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A survey of the mechanism in catalytic isomerization of alkanes

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Abstract

The isomerization of alkanes into corresponding branched isomers is one of the important processes in petroleum refining. Though the so-called bifunctional catalysts are used in industrial processes, the better catalysts are still sought for the improvement of the catalytic performance. The catalysts used in industrial processes and those of academic interest are described with emphasis on the mechanistic aspect. The catalysts include Pt supported on solid acids, sulfated zirconia, tungsten oxide supported on zirconia, oxycarbides of tungsten and molybdenum, and partially reduced MoO_3. The mechanism of the isomerization over each catalytic system is described. The role of transition metals and hydrogen in bifunctional catalysts and the controversial mechanisms of alkane isomerization over sulfated zirconia are discussed in detail. Finally, recent development of the computational modeling and quantum mechanical calculations on alkanes activation and their transformations over zeolites are discussed with respect to the role of acid sites in the isomerization.

Keywords: Alkanes; Sulfated zirconia; Tungsten oxide

1. Introduction

Isomerization of *n*-alkanes into the corresponding branched alkanes is an important way to enhance the octane number of gasoline. The octane numbers (RON) of pentane and hexane are 61.7 and 24.8, respectively, while those of isopentane and 2,3-dimethylbutane are 92.3 and 103.6, respectively. The isomerization of C_4–C_6 hydrocarbons is performed in industrial scale. Isobutane obtained by the isomerization of butane is also used for alkylation process and for MTBE synthesis after dehydrogenation to isobutene. Isomerization of heptane has been extensively studied. Skeletal rearrangement of hydrocarbons is also important in hydrocracking of higher hydrocarbons to obtain the products with higher octane numbers.

The mechanism of alkane isomerization has been discussed for years and is seemingly established. The details of the mechanism are, however, still unresolved. The main problems to be solved include the way of formation of carbenium ions, acidity requirement of the catalysts, and the roles of a metallic component and hydrogen during isomerization. This short review surveys the recent progress on the catalysts and the mechanisms in alkane isomerization.

2. Catalysts for alkane isomerization

The main catalysts of importance in alkane isomerization are briefly discussed. The mechanistic aspects of the catalytic systems are discussed later.

2.1. Friedel–Crafts catalysts

The catalysts used for the earlier industrial isomerization processes are Friedel–Crafts catalysts such as

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$AlCl_3$ with additives such as $SbCl_3$ and HCl. The catalysts are strongly acidic and very active even at 300–390 K. The low-temperature activity is very favorable since the equilibrium shifts to branched isomers at lower temperature. The processes using these catalysts, however, do not exist any more, because of the problems of corrosion of the reactor and the disposal of the used catalysts. The carbenium ion mechanism of the isomerization with acid catalysts is well developed through the works on these types of catalysts.

2.2. Chlorinated alumina or zeolites loaded with transition metal - bifunctional catalysts

Solid acids such as zeolites and modified alumina are active for alkane isomerization, though the higher temperature is required compared to Friedel–Crafts catalysts. The catalytic performance is greatly improved in terms of the selectivity and catalyst life by loading a transition metal on a solid acid and operating at high hydrogen pressure. The acidic components (chlorinated alumina or zeolite) participate in the reaction steps where carbenium ions are involved, while the metallic component offers hydrogenation–dehydrogenation activity. Therefore, this type of catalysts is called bifunctional (or dual-functional) catalyst. The mechanism of the bifunctional catalysis will be discussed later.

The industrial processes utilize dual-functional catalysts and are operated under high pressure of hydrogen (20–70 $kg\,cm^{-2}$), which is not consumed in the process. Because of the presence of hydrogen, these processes are referred to hydroisomerization.

In the case of Pt/Al_2O_3 catalysts, Al_2O_3 is chlorinated to improve acidic character by a chlorine-containing organic compound, which is continuously supplied during operation to compensate the loss of chlorine on the surface. The reaction temperature is 370–470 K. In the case of Pt-supported zeolite catalysts, the chlorination (and feed of chlorine-containing compounds) is not required because of higher acidity of zeolites, though higher reaction temperature has to be applied.

In the industrial processes, the reactants are butane, pentane, hexane and their mixtures (light naphtha). The reaction conditions depend on the reactant and the nature of the catalysts.

2.3. Sulfated zirconia and Pt-supported sulfated zirconia

In 1979, Hino and Arata found that ZrO_2 was very highly acidic when it was treated with concentrated sulfuric acid and then calcined at 850–920 K [1]. The catalyst, “sulfated zirconia” was active for the isomerization of alkanes including *n*-butane at room temperature. The material was assigned to a “superacid” because the solid surface changed the color of the indicator 1,3,5-trinitrobenzene [2]. Thus, the *H*o value was estimated as below -16.04. Sulfated zirconia is designated as S-ZrO_2, hereafter. The discovery of “superacid” gave an great impact on solid-acid chemistry, and many works followed to elucidate the optimum conditions for catalyst preparation and the acidic nature of this unique catalysts [3].

Later, it was found that the catalyst was more active and stable when Pt was supported on it and the reaction was carried out under hydrogen. The joint research of Cosmo Oil Ltd. and Mitsubishi Heavy Industries led to development of the process for the isomerization of light naphtha. The process was commercialized by UOP LLC. The catalyst has advantage of lower temperature operation compared with zeolite-based catalysts. This process is described by Kimura in this issue [4].

Hsu et al. [5] reported that the S-ZrO_2 containing Mn and Fe is about three orders of magnitude more active than S-ZrO_2 at 301 K. They claimed the higher acidity from the result of temperature programmed desorption (TPD) of benzene [6]. The high activity of Mn, Fe-containing S-ZrO_2 was confirmed by Jatia et al. [7]. They also found that the TPD peak from adsorbed benzene was not due to benzene, but to carbon dioxide. Later, Ni ion was also found to promote the activity of S-ZrO_2 [8].

Recent discussion on the mechanism of alkane isomerization over S-ZrO_2 will be described in a later section.

2.4. Tungsten oxide supported on zirconia

Hino and Arata [9] reported that a catalyst, which was prepared by impregnating $Zr(OH)_4$ or amorphous ZrO_2 with aqueous ammonium metatungstate followed by calcination in air at 1073–1123 K, was active for the isomerization of butane to isobutane at

323 K, and pentane to isopentane at 303 K, though the reaction rates were low at these temperatures. The catalyst was assigned as a superacid (Ho <-14.52) from the color change of indicator molecules.

