Structures of molybdenum silica catalysts reduced by ethanol, and their relations to catalytic oxidation reactions
II. Redox mechanism for catalytic oxidation of ethanol and methanol

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Abstract

Catalytic oxidation reactions of ethanol and methanol over Mo/SiO_2 were investigated. It was found that the dependence of the activities on the preparation method was small. The catalyses were suggested to proceed with redox cycles. Using structural information obtained in the part I, oxidation states responsible for the redox cycle were estimated. Aggregates which showed IVCT absorption were suggested to be candidates for the redox cycle. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Molybdenum; Fixed catalysts; EXAFS; UV–VIS; Ethanol oxidation; Methanol oxidation; Redox mechanism; Intervalence charge transfer (IVCT)

1. Introduction

Catalysts prepared by reaction between organometallic complexes and oxide supports are called fixed catalysts and some researchers believe that the fixed catalysts have molecularly well-defined active sites. Unlike ordinary solid catalysts with variety of non-uniform sites, they thought, fixed catalysts had uniform active sites and made it possible to elucidate the reaction mechanism and the origin of catalysis [1–4].

Iwasawa et al. investigated ethanol oxidation over fixed molybdenum monomer and dimer catalysts [5–7]. Redox cycle between Mo(6 +) and Mo(4 +) monomer structures and that be-

tween Mo(6 +)–Mo(6 +) and Mo(5 +)–Mo(5 +) dimer structures were proposed as reaction mechanisms for ethanol oxidation over the monomer and the dimer catalysts, respectively. With EXAFS spectra of the dimer catalysts after calcination and after reduction by ethanol, they asserted that they succeeded in visualizing dynamic structural changes of active sites during the catalysis.

They asserted that the unique and uniform structures of the fixed catalysts were valid, because ethanol oxidation can be rationalized by the redox mechanisms based on the monomer and the dimer active sites. But the structure models for the monomer and dimer catalysts

were rejected in the part I. Reduction of Mo/SiO_2 by ethanol was proven to be a complicated process rather than the simple one-step reactions proposed for the fixed catalysts. Also the structures of calcined or reduced Mo/SiO_2 were shown to be not dependent on the preparation method. Reaction mechanisms based on the uniform monomer and dimer active sites thus have to be reconsidered.

In the present study, mechanism for ethanol and methanol oxidation over Mo/SiO_2 in general is proposed.

2. Experimental

2.1. Preparation of catalysts

Mo/SiO_2 were prepared from $MoO_2(acac)_2$ $\cdot 2H_2O$, $Mo_2(C_3H_5)_4$, $[Mo_3O_2(OAc)_6(H_2O)(OH)_2] \cdot xH_2O$, AHM (ammonium heptamolybdate) in the same way as described in the part I. In the following, these catalysts are denoted as $Mo1/SiO_2$, $Mo2/SiO_2$, $Mo3/SiO_2$ and $Mo7/SiO_2$, respectively.

SiO_2 used as supports were Fuji-Davison's No. 952 silica: 250 m^2/g (for Mo1, Mo2, Mo3, Mo7), Fuji-Silysia's Cariact Q-10: 300 m^2/g (for Mo1), Aerosil 300 by Nippon Aerosil: 300 m^2/g (for Mo1), and Snowtex-O by Nissan Kagaku: 285 m^2/g (for Mo3).

2.2. EXAFS and diffuse reflectance UV–VIS spectroscopies

EXAFS and DR UV–VIS spectroscopies were taken in the same way as described in the part I.

2.3. Alcohol oxidation reactions

Prior to each reaction, catalysts were calcined under ca. 70 Torr (1 Torr = 133 Pa) of O_2 at 773 K in a closed circulating system (dead volume ca. 150 cm^3), and were evacuated at the same temperature and cooled to reaction temperature. About 50 mg catalysts were used for 2 wt.% loading samples. Ethanol or methanol were purified by freeze–thaw method and dried with Molecular Sieve 5A.

3. Results

3.1. Mo/SiO_2 during catalytic ethanol oxidation

Fig. 1 shows a typical reaction profile of catalytic ethanol oxidation on the silica supported molybdenum oxide catalysts. The main product was acetaldehyde. Diethyl ether was the second, but selectivity for it was less than 10%. Production of ethene was about 1%, and neglected in the plot. No ethyl acetate or dihydrogen could be detected.

