Surface Design and Characterization of New Al$_2$O$_3$-Attached "Mo-Pair" Catalysts

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New attached molybdenum catalysts with well-defined surface structures were molecularly prepared on the basis of the reaction between Mo$_2$(η^3-C$_3$H$_5$)$_4$ and surface OH groups of Al$_2$O$_3$, followed by chemical treatments. The surface Mo$_2$-structures were characterized by means of EXAFS, uv diffuse reflectance, XPS, ESR, temperature-programmed hydrogenolysis, volumetry, and chemical analysis. The high activities of the well-defined-attached Mo$_2$ catalysts were also mentioned.
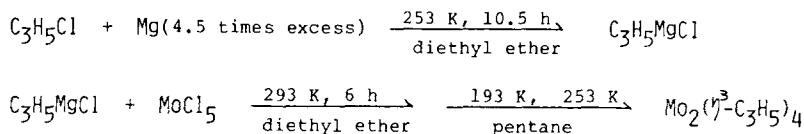
INTRODUCTION

It is known that the ill-defined and heterogeneous nature of conventional supported catalysts can be the cause of conflicting experimental results. Tailored metallic catalysts with well-defined reaction sites provide clear information on reaction mechanisms and active factors or origin of catalysis as well as a new implication for preparations of excellent solid catalysts. However, molecular design in surface monolayer on inorganic oxide supports has been one of the most difficult challenges.

We have reported the preparations of highly active, well-defined-attached molybdenum or chromium catalysts using Mo(η^3-C$_3$H$_5$)$_4$ (*1*), Mo$_2$(η^3-C$_3$H$_5$)$_4$ (*2*), Cr(η^3-C$_3$H$_5$)$_3$ (*3*), or Cr$_2$(η^3-C$_3$H$_5$)$_4$ (*3b, 4*). In the present study the surface design and characterization of the molybdenum-pair catalysts derived from Mo$_2$(η^3-C$_3$H$_5$)$_4$/alumina are reported.

EXPERIMENTAL

Mo$_2$(η^3-C$_3$H$_5$)$_4$ (*5–7*) was synthesized under strictly oxygen-free conditions via the following steps, as previously reported (*2*),

$$\text{C}_3\text{H}_5\text{Cl} + \text{Mg}(4.5 \text{ times excess}) \xrightarrow[\text{diethyl ether}]{253 \text{ K, } 10.5 \text{ h}} \text{C}_3\text{H}_5\text{MgCl}$$

$$\text{C}_3\text{H}_5\text{MgCl} + \text{MoCl}_5 \xrightarrow[\text{diethyl ether}]{293 \text{ K, } 6 \text{ h}} \xrightarrow[\text{pentane}]{193 \text{ K, } 253 \text{ K}} \text{Mo}_2(\eta^3\text{-C}_3\text{H}_5)_4$$

SCHEME 1

Allyl chloride (guaranteed grade) was refluxed for 5 h over 5-Å molecular sieve, followed by distillation in a flow of high purity (99.9995%) Ar. Diethyl ether and pentane (GR grade) were purified by reflux over Na wire, followed by distillation in a flow of

high purity Ar. MoCl$_5$(99%, Mitsuwa Kagaku Inc.) and Mg(99.99%, Mitsuwa) were used without further purification. The syntheses were performed in a specially devised Pyrex-glass apparatus under vacuum (1.33 × 10^{-3} Pa) or in a flow of high purity Ar at atmospheric pressure. Mo$_2$ (η^3-C$_3$H$_5$)$_4$ was purified by two recrystallizations in pentane at 193K.

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The reaction (7) between surface OH groups of alumina and $Mo_2(\eta^3\text{-}C_3H_5)_4$ in pentane at 273K was carried out under vacuum in a Pyrex-glass-attaching apparatus equipped with six U-shaped tubes with breakseals.

