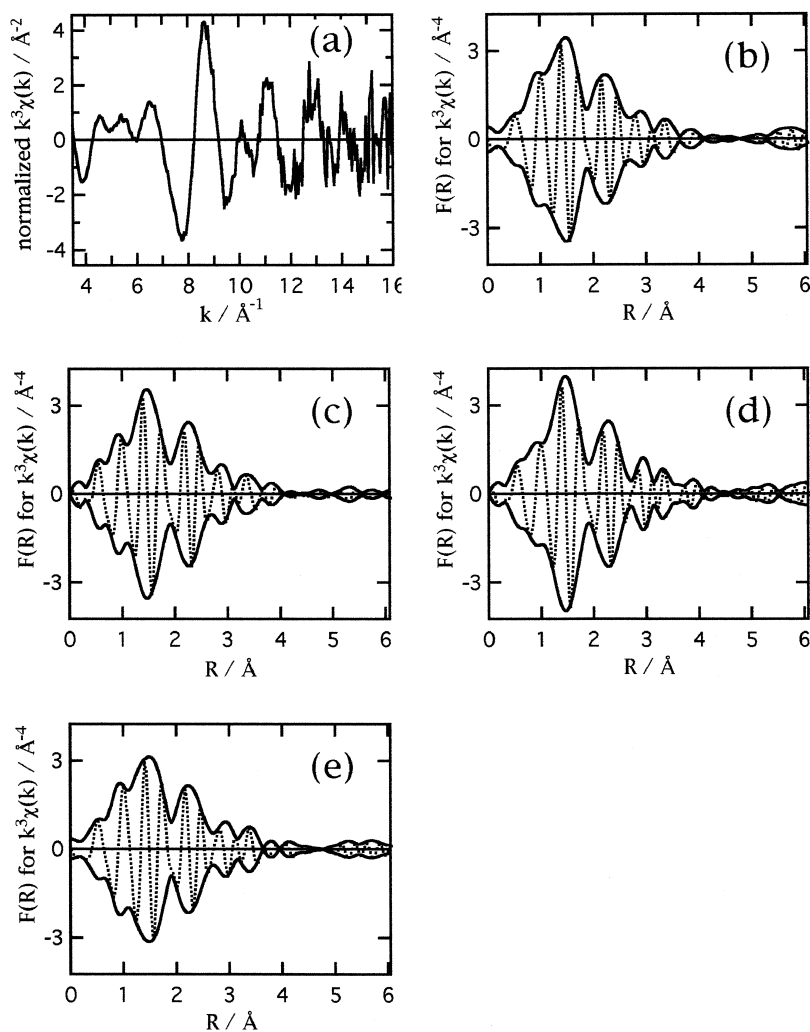
Fig. 3. Mo K-edge EXAFS spectra of molybdenum silica catalysts from various precursors reduced by ethanol at 433 K. (a) k^3-weighted EXAFS spectrum of 2.5 wt.% Mo3/SiO$_2$ reduced by ethanol at 433 K. Fourier transforms of k^3-weighted Mo K-edge EXAFS for molybdenum silica catalysts reduced by ethanol at 433 K: (b) 2.0 wt.% Mo1/SiO$_2$; (c) 2.1 wt.% Mo2/SiO$_2$; (d) 2.5 wt.% Mo3/SiO$_2$; (e) 2.0 wt.% Mo7/SiO$_2$ (Fuji-Davison #952 silica was used as supports. Initial pressures of ethanol were about 30 Torr and reaction time was 180 min).

formed but was not measured). Fig. 3 shows k^3-weighted EXAFS Fourier transformed (FT) spectra of the catalysts when the formation of acetaldehyde was virtually stopped in the reduction with ethanol at 433 K, namely at the point where structural change of the catalysts at this temperature was almost completed. The spectra of the catalysts prepared from different precursors are similar to each other and also to the spectra of the fixed dimer catalysts obtained previously in the literature under comparable conditions [9].

Fig. 4(a) shows a profile of product formation in the reaction of 2.5 wt.% $Mo3/SiO_2$ with ethanol at 513 K. When the reaction temperature was above 473 K, ethane was formed together with ethene, diethyl ether and acetaldehyde, but dihydrogen was not detected. Forma-
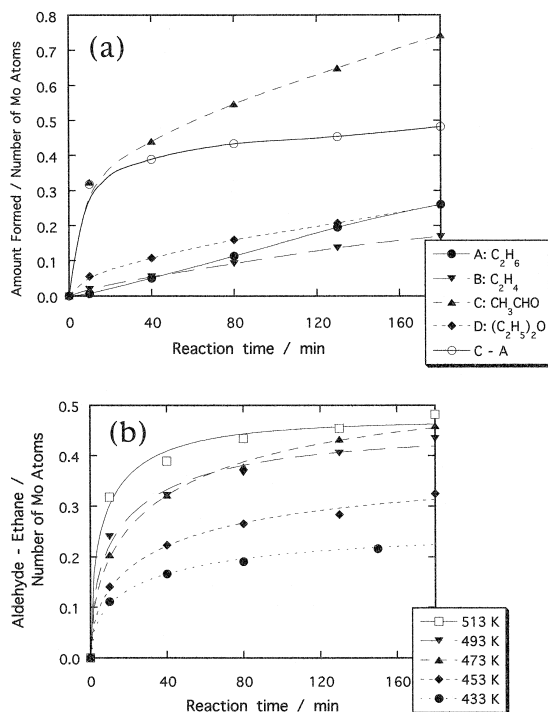