To investigate precursor effect on the selectivities, 2.0 wt.% $Mo1/SiO_2$, 2.1 wt.% $Mo2/SiO_2$, 2.5 wt.% $Mo3/SiO_2$, and 2.0 wt.% $Mo7/SiO_2$ with Fuji-Davison No. 952 silica as supports were compared. No differences were found among them. Mo3 with Snowtex silica, Mo1 and Mo7 with Aerosil 300 gave almost the same results except that selectivities of the catalysts supported on Aerosil 300 for diethyl ether
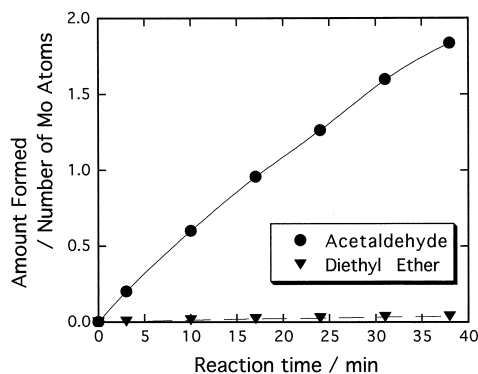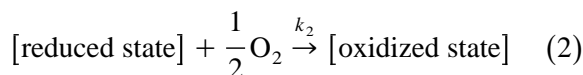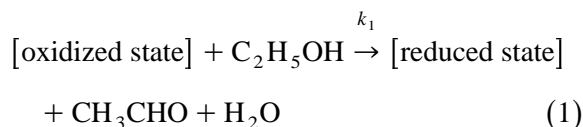

Fig. 1. Typical reaction profile of catalytic ethanol oxidation over Mo/SiO_2. An amount of 2.5 wt.% Mo3/Fuji-Davison No. 952 silica was used. Reaction temperature was 433 K. Partial pressure of ethanol and oxygen were 8 and 42 Torr, respectively.

were about two times greater than those of the rests. Aerosil 300 silica itself had no catalytic activities for the dehydration of ethanol.

As described by Iwasawa and Tanaka [5], if the acetaldehyde formation would proceed with a redox mechanism such as described by the Eqs. (1) and (2), a steady state rate equation for the reaction would be given by the Eq. (3).

$$[\text{oxidized state}] + C_2H_5OH \xrightarrow{k_1} [\text{reduced state}]$$

$$+ CH_3CHO + H_2O \qquad (1)$$

$$[\text{reduced state}] + \frac{1}{2}O_2 \xrightarrow{k_2} [\text{oxidized state}] \qquad (2)$$

$$\frac{P_e}{r} = \frac{1}{k_1} + \frac{P_e}{k_2\sqrt{P_o}} . \qquad (3)$$

Here P_e denotes partial pressure of ethanol and P_o denotes the partial pressure of dioxygen. r is the reaction rate normalized by the number of the active sites. [oxidized state] and [reduced state] represent proportions of active sites in the oxidized and reduced stage in the redox cycle, respectively. In the following argument, the total number of molybdenum atoms is chosen as the number of active sites for convenience (see Section 4). Linear correlation should be observed when P_e/r is plotted against $P_e P_o^{-1/2}$, and the rate constants k_1 and k_2 could be determined from an intercept and a slope of the graph, respectively.

Fig. 2(a) shows thus obtained P_e/r vs. $P_e P_o^{-1/2}$ plot for 2.5 wt.% Mo3/SiO$_2$. P_e and P_o were varied in the range of 5–40 and 10–150 Torr, respectively. Linear correlation can be seen for all the reaction temperatures examined. Using the k_1 and k_2 values obtained from Fig. 2(a), activation energies of the two steps were determined to be 39 and 77 kJ/mol, respectively (Fig. 3(a)). A quantity of 2.0 wt.% Mo1 and Mo7/SiO$_2$ were also investigated. P_e/r against $P_e P_o^{-1/2}$ for Mo1/SiO$_2$ and Mo7/SiO$_2$ are plotted in Fig. 2(a) to compare with the Mo3/SiO$_2$. Similar linear correlation can be
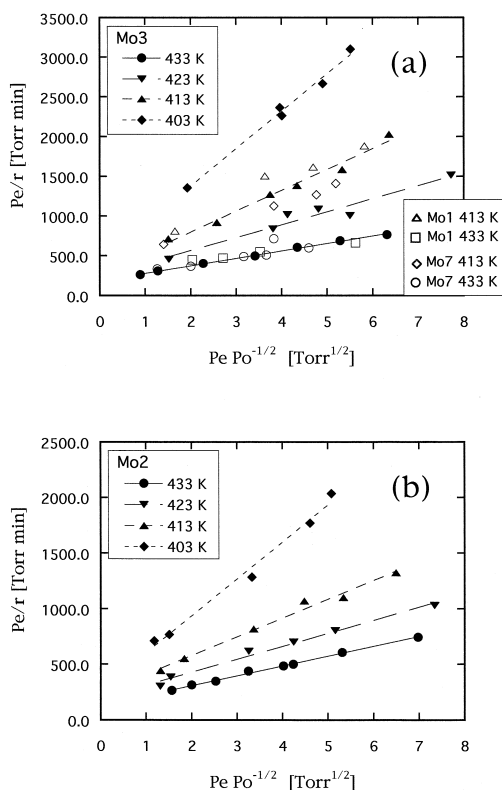

