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ACTIVITY SEQUENCE OF Mo(II) STRUCTURES CHEMICALLY ATTACHED ON SiO_2 IN THE CATALYTIC HYDROGENATION OF ETHENE AND 1,3-BUTADIENE

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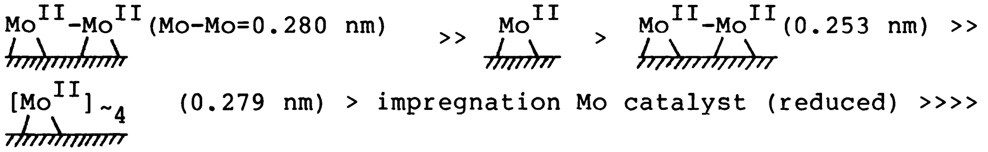
The catalytic activities of well-characterized SiO_2-attached Mo(II)-monomer, Mo(II)-dimer and Mo(II)-cluster catalysts in the hydrogenation of ethene at 200 K and 1,3-butadiene at 273 K were studied to find a structural property of active sites controlling the catalysis in combination with EXAFS(Extended X-ray Absorption Fine Structure) studies. The hydrogenation activity markedly depended upon the separation(bond distance) and assembly of Mo atoms, the activity decreasing in the following order;

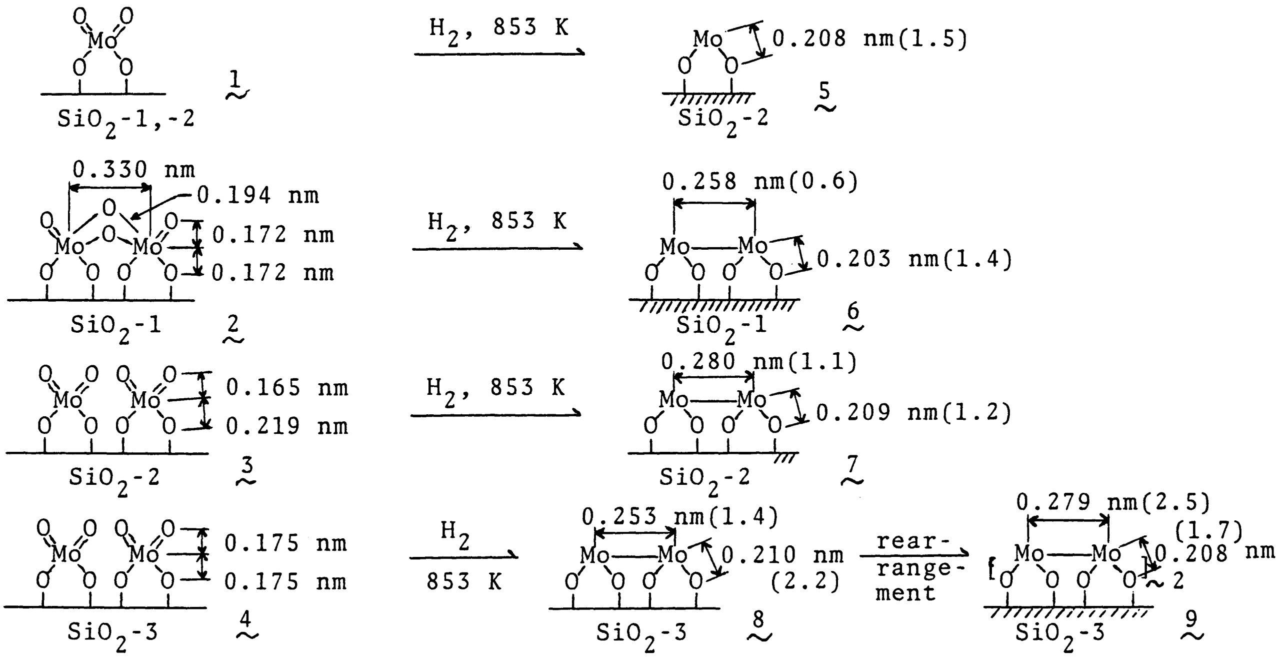


Mo^{II}-Mo^{II}(Mo-Mo=0.280 nm) >> Mo^{II} > Mo^{II}-Mo^{II}(0.253 nm) >> $[Mo^{II}]_{\sim 4}$ (0.279 nm) > impregnation Mo catalyst (reduced) >>>>

Mo^{IV} catalyst ~ Mo^{VI} catalyst (inactive).

