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HYDROGEN EXCHANGE, ISOMERIZATION, HYDROGENATION AND METATHESIS OF OLEFINS ON SOLID SURFACES —UNSATURATED COORDINATION MODEL OF ACTIVE SITES

By

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(Received Nobember 28, 1980)

Abstract

A review is given on the results ever obtained in the author's laboratory with olefin reactions over nickel, sulfided nickel, molybdenum disulfide and titania-supported molybdenum oxide catalysts. Some detailed discussions are given on the stereoselectivity observed in $[D_4]$-2-butene formation by metathesis of a $[D_0]/[D_8]$ (1 : 1) mixture of *cis* or *trans*-2-butene, and it is suggested by the extended Hückel theory (EHT) calculation that this stereoslectivity may be caused by the restricted orientation of C_2-carbene and metallacyclobutane intermediates on surface molybdenum ion surrounded by lattice oxygen. Taking account of the results obtained by X-ray photoelectron spectroscopy of the catalyst, it is emphasized that specially unsaturated coordination of legands (*e.g.* sulfur, oxygen *etc.*) to central metal ion is essential for an active site for the selective catalyses over these solid surfaces.

Introduction

This report concerns mainly with olefin metathesis reaction catalyzed by titania-supported molybdenum oxide. As an introduction to this problem, the author would like to summerize the results ever obtained in the author's laboratory on reactions of olefins over solid surfaces. These works have been started from the mechanistic analysis of ethylene hydrogenation on metallic catalysts using deuterium as a tracer, which has lasted for more than a decade[1] under the kind encouragement given by the late Professor Emeritus Juro Horiuti and been summerized in a monograph.[2] The results were that the associative mechanism ever proposed by Horiuti and Polanyi,[3]

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$$\begin{array}{l} C_2H_4 \xrightarrow{\text{I}} C_2H_4(a) \\ \qquad\qquad\quad H(a) \xrightarrow{\text{III}} C_2H_5(a) \\ H_2 \xrightarrow{\text{II}} \qquad\qquad\qquad\quad \xrightarrow{\text{IV}} C_2H_6, \\ \qquad\qquad\quad H(a) \end{array} \qquad (1)$$

is the most appropriate one; the hydrogenation is rate-determined by step II[2] and the variation of activity of metallic catalysts is caused by the competition of two mechanistic factors, *i. e.*, the activity of metals for step II and its retardation caused by irreversible chmisorption of ethylene.[4] The main difficulty in these experiments was in carrying out steady deuterations with high reproducibility.[1] In this respect, elimination of subreactions, *e. g.*, decomposition and polymerization of ethylene *etc.*, was achieved by poisoning a freshly evaporated metal surface with some products of ethylene decomposition taking place during preliminar runs of ethylene deuteration itself. Active sites for hydrogenation on nickel is thus surrounded by adsorbed ethylene and/or its decomposition products, however, the nature of interme-

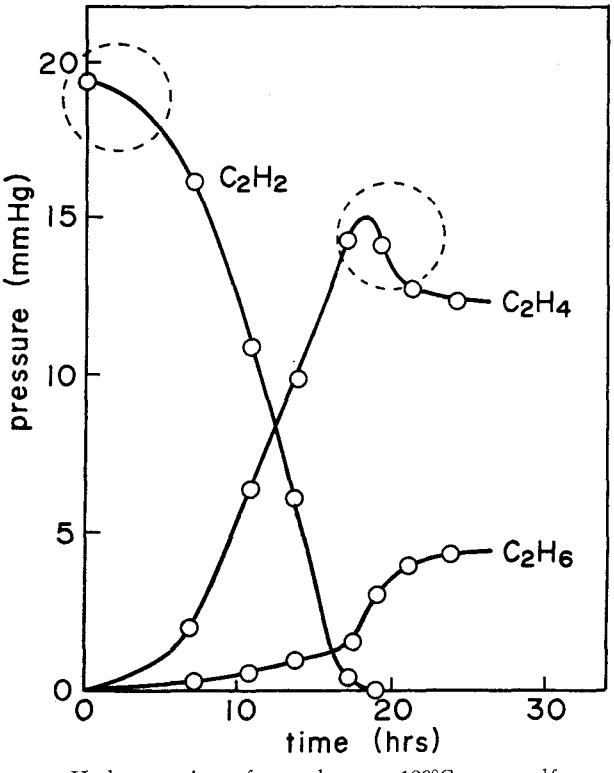


Fig. 1. Hydrogenation of acetylene at 120°C over sulfur-coated nickel catalyst.

diates or active sites were out of the mechanistic consideration as seen from the simple description of adsorbed state as (a).