Fig. 2. Plots of P_e/r against $P_e P_o^{-1/2}$ for ethanol oxidation over Mo/SiO$_2$: (a) 2.5 wt.% Mo3/SiO$_2$; (b) 2.1 wt.% Mo2/SiO$_2$. The rates were measured at 403, 413, 423 and 433 K. P_e/r values against $P_e P_o^{-1/2}$ for 2.0 wt.% Mo1/SiO$_2$ and 2.0 wt.% Mo7/SiO$_2$ measured at 413 and 433 K are also plotted in the graph (a).

found in the both cases, and reaction rate dependence on precursor is small as considering relatively large error in those experiments. Rates for 2.1 wt.% Mo2/SiO$_2$ prepared in the present experiment were about 30% faster than that for the Mo3/SiO$_2$, but kinetic features were quite similar (Fig. 2(b)). Arrhenius plots of k_1 and k_2 for Mo2/SiO$_2$ are plotted in Fig. 3(b) and the activation energies were determined to be 38 and 67 kJ/mol, respectively. Iwasawa et al. reported only one activation energy for ethanol oxidation over the fixed monomer or dimer catalysts as if it were an single-step reaction though they have insisted on the two-stage redox mechanism. It is difficult to directly compare the activation energies because these au-
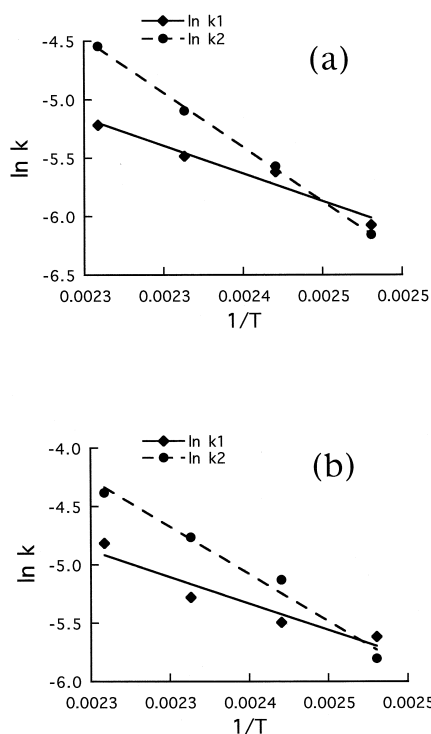
Fig. 3. Arrhenius plot for the two rate constants of ethanol oxidation over 2.5 wt.% $Mo3/SiO_2$ (a), and 2.1 wt.% $Mo2/SiO_2$ (b).

thors did not clearly show the reaction conditions.

In Fig. 4, effect of loadings are presented in a plot of P_e/r against $P_e P_o^{-1/2}$ for $Mo1/SiO_2$. Though the catalysts of loadings higher than ca. 1 wt.% showed only slight dependence, those of lower loadings were considerably less active and the catalysts of 0.6 wt.% were about half as active as the catalysts of higher loadings. In spite of the fact, all of them showed linear correlations in the plot suggesting that similar reaction might occur in different quantities on those catalysts. Catalytic activity of the 3:7 physical mixture of 2.0 wt.% catalysts and the support was almost the same as that of the 0.6 wt.% catalysts, though 2.0 wt.% catalysts and the support placed at different part in the reactor showed activities the same as those of 2.0 wt.% catalysts.