Sentiesteban et al. [10] reported a preparation method which involved the simultaneous coprecipitation of tungsten with the formation of the hydrous zirconia. The catalyst thus prepared yielded a catalyst with about a twofold increase in strong acid site density as compared to catalysts prepared by tungsten impregnation of hydrous zirconia. The optimum loading of WO_3 was about 16 wt.%, which represents about two monolayers coverage.

The calcination temperature is also important. The catalyst exhibited little catalytic activity when calcined at 1023 K, while near equilibrium conversion was attained when calcined at 1103 K [11]. They estimated the number of strong acid sites by catalytic titration with 2,6-dimethylpyridine in pentane isomerization. The number is very low (4×10^{-6} mol g^{-1}), but the turnover frequency of these sites are about four orders of magnitude higher than the sites present in β-zeolite. The acidic properties of the materials as determined by heat of adsorption of ammonia did not correlate with the catalytic activity for pentane isomerization [11].

Loading of Pt on WO_3/ZrO_2 drastically enhances the rate and selectivity of alkane isomerization in the presence of hydrogen [12–15]. The yield of branched isomers was only 6.1% at the selectivity of 50.8% even at 573 K over WO_3/ZrO_2 in the isomerization of hexane [14]. Modification of the catalyst with Pt lead to an increase in the isohexane yield up to 78.9% and the selectivity reached 98.6% at 533 K. Here again, the calcination temperature is important. Pt–WO_3/ZrO_2 calcined at 998 K exhibits the low activity in pentane isomerization (21.8% isopentane yield). When calcined at 1073 K, the isopentane yield increased threefold. However, the addition of $SO_4{}^{2-}$ ions to WO_3/ZrO_2 calcined at 988 K improves the catalytic activity at lower reaction temperatures (553–573 K). The isopentane yield reached at 66.1% and the selectivity to 93.2%.

Iglesia et al. [15] reported that WO_3/ZrO_2 loaded with Pt showed a reasonable selectivity for the isomers in the reaction of heptane. When the reaction was carried out at 473 K under hydrogen pressure of 100 kPa, the isomerization selectivity at about 50% conversion was 85% over Pt–WO_3/ZrO_2, while it was only 35% over Pt/S-ZrO_2. The reaction orders were 0.9 and −0.5 with respect with heptane and hydrogen, respectively. From X-ray absorption and UV spectroscopy, they concluded that distorted octahedral WO_x domains were formed on the ZrO_2 surface and this inhibited sintering of ZrO_2 and its tetragonal to monoclinic transformation.

Though this catalytic system is advantageous compared to S-ZrO_2 because sulfate ions are not contained in the catalyst, the acidity–activity relationship has not been studied extensively.

2.5. Heteropoly acids and their metal salts

Heteropoly acids such as $H_3PW_{12}O_{40}$ (WPA) is known to be highly acidic and catalyze many kinds of reactions as a solid-acid [16–19]. Ono and coworkers [16,20,21] reported that Pd salts of WPA supported on silica were highly active for the isomerization of hexane under hydrogen. WPA supported on commercial Pd/carbon was more active. As shown in Fig. 1, this catalyst gave 96.4% selectivity for hexane isomers at the conversion of 77.9% at 523 K. The unique role of Pd and heteropoly anions was proposed [16,21]. The metal dissociates H_2 to form H atoms, which in turn react with heteropoly anion to form proton and reduced form of the anion.

$$H_2 \overset{Pd}{\rightleftharpoons} 2H \tag{1}$$

$$H + PW_{12}O_{40}{}^{3-} \rightleftharpoons H^+ + PW_{12}O_{40}{}^{4-} \tag{2}$$

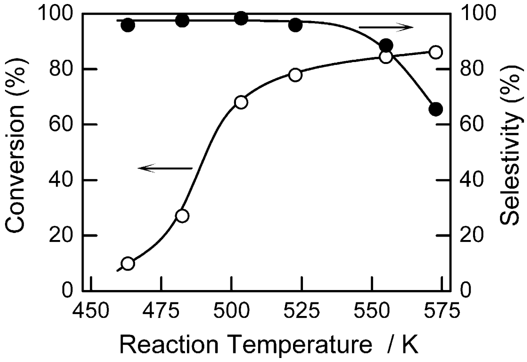


Fig. 1. Effect of reaction temperature on the isomerization of hexane over $H_3PW_{12}O_{40}$ supported on Pd/carbon [21]. Hexane 30 kPa, H_2 = 71 kPa.

The formation of protons is confirmed by the enhancement of the catalytic activity for methanol to hydrocarbons, an acid catalyzed reaction, with hydrogen over Pd-WPA on silica. The catalytic activity reversibly changed with hydrogen pressure, indicating that reactions (1) and (2) are reversible.

The group of Misono and Okuhara [17–19] found that $H_3PW_{12}O_{40}$ gave highly acidic materials with high surface area when the part of three protons were replaced with Cs. Thus, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ was active for alkane isomerization and the activity was more stable under hydrogen when the material was loaded with Pt [19,22,23].

2.6. Molybdenum/tungsten oxycarbide and partially reduced MoO_3

Iglesia and coworkers [24–26] found that tungsten carbides treated with oxygen at 800 K is active for isomerization of hexanes and heptanes. From the product distribution in the isomerization of heptane and 3,3-dimethylpentane, they proposed a bifunctional mechanism and refuted the mechanisms involving cyclopentane-ring or metallocyclobutane intermediates. The measurable steady-state concentrations of alkene intermediates were confirmed in the products. The experiments using 1-^{13}C-heptane were in conformity with the mechanism. The dehydrogenation–hydrogenation function is offered by the patches of carbide, while the acidic function is offered by patches of tungsten oxide.

Ledoux and coworkers [27–30] observed the large improvement in isomerization selectivity, when the surface of Mo_2C was oxidized. The molybdenum oxycarbide (MoO_xC_y) thus prepared was highly selective even for the isomerization of heptane and octane. They also showed that the active catalyst could be prepared by directly reacting MoO_3 with a flow of H_2/hydrocarbon. The surface area increases from 4 to 140 $m^2\,g^{-1}$ (80–90 $m^2\,g^{-1}$ after passivation) with this treatment. The carbide can be prepared also from Mo metal.

