

# Reaction of linear, branched, and cyclic alkanes catalyzed by Brønsted and Lewis acids on H-mordenite, H-beta, and sulfated zirconia

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## Abstract

The isomerization and cracking of pentane, cyclohexane, and C5–C6 branched alkanes (isopentane, 2-methylpentane, 2,2-dimethylbutane, and 2,3-dimethylbutane) were performed on H-mordenite and H-beta at 473 K, and sulfated zirconia at 273 K and 323 K. Pentane and 2-methylpentane were converted into the corresponding isomers on Brønsted acids of mordenite and beta-zeolite in the initial stage of the reaction. The major final product was isobutane, formed by bimolecular reaction in the later stage of the reaction. In contrast, pentane and 2-methylpentane were converted into their isomers by monomolecular reaction on sulfated zirconia with high selectivity. No reaction was observed in isopentane isomerization on sulfated zirconia because the product has the same structure. These highly selective isomerizations are considered to be catalyzed by Lewis acid sites on sulfated zirconia, because it has superacidic Lewis acid sites. Multi-branched alkanes showed higher reactivity than linear, mono-branched and cyclic alkanes. Isobutane formation as the main product and remarkable deactivation were found in the isomerization of 2,2-dimethylbutane and 2,3-dimethylbutane on sulfated zirconia. The Brønsted acid sites on sulfated zirconia were not strong enough to promote the skeletal isomerizations of linear and mono-branched alkanes. However, these acid sites were active enough to form intermediates by bimolecular reaction of multi-branched alkanes, and were the source of catalyst poisoning species formed by dehydrogenation. Cyclohexane was converted into methylcyclopentane on both Brønsted and Lewis acid sites with high selectivity.

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**Keywords:** Sulfated zirconia; Mordenite; Beta zeolite; Skeletal isomerization; Pentane isopentane; 2-Methylpentane; 2,2-Dimethylbutane; 2,3-Dimethylbutane; Cyclohexane; Monomolecular reaction; Bimolecular reaction; Intermediate

## 1. Introduction

Sulfated zirconia (SZ) and related catalysts [1,2] are environmentally benign alternative substitutes for liquid acids, thus satisfying the demand for green chemistry technologies. SZ is active for the skeletal isomerization of alkanes at low temperature [3,4], alkylation of light alkanes with alkenes [5], and the Friedel–Crafts alkylation and acylation [6–9], as well as the reaction of propane and ethane [10,11]. The skeletal isomerization of alkanes and cycloalkanes is highly desired for producing reformulated fuels (branched alkanes from linear alkanes and methyl-substituted cycloalkanes from cycloalkanes) owing to their high octane numbers (both

RON and MON) and their clean combustion. The isomerization of alkanes over superacidic catalysts at low temperature is a characteristic action, and thus investigation of the reaction mechanism of isomerization of linear and branched alkanes is essential for clarification of their character.

The alkane isomerization proceeds as follows [2,12]; the formation of an intermediate carbenium ion species, migration of an alkyl group, and transfer of hydride to the carbenium ion. The formation of carbenium ion from alkanes catalyzed by superacids has been explained by several plausible mechanisms, including protonation of the C–H or C–C bond by Brønsted acid followed by elimination of H<sub>2</sub>, abstraction of hydride ion by Lewis acid, and oxidative dehydrogenation of the alkanes followed by protonation of produced alkenes. In the migration of the alkyl group catalyzed by a superacidic site, it is known that the reaction proceeds through a proto-

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nated cyclopropane [2,12] or cyclobutane intermediates [13] following the formation of a carbenium ion. After the migration, the carbenium ion accepts the hydride on the Lewis acid site, or from another molecule [14,15], and then it is desorbed from the catalytic surface.

In the rearrangement step, two possible mechanisms have been proposed; either monomolecular or bimolecular reaction. In the monomolecular mechanism, a linear alkane is converted into the corresponding branched alkane with the same carbon number as a substrate. The monomolecular process is easy for the isomerization of alkanes with the carbon number greater than 4. Butane is converted into isobutane via the branched primary carbocation, which is thermodynamically unstable, following the formation of a protonated cyclopropane intermediate. On the other hand, pentane can be isomerized to isopentane through the relatively stable secondary carbocation.

In the bimolecular mechanism, the reaction proceeds through the formation of a bimolecular intermediate by the reaction of a carbenium ion with an alkene produced during reaction with the successive migration of alkyl groups, followed by its beta-scission to form a branched carbenium ion and an alkene. In such a case, the main product is isobutane together with disproportionated products, whose carbon number is different from that of a substrate. The bimolecular mechanism includes a surface alkene intermediate for the formation of dimer cation. The reaction is characterized by the observation of an induction period for the formation of surface alkenes [14], and the formation of isobutane and disproportionated products after the period. Recently, we reported that cyclodecane was converted into *cis*- and *trans*-decaline by dehydrogenation catalyzed by the solid superacid of SZ [13]. This result indicates that the hydride, on the Lewis acid site and/or Brønsted acid site that loses its proton (conjugated base), works as a base and will show the activity for the dehydrogenation when the structure of carbenium ion is suitable for the abstraction of a proton. It is expected that the difference in base property between Brønsted base sites and Lewis acid sites with hydride ions reflects the reaction mechanism, monomolecular and bimolecular reactions. It is presumed that the bimolecular reaction takes place on the Brønsted acid when the proton abstraction ability of conjugated Brønsted base is high. On the other hand, the dehydrogenation will be predominant on the Lewis acid when the hydride ion on Lewis acid site has a high proton affinity. The purpose of this paper is to show the difference in catalytic action between Brønsted and Lewis acid sites for skeletal isomerization of alkanes. To achieve this purpose, several kinds of branched alkanes greater than C<sub>4</sub> were used as the substrates. Branched alkanes were expected to show higher reactivity for the isomerization and dehydrogenation than linear alkanes, because a tertiary carbon has a hydride donating ability and tertiary carbenium ion is stabilized by an electron donating property of methyl (alkyl) groups.