In this point of view, our work was extended to the sulfur-coated nickel catalyst which has been reported by T. Kwan[5] as a highly selective catalyst for partial hydrogenation of acetylene to ethylene. The catalyst was prepared by heating reduced nickel powder with a small amount of hydrogen disulfide and evacuated at 300°C. The key to elucidate the selectivity was given by noting the transition periods before and after a steady hydrogenation of acetylene as shown in Fig. 1 by broken circles.[6] These transition periods suggest some changes of catalyst surface, that is, active sites for hydrogenation is generated at 120°C during several hours after the contact with acetylene and survive for several hours after the consumption of acetylene. The activities of the catalyst in these various surface states were examined with a variety of reactions as shown in Table 1.[7] Surface [I] in the Table is a freshly prepared one, [I-H_2] is that brought into contact with hydrogen. The surface [II] active for acetylene hydrogenation was realized by trapping off acetylene from the reaction system. Catalytic characteristics of the surfaces [I-H_2] and [II] are quite similar to those of rhodium complexes, $RhH(CO)(PPh_3)_3$ and $RhCl(PPh_3)_3$, respectively,[8] which have been well explained by the degree of coordinative unsaturation of central metal. The surface composition of [I] was found as $Ni/S \simeq 1.5$ by AES analysis[9] and the compound, Ni_3S_2 (nickel is surrounded by four sulfur atoms), is active for selective partial hydrogenation,[10] while NiS (nickel is surrounded by six sulfur atoms) has no catalytic activity.[9] The similar selectivity for partial hydrogenation was achieved over nickel catalyst when a little of CO was admixed with acetylene.[11]

TABLE 1. Catalytic activities of sulfur-coated nickel+

Reaction	Surface*		
	[I]	[I-H_2]	[II]
Isomerization of butene	−	+	
Exchange of C_2H_4-C_2D_4	−	+	
Hydrogenation of C_2H_2, C_2H_4 or C_4H_8	−	−	+
H_2-D_2 equilibration	−	−	+
Exchange of H_2-C_2D_4, D_2-C_2H_4	−	−	+
Dimerization of C_2H_2	−	−	+

+: + active; − inactive.

*: [I], freshly prepared sulfur-coated nickel; [I-H_2], [I] under coexistence of gaseous hydrogen; [II], [I] under coexistence of gaseous C_2H_2.

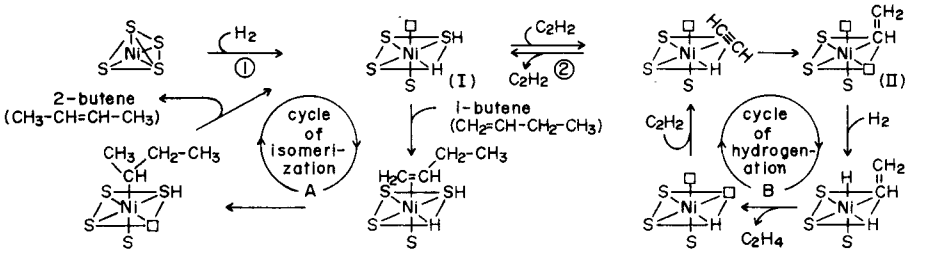


Fig. 2. Model of active sites on sulfur-coated nickel catalyst and its selectivity for isomerization and hydrogenation of olefin. (Hydrogenation activity is generated by step 2.)

Accordingly, a model of active site (Fig. 2) with coordinative unsaturation similar to the rhodium complexes mentioned above was proposed[9] for the catalytic selectivity of sulfur-coated nickel. The surface active for olefin hydrogenation as well as H_2-D_2 equilibration is understood as to be generated by substitution of coordinating sulfur by acetylene and the transition periods shown in Fig. 1 is caused by changes of catalyst surface due to the order of coordination strength as $C_2H_2 > S$, $CO > C_2H_4$, H_2.