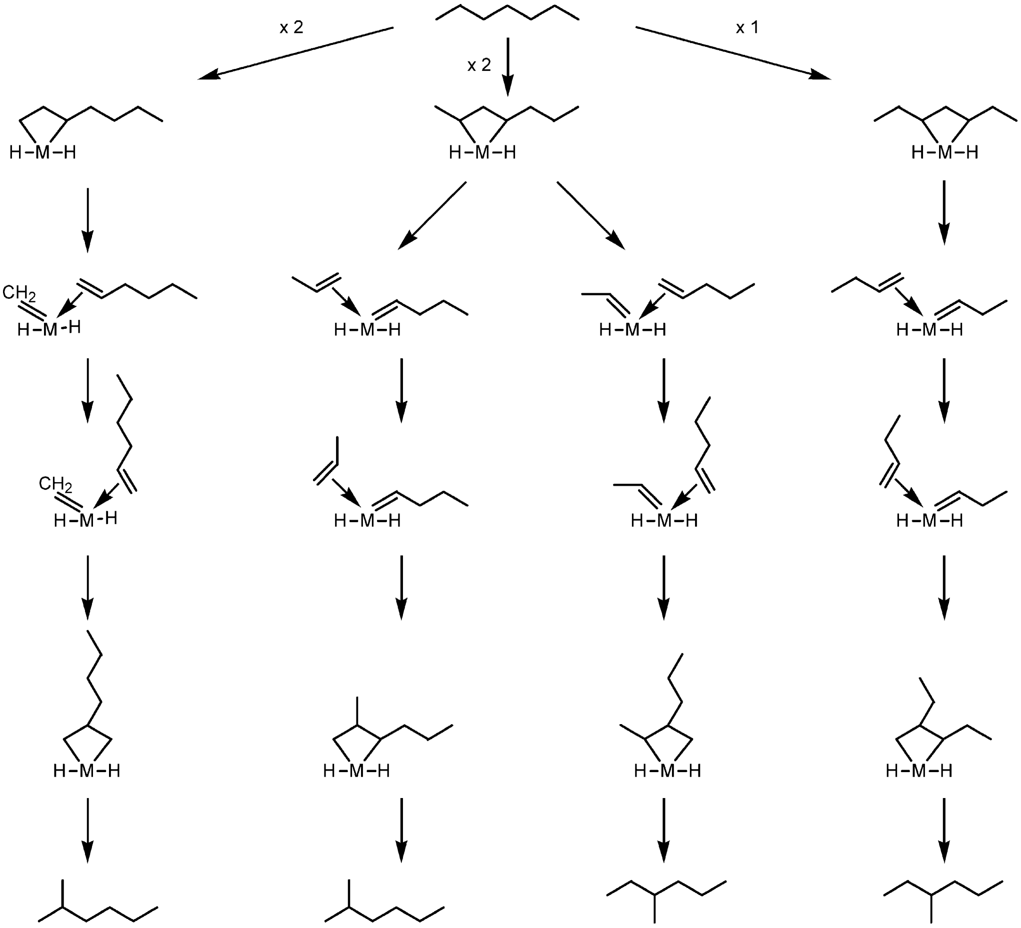
Table 1 compares the catalytic activity and selectivity for octane isomerization over MoO_xC_y and Pt-loaded β-zeolite [30]. The reaction temperatures were 563 and 523 K for the oxycarbide and the zeolite, respectively, showing that the latter is more active. Table 1 shows that both catalysts show a high selectivity for the isomers. The selectivity values at higher conversion level are different in the two catalysts. Over the carbide catalyst, the selectivity for isomers is very high (95%) even at high conversion (75%), while it decreases significantly with the conversion in the case of β-zeolite. The high selectivity was observed also for heptane [29]. The selectivity for the isomers were about 90% even at 78% conversion.

Table 1
Isomerization of octane over molybdenum oxycarbide and Pt/β-zeolite catalysts at 15 bar [30]

Catalyst	Mo oxycarbide	Pt/β-zeolite
Reaction temperature (K)	563	523
Conversion (%)	37	28
Rate (10^{-7} mol g^{-1} s^{-1})	28.3	117.5
C_8 selectivity (%)	97	93
Isomer products (%)		
TPM + DMH[a,b]	15.6	18.4
3-Ethylhexane	5.3	4.0
Methylheptanes	78.9	77.3
Cyclic compounds	0.1	0.2
Cracking products (%)		
$C_7 + C_1$	30.6	3.2
$C_6 + C_2$	4.9	0.0
$C_5 + C_3$	40.0	51.5
$2 \times C_4$	23.9	45.0

[a] TMP: trimethylpentanes.
[b] DMH: dimethylhexanes.

In contrast to Iglesia and coworkers, the authors proposed a mechanism which involved metallocyclic intermediate (Scheme 1). The mechanism is unique; it does not involve carbenium ion intermediates, which are easily cracked when the carbon number is 7 or more. This mechanism explains higher selectivity in isomerizations of heptane and octane. The supporting evidence for this mechanism is the fact that the cracking products contain a rather large amount of methane, but a small amount of C_3 and C_4 (Table 1). They found a new phase, $MoO_{2.42}C_{0.23}H_{0.78}$ by treating MoO_3 or molybdenum bronze with H_2 and heptane at 623 K and studied the structure of this new phase by XRD, selected area electron diffraction, and high resolution transmission electron microscopy [31]. They concluded that the catalytically active phase is a suboxide of molybdenum containing many vacancies and the role of carbon atoms should be to stabilize a metastable intermediate phase between MoO_2 and MoO_3 [31].



Scheme 1. Isomerization of heptane via metallocyclobutane intermediates [28].

