[Review Paper]

Skeletal Isomerization of *n*-Heptane to Clean Gasoline

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Skeletal isomerization of *n*-heptane to clean gasoline can be catalyzed by solid acids such as zeolites, sulfated zirconia, heteropoly compounds, and WO_3/ZrO_2 and their Pt or Pd-modified catalysts (bifunctional catalysts). The catalytic properties of these catalysts for isomerizations of *n*-butane and *n*-pentane are generally reviewed. The activation steps of alkane and factors influencing the activity and selectivity are discussed. Our study on the reaction mechanism for the isomerization of *n*-butane using ^{13}C-*n*-butane is interpreted. The bimolecular mechanism is the main contributor on solid acid catalysts (sulfated zirconia and $Cs_{2.5}H_{0.5}PW_{12}O_{40}$). In contrast, the monomolecular mechanism is predominant over the bifunctional catalysts in the presence of H_2. The reaction pathways of *n*-heptane isomerization are presented and the characteristics of this reaction are discussed. Recent reports and our data for the isomerization of *n*-heptane are summarized and discussed. Pt–$Cs_{2.5}H_{0.5}PW_{12}O_{40}/SiO_2$ and Pd–$H_4SiW_{12}O_{40}/SiO_2$ are comparable to Pt–H–β in selectivity to branched heptanes and the latter heteropoly catalyst has superior activity.

1. Introduction

One of the important targets in the petroleum industry is the production of branched alkanes by skeletal isomerizations of *n*-alkanes or alkylation of isoalkane with alkenes using solid acid catalysts. Environmental concerns are now promoting the synthesis of clean gasoline with high research octane number (RON) and low content of aromatics such as benzene. Recent worldwide legislation also calls for ultra-low sulfur levels in gasoline. Isomerization of light straight run naphtha has the potential to satisfy these requirements[1].

Conventional technologies using zeolite-based catalysts and chloride alumina-based catalysts are available for the skeletal isomerization of heavy alkanes[2]. Zeolite catalysts are characterized by outstanding tolerance of feedstock poisons such as sulfur and water, but chlorinated catalysts suffer from extreme sensitivity to all types of feed contaminants.

Sulfated zirconia, SO_4^{2-}/ZrO_2, has outstanding catalytic activity together with greatly improved tolerance towards water[2]. A light naphtha isomerization process was operated in 1996 with a catalyst, Pt–SO_4^{2-}/ZrO_2, developed by Cosmo Oil Co., Ltd., Mitsubishi Heavy Industries, Ltd., and UOP LLC[2]. The isomer-

ization of light naphtha consists mainly of the conversions of *n*-pentane and *n*-hexane to the corresponding branched alkanes. Commercial processes of isomerization with Pt–SO_4^{2-}/ZrO_2 had a total capacity of 1,400,000 barrels (1 barrel = 159 *l*) per day in the world by 2000. Although sulfated zirconia showed a high activity at the initial stage of the reaction, catalyst deactivation occurred rapidly. The addition of Pt increased the activity and reduced the amount of coke greatly.

Recently the conversion of heavy linear alkanes such as *n*-heptane and *n*-octane to the corresponding branched alkanes has become important for clean gasoline synthesis. However, the selective isomerization of these alkanes to multi-branched alkanes is rather difficult because of the ease of cracking by β-scission. Therefore, a catalyst with high activity, selectivity, and acceptable poison resistance is needed.

Here, the outlines of skeletal isomerization of alkanes (mainly C4 and C5) including the mechanism will be reviewed to clarify the catalytic properties of solid acids and bifunctional catalysts. Recent data for the isomerization of *n*-heptane will also be discussed.

2. General Aspects

There are two types of catalysts effective for the isomerization of alkanes, solid acid catalysts and transition

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Table 1   Activity and Selectivity for Skeletal Isomerization of n-Butane

Catalyst	Acid sites[a]	Rate[b]	Temp. [K]	Selectivity [mol%]	Refs.
$Cs_{2.5}H_{0.5}PW_{12}O_{40}$	0.06	2.3	573	84.0	4a
SO_4^{2-}/ZrO_2	0.20	0.4	573	60.7	4a
	0.20	4.2	473	91.8	4a
WO_3/ZrO_2	0.10	1.1	573	92.9	4b
H–ZSM-5(Si/Al = 11.7)	0.33	2.8	573	14.1	4a
H–β (Si/Al = 12.5)	0.31	1.8	573	27.0	4c
Pt–$Cs_{2.5}H_{0.5}PW_{12}O_{40}$		12.0	573	91.0	4d
Pt–SO_4^{2-}/ZrO_2		10.6	573	48.6	4d
		0.9	473	74.4	4d
Pt–WO_3/ZrO_2		22.3	673	87.0	4e
Pt–H–ZSM-5 (Si/Al = 11.7)		11.9	573	34.0	4d

a) $mmol \cdot g^{-1}$.

b) $10^{-8} \, mol \cdot g^{-1} \cdot s^{-1}$.

