JOURNAL OF CATALYSIS **82**, 373–381 (1983)

New SiO_2-Attached "Mo-Pair" Catalysts—Preparations, Surface Structures, and Chemical Nature

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Received November 2, 1982; revised February 16, 1983

New attached molybdenum-pair catalysts with well-defined surface structures were molecularly prepared by taking advantage of the reaction between a $Mo_2(\eta^3\text{-}C_3H_5)_4$ complex and surface OH groups of SiO_2 followed by chemical treatments. The surface-Mo_2 structures were characterized by means of ultraviolet diffuse reflection, photoluminescence, x-ray photoelectron spectroscopy, infrared, electron spin resonance, temperature-programmed hydrogenolysis, volumetry, and chemical analysis. The Mo(II)-pair chemically attached on a silica functioned as a reversible dioxygen carrier at 273–428 K. The high catalytic activities of the attached Mo_2 catalysts are also described.

INTRODUCTION

The ill-defined and heterogeneous properties of conventional supported catalysts restrain the molecular-level study on reaction mechanisms and active factors or origin of catalysis. A new class of supported molybdenum catalysts with more definitive properties has been developed using $Mo(CO)_6$ (*1*), $Mo(\eta^3\text{-}C_3H_5)_4$ (*2*), $Mo_2(\eta^3\text{-}C_3H_5)_4$ (*3*), $Mo_2(O_2CCH_3)_4$ (*4*), Mo vapor (*5*), etc. (*6*). Tailored metal catalysts with well-defined structures of active sites seem to have a great advantage for those fundamental researches in catalytic chemistry and to provide a new way to prepare excellent solid catalysts. However, molecular design of active structures in surface monolayer of oxide supports is still one of the most difficult challenges. We have demonstrated the possibility of the chemical design of catalyst surfaces with high catalytic activities using $Mo(\eta^3\text{-}C_3H_5)_4$ (*7*), $Mo_2(\eta^3\text{-}C_3H_5)_4$ (*8*), $Cr(\eta^3\text{-}C_3H_5)_3$ (*9*), and $Cr_2(\eta^3\text{-}C_3H_5)_4$ (*9b, 10*). In the present study the surface design, characterization, chemical nature, and catalysis of the molybdenum-pair catalysts derived from $Mo_2(\eta^3\text{-}C_3H_5)_4/SiO_2$ are reported.

EXPERIMENTAL

$Mo_2(\eta^3\text{-}C_3H_5)_4$ was synthesized under strictly oxygen-free conditions as previously reported (*3, 11*). $Mo_2(\eta^3\text{-}C_3H_5)_4$ was purified by two recrystallizations in pentane at 193 K. Pentane (guaranteed grade) was purified by reflux over Na wire for 15 h, followed by distillation in a flow of high purity (99.9995%) Ar.

The reaction between surface OH groups of silica and $Mo_2(\eta^3\text{-}C_3H_5)_4$ in pentane at 273 K was carried out in a Pyrex-glass apparatus equipped with six U-shaped glass tubes with breakseals under vacuum. Two types of silica, SiO_2-1(surface area: 120 m^2g^{-1}, obtained from Snowtex-30 of Nissan Kagaku Inc.) and SiO_2-2 (285 m^2g^{-1}, from Snowtex-O) were employed as supports. The numbers of surface OH groups of SiO_2-1 and SiO_2-2 were controlled to be 3.5 and 4.6 OH nm^{-2}, respectively, by heating in oxygen (9.33 kPa) followed by evacuation at 473 K *in situ* prior to the Mo attachment; the OH quantity was determined using $Al(C_2H_5)_3$ (*9c*). The attaching reaction of

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0021-9517/83 $3.00

$Mo_2(\eta^3\text{-}C_3H_5)_4$ with the silica at 273 K was completed within 15 min. The surface allyl-type complexes obtained were washed four times with pentane under vacuum in order to remove the residual free Mo_2 complex. The amount of molybdenum attached on a support was determined from the initial (before attachment) and the final (after attachment) concentrations of $Mo_2(\eta^3\text{-}C_3H_5)_4$ in pentane by colorimetry at 470 nm using a thiocyanate–$SnCl_2$ method (*7*). After attaching molybdenum onto silica, pentane, used as a solvent for the $Mo_2(\eta^3\text{-}C_3H_5)_4$, was evacuated at room temperature for 1 h. These attached catalysts in the attaching apparatus were transferred to each U-shaped tube with two breakseals and kept in dark until their use. The complex-type catalysts were further evacuated at 350 K for 1 h before use. Then the surface complexes were converted to various structures by H_2 reduction or O_2 oxidation at given temperatures.

Ultraviolet diffuse-reflectance spectra were measured on a JASCO-505 spectrophotometer in a thin quartz cell combined with a closed circulating system in which a variety of treatments were carried out; the difference spectra were always recorded placing pure supports, SiO_2-1 or SiO_2-2, on the reference side. ESR peaks were measured at 77 or 293 K without contacting air using a JEOL ESR spectrometer. Infrared spectra were taken by the self-supporting disk method in a quartz cell combined with a closed circulating system. Photoluminescence was monitored in a quartz cell connected to a vacuum line by a JASCO-FP4 spectrometer. X-Ray photoelectron spectroscopy (XPS) emissions of the attached Mo_2 catalysts were measured by a VG-ESCA-3.