Matsuda et al. [32–34] found that MoO_3 gave a high surface area and a high catalytic activity and selectivity for heptane isomerization when reduced with hydrogen at 623 K. The activity was very much dependent on the degree of reduction (on time and temperature of exposure to hydrogen). The catalyst is most active when the Mo oxidation number is between 2.5 and 3.5. The dependence of the activity for isomerization on the degree of reduction was similar to that of the activity for isopropyl alcohol dehydration catalyzed by acid sites. They concluded that the isomerization proceeded via dual functional mechanism, though they did not give any evidence for hydrogenation–dehydrogenation activities of the catalysts for alkenes or alkanes. Later, they also found that MoO_3 loaded with transition metals was more active than MoO_3 without metal-loading for heptane isomerization under hydrogen after it was reduced with hydrogen [35,36]. Among transition metals, Pt was most effective. The role of Pt is suggested to enhance the formation of H_xMoO_3 phase, which is the precursor of the active MoO_xH_y phase.

Though elucidation of the mechanism of the isomerization over the oxycarbides and reduced MoO_3 clearly needs further investigation, it is worthy of note that these groups of catalysts are very selective for heptane isomerization.

3. Mechanism of alkane isomerization

As described above, there are two types of catalysts for isomerization of alkanes; acid catalysts (homogeneous or heterogeneous) and solid acids loaded with a transition metal (mostly Pt), except a unique metallocycle mechanism proposed for molybdenum oxycarbonate. In both cases, carbenium ions are considered to be responsible for the skeletal rearrangements. Therefore, the most important steps in the isomerization are the formation of carbenium ions and its rearrangement on the catalyst surface.

3.1. Acid catalyst

3.1.1. Main reaction pathway

Isomerization of alkanes by acids proceeds through elementary steps

$$^{n}\mathrm{RH} + \mathrm{H}^+ \rightleftharpoons {}^{n}\mathrm{R}^+ + \mathrm{H}_2 \qquad (3)$$

$$^{n}\mathrm{R}^+ \rightleftharpoons {}^{iso}\mathrm{R}^+ \qquad (4)$$

$$^{iso}\mathrm{R}^+ + {}^{n}\mathrm{RH} \rightleftharpoons {}^{n}\mathrm{R}^+ + {}^{\mathrm{iso}}\mathrm{RH} \qquad (5)$$

The formation of carbenium ions is induced by the reaction of protons with alkanes (reaction (3)). The carbenium ions thus formed undergo skeletal rearrangement (reaction (4)). The newly formed carbenium ions turn into isomerized alkanes by a hydride-transfer reaction with reactant alkanes (reaction (5)). The chain reactions composed of reactions (4) and (5) make the isomerization catalytic. In isomerization of *n*-alkanes to branched alkanes, reaction (5) usually converts a tertiary carbenium ion into a secondary one. Therefore, this step is not easy in the energetic respect.

Under high pressure hydrogen, the reaction of carbenium ions with dihydrogen becomes more important than reaction (5)

$$^{iso}\mathrm{R}^+ + \mathrm{H}_2 \rightleftharpoons {}^{\mathrm{iso}}\mathrm{RH} + \mathrm{H}^+ \qquad (6)$$

The occurrence of elementary reaction (6) was confirmed in the homogeneous systems [37]. Minachev et al. [38] found that the rate of isomerization of pentane over mordenite under hydrogen is expressed as $r = kp_{\mathrm{C}_5}/p_{\mathrm{H}_2}$, and proposed a mechanism composed of the steps (3), (4), and (6). Hydrogen in this case is considered to be a chain transfer agent.

The formation of carbenium ions occurs very easily if the feed contains alkenes as impurities. Addition of a small amount of alkene to the reaction system often enhances the rate of isomerization.

3.1.2. Side reactions

The side reactions in alkane isomerization lower the selectivities for desired products and lower the catalyst life. They always involve carbenium ions or alkenes as reactive intermediates. Alkenes are formed by deprotonation of carbenium ions

$$\mathrm{C}_n\mathrm{H}_{2n+1}{}^+ \rightleftharpoons \mathrm{C}_n\mathrm{H}_{2n} + \mathrm{H}^+ \qquad (7)$$

Alkenes react easily with carbenium ions to form those with longer carbon chains

$$\mathrm{C_4}^+ \xrightarrow{+\mathrm{C}_4^=} \mathrm{C_8}^+ \xrightarrow{+\mathrm{C}_4^=} \mathrm{C_{12}}^+ \qquad (8)$$

The higher hydrocarbons on the surface do not desorb easily at the reaction temperature and accumulate as coke or coke precursors.

When the number of carbon atoms is 7 or more, the carbenium ions undergoes β-scission to form alkenes and carbenium ions, whose carbon numbers are different from the starting alkane [39–42]

$$\mathrm{C_8}^+ \rightarrow \mathrm{C}_3^= + \mathrm{C_5}^+ \qquad (9)$$

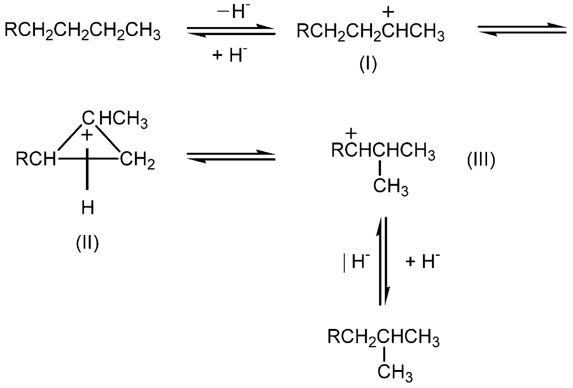
$$\mathrm{C_8}^+ \rightarrow \mathrm{C}_5^= + \mathrm{C_3}^+ \qquad (10)$$

The repetition of oligomerization (reaction (8)) and cracking (reactions (9) and (10)) lowers the selectivity of alkane isomerization significantly. This explains why the isomerization of heptane or octane is difficult. Therefore, to obtain high selectivity, it is essential to keep the concentration of alkenes very low.

3.1.3. Rearrangement of carbenium ions-monomolecular mechanism

In the isomerization of alkanes, elementary reaction (5) proceeds via protonated cyclopropane intermediate. Detailed discussion on this mechanism is given by several authors [39–42]. In the case of pentane, isomerization proceeds in Scheme 2 ($\mathrm{R} = \mathrm{CH}_3$).

