A General Aspect of Catalytic Hydrogenation and Isomerization Reactions on Oxide Catalyst

Characteristics of the Reactions via Ionic and Nonionic Intermediates

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Hydrogenation and isomerization reactions taking place on oxide and/or on sulfide catalysts are divided into two types depending on the intermediates being either ionic or nonionic. The reactions via nonionic species such as σ-alkyl and σ- or π-allyl intermediates require specific structure for active sites, while the reactions via ionic intermediates such as alkyl cation or allyl carbanion require no specific structure for active sites and depend entirely on acidity or basicity of the surface. The reactions on such oxides as Co_3O_4, Cr_2O_3, ZrO_2, ThO_2, and La_2O_3 are the former case, which are controlled by the structure of active sites. CdO and MgO are a typical case of ionic intermediates and are active for the hydrogenation of conjugated diene via allyl carbanion but not for the hydrogenation of olefin. Allyl as well as allyl carbanion bring about both the 1,2- and 1,4-additions, and the relative contribution of these two types of addition depends on kinetic facility. A larger *cis/trans* ratio in the 1,4-addition reflects allyl carbanion intermediates because of preferential Z-conformation of allyl carbanions. From a view of ionic and nonionic intermediates in catalysis, a new type of hydrogenation reaction via cationic intermediates is predicted.

INTRODUCTION

The concept of "demanding and facile" properties in heterogeneous catalysis proposed by Boudart *et al.* (*1*) has been rationalized on stepped platinum single crystal by Somorjai and his co-workers (*2*). However, we should give due consideration to the fact that apparent structure sensitivity in heterogeneous catalysis appears only when the rate-controlling step or steps is sensitive to the structure of catalyst. As a catalytic reaction is in general composed of several elementary processes, and if the reaction includes a process which proceeds on sites having specific structures, the catalyst should fulfill this structural requisite. In this sense, this catalytic reaction is a structure requisite reaction. In spite of this, if the structure

requisite process is not the rate-controlling step of the reaction, the reaction will be structure insensitive. The term "structural prerequisite" used in this paper has a more precise and essential meaning than the term "structural sensitivity" previously used in heterogeneous catalysis.

The authors (*3–5*) proved that the isomerization and/or the hydrogen exchange reaction of olefins taking place on MoS_2 usually proceeds on the edge plane of MoS_2 crystal via alkyl intermediates. However, the isomerization of 2-methyl but-1-ene is entirely catalyzed on the basal plane of MoS_2 crystal composed of sulfur sheets, and this isomerization reaction proceeds via a tertiary carbonium cation. These results lead us to an important concept, that the reaction via alkyl intermediates requires such specific structures as certain degrees of coordinative unsaturation for active sites, but the reaction through ionic intermediates does not require such specific structures a priori for the sites. Furthermore, it was

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demonstrated that the alkyl intermediates for the hydrogenation reaction are strictly distinctive from those for the isomerization reaction. Such a distinction of alkyl species for the hydrogenation and the isomerization reactions may be caused by the difference of structural prerequisites of these two reactions for the active sites (6–8). An interesting question may arise concerning whether the intermediates of the hydrogenation of 1,3-butadiene and those of the isomerization of n-butene on basic oxides are identical or not, because the formation of ionic species such as allyl carbanion and alkyl cation may not require specific structures for active sites. Accordingly, another interesting problem is what different characteristics will be expected for the reactions via ionic and nonionic intermediates.

A general aspect based on ionic and nonionic intermediates proposed in this paper will predict a new catalytic hydrogenation reaction via cationic intermediates on heterogeneous catalyst. This type of hydrogenation reaction has been reported only in super acid media.