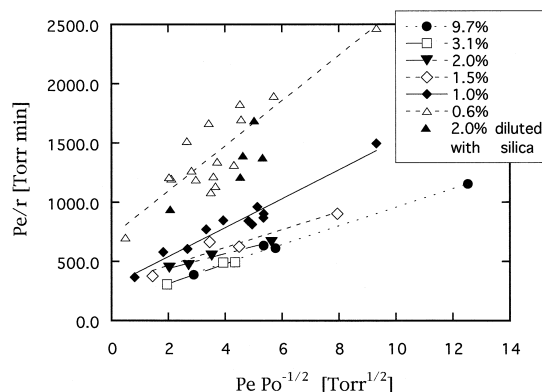From the k_1 and k_2 values obtained above, it can be calculated what percentage of the active

Fig. 4. Plots of P_e/r against $P_e P_o^{-1/2}$ for ethanol oxidation over $Mo1/SiO_2$ of various loadings. The rates were measured at 433 K.

sites were in the reduced stage as is shown in Eq. (4).

$$[\text{reduced state}] = \frac{k_1 \times P_e}{k_1 \times P_e + k_2 \times \sqrt{P_o}} \qquad (4)$$

It can be seen that about half of the active sites were in the reduced state under a steady state condition typically applied in the series of experiments (Fig. 5). If this is the case, the catalysts quenched during the ethanol oxidation will give the spectra containing the two states equally.

Fig. 6 shows an EXAFS spectrum of the $Mo2/SiO_2$ under a catalytic ethanol oxidation. There seem to exist several very weak components in the region where distances of adjacent Mo atoms should take place, but peak corresponding to the 2.6 Å Mo–Mo bonds cannot be seen clearly.
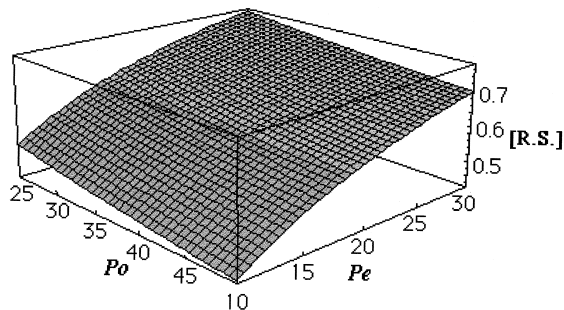

Fig. 5. Rough estimation of the percentage of reduced stage in the redox cycle of catalytic ethanol oxidation over Mo/SiO_2.
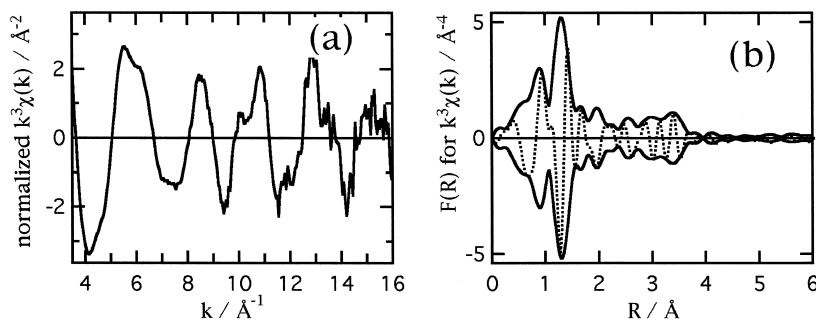
Fig. 6. Mo K-edge EXAFS of Mo/SiO$_2$ during catalytic ethanol oxidation. k^3-weighted EXAFS spectrum of 2.1 wt.% Mo2/SiO$_2$ quenched during catalytic ethanol oxidation (a), and its Fourier transformation (b). Partial pressure of ethanol and oxygen were 31 and 50 Torr, respectively.