Table 2   Activity and Selectivity for Skeletal Isomerization of n-Pentane

Catalyst	Acid sites[a]	Rate[b]	Temp. [K]	Selectivity [mol%]	Comments	Refs.
$Cs_{2.5}H_{0.5}PW_{12}O_{40}$	0.06	0.4	453	100.0	Flow (stationary)	5a
SO_4^{2-}/ZrO_2	0.20	3.4	523	77.9	Flow (1 h)	5b
	0.20	4.2	473	47.7	Circulation (initial)	5a
WO_3/ZrO_2	0.10	0.5	523	45.1	Circulation (initial)	5a
	0.10	0.1	523	67.0	Flow (8 h)	5c
H–ZSM-5 (Si/Al = 11.7)	0.33	2.0	473	13.2	Circulation (initial)	5a
	0.33	2.5	473	18.3	Flow	5d
Pt–$Cs_{2.5}H_{0.5}PW_{12}O_{40}$		145.4	523	79.6	Circulation (initial)	5a
Pt–SO_4^{2-}/ZrO_2		852.8	523	87.7	Circulation (initial)	5a
Pt–SO_4^{2-}/ZrO_2		37.6	523	89.3	Flow (1 h)	5b
Pt–WO_3/ZrO_2		208.7	523	91.4	Circulation (initial)	5a
Pt–H–ZSM-5 (Si/Al = 11.7)		201.4	523	93.9	Flow	5d

a) $mmol \cdot g^{-1}$.

b) $10^{-8} \, mol \cdot g^{-1} \cdot s^{-1}$.

metal-modified solid acid catalysts (so-called bifunctional catalysts). Carbenium ions are the reaction intermediates for the skeletal isomerization in both cases[3], but the initial activation step is often different depending on the catalyst and reaction conditions. Acid strength, number of acid sites, types of acid sites, and pores of the catalysts all influence the activity and selectivity for the solid acid catalyst. Dehydrogenation of alkane on metallic sites and hydrogen spillover are sometimes important in the reaction on the bifunctional catalysts. In the case of n-heptane isomerization, β-scission of heptyl cation is critical for the selectivity[3].

2. 1. Skeletal Isomerizations of n-Butane and n-Pentane

Catalytic activities and selectivities for the isomerizations of n-butane and n-pentane over various catalysts are summarized in **Tables 1** and **2**[4),5)]. Note that these data are only typical example values because the activity and selectivity depend on the conditions of reaction and catalyst preparation. SO_4^{2-}/ZrO_2 (abbreviated as SZ), $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (Cs2.5), WO_3/ZrO_2 (WZ), and zeolites (H–ZSM-5 (Si/Al = 11.7) and H–β (Si/Al = 12.5)) are typical active solid acid catalysts for these reactions. In addition, Pt-modified catalysts (typical bifunctional catalysts) are much more effective.
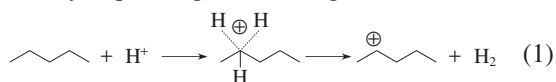
For the n-butane isomerization, the order of activity is   SZ > H–ZSM-5 > Cs2.5 > WZ > H–β (**Table 1**). Generally, severe deactivations occur over solid acid catalysts. Addition of Pt promoter to the solid acid catalyst results in large increase in the activity with small deactivations. Such observations are also found for the isomerization of n-pentane (**Table 2**). The activities of Pt-modified catalysts are noticeably higher for the isomerization of n-pentane.

Tables 1 and **2** also present the selectivities for both reactions. In n-butane isomerization (**Table 1**), SZ, Cs2.5 and WZ are selective, whereas zeolites (H–ZSM-5 and H–β) are less selective. These bifunctional catalysts are highly selective except for Pt–H–ZSM-5. In contrast, in n-pentane isomerization, these solid acid catalysts show low selectivity except for Cs2.5. On the other hand, the bifunctional catalysts were also
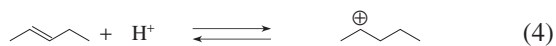
highly selective for *n*-pentane isomerization. As described below, there are decisive differences in the isomerization reaction pathways for *n*-butane and *n*-pentane between solid acids and bifunctional catalysts.