RESULTS AND DISCUSSION

So far the isomerization and/or the hydrogen exchange of olefin via alkyl intermediates have been explained by the reverse process of the hydrogenation reaction, that is, common intermediates were tacitly assumed (9). However, it was proved that isomerization and/or hydrogen exchange reactions of olefin taking place on sulfided nickel (4, 6) as well as on molybdenum disulfide (4, 8, 10) proceeded through alkyl intermediates which are distinctive from those of the hydrogenation reaction. Such distinction of alkyl species is caused by the fact that the structural prerequisite for the hydrogenation reaction is different from that for the isomerization reaction. If the active sites are entirely isolated from one another, the isomerization reaction occurs on the sites having two degrees of coordinative unsaturation to which one hydrogen atom is bound as shown in Scheme I, while
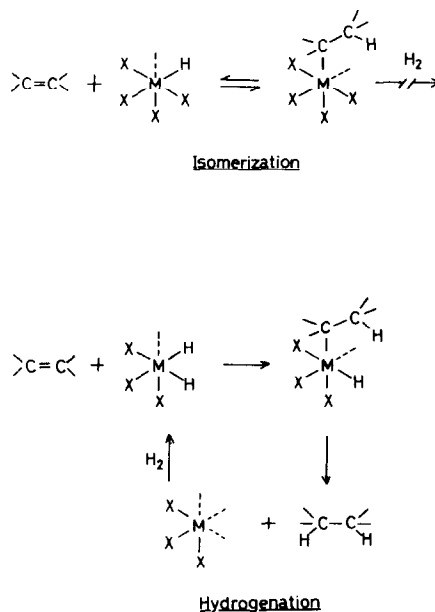
SCHEME I. Different structural prerequisites for hydrogenation and isomerization reactions.

the hydrogenation reaction will require three degrees of coordinative unsaturation for active sites in a similar manner as the Wilkinson hydrogenation catalyst.

The determination of the importance of such structural prerequisites for catalytic reactions was first attempted on reactions on transition metal oxides (7). If a catalytic hydrogenation reaction proceeds on such isolated active sites, the hydrogen molecular identity will be maintained providing that the reverse process is slow. In fact, the reaction of olefin or diene with a mixture of H_2 and D_2 yields d_0- and d_2-adducts on Cr_2O_3 (12, 13), Co_3O_4 (14), and MoS_2 (10, 11). However, such precise conservation of hydrogen molecular identity is not a specific character of transition metal oxides. The deuteration of 1,3-butadiene on ZnO (12, 15), CdO (16), and MgO (17) also maintains the deuterium molecular identity to yield but-1-ene-d_2 and/or but -2-ene-d_2 predominantly. Catalytic activity of various oxides for the hydrogenation of olefins as well as of dienes and for the H_2–D_2 equilibration reaction is summarized in Table 1. Relative contributions of the 1,2- and 1,4-

TABLE 1

Catalytic Activity and Selectivity of Various Oxides in the Hydrogenation of Butadiene and Olefin

Oxides	Temperature (°C)	C=C—C=C		$\left[\dfrac{cis}{trans}\right]$	$\diagdown\diagup_{C=C}\diagup\diagdown$	H_2–D_2	Reference
		1,2-add. (%)	1,4-add. (%)				
CdO	r.t.	60	40	(20)	−	−	16
MgO	0	10	90	(10)	−	−	17
ZnO	r.t.	90	10	(10)	+	+	15
Co_3O_4	r.t.	20	80	(1)	+	+	a
Cr_2O_3	r.t.	80	20	(1)	+	+	a
ThO_2	18	10	90	(0.1)	+	+	31
ZrO_2	50	16	84	(0.08)	+	+	30,b
La_2O_3	0	4	96	(0.2)	+	+	31
MoS_2	r.t.	100	0	(—)	+	+	29

a Unpublished data.

b In Ref. (30) no activity for the H_2–D_2 equilibration was reported, but Yamaguchi's repeated experiment according to my suggestion showed activity for the equilibration reaction.

additions of hydrogen to 1,3-butadiene are also listed. From this table, one can derive the following characteristics of various oxides for the hydrogenation reaction.