In Fig. 7, the UV–VIS spectrum of 0.6 wt.% Mo1/SiO$_2$ quenched under the catalytic reaction condition is presented. It resembles to the spectra of the catalysts not deeply reduced (see Fig. 7 in the part I), but the color was more dilute. Lower-temperature (403 K) and shorter-time reductions were conducted to obtain UV–VIS spectra of less reduced catalysts (dotted lines in Fig. 7). Absorption at 710 nm of those shallowly reduced samples were compared with that of the catalysts under catalytic reaction condition. Fig. 8 shows correlation between ab-
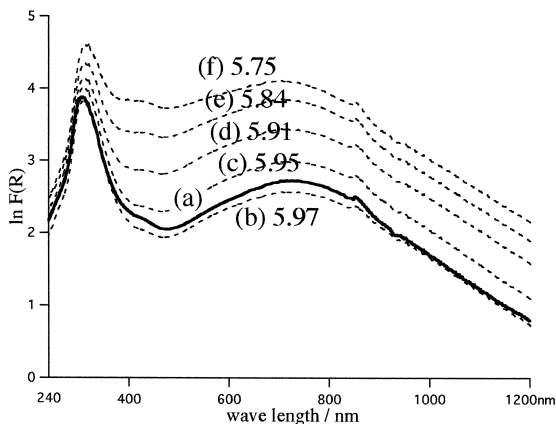
sorption strength and oxidation states of the catalysts estimated by acetaldehyde formation from the shallowly reduced samples. The absorption of the catalysts under catalytic condition was about In $F(R) = 2.7$ and it coincides with oxidation state of $+5.95$. (Average oxidation state of 2.0 wt.% Mo1/SiO$_2$ under catalytic reaction condition was also estimated in the same way to be $+5.9$.) The estimation of average oxidation states by monitoring acetaldehyde formation at the time of quenching might tend to give higher oxidation value, because acetaldehyde adsorbed on the catalysts or formed during short times of quenching processes were not counted on. Nevertheless it can safely be concluded that the UV–VIS spectrum of the catalysts under reaction condition is similar to those at high oxidation states close to $+6$.

Fig. 7. UV–VIS spectra of 0.6 wt.% Mo1/SiO$_2$ quenched in catalytic ethanol oxidation at 433 K (a). Partial pressure of ethanol and oxygen were 43 and 19 Torr, respectively. Dotted lines (b)–(f) are UV–VIS absorption of 0.6 wt.% Mo1/SiO$_2$ reduced by ethanol at 403 K 3–90 min. Estimated values of oxidation states of Mo are affixed. Distortions near 850 nm were due to incompleteness of smoothing discontinuities accompanied with exchange of detectors.
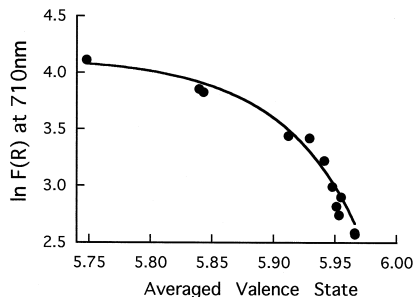

Fig. 8. Correlation between absorption strength at 710 nm and average oxidation states of Mo species estimated by amount of acetic acetaldehyde formation. An amount of 0.6 wt.% Mo1/SiO$_2$ was used.

3.2. *Mo / SiO$_2$ during catalytic methanol oxidation*

Methanol oxidation at 433 K over molybdenum silica (Fuji Davison No. 952) catalysts derived from different precursors (Mo1, Mo2, Mo3 and Mo7) were compared. Evolution of products was almost the same for all the catalysts, except that Mo2/SiO$_2$ was slightly more active than the other three, just as in the case of ethanol oxidation.

The reaction products were formaldehyde, methyl formate, dimethoxymethane, dimethyl ether and water (CO and CO$_2$ were negligible for reaction at 433 K). Unlike acetaldehyde formation in ethanol oxidation, three products in methanol oxidation (formaldehyde, methyl formate and dimethoxymethane) did not formed linearly. Furthermore partial pressure of water or amount of catalysts affected reaction profiles of them. Mo/Aerosil silica showed higher dehydration activities than those with No. 952 or Cariact Q-10 silica, and larger amount of produced water resulted in different reaction profiles of the oxidation products.

This phenomenon was found to be caused by interconversion of the oxidation products catalyzed by Mo/SiO$_2$ catalysts at that temperature:

$$HCHO + 2CH_3 \rightleftarrows 2CH_3OCH_2OCH_3 + H_2O \quad (5)$$
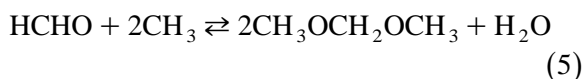
Each molecule of methyl formate, dimethoxymethane and formaldehyde can be formed by four, two and two electron oxidation of two, three and one methanol molecules, respectively. Methyl formate formation and dimethoxymethane formation can be converted with this rule to formaldehyde formations of equivalent oxidation activity. Amount of oxidation products measured by the formaldehyde equivalents developed linearly, and reaction rate r could be measured with it.