Fig. 5. Reduction temperature dependence of Mo K-edge EXAFS of Mo/SiO_2 reduced by ethanol. (a) EXAFS Fourier transformed spectra of 2.5 wt.% $Mo3/SiO_2$ reduced by ethanol in the temperature range of 403–513 K, and (b) those of 2.1 wt.% $Mo2/SiO_2$ in the range of 433–513 K. In each case, spectrum was taken after the reduction virtually had ceased. For $Mo2/SiO_2$ reduced at 513 K, a sample with prolonged contact with ethanol was also measured. Reaction time was 150 and 360 min, respectively.

Fig. 4. Estimation of acetaldehyde formation accompanied with reduction of Mo/SiO_2 by ethanol at various temperatures. (a) Products in a reaction of 2.5 wt.% $Mo3/SiO_2$ with ethanol at 513 K. (b) Net amount of acetaldehyde formation with reduction of the catalysts, estimated by substructing amount of the ethane formation from the total acetaldehyde formation (Reaction temperatures: 433–513 K).

tion of one molecule of acetaldehyde is accompanied with two electron reduction of the catalysts. Ethane may be formed by a disproportionation reaction of two molecules of ethanol into acetaldehyde and ethane (Eq. (1)), though detailed reaction mechanism is not clear

$$2C_2H_5OH \rightarrow CH_3CHO + C_2H_6 + H_2O \qquad (1)$$
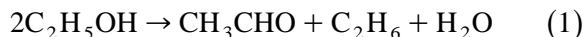
Thus, change in the average oxidation states of molybdenum species can be deduced from the amount of acetaldehyde formation minus the amount of ethane formation. Time courses of

net acetaldehyde formation accompanied by the reduction of the catalysts are plotted in Fig. 4(b) for reduction temperatures from 433 to 513 K (for temperatures lower than 473 K, the lines coincide with amounts of acetaldehyde formation, because ethane was not detectable). Each line seems to asymptotically converging to a certain value and the value depends on the reduction temperature. In other words, molybdenum species will be reduced to a certain limit for a given temperature and further reduction proceeds only slowly. Above 473 K the temperature dependence of the limit gets smaller and the molybdenum species would not be reduced lower than $+5$, which corresponds to 0.5 acetaldehyde formation per molybdenum atom. The same phenomena were observed with the catalysts from the other precursors.

EXAFS FT spectra of 2.5 wt.% $Mo3/SiO_2$ reduced by ethanol at 403–513 K are shown in

Table 1
Curve fitting results for silica supported molybdenum catalysts reduced by ethanol