Proton-type mordenite (H-MOR) was used as the representative Brønsted acid. Proton-type beta zeolite (H-BEA)

has Lewis acid sites as well as Brønsted acid sites [16–18]. The acid strength of H-BEA is marginally lower than that of H-MOR [19,20], but it is strong enough to promote skeletal isomerization of alkanes. Additionally, H-BEA has an advantage in the isomerization of larger molecules owing to its larger pore size. The active acid sites on SZ for alkane isomerization were estimated to be the Lewis type. The catalytic activity of SZ in the isomerization of butane is reversibly suppressed by the addition of CO because of poisoning the acid sites [21]. The adsorption interaction of CO is stronger on the Lewis acid sites than on the Brønsted acid sites.

## 2. Experimental

### 2.1. Catalyst preparation

Zirconia gel was obtained by hydrolyzing ZrOCl<sub>2</sub> with aqueous ammonia to pH 8 at 343 K [22]. Aqueous ammonia solution (25%) was added dropwise with stirring into 100 g of ZrOCl<sub>2</sub>·8H<sub>2</sub>O dissolved in 3 L of distilled hot water; then the suspension was kept in a water bath warmed at 343 K for 2 h. Finally the precipitate was washed twice with 1 L of hot water, dried at 373 K for more than 24 h after filtration, and powdered to 32–50 mesh. Two kinds of hydrated zirconia, named JRC-ZRO-2 and -5, which were the reference catalysts supplied by the Reference Catalyst Committee of the Catalysis Society of Japan, were also examined. The gel was treated with sulfate ion by exposing 2 g of the dried and powdered matter in 30 mL of 1N H<sub>2</sub>SO<sub>4</sub> on a glass filter for 1 h. The treated gel was filtrated, dried in a desiccator at room temperature, and finally calcined in air at 873 K for 3 h in a glass ampoule. The ampoule was sealed while hot and the sample was kept in the ampoule until use. The catalysts of sulfated zirconia obtained using prepared gel, JRC-ZRO-2, and JRC-ZRO-5 are named SZ, S/ZRO-2, and S/ZRO-5, respectively. Additionally, alumina-promoted sulfated zirconia (SZA) supplied by Japan Energy Co. was also examined. H-MOR and H-BEA were the reference catalysts supplied by the Catalysis Society of Japan, JRC-Z-HM20 and JRC-Z-HB25, respectively.

### 2.2. Reaction procedure

The skeletal isomerization of alkanes was performed in a closed recirculation system made of glass. The catalyst (0.5 g, 32–50 mesh) was set in the reactor and pretreated in a vacuum at 473 K (sulfated zirconias) or 773 K (H-MOR and H-BEA) for 3 h. Furthermore, SZ catalyst pretreated at 673 K was examined for the isomerization of 2,3-dimethylbutane and cyclohexane to examine the catalytic action of Brønsted acid sites. The high-temperature treatment in a vacuum provides the sample with a reduced number of Brønsted acid sites. After the catalyst activation, 6.7 kPa of substrate was introduced into the reactor. All substrates were degassed and purified by passing through molecular sieve 4A before the

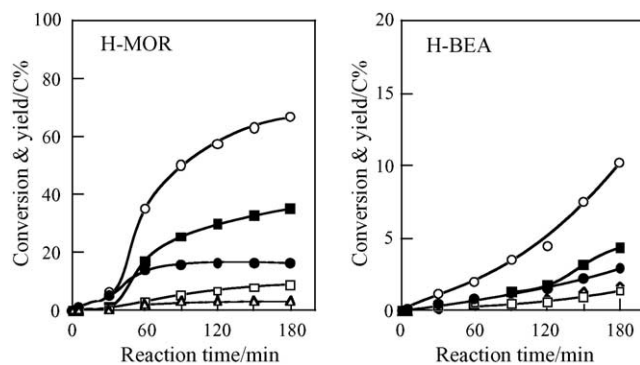


Fig. 1. Isomerization and disproportionation of pentane on H-MOR and H-BEA at 473 K: (○) conversion, (□) butane, (■) isobutane, (●) isopentane, (△) hexanes.

reaction. Products were analyzed by GLC connected to the reaction system using a 60 m capillary column of TC-1 (GL Science) operated at 343 or 343–403 K at the programmed rate of 10 K min<sup>-1</sup>.

### 3. Results

#### 3.1. Pentane

Pentane isomerization was performed on H-MOR, H-BEA, and SZ catalysts in order to compare their catalytic performance for linear alkanes. The changes of product yields against reaction time are shown in Figs. 1 and 2. The reaction was carried out at 273 K for SZ and 473 K for zeolites. The initial activities of H-MOR and SZ at 30 min were on a similar level; these being 6.0% (H-MOR), and 3.0–4.2% (SZ).

As shown in Fig. 1, a short induction period was observed on H-MOR for catalytic activity and product selectivity. Production of isopentane was predominant in the induction period. Later, an increase in the activity was observed along with the formation of isobutane, butane, and hexanes, which were different in the carbon number from the substrate of pentane.