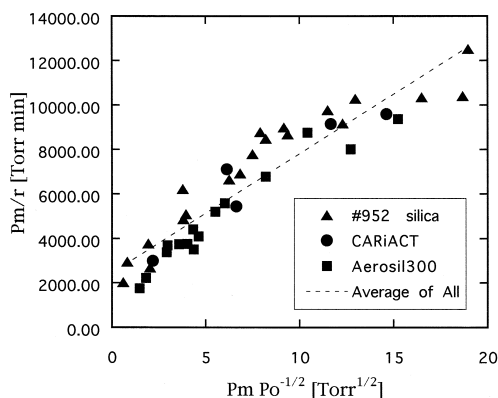In Fig. 9, P_m/r values were plotted against $P_m P_o^{-1/2}$ for 2.0 wt.% Mo1/SiO$_2$ at 433 K

Fig. 9. Plot of P_m / r against $P_m P_o^{-1/2}$ for methanol oxidation reactions over Mo1/SiO$_2$ at 433 K. Fuji-Davison No. 952, Cariact Q-10 and Aerosil 300 silica were used as supports.

(P_m is partial pressure of methanol). Partial pressure of methanol and oxygen were changed in the range of about 5–70 Torr and 10–230 Torr, respectively. Linear correlation similar to those in the corresponding plots of ethanol oxidation was observed. There cannot be seen difference by variation of the silica supports. k_1 and k_2 values for the two reaction steps in catalytic methanol oxidation are 4×10^{-4} [Torr^{-1}] and 2×10^{-3} [Torr$^{-1/2}$] and which were about 15 times and 5 times smaller than those of ethanol oxidation.

In Fig. 10, UV–VIS spectra of 0.6 wt.% Mo1/SiO$_2$ (No. 952) are shown. They are similar to those of samples treated with ethanol. Spectra taken with the sample quenched under catalytic methanol oxidation (Fig. 10, line (c)) was less colored compared with the one under ethanol oxidation reaction.

In contrast to fewer reports handling ethanol oxidation reactions catalyzed by molybdenum silica catalysts, methanol oxidation reactions were often examined over silica supported molybdenum catalysts [8–11]. In most of those cases, reaction were performed in the flow type reactors and at reaction temperatures about 500 K. Thus molybdenum silica catalysts under methanol and oxygen atmosphere at about 500 K were also investigated in the present study
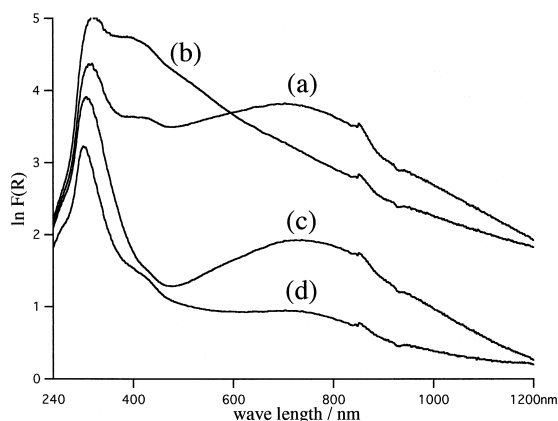
Fig. 10. UV–VIS spectra of 0.6 wt.% Mo1/SiO$_2$: (a) reduced by methanol (initial pressure 67 Torr) at 433 K, 180 min; (b) reduced by methanol (initial pressure 71 Torr) at 513 K, 360 min; (c) quenched under catalytic methanol oxidation reaction at 433 K. ($P_m = 45$, $P_o = 58$ Torr.); (d) quenched under catalytic methanol oxidation reaction at 503 K. ($P_m = 44$, $P_o = 47$ Torr.)

shortly. UV–VIS spectrum of 0.6 wt.% Mo1/SiO$_2$ treated with methanol and oxygen gas is shown in Fig. 10 (line (d)). Color of the catalysts was almost white but there was weak absorption in visible range. An EXAFS spectrum of 2.1 wt.% Mo2/SiO$_2$ treated with methanol and oxygen gas (initial pressure ca. 50 and 35 Torr, respectively) at 503 K for 54 min didn't show prominent Mo–Mo peaks.

4. Discussion

4.1. Redox cycle in catalytic alcohol oxidation

Catalytic oxidation of methanol and ethanol was studied here on Mo/SiO$_2$. The redox mechanism might be essentially not different between the two alcohols.