Two types of γ-alumina, Al_2O_3-1 (190 m^2 g^{-1}) and Al_2O_3-2 (385 m^2 g^{-1}), were employed as supports. The number of surface OH groups on Al_2O_3-1 and Al_2O_3-2 was controlled to be 2.6 and 4.5 OH nm^{-2}, respectively, by heating in oxygen (9.33 kPa) followed by evacuation at 773K *in situ* prior to the Mo fixation. The OH quantity was determined from the amount of ethane evolved by the reaction of the OH groups and $Al(C_2H_5)_3$ (8). The fixing reactions of $Mo_2(\eta^3\text{-}C_3H_5)_4$ with the alumina at 273K were rapid and completed within 10 min. The surface allyl-type complexes obtained were washed 4 times with pentane under vacuum in order to remove the residual free Mo_2 complex. Some Mo remained in the pentane solution after the Mo_2 attaching and the washing solution was analyzed by colorimetry at 470 nm using a standard thiocyanate–SnCl$_2$ method. 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. The amount of molybdenum was also analyzed by decomposing the alumina-supported Mo catalysts with a 1 : 1 mixture of nitric acid (20.3%) and sulfuric acid (32.3%). After attaching molybdenum onto alumina, the pentane, used as a solvent for the $Mo_2(\eta^3\text{-}C_3H_5)_4$, was removed by evacuation at room temperature for 1 h. These attached catalysts in the attaching apparatus were transferred to each U-shaped tube equipped with two breakseals and kept in dark until used. The complex-type catalysts were further evacuated at 350K for 1 h before use. The surface complexes were converted to various structures by H$_2$ or O$_2$ treatments at specific temperatures.

X-Ray absorption spectrum of the attached Mo_2 catalyst was taken on a laboratory EXAFS (extended X-ray absorption
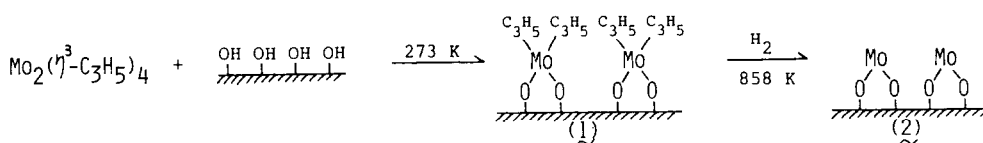
fine structure) spectrometer equipped with a high-power rotating-anode (Cu target) X-ray generator (Rigaku RU-1000) which operated at a tube voltage of 45 kV and a tube current of 950 mA (9). The energy resolution in the MoK edge region was about 20 eV. The period of data collection was about 24 h and the accumulated counts for I and I_0 were 140,000. K_2MoO_4 and Mo powder (99.9% purity) were chosen as the standards for empirical curve-fitting procedure. 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, Al_2O_3-1 or Al_2O_3-2, on the reference side. ESR peaks were measured at 77 or 293K without contacting air using a JEOL ESR spectrometer. XPS emissions of the attached Mo_2 catalysts were measured by a VG-ESCA-3.

The uptake of H$_2$ or O$_2$ in reduction or oxidation of surface molybdenum species was followed manometrically in a closed circulating system equipped with a liquid N$_2$ trap. The temperature-programmed hydrogenolysis of the allyl ligands of the attached complexes was carried out under H$_2$ partial pressure of 8.0 kPa; the heating rate was 4K min^{-1}. The products desorbed were analyzed at adequate intervals by gas chromatography using VZ-10 and 5-Å molecular sieve columns.

RESULTS AND DISCUSSION

Mo Attachment to Form Surface Complexes

Al_2O_3-1 (190 m^2 g^{-1}, 2.6 OH nm^{-2}) and Al_2O_3-2 (385, 4.5) with the definite amounts of surface OH were employed as supports. $Mo_2(\eta^3\text{-}C_3H_5)_4$ with a Mo–Mo distance of 0.2183 nm (6), 2.5–5 mmol dm^{-3} in pentane, reacted exclusively with the surface OH groups of alumina at 273K. The Al–O–Al bonds were less reactive toward the $Mo_2(\eta^3\text{-}C_3H_5)_4$; no Mo_2–complex reacted with the surface lattice oxygen within 30 min under the present conditions. The Mo

$$Mo_2(\eta^3\text{-}C_3H_5)_4 \;+\; \underset{\text{OH OH OH OH}}{\text{////////}} \quad\xrightarrow{273\ K}\quad (1) \quad\xrightarrow[858\ K]{H_2}\quad (2)$$

SCHEME 2

quantities chemically attached on Al$_2$O$_3$-1 and Al$_2$O$_3$-2 were in the range of 0.2–1.0 wt% as Mo/Al$_2$O$_3$ according to chemical analysis.

