Mechanism of the catalytic oxidation of CO with O₂ on an Mo catalyst supported on silica and on bulk MoO₃

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The mechanism of the catalytic oxidation of CO with O_2 on an Mo catalyst supported on silica has been studied by a tracer technique using ${}^{18}O_2$. The supported Mo catalyst was prepared by using the ready reaction between $Mo(\eta^3 - C_3H_5)_4$ and the OH groups on silica. Extended X-ray absorption fine structure (EXAFS) spectroscopy showed that the Mo species attached to silica are dispersed atomically and have a dioxostructure. At steady state during oxidation with $CO/O_2 = 2/1$, 32% of the attached Mo species were estimated to be present as Mo^{6+} and 68% as Mo^{4+} . The catalytic oxidation was accompanied by oxygen isotope exchange between O_2 molecules. The oxidation of the oxostructure (Mo^{4+}) to the dioxostructure (Mo^{6+}) by O_2 molecules during the catalytic oxidation produces O atoms on the silica surface. Recombination of two migrating O atoms leads to oxygen isotope exchange between O_2 molecules. The mechanism of the catalytic oxidation of CO with O_2 on bulk MoO_3 was re-examined with reference to that elucidated on the SiO₂-supported Mo catalyst.

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It is generally accepted that the catalytic oxidation of hydrocarbons and CO over several metal oxides proceeds by repeated reduction of oxide ions at active sites on the catalyst surface by the reducing gas and replenishment of oxide vacancies by O_2 . Oxide ions and metallic cations are arranged regularly on the surface of the oxide catalyst. However, it is, at present, difficult to specify the active sites. In consequence, even the initial adsorption of O_2 molecules on the catalyst surface is not well elucidated.

We have shown previously that O_2 molecules are adsorbed irreversibly and dissociatively on two adjacent vacancies of active oxygen during catalytic oxidation of CO with O_2 on the surface of MOO_3 .¹ We also showed that the concentration of oxygen vacancies is only 0.13% of the total surface lattice oxide ions of MOO_3 .¹ This concentration seems to be too low to assume that the dissociative adsorption of O_2 molecules occurs on two adjacent oxygen vacancies in the catalytic oxidation.

In order to obtain further information about the oxidation process by O_2 molecules at active sites during the catalytic oxidation, it is necessary to prepare a catalyst which has a definite number of active sites with a clear structure on a molecular level and to examine how the oxidation proceeds on such a catalyst.

It has been shown that the supported Mo catalyst that can be prepared via the facile reaction between $Mo(\eta^3-C_3H_5)_4$ and the surface OH groups of SiO₂ or Al₂O₃ has almost all Mo atoms on the catalyst surface that can be reduced by H₂ and re-oxidized by O₂.^{2.3} The amount of Mo atoms can be determined by the usual analytical methods.^{2.3} A recent EXAFS study has given information about the structure around a Mo atom attached to a silica surface.⁴ This catalyst may be useful to examine the reaction mechanism of the catalytic oxidation of CO with O₂ by the ¹⁸O₂ tracer technique.

Experimental

The supported Mo catalyst was obtained from the ready reaction between $Mo(\eta^3-C_3H_5)_4$ and the surface OH groups of silica (Aerosil 200, Japan Aerosil, BET surface area 189 $m^2 g^{-1}$).⁵ All procedures for synthesis were carried out using Pyrex-glass apparatus under vacuum (base pressure 1.3×10^{-3} Pa) or in a flow of high purity Ar (99.999%, H₂O <5 ppm, Sumitomo Seika) at atmospheric pressure. Unless otherwise noted, reagents used in the synthesis were purchased from Wako Pure Chemical Industries. Diethyl ether and pentane, dried in the presence of calcium hydride for 5 days, were further refluxed for 3 h over Na wires before distillation. Allyl chloride was dried with molecular sieve 4A before distillation. Mg (>99.5% purity) was degassed at 423 K for 1 h before being reacted with allyl chloride.

 $Mo(\eta^3-C_3H_5)_4$ was synthesized according to the method described by Wilke *et al.*⁶

$$C_3H_5Cl + Mg(large excess) \xrightarrow[diethyl ether]{258 K, 12 h} C_3H_5MgCl (1)$$

$$_{3}H_{5}MgCl + MoCl_{5}$$

$$\xrightarrow{233 \text{ K}, 1.5 \text{ h}} 195 \text{ K}, 20 \text{ h}} \xrightarrow{233 \text{ K}} Mo(\eta^{3}-C_{3}H_{5})_{4} \quad (4)$$
diethvl ether
pentane

Silica (ca. 1.3 g) was heated at 773 K in the presence of 9.1 kPa O₂ for 1 h and then evacuated at the same temperature for 1 h.⁵ The reaction between $Mo(\eta^3-C_3H_5)_4$ complex in pentane and silica was carried out initially at 273 K and then at room temperature. The supported Mo catalyst was washed three times with pure pentane to remove unreacted Mo complex. After removing pentane by evaporation, the Mo catalyst, which still had some allyl ligands was transferred into a U-shaped quartz tube reactor in a closed circulation Pyrexglass apparatus without exposure to air. The amount of Mo on the silica surface was determined to be 1.4 wt.% by a gravimetric method based on precipitation of Mo with α -benzoinoxime.