Selectivity to the partially oxidized products in methanol oxidation have been often used as indicators of the nature of active sites. However, it was found that the selectivity is not necessarily reflecting the initial selectivity of oxidation because secondary reactions among those products could occur. Many factors such as partial pressure of water may affect them in too complicated ways for a simple explanation. The

reason why performance of total oxidized products formation showed simple linear relation whilst interconversions between methyl formate and the other two partially oxidized products were not observed might be because all those products evolved from the same intermediates which were formed with a rate determining step, e.g., C–H bond scission.

It should be stressed that the Eq. (3) only suggests a redox mechanism and it has no ability to determine the number of Mo atoms in an active site. Assigning different number of Mo atoms for an active site is only a matter of multiplying the rate constants per active site by a certain constant and dividing the number of active sites by the same constant. The form of the rate equation does not change by that. Rate constants proposed by Iwasawa et al. for the fixed dimer site were twice as large as those for the monomer site [5]. That means the fixed monomer and dimer catalysts also had the same activity per molybdenum atom.

All the four Mo/SiO$_2$ prepared in the present study from different precursors showed almost the same kinetic features. It strongly suggests that the redox mechanism is not indicating uniqueness of the fixed catalysts but is common to any Mo/SiO$_2$. As described in the part I, structural changes of Mo/SiO$_2$ with reduction by ethanol were also not dependent on preparation methods. In the following, comparing with the results obtained in the part I, what the redox reactions really are will be discussed.

Fig. 1 shows the reaction profile of the catalytic ethanol oxidation. There was no problem in adopting the initial rate method in the measurements of activities of the alcohol oxidation. That means steady states of the reactions were attained almost instantly. As can be seen in Fig. 5, at steady states, quite high percentage of active sites were on reduced side of the redox cycle, which also can be understood from the fact that reaction rates were dependent on partial pressure of oxygen. If we assume a redox cycle between well-defined uniform Mo(6 +)–Mo(6 +) and Mo(5 +)–Mo(5 +) dimer struc-

tures, it follows that the structure which requires about 500 K and considerable time for complete formation would be built instantly at 433 K with oxygen coexistence. The assumption also contradicts with the spectra under catalytic reactions with neither the characteristic Mo–Mo peaks nor brown color.

It is more reasonable to think of lesser oxidation state change in the redox cycle, namely infinitesimal redox cycle of aggregated molybdenum oxo species. Such redox mechanisms are popular in oxidation reactions on surfaces of bulk oxides [12,13] and on polyoxometalate catalysts [14,15]. For example, Mizuno et al. [16] had shown the redox mechanism of catalytic H_2 and CO oxidation over Keggin-type polyacids. Infinitesimal redox cycles were balanced at the level where the catalysts were reduced by about 0.3 and 0.04 electrons per anion for the reaction of H_2 and CO, respectively. Probably the aggregates in the blue states introduced in the part I can be regarded as candidates for such infinitesimal redox cycles, because the kinetic and spectroscopic results can be explained fairly well by this assumption. With these models, it should be kept in mind that the notation 'blue state' is generally referred to many kinds of aggregates which are not well-definable substances. For example, oxidized and reduced states in the redox cycles for methanol and ethanol oxidation are not necessarily the same. Intensity of IVCT band under methanol oxidation was much weaker than that for ethanol oxidation and that is in accord with smaller k_1/k_2 value for methanol oxidation. But it does not necessarily mean that the two reactions share the same oxidized and reduced states and only the proportions of the states were different between the two reactions. Not discreet oxidation levels but reduction and reoxidation rates that show approximately linear dependence on degree of reduction are needed for the redox rate equations to get fulfilled. It can be only anticipated that the cycle for methanol oxidation might be running at around higher average oxidation states than that for ethanol oxidation.

As shown in the part I, the reduction of Mo/SiO_2 by ethanol cannot be explained by the assumption of uniform monomeric or dimeric sites. Thus if monomeric or dimeric sites were responsible for the catalysis, these sites should be very scarcely populated and ignorable in the non-catalytic reduction of the catalysts. Under the catalytic conditions they must be reduced and oxidized so rapidly that they govern the whole reaction rates. There are no conclusive evidence but this assumption is not realistic because isolated metal oxo species are often less reducible than aggregated oxo species and it is hard to imagine only few of those isolated sites are prominently active even how highly non-uniform the surfaces are. The fact that catalysts with extremely low loadings had lower activities also suggests aggregated molybdenum as the active species. Some isolated molybdenum species probably existed, but they might be inactive.