The uptakes of H_2 or O_2 in reduction or oxidation of surface molybdenum species were followed by manometer in a closed circulating system with a liquid N_2 trap. The temperature-programmed hydrogenolysis of the allyl ligands of the fixed complexes was carried out under H_2 partial pressure of 8.0 kPa; the heating rate was 4 K min^{-1}. The products desorbed were analyzed at adequate intervals by gas chromatography using a VZ-10 column and a 5 Å molecular sieve column commercially obtained.

RESULTS AND DISCUSSION

Attachment of Molybdenum

SiO_2-1 (120 $m^2\ g^{-1}$, 3.5 OH nm^{-2}) and SiO_2-2 (285, 4.6) with the definite amounts of surface OH were employed as supports. $Mo_2(\eta^3\text{-}C_3H_5)_4$ with a Mo–Mo bond distance of 0.2183 nm (*11b*) (2.5–5 mmol dm^{-3} in pentane) reacted exclusively with the surface OH groups of silica at 273 K. The intensity of the OH stretching band for SiO_2 decreased by the Mo_2 fixation similarly to the case of the mononuclear Mo fixation (*7a*). The fixing reactions were completed within 15 min. The Si–O–Si bonds were less reactive toward the $Mo_2(\eta^3\text{-}C_3H_5)_4$; no significant amount of the complex reacted with the surface lattice oxygen within 30 min under similar conditions. The Mo quantities of the attached catalysts employed were in the range of 0.2–1.0 wt% as Mo/SiO_2 according to chemical analysis.

The number of the allyl ligands on a Mo atom in the surface complex derived from $Mo_2(\eta^3\text{-}C_3H_5)_4/SiO_2$ was determined in the same manner as that for the Al_2O_3-attached Mo_2 complex (*8e*). The results are given in Table 1. It was found that the surface complex obtained by the reaction of $Mo_2(\eta^3\text{-}C_3H_5)_4$ and SiO_2-1 has about one C_3 ligand per Mo atom, while on SiO_2-2 two C_3 ligands coordinate to a Mo atom. In other words, $Mo_2(\eta^3\text{-}C_3H_5)_4$ released no C_3 ligand during the attaching reaction with SiO_2-2, whereas one C_3 ligand per Mo atom was lost over SiO_2-1. The allyl ligands of the surface complexes were eliminated with H_2. It was clarified from the amount of dioxygen consumed in the oxidation of the ligand-eliminated molybdenum to the hexavalent level, taking into account the small amounts of CO_2 formed, that the ligand-free Mo is in bivalent level, that is, in bidentate form.

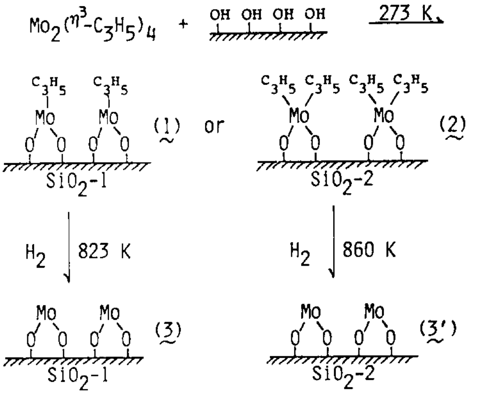
TABLE 1

Stoichiometries (allyl ligand/Mo) in the Surface Complexes Obtained by the Reaction between $Mo_2(\eta^3\text{-}C_3H_5)_4$ and Silica with Given Numbers of Surface OH Groups at 273K

Support	SiO_2-1			SiO_2-2		
Surface area of support (m^2g^{-1})	120			285		
Surface OH number (OH nm^{-2})	3.5			4.6		
Chemical analysis of molybdenum[a]	0.42	0.68	1.0	0.21	0.49	0.70
Number of C_3-ligand per Mo atom in the surface complex	1.04	1.10	1.10	1.95	2.05	1.98

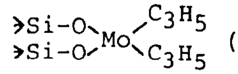
[a] Wt% as Mo/SiO_2.

Accordingly, the Mo_2 attachment is best expressed by Scheme 1. The molybdenum is formally oxidized to Mo^{III} or Mo^{IV} from Mo^{II} by the attachment onto the silica, liberating H_2 which was detected by mass spectrometry.