The allyl ligands of the surface complexes derived from Mo$_2$(η^3-C$_3$H$_5$)$_4$/Al$_2$O$_3$ were decomposed with H$_2$ at 858K, evolving C$_1$–C$_4$ hydrocarbons. Small amounts of carbon remained at the surface after the ligand decomposition. The C amounts were determined by oxidizing with O$_2$ to CO$_2$ at 838K; O$_2$ was carefully admitted onto the surface at first at room temperature in order to avoid too rapid (exothermic) oxidation of bivalent molybdenum. Thus the number of the allyl ligands on a Mo atom in the surface complexes was calculated from the equation $\left(i\sum_{i=1}^{4}C_i + CO_2\right)/3$. The results are given in Table 1. The surface complexes obtained by the reaction of Mo$_2$(η^3-C$_3$H$_5$)$_4$ and Al$_2$O$_3$-1 or Al$_2$O$_3$-2 were found to have two (1.95–2.00) C$_3$-ligands per Mo atom, that is, Mo$_2$(η^3-C$_3$H$_5$)$_4$ released no C$_3$-ligand

during the attaching reaction. Furthermore, it is evident 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 bivalent molybdenum species were formed by the ligand decomposition of the surface complexes.

Accordingly, the Mo$_2$ attachment is best expressed by Scheme 2. The molybdenum is formally oxidized to Mo^{IV} from Mo^{II} by its attaching onto the alumina.

Figure 1 depicts a typical temperature-programmed hydrogenolysis (TPH) curve of the surface complex (A)
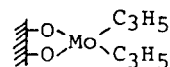
(1b, c, e), obtained by use of a mononuclear Mo(η^3-C$_3$H$_5$)$_4$ complex (10). A major peak attributed to ethene evolution and a minor ethane peak were observed at 520K.

In contrast to the TPH chromatogram of

TABLE 1

Stoichiometries (Allyl Ligand/Mo) in the Surface Complexes Obtained by the Reactions between Mo$_2$(η^3-C$_3$H$_5$)$_4$ and Al$_2$O$_3$ with Given Numbers of Surface OH Groups at 273K

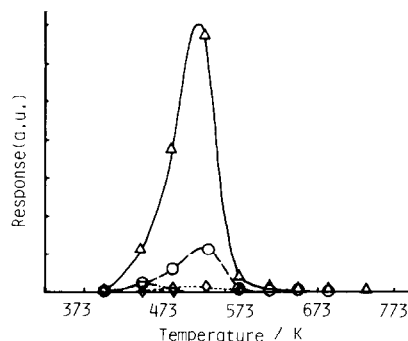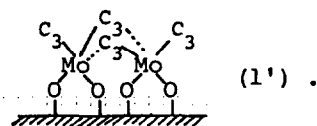|	Support				
	Al$_2$O$_3$-1		Al$_2$O$_3$-2		
Surface area of support, m^2 g^{-1}	190		385		
Surface OH number, OH nm^{-2}	2.6		4.5		
Chemical analysis[a] of molybdenum	0.66	0.95	0.22	0.56	0.83
Number of C$_3$-ligand per Mo atom in the surface complex	1.9$_5$	1.9$_9$	1.9$_5$	2.0$_0$	1.9$_8$

[a] Wt% as Mo/support.

FIG. 1. Temperature-programmed hydrogenolysis (TPH) chromatogram of the Al$_2$O$_3$-1-attached Mo–allyl complex(A); Mo/Al$_2$O$_3$: 0.73 wt%, promotion rate: 4°K min^{-1}, H$_2$ flow: 70 cm^3 min^{-1}. ($\triangle$) Ethene, ($\bigcirc$) ethane, ($\triangledown$) propane, ($\lozenge$) butene.

the single Mo complex (A), the TPH curves of the Al_2O_3-1- and Al_2O_3-2-attached Mo_2–allyl complexes (1) in Figs. 2 and 3 showed the two-peak patterns (peak I and peak II). The allyl ligands of (1) displayed remarkable thermal stability compared to a free $Mo_2(\eta^3$-$C_3H_5)_4$ (5). The products in peak I at ca. 508K in Fig. 2 were propane and ethane, while various hydrocarbons like propane, ethene, ethane, propene, and butene were desorbed in the higher temperature range (peak II). The different chromatograms of peak I and peak II imply two types of allyl ligands with different environments or bondings. The peak II may be due to two allyl groups of the four groups which interact with the adjacent molybdenum in the paired structure as follows,

$$\begin{array}{c} C_3 \quad C_3 \quad C_3 \\ \diagdown \quad / \diagdown \quad / \\ C_3 \\ Mo \quad Mo \\ O \quad O \quad O \quad O \end{array} \qquad (1') \ .$$