Such a coodinative unsaturation model of active sites was further successively applied to the characteristic selectivity of molybdenum disulfide catalyst[12] for hydrogen exchange, isomerization and hydrogenation of olefins. The model was confirmed by the obserbed anisotropy of MoS_2 single crystal for these catalyses; they were caused only on the edged surface of the crystal which exposes coordinatively unsaturated molybdenum, but never on the basal plane fully covered by sulfur layer. Furthermore, that the olefin intermediate of these catalyses should be σ-alkyl, that is, the associative mechanism as assumed in the scheme (1) was verified for the first time and the type of σ-alkyl, normal or secondary, was made clear by microwave spectroscopic analysis of deuterated products formed from propene and butene.

The methods used for sulfur-coated nickel and MoS_2 catalysts were recently extended to the study on molybdenum oxide catalyst which is interested by its structure resembling to MoS_2 and its potential uses in practical catalyses.

Characteristics of Titania-Supported Molybdenum Oxide Catalyst

1. *Preparation of the catalyst and its catalytic selectivity.*[13]

Powder of β-titanic acid (H_2TiO_3) impregnated with an aqueous solution of ammonium molybdate was dired at 120°C, evacuated and oxidized with oxygen at 500°C. The amount of supported molybdenum are given in what

follows by the weight percent of MoO_3 over TiO_2 in this oxidized state. The amount of hydrogen consumed in the reduction of this oxidized sample at 500°C for 1 h is shown in Fig. 3. As this result was reproducible by this redox pretreatment of the catalyst sample and Ti^{3+} ion was never detected by ESR and XPS, we see that molybdenum oxide but none of titania was reduced and/or oxidized and molybdena supported by less than 10 wt% is easily reduced completely.

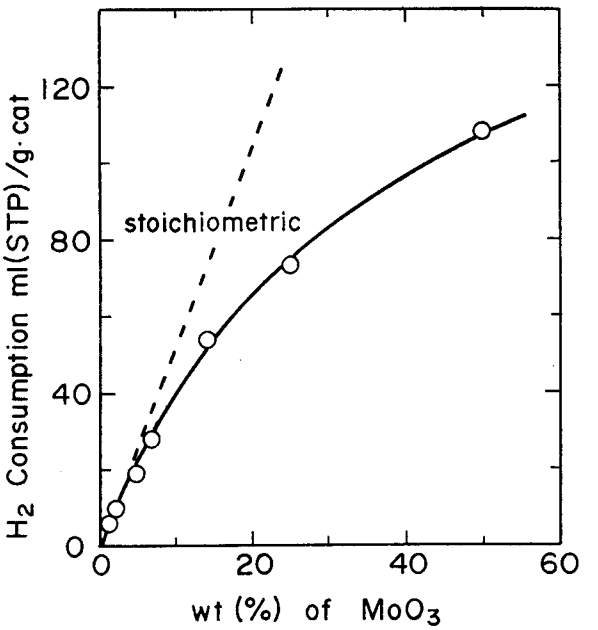


Fig. 3. Reducibility of MoO_3/β-TiO_2 catalyst by hydrogen (500°C, 1 h).

Figure 4 shows the characteristics of a catalyst of 6.7 wt% MoO_3 for olefin reactions at room temperature. Before use, an oxidized catalyst sample was reduced by hydrogen at various extent. Olefin was completely oxidized to CO_2 over a catalyst of $x=3.0$. A catalyst (I) of $x=2.9\sim2.3$ is active for olefin metathesis which hardly accompanies the hydrogen scrambling among olefin molecules as clearly seen from the exclusive formation of $[D_0]$, $[D_2]$ and $[D_4]$-ethylene, $[D_0]$, $[D_4]$ and $[D_8]$-butene, and $[D_2]$ and $[D_4]$-propene from 1 : 1 mixture of $[D_0]$ and $[D_6]$-propene.[14] The activity of the catalyst for metathesis decreased steeply with decrease of x. A catalyst (II) of $x=2.3\sim2.0$ is active for olefin isomerization only under the coexistence of hydrogen, while the one (III) of x less than 2.0 causes isomerization of olefin even when hydrogen is absent. The catalyst (II) is slightly and that (III) is