The catalyst pretreatment was carried out in an apparatus with two circulation pathways, as described elsewhere.^{7,8} One pathway was coupled to a quadrupole mass spectrometer (ULVAC MSQ-150) through a Granville–Phillip variable-leak valve. All cocks used in the circulation loops were metallic or greaseless. Traps before the circulation loops were cooled continuously with liquid nitrogen or a dry-ice–ethanol mixture to protect the catalyst from contamination by grease or mercury vapour. CO and O₂, obtained commercially, were fractionally distilled at liquid-nitrogen temperature. H₂ was purified by passing through liquid-nitrogen-cooled traps. ¹⁸O₂ (¹⁸O atom fraction, 98.6%) from Commissariat L'Energie Atomique was used without further purification.

The number of OH groups on the silica was determined by Sato's method.⁹ Silica was degassed at a fixed temperature before the reaction with $Al(C_2H_5)_3$. $Al(C_2H_5)_3$ obtained from Tokyo Chemicals was dissolved in decalin at a concentration of 10%. The reaction between silica and $Al(C_2H_5)_3$ was carried out at room temperature in Ar at atmospheric pressure. The amount of C_2H_6 evolved was determined volumetrically.

For the characterization by transmission electron microscopy (TEM) the Mo/SiO₂ sample dispersed in acetone was placed on a holey carbon film on a copper grid. After evaporation of acetone, the specimen was transferred into a JEM-200CX transmission electron microscope with LaB₆ filament, which was operated at 200 kV.

Mo K-edge EXAFS spectra of the catalyst were taken in a transmission mode at BL 10B of the Photon Factory in the National Laboratory for High Energy Physics with an Si (311) channel-cut monochrometer (Proposal No. 93G164). The spectra were recorded at room temperature and at 100 K. Prior to the EXAFS measurements, the catalyst was oxidized by O_2 (*ca.* 13 kPa) at 773 K for 30 min. Subsequently, it was transferred to an EXAFS cell without exposure to air. The 17 cm ionization chamber filled with N₂(50%)–Ar (50%) and the 34 cm chamber filled with Ar (100%) were used as detectors for I_0 and I signals, respectively.

The following EXAFS formula was used in the curve-fitting analysis of the Mo K-edge EXAFS data,

$$\chi(k'_j) = \sum N_j F(k'_j) \exp(-2R_j/\lambda) \exp(-2k'_j \sigma_j^2)$$

$$\times \sin[2k'_j R_j + \phi(k'_j)]/k'_j R_j^2 \qquad (3)$$

$$k'_j = (k_j^2 - 2m\Delta E_{0j}/\hbar)^{1/2}$$

where k_j is the photoelectron wavenumber, $F(k'_j)$ is the backscattering amplitude function, and ϕ (k'_j) is the phase shift function. Model compounds used were Mo foil and K₂MoO₄ for Mo—Mo and Mo—O, respectively. The theoretical parameters based on FEFF were used for Mo—Si.¹⁰ N_j, σ_j , and R_j are the coordination number, the Debye-Waller factor and the interatomic distance, respectively. The fitting parameters are N_j , R_j , ΔE_{0j} (difference between the origin of the photoelectron wave vector and that conventionally determined), and σ_j .

Results

Pretreatment of the Mo/SiO₂

The Mo/SiO₂ was reduced with H₂ to remove remaining allyl ligands. The catalyst temperature was raised from room temperature to 823 K at a rate of 6 K min⁻¹ in circulating H₂ (*ca.* 7.8 kPa) with a liquid-nitrogen-cooled trap. The treatment with circulating H₂ was continued for a further 4 h at 823 K. Fig. 1 shows a mass spectrum of the reduction products trapped at 77 K. Peaks at mass numbers between 44 and 39 and those between 30 and 26 and those between 16 and 12 indicate that saturated and unsaturated C₃ and C₂ hydrocarbons are the main products of the hydrogenolysis. The H₂ reduction changed the catalyst colour from grey to black.

The black catalyst was then exposed to oxygen at a pressure of 27 Pa at room temperature. An abrupt decrease in O_2 pressure occurred within 30 s followed by an extremely slow decrease in O_2 pressure for a further 60 min. The O_2 uptake at room temperature did not cause any notable change in the catalyst colour. The catalyst was then oxidized at 573 K by



Fig. 1 Mass spectrum of hydrogenolysis products from Mo/SiO_2 . The products were trapped at the temperature of liquid nitrogen.

 O_2 (ca. 4 kPa). The O_2 pressure decreased initially then became almost constant after 240 min. The catalyst colour was then pale grey. The catalyst was then further oxidized at 673 K. The decrease in O_2 pressure occurred again but this time it ceased within 30 min. Further decrease in the O_2 pressure was not observed above 673 K. The catalyst changed to a bright white colour after the oxidation at 673 K.