The fact that the Mo_2 complexes attached on Al_2O_3 showed almost the same TPH pattern regardless of the Mo quantity (0.2–1.0 wt%), indicates that individual surface Mo^{IV}-pairs (1) have a nearly uniform nature. These complex-type catalysts were found to be highly active for propene metathesis at 273K (2b). The turnover frequency was independent of the Mo loading in the range 0.2–1.0 wt%, e.g., 0.013 s^{-1} at 273K and propene pressure of 2.6 kPa for the Al_2O_3-2-attached species (1). This also indicates uniformity.
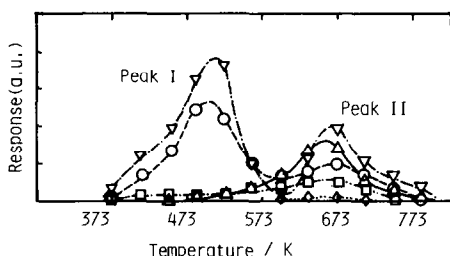

FIG. 3. TPH chromatogram of the Mo_2–allyl complex (1) attached on Al_2O_3-2; Mo/Al_2O_3: 0.56 wt%. ($\triangle$) Ethene, ($\bigcirc$) ethane, ($\square$) propene, ($\triangledown$) propane.

It would be useful to discuss briefly the molybdenum distribution on catalyst surface referring to the simulated distribution of OH groups on an alumina. Figure 4 shows an Al_2O_3-1 surface when 79% of the full monolayer of OH groups are removed. The figure was obtained by inspection using Peri's simulation (11) to fit the present OH population, 2.6 OH nm^{-2}. The molybdenum-pairs (0.6 wt% as Mo/Al_2O_3) were distributed on four-OH assemblies as shown in Fig. 4 on the basis of the stoichiometric reactions of $Mo_2(\eta^3$-$C_3H_5)_4$ with four OH groups. Figure 4 illustrates that the distance between two nearest-neighbor molybdenum-pairs (Mo_2—Mo_2) ranged from 2.4 to 3.3 nm, which is compatible with the estimated value of 3.0 nm assuming an ideal distribution of molybdenum on the support surface. These values suggest that the Mo_2 species are molecularly distributed on the Al_2O_3 surface. The Mo–Mo distance in a
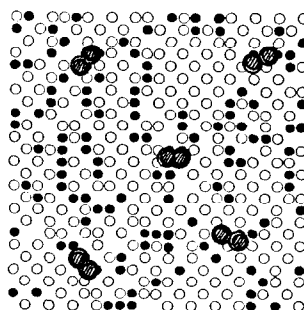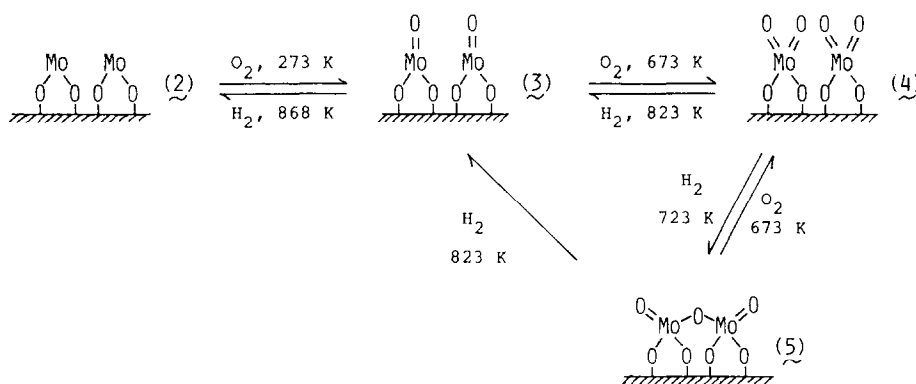

FIG. 2. TPH chromatogram of the Al_2O_3-1-attached Mo_2–allyl complex (1); ($\triangle$) ethene, ($\bigcirc$) ethane, ($\square$) propene, ($\triangledown$) propane, ($\lozenge$) butene, Mo/Al_2O_3: 0.66 wt%.

FIG. 4. Distribution of molybdenum-pairs on Al_2O_3-1 surface showing 79% removal of OH groups; ($\bigcirc$) surface lattice oxygen, ($\bullet$) surface OH groups, (◎◎) molybdenum pair, Mo_2—Mo_2 : 3.0 nm on average.