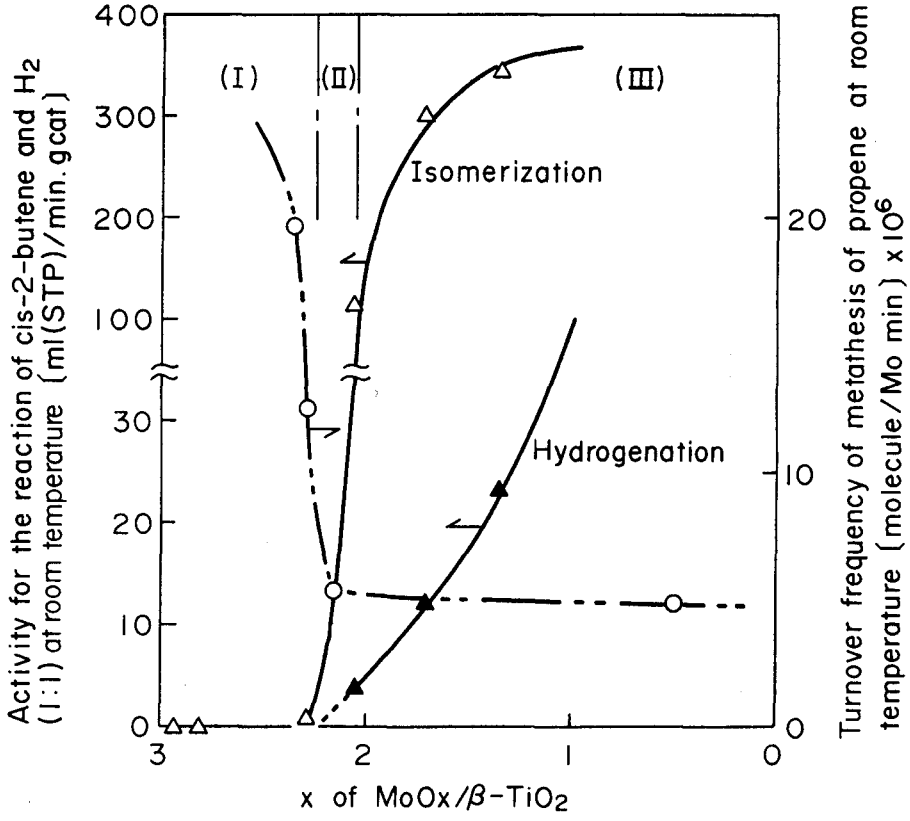


Fig. 4. Characteristics of MoO_x/β-TiO_2 catalyst for olefin reactions at room temperature.

highly active for olefin hydrogenation. The detailed profiles of isomerization and hydrogenation on the catalyst (II) are quite similar to those over sulfur-coated nickel and MoS_2 catalysts,[15] indicating that the unsaturated coordination model is valid again for the active sites on this catalyst. A new result was additionally obtained, that is, 1-butene was selectively hydrogenated from its mixture with 2-butene.[14]

Relating to a report[16] that the present catalyst was surpassingly active for reduction of N_2O with H_2 among various metal oxides, this reaction at 200°C as well as reduction of N_2O with CO at room temperature, each for 1 h, were conducted over the catalyst sample of reduced state. We found that the characteristic catalyses over the catalysts (I) and (II), respectively, were reproducibly realized by these pretreatments of reduced catalyst. The catalyst for olefin metathesis were thus prepared by conducting the reduction

of N_2O (*ca.* 5×10^3 Pa) by H_2 (*ca.* 1.3×10^4 Pa) at 200°C for 1 h over a catalyst sample reduced and evacuated at 500°C for 1 h.