H₂ and CO uptake by the oxidized Mo/SiO₂ catalyst

The supported Mo catalyst, oxidized with O_2 (*ca.* 6.5 kPa) at 673 K for 2 h was exposed to H_2 (*ca.* 6.5 kPa) and CO (*ca.* 6.5 kPa) at 723 and 873 K. The ratios of the amounts of H_2 and CO consumed in the reduction to the number of Mo atoms attached to the silica $(1.5 \times 10^{-5} \text{ mol})$ are plotted *vs.* time in Fig. 2. Reduction of the oxidized SiO₂-supported Mo catalyst by H_2 at 873 K proceeded rapidly initially but H_2 consump-



Fig. 2 Changes of H_2/Mo and CO/Mo ratios with time. The catalyst was oxidized at 673 K by O_2 prior to reduction by H_2 and CO at 723 and 873 K. \bullet ; H_2 reduction at 873 K, \blacksquare ; CO reduction at 873 K, \bigcirc ; H_2 reduction at 723 K, \Box ; CO reduction at 723 K.

Reduction of the oxidized Mo/SiO₂ by CO at 723 K proceeded more rapidly than that by H_2 at the same temperature. The reduction almost ceased within 30 min. The total amount of CO consumed at 723 K agreed well with that of H_2 consumed at the same temperature. On the other hand, the reduction of the oxidized catalyst by CO at 873 K proceeded more slowly compared with that by CO at 723 K in the initial period. The reduction curve of CO does not reach the same level as that of H_2 at 873 K.

EXAFS spectroscopy

Fig. 3(a) shows the Fourier transform of the k^3 -weighted Mo K-edge EXAFS spectrum for the oxidized SiO₂-supported Mo catalyst at 100 K over k = 30-130 nm⁻¹. The Fourier transform depicts a large asymmetric peak in the region 0.09-0.22 nm. This peak may be straightforwardly assigned to the Mo-O bond.⁴ In order to obtain detailed structural information on the Mo sites, we performed a curve fitting analysis for the k-space oscillation obtained by the reverse Fourier transform in the region around this peak. However, the Mo-O one-wave curve fitting did not give reasonable converging values. Next, as expected from a main peak with a shoulder in the Fourier transform of Fig. 3(a), we conducted two-wave (Mo-O and Mo-O) curve-fitting analysis as shown in Fig. 3(b). The theoretical curve fits the experimental one well. Table 1 summarizes the curve-fitting parameters which gave the best fit. Fig. 3(a) shows a small peak around 0.2-0.3 nm which almost corresponds to the Mo-Mo bond distance reported previously.⁴ However, the curve-fitting analysis, assuming it to be due to Mo-Mo or Mo-Si, did not give any reasonable converging values. Both the form and position of this peak were confirmed to vary substantially with the Fourier-transform range, indicating that this peak was due to noise.



Fig. 3 (a) Fourier transform of k^3 -weighted Mo K-edge EXAFS spectrum of the oxidized catalyst over $k = 30-130 \text{ nm}^{-1}$. The catalyst was held at 100 K during EXAFS measurement. (b) Two-wave curve fitting analysis of the peak at 0.09–0.22 nm [calc. (····), obs. (---)].

Table 1 Curve-fitting analysis of EXAFS data for the ${\rm SiO_2}$ -supported Mo

back- scattering atom	bond distance /nm	coordination number, N	$\Delta E_{\rm o}$ /eV	Debye–Waller factor, σ /nm
0	0.170	2.3	-4.2	0.0060
0	0.198	1.5	1.0	0.0060

Fourier-transform range: $30-130 \text{ nm}^{-1}$; Fourier-filtering range: 0.09-0.22 nm; amplitude and phase shift function are extracted from the spectra for K₂MoO₄ measured at room temperature; (*N*, *R*, ΔE_0 , σ) = (4, 0.176 nm, 0.0 eV, 0.0060 nm)

Characterization of silica

The mean particle size of Aerosil 200 was calculated to be 14 nm from its BET specific area (189 m² g⁻¹) and density (2.2 g cm⁻³) assuming a spherical shape. On the other hand, the mean diameter of primary particles of Aerosil 200 determined from the TEM photograph was 12 nm which agrees with the manufacturer's data.¹¹ The agreement between the calculated and observed mean particle sizes suggests that a particle of Aerosil 200 has a flat surface.

X-Ray powder diffraction revealed that Aerosil 200 is crystallographically amorphous. The TEM photograph (5×10^6 magnifications) of the Mo-supported silica also showed that the catalyst carrier is crystallographically amorphous. However, the detailed TEM observation of the Mo-supported silica that had been heated above 773 K for a sufficiently long period showed a small crystallized part. Fig. 4 shows the electron diffraction pattern of the crystalline part. The values of interplanar spacings calculated from Debye–Scherrer rings satisfactorily agreed with those of β -cristobalite, which has a cubic crystal structure.¹² Fig. 5 shows the schematic diagram of the top view of the (111) plane of β -cristobalite.¹³ We assumed from this figure that the density of an OH group on Aerosil 200 is 4.6 (OH) nm⁻² at most.

Fig. 6 shows the time dependence of the amounts of C_2H_6 evolved in the reaction between silica and $Al(C_2H_5)_3$ in decalin. Prior to the reaction with $Al(C_2H_5)_3$, the silica was degassed at 393 and 773 K, respectively. A large part of the C_2H_6 is evolved rapidly initially, indicating that the reaction proceeds almost completely within the first 20 min. Since one molecule of $Al(C_2H_5)_3$ reacts with one surface OH group on silica and produces one molecule of C_2H_6 , according to Sato *et al.*,⁹ the number of surface OH groups on silica was determined to be 1.2 (OH) nm⁻² after degassing at 393 K and 0.5 (OH) nm⁻² after degassing at 773 K.