SCHEME 3

Mo-pair was determined using EXAFS as discussed in the next section.

Surface Design of Molybdenum-Pair Structures

(1) Molybdenum structures on Al_2O_3-1 surface. The surface molybdenum–allyl complex (1) chemically attached on Al_2O_3 was reduced to the bivalent molybdenum (2) with the concomitant release of the allyl groups as mentioned above. The species (2) was oxidized to the hexavalent level (4) with O_2, consuming the stoichiometric amount of O_2 as shown in Scheme 3. The Mo^{VI} ions obtained (4) showed the
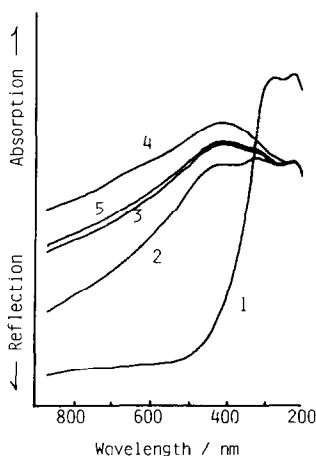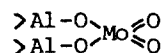

FIG. 5. Ultraviolet diffuse reflectance spectra of the Al_2O_3-1-attached Mo-pair species in various oxidation levels; (1) Mo(VI), (2) Mo(V), (3) Mo(IV) derived from Mo(V), (4) Mo(II), (5) Mo(IV) derived from Mo(II).

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 236.5 and 233.6 eV, respectively. The XPS emission spectrum reveals that the molybdenum species (4) molecularly synthesized via (2) are genuinely in a hexavalent level; no impurity Mo^V ion was detected by means of ESR spectroscopy at any temperatures.

The absorption wavelength of the charge transfer band of a $Mo^{6+}=O^{2-}$ bond correlates, on the whole, with the symmetry of Mo ions in the supported catalysts (*1c, 12*). The uv diffuse reflectance spectrum of the Al_2O_3-1-attached Mo(VI)₂ species (4) in Fig. 5 (curve 1) showed a $2t_2 \rightarrow 3t_2$ transition at 225 nm and a $t_1 \rightarrow 3t_2$ absorption at 283 nm referred to the CT bands of a tetrahedral Mo^{VI} ion (*13*). The uv spectrum was similar to the CT absorption (235 and 281 nm) for the tetrahedral dioxo-Mo^{VI} structure (B)

$$\begin{matrix} >Al-O \\ >Al-O \end{matrix} Mo \begin{matrix} O \\ O \end{matrix}$$

derived from the attached single Mo complex (A) (*1c*), suggesting that each Mo^{VI} ion of the "paired" structure (4) has a similar structure to (B).

Molecular structures containing Mo^{IV} or Mo^V were produced by transformations of the (2) or (4) as shown in Scheme 3. The stoichiometries in reduction or oxidation steps for the mutual transformation are

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	
			Al_2O_3-1^a	Al_2O_3-2^b
H/Mo	723	$Mo^{VI} \rightarrow Mo^V$	0.97^c	1.0_0
H/Mo	823	$Mo^V \rightarrow Mo^{IV}$	0.93	0.93
H/Mo	868	$Mo^{IV} \rightarrow Mo^{II}$	2.0_3	2.1_3
O/Mo	273	$Mo^{II} \rightarrow Mo^{IV}$	0.97	0.97
O/Mo	673	$Mo^{IV} \rightarrow Mo^{VI}$	1.0_2	1.0_7

^{a} $Mo/Al_2O_3 = 0.66$ wt%.
^{b} $Mo/Al_2O_3 = 0.56$ wt%.
^{c} After reduction for 3 h.

given in Table 2. The paired tetrahedral dioxomolybdenum(VI) (4) was converted to the dinuclear MO_2^V species (5) by H_2 reduction at 723K. Two characteristic absorption peaks at 310 and 405 nm (curve 2 of Fig. 5) developed in the course of the stoichiometric reduction of Mo^{VI} to Mo^V, which suggests the formation of bismolybdenyl(V) (14) structure (5). This Mo^V species (5) was essentially diamagnetic due to the strong interaction between two adjacent d^1 spins; the paramagnetic minor species (only 4–6% of total Mo quantity) which may be assigned to a distorted Mo^V ion

$$>Al-O\diagdown_{Mo}\diagup^O$$
$$>Al-O\diagup^{Mo}\diagdown_{OH}$$
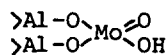
with no interaction with adjacent Mo ions due to large separations, were also observed.