On H-BEA, the isomerization activity continued to increase during the reaction period. Products in the gas phase were isobutane, isopentane, and butane. In particular, the content of isobutane increased after 2 h of reaction.

In contrast, the reaction rate on SZ was almost constant during the examined reaction period (Fig. 2). The main product was isopentane and very small amounts of isobutane and hexanes were detected. The isopentane selectivities of sulfated zirconias were 86% (SZ) and higher than 99% (SZA, S/ZRO-2, and S/ZRO-5) at 180 min. As shown in Fig. 2, the four kinds of sulfated zirconias showed a very similar catalytic action for pentane isomerization. These catalysts also gave very similar results for other substrates. Therefore, the results of SZA, S/ZRO-2, and S/ZRO-5 will be omitted hereafter.

#### 3.2. Isopentane

The changes of the product yields on each catalyst are shown in Fig. 3. An induction period and increase in the reaction rate were observed in the course of reaction on H-MOR and H-BEA. The main product in the later stage was isobutane on H-MOR, as in the previous result of pentane conversion. H-BEA showed similar catalytic action to H-MOR; isobutane production and increase in the activity. The conversions of isopentane and pentane on H-MOR at 60 min were 56.6% and 35.1%, respectively. The high reactivity of isopentane was also observed on H-BEA. The isopentane conversion on H-BEA was much higher than that of pentane and the induction period was extremely short, being less than 60 min. The reaction rate of the bimolecular reaction was higher than that of the monomolecular reaction due to the lower activation energy of the bimolecular reaction [14].

In contrast to the cases of proton-type zeolites, no change in gas phase composition was observed on SZ, as is seen in Fig. 3. Very small amounts of isobutane and hexanes were detected in the gas phase during the reaction. This does not mean that the SZ was inactive for isopentane isomerization. Isopentane showed higher reactivity than pentane, as observed on zeolites. In addition to this observation, SZ

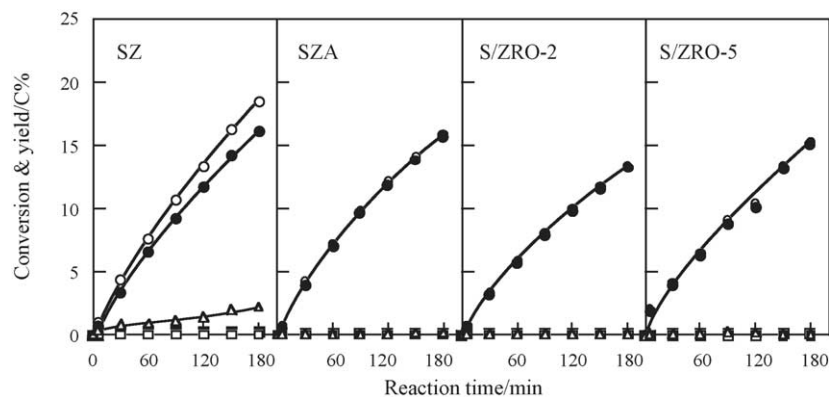


Fig. 2. Isomerization and disproportionation of pentane on sulfated zirconia catalysts at 273 K: (○) conversion, (□) butane, (■) isobutane, (●) isopentane, (△) hexanes.

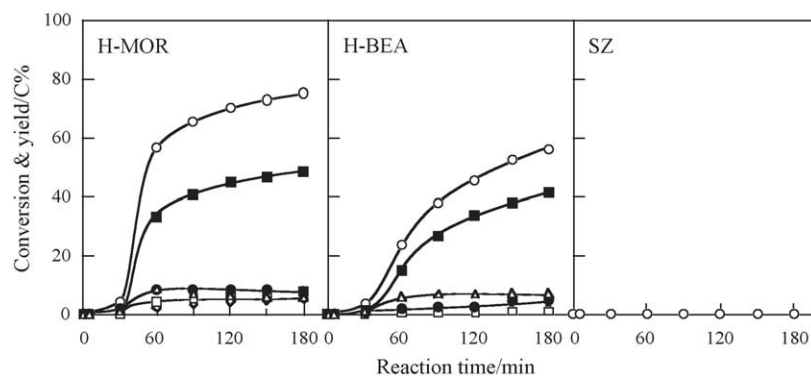


Fig. 3. Isomerization and disproportionation of isopentane on H-MOR and H-BEA at 473 K, and SZ at 273 K: (○) conversion, (◇) propane, (□) butane, (■) isobutane, (●) pentane, (△) hexanes.

showed isomerization activity for the mono-branched alkane of 2-methylpentane, as is shown in the next section. The product of methyl group migration has the same structure as the substrate. This result indicates that only the 1,2-migration of a methyl group took place on SZ.

### 3.3. 2-Methylpentane

As shown in Fig. 4, 2-methylpentane showed higher reactivity than isopentane (2-methylbutane). No induction period was observed for any catalysts. Products as a result of isomerization and disproportionation were detected from the beginning of the reaction on proton-type zeolites. This observation is in remarkable contrast to the cases of the other substrates described above. The production of isobutane, isopentane, and 3-methylpentane was predominant on H-MOR. The formation of hexanes, mainly 3-methylpentane, was terminated at 5 min and the concentration of hexanes in the gas phase decreased gradually during the reaction; a marked deactivation of H-MOR was found. The activity of H-BEA was a slightly lower than that of H-MOR, similar to the above cases. However, it showed higher conversion than H-MOR due to slower deactivation.