Though molybdenum is believed to be reluctant to migrate onto the silica support once incorporated in bulk MoO_3 lattices [17,18], Mo species prior to take crystalline MoO_3 form might easily spread on the support in micrometer scale under calcination and/or reaction conditions and at low loadings proportion of molybdenum which settled in less active dispersed states were large as can be seen in Fig. 4. This flexibility of molybdenum on silica may be also the reason for the little precursor effects.

4.2. Comparison with results of alcohol oxidation over Mo/SiO_2 investigated by other researchers

In the present study, it was confirmed that oxidation of methanol and ethanol over Mo/SiO_2 are not seriously affected by the preparation method. It is regarded as reflecting the average structures of Mo/SiO_2, of which dependence on the preparation method was also negligible. If the structure is really not dependent on the preparation method and the alcohol oxidation reactions reflect the average struc-

tures, it can be anticipated that alcohol oxidation over Mo/SiO$_2$ prepared by other researchers have the same characteristics as in the present experiments.

For ethanol oxidation reactions over Mo/SiO$_2$, recently Oyama and Zhang [19–21] have presented some results by the kinetic investigations. As they used higher loading catalysts, most of molybdenum on silica were in the microcrystallite of MoO$_3$. Therefore, it cannot be directly compared to the present results, and the rate equations given by them did not fit with the present data.

Ono et al. have investigated the effect of loadings on the catalytic activity of Mo/SiO$_2$ for the oxidation of ethanol [22]. Though dependence of the activity on the loadings were little different from the present results, they also deduced that aggregated molybdenum species are more active than dispersed ones.

Some data proposed by Iwasawa et al. do not agree with the present results. They insisted that initial rates of acetaldehyde formation with reduction of the fixed catalysts by ethanol under O$_2$ free condition were coincide with rate constants derived by the redox rate equations and assumption of monomer and dimer active sites. Initial rates can hardly be measured accurately where the reaction conditions change significantly. Careful inquiry about the rates reported by Iwasawa et al. demonstrates that they did not properly reduce the partial pressure of ethanol to avoid getting the catalysts reduced and linearity of the acetaldehyde formation lost [5,6].

For catalytic methanol oxidation at about 500 K, Bañares et al. investigated using Raman spectroscopy structures and activities of molybdenum silica catalysts prepared by various methods [8]. They had suggested that a part of molybdenum initially dispersed as monomers agglomerated under the catalytic reaction condition to β-MoO$_3$ particles, extent of which depended on the loading. They also get similar conclusion with the present one, in that the molybdenum undergoes aggregation under the catalytic reactions. UV–VIS spectra showed existence of the blue state at 500 K only faintly, but that may because at that temperature the reoxidation step was relatively faster than the reduction step. Contradiction is that no β-MoO$_3$ could be found in the EXAFS spectrum whereas if they had been formed as much as Bañares' estimation it should have been. (β-MoO$_3$ has structure similar to that of ReO$_3$ [23]. Because in this structure, Mo–O–Mo align almost linearly and Mo–Mo distances are almost equal, a strong EXAFS signal of Mo–Mo, which is enhanced by focusing effect of midway O atom, should be observed.) Another serious problem is that they have proposed that monomerically dispersed molybdenum showed similar activity as those on the surface of aggregates. It can be possible that under their reaction conditions the dispersed species can easily reduced to oxidation state +4 or +5 and can participate effectively in the redox cycles in the catalysis, because catalytic performances that they reported were higher than the present results.

Louis and Tatibouët, Che et al., and Louis and Che [10,24–26] proposed that two distinctive species existed on silica supported molybdenum, one is dispersed and strongly interacts with the support and the other interacts with support weakly. The former may correspond to the less active dispersed species and the latter might be the active species in the present experiments, because they reported that the former was hard to get reduced. On the contrary they insisted that the dispersed species are more active for the catalytic oxidation of methanol by a redox mechanism.

As written above, there are still some inconsistencies. Especially the monomer active sites proposed for methanol oxidation at 500 K are opposite to the results obtained in the present study. There must be some unknown parameters which are different from one research group to another. Just as the present study has rationally explained the contradictions about the fixed catalysts, new researches which can solve the problem of contradictions among the different researchers are needed.

5. Conclusions

It was confirmed that catalytic oxidation of methanol and ethanol over Mo/SiO_2 cannot be explained by the simple well-defined active site models which demand drastic transformation of the oxidation states. Redox cycles with much more subtle oxidation state change were proposed for the catalyses.

Acknowledgements

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