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Molecular Mechanisms of Catalytic Isomerization and Hydrogen Exchange of Olefins over the MoS_2 Single Crystal Catalysts: Regulation of Catalytic Processes by the Conformation of Active Sites[1]

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Reaction mechanisms and crystallographic specification of active sites were attained by using deuterium tracer for the reactions taking place on MoS_2 single crystal catalysts. The isomerization reaction as well as the hydrogenation reaction of olefins via alkyl intermediates were found to proceed on the edge surface of the MoS_2 crystal, while the isomerization of 2-methyl 1-butene via tertiary carbonium cation occurred on the basal plane of the MoS_2 crystal. Both the hydrogenation and the hydrogen exchange or the isomerization reactions of olefins occurred on the edge surface of the MoS_2 crystal, but the active sites for these two reactions were entirely different in catalytic ability. Such different catalytic ability of the active sites exposed on the edge surface may be referable to the different degrees of coordinative unsaturation. Some reactions via alkyl intermediates on the edge surface accompanied certain induction times. It was shown that the edge surface has the ability to produce alkyl species in the period of the induction time for the isomerization and certain hydrogen exchange of olefins. It was deduced that the rotational motion of bulky groups in these alkyl species is restricted during the induction time. The coordination of bulky groups in these alkyl species seems to undergo the reconstruction of the local structures of active sites, which results in being off the latch for the rotation of bulky groups being one elementary step in the catalysis.

INTRODUCTION

A catalytic reaction is in general composed of several elementary processes, and, if one of these processes requires specific structures for active sites, the catalytic reaction which includes this elementary process is a structure requisite type catalytic reaction. In other words, apparent structure sensitivity in heterogeneous catalysis is undoubtedly a kinetic phenomenon referring to the rate controlling step or steps, which is either sensitive or insensitive to the structures of active sites. Based on this concept, the terms "structural prerequisite" or "structure requisite reaction" will be used in this paper to describe more precise and essential properties than the apparent structural sensitivity which has been used in the past.

As the authors mentioned in a previous paper (*1*), the reaction via ionic intermediates is a structure nonrequisite type reaction, because the formation of the intermediates depends on an intensive property such as proton activity and/or proton affinity, and they are held on the surface by an ionic bond being insensitive to bond angle and/or to bond length as compared with the covalent bond. As a result, the reaction via ionic intermediates does not require any specific structures for active sites a priori, while the reaction via σ- or π-bonded intermediates requires specific structures prior to being catalyzed on it.

Typical examples are the isomerization

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and hydrogenation reactions of olefin catalyzed on isolated single sites; that is, the hydrogenation reaction via alkyl intermediates requires three degrees of coordinative unsaturation, but the isomerization reaction via alkyl intermediates can proceed on sites with two degrees of coordinative unsaturation. The reactions via ionic intermediates are quite different. For example, the isomerization of 2-methyl 1-butene occurs on the basal plane of MoS_2 but that of 1-butene does not, because although proton activity of the basal plane is sufficient to make the tertiary carbonium cation, it is insufficient to make sec-carbonium cations. As a result, the isomerization of *n*-butenes on the MoS_2 is catalyzed by the edge surface of the MoS_2 by making sec-butyl intermediates in the presence of hydrogen (*2*, *3*). In the present paper, molecular level details of the catalytic reactions taking place on the MoS_2 single crystal catalyst were elucidated by microwave spectroscopic analysis using deuterium-labeled compounds.

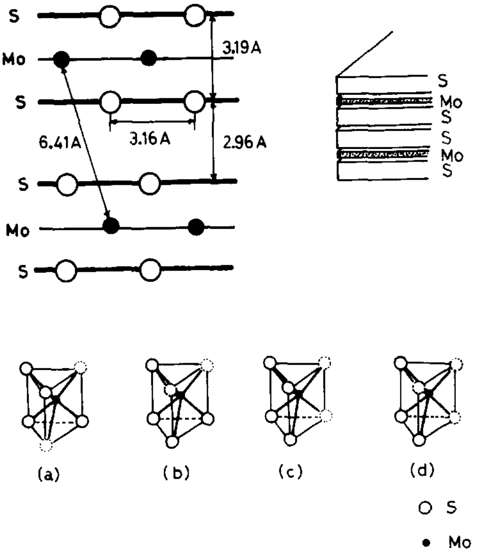


FIG. 1. Schematic layer structure of the MoS_2 crystal and variety conformation of molybdenum ions exposed on the edge surface of a single crystal. (a), (b), (c) Molybdenum ion having two degrees of coordinative unsaturation. (d) Molybdenum ion having three degrees of coordinative unsaturation.