Sample	B.S.	C.N.	R	ΔE_0	D.W.	R_f
Mo1/SiO$_2$ 433 K	Mo	0.4 (0.2)	2.63 (0.02)	-2 (8)	0.059 (0.019)	4.8%
	O	0.5 (0.2)	1.70 (0.02)	-1 (10)	0.054 (0.019)	
	O	1.4 (0.7)	2.01 (0.02)	-4 (8)	0.083 (0.020)	
Mo2/SiO$_2$ 433 K	Mo	0.5 (0.2)	2.63 (0.02)	-5 (7)	0.059 (0.017)	4.7%
	O	0.6 (0.3)	1.70 (0.02)	-1 (9)	0.066 (0.018)	
	O	2.4 (0.9)	1.99 (0.02)	-8 (7)	0.097 (0.015)	
Mo2/SiO$_2$ 483 K	Mo	0.8 (0.3)	2.62 (0.02)	0 (6)	0.069 (0.016)	4.2%
	O	0.4 (0.2)	1.68 (0.04)	8 (18)	0.04 (0.05)	
	O	2.8 (0.9)	2.01 (0.02)	-6 (7)	0.090 (0.015)	
Mo2/SiO$_2$ 513 K (150 min)	Mo	0.9 (0.3)	2.62 (0.02)	0 (5)	0.068 (0.012)	2.8%
	O	0.5 (0.3)	1.69 (0.03)	8 (13)	0.06 (0.03)	
	O	3.0 (0.9)	2.00 (0.02)	-6 (5)	0.093 (0.012)	
Mo2/SiO$_2$ 513 K (360 min)	Mo	0.9 (0.3)	2.61 (0.02)	-0 (5)	0.070 (0.013)	3.4%
	O	0.2 (0.2)	1.68 (0.05)	3 (26)	0.03 (0.12)	
	O	3.3 (0.9)	2.00 (0.02)	-8 (5)	0.091 (0.011)	
Mo3/SiO$_2$ 403 K	Mo	0.3 (0.2)	2.65 (0.04)	3 (13)	0.06 (0.04)	5.1%
	O	0.7 (0.2)	1.69 (0.01)	-3 (6)	0.054 (0.014)	
	O	1.1 (0.7)	2.02 (0.04)	5 (13)	0.09 (0.04)	
Mo3/SiO$_2$ 433 K	Mo	0.5 (0.2)	2.63 (0.02)	-5 (7)	0.056 (0.018)	4.0%
	O	0.5 (0.2)	1.69 (0.02)	-1 (10)	0.054 (0.023)	
	O	1.9 (0.7)	1.99 (0.02)	-8 (7)	0.085 (0.016)	
Mo3/SiO$_2$ 448 K	Mo	0.6 (0.2)	2.65 (0.02)	2 (7)	0.056 (0.017)	3.2%
	O	0.5 (0.2)	1.69 (0.02)	8 (10)	0.049 (0.020)	
	O	2.0 (0.7)	2.00 (0.02)	-5 (5)	0.079 (0.017)	
Mo3/SiO$_2$ 513 K	Mo	0.8 (0.3)	2.61 (0.02)	0 (6)	0.061 (0.015)	4.2%
	O	0.7 (0.8)	1.68 (0.04)	-2 (13)	0.08 (0.03)	
	O	4.2 (1.2)	1.97 (0.02)	-9 (5)	0.101 (0.014)	
Mo7/SiO$_2$ 433 K	Mo	0.4 (0.2)	2.63 (0.02)	-3 (8)	0.056 (0.020)	5.2%
	O	0.4 (0.2)	1.70 (0.02)	-1 (11)	0.047 (0.023)	
	O	1.1 (0.6)	2.01 (0.02)	-4 (9)	0.076 (0.020)	

B.S.: backscatterer.
C.N.: coordination number.
R: distance/Å.
ΔE_0: energy correction/eV.
D.W.: Debye–Waller factor/Å^2.
R_f: R-factor.
Fourier transformation range: 3.5–16 Å^{-1}.
Inverse Fourier transformation range: 1.03–2.67 $\pm$ 0.05 Å.
Numbers in parentheses are errors. They represent the maximum ambiguities of the parameters not to make R_f value twice at the local minima.
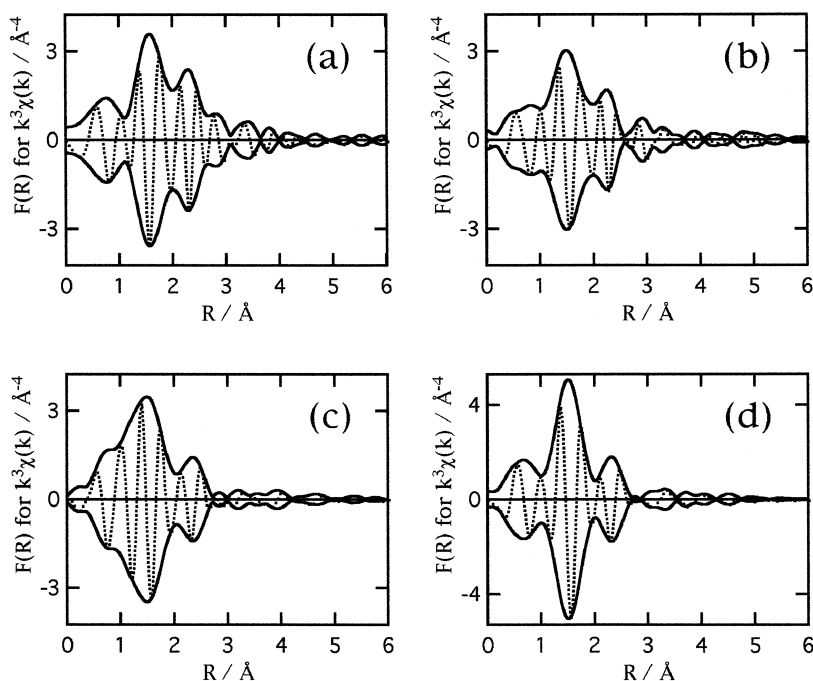
Fig. 6. Mo–Mo EXAFS peaks of reduced molybdenum oxides on supports. Fourier transforms of k^3-weighted Mo K-edge EXAFS for the following: (a) 2.5 wt.% Mo3/SiO$_2$ reduced by methanol at 513 K; (b) 2.5 wt.% Mo3/SiO$_2$ reduced by H$_2$ at 773 K (average oxidation state of the latter was estimated to be ca. +5 with H$_2$ consumption); (c) 2.5 wt.% Mo3/Al$_2$O$_3$ reduced by ethanol at 513 K; (d) 9.7 wt.% Mo1/Al$_2$O$_3$ reduced by ethanol at 513 K. Fourier transformation range for 2.5 wt.% Mo3/Al$_2$O$_3$ was 3.5–12.9 Å^{-1}.