Fig. 4 Electron diffraction pattern of the crystalline part of Aerosil 200.



Fig. 5 Schematic diagram of top view of (111) plane of β -cristobalite. Large open circles designate oxygen atoms. Small dashed circles designate silicon atoms which are located in silica tetrahedra pointing out of the surface (upward from page) and are responsible for OH groups. Small and partly closed circles are silicon atoms located in the silica tetrahedra pointing into the silica particle (downward into page).

Catalytic oxidation of CO with O₂ on the supported Mo catalyst

After oxidizing the supported Mo catalyst with O_2 (ca. 4 kPa) at 673 K, a stoichiometric mixture of CO and O_2 was introduced into the reactor. After a gradual decrease in the initial catalytic activity, the catalyst showed a steady activity. It was confirmed that silica is inactive for the catalytic oxidation of CO with O_2 at 773 K, indicating that the Mo atoms on silica must serve as active sites for the oxidation.

Fig. 7 presents the first-order plots of the decrease in the total pressure of the reaction mixture due to the catalytic oxidation at 673, 693, and 713 K. The apparent activation energy was found to be 143 kJ mol^{-1} . The reaction order was 1.0-1.3 with respect to the total pressure.

Oxygen isotope exchange during oxidation

The reaction mixture with molar ratio of CO: ${}^{16}O_2$: ${}^{18}O_2 = 2: 0.6: 0.4$ was introduced over the catalyst which showed a steady catalytic activity with the stoichiometric mixture of CO and O₂ at 733 K. Fig. 8 shows the time dependence of the composition of each isotopic form of O₂ during the oxidation and that of the atomic fraction of ${}^{18}O$ in total O₂ (%) in the gas phase. The composition of ${}^{16}O$ ${}^{18}O$ in O₂ evidently



Fig. 6 Time dependence of the amount of C_2H_6 evolved in the reaction between silica (*ca.* 300 mg) and $Al(C_2H_5)_3$ in decalin. Prior to the reaction, silica was degassed at 393 K ((\bigcirc) and at 773 K (\bigcirc).

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Fig. 7 First-order plots of the decrease in the total pressure of the reaction mixture $(CO/O_2 = 2/1)$ owing to the catalytic oxidation at (a) 673, (b) 693 and (c) 713 K.

increases with time, while the atomic fraction of ¹⁸O in O_2 remains almost constant. This shows that oxygen isotope exchange between O_2 molecules proceeds simultaneously with the catalytic oxidation.

A mixture of ${}^{16}O_2$ and ${}^{18}O_2$ with molar ratio of ${}^{16}O_2$: ${}^{18}O_2 = 6:4$ was introduced at 733 K over the catalyst after it had reached steady catalytic activity for CO oxidation at the same temperature. Fig. 9 shows the time dependence of the composition of each isotopic form of O_2 . The ratio of ${}^{18}O^{16}O$ in O_2 shows no increase with time. Evidently oxygen isotope exchange occurs only during the catalytic oxidation of CO with O_2 over the supported Mo catalyst. The results shown in Fig. 8 and 9 suggest that oxygen isotope exchange is correlated closely with the catalytic oxidation.

Extent of reduction and oxidation of the supported Mo catalystat steady state

The catalyst was evacuated after establishment of the steady state for the reaction of stoichiometric amounts of CO and O_2



Fig. 8 Time dependence of the composition of each isotopic O₂ and ¹⁸O atomic fraction in O₂ during the catalytic oxidation on the SiO₂-supported Mo catalyst. The reaction was performed at 733 K using the mixture CO: ¹⁶O₂: ¹⁸O₂ = 2:0.6:0.4. (a)¹⁸O¹⁶O, (b) ¹⁸O₂, (c)¹⁶O₂, (d) atomic fraction of ¹⁸O in O₂.



Fig. 9 Time dependence of the composition of each isotopic species of O₂. The mixture ${}^{16}O_2 : {}^{18}O_2 = 6 : 4$ was introduced over the catalyst at 733 K. (a) ${}^{18}O {}^{16}O$, (b) ${}^{18}O_2$ and (c) ${}^{16}O_2$.

at 723 K. The catalyst was then oxidized by O_2 (*ca.* 6.5 kPa) at the same temperature. The pressure of O_2 first decreased and then soon attained a constant value, indicating that the catalyst was in a partially reduced state, different from the fully oxidized state. The extent of the reduction was determined volumetrically from the decrease in the O_2 pressure. In a second experiment, the catalyst, treated as above with CO and O_2 at 723 K, was reduced by CO (*ca.* 6.5 kPa) at the same temperature. The pressure of CO first decreased then soon attained a constant value, indicating that the catalyst was in a higher oxidized state than the reduced state achieved by CO reduction at 723 K in Fig. 2. The extent of oxidation was similarly determined from the decrease in the CO pressure.

The results are summarized in Table 2. The sum of consumed CO molecules and consumed oxygen atoms, *i.e.*, Δ (CO) + 2Δ (O₂) = 1.40 × 10⁻⁵ mol, agrees well with the amount of Mo supported on silica determined gravimetrically as well as by the H₂ and CO uptake at 723 K shown in Fig. 2. The respective ratios of the amounts of consumed CO molecules and consumed oxygen atoms to that of total attached Mo atoms are 0.32 and 0.68, respectively.