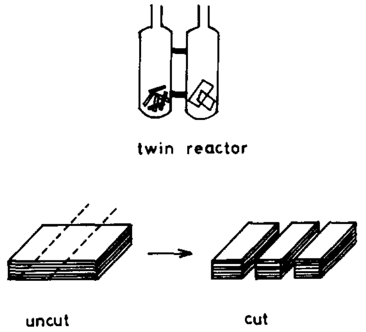


FIG. 2. Schematic description of cut and uncut MoS_2 single crystal catalysts and twin reactor cells.

EXPERIMENTAL

Molybdenum disulfide has a sandwich-like layer structure, such as that shown schematically in Fig. 1, which is easily peeled off between the sulfur layers. Accordingly, the basal plane of the crystal is composed of a monolayer of sulfur; however, the edge surface is composed of one-dimensionally arranged sulfur and molybdenum ions. By cutting a MoS_2 wafer, as shown in Fig. 2, one can enlarge the edge surface area without causing changes of the basal plane area. That is, the cut catalyst has a large edge surface area but its basal plane area is approximately equal to the uncut catalyst. Two single crystal catalysts, the cut and the uncut catalysts, were placed in a twin reactor of 50 ml per cell as shown in Fig. 2. Substantially equal experimental conditions were maintained for the two catalysts to minimize experimental errors. The two catalysts in the twin reactor were pretreated by evacuation at 450°C for 4 hr. The subsequent reactions were performed at 100°C unless otherwise stated.

The reactions were monitored by gas chromatography by sampling the gases one after the other from each cell of the twin reactor. Mass spectroscopic analyses of the deuterium-labeled compounds were also performed in the same way. The experiments for microwave spectroscopic analysis were carried out by using a batch reactor with a volume of 150 ml. The details of the microwave spectroscopic analysis were described in a previous paper (*4*).

RESULTS

A typical result of the isomerization of 1-butene and of 2-butene in the presence of hydrogen is shown in Figs. 3a and b. It was clear that the double bond migration as well as the *cis* to *trans* isomerization occurred on the edge surface of the MoS_2 crystal. In contrast to the isomerization reactions of *n*-butenes promoted in the presence of hydrogen, the double bond migration of 2-methyl 1-butene occurred without hydrogen on the cut and uncut catalysts in nearly equal rates as shown in Fig. 3c, and it was influenced little by the addition of hydrogen as was observed on the MoS_2 powder catalyst (*2*). As observed in Figs. 3a, b, and c, the isomerization of *n*-butene taking place on the cut catalyst has a distinct induction time but that of 2-methyl 1-butene does not. The mechanisms responsible for the appearance of the induction time will be discussed later.

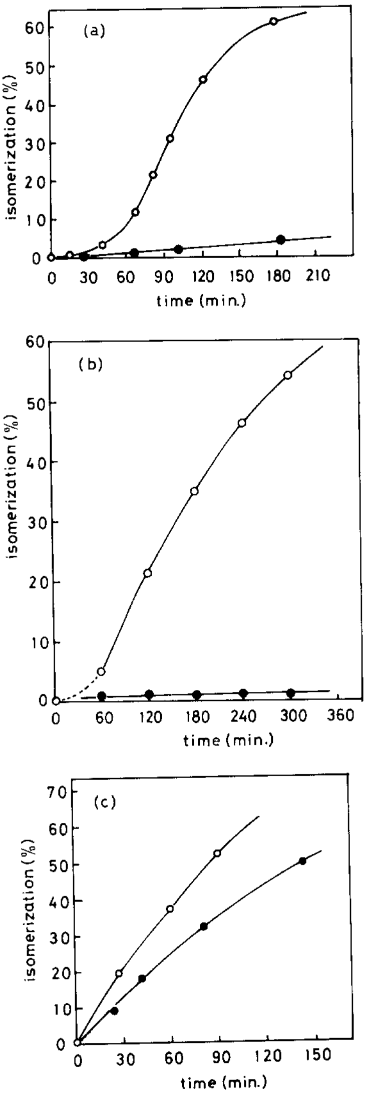


FIG. 3. Isomerization reactions taking place on cut (○) and uncut (●) MoS_2 single crystal catalysts at 100°C. (a) Isomerization of 1-butene (25 mm Hg) in the presence of hydrogen (25 mm Hg). (b) Isomerization of *cis*-2-butene (6.2 mm Hg) in the presence of hydrogen (3.8 mm Hg). (c) Isomerization of 2-methyl 1-butene (25 mm Hg) in the absence of hydrogen.