Fig. 5(a), and those of 2.1 wt.% Mo2/SiO$_2$ reduced at 433–513 K are in Fig. 5(b). Again, the catalysts derived from different precursors show quite small differences. At first sight of the spectra, it can be recognized that the Fourier components mainly comprise of two distinct shells. The two peaks grow as the reduction temperature is raised from 433 up to 473 K, but the positions of the peaks scarcely change. Over 473 K, changes in the spectra are less signifi-

Table 2
Curve fitting results for silica supported molybdenum catalysts reduced by methanol and H$_2$

Sample	B.S.	C.N.	R	ΔE_0	D.W.	R_f
Mo3/SiO$_2$ reduced by MeOH	Mo	0.7 (0.3)	2.63 (0.02)	−1 (7)	0.070 (0.017)	4.2%
	O	0.4 (0.2)	1.67 (0.03)	−1 (15)	0.05 (0.04)	
	O	2.4 (0.7)	2.01 (0.02)	−5 (6)	0.086 (0.013)	
Mo3/SiO$_2$ reduced by H$_2$	Mo	0.4 (0.2)	2.62 (0.02)	−6 (8)	0.07 (0.02)	4.1%
	O	0.2 (0.1)	1.65 (0.04)	−3 (18)	0.05 (0.05)	
	O	2.2 (0.7)	2.00 (0.02)	−8 (6)	0.095 (0.013)	

B.S.: backscatterer.
C.N.: coordination number.
R: distance/Å.
ΔE_0: energy correction/eV.
D.W.: Debye–Waller factor/Å^2.
R_f: R-factor.
Fourier transformation range: 3.5–16 Å^{-1}.
Inverse Fourier transformation range: 1.0–2.67 Å (MeOH) and 1.0–2.6 Å (H$_2$).

cant, as synchronizing with the oxidation level change of the molybdenum which can be seen in Fig. 4(b).

The EXAFS curve fitting results for the reduced Mo/SiO_2 are summarized in Table 1.

Fig. 6(a) shows EXAFS FT spectrum of 2.5 wt.% $Mo3/SiO_2$ reduced with methanol of an initial pressure of 40 Torr at 513 K 360 min. Fig. 6(b) shows EXAFS FT spectrum of 2.5 wt.% $Mo3/SiO_2$ reduced by dihydrogen at 773 K 180 min. The spectra for these two types of catalysts contain the same characteristic Mo–Mo peaks. Curve fitting results for them are summarized in Table 2.

Structural change of molybdenum catalysts supported on alumina was also compared. Ethanol of initial pressure 40 Torr was introduced to 2.5 wt.% $Mo3/Al_2O_3$ at 513 K. Alumina supports catalyze competing dehydration reaction so efficiently that ethanol in a closed circular system will consumed rapidly. So reaction gas was evacuated and ethanol was added in each 30 min. Spectrum obtained after 90 min of reduction are shown in Fig. 6(c). Spectrum of 9.7 wt.% $Mo1/Al_2O_3$ treated in the same way as above were shown in Fig. 6(d). Curve fitting parameters for them are listed on Table 3. Mo–Mo peaks were also observed but the EXAFS oscillation amplitudes were smaller than those of corresponding silica supported catalysts because of larger Debye–Waller-like factors of the
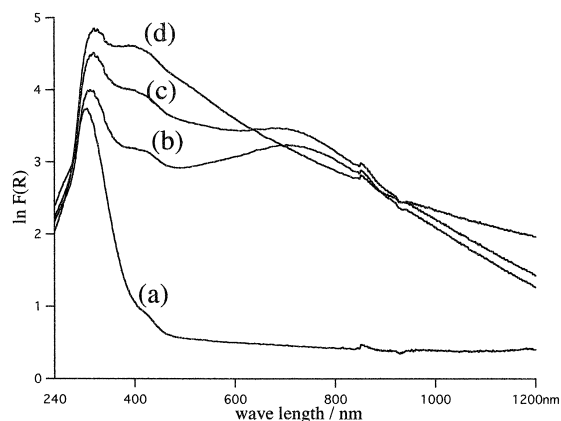

Fig. 7. UV–VIS spectra of 0.6 wt.% $Mo1/SiO_2$: (a) with ethanol adsorbed at room temperature; (b) reduced by ca. 20 Torr of ethanol at 433 K, 10 min; (c) at 433 K, 60 min; (d) at 513 K, 120 min. Distortions near 850 nm were due to incompleteness of smoothing discontinuities accompanied with exchange of detectors.

Mo–Mo bonds in the molybdenum species supported on alumina.