(1) Transition metal oxides are active for hydrogenation of olefin as well as of diene, but alkaline earth oxides are merely active for the hydrogenation of conjugated diene. ZnO is exceptional because it is active for both olefin and diene.

(2) Oxides which are active for the hydrogenation of olefin are also active for the H_2–D_2 equilibration reaction.

(3) Hydrogenation of butadiene on oxides is brought about by both or either the 1,2- and 1,4-additions, and the 1,4-addition on basic oxides such as MgO, CdO, and ZnO yields preferential cis-but-2-ene to trans-but-2-ene.

(4) Relative contribution of the 1,4-addition on various oxides has no apparent trend with respect to the basicity of oxides.

A parallel correlation of the catalytic activity of metals for the hydrogenation of olefin and the H_2–D_2 equilibration proves a necessary condition of hydrogen dissociation for the hydrogenation reaction on metallic catalyst. In fact, gold is an inactive metal for either the hydrogenation or the H_2–D_2 equilibration, but if hydrogen atoms are furnished to it by diffusing from the other side of Au foil, the hydrogenation of cyclohexene is brought about on the Au surface as Wood and Wise demonstrated (18). A similar type of hydrogenation reaction can be brought about on an inert surface by using hydrogen donor substances (19). Quantum chemistry also supports a necessary condition of hydrogen dissociation for the catalytic hydrogenation reaction, that is, the orbital symmetry rule prohibits the direct addition of hydrogen molecule to the bonding π-orbital of olefin. In conformity with these facts, a correlation observed in Table 1 seems to indicate the necessary condition of hydrogen dissociation on oxide catalyst for the hydrogenation of olefin. If this is true, a question may arise as to why CdO and MgO are active for the hydrogenation of conjugated dienes although they are not active for the hydrogenation of olefin as well as for the H_2–D_2 equilibration reaction. Selective partial hydrogenation of diene and/or acetylene has been observed on several catalysts, and two mechanisms have been proved in the past: selective hydrogenation of acetylene or diene on metals or on transition metal oxides which is caused by competitive adsorption of diene or acetylene and olefin,

and the selective partial hydrogenation regulated by reversible change of catalyst surface. In the former case, if olefin alone is added to the catalyst, rapid hydrogenation of it will occur, but in the latter case no hydrogenation of olefin is brought about. The partial hydrogenation of acetylene and of 1,3-butadiene attained on sulfided nickel is a typical example of the latter case. That is, the sulfided nickel surface is inactive for the hydrogenation reaction of acetylene as well as of ethylene, but it becomes active for the hydrogenation reaction by contacting with acetylene or 1,3-butadiene. If acetylene or butadiene in the gas phase is consumed, the surface is deactivated which results in selective partial hydrogenation of acetylene or diene to olefins (4, 6).

It should be emphasized here that the partial hydrogenation of conjugated diene on CdO and on MgO is attained by an entirely different mechanism. The characteristics of CdO and MgO are quite similar to those of alkali metals deposited on alumina (20) and alkali metal hydrides (21) which are active only for the hydrogenation of conjugated dienes. In conformity with these facts, plausible intermediates of the hydrogenation of conjugated dienes are allyl carbanions. As shown in Scheme I, the hydrogenation as well as the isomerization reactions which proceed through σ-alkyl intermediates require specific structures for active sites, and the different structural prerequisites for the hydrogenation and the isomerization reactions distinguish the intermediates for the two reactions. In contrast to this, the hydrogenation of 1,3-butadiene on CdO proceeds through allyl carbanion intermediates, and the intermediates for the hydrogenation was proved to be the same species as those for the double bond migration reaction of n-butene (16). This fact seems to indicate that the catalytic reaction through ionic intermediates may require no structural prerequisite a priori for active sites. In fact, the results on MoS₂ single crystal catalyst proved that the isomerization reaction via alkyl cation proceeds on the basal plane of MoS₂ crystal composed of sulfur sheets, but the isomerization reaction via σ-alkyl intermediates occurs entirely on the edge plane of MoS₂ crystal as shown schematically in Fig. 1 (3–5). According to this concept, the isomerization reaction may be described with ionic or nonionic intermediates as shown in Scheme II.