Discussion

Reaction between Mo(η^3 -C₃H₅)₄ and the OH groups on silica

The maximum number of OH groups on the silica surface is 4.6 (OH) nm⁻², see Fig. 5. However, the number of OH groups which remain on silica after de-gassing at 773 K was 0.5 (OH) nm⁻², Fig. 6. The fraction of the top layer surface oxygen which can fix $-Al(C_2H_5)_2$ to the total top layer surface oxygen is only 0.14. We consider that a large part of the OH groups is converted into a siloxane form on the surface and that the possibility of two adjoining OH groups seems to be very small.

Table 2 Extents of the reduction and oxidation of the SiO_2 -supported Mo catalyst during the oxidation

reaction	amount of gas consumed $/10^5$ mol	estimated amount of Mo /10 ⁵ mol	% of total attached Mo
CO reduction $(\pm 6 \rightarrow \pm 4)$	0.45	0.45ª	32
$O_2 \text{ oxiation}$ (+4 \rightarrow +6)	0.475	0.95 ^b	68

^a Hexavalent Mo. ^b Tetravalent Mo.

According to previous studies,^{2,3} one molecule of $Mo(\eta^3 - C_3H_5)_4$ interacts with one or two adjoining OH groups on the silica surface and liberates one or two molecules of C_3H_6 into the gas phase. The number of Mo species attached to the silica was calculated to be 0.45 (Mo) nm⁻², an average result from the gravimetric analysis and the H₂ and CO uptake experiments shown in Fig. 2. If all Mo species attached to silica are produced via the reaction with two paired OH groups, the number of OH groups must at least be larger than 0.9 (OH) nm⁻². Since silica was de-gassed at 773 K before the reaction with Mo(η^3 -C₃H₅)₄, the number of OH groups must be controlled near 0.5 (OH) nm². Accordingly, a large part of the Mo fixation may take place according to eqn. (5) rather than eqn. (4) under the present conditions.^{2,3}

+ Mo(
$$\eta^3$$
-C₃H₅),

⇒si−он

$$Mo(\eta^{3}-C_{3}H_{5})_{2} + 2C_{3}H_{6}(g) \quad (4)$$

Si-O

$$\begin{array}{c} \Rightarrow Si - OH \\ \Rightarrow Si \\ O \\ \Rightarrow Si \end{array} + Mo(\eta^{3} - C_{3}H_{5})_{4} \rightarrow \\ O \\ \Rightarrow Si \end{array}$$

$$\begin{array}{c} Si - O \\ Si - O \\ Si - O \\ Si - O - C_{3}H_{5} \end{array}$$

$$\begin{array}{c} (5) \\ Si - O \\ Si - O - C_{3}H_{5} \end{array}$$

Si = O

The principal C_2 and C_3 hydrocarbon formation during the hydrogenolysis of the Mo-allyl complex attached to the silica (Fig. 1) almost agrees with the result observed during the hydrogenolysis of the Mo mononuclear allyl complex attached to Al_2O_3 .¹⁴

Since instantaneous oxygen incorporation took place at room temperature, at least a part of the Mo attached to silica must be reduced to the Mo^{2+} state after treatment with H_2 at 823 K.²

Catalyst characterization

The amount of Mo attached to silica, as determined by gravimetry, agreed well with the amount of H_2 consumed in the reduction at 723 K, as shown in Fig. 2. This agreement confirms the previous studies.^{2,3,15} If attached Mo atoms form Mo—Mo dimer on silica, one H_2 molecule per dimeric Mo₂ should be taken up in the reduction at 723 K, according to the previous results.¹⁴ Therefore, the satisfactory coincidence between the amount to Mo attached to silica and that of H_2 consumed at 723 K indicates that the amount of Mo—Mo pairs which may be formed on silica is negligible. In fact, the EXAFS spectroscopy in Fig. 3 does not show any distinct peak attributable to an Mo—Mo bond. These facts are also consistent with the extremely small possibility of the existence of an adjoining OH assembly on silica surface.

The amount of H_2 consumed in the reduction of the oxidized Mo/SiO₂ catalyst at 873 K is twice as much as that consumed in the reduction at 723 K, Fig. 2. Accordingly, almost all Mo⁶⁺ ions are reduced to Mo⁴⁺ and Mo²⁺ by reduction with H₂ at 723 and 873 K.

Aigler *et al.* recently prepared a monomeric-attached Mo catalyst by the sublimation of $Mo(\eta^3-C_3H_5)_4$ onto silica at

313 K.¹⁵ They first prepared a lemon-yellow crystal of $Mo(\eta^3-C_3H_5)_4$ through reaction between $MoCl_2 \cdot 2THF$ and C_3H_5MgCl in THF at 273 K, where THF denotes tetra-hydrofuran.¹⁵ The purity of the crystal was authenticated by ¹H NMR, IR and C, H analysis. They performed redox measurements on the monomeric-attached Mo catalyst (1.7 wt.% Mo) with H₂ and O₂, using a BET system with a glass circulation loop, and confirmed the stoichiometric redox transformation of Mo species ($Mo^{6+} \rightleftharpoons Mo^{4+} \rightleftharpoons Mo^{2+}$) manometrically.¹⁵ Their observation is consistent with the results obtained in the present study and those reported previously.^{2,3}