The hydrogen scrambling reaction of ethylene, propene, and *n*-butene was also catalyzed preferentially in the presence of hydrogen on the cut catalyst, because the uncut catalyst had very poor activity for this reaction. Figure 4 shows the results of hydrogen scrambling of ethylene on both the cut and the uncut catalysts. It is noteworthy that no induction time such as that observed in the isomerization of *n*-butenes was observed in the hydrogen scrambling of ethylene on the cut catalyst. The H_2–D_2 equilibration reaction was also promoted preferentially on the cut catalyst, but it

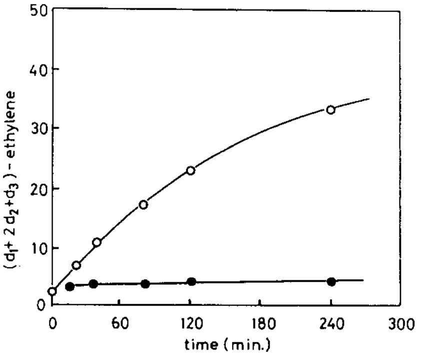


FIG. 4. Hydrogen exchange reaction of C_2H_4 and C_2D_4 (total pressure 6 mm Hg) on cut (○) and uncut (●) MoS_2 single crystal catalysts at 100°C in the presence of hydrogen (4 mm Hg).

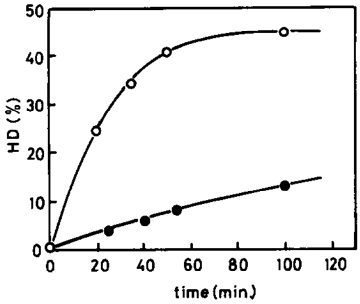


FIG. 5. The H_2–D_2 equilibration reaction (total pressure 8 mm Hg) on cut (○) and uncut (●) MoS_2 single crystal catalysts at −40°C.

showed no induction time as shown in Fig. 5. Here the question arises as to why the isomerization reaction which took place on the cut catalyst had a distinct induction time while the hydrogen scrambling of ethylene as well as the H_2-D_2 equilibration on the cut catalyst did not.

On the MoS_2 powder catalyst, it was proved that the hydrogen exchange of α-olefins such as propene and 1-butene proceeds via the *n*- and sec-alkyl intermediates in a ratio of 7 to 3 of the relative contribution independent of the chain length (*4*).

Considering these facts, we first focused on the relative contribution of *n*- and sec-alkyl species formed on the edge surface of the MoS_2 single crystal in the hydrogen exchange reaction of α-olefins. For this purpose, coisomerization of 1-butene-d_0 and 1-butene-d_8 was performed on the cut catalyst. Hydrogen scrambling as well as the isomerization reactions of 1-butene were catalyzed in the presence of hydrogen on the edge surface of MoS_2 but the induction time appeared only on the isomerization reaction as shown in Fig. 6. This fact proves that the hydrogen exchange via alkyl intermediates can take place on the edge surface which is inactive for the isomerization reaction: that is, though the edge surface is inactive for the isomerization reaction, it has the ability to catalyze the hydrogen exchange of 1-butene. In order to shed light on this curious hydrogen exchange of α-olefins taking place during the induction time for the isomerization reaction, the conformational isomers of 1-butene-d_1 obtained at 20 and 40 min which corresponded to the products obtained within and after the induction time were determined by microwave spectroscopic analysis. The 1-butene-d_1 formed in the coisomerization of 1-butene-d_0 and 1-butene-d_8 over the cut catalyst and also the 1-butene-d_1 obtained on the MoS_2 powder catalyst are shown in Table 1. The reaction temperatures are different on the cut catalyst and the powder catalyst, 100°C and room temperature, respectively, but the distribution of the geometrical isomers is surprisingly in good agreement with each other. Based on these results, we may conclude that the hydrogen exchange of 1-butene on the edge surface both during and after the induction time proceed via the same mechanism as that deduced on the MoS_2 powder catalyst