The Mo^{IV} species produced by reduction of the species (5) at 823K for 1.5 h showed almost the same uv spectrum (410 nm (main) and 317 nm (sh), curve 3 of Fig. 5) as the spectrum of the Mo^{IV} ion (curve 5) obtained by stoichiometric oxidation of the attached Mo^{II}-pair (2) at 273K. Thus the coordinatively unsaturated oxo-Mo(IV) structure (3) is made by two routes. The oxidation of (2) to (3) at 273K took 2 h, while the single Mo^{II} ion derived from the surface complex (A) was almost instantaneously oxidized. Very slow oxidation of

Mo^{II} to Mo^{IV} seems to be a common feature of the pair structures attached on Al_2O_3 or SiO_2 (15).

The $Mo^{IV} \rightarrow Mo^{II}$ step took ca. 15 h at 868K, uptaking the stoichiometric amount of H_2 and evolving the stoichiometric (100%) amount of water. This reduction step does not quantitatively proceed over a conventional Al_2O_3-supported catalyst. It is to be noted that the Mo^{II}-pair (2) showed a much higher activity for ethene hydrogenation at 200K (turnover frequency > 5 s^{-1} at C_2H_4 of 20.3 kPa and H_2 of 81.1 kPa) than a usual Mo catalyst (2a).

Thus surface structures (2)–(5) were found to be chemically designed via (1) taking advantage of the attaching reaction, where the behaviors of the paired molybdenum species in the mutual structure-transformations were different from those of the single Mo structures. No unfavorable surface reconstruction of the attached Mo_2 catalyst occurred by repeated redox treatments (4) $\rightleftharpoons$ (2), judging from unchanged redox curves and constant catalytic activities of the Mo-pairs.

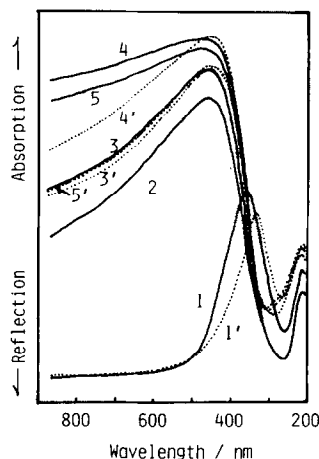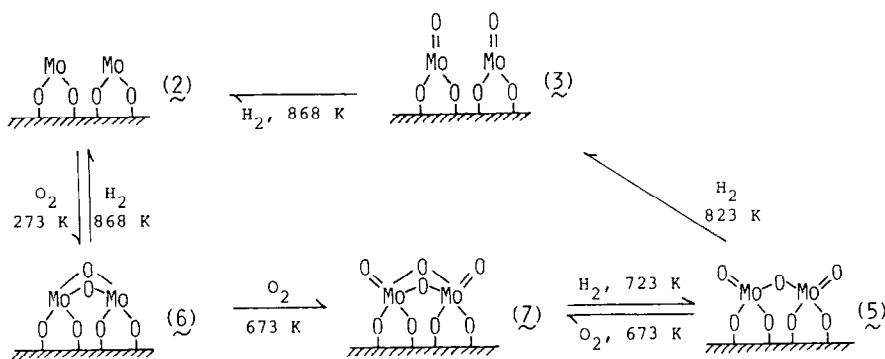(2) *Molybdenum structures on Al_2O_3-2 surface.* In contrast to the "paired" struc-

FIG. 6. Ultraviolet diffuse reflectance spectra of the Al_2O_3-2-attached Mo_2 species (solid line, 1, 2, 3, 4, 5) and Mo species (dotted line, 1', 3', 4', 5'). (1,1') Mo(VI), (2) Mo(V), (3,3') Mo(IV) formed from Mo(V) or Mo(VI), (4,4') Mo(II), (5,5') Mo(IV) formed from Mo(II).

SCHEME 4

ture **(4)**, the Al$_2$O$_3$-2-attached Mo$_2$^{VI} cata-
lyst showed a CT (Mo^{6+}=O^{2-}) transition
peak at 353 nm which is much different in
position from the 333-nm absorption for the
Al$_2$O$_3$-2-attached single Mo^{VI} catalyst in
Fig. 6. The latter peak is owing to a typical
octahedral Mo^{VI} ion. The absorption wave-
length is also different from 283 nm for tet-
rahedral coordination. The Al$_2$O$_3$-2-at-
tached Mo^{VI}$_2$ species may be assigned to a
five-coordinated oxygen-bridged structure
(7) as shown in Scheme 4.