2. *Stereoselectivity of olefin metathesis reaction.*

Various selectivities observed in the metathesis over the catalyst (I) have been reported previously.[13] In what follows, the discussion is concentrated to the stereoselectivity observed in metathesis of *cis* or *trans*-2-butene over the catalyst (I), on which *cis*-2-butene is selectively formed by productive metathesis of propene.[13]

Figure 5 shows the relative amounts of *cis* and *trans*-isomers in [D_4]-butene formed by metathesis of 1 : 1 mixture of [D_0] and [D_8] isomers of *cis* or *trans*-2-butene. We see that *cis* or *trans* geometry of the reactant is retained in the [D_4]-product formed at the early stage of metathesis. The similar phenomena have been observed with metal complexes of Cr, Mo and W[17,18] in homogeneous phase and also with some heterogeneous catalysts.[19] The metatheses ever observed with metal complex catalysts have been well interpreted by metal carbene and metallacyclobutane intermediates[17,18] as

$$C=C+R-{}^*C=M\rightarrow \begin{matrix} C-C \\ | \quad | \\ R-{}^*C-M \end{matrix} \rightarrow R-{}^*C-C+C=M, \quad (2)$$

and the stereoselectivities were attributed[18] to a repulsion which surpasses

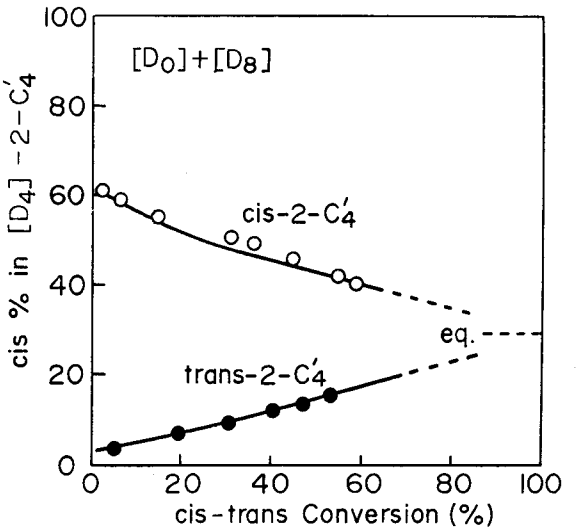


Fig. 5. *cis/trans*-Stereoselectivity in [D^4]-2-butene formation from 1:1 mixture of [D_0] and [D_8] isome of *cis* or *trans*-2-butene.

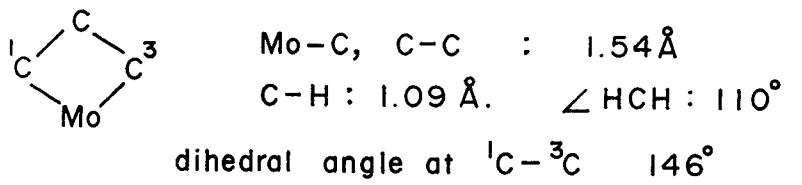


Fig. 6. Structure parameters of metalla cyclobutane intermediate.