TABLE 1

Microwave Spectroscopic Analysis of 1-Butene-d_1 Formed in the Coisomerization of 1-Butene-d_0 and 1-Butene-d_8 on Cut Catalyst of the MoS_2 Single Crystal and on MoS_2 Powder Catalyst

Time (min)	Z-1-d_1	E-1-d_1	2-d_1	3-d_1	4-d_1	Reference
Single crystal						
20	14.2	14.5	71.3	0	0	This work
40	19.3	23.3	57.2	0	0	
Powder						
3	15.9	16.0	68.1	0	0	(*3*)
5	24.9	29.1	46.1	0	0	

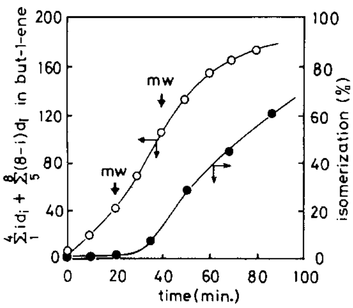


FIG. 6. Hydrogen exchange between 1-butene-d_0 and 1-butene-d_8 (total pressure 30 mm Hg) and their isomerization on the cut MoS_2 single crystal catalyst in the presence of D_2 (12 mm Hg) at 100°C. mw indicates sampling time for microwave spectroscopic analysis.

(5). Here we may ask why the hydrogen exchange through sec-butyl intermediates can occur on the inactive edge surface (during the induction time) via sec-butyl species, and what changes occur on the edge surface during the induction time?

In order to answer this question, the surface was exposed to either hydrogen or olefin for a sufficiently longer time than the induction time and another gas was subsequently added. Figure 7 shows a typical result of the previous contact with 7 mm Hg of 1-butene for 2 hr at 100°C followed by the addition of about 25 mm Hg of hydrogen. It is clear that the induction time for the isomerization reaction was neither diminished nor shortened by this procedure.

This phenomena was the same for the reverse sequence of the contact of gases. This fact indicates that the edge surface may be altered by the coordination of alkyl species with molybdenum ions exposed on the edge surface. In order to clarify the activation process of the edge surface during the induction time, the two types of reactions, one having induction time and the other without, were performed together.

The hydrogen exchange of ethylene occurred with no induction time in the presence of hydrogen as shown in Fig. 4, but the hydrogen exchange between C_2D_4 and *cis*-2-butene-d_0 occurred after the induction time concomitantly with the isomerization reaction as shown in Fig. 8a. This result is consistent with the fact that the isomerization reaction on the MoS_2 powder catalyst occurs necessarily with one hydrogen atom exchange (5).

In contrast to this finding, when a mixture of C_2H_4 and C_2D_4 was added together with *cis*-2-butene-d_0, the hydrogen exchange between C_2H_4 and C_2D_4 proceeded with no induction time while the isomerization of *cis*-2-butene-d_0 and the hydrogen exchange between C_2D_4 and *cis*-2-butene-d_0 started after the same induction time as shown in Fig. 8b. However, the hydrogen exchange between 1-butene-d_0 and ethylene-d_4 or propene-d_6 occurred within the induction time of the isomerization reaction as shown in Figs. 9a and b. In order to assure the mechanism of such characteristic hydrogen exchange of α-olefins, the propene-$h_1(d_5)$ and 1-butene-d_1 which were formed by the hydrogen exchange between propene-d_6 and 1-butene-d_0 on the cut catalyst were monitored by microwave spectroscopic analysis. As shown in Table 2, the ratios of the 2-d_1 to 1-d_1 isomers of 1-butene-d_1 and 2-h_1 to 1-h_1 of propene-$h_1(d_5)$ had approximately equal values of 7 to 3 and were in good agreement with the ratio of the isomers of 1-butene-d_1 in Table 1. Finally, we confirmed the anisotropic activities of the MoS_2 crystal by changing the crystal size of MoS_2. That is, relativistic

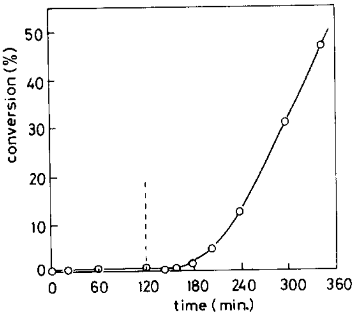


FIG. 7. Induction time observed on the cut MoS_2 single crystal catalyst which had been previously contacted with about 25 mm Hg of 1-butene for 2 hr at 100°C, followed by the addition of 75 mm Hg hydrogen at dotted line.