In Fig. 7 the UV–VIS spectra of a low loading 0.6 wt.% $Mo1/SiO_2$ are presented. Here, the low loading catalysts were chosen because those of higher loadings had so strong absorption that reflection from them were very weak. Though the low loading catalyst may have fewer active components as will be described in the part II, the feature of them was the same as that of higher loading one (UV–VIS spectra of 2.0 wt.% $Mo1/SiO_2$ were basically the same as the 0.6 wt.% ones but contained

Table 3

Curve fitting results for alumina supported molybdenum catalysts reduced by ethanol

Sample	B.S.	C.N.	R	ΔE_0	D.W.	R_f
$Mo3/Al_2O_3$ 2.5 wt.%	Mo	0.8 (0.3)	2.66 (0.02)	2 (6)	0.094 (0.016)	1.6%
	O	0.5 (0.1)	1.67 (0.01)	−6 (6)	0.050 (0.013)	
	O	1.3 (0.2)	2.03 (0.01)	−4 (4)	0.067 (0.009)	
$Mo1/Al_2O_3$ 9.7 wt.%	Mo	1.0 (0.4)	2.63 (0.02)	4 (5)	0.098 (0.016)	1.3%
	O	0.4 (0.2)	1.66 (0.02)	−0 (9)	0.06 (0.02)	
	O	2.9 (0.4)	2.01 (0.01)	−7 (3)	0.086 (0.006)	

B.S.: backscatterer.
C.N.: coordination number.
R: distance/Å.
ΔE_0: energy correction/eV.
D.W.: Debye–Waller factor/$Å^2$.
R_f: R-factor.
Fourier transformation range: 3.5–12.9 (2.5 wt.%) and 3.4–16.0 (9.7 wt.%) $Å^{-1}$.
Inverse Fourier transformation range: 0.98–2.67 Å.

considerable uncertainties). The spectra of calcined catalysts had peaks near 300 nm and they may correspond to LMCT from oxygen to molybdenum. For the catalysts reduced at 433 K, a strong absorption appears at about 750 nm, which is a well known absorption band of molybdenum blue due to intervalence charge transfer (IVCT) between Mo(5 +) and Mo(6 +) centers [21,34–36]. Evolution of the absorption of the catalysts in the course of reduction did not progress in a linear way. IVCT band grew at the first stage, but as the catalysts were reduced further broad absorption expanding from 400 nm into the visible region got stronger and finally the IVCT band slightly diminished.

4. Discussion

4.1. Calcined catalysts

It was confirmed in the present experiments that no Mo–Mo EXAFS peak is observable for calcined low loading Mo/SiO$_2$, and that is totally in line with the results of researchers who claim that the fixed catalysts are not correct. It is also not contradict with the results for the fixed monomer and dimer catalysts by Iwasawa et al., as far as spectra taken at room temperature are concerned. Only the Mo–Mo peak observed at low temperature for the dimer catalysts was inconsistent, because it did not appear this time. To get a collective view, rational explanation for the appearance of the Mo–Mo peak is inevitable. So the peak will be considered thoroughly in the following.

It should be underscored that position of the Mo–Mo peak for the fixed dimer catalysts is remarkably close to that of hydrated Mo/SiO$_2$ catalysts.

Effect of adsorbed water on the structures of Mo/SiO$_2$ has been investigated by EXAFS [15], UV–VIS spectroscopy [11], and ^{29}Si NMR [37]. Among them the NMR result is most eminent because whereas other method could suggest only the formation of polymolybdate-like structure in the presence of adsorbed water, NMR

could present that Si was incorporated into the position which is similar to the tetrahedral site in [SiMo$_{12}$O$_{40}$]$^{4-}$. De Boer et al. had tried EXAFS curve fitting method with hydrated structure of molybdenum silica catalysts though they did not commented what type of molybdate it was. They might have thought that it is beyond the limitation of this spectroscopy. SMA's EXAFS FT spectrum has two characteristic shells. One is a very vague Mo–O shell which may be caused by interference of signals from different bond lengths [38]. The other is a Mo–Mo shell near 3.0 Å which is accompanied with a smaller peak at 3.5 Å. Both of the characteristics were found also in the spectrum of the Mo/SiO$_2$ catalysts exposed to moist air for a long time (Fig. 2(d)), and it is quite reasonable to consider the structure of molybdenum under that condition to be similar to SMA. By model calculation using the Feff 6 program [39] and X-ray crystal structure parameters of a Keggin anion [40], it was realized that the shape of the second shell is mainly derived from the overlapped backscatterings of edge- and corner-sharing molybdenum atoms getting back directly or with a reflection at an oxygen atom. Such an overlap of many comparably weighted EXAFS oscillations with different path length usually gives a spectrum difficult to analyze with curve fitting methods. It is noteworthy that when the larger peak of the second shell was inverse Fourier transformed and curve fitting was done with the oscillations, they could be fitted with only one Mo backscatterer model quite well, though the parameter of coordination number was liable to get too small for the real Keggin structure. The peak alters its position nearly 0.1 Å with different choice of FT filtering range, and the variation is quite larger than a peak from a single distance. That is because of the interference of many contributions [41]. Mo/SiO$_2$ which was not so completely hydrated (Fig. 2(b)) had a second shell almost at the same position as SMA. There were some differences in the dependence on different choice of FT filtering range. Whether there existed a

structure other than SMA or it was a result of interference between signal from SMA and signal from molybdenum remaining in different states is not clear. Because the distance is similar to SMA, the structure of hydrated Mo/SiO_2 must contain edge-shared Mo coordination spheres in any way.