The EXAFS were recorded after oxidization of the SiO₂supported Mo catalyst at 773 K, where Mo⁶⁺ species must be formed on silica surface, as mentioned above. Table 1 shows that there are two kinds of Mo—O bonds around the Mo atoms on silica. Considering the previous results, the Mo—O bond with a distance of 0.170 nm and a coordination number of 2.3 can be ascribed to the Mo=O double bond, and the other Mo—O bond with a distance of 0.198 nm and a coordination number of 1.5 can be ascribed to an Mo—O(surface) single bond.⁴ In the present EXAFS analysis, the number of independent information, *i.e.*, $N_{\rm I} = 2\Delta R\Delta k/\pi + 2$ where $\Delta R = 0.13$ nm and k = 100 nm⁻¹, is 10.3.¹⁶ Therefore, it is valid to perform two-wave (Mo—O + Mo—O) fitting for the EXAFS data, by changing R, N, ΔE_0 and σ . Accordingly, the structure of an active Mo site on silica can be schematically depicted as follows;



The reduction curve for the oxidized Mo catalyst with CO at 723 K rises sharply and then reaches the same level as the reduction curve by H_2 at the same temperature (see Fig. 2). This shows that almost all the hexavalent Mo with the dioxostructure are readily reduced to tetravalent Mo with the oxostructure by CO at 723 K. However, further reduction to divalent Mo does not occur at this temperature.

The reduction of the oxidized Mo catalyst by CO at 873 K proceeds more slowly than that at 723 K and stops when the amount of consumed CO is 1.3 times the Mo quantity. This indicates that only a part of the Mo can be reduced from hexavalent to divalent in the reduction with CO at 873 K.

Mechanism of the catalytic oxidation of CO with O_2 on the SiO₂-supported Mo catalyst

Oxygen isotope exchange between O_2 molecules apparently proceeds during the catalytic oxidation of CO with O₂, as shown in Fig. 8, while it does not occur in the isotope mixture of ${}^{18}O_2$ and ${}^{16}O_2$ without CO, as shown in Fig. 9. Since all Mo atoms attached to silica are oxidized to the hexavalent dioxostructure under the isotope mixture of ${}^{18}O_2$ and ${}^{16}O_2$ at 733 K, it is suggested that the hexavalent dioxomolybdenum species do not serve as active sites for oxygen isotope exchange. The active sites for oxygen exchange should be produced only when CO is present in the gas phase. When the catalytic oxidation of CO with O₂ proceeds on the SiO₂supported Mo catalyst, at least a part of the Mo ions must be reduced to an oxidation state below hexavalency by CO in the gas phase. On the other hand, Fig. 2 shows that Mo ions attached to silica cannot be reduced below the tetravalent state by CO at 723 K. Therefore, Mo atoms on silica may exist in either the hexavalent or tetravalent state during the

catalytic oxidation. On this assumption, we estimate that 32% of the attached Mo atoms are in a hexavalent state and the rest are in a tetravalent state under steady state catalysis conditions, as tabulated in Table 2.

When an O_2 molecule converts a tetravalent Mo with the oxostructure to a hexavalent Mo with the dioxostructure, only one of two O atoms in an O_2 molecule can bind with the Mo. In other words, the oxidation of a tetravalent Mo with the oxostructure causes dissociation of an O_2 molecule. In this case, another O atom must remain on the silica surface. Since each Mo site is separate from the other Mo sites on the silica surface, the remaining O atom must migrate on the silica surface until it recombines with another O atom or reacts with one of the tetravalent Mo sites. The increase in the ¹⁸O ¹⁶O composition in O_2 in Fig. 8 suggests that the recombination between two migrating O atoms to form an O_2 molecule occurs during the catalytic oxidation.

Fig. 8 also shows that the atomic ratio of ¹⁸O in O₂ holds its initial value during catalytic oxidation of CO with ¹⁸O₂, ¹⁸O ¹⁶O and ¹⁶O₂. This implies that migrating O atoms are not exchanged with the surface lattice oxygen of silica. Migrating O atoms probably do not carry electric charges since recombination between two negatively charged species would be difficult due to mutual electric repulsion.

The reduction of hexavalent Mo with the dioxostructure by CO produces CO_2 . The production of CO_2 accompanies the liberation of two valence electrons bound in one of two Mo=O double bonds. Each Mo site is insulated from the other Mo sites on the silica surface. Liberated electrons must be localized on the reduced Mo sites. Thus tetravalent Mo sites are regenerated on the silica surface.

We propose the reaction scheme for the catalytic oxidation of CO with O_2 on the monomeric Mo catalyst, as shown in Fig. 10.

In the steady state of the catalysis in the mixture with a composition of $CO/O_2 = 2/1$, 68% of the attached Mo sites are tetravalent, as shown in Table 2. This result suggests that the reduction of Mo⁶⁺ to Mo⁴⁺ proceeds a little more rapidly than the oxidation of Mo⁴⁺ to Mo⁶⁺.