In the case of butane ($\mathrm{R} = \mathrm{H}$), the isomerization via a protonated cyclopropane intermediate is not easy because the reaction involves the conversion of a secondary into a primary carbenium ion (III). This is energetically not feasible. In the case of pentane or hexane isomerization, the intermediates are secondary carbenium ions. In fact, there is a pronounce difference in the rate of isomerization between butane and pentane. However, the rate of isomerization of 1-^{13}C-butane to 2-^{13}C-butane is as high as



Scheme 2. Rearrangement of carbenium ions via a protonated cyclopropane intermediate [37].

that of pentane skeletal isomerization [37]. This is also explained by Scheme 2, since the intramolecular scrambling of the ^{13}C position in butane molecule does not need to go through a primary carbenium ion (III).

3.1.4. Bimolecular mechanism

It is often observed that 1,4-^{13}C-butane over a solid acid catalyst undergoes intermolecular scrambling of ^{13}C. Isobutane with the number of ^{13}C atoms other than 2 are formed. This cannot be explained by a monomolecular mechanism described above and indicates the existence of bimolecular mechanism (oligomerization-cracking) for butane isomerization. The intermolecular ^{13}C scrambling occurs through the skeletal rearrangement of $C_8{}^+$ carbenium ions, whose decomposition give isobutane with the number of ^{13}C atoms other than 2

$$ {}^{n}C_4{}^{+} + {}^{n}C_4{}^{=} \rightleftharpoons C_8{}^{+} \tag{11}$$

$$ C_8{}^{+} \rightleftharpoons C_8'^{+} \tag{12}$$

$$ C_8'^{+} \rightleftharpoons {}^{iso}C_4{}^{=} + {}^{iso}C_4{}^{+} \quad (\text{or } {}^{n}C_4{}^{+}) \tag{13}$$

The detailed mechanism of ^{13}C scrambling in $C_8{}^+$ intermediates is discussed by Adeeva et al. [43,44]. The characteristics of butane isomerization via bimolecular mechanism is that the reaction products always contain C_3 and C_5 hydrocarbons as a result of reactions (9) and (10). The catalysts, on which extensive ^{13}C scrambling during butane isomerization were observed, include mordenite [45], S-ZrO$_2$ [46,47], Fe, Mn-containing S-ZrO$_2$ [48], $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ [47]. Almost binominal distribution of number of ^{13}C atoms in product isobutane in the case of sulfated zirconia [46,48].

On the other hand, ^{13}C scrambling was not significant in the butane isomerization in the presence of hydrogen over Pt-loaded sulfated ZrO$_2$, Pt-loaded $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ [47]. This indicates that the reactions of carbenium ions and alkene molecules hardly occur due to low alkene concentration under hydrogenation conditions.

Adeeva and Sachtler [43] studied the ^{13}C-scrambling over industrial catalysts, chlorinated alumina loaded with Pt. They found extensive scrambling of the isotope and concluded that bimolecular mechanism was prevailing though monomolecular mechanism was also involved. Their experiments were done under 40 mm Hg of hydrogen pressure, which is far below that in industrial operation (20–30 kg cm^{-2}). The contribution of monomolecular mechanism would be much more important under the industrial conditions of butane isomerization.

The bimolecular mechanism is less important in the isomerization of higher alkanes. First of all, the isomerization via monomolecular mechanism is much faster compared with that in butane isomerization. Secondly, oligomeriztion-cracking usually give by-products with varied numbers of carbon atoms rather than the isomerization products. Blomsman et al. [49] reported that the bimolecular mechanism is involved in addition to monomolecular mechanism in the isomerization of heptane over Pt-loaded β-zeolite.

4. Bifunctional mechanism

As mentioned above, solid acids loaded with transition metal (Pt) are used in the industrial isomerization processes. The catalysts are often called bifunctional. One function is a function as an acid catalyst, the other being a function as a hydrogenation–dehydrogenation catalyst.

The original idea of "bifunctional catalysis" stems from the use of alumina loaded with a transition metal used for reforming processes. The idea was transferred to isomerizaton. Thus, it is supposed that alkane is dehydrogenated on metallic sites to the corresponding alkene, which is isomerized by acid sites into a branched alkene. The branched alkene is then hydrogenated into the branched alkane again on the metallic sites

$$ {}^{n}C_5H_{12} \rightleftharpoons {}^{n}C_5H_{10} + H_2 \quad \text{(on Pt)} \qquad (14)$$

$$ {}^{n}C_5H_{10} + H^+ \rightleftharpoons {}^{n}C_5H_{11}{}^+ \quad \text{(on solid acid)} \qquad (15)$$

$$ {}^{n}C_5H_{11}{}^+ \rightarrow {}^{iso}C_5H_{11}{}^+ \quad \text{(on solid acid)} \qquad (16)$$

$$ {}^{iso}C_5H_{11}{}^+ \rightleftharpoons {}^{iso}C_5H_{10} + H^+ \quad \text{(on solid acid)} \qquad (17)$$

$$ {}^{iso}C_5H_{10} + H_2 \rightleftharpoons {}^{iso}C_5H_{12} \quad \text{(on Pt)} \qquad (18)$$

According to this mechanism, acidic sites do not participate in the difficult step of alkane activation, which requires high acid strength. When a loaded amount of a transition metal exceeds a certain level, the hydrogenation–dehydrogenation steps, reactions (14) and (18) reach the equilibrium under hydrogen. The rate-determining step of the isomerization is the rearrangement of carbenium ions, reaction (16). Therefore, it is of utmost importance to know how the rate of this step depends on the acidic properties of the catalyst.

The positive evidence for the bifunctional mechanism were as follows:

(a) A high catalytic activity is obtained only when both a metallic component and hydrogen are present.

This was observed in the case of hexane isomerization over Pt/Al_2O_3. Without Pt, Al_2O_3 had no activity even in the presence of hydrogen. Pt/Al_2O_3 was not active if H_2 was replaced by N_2 [50].

(b) The negative reaction order with respect to hydrogen.

Since hydrogen shift the equilibrium of reaction (14) to the left-hand side, the concentration of the carbenium ion decreases with H_2 pressure. This results in the rate retardation of the rate-determining step (16). The rate of pentane isomerization r over Pt/Al_2O_3 was expressed as $r = k(p_{nC_5}/p_{H_2})^{1/2}$ [51].