If this concept is applicable to the hydrogenation reaction, the characteristics of the hydrogenation reaction may be described by the intermediates which are either ionic or nonionic species. The hydrogenation via ionic intermediates might be controlled by the surface acidity or basicity, while the hydrogenation reaction via σ-alkyl and σ- or π-allyl intermediates will be controlled by the structures of active sites as described in Scheme III. The catalytic hydrogenation of 1,3-butadiene on CdO and MgO seems to verify the hydrogenation reaction via ionic intermediates. The basicity of CdO and MgO surfaces may be sufficient to make allyl carbanion in the reaction of conjugated diene with hydrogen molecule, and allyl anions are also formed by hydrogen abstraction from olefins. However, these oxides have no active sites which fulfill the structural prerequisite for the catalytic hydrogenation reaction via nonionic intermediates such as σ-alkyl and σ- or π-allyl species. As a result, the hydrogenation reaction of olefins cannot be brought about on these
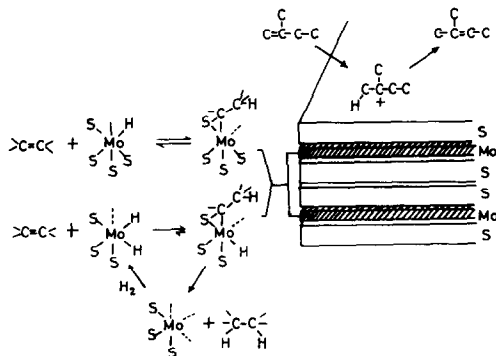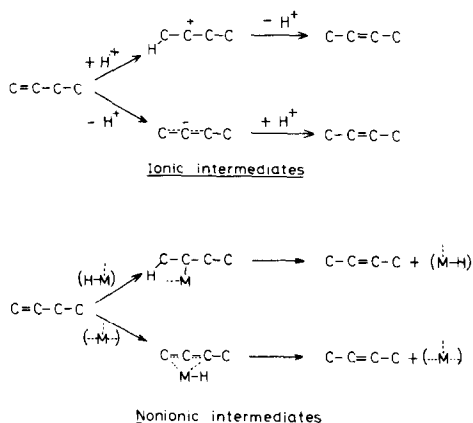

FIGURE 1. Structure required and nonrequired reactions taking place on edge and basal plane of MoS₂.

$$C=C-C-C \begin{array}{c} \xrightarrow{+H^+} \overset{+}{H_2}C-\overset{}{C}-C-C \xrightarrow{-H^+} C-C=C-C \\ \xrightarrow{-H^+} C\overset{-}{=}C\overset{}{=}C-C \xrightarrow{+H^+} C-C=C-C \end{array}$$

Ionic intermediates

$$C=C-C-C \begin{array}{c} \xrightarrow{(H-M)} \overset{\cdot}{C}-C-C-C \quad H\cdots M \longrightarrow C-C=C-C + (\overset{\cdot}{M}-H) \\ \xrightarrow{(-M-)} C\overset{}{=}C\overset{}{=}C-C \quad \overset{\cdot}{M}-H \longrightarrow C-C=C-C + (-\overset{\cdot}{M}-) \end{array}$$

Nonionic intermediates

SCHEME II. Characteristics of the isomerization reaction via ionic and nonionic intermediates.

oxides because the surface basicity is not strong enough to stabilize alkyl carbanions.