2-Methylpentane was converted into 3-methylpentane with high selectivity on SZ. The other observed products

were 2,2-dimethylbutane and hexane. In addition to these, trace amounts of the products of the bimolecular reaction, which were different in the carbon number from the substrate, were obtained on SZ. Rapid deactivation was also observed, as was the case for proton-type zeolites.

### 3.4. 2,2-Dimethylbutane

2,2-Dimethylbutane was mainly converted into isobutane on H-MOR (Fig. 5). Another major product observed in the gas phase was isopentane. In addition to these, 2- and 3-methylpentane and hexane were obtained. However, 2,3-dimethylbutane was produced in only a trace amount.

H-BEA showed higher activity than H-MOR for 2,2-dimethylbutane conversion, as shown in Fig. 5. The product selectivity was very different from that on H-MOR. The main product was neopentane and an equimolar amount of methane was obtained by cracking. The methane formation was negligible on either H-MOR and SZ. In addition to the cracking, a large amount of isobutane, the main product of the bimolecular reaction, was obtained. The composition of hexanes was similar to that observed on H-MOR.

The reaction selectivity of SZ for 2,2-dimethylbutane was completely different from that of the previous substrates of linear and mono-branched alkanes. The yield of hex-

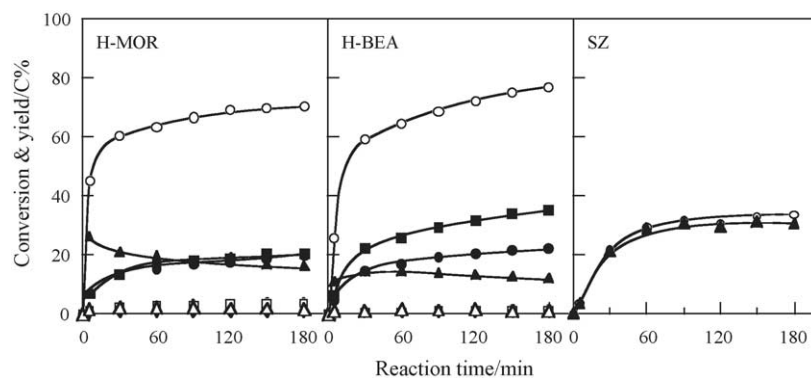


Fig. 4. Isomerization and disproportionation of 2-methylpentane on H-MOR and H-BEA at 473 K, and SZ at 273 K: (○) conversion, (□) butane, (■) isobutane, (●) isopentane, (▲) 3-methylpentane, (△) heptanes.

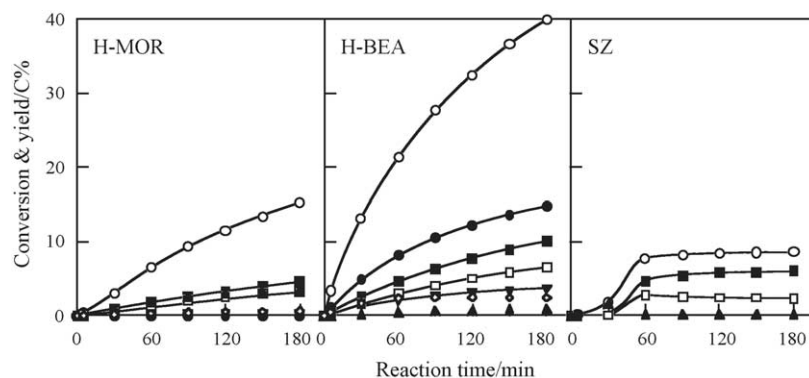


Fig. 5. Isomerization and disproportionation of 2,2-dimethylbutane on H-MOR and H-BEA at 473 K, and SZ at 273 K: (○) conversion, (▼) methane, (■) isobutane, (●) neopentane, (□) isopentane, (▲) 2-methylpentane + 3-methylpentane + hexane, (◇) heptanes.

ane isomers was very low. The main product in hexanes was 3-methylpentane, as the case of H-MOR and H-BEA. After the short induction period, 2,2-dimethylbutane was converted into isobutane and isopentane, which were produced by the bimolecular reaction. The activity of SZ was strongly depressed after 60 min of reaction.

### 3.5. 2,3-Dimethylbutane

As shown in the above section, 2,3-dimethylbutane was formed in a trace amount on H-MOR, and was negligible on H-BEA. This was not formed on SZ. Therefore, 2,3-dimethylbutane was used as the substrate to confirm the reactivity. The reaction was performed on SZ treated at 673 K in a vacuum as well as on SZ treated at 473 K to estimate the catalytic action of Brönsted acid. The number of Brönsted acid sites over SZ is reduced by the pretreatment at elevated temperatures [23]. Results are shown in Figs. 6 and 7.

2,3-Dimethylbutane showed much higher reactivity on H-MOR than did other substrates. The hexane isomers, 2- and 3-methylpentane, were produced at 5 min. After that, hexanes were decreased and the main products changed to isobutane and isopentane. These observations of the catalytic activ-

ity and product changing were similar to those on H-BEA (Fig. 6).

2,3-Dimethylbutane also showed high reactivity on SZ treated at 473 K in vacuum (Fig. 7). Isobutane and isopentane were observed from the initial stage of the reaction. In contrast to the reaction on zeolites, the activity of SZ rapidly disappeared and hexanes were not consumed. The time for deactivation was prolonged and selectivity of hexanes was increased by heat treatment at 673 K. The yield of hexane isomers on SZ treated at 673 K was higher than those of isobutane and isopentane.