Mechanism of CO oxidation with O2 on MoO3

 MoO_3 is an n-type semiconductor metal oxide, composed of an orderly periodic array of a huge amount of Mo^{6+} and O^{2-} ions. We reported previously that the catalytic oxidation of CO with O_2 on MoO_3 proceeds by the cyclic repetition of the following two steps;

$$CO(g) + O(s) \rightarrow CO_2(g) + (s)$$
 (6)

$$2(s) + O_2(g) \rightarrow 2O(s) \tag{7}$$

where O(s) refers to active oxygen on the surface of MoO_3 and (s) refers to an active oxygen vacancy on the surface.¹ The



Fig. 10 Schematic of the reaction mechanism for the catalytic oxidation of CO with O_2 on Mo/SiO₂

temperature range in which this catalysis proceeds on MoO_3 (673–873 K) almost overlaps with that studied for the SiO_2 supported Mo catalyst. It may be significant to re-examine the reaction mechanism of the catalytic oxidation of CO with O_2 on MoO_3 with reference to that elucidated for the SiO_2 supported Mo catalyst.

All the hexavalent attached Mo species are readily reduced to tetravalency with CO at 6.5 kPa and at 723 K (Fig. 2), while the reduction of bulk MoO_3 with CO hardly proceeds under the same conditions.¹ At the most, only 7.9% of the total surface lattice oxide ions can be converted to CO_2 by CO at this temperature, irrespective of the CO pressure.¹ We have called such reducible surface lattice oxide ions, active oxygen. In the case of the SiO₂-supported Mo catalyst, the electrons liberated with the production of CO_2 are localized on the reduced Mo sites. On the other hand, the electric conductivity of MoO_3 increases gradually on reduction by CO, indicating that the electrons liberated with the breakage of the Mo-O bond at the surface of MoO_3 are not localized at the reduced sites and are easily excited into the conduction band.

In contrast to the SiO₂-supported Mo catalyst, where the reduction rate of Mo⁶⁺ to Mo⁶⁺ by CO and the re-oxidation rate of Mo⁶⁺ to Mo⁶⁺ by O₂ are almost comparable, the re-oxidation of the reduced MoO₃ by O₂ proceeds much more rapidly than the reduction of oxidized MoO₃ by CO.¹ In fact, the rate constant for the re-oxidation of the reduced MoO₃ by O₂, *i.e.*, k_{O_2} is *ca.* 3600 times larger than that of the reduction of the oxidized MoO₃ by CO, *i.e.*, k_{CO} at 723 K.¹

The re-oxidation of the reduced MoO_3 accompanies the abrupt decrease in the electric conductivity of MoO_3 .¹ The decrease in the electric conductivity suggests that the reaction in which O_2 molecules are converted to oxide ions at active oxygen vacancies, *i.e.*

$$O_2(g) + 2(s) + 4e \rightarrow 2O^{2-}(s)$$
 (8)

consumes the electrons in the conduction band of MoO_3 . The rapid decrease in the electric conductivity suggests that the transfer of electrons from the conduction band to O_2 molecules occurs promptly.

As reported previously, the following relation holds between k_{CO} and k_{O_2} :

$$k_{\rm CO} P_{\rm CO} \theta = 2k_{\rm O_2} P_{\rm O_2} (1-\theta)^2 \tag{9}$$

where θ and $(1 - \theta)$ denote the coverage and deficient ratio of active oxygen, respectively.¹ As to be expected from $k_{O_2} \gg k_{CO}$, the measured value of $(1 - \theta)$ during the oxidation is quite small, *i.e.* the percentage of active oxygen vacancies is only 1.58% of the total amount of active oxygen. Since active oxygen occupies 7.9% of the total surface lattice oxide ions at this temperature,¹ the percentage of the active oxygen vacancies which exist during the oxidation is only 0.13% of the total surface lattice oxide ions of the total surface lattice oxide ions of MoO₃.

On the other hand, the rate of oxidation of the reduced MoO₃ by O₂ is proportional to the second power of $(1 - \theta)$, as described in eqn. (9). We have assumed from this that the oxygen molecule is chemisorbed dissociatively on such sites, which are composed of two adjacent active oxygen vacancies during the oxidation.¹ In fact, oxygen isotope exchange between O₂ molecules did not proceed at all on MoO₃ during the catalytic oxidation of CO with ${}^{18}O_2$ and ${}^{16}O_2$ at 780 K,¹ which is consistent with the dissociative adsorption of an O₂ molecule on two coupled active oxygen vacancies. However, the concentration of vacancies active oxygen is no more than 0.13% of the total surface lattice oxide ions of MoO_3 . The opportunity that two active oxygen vacancies will occur on adjacent sites seems to be extremely scarce as long as we assume that CO could react with any oxide ion on active sites on MoO_3 during the oxidation.

In the case of the SiO_2 -supported Mo catalyst, 68% of the attached Mo are tetravalent. The mean distance between the

nearest-neighbour Mo⁴⁺ ions can be estimated to be ca. 1.8 nm. An O₂ molecule cannot oxidize two isolated tetravalent Mo sites simultaneously. The reaction of one O_2 molecule with one isolated Mo⁴⁺ site liberates one migrating O atom onto the silica surface, as described previously. Accordingly, oxygen isotope exchange proceeds on the SiO₂-supported Mo catalyst, as presented in Fig. 8. If we assume that active oxygen and active oxygen vacancies are distributed ideally on the surface of MoO₃, the concentrations of active oxygen and active oxygen vacancies are 1.34 nm⁻² and 0.021 nm⁻², respectively. The mean separation between two nearest oxygen vacancies could be calculated to be 6.9 nm, which is 3.8 times larger than that of attached Mo^{4+} ions on silica. Consequently, the absence of oxygen isotope exchange during the catalytic oxidation of CO with O₂ on MoO₃ suggests that active oxygen and active oxygen vacancies are not distributed at random on the surface of MoO_3 .