Though the original idea of the bifunctional catalysis is generally accepted, the mechanism of the isomerization over “bifunctional catalysts” are often not that simple, especially the roles of the metal and hydrogen.

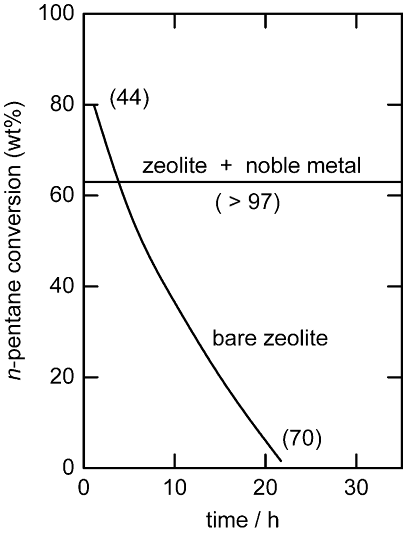


Fig. 2. Isomerization of pentane over mordenite and Pt/mordenite [52]. Numbers in parentheses show the selectivity for branched isomers. 523 K, 30 kg cm^{-2}, H_2/n-C_5 = 2.5.

Fig. 2 shows the effect of Pt loading on the time course in pentane isomerization over mordenite, which is used in Hysomer process [52]. The reaction was performed under pressure of 30 kg cm^{-2} (abs.) with $H_2/{}^{n}C_5 = 2.5$. Without Pt, the activity decays quickly under hydrogen pressure of 30 kg cm^{-2} (abs.) with $H_2/{}^{n}C_5 = 2.5$. Without Pt, the activity decays quickly and is lost in 20 h. The selectivity for isopentane was 44% at the beginning and increased to 70% after 20 h. With Pt, on the other hand, the activity was stable and no decay was observed within 30 h. The selectivity for isopentane was always very high (>97%). The positive effect of Pt (and H_2) is obvious. The important characteristic of this catalytic system is that the zeolite is active even without Pt, even though the activity decays with time on stream. Mordenite has an intrinsic activity for isomerization and the initial rate is rather lowered by the presence of Pt and hydrogen. It follows that pentane is activated by acid sites as given by reaction (2) even in the presence of Pt. Thus, the most important role of the metal component is to stabilize the catalytic activity and to offer higher selectivity for isomerization.

As described above, carbenium ions are easily deprotonated to form alkenes, which polymerize to give coke precursors. The decomposition of oligomers is a main source of by-products. It is clear that Pt–H_2 reduces the concentration of alkenes in the system by hydrogenation. Apart from the real mechanism of alkane activation, the following equilibrium is reached when enough amount of a metallic component and H_2 exist in the system

$$C_nH_{2n+1}{}^{+} \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} C_nH_{2n} \underset{-H_2}{\overset{+H_2}{\rightleftharpoons}} C_nH_{2n+2} \tag{19}$$

The significant effect of Pt on the selectivity and stability was reported also in hexane isomerization over S-ZrO_2 and S-ZrO_2 loaded with 0.5 wt.% Pt [53]. The reactions were carried out under 6 kg cm^{-2} of H_2 at 473 K. S-ZrO_2 has a high activity though the catalytic activity rate drops very quickly and is completely lost in 100 min, while the reaction produces a lot of cracking products. Over Pt/S-ZrO_2, the activity is much more stable and the selectivity for isomers are very high during the run.

Hexane isomerization over alumina proceed only when Pt is supported, as described above [50]. It is, however, worthy of note that most of the very active isomerization catalysts (chlorinated Al_2O_3, zeolites, heteropoly compounds, S-ZrO_2, oxicarbides, reduced MoO_3) have intrinsic activities for isomerization. It seems that the role of a metallic component is to reduce the concentration of alkenes in the system rather than to generate alkenes by dehydrogenation of the starting alkanes. Many recent papers of the isomerization catalysts simply describe that their catalyst is bifunctional. Of course, this is not totally in error, since the metallic component has a definitive role of dehydrogenation and hydrogenation, the mode of activation of alkanes has to be more keenly discussed for the respective systems.

Hydrogen can be converted into acid sites. As described earlier, Ono and coworkers [16,21] proposed that hydrogen dissociates on Pd to form protons, which are very active for the isomerization. The reversible effect of hydrogen on proton generation was confirmed by the activity for acid-catalyzed reaction, conversion of methanol into hydrocarbons.

Similar effect of spilt-over hydrogen was reported by Hattori and coworkers [54–56] for the isomerization over Pt/S-ZrO_2. Spilt-over hydrogen reacts with surface Lewis acids to convert them into protonic acid sites, which are active for isomerization. They confirmed that the number of protonic acid sites as well as the rate of isomerization reversibly changed with the change in the partial pressure of hydrogen. It is of interest how the nature of protons formed by spilt-over hydrogen is different from those originally present on Pt/S-ZrO_2 surface.

Reversible formation of very reactive protons under hydrogen was observed in the catalytic systems such as Ag^+-heteropolyacid [57–59], and Ag^+-ion exchanged zeolites [60].

Iglesia et al. [61] found that addition of adamantane enhanced the rate and selectivity of heptane isomerization over Pt-loaded sulfated ZrO_2 and concluded that adamantane acts as a hydride transfer agent. The effects of hydrogen on the rate and selectivity were similar to those of adamantane. In addition, the rate was the first order with respect to hydrogen pressure. From these fact, they concluded that dissociated hydrogen also acts as a hydride transfer agent to facilitate the reaction, $R^+ + R'H \rightarrow RH + R'^+$. Since efficient hydride transfer shortens the life of carbenium ions on the surface, the chance of β-scission of the carbenium ions are reduced and this results in higher selectivity for the isomers.

5. Activation of alkanes on S-ZrO_2

As described above, Hino and Arata [2,3] claimed that S-ZrO_2 is an superacid from the color change of Hammett indicators. Lin and Hsu [6] claimed the superacidity by TPD of benzene for Fe, Mn-containing S-ZrO_2. Another “strong evidence” was that S-ZrO_2 could activate even butane molecules. Though many papers designate this material as superacid in their titles, these three pieces of “evidence” are recently questioned. Do we really need superacid to activate butane molecules?

The application of Hammett indicators to solid acids is questioned, since the interaction of chemisorbed indicators involve the various kinds of interactions with surfaces [62,63]. The acid strength determined by indicators and the catalytic activities could not be correlated [63].