### 3.6. Cyclohexane

The isomerization of cyclohexane was performed on H-MOR and H-BEA at 473 K, and on SZ at 323 K. The reaction proceeded with very high selectivity (Figs. 8 and 9). Small amounts of methane and C3–C6 hydrocarbons were formed by cracking, disproportionation, and ring opening. H-MOR and SZ treated at 473 K showed higher activity for this reaction and the equilibrium composition of methylcyclopentane was obtained at the respective reaction temperatures; the

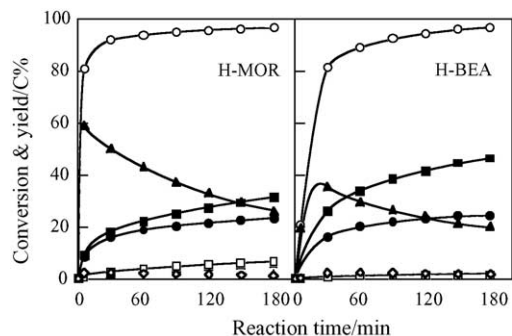


Fig. 6. Isomerization and disproportionation of 2,3-dimethylbutane on H-MOR and H-BEA at 473 K: (○) conversion, (△) propane, (□) butane, (■) isobutane, (●) isopentane, (▲) hexanes except 2,3-dimethylbutane, (◇) heptanes.

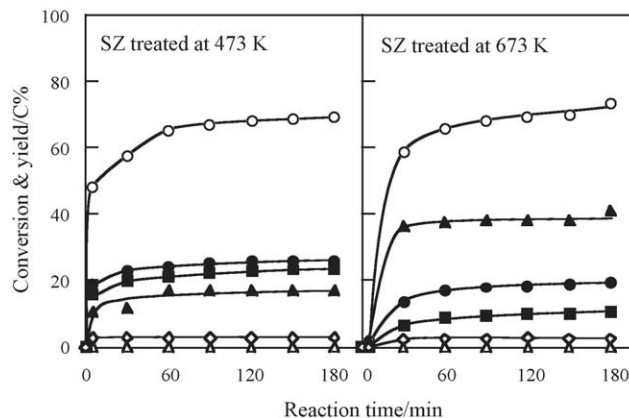


Fig. 7. Isomerization and disproportionation of 2,3-dimethylbutane at 273 K on SZ treated at 473 and 673 K: (○) conversion, (△) propane, (■) isobutane, (●) isopentane, (▲) hexanes except 2,3-dimethylbutane, (◇) heptanes.

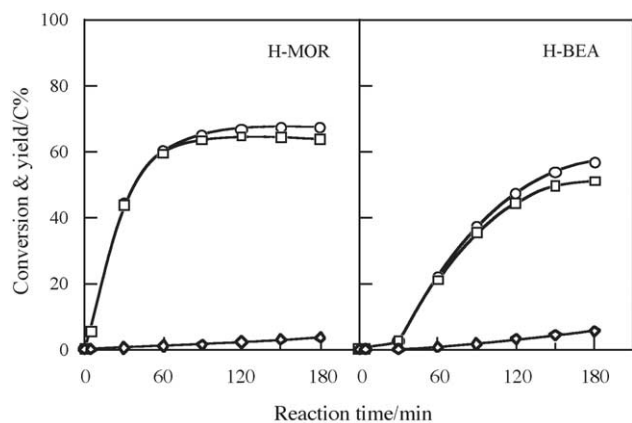


Fig. 8. Isomerization of cyclohexane on H-MOR and H-BEA at 473 K: (○) conversion, (□) methylcyclopentane, (◇) others.

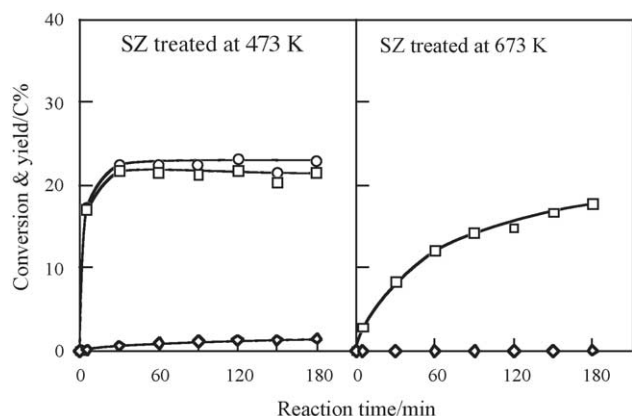


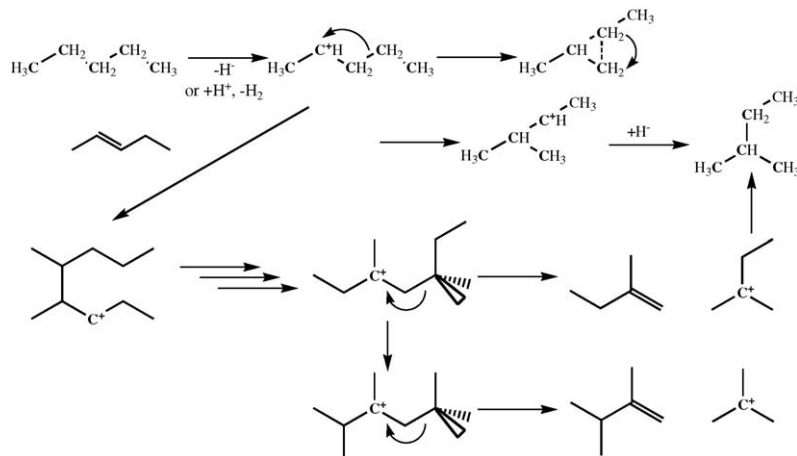
Fig. 9. Effect of heat treatment temperature on the activity and selectivity of SZ for cyclohexane isomerization at 323 K: (○) conversion, (□) methylcyclopentane, (◇) others.

calculated equilibrium compositions of methylcyclopentane were 69.7% at 473 K and 24.8% at 323 K. Heat treatment at 673 K decreased the activity on SZ. It showed much higher isomerization selectivity, exceeding 99.8%.