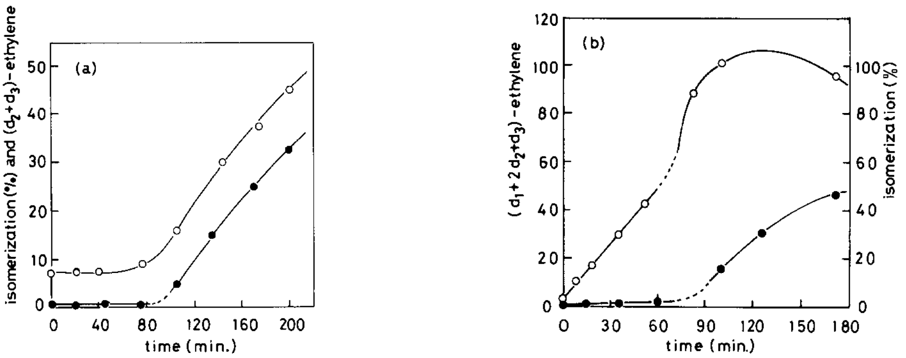


FIG. 8. Hydrogen exchange reactions taking place concomitantly with *cis* to produce *trans* isomerization reaction on cut MoS_2 single crystal catalyst at 100°C in the presence of D_2. (a) Hydrogen exchange between C_2D_4 (3 mm Hg) and *cis*-2-butene-d_0 (17 mm Hg) (○) and isomerization of *cis*-2-butene (●). (b) Hydrogen exchange between C_2D_4 and C_2H_4 (total pressure 3 mm Hg) in the presence of *cis*-2-butene (27 mm Hg), and hydrogen mixing of C_2D_4 and *cis*-2-butene-d_0 (○) superimposed concomitantly with isomerization of *cis*-2-butene (●).

activity for the isomerization of 2-methyl 1-butene and that for the hydrogen exchange between C_2H_4 and C_2D_4 were compared by using five different size catalysts. The results are summarized in Table 3. It is clear that the reaction catalyzed on the edge surface is sensitive to the crystal size but that on the basal plane is not.

DISCUSSION

The result shown in Fig. 3c demonstrates that the isomerization of 2-methyl 1-butene occurs without hydrogen on the basal plane on MoS_2. This fact indicates that acidic hydrogen may exist on the basal plane of MoS_2 which is evacuated at 450°C, and that although the proton activity is sufficient to make a tertiary carbonium cation from 2-methyl 1-butene, it is not high enough to make primary and/or secondary carbonium cations. As a result, the basal plane of MoS_2 is inactive for the isomerization of *n*-butenes (*2*).

By inelastic neutron scattering spectroscopy it was proved that the absorption of hydrogen at 300°C by MoS_2 produces a hydrogen bonding with sulfur atom and that such hydrogen does not contribute to the

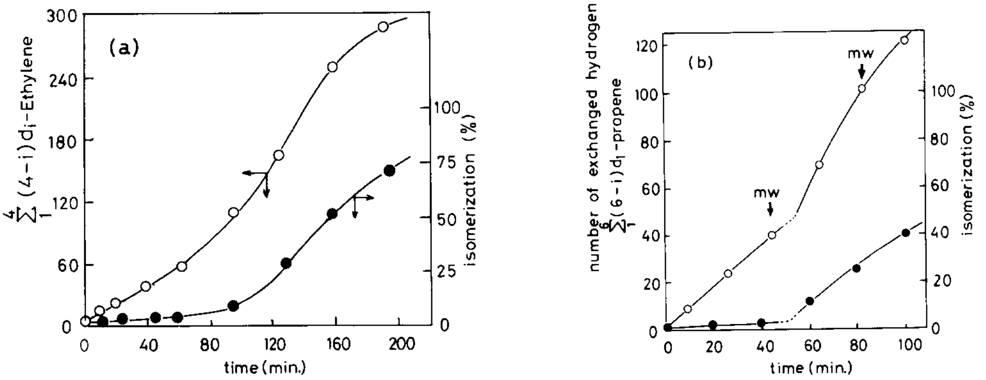


FIG. 9. Hydrogen exchange reactions taking place concomitantly with double bond migration of 1-butene on the cut MoS_2 single crystal catalyst at 100°C in the presence of D_2. (a) Hydrogen exchange between C_2D_4 (3 mm Hg) and 1-butene-d_0 (16 mm Hg) and isomerization of 1-butene. (b) Hydrogen exchange between propene-d_6 and 1-butene-d_0. Microwave spectroscopic analysis was performed by sampling at mw both within and after the induction time.