As shown previously, the electric conductivity of MoO_3 maintains a constant value under steady state catalysis,¹ indicating that the number of oxygen vacancies neither increases nor decreases during the oxidation. This should arise from the dynamic balance between the production rate of oxygen vacancies by CO and the extinction rate of two paired oxygen vacancies by O_2 . In other words, CO molecules cannot produce any oxygen vacancies that cannot be oxidized dissociatively by O_2 molecules during the steady state of the oxidation.

Thus, at present, we conclude: (1) CO does not react at random with any oxide ions on active sites on MoO_3 during the catalytic oxidation. (2) CO reacts regularly with the oxide ion at the active site adjacent to an oxygen vacancy. (3) Therefore, at least two active sites must be linked in their immediate neighbourhoods. (4) Oxygen molecules are dissociatively chemisorbed on linked vacancies.

Gai *et al.* studied the reduction of the (010) surface of MoO_3 by CO and H_2 in a gas reaction cell set inside a 1 MeV electron microscope (EM).¹⁷ The reduction of MoO_3 with CO and H_2 produces anion vacancies. The non-stoichiometry introduced by these gas reactions entails the switch from corner to edge shearing of MoO_6 octahedra on the crystal structure of MoO_3 . The shearing finally creats a crystallographic shear plane (CSP) at >673 K, as shown in a series of *in situ* EM photographs.¹⁷ They observed that CSPs apparently grow in length with increasing temperature (673, 773 and 823 K).¹⁷ These temperatures are within our range of study of the catalytic oxidation of CO with O_2 on MoO_3 . The observation supports the presumption that oxygen vacancies are linked together on the surface of MoO_3 .

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References

- 1 Y. Iizuka, Y. Onishi, T. Tamura and T. Hamamura, J. Catal., 1980, 64, 437.
- 2 Y. Iwasawa, Y. Nakano and S. Ogasawara, J. Chem. Soc., Faraday Trans. 1, 1978, 74, 2968; Y. Iwasawa and S. Ogasawara, J. Chem. Soc., Faraday Trans. 1, 1979, 75, 1465; Y. Iwasawa, Adv. Catal., 1987, 35, 187.
- 3 Yu. I. Yermakov and B. N. Kuznetsov, Preprint, Second Japan-Soviet Catalysis Seminar, Tokyo, 1973, p. 65; Yu. I. Yermakov, *Catal. Rev. Sci. Eng.*, 1976 13, 77.
- 4 Y. Iwasawa, K. Asakura, H. Ishii and H. Kuroda, Z. Phys. Chem., 1985, 144, 105.
- 5 Y. Iwasawa, Shokubai/Catal. (Japanese), 1981, 23, 232.
- 6 G. Wilke, B. Bogdanovic, P. Hardt, P. Heimbach, W. Keim, M. Kroner, W. Oberkirch, K. Tanaka, E. Steinrucke, D. Water and H. Zimmermann, Angew. Chem. Int. Ed. Engl., 1966, 5, 151; F. A. Cotton and J. R. Pipal, J. Am. Chem. Soc., 1971, 93, 5441.
- 7 Y. Iizuka, J. Chem. Soc. Faraday Trans., 1994, 90, 1301.

- 8 Y. Iizuka, H. Tanigaki, M. Sanada, J. Tsunetoshi, N. Yamauchi and S. Arai, J. Chem. Soc., Faraday Trans., 1994, 90, 1307.
- M. Sato, T. Kanbayashi, N. Kobayashi and Y. Shima, J. Catal., 1967, 7, 32. 9
- J. J. Rehr, J. M. Leon, S. I. Zabinsky and R. C. Albers, J. Am. Chem. Soc., 1991, 113, 5135; J. J. Rehr and R. C. Albers, Phys. 10 Rev. B, 1990, 41, 8139; J. Mustre de Leon, J. J. Rehr, S. I. Zabinsky, and R. C. Albers, Phys. Rev. B, 1991, 44, 4146.
- 11
- J. V. Smith, X-Ray Powder Data File, Sets 1–5 Inorganic, 4-0359, 12 ASTM, 1960.
- R. W. G. Wyckoff, Crystal Structures, Wiley, New York, 2nd edn., 1965, vol. 1, p. 318. 13

- Y. Iwasawa, Y. Sato and H. Kuroda, J. Catal., 1983, 82, 289.
 J. M. Aigler, J. L. Brito, P. A. Leach, M. Houalla, A. Proctor, N. J. Cooper, W. K. Hall and D. M. Hercules, J. Phys. Chem., 1993, **97**, 5699.
- 16 E. A. Stern, Phys. Rev. B, 1993, 48, 9825.
- 17 P. L. Gai-Boyes, Cat. Rev.-Sci. Eng., 1992, 34, 1; P. L. Gai, Philos. Mag., 1981, 43, 841; P. L. Gai and M. J. Goringe, Krist. Tech., 1979, 14, 1385.

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