Kustov et al. [64] studied the infrared spectrum of benzene adsorbed on ZrO_2 and S-ZrO_2. The band shift of the surface OH stretching band due to hydrogen bonding upon benzene adsorption is larger in the case of S-ZrO_2 than non-modified ZrO_2, indicating the former has stronger Bronsted acid sites. The extent of the shift, however, is smaller than that of benzene adsorption on HY zeolite and much smaller than on mordenite. Therefore, S-ZrO_2 is weaker than HY as acid and thus concluded that it cannot be a superacid. Adeeva et al. [62] reached a similar conclusion that the strength of Bronsted acid sites is similar to that of HY, but weaker than that of the protons in H-ZSM-5 from the shifts of OH stretching band and a ^1H MAS NMR peak upon adsorption of accetonitrile.

Hsu et al. [5] reported that the S-ZrO_2 containing Mn and Fe is about three orders of magnitude more active than S-ZrO_2 at 301 K. They claimed the higher acidity from the result of TPD of benzene. The method is questioned by later works. The high activity of Mn, Fe-containing S-ZrO_2 was confirmed by Jatia et al. [7] who found, however, the TPD peak from adsorbed benzene was not due to benzene but to carbon dioxide. Thus, the TPD of benzene cannot be taken as evidence for strong acidity of Mn, Fe-containing sulfated ZrO_2. The same conclusion was also reached by other groups [65,66].

Coelho et al. [67] also concluded that from the infrared spectrum of adsorbed ammonia adsorbed on Fe, Mn-promoted S-ZrO_2, Ni-promoted S-ZrO_2, and non-promoted sulfated ZrO_2, the density of Bronsted acid and Lewis acid did not correlate with the catalytic activity for butane isomerization. The shift of OH stretching band and ^1H MAS NMR peak upon adsorption of acetonitrile did not differ appreciably between S-ZrO_2 and Fe, Mn-modified S-ZrO_2 [62]. These findings also suggest that there are no essential differences in acid strength between the two catalysts.

The findings described above indicates that S-ZrO_2 and Fe, Mn-modified ZrO_2 are not superacid. It follows that their acid sites may not activate butane molecules, and that the surface properties other than acidity are involved in alkane activation.

Fărcaşju et al. [63] proposed the one-electron oxidation of alkane molecules by the surface sulfate ions to form the cation radicals, which are converted into surface esters of sulfite or sulfate on the surface.

The activity of S-ZrO_2 for butane isomerization is high only when the catalyst was pretreated under oxygen. The catalyst pretreated under helium was much less active. From these facts, Wan et al. [66] concluded that the surface oxy species are involved in the activation of butane. Furthermore, the higher activity of Fe, Mn-promoted S-ZrO_2 was suggested to be due to the presence of Fe(III) ions. Both oxy species and Fe(III) ions act as dehydrogenation center of butane to butenes, which is isomerized to isobutane through oligomerization-cracking mechanism [66]. Adeeva et al. [62] also suggested that the high activity can be due to high dehydrogenation activities of metal (Fe, Mn) oxides to increase butene concentration on the surface. The isomerization over Fe, Mn-containing S-ZrO_2 proceeds through bimolecular mechanism, which requires alkene intermediates as already mentioned [43]. Oxidation of adsorbed benzene to carbon dioxide also support that Fe, Mn-modified S-ZrO_2 has oxidation capability.

Participation of butenes was studied by Tabota and Davis [68]. When the butene impurity was eliminated from the feed butane by adsorption, the activity of S-ZrO_2 dropped sharply. On the other hand, high activity was maintained in the case of S-ZrO_2 loaded with Pt, even when butene impurity was eliminated. This implies that, the equilibrium is reached between *n*-butenes and butane in this case.

Discussion above indicates that the isomerization of butane starts with the dehydrogenation to butenes on oxidative sites on S-ZrO_2 or Fe, Mn-ZrO_2 or on Pt. In the presence of Pt and hydrogen, the ^{13}C experiments clearly shows that the isomerizatrion goes through monomolecular mechanism. In this case, the rearrangement of carbenium ions must occur on the surface and the rate-determining step. It follows that, even if alkene formation occurs on the redox sites or on metals, S-ZrO_2 still behaves like a very strong acid under isomerization conditions. The carbenium ions might be stabilized as surface esters, which are reactive enough to undergo the skeletal rearrangement. The acid strength of as-synthesized catalysts might not represent the surface properties of S-ZrO_2 under the reaction conditions.

6. Quantum chemical modeling of alkane rearrangement

Most of our knowledge on the mechanism of alkane isomerization is based on the theory developed for accounting the findings in the isomerization in liquid phase. The applicability of the idea deduced from the events in homogeneous phase to those on

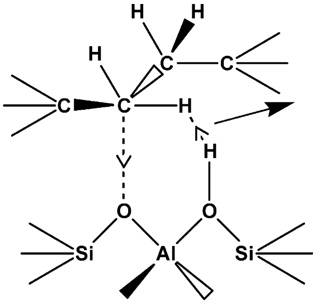


Fig. 3. The transition state of butane adsorption on zeolite [69].

solid surfaces has been a recent subject of quantum chemical calculations. The calculation has been made mainly on the transformations on zeolite surface.

6.1. *Adsorption of alkanes*

The adsorption from *n*-alkanes on acid sites on zeolite has been studied by quantum mechanical modeling [69,70]

$$R\text{–}H + Z\text{–}OH \rightarrow Z\text{–}OR + H_2 \tag{20}$$

Here, Z–OH and Z–OR stand for the acidic OH group and alkoxy group on zeolite surface, respectively.

The transition state of adsorption of butane is shown in Fig. 3 [69]. A C–H bond of butane molecule is stretched and the corresponding hydrogen atom to react with zeolite hydroxyl group to form H_2, while the positive charge on the carbon is compensated by the short distance to the negatively charged lattice oxygen. The transition state is similar to the carbonium ion, $C_4H_{11}^+$. Here, $C_4H_{11}^+$ like species is not an intermediate, but the transition state of the reaction. It is also noted that the oxygen site on zeolite is involved in addition to the hydroxyl group in the adsorption step. The stable form is not a carbenium ion, $C_4H_9^+$, but the alkoxy group covalently bonded on the zeolite surface. The chemistry is different from that we find in solution chemistry. The order of the values of activation energies for adsorption of small alkanes has been calculated to be $CH_4 > C_2H_6 > C_3H_8 > {}^{iso}C_4H_{10}$ [70]. The order is in agreement with the order of the stability of the corresponding carbenium ions.