TABLE 2

Microwave Spectroscopic Analysis of Propene-h_1 and 1-Butene-d_1 Formed in the Reaction of Propene-d_6 and 1-Butene-d_0 on Cut Catalyst of the MoS_2 Single Crystal

Time (min)	Propene-h_1			1-Butene-d_1			
	1-h_1	2-h_1	3-h_1	1-d_1	2-d_1	3-d_1	4-d_1
45	27.4	63.7	8.9	33.6	66.4	0	0
82	36.5	57.0	6.5	47.9	52.1	0	0

H_2–D_2 equilibration reaction (*6*). However, a part of such hydrogen might be effective to catalyze the isomerization of 2-methyl 1-butene if its proton activity is sufficient.

The formation of carbonium cationic intermediates depends mainly on the proton activity of the catalyst and the proton affinity of the olefins and will be less sensitive to the structures of active sites, because the ionic interaction is less sensitive to the bond length as well as to the bond angle. Furthermore, proton activity of the surface may have no regular relations with respect to the structures of active sites. As a result, the reaction via ionic intermediates will be a structure nonrequisite reaction.

In contrast to such structure nonrequisite reactions, the reaction via σ- or π-bonded alkyl or allyl intermediates will be sensitive to the structures of active sites, because the formation and stability of these species are quite sensitive to the bond length and the bond angle. As a result, the formation of such intermediates requires specific structures for the active sites on which the orbitals can overlap. The enhancing effect of H_2 on the reactions taking place on the edge surface indicates that the sites exposed on the edge surface of MoS_2 may have specific structures to accelerate the dissociation of the H_2 molecule. The coordination of olefin with such sites undergoes the insertion reaction of the hydrogen atom to make the alkyl species. The H_2–D_2 equilibration reaction is also a reaction which requires the dissociation of the hydrogen molecule. It should be noted here that the H_2–D_2 equilibration as well as the hydrogen exchange between C_2H_4 and C_2D_4 occur on the edge surface with no induction time. These two reactions remind us of our previous work on the MoS_2 powder catalyst; when C_2H_4 and C_2D_4 in a ratio of 3/2 and H_2 and D_2 in a ratio of 2/3 were added together on the MoS_2 powder catalyst, both the H_2–D_2 equilibration and the hydrogen scrambling of ethylene occurred simultaneously but no hydrogen exchange between ethylene and hydrogen proceeded appreciably (*7*). A similar phenomenon was that the isomerization of 1-butene enhanced by D_2 yielded 2-butene-d_0 predominantly, but the hydrogenation taking place simultaneously yielded only butane-d_2 as a major product (*7*). To understand these enigmatic results, the intermediates for the isomerization and for the hydrogenation reactions should be identified. As shown in Table 1, the hydrogen exchange of α-olefins taking place on the edge surface proceeds via the *n*- and sec-alkyl intermediates and their relative contribution is about *n*/sec = 7/3 for 1-butene as well as for propene (*4, 5*). The question arises, if the isomerization of 1-butene proceeds via the sec-butyl intermediates on the edge surface of MoS_2, why did the isomerization of 1-butene enhanced by D_2 yield mainly 2-butene-d_0 although the concomitant hydrogenation gave butane-d_2?

To answer this question, we attempted to identify whether *n*- or sec-alkyl species are the intermediates of the hydrogenation of

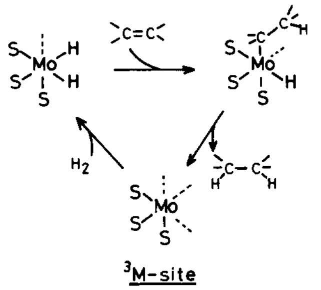
TABLE 3

Effect of Crystal Size of MoS_2 on the Relative Activities for Isomerization of 2-Methyl 1-Butene and for Hydrogen Exchange Between C_2H_4 and C_2D_4

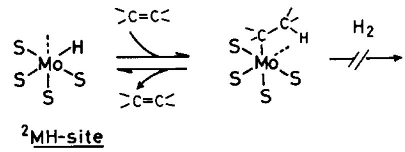
	Mesh of MoS_2 crystal				
	<10	10–20	20–42	42–100	>100
Isomerization of 2-methyl 1-butene	1	1	1	2	4
C_2H_4-C_2D_4	10^{-4}	5×10^{-3}		1	