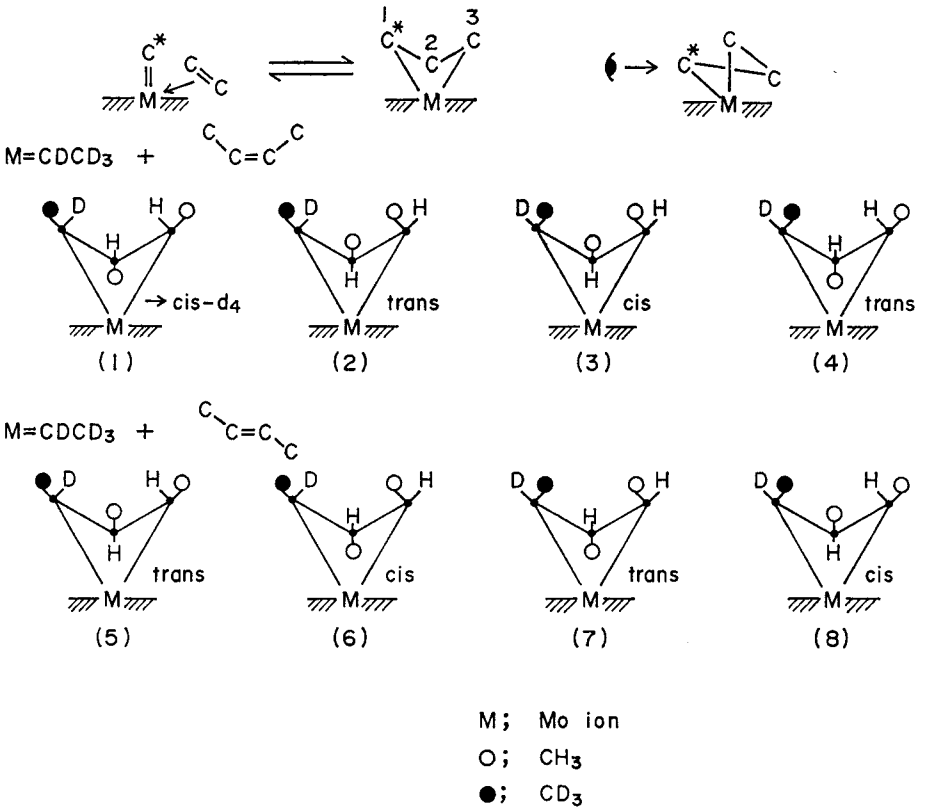


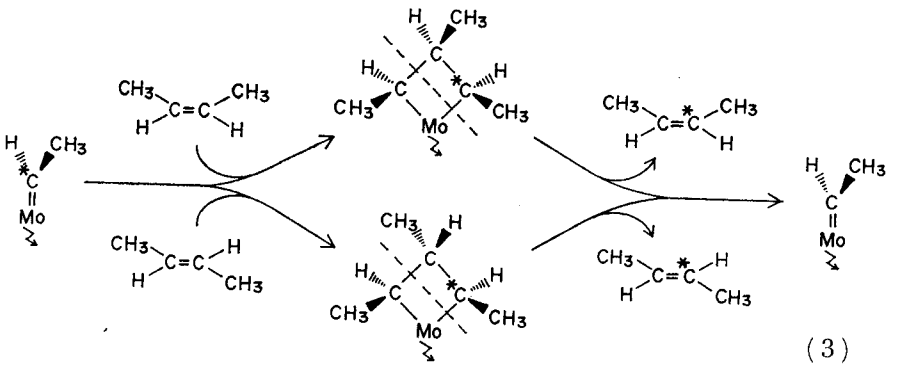
Fig. 7. Stereoisomers of metallacyclobutane intermediate formed from C_2-carbene and *cis* or *trans*-2-butene.

between two methyl groups bonding to 1 C and 3 C carbons (Fig. 6) of metallacyclobutane intermediate.

This conclusion was examined[20] by a calculation using the extended Hückel theory (EHT) for the total energies of eight conformations, as given in Fig. 7,[18,20,21] of metallacyclobutane intermediate formed on isolated molybdenum ion on the catalyst surface. The structure parameters used in this calculation (Fig. 6) were assumed to be the same as those of cyclobutane.

The result is that, among the intermediates (1)~(4) formed form C_2-carbene and *cis*-2-butene or those (5)~(8) from *trans*-2-butene, (1) or (6) has the lowest energy, respectively. This result does not agree with the observed high selectivity for *trans* from *trans*. The relative magnitudes of the total energies of these intermediates are not affected by the change of the charge of molybdenum ion.

The observed stereoselectivity is, on the other hand, necessarily derived from a model as shown in the scheme (3) that the orientation of C_2-carbene should be same as that of starting C_2-carbene.[22]



(3)

The possibility of such an orientation of intermediates was examined, too, by EHT calculation taking into account the effect of oxygen atoms surrounding molybdenum.[20] The calculation was carried out with a model as shown in Fig. 8, in which the outermost oxygen atom of the MoO_3 layer structure is assumed to be substituted by C_2-carbene. The total energy of this system changes as shown in Fig. 9 by rotation of C_2-carbene around C=Mo bond. This result strongly suggests that the orientation of C_2-carbene is confined on MoO_x surface in the way that methyl group of C_2-carbene points to the oxygen which is nearest to the central molybdenum. With respect to metallacyclobutane, similar restriction of its orientation is suggested and the total energy is concluded to be the lowest for (1) or (5) among (1)~(4) or (5)~(8) conformations (Fig. 7) of metallacyclobutane, respectively. These results of EHT calculation are in good agreement with the observed steereoselctivity.

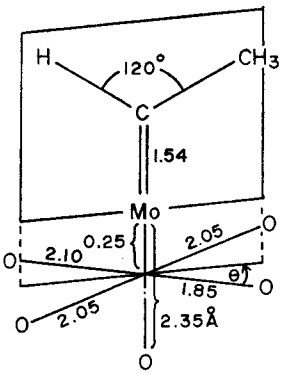


Fig. 8. Structure parameters of C-carbene intermediate on (MoO) cluster.