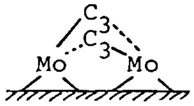
SCHEME 1

Figure 1 depicts the temperature-programmed hydrogenolysis (TPH) chromatogram of the SiO_2-1-attached Mo^{III}-pair complex (**1**). Propane and ethane were mainly desorbed, showing a one-peak pattern around 590 K. Propene peak was also observed at a similar temperature. The TPH chromatogram was almost unchanged with the Mo quantity in the range of 0.2–1.0 wt%; it implies that the species (**1**) are approximately uniformly distributed on the SiO_2-1 surface. On the other hand, the single Mo complex on SiO_2-1,



(A),

which is prepared by the reaction between a mononuclear $Mo(\eta^3\text{-}C_3H_5)_4$ complex and silica, was decomposed, evolving mainly ethane, at much lower temperatures (peak position: 438 K) as shown in Fig. 2. The thermal stability and decomposition pattern of the allyl ligands coordinated to the Mo^{III}-pair (**1**) are evidently different from those of the single Mo^{IV}–allyl species (A). The difference may be derived from the different oxidation states of molybdenum ions as well as the μ-type ligand-coordination as



Photoluminescence data revealed that two molybdenum atoms are adjacently located at a short distance as described in the next section.

The TPH analysis of the SiO_2-2-attached Mo^{IV}_2–allyl complex (**2**) is shown in Fig. 3. The complex (**2**) was also thermally stable, compared to a free $Mo_2(\eta^3\text{-}C_3H_5)_4$ complex. In contrast to the TPH chromatogram of the single Mo^{IV} complex (A) in Fig. 2, the two-peak pattern (peak I and peak II) was observed. The products in peak I at ca. 508 K in Fig. 3 were mainly ethane and pro-

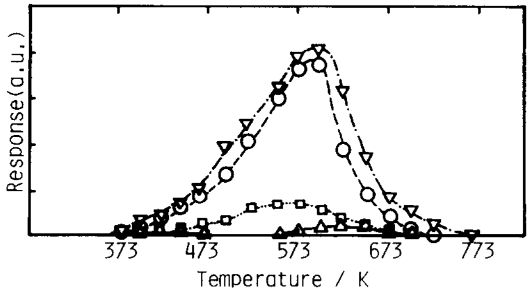


FIG. 1. Temperature-programmed hydrogenolysis (TPH) chromatogram of the SiO_2-1-attached Mo_2–allyl complex (**1**); Mo/SiO_2 = 0.68 wt%, heating rate: 4K min^{-1}, H_2 flow: 50 cm^3 min^{-1}, (○) ethane, (△) ethene, (▽) propane, (□) propene.

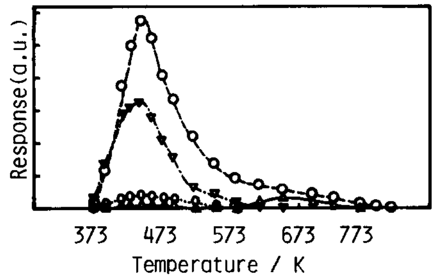
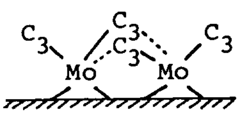


FIG. 2. TPH chromatogram of the single Mo complex (A) (1.0 wt%) on SiO_2-1; (○) ethane, (△) ethene, (▽) propane, (0) butane.

pane, while ethene and propene were desorbed in the higher temperature range (peak II). The different chromatograms of peak I and peak II suggest the presence of two types of allyl ligands with different environments and bondings. The peak II for the species (**2**) may be due to two allyl groups of the four groups which interact with the adjacent molybdenum in the paired structure as



Since the attached Mo_2–allyl complex on SiO_2-2 showed always almost the same TPH pattern, regardless of the Mo quantity, individual surface Mo^{IV}-pairs (**2**) seem to have a nearly uniform nature. The species (**2**) was found to be highly active for propene metathesis at 273 K. The turnover frequency was independent of the Mo quantity in the range 0.2–0.7 wt%; e.g., 0.056 s^{-1} at 273 K and propene pressure of 2.6 kPa. This also indicates a uniformity of each Mo ion.

Surface Design of Molybdenum-Pair Structures

1. Molybdenum structures on SiO_2-1 surface. The surface molybdenum–allyl complex (**1**) was reduced with H_2 to the bivalent molybdenum as above mentioned. The Mo^{II} ion was quantitatively oxidized to the hexavalent level with O_2 at 838 K. The obtained Mo^{VI} ion (**6**) in Scheme 2 showed the XPS doublet peak stemming from emissions from the $3d$ level. The binding energies of Mo $3d_{3/2}$ and $3d_{5/2}$ levels, referred to 83.8 eV of Au $4f_{7/2}$, were 235.8 and 232.8 eV, respectively. The binding energies of the Mo $3d$ levels of this attached catalyst were similar to those of Mo^{VI} ions of pure MoO_3 (235.6 eV for $3d_{3/2}$ and 232.6 eV for $3d_{5/2}$). The XPS emission spectrum reveals that the molybdenum species (**6**) molecularly synthesized via (**3**) are genuinely in a hexavalent level. No impurity-Mo^V ion in the attached-$Mo^{VI}{}_2$ catalyst was detected by means of ESR spectroscopy at any temperature.