The existence of structure **(7)** is sup-
ported by EXAFS data (*9, 16*). The MoK
absorption spectrum and the Fourier trans-
form of the observed EXAFS data of the

attached Mo^{IV}$_2$ catalyst are shown in Fig. 7.
Two definite peaks were observed in Fig.
7b. The first peak at about 0.13 nm was as-
signed to Mo–O distance. Fourier filtering
and curve-fitting for the second shell re-
vealed that the second-shell atom is molyb-
denum. The peak existing in the range of R
> 0.4 nm is probably due to statistical
counting noise. Both empirical and theoret-
ical curve-fitting were performed with O
atom in the first shell and Mo atom in the
second shell using a k^3-weighting scheme
over the k-range 40–120 nm^{-1}. The theoreti-
cal curve-fitting is shown in Fig. 8 where
$k^3\chi(k)$ spectra were dominated by the first
nearest-neighbor atom (O), and the contri-
bution from the second nearest-one (Mo)
was observed in the range of 90–120 nm^{-1}.
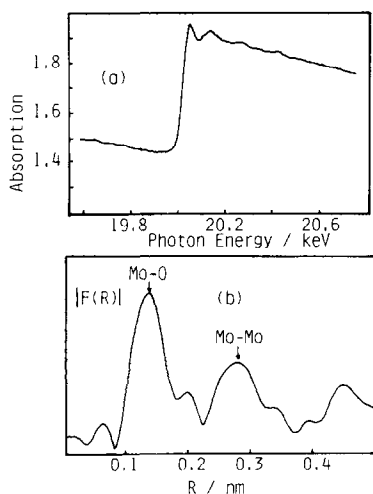The distance and coordination number of

FIG. 7. (a) X-Ray absorption spectrum of the Al$_2$O$_3$-
2-attached Mo(VI)$_2$ catalyst **(7)**. (b) Fourier transform
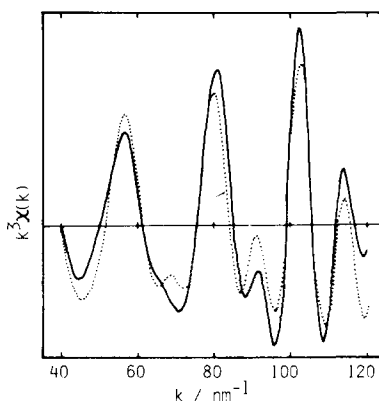of the EXAFS spectrum of the Mo$_2$ catalyst **(7)**.

FIG. 8. Theoretical curve-fitting of EXAFS signal
$k^3\chi(k)$ for the Mo$_2$ catalyst **(7)**. (—), Experimental,
(---), calculated.

TABLE 3

Mo–Mo and Mo–O Distances and Coordination Numbers Determined by Empirical and Theoretical
Curve-Fitting for EXAFS Spectrum of Mo_2/Al_2O_3-2

Absorber-backscatterer	Empirical			Theoretical		
	Distance (nm)	No.	$R_f{}^a$	Distance (nm)	No.	$R_f{}^*$
Mo–O	0.176(1)	4.4(2)	0.363	0.178(1)	4.8(5)	0.423
Mo–Mo	0.325(2)	0.6(1)	0.326	0.312(2)	1.7(3)	0.373

^{a} Reliability factor which indicates the quality of curve-fitting, defined by:

$$R_f = \left[\frac{\Sigma\{(k^3\chi)_{experimental} - (k^3\chi)_{calculated}\}^2}{\Sigma(k^3\chi)_{experimental}} \right]^{1/2}.$$

the first shell, shown in Table 3, demonstrate that a Mo atom has about 5 nearest-neighbor oxygen atoms at an average distance of 0.176–0.178 nm. The second shell data in Table 3 suggest that one Mo atom is located at the distance of 0.31–0.32 nm around an absorbing Mo atom. These EXAFS data are consistent with the proposed five-coordinate di-μ-oxo-Mo^{VI}_2 structure (7).