#### 4. Discussion

The skeletal isomerization of alkane takes place through three steps, carbenium ion formation, alkyl (methyl) group migration, and hydride ion transfer. An overall reaction path of pentane isomerization is illustrated in Scheme 1 as an example. The secondary carbenium ion is formed by abstraction of hydride ion by Lewis acid sites, or by protonation of the C–H bond followed by elimination of hydrogen. After the formation of carbenium ion, migration of an alkyl group takes place and a branched carbenium ion is produced. The carbenium ion accepts a hydride ion, which has been captured by Lewis acid or supplied by another substrate. This process is called the monomolecular mechanism. The substrate, which gives a hydride ion to the carbenium ion, is converted into another carbenium intermediate. Therefore, a part of the isomerization is a type of chain reaction. The monomolecular mechanism is distinguished by a substrate being converted into an alkane with the same carbon number.

As the mechanism for the alkyl group migration step, a bimolecular mechanism has been proposed. In the bimolecular mechanism, the process occurs through formation of a bimolecular intermediate, produced by the addition of a carbenium ion to a surface alkene species, called a dimer cation. The dimer cation is converted by successive migration of alkyl groups followed by beta-scission to form a branched carbenium ion and an alkene. In such a case, the main product is isobutane, together with materials such as propane and pentanes, which are different in carbon number from the substrate. The intermediate of the bimolecular reaction is composed of a quaternary carbon (*tert*-butyl group in many cases), and a secondary or tertiary carbenium ion at the beta-position of the quaternary carbon, as is shown in Scheme 1. The intermediates of the bimolecular reaction must have a carbon number greater than 6 to construct this structure. The C–C bond at the quaternary carbon is cleaved by the cooperative effect of electron donation from the *tert*-butyl group and electron withdrawal by the secondary or tertiary carbenium



Scheme 1. Monomolecular and bimolecular mechanisms of pentane isomerization on solid acids.

ion. The electron donating effect of the *tert*-butyl group is the strongest. This is one of the reasons for the predominant formation of isobutane by the bimolecular mechanism.

As is mentioned above, the bimolecular reaction needs a surface alkene species. A simple dehydrogenation proceeds on acid sites. We have reported that the reaction of cyclodecane on SZ led to dehydrogenation into the bicyclic compounds, *cis*- and *trans*-decalines, with the evolution of hydrogen [13]. In general, the carbenium ion has strong acidity. If there is a base and the dehydrogenated compound has a more stable structure, the carbenium ion gives its proton to the base and is converted into the corresponding alkene. It is well known that *tert*-butyl alcohol is converted into isobutene via the isobutyl cation by acid catalyzed dehydration. In the case of cyclodecane, the stability of the six-membered ring structure seems to be the driving force for proton donation. Recently, Seki and Onaka reported that the alumina catalyst modified with sulfate shows catalytic base activity in acidic super-critical CO<sub>2</sub> [26]. This shows that a proton-accepting site can be formed on solid acids. The conjugated Brønsted base sites are candidates as proton acceptors. The catalyst surface is expected to be proton-deficient due to the elimination of proton as hydrogen in the carbenium ion formation step. As a result of hydrogen evolution, negative charges accumulate on the catalyst surface. The basicity of the surface base sites, the conjugated Brønsted base sites, would be enhanced by the accumulated negative charges. As shown in Figs. 1 and 3, the bimolecular reaction took place on the Brønsted acids of H-MOR and H-BEA, when the linear and mono-branched alkanes were used as the substrates. Therefore, it is considered that the conjugated Brønsted base is the proton acceptor.

The carbenium cation formed on the Brønsted acid sites is the same intermediate species as that of the monomolecular reaction on Lewis acid sites (Scheme 1). The monomolecular reaction would also begin at this stage. Production of isopentane from pentane by a monomolecular reaction was predominant on H-MOR in the observed short induction period, as shown in Fig. 1. However, the catalyst surface is in a proton-deficient condition, as mentioned above. As a result, the cation gives its proton to the conjugated Brønsted base and is converted into the alkene. After accumulation of the surface alkenes, isomerization via bimolecular intermediates should proceed; isobutane begins to be produced (the reaction path bottom in Scheme 1). The time needed for the surface alkenes to accumulate results in the induction period. After the surface alkenes accumulate, the bimolecular reaction begins [24] and acceleration of the isomerization is observed. The reaction rate of the bimolecular reaction is higher than that of the monomolecular reaction because of its lower activation energy [14].

The lower activity of H-BEA can be attributed to its lower acid strength and small number of acid sites. On H-BEA, the isomerization activity continued to increase during the reaction. This indicates that the induction period for the accumulation of surface alkenes stretched over 3 h. The long induction period is also attributed to the lower acidity of H-

BEA, because the formation of surface alkenes is related to the formation of carbenium ions catalyzed by Brønsted acid sites.