α-olefins. For this purpose, a novel method derived from a kinetical relation between the orientation in the addition of the HD molecule and the isotope effect for H_2 and D_2 addition has been developed (*8, 12*). Using this method, we concluded that the hydrogenation of α-olefins proceeds via sec-alkyl intermediates on the MoS_2 catalyst, and that the active sites for the hydrogenation reaction are composed of dihydride species. These facts prove that the hydrogenation reaction as well as the isomerization reaction of 1-butene occur on the edge surface of MoS_2 via sec-butyl intermediates. However, the isomerization via sec-butyls in the presence of D_2 produces 2-butene-d_0 but the hydrogenation with D_2 via sec-butyls yields butene-d_2. These facts seem to suggest that the two kinds of active sites with different catalytic abilities exist on the edge surface of MoS_2. The fact that the H_2–D_2 equilibration and the hydrogen exchange of ethylene proceeded independently on the edge surface of MoS_2 is also explained by the presence of sites with different catalytic abilities. That is, the molybdenum ion exposed on the edge surface has certain degrees of coordinative vacancies, and if the hydrogenation reaction is accomplished on such sites, the hydrogenation reaction may require three degrees of coordinative unsaturation in a way similar to Wilkinson's hydrogenation catalyst.

On the other hand, the alkyl species which are coordinated with the sites having two degrees of coordinative unsaturation can undergo isomerization and/or hydrogen exchange reactions but cannot be hydrogenated to alkanes provided that all elementary processes are accomplished on an isolated single site (*9, 10*). In conformity with dihydride type homogeneous hydrogenation catalysis, it is quite reasonable to assume that dihydride sites with one coordinative vacancy are active for the hydrogenation reaction but that monohydride sites with one coordinative vacancy can catalyze only the isomerization and/or the hydrogen exchange of olefins. Scheme I describes the reactions of alkyl species coordinated to ^{2}M-sites and to ^{3}M-sites (*3, 10*).



Hydrogenation on ^{3}M-site



Isomerization or Hydrogen Exchange on ^{2}MH-site

The molybdenum ions having three degrees of coordinative unsaturation (^{3}M-sites) may locate mainly at the corner of the MoS_2 crystal while the ^{2}M-sites may appear randomly over the edge surface, and the migration of intermediates between the sites may be rather prohibited. As a result, the two types of reactions catalyzed on ^{2}M-sites and ^{3}M-sites proceed independently on the edge surface of MoS_2. On the other hand, the isomerization reaction catalyzed on the basal plane of MoS_2 is controlled by proton activity and affinity, that is, this type of reaction requires sufficient proton activity but not specific structures for active sites.

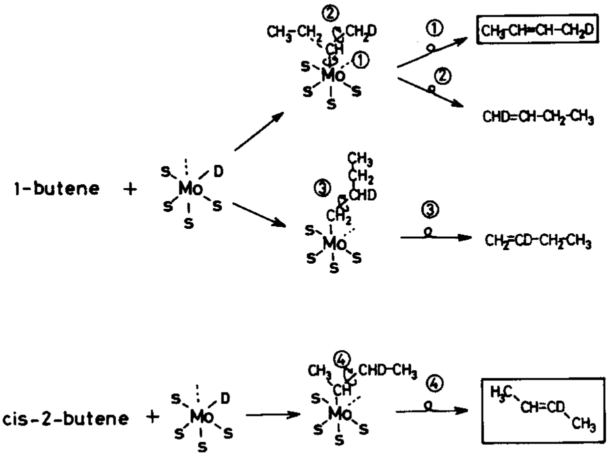
It is noteworthy that the relative contributions of *n*-butyl and sec-butyl intermediates in the coisomerization of 1-butene-d_0 and 1-butene-d_8 are about 70 and 30%, respectively, either on the single crystal or the powder MoS_2 catalyst. The hydrogen exchange of propene also proceeds in a quite similar manner to that of 1-butene, that is, sec-propyl contributes about 30% of the total hydrogen exchange. If the hydrogen exchange via sec-propyl would occur in a statistical manner, propene-1-d_1 and propene-3-d_1 should be formed in a ratio of 2/3. This was not the case on the MoS_2 catalyst; instead, unusually small numbers of propene-3-d_1 were formed on the MoS_2 catalyst as shown in Table 2.