The uv diffuse-reflectance spectra of the SiO_2-1-attached $Mo(VI)_2$ catalyst (**6**) in Fig. 4(a) showed a $t_1 \rightarrow 3t_2$ absorption (*12*) at 34.5×10^3 cm^{-1} (290 nm) referred to the charge-transfer band (Mo^{6+}=O^{2-}) of a tetrahedral Mo^{VI} ion (*13*). No shoulder at longer wavelengths than 290 nm was observed. The uv spectrum of the (**6**) was sim-

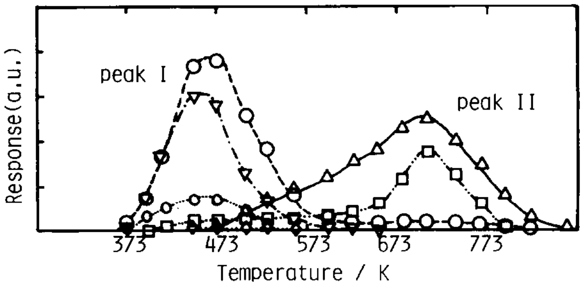


FIG. 3. TPH chromatogram of the SiO_2-2-fixed Mo_2 complex (**2**); Mo/SiO_2 = 0.49 wt%, (○) ethane, (△) ethene, (▽) propane, (□) propene, (0) butane, (◇) butene.

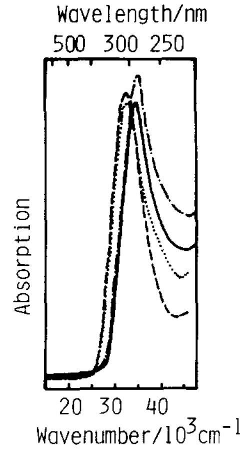


FIG. 4. Ultraviolet diffuse-reflectance spectra; (a) single Mo(VI) (-·-·) and Mo(VI)-pair (—) on SiO_2-1, (b) single Mo(VI) (···) and Mo(VI)-pair (---) on SiO_2-2. The spectra were essentially unchanged with Mo loadings in the range 0.2–1.0 wt%.

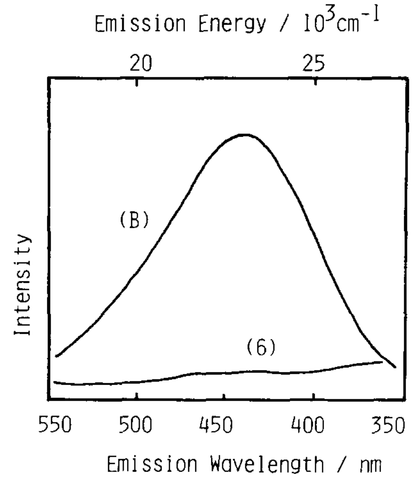
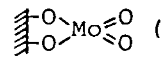


FIG. 5. Photoluminescence of the SiO_2-1-attached single Mo^{VI} ion (B) and Mo^{VI}-pair species (6); E_x: 33.9 × 10^3 cm^{-1}.

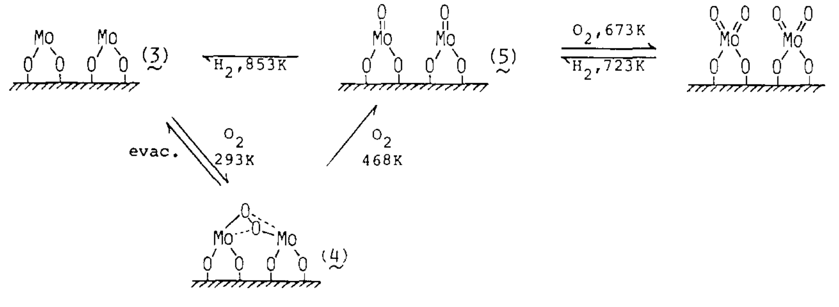
ilar to a CT absorption (35.1 × 10^3 cm^{-1}, 285 nm) of the tetrahedral dioxostructure,


(B),

derived from the single Mo complex (A), as shown in Fig. 4(a). Thus each Mo ion of the "paired" structure (6) seems to have a similar tetrahedral structure to (B).

The two molybdenum atoms of a Mo-pair at SiO_2-1 surface were located closely with some interaction as evidenced by a photoluminescence technique. The isolatedly distributed "single" Mo^{VI} structure (B) showed an emission at 22.9 × 10^3 cm^{-1} from the lowest triplet T_1 state by an illumination of the CT band ($Mo^{6+}{=}O^{2-}$) in Fig. 5. The emission energy was independent of the excitation energy in the range of 31.2–35.1 × 10^3 cm^{-1}, indicating the uniform nature of the Mo^{VI}-emitting species. It was found that the paired structure (6) on SiO_2-1 (0.2–1.0 Mo wt%) did not luminesce. The quenching of emission implies a strong interaction between two adjacent Mo ions. Again the complete quenching suggests the absence of a single species in the pair catalysts.

The tetrahedral dioxomolybdenum(VI)-pair (6) was reduced stepwisely to the $Mo(IV)_2$ species (5) at 723 K and then at 853 K to the Mo^{II} level (3), uptaking the stoichiometric amount of H_2 as shown in Fig. 6 and Table 2. That the oxidation number was 2 is indicated also from the stoichiometric uptake of O_2 in the oxidation of



SCHEME 2. SiO_2-1.