With the same choice of FT range, the Mo–Mo peak in the partly hydrated Mo/SiO_2 coincided well with that of the fixed dimer's peak. So it is highly probable that the leakage of the cell had led to the partial construction of polymolybdate-like structure in the low temperature measurement by Iwasawa et al., and the second shell peak was mistaken as an indication of paired molybdenum ions fixed on the support.

The structure of the dimer catalysts proposed by Iwasawa et al. was comprised of two molybdenum atoms which were nearby but with no oxygen ion to bind them together. They thought that random and independent thermal vibration of the two molybdenum atoms caused the large Debye–Waller-like factor. But this model is not realistic in itself. Considering simple geometry with Mo–O distances of about 1.7 Å and repulsion between two $Mo(6+)$ ions, the structure proposed by Iwasawa et al. is unfeasible [36]. If two molybdenum oxo species were placed without sharing any oxygen ligands, the distance between the two molybdenum should be much larger than the value of 3.3 Å (Iwasawa et al. reported the distance was 3.0 Å, but it might have been a local minimum of the curve fitting). Even in $MgMo_2O_7$, which has $Mo_2O_7^{2-}$ anion where two MoO_4 tetrahedra share a vertex, the shortest distance between Mo–Mo is 3.685 Å [42]. The observed Mo–Mo distance is attributed to that of edge-shared $Mo(6+)$ coordination polyhedra. It is hard to think of a thermal Debye–Waller-like factor so large as to obscure Mo–Mo signal with such a strong interaction.

De Boer et al. [15] also argued with a spectrum of calcined Mo/SiO_2 without contacting air humidity that molybdenum species were spread over the silica support as monomers because there no Mo–Mo derived oscillations in

the EXAFS were observed. The present experiments support the absence of the peak, but it cannot be said unambiguously that molybdenum were really spread monomerically. If there were large static disorders around molybdenum, many slightly different Mo–Mo distances can result in destructive interference of the EXAFS waves. Peak of heteropoly anions were often much smaller than expected from the real number of near atoms, and for molybdenum oxo species on amorphous supports, static disorder must be much larger. It was observed that EXAFS oscillation of silica supported zirconia contained no clear Zr–Zr peaks whereas the loading was corresponding to monolayer zirconium oxide [43].

4.2. Reduced catalysts

The 2.6 Å Mo–Mo bond observed in the fixed dimer catalysts was proposed as the most distinctive feature for unique and well-defined dimeric active sites [9]. In the present experiments, it was shown that Mo/SiO_2 prepared by different methods also had the same characteristic, and it conclusively denies uniqueness of the fixed catalysts. Now we have to reinterpret the experimental results as representing some structures generally appearing on Mo/SiO_2 with comparable loadings and conditions.

Iwasawa et al. thought that formation of the 2.6 Å Mo–Mo bond was direct transformation of the $Mo(6+)–Mo(6+)$ pair into $Mo(5+)–Mo(5+)$ dimer, but it is groundless. Time courses of acetaldehyde formation in Fig. 4 and EXAFS spectra in Fig. 5 suggest that the structure was made with more complicated processes rather than a simple one step reduction. From some graphs presented by Iwasawa et al. themselves, it is confirmed that at 423 K or 436 K, the old monomer [5] and the dimer catalysts [8] were also not reduced by ethanol to average oxidation state $+5$, though these authors did not seem to be aware of it. UV–VIS spectra in Fig. 7 also support that. At least two states of reduced molybdenum oxo species should be

considered to understand the structural changes, which are called in the present report the blue state (IVCT absorption at 750 nm) and the brown state (absorption at 400 nm), respectively, from their colors.