This strange phenomenon was explained by the restricted rotation of the sec-propyl species around the coordination bond (*4*). That is, the two methyls in a sec-propyl which is bonded-to the ^{2}M-site have a different probability for undergoing hydrogen giving and receiving with a vacant coordination site on the ^{2}M-site. If this speculation is correct, the sec-butyl species bonded to ^{2}M-sites may also be considered to be restricted from rotating freely around the coordination bond. In fact, it is a unique characteristic of MoS_2 that the double bond migration of 1-butene via sec-butyl is slow although the hydrogen exchange as well as the *cis–trans* via sec-butyl intermediates occur rapidly. This result may prove that the sec-propyl species on the edge surface of MoS_2 are restricted from free rotation.

An interesting phenomenon observed on single crystal catalysts is that the *cis* to *trans* isomerization as well as the double bond migration reaction of *n*-butenes start after a certain induction time. In other words, the edge surface of MoS_2 evacuated at 450°C is inactive for these isomerization reactions in the initial stage although it is active for the hydrogen scrambling reaction of α-olefins including ethylene. The formation of alkyl intermediates was proved for the hydrogen scrambling reaction occurring during the induction time. This fact indicates that the edge surface has an inherent ability to create *n*-alkyl and sec-alkyl species in the presence of hydrogen even if the surface is inactive for the isomerization reactions.

Furthermore, the relative contributions of *n*- and sec-butyl species in the hydrogen scrambling reaction during the induction time is also a ratio of 7 to 3 as shown by the geometrical isomers of 1-butene-d_1 at 20 min in Table 1. Further evidence for the formation of alkyl species on the edge surface of MoS_2 during the induction time is presented in Fig. 8b, where ethyl species are evidently formed in the presence of hydrogen on the edge surface which is inactive for the isomerization of *cis*-2-butene. Taking into account the fact that the *cis–trans* rotation over the ^{2}M-sites necessarily accompanies one hydrogen atom exchange, it is quite reasonable to assume that the hydrogen exchange between C_2D_4 and *cis*-2-butene-d_0 does not proceed appreciably during the induction time for the isomerization as shown in Fig. 8a, although the hydrogen exchange between C_2H_4 and C_2D_4 does. From these facts, we concluded that the edge surface of the MoS_2 crystal has an ability to form *n*- and sec-alkyl species in the presence of hydrogen but that some necessary conditions for the isomerization reaction may not be fulfilled on the edge surface during the induction time.

Catalytic processes taking place on the ^{2}M-sites via *n*-butyl and sec-butyl intermediates are shown schematically in Scheme II, and the reactions with an induction time are enclosed in the square. It may be deduced that the reactions having an induction time require necessarily the rotation of bulky groups through sec-butyl intermediates. That is, the double bond migration reaction on ^{2}M-sites requires the rotation of sec-butyl intermediates around the coordination bond and the *cis–trans* rotation of 2-butene requires the rotation of the ethyl group. The fact that such induction time is not shortened by the preceding contact of either olefins or hydrogen may indicate that the induction time for these two reactions may correspond to a rearrangement process caused by the coordination of alkyl species to the ^{2}M-sites. In other words, the rotational barriers of bulky groups might be lowered by the rearrangement of the active sites. The ^{2}M-sites can take various conformations, such as these shown in Fig. 1, and some of them are stable under evacuation



Scheme for required rotational motion of intermediates.

at 450°C. However, the coordination of alkyls with these sites will cause some kind of reconstruction, and therefore the conformational changes result in more space around the ^{2}M-sites which are favorable to the rotational motion of bulky groups. It should be emphasized here that the rotational motion of sec-alkyl species around the coordination bond is still restricted from free rotation and is slow as compared with the other elementary processes on the rearranged ^{2}M-sites; these are referred to as the characteristic properties of the MoS_2 catalyst as described above.

A catalytic reaction is in general composed of several elementary processes. And, if the rotational motion and/or the surface migration of the intermediates are necessary elementary processes, the restriction of such dynamic motions of the intermediates as the rotation or the surface migration causes retardation of the corresponding catalytic reaction.

This work might be the first experiment in which reactions on single crystal catalysts were analyzed by using microwave spectroscopy. The combination of microwave spectroscopy and well-defined single crystal catalyst is a great advantage for understanding catalysis at the molecular and atomic level.

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