The dimolybdenum structure (7) was transformed to the diamagnetic bismolybdenyl(V) structure (5) (Scheme 4) in 3 h with H_2 at 723K. One H_2 molecule per a Mo_2 was uptaken as shown in Fig. 9a. The uv spectrum of this Mo^V-level species showed a single peak at 452 nm (curve 2 of Fig. 6) in contrast to the two-peak spectrum observed for the Mo^V_2 species on the Al_2O_3-1 support (curve 2 of Fig. 5). Neither a peak nor a shoulder at 353 nm was observed, tending to rule out the existence of an asymmetric structure consisting of Mo^{IV}–Mo^{VI} pair. Another possible structure
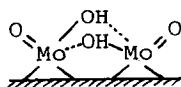
was also ruled out based upon the uv-spectral changes and H_2O desorption pattern data obtained during reduction and thermal treatments. The environment (coordination, distortion, or bond distance) of the Al_2O_3-2-attached bismolybdenyl(V) species

(5) may be different from that of the (5) on Al_2O_3-1.[2]

The species (5) was converted to the paired oxo-Mo^{IV} species (3) (Scheme 4) by the stoichiometric reduction at 823K as shown in Fig. 9a and Table 2 as corroborated by the fact that (3) gave essentially the same spectrum as the spectrum of the single oxo-molybdenum(IV) structure
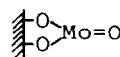
on Al_2O_3-2 (curves 3 and 3' or 5' of Fig. 6).

The oxidation of the Mo^{II}-pair (2) at 273K, which required about two oxygen atoms (Fig. 9b and Table 2), led to the formation of another kind of quadrivalent molybdenum (6). This species may have the di-μ-oxo-structure (6) (Scheme 4). It displays a different uv spectrum from the paired oxo-structure (3) and can be converted to the di-μ-oxo-Mo(VI) structure (7) by uptaking two oxygen atoms/Mo-pair.

The species (3) was further reduced to the bivalent molybdenum (2) with H_2 at 868°K, uptaking the stoichiometric amount of H_2 and evolving 1.7 molecules of H_2O per Mo-pair. The residual water remained adsorbed on the Al_2O_3-2 support. The dinu-

[2] When the bismolybdenyl(V) structure (17), $[OCl_4Mo–O–MoCl_4O]^{4-}$, in aqueous solution of HCl was supported on Al_2O_3-1 or Al_2O_3-2, followed by drying at room temperature, the two supported bismolybdenyls showed different uv spectra.
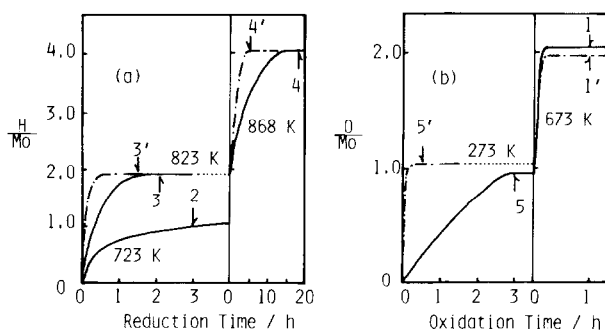
FIG. 9. (a) Reduction curves of the Al₂O₃-2-attached Mo(VI) (---) and Mo(VI)₂(—) (0.56 wt%) species with H₂ (8.0 kPa) in a closed circulating system equipped with a liquid N₂ trap; the numbers denoted in the figure correspond to those in Fig. 6. (b) Oxidation curves of the Al₂O₃-2-attached single Mo(II) (---) and Mo(II)-pair (—) species with O₂ (8.0 kPa).

clear Mo^{II} complexes with a metal–metal (single to quadruple) bond between the two adjacent Mo atoms show new absorption bands associated with d_σ, d_π, or δ orbitals (18). The d–d absorption in the range > 500 nm for the Mo^{II}-pair (2) which is absent for the single Mo^{II} ion, suggests direct Mo–Mo bonding. The Al₂O₃-2-attached Mo^{II}_2 catalyst was found to show cooperative catalysis by the two adjacent Mo(II) ions in the hydrogenation of 1-butene and 1,3-butadiene (19).

CONCLUSION

Several molecularly designed catalysts with molybdenum-pair structures having Mo(II), Mo(IV), Mo(V), and Mo(VI) ions are produced on alumina surfaces via the reaction between the surface OH groups and $Mo_2(\eta^3\text{-}C_3H_5)_4$ in pentane at 273K, followed by chemical treatments as shown in Schemes 2, 3, and 4. The molybdenum-pair species chemically attached on support surfaces in the range of Mo loadings 0.2–1.0 wt% are nearly uniform catalytically, volumetrically, and also spectroscopically. The surface structures are stable below 870K.

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