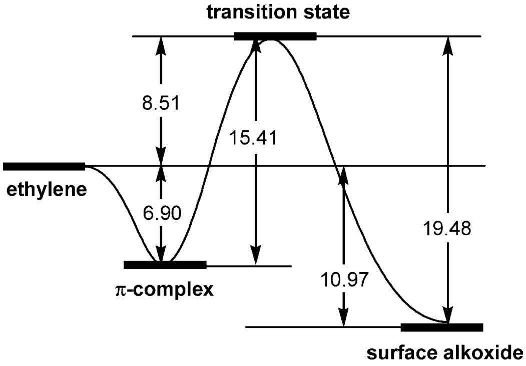


Fig. 5. The energy diagram of ethylene adsorption on zeolite [71]. The numbers in the figure represents the energy differences in kcal mol^{-1}.

6.2. *Adsorption of alkenes*

Kazansky [71] calculated the adsorption of ethylene on acidic zeolite. Figs. 4 and 5 show the conformation of adsorbed ethylene and the energy diagram, respectively. At first, ethylene is adsorbed as a π-complex (Fig. 4(a)). The π-complex is transformed into surface

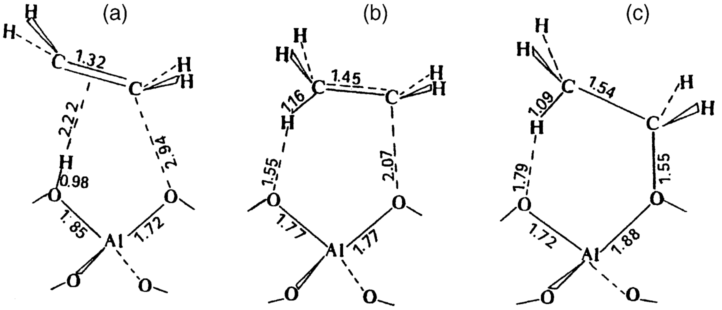


Fig. 4. The adsorbed state of ethylene on zeolite [71].

ethoxide (Fig. 4(c)) via the transition state (Fig. 4(b)). The geometry and the electronic state of the C_2H_5 fragment at the transition state are very similar to those of classical form of the ethyl cation; The charge is +0.565e and C–C bond length is between those of a double and a single bond. The surface ethoxide is a stable form and the transition state is about 80 kJ mol^{-1} above the alkoxide form. This shows that the free carbenium ions, $C_2H_5{}^+$ is not an intermediate, though it resembles the transition state of adsorption.

Adsorption of various alkenes have been calculated [72,73]. The main conclusion is same as in the case of ethylene adsorption. Alkoxy groups covalently bonded to the zeolite framework are stable intermediate, whereas transition states resemble carbenium ions. The energy of the transition state is consistent with the carbenium ion like character of the transition state [72,73]. The transition state from isobutane is much more stable than that from but-1-ene or (*E*)-but-2-ene. At the transition state, the tertiary carbon from isobutene bears a charge of 0.565 [73]. The stability of the alkoxides, however, does not display similar stability ordering of the corresponding carbenium ions. *t*-Butoxide is less stable than *n*-butoxide because of the steric repulsion [73].

6.3. Hydrocarbon conversions

These calculations show the stable form of the adsorbed state of alkenes are alkoxides on zeolite surface. This means that the various elementary reactions involving carbenium ions have to be reconsidered as the reactions of stable alkoxides. Thus, calculations have been performed for various reactions involving surface alkoxide, such as hydride transfer, hydride shift and cracking [70,74]. These theoretical calculations offer us some important differences of the chemistry on the surface and the carbenium ion chemistry in solution. Followings are some examples.

1. The activation energies of elementary reactions depend on the acid strength (deprotonation energy) of zeolite. The activation energies of the elementary reactions related to isomerization decreases with increasing acidity.
2. The rates also depends on the proton affinity of the oxygen anion next to acidic OH group, since the oxygen anion is always involved in the ring-like transition states of the reactions.
3. Bulkiness of the *t*-butyl group causes steric hindrances in the transition state. Therefore, In the reactions involving tri-substituted carbenium ion-like species as transition state, the activation energy is only slightly lower than or close to those involving *s*-propyl group.

Further development in theoretical modeling of surfaces and the reaction pathway is expected to answer more questions in more details of alkane activation and skeletal rearrangement of the intermediate species.

7. Summary

The isomerization of alkanes has been industrially performed for years. The catalysts used in commercial processes have some disadvantages such as need for chlorinated compounds, high working temperature and high hydrogen pressure. The novel catalysts, which overcome these disadvantages of the present industrial catalysts are highly desired. The catalysts, which have a high selectivity in the isomerization of heptane and higher alkanes are also sought. As for the mechanism of the isomerization, the activation of alkane molecules has been the subject of main concern. The acidity of the surface has been discussed in the respect of alkane activation. However, in many cases, the rate-determining step is the skeletal rearrangement of carbenium ions. The nature of carbenium ions on the surface determine the rate and the selectivity of the isomerization. For example, why one catalyst gives a reasonable selectivity for isomers by the skeletal rearrangement, while the other gives mainly cracking by β-scission. The dependence of the behaviors of "carbenium ions" on the acidic properties of the catalyst has to be more focused. In this respect, further development of theoretical quantum chemical modeling and calculation is highly desired.

The recent development on alkane reactions has to be watched. Ga, Zn, Ag-containing ZSM-5 have high catalytic activities for aromatization of lower alkanes and these cations offer high dehydrogenation activity of lower alkanes [75,76]. Baba et al. [77,78] reported that methane reacts with ethylene and benzene over Ag^+-exchanged zeolites. As described earlier, metal oxycarbides and partially reduced molybdenum oxides show high selectivities in the isomerization of heptane.

Closer examination of these systems might offer some important insight for alkane activation in general.

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