2. 2. Activation of Alkane

On a solid acid catalyst, alkane can be activated on a Brønsted acid site to form a carbenium cation through protonation to a five-coordinate carbonium ion (Eq. (1)) or on a Lewis acid site through hydride abstraction from the alkane[3] (Eq. (2)). These activation processes generally require high acid strength.

$$\sim\!\!\sim + \text{H}^+ \longrightarrow \overset{\text{H} \oplus \text{H}}{\underset{\text{H}}{\sim\!\!\sim}} \longrightarrow \overset{\oplus}{\sim\!\!\sim} + \text{H}_2 \quad (1)$$

$$\sim\!\!\sim + \text{L} \longrightarrow \overset{\oplus}{\sim\!\!\sim} + \text{LH}^{\ominus} \quad (2)$$

On a bifunctional catalyst, alkane can be dehydrogenated on a metallic site to the corresponding alkene (Eq. (3)). The alkene is activated on a protonic site to form a carbenium cation, which is an intermediate in the isomerization (Eq. (4)). High acid strength is not necessarily required, because the alkene is readily transformed to the carbenium cation. On the bifunctional catalysts, the rate-determining step is supposed to be the rearrangement of carbenium cations (Eq. (5)) from secondary to primary carbenium cation for *n*-butane and from secondary carbenium cation to protonated cyclopropyl intermediate for longer alkanes[3]. This mechanism is supported by the following experimental results: (a) The catalytic activity is greatly enhanced by the combination of the metallic component with the solid acid and (b) the reaction order with respect to hydrogen is negative. Generally the step shown by Eq. (3) is in equilibrium, which is supported by the observation that the total reaction rate is independent of the loading amount of transition metals such as Pt and Pd in a certain range. If so, the concentration of alkene intermediate depends on the temperature and the concentrations of alkane and H_2, which actually influence the total reaction rate.

$$\sim\!\!\sim \underset{\longleftarrow}{\overset{\text{metal}}{\longrightarrow}} \sim\!\!\sim + \text{H}_2 \quad (3)$$

$$\sim\!\!\sim + \text{H}^+ \underset{\longleftarrow}{\longrightarrow} \overset{\oplus}{\sim\!\!\sim} \quad (4)$$

$$\overset{\oplus}{\sim\!\!\sim} \longrightarrow \overset{}{\underset{\oplus}{\triangle}}\!\!\sim \quad (5)$$

2. 3. Factors Influencing Activity and Selectivity

The acid strength of the catalyst must influence the activity and selectivity. Especially for *n*-heptane, the selectivity is considered to be sensitive to the acid strength as described in **Section 4**.

The pore diameter of the catalyst also affects the selectivity[6]. Ultramicroporous (< 0.7 nm of pore diameter) bifunctional catalysts such as Pt–H–ZSM-5 and 0.5 wt%Pt–$Cs_{2.1}H_{0.9}PW_{12}O_{40}$ are less selective and propane is the main product over these catalysts. This

is due to restriction of the formation of branched alkanes in the constrained pores called for the shape selectivity[6]. Generation of protonic sites through hydrogen spillover is a possible reason for the high activity of some types of bifunctional catalysts like Pt–WO_3/ZrO_2 and Pt–SO_4^{2-}/ZrO_2[7].

Dehydrogenation of alkane to alkene on metallic sites is essential over bifunctional catalysts. Since the concentration of carbenium cation is proportional to that of alkene, the reaction rate will increase as the concentration of alkene increases. On the other hand, alkene readily reacts with carbenium cation to form the corresponding dimers (oligomerization). The carbenium cations from the dimer species undergo formation of smaller hydrocarbons by β-scission and at the same time further oligomerization to form coke precursor or coke. Therefore, the concentration of alkene greatly effects both the activity and selectivity. Hydrogenolysis of alkane on Pt also causes reduction of the selectivity.

## 2. 4. Reaction Mechanism of Skeletal Isomerization of Alkane

Two reaction pathways have been proposed for the transformation of carbenium cation[3], the monomolecular mechanism (through intramolecular rearrangement) and the bimolecular mechanism (through intermolecular rearrangement). These reaction pathways for the *n*-butane and *n*-pentane isomerizations are shown in **Scheme 1**.

In the case of *n*-butane, the isomerization *via* the protonated methylcyclopropane (monomolecular mechanism) involves the conversion of a secondary into a primary carbenium cation[3]. However, the reactions of alkanes with more than 5 carbon atoms involve the change of protonated cyclopropane intermediates to secondary carbenium cation. The energy level of a secondary carbenium cation is lower than that of primary one. The isomerization of *n*-pentane is easier than that of *n*-butane over solid acid catalysts. If the reaction proceeds through only the monomolecular mechanism, the selectivity becomes 100% because of the absence of the cracking of the C4 carbenium cation.