TABLE 2

Stoichiometries in Reduction and Oxidation of Molybdenum Ions Contained in the Attached Mo_2 Catalysts

H_2 or O_2 uptake per Mo atom	Temperature (K)	Step	Support	
			SiO_2-1[a]	SiO_2-2[b]
H/Mo	723	$Mo^{VI} \rightarrow Mo^{IV}$	2.0_8	
H/Mo	723	$Mo^{VI} \rightarrow Mo^{V}$		0.97[c]
H/Mo	773	$Mo^{V} \rightarrow Mo^{IV}$		1.0_1
H/Mo	853	$Mo^{IV} \rightarrow Mo^{II}$	2.0_3	2.0_2
O/Mo	273	$Mo^{II} \rightarrow Mo^{III}$	1.0_0[d]	
O/Mo	273	$Mo^{II} \rightarrow Mo^{IV}$		1.0_2
O/Mo	468	$Mo^{II} \rightarrow Mo^{IV}$	1.0_9	
O/Mo	673	$Mo^{IV} \rightarrow Mo^{VI}$	0.99	0.99

[a] Mo/SiO_2-1 = 0.68 wt%.
[b] Mo/SiO_2-2 = 0.49 wt%.
[c] After reduction for 2 h.
[d] Reversible, at 13.3 kPa of O_2.

the (**3**) to the Mo(VI) level in Table 2. The reduction of Mo^{VI}-pair at 723 K was slower than that of single Mo^{VI}. The Mo^{IV} and Mo^{II} ions on SiO_2-1 showed structureless uv peaks. The SiO_2-1-attached Mo^{II}-pair catalyst showed a much higher activity than the corresponding single Mo^{II} catalyst for ethene hydrogenation at 293 K (*8a*).

It was found that the Mo^{II}-pair structure (**3**) chemically attached on SiO_2-1 surface, which was prepared by stoichiometric reduction (Fig. 6) of the Mo^{VI}-pair (**6**) with a direct interaction between the adjacent Mo ions, reversibly binds dioxygen in the temperature range 273–428 K. It is known that the single Mo^{II} ion was instantaneously and irreversibly oxidized to a Mo^{IV} ion with O_2 at 273 K (*2*, *7*). The attached Mo^{II}-pair is the first reversible oxygen carrier among the group 6A metals. The dioxygen uptake at 273 K reached equilibrium within 25 min as shown in Fig. 7, while the coordinated dioxygen was completely desorbed within 15 min *in vacuo*. Irreversible uptake started at about 455 K to form the oxomolybdenum (IV) species (**5**), with stoichiometric uptake at 673 K to give the Mo^{VI} species (**6**), as shown in Fig. 7. The stoichiometries in the mutual transformations of (**3**), (**4**), (**5**), and (**6**) are given in Table 2. Figure 8 shows typical Langmuir plots for reversible dioxygen uptake at 273, 326, 377, and 404K. The linear relations and the mass adsorbed at saturation which was independent of temperature indicate that one molecule of dioxygen coordinates to one Mo^{II}-pair. The reversible dioxygen complex was diamagnetic according to ESR studies. Thus the surface dioxygen complex (**4**) in Scheme 2 may be represented formally as Mo^{3+}–O_2^{2-}–Mo^{3+}.

ΔH^0 and ΔS^0 for the process were calcu-

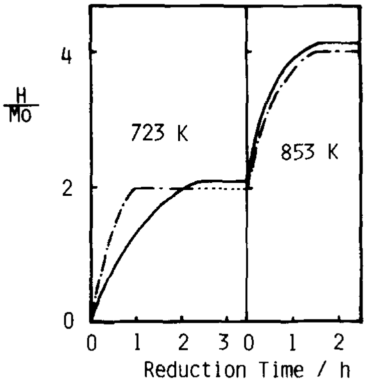


FIG. 6. Stoichiometric reductions of single Mo^{VI} ions (-·--) and Mo^{VI}-pairs (—) on SiO_2-1; H_2 pressure: 8.0 kPa.

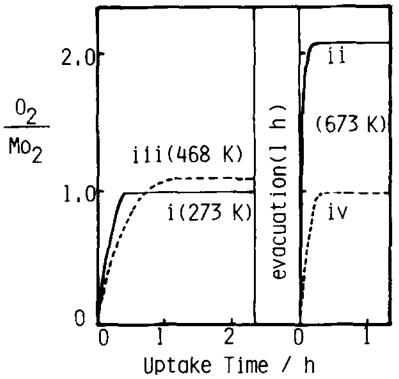


FIG. 7. O_2 uptake on the Mo(II)-pair structure (**3**) (Mo/SiO_2 = 0.68 wt%). Step a (—) (i), O_2 (13.3 kPa) at 273°K followed by evacuation at 273°K for 1 h, then (ii), O_2 (9.3 kPa) at 673°K. Step b (---) (iii), O_2 (9.3 kPa) at 468°K followed by evacuation at 468°K for 1 h, then (iv), O_2 (9.3 kPa) at 673°K.