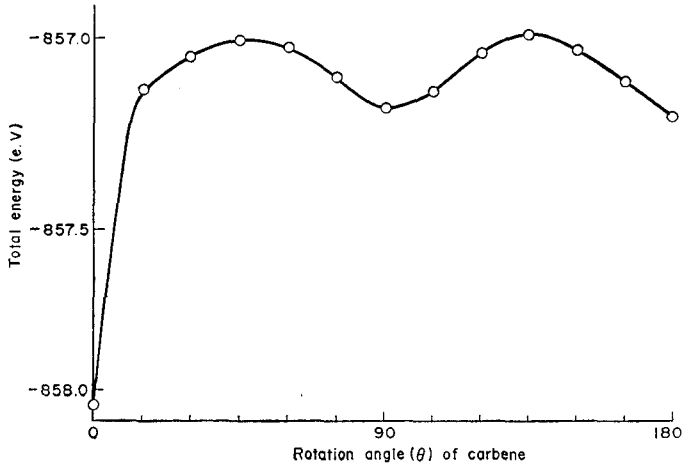


Fig. 9. The total energy change of a system given in Fig. 8 by rotation of C_2-carbene around C=Mo bond axis.

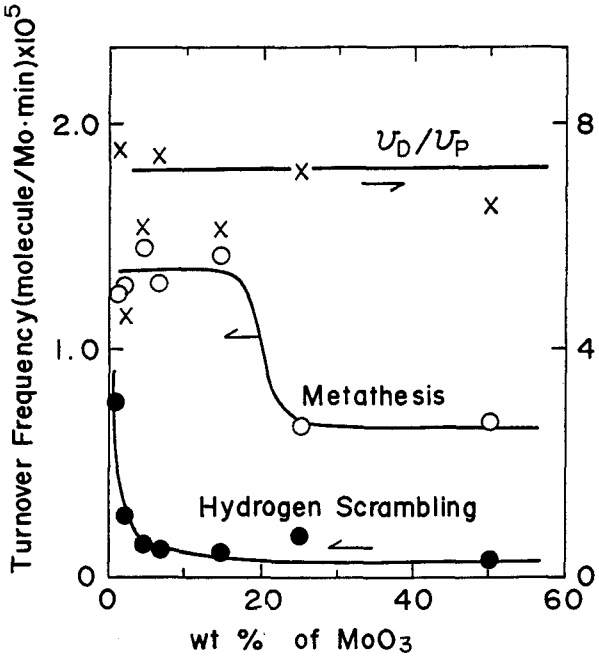


Fig. 10. Activities of MoO_x/β-TiO_2 catalyst of various wt% MoO_3 for metathesis and hydrogen scrambling of olefin.

3. *Surface characterization of MoO_x/β-TiO_2 catalyst.*[23]

Activities of the catalyst for metathesis and simultaneous hydrogen scrambling of olefin changed as shown in Fig. 10[13,23] with increase of the amount of supported molybdenum oxide. The selectivity, v_D/v_P, of degenerative metathesis over productive one is unchanged, clearly indicating that the activity for metathesis is attributed to surface MoO_x. The fact that the results given in Fig. 10 were reproducible after the redox pretreatment of catalyst indicates that the dispersion of molybdenum oxide on TiO_2 surface is affected little by this pretreatment. Therefore, the surface state of the catalyst was examined by XPS in its oxidized state and obtained the spectra of O(1s), Ti(2p) and Mo(3d) electrons, the peak areas of which are plotted