Schlosser and Hartmann (22) showed that the delocalization of π-electrons in allyl carbanion depends on countercations, and the conformation of 2-butenyl metallic compounds, $[CH_3CH-CH-CH_2]^-M^+$, in hexene increasingly prefers the Z-conformation (cis) as the electropositivity of M^+ increases. The electropositivity of metal ions may correspond to the values of opposite sign of electronegativity of metal ions given by Tanaka and Ozaki (23). The delocalizability of π-electrons influences the resonance stabilization of allyl carbanion, and the larger the resonance stabilization the higher the rotational barrier about the carbon–carbon bond. For example, the rotational barrier of allyl alkali metal complexes changes, being 10.7 kcal/mole for allyl-Li, 16.7 kcal/mole for allyl-K, and 18.0 kcal/mole for allyl-Cs in THF solution, and free allyl carbanion might have more than 18 kcal/mole of rotational barrier about the carbon–carbon bond (24). On the other hand, the resonance energy of the allyl radical is 9.6 kcal/mole (25) but that of the allyl carbanion is 14.5 kcal/mole (26). This fact suggests that the rotation about the carbon–carbon bond will be more prohibited from free rotation in reaction via allyl carbanion intermediates. In fact, the iso-

merization of cis-but-2-ene on Na/Al_2O_3 (27) and on CdO (16) gives preferential but-1-ene formation although trans-but-2-ene is thermodynamically favored. The rotational barrier of allyl carbanions formed on CdO and Na/Al_2O_3 is higher than that on ZnO and MgO, which indicates that the rotational barrier of allyl carbanions formed on oxides depends on the electropositivity of the sites on which the allyl carbanions are stabilized.

In contrast to this, the rotational barrier of σ- or π-allyl species formed on transition metal oxides is undoubtedly lower than that of allyl carbanions. As a result, the hydrogenation of butadiene on transition metal oxides gives rather small values of the cis/trans ratio. It is worthy of note that the isomerization of but-1-ene on Cr_2O_3 gives a wide range of the cis/trans ratio depending on pretreatment of the oxide (28), and this unusual ratio remains to be proved.

If the intermediate of hydrogenation of 1,3-butadiene is σ-allyl, but-1-ene will be a predominant product as is the case on MoS_2 catalyst (29). However, the hydrogenation of butadiene on transition metal oxides gives but-2-ene as well as but-1-ene in a variety ratio as shown in Table 1, which reflects the contribution of the 1,2- and 1,4-additions. The hydrogenation of 1,3-butadiene on transition metal oxides gives both but-1-ene and but-2-ene, but it is not obvious whether the π-allyl species formed on transition metal oxide would react in a form of 1,2-addition without the π- to σ-allyl interconversion on active sites. On the other hand, it was proved that allyl carbanion formed on CdO reacts to give the 1,2- and 1,4-additions without the σ-π interconversion, and that their relative contribution in the hydrogenation reaction depends on the kinetic facility of these two types of addition (16).

From these results, it may be concluded that the cis/trans ratio in the 1,4-addition reflects allyl carbanion intermediates, while the relative contribution of the 1,2- and 1,4-additions depends on the kinetic facility of

the two types of reactions. In this sense, ThO_2 and La_2O_3 are interesting oxide on which preferential 1,4-addition taking small values of cis/trans ratio is brought about. Imizu et al. (31) conjectured allyl carbanion intermediates for the hydrogenation of conjugated dienes on these oxides for reason of preferential 1,4-addition, but it carries no validity as cited above. The characteristics of ThO_2 and La_2O_3 in Table 1 are quite analogous to the transition metal oxides which are active for the hydrogenation of olefin as well as for the H_2–D_2 equilibration reactions. These results suggest that the active sites for the hydrogenation reaction on La_2O_3 are perhaps oxygen vacancies with certain degrees of coordinative unsturation. The La_2O_3 surface has undoubtedly some basicity which catalyzes the isomerization of n-butene via allyl carbanion intermediates. The basic strength of La_2O_3, however, may not be sufficient to promote the hydrogenation of conjugated dienes by making allyl carbanion intermediates.