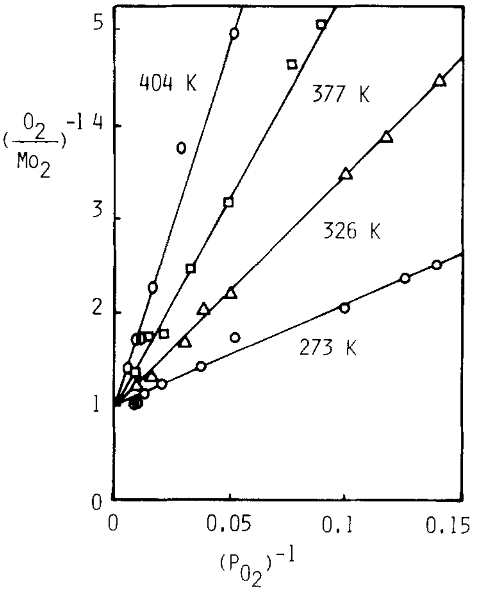


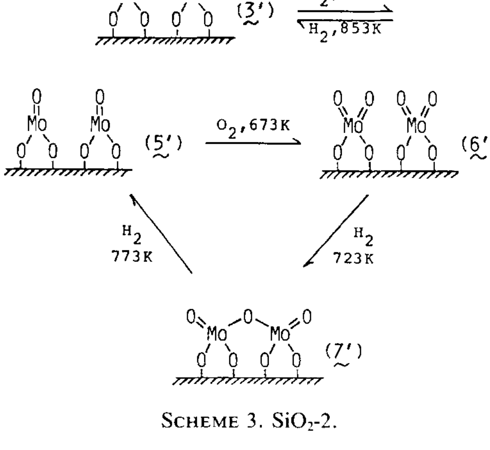
FIG. 8. Langmuir plots for reversible O_2 uptake on the SiO_2-1-fixed Mo_2 structure (3) according to the equation $(O_2/Mo_2)^{-1} = 1 + K_{eq}{}^{-1}P_{O_2}{}^{-1}$, where (O_2/Mo_2) represents the fraction of saturation at equilibrium.

lated to be −14 kJ mol^{-1} and −71 J K^{-1} mol^{-1}, respectively, using the Van't Hoff isotherm. Comparison of the equilibrium constant (K_{eq} = 0.069 $Torr^{-1}$, or $P_{1/2}$ = 14 Torr, at 293 K), ΔH^0 and ΔS^0 for the Mo_2–O_2 complex formation with those for other oxygen carriers demonstrates that the attached Mo_2 species binds dioxygen more easily than Co–myoglobin (*14*), Co–"picket fence" porphyrins (*15*), and Co–protoporphyrins (*16*), but more weakly than human myoglobin (*17*), Fe–"picket fence" porphyrins (*18*) and Co–Schiff base complexes (*16*). The surface Mo^{II}-pair (**3**) functioned as an oxygen carrier under mild conditions over a wide range of temperatures.

The fact that an ir absorption at 1415 cm^{-1}, which may be assigned to an ONO group (*19*) coordinated to molybdenum, appeared when NO was admitted onto the Mo_2–O_2 complex (**4**) at 293–373 K, indicates the presence of reactive dioxygen. The dioxygen of the (**4**) also reacted with cyclohexene or carbon monoxide to form benzene or carbon dioxide at 423 K, respectively. The turnover frequency of catalytic CO oxidation with O_2 over (**4**) was 1.2 × 10^{-5} s^{-1} at 423 K and 29.7 Torr of CO; the rate of CO_2 formation at 423 K was compared to that at 678 K on the Mo^{VI} catalyst (**6**). Thus the reversibly bound dioxygen is activated by electron transfer from the adjacent Mo^{II} ions.

2. Molybdenum structures on SiO_2-2 surface. The Mo^{II}-pair species (**3′**) formed by the ligand elimination of the surface complex (**2**) on SiO_2-2 was stoichiometrically oxidized with O_2 to the hexavalent level (**6′**) as shown in Scheme 3. The CT absorption ($Mo^{6+}{=}O^{2-}$ bond) of the SiO_2-2-attached $Mo(VI)_2$ catalyst (**6′**) at 32.7 × 10^3 cm^{-1} (306 nm) with half-value width of 8.8 × 10^3 cm^{-1} (80 nm) was similar to that observed at 33.0 × 10^3 cm^{-1} (303 nm) (9.4 × 10^3 cm^{-1}), 87 nm in width) for the single Mo^{VI} ion as shown in Fig. 4(b). The hexavalent molybdenum on SiO_2-2 derived from the dinuclear $Mo_2(\eta^3\text{-}C_3H_5)_4/SiO_2\text{-}2$ seems to take a pair-structure consisting of two Mo^{VI} ions. The CT-peak position suggests that a Mo ion is situated in octahedral coordination (*13*), or probably five-coordination taking into account the low Mo loading on the tetrahedral SiO_2 framework.