A new class of inorganic oxide-attached metal-monomer, -dimer, or -cluster catalysts which are prepared by use of suitable organometallics via well-controlled attaching reactions and subsequent surface transformations, has been demonstrated to provide a new approach for understanding the origin of catalysis as well as elucidating reaction mechanisms on solid surfaces in a molecular scale.1) In the present report we indicate the significance of the separation and assembly of Mo atoms of SiO_2-attached Mo(II) catalysts for the catalysis in the hydrogenation of ethene and 1,3-butadiene.

The SiO_2-attached Mo(II)-monomer and Mo(II)-dimer catalysts were prepared from the Mo(VI)-monomers or Mo(VI)-dimers attached on SiO_2 by H_2 reduction under similar conditions to those previously reported.2) Three types of SiO_2 having different surface areas were used as supports; SiO_2-1(510 m^2g^{-1}) was purchased from Nishio Industry Ltd., while SiO_2-2(285 m^2g^{-1}) and SiO_2-3(120 m^2g^{-1}) were obtained from colloidal silicas(Snowtex-O and Snowtex-30 of Nissan Kagaku Co. Ltd., respectively). The distances and coordination numbers of Mo-Mo and Mo-O bonds in the Mo catalysts were determined by the EXAFS analysis of the Mo K-edge EXAFS data obtained by use of synchrotron radiation. The details of analysis will be

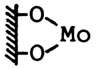
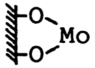
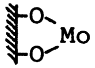
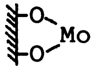
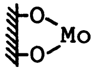
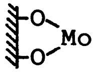


described elsewhere.3) The catalytic reactions were carried out in a closed circulating system (180 cm^3).

The dioxomolybdenum(VI)-dimers(**3**) on SiO_2-2 had a more distorted structure compared to the Mo(VI)-dimers(**4**) on SiO_2-3, whereas the Mo-O bond lengths attained to similar values by reduction with H_2 (**7** & **8**). Also on SiO_2-1 surface the Mo-O bond length of the reduced species(**6**) was similar. The direct bonding between the two adjacent Mo(II) ions in the Mo-dimer catalysts was found at the distances of 0.253-0.280 nm. The Mo-Mo separation of the new Mo(VI)-dimer(**2**) was shortened to 0.258 nm by the removal of bridging oxygens with H_2, while the Mo-O (surface) bond length was elongated from 0.172 nm to 0.203 nm. Another new Mo(II)-cluster(**9**) was obtained by surface rearrangement of **8** by repeated oxidation-reduction treatments at 868 K. The Mo-Mo separation increased by 0.026 nm and the coordination number of Mo atoms became larger about 2 times, which suggests the formation of Mo-clusters consisting of about 4 Mo atoms. The oxidation of the Mo-cluster(**9**) with O_2 led to octahedral Mo(VI) ions which show a charge transfer band of Mo=O bonds at 330 nm in contrast to the oxidation of **8** to tetrahedral Mo(VI) ions. The coordination numbers, 0.6-1.4, of Mo atoms around a Mo atom indicate the molybdenum-dimer structures. The Mo-O bond distance of the Mo(II)-monomers(**5**) was similar to those of the dimers, but there was no interaction among Mo(II) ions of the monomer catalysts.

The catalytic activities of Mo(II)-monomers, -dimers, and -clusters attached on SiO_2 in the hydrogenation of ethene at 200 K and 1,3-butadiene at 273 K are given in Table 1. The Mo(II)-dimer catalysts showed about two orders of magnitude higher activities than the corresponding traditional Mo catalysts prepared by an impregnation method. The activities of Mo(II)-dimers were profoundly affected by the kind of SiO_2 as shown in Table 1; the turnover frequencies (T.F.; $10^{-3}s^{-1}$) for 1,3-butadiene hydrogenation: 3.7(SiO_2-1), 32.1(SiO_2-2), 0.01(SiO_2-3). The T.F. of

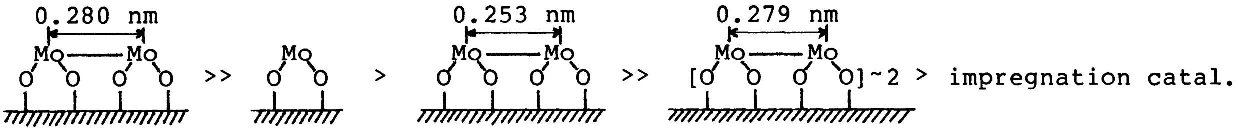
Table 1. Comparison of Activities of Mo(II)-Monomers, Mo(II)-Dimers and Impregnation Mo Catalysts[a) in the Hydrogenation of Ethene[b) and 1,3-Butadiene[c)