The dark brown color which appears on the catalysts reduced at higher temperatures may be due to an excitation to the energy levels of the 2.6 Å Mo–Mo bonds. Simple d-electron transitions of isolated molybdenum should have much weaker absorbance. This bond length and the coordination number as large as 0.8 are uncommon in bulk molybdenum oxides, and it is not attributable to known compounds. In the shear structures of the partially reduced molybdenum oxides and in the so-called molybdenum bronzes, d-electrons were delocalized and do not form such a strong metal–metal bond as short as 2.6 Å. In $Mo_{17}O_{47}$, Mo–Mo distance of 2.63 Å can be found but average oxidation state of the solid is much higher than $+5$ and the contribution from the short Mo–Mo bond to the whole structure is much smaller [44]. MoO_2 has a rutile-like structure in which a double-bond-like interaction keeps two Mo(4+) atoms at 2.51 Å (coordination number 1). So it is incapable to draw a distinct picture of the brown state structure from the EXAFS data. The bond length 2.6 Å can be thought of as that of a single bond. But even when Mo–Mo single bond is assumed a structure containing triangular $Mo(4+)_3$ unit, for example, may also be possible besides $Mo(5+)_2$ dimer structure. The structural units containing 2.6 Å Mo–Mo bond can exist as isolated ones dispersed on the silica supports, or they may be a part of more aggregated polyanion or particles. For example, aggregation of Mo(5+) oxochloride alkoxide is thought to proceed via polymerization of dimeric units with a Mo–Mo bond [45]. Whether the units are isolated or aggregated cannot be determined only by EXAFS.

There must be some interaction between the supports and the molybdenum species with the Mo–Mo bonds. Quite larger Debye–Waller-like factors of the Mo–Mo bonds in the alumina supported catalysts may be derived from interaction stronger than that of Mo/SiO_2 catalysts. This does not imply that dispersed species are more likely, because if the aggregates were sufficiently small, the interactions with the supports may alter the structures in the aggregates significantly.

The large Debye–Waller factors remind us of the EXAFS measurements of reduced Mo–Mg mixed oxides reported by Aritani et al. [46]. Mixed oxides containing low molybdenum proportions reduced by dihydrogen showed a second shell in Mo K-edge EXAFS FT spectra at similar position as in the present experiments with Mo/SiO_2 and Mo/Al_2O_3. They concluded using the curve fitting method that the peaks were from Mo–Mg bonds. It is also possible to use Mo–Al model for the EXAFS spectra of the Mo/Al_2O_3 catalysts, for example, as shown in Table 4. Mg and Al have similar backscattering properties because atomic numbers of them only differ by one. Magnesium oxide supports are also suggested to have strong interactions with supported materials. It may be possible that the strong interaction caused large Debye–Waller-like factors to make large k part of the Mo–Mo EXAFS oscillation to diminish and render the shape of overall amplitude resembling that of lighter elements. The same situation may be concluded in this experiment because no attractive interactions can be expected between Mo and Mg or Al to get them as close to 2.6 Å.

To summarize, the brown state of the reduced molybdenum species may be considered to have molybdenum units with the 2.6 Å Mo–Mo bond(s), but the extent of aggregation of the units is not clear. They have some interactions with supports and are so stable as to be formed with a variety of oxide supports.

The strong IVCT absorption is responsible for the blue state of reduced molybdenum species. This kind of absorption is associated with electron transfer from Mo(5+) to Mo(6+). The structure may be similar to those of other molybdenum compounds which exhibit

Table 4

Curve fitting results using Mo–Al parameters for alumina supported molybdenum catalysts reduced by ethanol

Sample	B.S.	C.N.	R	ΔE_0	D.W.	R_f
Mo3/Al$_2$O$_3$ 2.5 wt.%	Al	0.7 (0.4)	2.70 (0.03)	8 (8)	0.05 (0.05)	3.0%
	O	1.0 (0.3)	1.68 (0.02)	−6 (7)	0.080 (0.016)	
	O	2.1 (0.7)	2.02 (0.02)	−4 (4)	0.082 (0.016)	
Mo1/Al$_2$O$_3$ 9.7 wt.%	Al	1.0 (0.6)	2.68 (0.04)	8 (7)	0.07 (0.03)	2.5%
	O	0.4 (0.2)	1.67 (0.03)	−0 (11)	0.06 (0.03)	
	O	3.3 (0.7)	2.00 (0.01)	−7 (4)	0.093 (0.010)	

B.S.: backscatterer.
C.N.: coordination number.
R: distance/Å.
ΔE_0: energy correction/eV.
D.W.: Debye–Waller factor/Å^2.
R_f: R-factor.
Fourier transformation range: 3.5–12.9 (2.5 wt.%) and 3.4–16.0 (9.7 wt.%) Å^{-1}.
Inverse Fourier transformation range: 0.98–2.67 (2.5 wt.%) and 1.01–2.67 (9.7 wt.%).

IVCT absorption. So, the structure may be suggested as aggregates of at least several molybdenum atoms, only a part of which are reduced to oxidation state +5.