These results suggest a dual character of the La_2O_3 surface which is similar to the MoS_2 surface shown in Fig. 1, that is, the La_2O_3 surface is composed of lanthanum ions with certain degrees of coordinative unsaturation and oxygen ions with some basicity. The hydrogenation of olefin as well as of conjugated diene proceeds on lanthanum ions which fulfill the structural prerequisites for the catalytic hydrogenation reaction. The isomerization reaction of n-butene on La_2O_3 occurs mainly on basic sites via allyl carbanion intermediates. In fact, cis/trans ratio in the hydrogenation of 1,3-butadiene on La_2O_3 has the low value of 0.22 as shown in Table 1, but the ratio in the isomerization reaction of but-1-ene to but-2-ene is as high as 7 to 8 at 0°C (32). Preferential trans-but-2-ene formation in the hydrogenation of 1,3-butadiene on these oxides was explained by the transoid conformation of butadiene in the gas phase (31), but it seems to be a temporizing idea
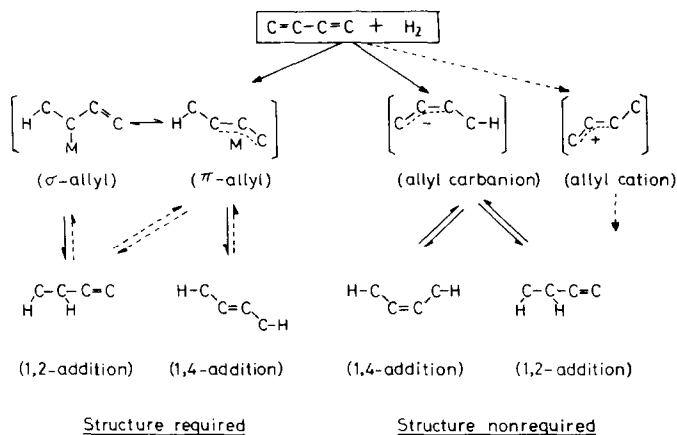
because they assumed high rotational barrier for butadiene with no evidence.

As a goal of this paper, we wish to propose the following reaction scheme for the catalytic hydrogenation reaction on oxides where the nature of the intermediates, being either ionic or nonionic, govern the characteristics of the reaction whether it requires specific structures for active sites or not.

A general idea proposed in this paper suggests a new type of hydrogenation reaction which proceeds through cationic intermediates. As far as we know, the hydrogenation reaction through cationic intermediates has never been recognized in heterogeneous catalysis. However, this type of hydrogenation reaction has been found in super acids (33), which is undoubtedly a structure nonrequired reaction because it contains no transition metal complexes or ions. As Brouwer and Hogeveen (34) showed explicitly, the reaction of secondary carbonium cations with H_2 in super acids is about 10^5–10^6 times faster than the tertiary cations. In conformity with the thermodynamic stability of the carbonium cations, the formation of primary and/or secondary cations on solid surface may need exceedingly high proton activity, and if we keep this in mind, the hydrogenation of primary and/or secondary carbonium cations on solid surfaces will be recognized in the future. The hydrogenation reaction via cationic intermediates might be strong for poisons because this type of reaction requires no specific structures which are sensitive for poisoning. Accordingly, this type of hydrogenation reaction will be an advantage for heavy duty systems such as coal hydrogenation reaction, and $ZnCl_2$ catalyst for coal hydrogenation might perhaps be a case of this type of hydrogenation reaction.

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$$C\text{-}C\text{-}C\text{=}C \ + \ H_2$$

(σ-allyl)   (π-allyl)   (allyl carbanion)   (allyl cation)

(1,2-addition)   (1,4-addition)   (1,4-addition)   (1,2-addition)

Structure required   Structure nonrequired

SCHEME III. Characteristics of hydrogenation reactions via ionic and nonionic intermediates.

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