In contrast, the isomerization took place on SZ with a constant reaction rate (Fig. 2). The high isopentane selectivity indicates that the monomolecular reaction is the main route to isomerization and catalyzed by the Lewis acid on SZ. The production of the small amount of isobutane indicates the small contribution of Brønsted acid sites for the selective isomerization. The SZ catalyst pretreated at 473 K mainly consists of Brønsted acid sites. The acid strength of Brønsted acid sites is lower than that of Lewis acid sites [27]. The Brønsted acid character was not appreciable in pentane isomerization on SZ because they were not strong enough to form the carbenium ion under the reaction conditions.

The product of methyl group migration of isopentane has the same structure as the substrate. Therefore, the progress in isomerization by the monomolecular mechanism provides no change in the gas phase species. All catalysts tested in this study showed the ability to convert 2-methylpentane into 3-methylpentane, as shown in Fig. 4. No change of species in the gas phase does not mean that SZ catalyst is inactive for the isopentane conversion. The formation of hydrocarbons of different carbon numbers from pentanes means the bimolecular reaction occurred. From this point of view, it is concluded again that the bimolecular reaction takes place on the Brønsted acids after the short induction period, not on the Lewis acids. No change in gas phase composition due to the Lewis acid of SZ indicates that only the monomolecular reaction takes place.

The reactivity of isopentane was slightly higher than that of pentane. The isopentane conversion of H-BEA was much higher than that of pentane and the induction period was extremely short, being less than 30 min. The high reactivity can be explained by the stability of the tertiary carbenium ion formed on the catalyst surface. The shortened induction period indicates that the formation of surface alkenes takes place easier from the branched carbenium ion than from the linear ion. On H-BEA, the dehydrogenation of isopentane may take place on the weaker acid sites, which are not active for pentane isomerization. In the case of pentane isomerization on proton-type zeolites, the formation of isopentane was predominant in the induction period. The isopentane produced may be converted into the surface alkenes by dehydrogenation and accumulate on the surface.

The reactivity of 2-methylpentane was higher than that of isopentane. The induction period disappeared on proton-type zeolites. Products of the monomolecular and bimolecular reactions were detected from the beginning of the reaction. This observation is in remarkable contrast to the cases of pentane and isopentane described above. The formation of 3-methylpentane was terminated at 5 min and decreased gradually during the reaction. This means that the active sites for the monomolecular reaction were deactivated within the first 5 min of reaction. A decrease in the yield of 3-methylpentane was observed after 30 min on H-BEA. Deactivation of the

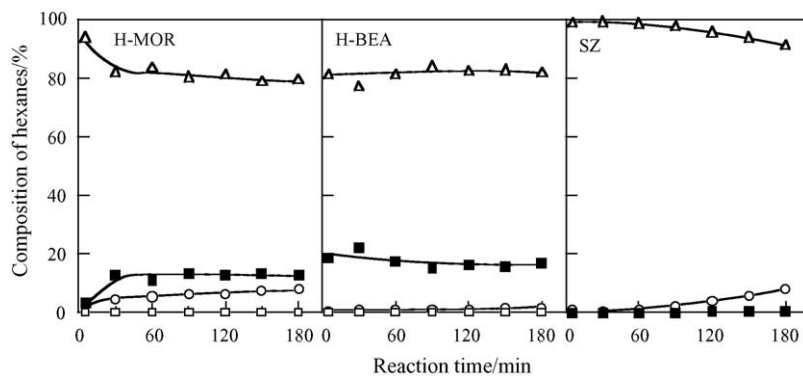
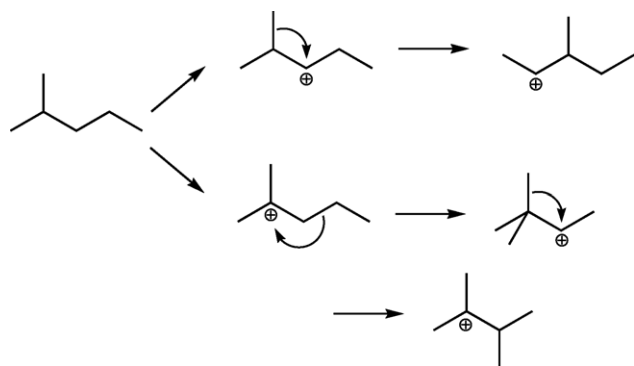


Fig. 10. Gas phase composition of hexanes in conversion of 2-methylpentane on H-MOR and H-BEA at 473 K, and SZ at 273 K: (○) 2,2-dimethylbutane, (□) 2,3-dimethylbutane, (△) 3-methylpentane, (■) hexane.

monomolecular reaction sites was also found. Because of slow deactivation of H-BEA, it showed higher conversion than H-MOR. Oligomers of alkenes and deposited carbon formed from oligomers have been proposed as the poisoning materials for skeletal isomerization activity of solid acids [24,25]. The formation of alkenes from 2-methylpentane with high reaction rate on Brønsted acid sites may provide the fast occurrence of the bimolecular reaction and deactivation.