Distances between molybdenum atoms in the aggregates must be not as short as 2.6 Å. The 2.6 Å bonds in the brown state means considerable mixing of the energy levels of the molybdenum atoms while there must be localized orbitals which can be considered as separate potential wells for IVCT to occur. It is known from X-ray crystallography that polyoxomolybdates which is reduced to the oxidation state with IVCT absorption have almost the same atomic positions as those of non-reduced anions [34]. On the other hand, molybdenum atoms in the aggregates must not be so far apart in order to make the charge transfer possible. Usually, there are bridging oxygen ions in aggregates which exhibit IVCT absorption. Thus, the distance between molybdenum atoms of Mo/SiO$_2$ in the blue state may be distributed around 3.5 Å which is typical for the distances of molybdenum atoms in oxidized polymeric molybdenum oxo compounds. But even in the EXAFS spectra of the catalysts reduced by ethanol at 433 K where the proportion of the brown state molybdenum species should be about 50% of the maximum, no other Mo–Mo bonds could be seen.

One possibility to explain the absence of EXAFS Mo–Mo peaks for the blue state is that proportion of molybdenum species in the blue state was small. Then the rest of the molybdenum might be dispersed monomerically and their contributions to EXAFS had no Mo–Mo characters. They were likely to be at oxidation state +6 because if they were monomeric Mo(+5)s, they should have exhibited EPR signals which were not observed in the previous reports of the reduced fixed Mo/SiO$_2$, and oxidation states lower than +5 were unlikely considering the limited amount of acetaldehyde formation with the reduction of the catalysts by ethanol. This assumption has one difficulty because IVCT band which rivals LMCT peak is too strong for minor impurities in the catalysts (relative intensities of IVCT to LMCT absorption in the case of Keggin type polyanion with reduction of one electron per one anion was reported to be roughly 1:5 [35]. UV–VIS DRS of amorphous molybdenum blue was shown by Che et al. in which LMCT and IVCT absorption have nearly the same intensities [21]). If the UV–VIS spectra represents correct absorption strength, the situation was that the proportion of molybdenum in the blue state was large though the Mo–Mo distance of them were not observable in EXAFS measurements. So second possibility to explain the spectra of Mo/SiO$_2$ reduced by

ethanol at 433 K is that extremely large static disorders in the aggregates of molybdenum in the blue state. Third possibility is a hybrid of the first and the second, namely that Mo–Mo bonds other than the 2.6 Å bond could not be observed because some parts of the molybdenum were dispersed and the other large part were aggregates with large disorder. The third explanation is most likely, considering effect of loadings on the catalytic activities which will be discussed in the following paper.

Whether the aggregates were already formed in the calcined catalysts or they were formed by contact with ethanol is not clear.

The reduction pathway of Mo/SiO_2 is also not clear. It may be an analog of those for polyoxoanions if the blue state plays a major role in the process as in the second and third assumptions. In the first stage of reduction of many polymolybdates, cyclic voltammetries showed several reversible one- or two-electron reduction sequences, which yield mixed-valence species with IVCT absorption [47]. Further reductions often alter the structures of polyanions more markedly. The most interesting among them is a brown-colored reduced Keggin-type tungstate $[SiW_3^{IV}W_9^{VI}O_{40}H_6]^{4-}$ [48]. In the reduced anion, six localized d-electrons make metal–metal bonds between three $W(4+)$s to form a structure similar to triangular $[W_3^{IV}O_4]^{4+}$ aqua cation. Further reduction is considered to result in the formation of more $W(4+)_3$ units inside the anions. In the case of Mo/SiO_2 catalysts structural changes with reduction might be different in detail as metal atoms are molybdenum and the final average oxidation state is $+5$, but similar scheme is possible to explain the experimental results, namely formation of some structural units with metal–metal bond from IVCT mixed-valence states by acquisition of more electrons. Proportion of the brown state units in the blue state aggregates may be determined by the reduction conditions. There was no firm evidence to eliminate the possibilities of direct formation of the brown state species from the oxidized state but it is harder to explain the

behavior of the catalysts on different temperature reductions.

Blue and dark brown colors of the fixed molybdenum monomer catalysts were observed by Iwasawa et al. and they were not aware that those absorption were too intense for d–d absorption of monomerically dispersed Mo oxo species [5,6,8]. They also reported some graphs from which the fixed monomer and dimer catalysts were not reduced by ethanol to average oxidation state $+5$, though they should be reduced to $+4$ and $+5$, respectively, according to their assumption [5,8]. Considering these results, also the fixed catalysts prepared by Iwasawa et al. were not special. These authors proposed much evidence for the monomer and dimer catalysts. For example, H_2 and O_2 uptake values of the fixed monomer and dimer catalysts coincided completely to the stoichiometric values for non-existing monomers and dimers. Why it happened like that is beyond explanation.

5. Conclusions

In this investigation, the dispute about the fixed molybdenum catalysts was settled by demonstrating that many features proposed for the unique fixed monomer and dimer catalysts can be also observed in Mo/SiO_2 catalysts prepared by other methods. It was also demonstrated that interpreting those features as evidence for uniform monomeric or dimeric sites is full of inconsistencies.

Reduction of Mo/SiO_2 catalysts by ethanol is a complicated process in which at least two distinctive structures are involved rather than a simple one-step reaction proposed for the fixed monomer and dimer catalysts.

Acknowledgements

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