The initial rate of the oxidative dehydrogenation of ethanol to form acetaldehyde over the attached single Mo(VI) catalyst



SCHEME 3. SiO_2-2.

showed a 1:1 correlation with the Mo quantity:

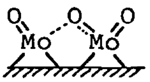
$$C_2H_5OH + Mo^{VI} \rightarrow CH_3CHO + H_2O + Mo^{IV}. \quad (a)$$

On the other hand, over the attached $Mo(VI)_2$ catalyst (**6′**) the rate had a linear relation with the Mo-pair quantity as expressed by (*20a*):

$$C_2H_5OH + Mo^{VI}–Mo^{VI} \rightarrow CH_3CHO + H_2O + Mo^{V}–Mo^{V}. \quad (b)$$

This cooperative catalysis of two Mo^{VI} ions strongly suggests the adjacent location of two Mo^{VI} ions with a suitable Mo–Mo separation. The reaction catalytically proceeded in the presence of O_2 by two-stage redox mechanism (*20a*).

The $Mo(VI)_2$ species (**6′**) was reduced at first to the Mo^{V} level with H_2 at 723 K as shown in Fig. 9, whereas the reduction pattern of a Mo^{VI} ion isolatedly distributed is generally given by the steps $Mo(VI) \rightleftharpoons Mo(IV) \rightleftharpoons Mo(II)$. The reduction behavior of (**6′**) is compatible with the cooperative mechanism for the two-electron transfer reaction of Eq. (b). The uv spectrum of the Mo(V)-level species (26.0×10^3 cm^{-1} (main) and 22.6×10^3 cm^{-1} (sh)) was not a superimposed one of Mo^{VI} (32.7×10^3 cm^{-1}) and Mo^{IV} (27.1×10^3 cm^{-1}) peaks. The Mo(V) species was diamagnetic by ESR studies. These results suggest the dinuclear bismolybdenyl(V) structure (**7′**) although a strongly interacted $Mo^{VI}–Mo^{IV}$ pair,



cannot be excluded. The species (**7′**) was reduced eventually to the bivalent level (**3′**) via a quadrivalent molybdenum (**5′**), uptaking the stoichiometric amount of H_2 as shown in Fig. 9 and Table 2 and evolving the quantitative amount of H_2O. In general the paired molybdenum was more hardly reduced with H_2 than the corresponding single structure.

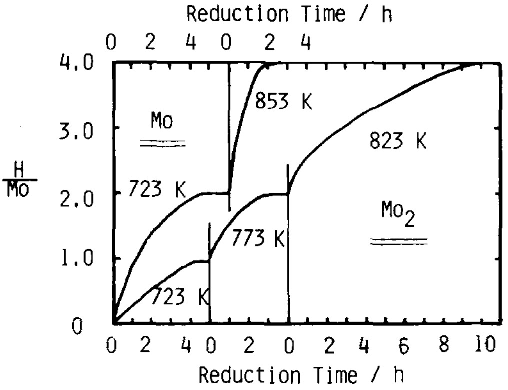
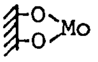


FIG. 9. Reduction behaviors of Mo^{VI} and Mo^{VI}_2 species attached on SiO_2-2 surface (Mo/SiO_2 = 0.49 wt%).

The Mo^{II}-pair (**3′**) on SiO_2-2 did not form a reversible dioxygen complex in contrast to the SiO_2-1-attached Mo^{II}-paired (**3**) as shown in Scheme 3. The arrangement and distance of two adjacent



in the paired structures (**3**) and (**3′**) may be different. EXAFS studies would give a distinct information on this problem (*20b*). The irreversible oxidation of the Mo^{II}-pair (**3′**) proceeded much more slowly than that of a single Mo^{II} ion which was nearly instantaneously oxidized at 273 K. The $Mo(VI)_2$ structure (**6′**) was recovered again by oxidation of (**5′**) at 673 K. The stoichiometries in the processes are given in Table 2. Thus various molybdenum-pair structures (**3′**)–(**7′**) were found to be chemically designed on silica surface via the attached allyl complex (**2**) with a uniform nature. The attached Mo_2 catalyst was very stable below 870 K judging from unchanged redox curves and stoichiometric behaviors in the mutual structure transformations and constant catalytic activities of the species (**5′**) or (**6′**) for propene metathesis or oxidative dehydrogenation of ethanol.