The dehydrogenation ability of 2-methylpentane is expected to be extremely high in comparison with that of isopentane. The yield of multi-branched hexanes in the gas phase was very small, in spite of the high stability of these carbenium ions. The gas phase compositions of hexanes are shown in Fig. 10. The main product of 2-methylpentane conversion was 3-methylpentane resulting from methyl group migration. In addition, 2,2-dimethylbutane was observed. The mechanism of 2,2-dimethylbutane formation is shown in Scheme 2. 2-Methylpentane is converted into the corresponding carbenium ion. Then, it is converted into 2,2-dimethylbutyl carbocation by migration of the ethyl group. It is expected that the carbenium ion of 2,2-dimethylbutane is easily converted into that of 2,3-dimethylbutane, as shown in Scheme 2, because the tertiary cation is more stable than the secondary cation. However, only a trace amount



Scheme 2. Conversion of 2-methylpentane into 3-methylpentane and 2,3-dimethylbutane via 2,2-dimethylbutane.

of 2,3-dimethylbutane was formed from 2,2-dimethylbutane, as shown in Fig. 10. 2,3-Dimethylbutane seems to be dehydrogenated and converted into alkenes and their oligomers, without desorption from the surface. On the cation of 2,3-dimethylbutane, the positive charge is stabilized on the *tert*-butyl carbon, and a proton on the adjacent carbon (beta-hydrogen) is easily released. The elimination rate of the beta-hydrogen as a proton increases with an increase in the number of methyl groups on carbenium ion. The rate is also increased by beta-branching [28]. The elimination rate is the highest on the cation of 2,3-dimethylbutane. As a result, the carbenium ion of 2,3-dimethylbutane will be converted into 2,3-dimethylbutene, surface alkene.

The Lewis acid of SZ catalysts is active for 2-methylpentane isomerization by the monomolecular mechanism. A very small amount of products by a bimolecular reaction were observed in the gas phase. This result indicates that the Lewis acid sites are active for selective isomerization by the monomolecular mechanism, and that surface alkene species are not formed on it. The hydride abstracted by the Lewis acid does not work as the proton acceptor.

For the conversion of 2,2-dimethylbutane on SZ, the bimolecular reaction was dominant, and the catalytic activity was terminated after 60 min of reaction. This behavior could be attributed to the high reactivity of 2,3-dimethylbutane for the dehydrogenation. 2,2-Dimethylbutane might be converted into 2,3-dimethylbutane by a monomolecular reaction and then dehydrogenated by the weak Brønsted acid sites on SZ. As stated above, Lewis acid sites are not involved in the formation of surface alkenes [25]. The weak Brønsted acid sites are not active for the formation of secondary carbenium ions from linear alkanes in the present reaction conditions, because the proton on the secondary carbon has low reactivity.

The alkenes formed are the source of oligomers, the poisoning species, as well as the intermediates in the bimolecular reaction. Furthermore, they would migrate to Lewis acid sites and be adsorbed strongly by  $\pi$ -electron donation. As a result, Lewis acid sites are poisoned and isomerization activity is diminished.



As stated above, an extremely high reactivity of 2,3-dimethylbutane was observed, as shown in Figs. 6 and 7. High conversion, close to 100%, was achieved on H-MOR and H-BEA. The high reactivity can be attributed to the high stability of its carbenium ion. The very short time for monomolecular reaction and isobutane formation at later times are in agreement with the explanation detailed above.

The bimolecular reaction products, isobutane and isopentane, were produced from the beginning of the reaction on SZ treated at 473 K (Fig. 8). The number of Brønsted acid sites over SZ is reduced when it is pretreated at elevated temperatures [23]. These acid sites are inactive for the linear and mono-branched alkanes. However, the Brønsted acid character was clearly shown in the reaction of 2,3-dimethylbutane. The acid strength of Brønsted acid sites on SZ is expected to be higher than that of H-MOR and H-BEA. These weak Brønsted acid sites show activity when the substrate has high reactivity, such as 2,3-dimethylbutane. The increase in the selectivity for hexanes observed on the SZ treated at 673 K in Fig. 7 is attributed to the reduction in the number of Brønsted acid sites.

Cyclohexane is composed solely of secondary carbons. The reactivity of cyclohexane is similar to that of pentane, which has primary and secondary carbons. The skeletal isomerization of cyclohexane took place with high selectivity giving methylcyclopentane on all tested catalysts. In this case, isomerization by the monomolecular mechanism takes place on both the Brønsted and Lewis acids. The decrease in activity of SZ by the higher temperature treatment is due to the decrease in the total number of acid sites, mainly Brønsted acid sites. The conversion might be related to the acid strength and acid amount. The type of acid site is not reflected in the product selectivity.

## 5. Conclusions

The isomerization and cracking of linear, cyclic, and branched C5 and C6 hydrocarbons were performed on H-MOR and H-BEA at 473 K, and SZ at 273 and 323 K. The reactivities of dimethylalkanes (2,2-dimethylbutane and 2,3-dimethylbutane) were higher than those of linear (pentane), mono-branched (isopentane and 2-methylpentane), and cyclic (cyclohexane) alkanes. The selective isomerization of pentane by a monomolecular mechanism took place on Brønsted acids of H-MOR and H-BEA in the initial stage of the reaction, and Lewis acid sites on SZ. On the Brønsted acids, the products by cracking and disproportionation, mainly isobutane, were obtained after an induction period with increasing reaction rate by changing the reaction mechanism to a bimolecular mechanism. The induction period was shortened when the more reactive branched alkanes were used as the substrate. The Brønsted acid sites

on SZ, which were not strong enough to promote linear and mono-branched alkane isomerization, showed activity for the bimolecular reaction of 2,2-dimethylbutane and 2,3-dimethylbutane. As the source of alkene intermediates for the bimolecular reaction, 2,3-dimethylbutane was carefully examined. 2,3-Dimethylbutane would be converted into the corresponding alkene by Brønsted acid sites. The conjugated Brønsted base is expected to be the proton acceptor. The basicity of conjugated Brønsted base sites would be enhanced by the accumulated negative charges. Cyclohexane was converted into methylcyclopentane on both Brønsted and Lewis acid sites with high selectivity.

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