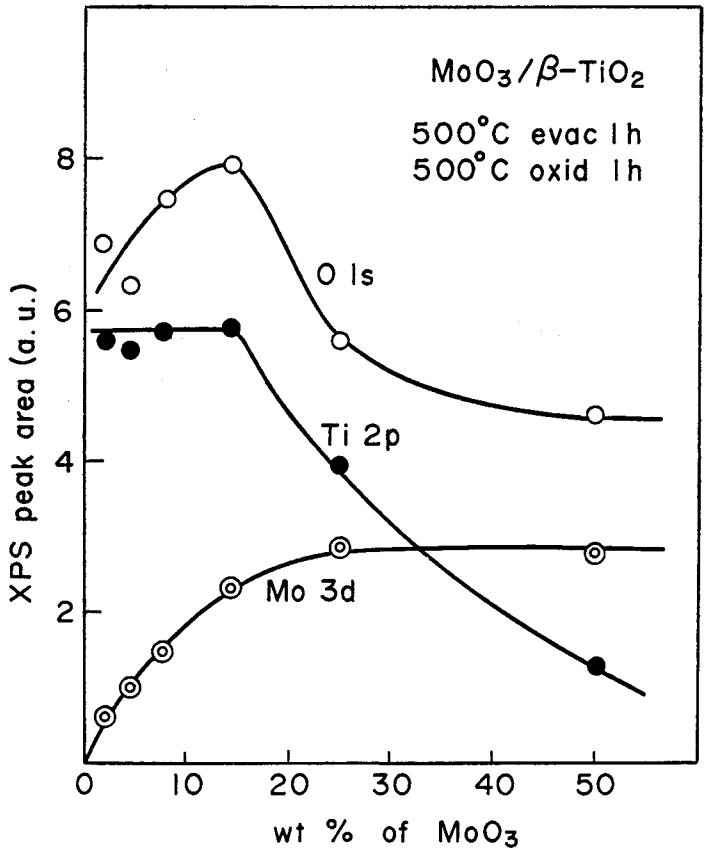


Fig. 11. Changes of O(1s), Ti(2p) and Mo(3d) XPS peak areas depending on the loaded amount of MoO_3 on β-TiO_2 support.

in Fig. 11 against the loaded amount of MoO_3. We see that, with catalysts loaded with MoO_3 more than *ca.* 15 wt%, the surface of TiO_2 decreased, while that of MoO_3 increased to a plateau, suggesting aggregation of MoO_3 loaded on TiO_2 surface. Such an estimation of surface state agrees with the results of Figs. 3 and 10. Molybdenum oxide loaded by less than 10 wt% may be well dispersed on TiO_2 and easily controlled by redox pretreatment to be active for metathesis, while agrregated MoO_3 is rather hard to be reduced as shown in Fig. 3 and, consequently, the specific activity for metathesis is lowered as shown in Fig. 10. The high activity for hydrogen scrambling of a catalyst loaded with a small amount of MoO_3 might be due to TiO_2 surface. The fact that XPS spectra with O(1s) peak of OH group and Ti(2p) peak of Ti^{3+} were obtained with a catalyst of 2.2 wt% MoO_3 but not with those loaded with MoO_3 more than 4.6 wt%, indicate that the change of β-titanic acid into TiO_2 or dehydration of TiO_2 is accelerated by MoO_3 loaded more than 4.6 wt%.

Figure 12[13,24] shows the XPS spectra of MoO_x supported on three typical oxides observed after the redox pretreatment and a contact with olefin. Molybdenum on MoO_x/β-TiO_2 is mainly Mo^{6+} ion with a small amount of Mo^{4+}, while those supported on GeO_2 and MgO have Mo^{4+}, however, they are quite inactive for metathesis and other reactions. The presence of Mo^{4+} ions is thus not sufficient for the metathesis activity. It may be concluded that Mo ions with an average positive charge less than 5+ are the active center for metathesis in conformity with some reports.[25] Taking into account that the isomerization and hydrogenation over MoO_x/TiO_2 of $x=2.3\sim2.0$ proceed quite similarly to those over metal sulfide catalyst,[12] it may be concluded that a specially unsaturated corrdination sites on surface metal ions are essential for the selectivity for these catalytic reactions.

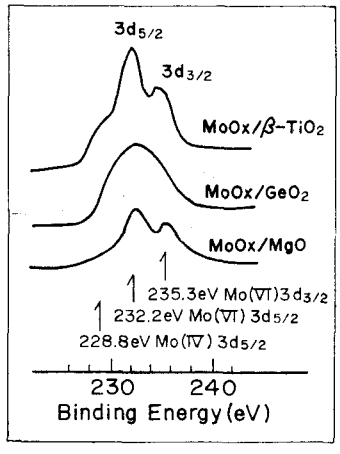


Fig. 12. Mo (3d) XPS spectra of MoO_x supported on β-TiO_2, GeO_2 and MgO.

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