REFERENCES

1. Davie, E. S., Whan, D. A., and Kemball, C., *Chem. Commun.* 1430 (1969); Burwell, R. L. Jr., *et al.*, *J. Amer. Chem. Soc.* **97,** 2565 (1975); Brenner, A., and Burwell, R. L. Jr., *J. Catal.* **52,** 364 (1978); Kazusaka, A., and Howe, R. F., *J. Mol. Catal.* **9,** 183 (1980); etc.
2. Yermakov, Yu. I., *Catal. Rev.* **13,** 77 (1976); Yermakov, Yu. I., Zakharov, V. A., and Kuznetsov, B. N., *in* "Catalysis by Supported Complexes." Elsevier, 1981.
3. Candlin, J. P., and Thomas, H., *Adv. Chem. Ser.* **132,** 212 (1974).
4. Best, S. A., Squires, R. G., and Walton, R. A., *J. Catal.* **60,** 171 (1979).
5. Francis, C. G., Huber, H., and Ozin, G. A., *Inorg. Chem.* **19,** 219 (1980).
6. Leal, O., Goldwarser, M. R., Lopez, R., and Arzoumarian, H., *in* "Proceedings, 7th Int. Congress on Catalysis, Tokyo, 1980" (Seiyama and Tanabe, Eds.), p. 1512. Elsevier, 1981.
7. (a) Iwasawa, Y., Nakano,. Y., and Ogasawara, S., *J. Chem. Soc. Faraday I* **74,** 2968 (1978); (b) Iwasawa, Y., Ogasawara, S., and Soma, M., *Chem. Lett.* 1039 (1978); (c) Iwasawa, Y., and Ogasawara, S., *J. Chem. Soc. Faraday I* **75,** 1465 (1979); (d) Iwasawa, Y., Nakamura, T., Takamatsu, K., and Ogasawara, S., ibid. **77,** 939 (1980); (e) Iwasawa, Y., Ichinose, H., Ogasawara, S., and Soma, M., ibid. **77,** 1763 (1981); (f) Iwasawa, Y., and Ogasawara, S., *Bull. Chem. Soc. Jpn.* **53,** 3709 (1980).
8. (a) Iwasawa, Y., Yamagishi, M., and Ogasawara, S., *J. Chem. Soc. Chem. Commun.* 871 (1980); (b) Iwasawa, Y., Kubo, H., Yamagishi, M., and Ogasawara, S., *Chem. Lett.* 1165 (1980); (c) Iwasawa, Y., Yamagishi, M., and Ogasawara, S., *J. Chem. Soc. Chem. Commun.* 246 (1982); (d) Sato, Y., Iwasawa, Y., and Kuroda, H., *Chem. Lett.* 1101 (1982); (e) Iwasawa, Y., Sato. Y., and Kuroda, H., *J. Catal.*, in press.
9. (a) Iwasawa, Y., and Ogasawara, S., *Chem. Lett.* 127 (1980); (b) Iwasawa, Y., Sasaki, Y., and Ogasawara, S., *J. Mol. Catal.* **16,** 27 (1982); (c) Iwasawa, Y., ibid. **17,** 93 (1982).
10. Iwasawa, Y., Sasaki, Y., and Ogasawara, S., *J. Chem. Soc. Chem. Commun.* 140 (1981).
11. (a) Wilke, G., *et al.*, *Angew. Chem. Int. Edn.* **5,** 151 (1966); (b) Cotton, F. A., and Pipal, J. R., *J. Amer. Chem. Soc.* **93,** 5441 (1971); Cotton, F. A., *Chem. Soc. Rev.* **4,** 27 (1975).
12. Wolfsberg, M., and Helmholz, L., *J. Chem. Phys.* **20,** 837 (1952); Ballhausen, C. J., and Liehr, A. D., *J. Mol. Spectrosc.* **2,** 342 (1958).
13. Che, M., Figueras, F., Forissier, M., McAteer, J., Perrin, M., Portefaix, J. L., and Praliaud, H., *in* "Proceedings, 6th Int. Congress on Catalysis, The Chemical Society, London, 1977," Vol. 1, p. 261; Asmolov, G. N., and Krylov, O. V., *Kinet. Katal.* **11,** 847 (1971).
14. Hoffman, B. M., and Petering, D. H., *Proc. Nat. Acad. Sci. USA* **67,** 637 (1970); Spilburg, C. A., Hoffman, B. M., and Petering, D. H., *J. Biol. Chem.* **247,** 4219 (1972).
15. Collman, J. P., Brauman, J. I., Doxsee, K. M., Halbert, T. R., Hayes, S. E., and Suslick, K. S., *J. Amer. Chem. Soc.* **100,** 2761 (1978).
16. Jones, R. D., Summervill, D. A., and Basolo, F., *Chem. Rev.* **79,** 139 (1979); Valentine, J. S., ibid. **73,** 235 (1973); McLendon, G. G., and Martell, A. E., *Coord. Chem. Rev.* **19,** 1 (1976); Vaska, L., *Acc. Chem. Res.* **9,** 175 (1976); Fallab, S., Hunold, H. P., Maeder, M., and Mitchell, P. R., *J. Chem. Soc. Chem. Commun.* 469 (1981). Most of the Co-complexes in homogeneous systems have been investigated at much lower temperatures for reversible dioxygen binding.
17. Fanelli, A. R., and Antonini, E., *Arch. Biochem. Biophys.* **77,** 478 (1958).
18. Collman, J. P., Brauman, J. I., and Suslick, K. S., *J. Amer. Chem. Soc.* **97,** 7185 (1975); Collman, J. P., *et al.*, ibid. **97,** 1427 (1975).
19. Nakamoto, K., *in* "Infrared and Raman Spectra of Inorganic and Coordination Compounds," 3rd edn., p. 220–226. Wiley, New York, 1978; Blyholder, G., and Allen, M. C., *J. Phys. Chem.* **70,** 352 (1966).
20. (a) Iwasawa, Y., and Tanaka, H., to be published; (b) Ishii, T., Iwasawa, Y., and Kuroda, H., to be published.