Catalyst	Support	Ethene ⟶ Ethane T.F./$10^{-3}s^{-1}$	Ethene ⟶ Ethane Relative[e) activity	Ethene ⟶ Ethane E_a/kJ mol^{-1}	1,3-Butadiene ⟶ Butene T.F./$10^{-3}s^{-1}$	1,3-Butadiene ⟶ Butene Relative[e) activity	1,3-Butadiene ⟶ Butene E_a/kJ mol^{-1}	1,3-Butadiene ⟶ Butene 1-B/2-B[f)
	SiO_2-1	140	1.4	8	4.7	1.3	17	3.6
[]$_2$	"	100	1	10	3.7	1	30	2.6
Impreg.cat.	"	—	—	—	0.024	0.006	31	3.4
]	SiO_2-2	90	< 0.14	20	4.0	0.12	10	2.4
[]$_2$	"	> 650	1	g)	32.1	1	8	4.4
Impreg.cat.	"	—	—	—	0.7	0.02	15	5.0
[]$_2$	SiO_2-3	2.8 d)	1	—	0.01	1	—	4.0
[]$_{\sim 4}$	"	0.05d)	0.018	—	≈0	≈0	—	—
Impreg.cat.	"	0 d)	0	—	0	0	—	—

a) Mo/SiO_2=0.5 - 1.7 wt%. b) C_2H_4=20 Torr, H_2=60 Torr(1 Torr=133.3 Pa), at 200 K. c) C_4H_6=H_2=20 Torr, at 273 K. d) At 293 K. e) Referred to each dimer catalyst. f) Ratio of 1- butene to 2-butene(cis+trans) in butene produced. g) Not observed by too rapid reaction.

the Mo(II)-monomers was not so different on SiO_2-1 and SiO_2-2. The most active species under the present conditions is the SiO_2-2-attached Mo(II)-dimers judging from the T.F. and the activation energies, the dimer catalyst(7) being about 10-fold active than the monomer catalyst(5). Reversely, the Mo(II)-dimers(6) on SiO_2-1 were less active than the corresponding monomers. On all the Mo(II) catalysts ethene hydrogenation more rapidly proceeded than the hydrogenation of 1,3-butadiene. The selectivity towards 1-butene and 2-butene was not observed to correlate with Mo structures, 1-butene being a main product. When the Mo-dimers on SiO_2-3$^{4)}$ were transformed to the Mo(II)-clusters(9), the hydrogenation activity decreased to about 2% of that of the dimers(8).

The alkene hydrogenation activity of various metals is known to vary with the lattice parameters of metal crystals, where there is an optimum separation of two adjacent metal atoms and hence preferable kinds of metals.$^{5)}$ When a certain metal element is taken into account, the activity (T.F.) does not drastically depend upon particle sizes of metal supported on inorganic oxides; thus this reaction is classified into a structure-insensitive reaction.$^{6)}$ However, Table 1 demonstrates that the catalytic activity of the Mo catalysts was much effected by the Mo-Mo separation (bond distance) and the assembly (monomer, dimer or cluster). Taking into account both the catalytic activities (T.F.) and the activation energies for the hydrogenation of ethene and 1,3-butadiene, the hydrogenation obviously demands the preferable structure and environment of Mo(II) sites. These factors can widely be controlled on a class of inorganic oxide-attached metal catalysts without changing the kinds of metal elements. Consequently, the activity sequence of the Mo(II) structures for the hydrogenation at low temperatures is shown as follows;



References

1) "Tailored Metal Catalysts," ed by Y. Iwasawa, D. Reidel Publishing Co., Holland (1985); Yu. I. Yermakov, B. N. Kuznetsov, and V. A. Zakharov, "Catalysis by Supported Complexes," Elsevier, Amsterdam (1981).
2) Y. Iwasawa and M. Yamagishi, J. Catal, 82, 373 (1983).
3) H. Ishii, N. Kosugi, H. Kuroda, and Y. Iwasawa, to be published.
4) SiO_2-3 is doped with Na ion (0.5 wt%) in order to promote the surface rearrangement of Mo-dimers to clusters; hence, the discussion is limited to the comparison of 8 and 9 attached on the identical SiO_2-3.
5) O. Beeck, Discuss. Faraday Soc., 8, 118 (1950).
6) M. Boudart, Adv. Catal., 20, 153 (1969).

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