The bimolecular pathway is more favorable than the monomolecular pathway for the *n*-butane isomerization, because the bimolecular pathway passes through secondary carbenium cation. In this mechanism for *n*-butane isomerization, oligomerization from butene and carbenium cation forms the C8 carbenium cation. The cracking of the C8 carbenium cation results in hydrocarbons such as propane and isopentane as well as isobutane. The selectivity to isobutane will be low in this mechanism.

3. Isotopic Studies

In **Scheme 2**, the rearrangements of the carbon

Monomolecular pathway for *n*-butane

Bimolecular pathway for *n*-butane

Monomolecular pathway for *n*-pentane

Bimolecular pathway for *n*-pentane

Scheme 1

Monomolecular pathway

● = ^{13}C

Bimolecular pathway

$C_3 + C_5$
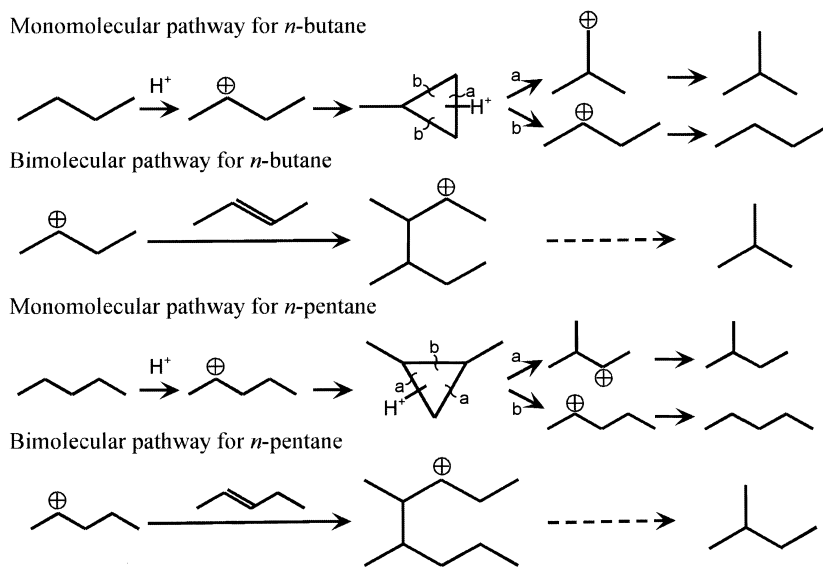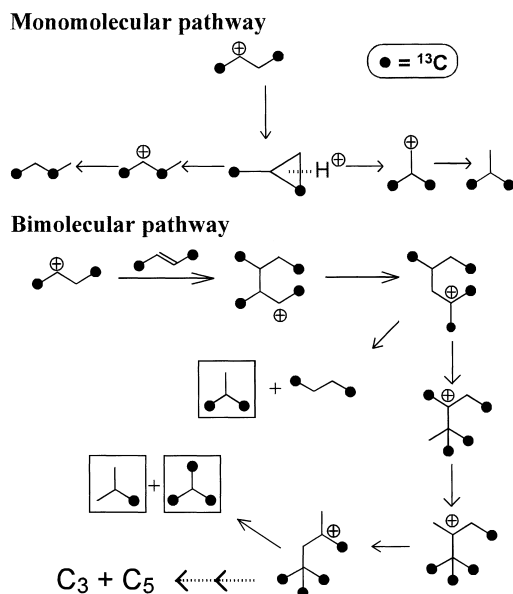
Scheme 2

atoms in the monomolecular and bimolecular mechanisms are illustrated, using 1,4-^{13}C$_2$-*n*-butane as a reactant[8]~[11]. In the monomolecular mechanism, the isomerization involves a protonated cyclopropane and the consequent primary carbenium cation as intermediates to form isobutane[11]. ^{13}C$_2$-Isobutane would be produced exclusively (intramolecular rearrangement), together with 1,3-^{13}C$_2$-*n*-butane as an isotopomer by self-isomerization. On the other hand, the bimolecular mechanism is possible, if butenes and *s*-butyl carbenium cation are formed on the catalyst surface to form C8 (octyl) cation[11]. In the C8 cation intermediate, rearrangements of hydride, followed by that of methyl

group occur. The β-scission of the C8 cation gives C4 moieties, together with C3 and C5 hydrocarbons as byproducts. In this case, intermolecular isotopic-scrambling in isobutane is expected. The contribution of each pathway can be estimated from the difference between the observed fraction of ^{13}C$_2$-isobutane and fraction of ^{13}C$_2$-isobutane of the binomial distribution, assuming that the bimolecular pathway gives a binomial distribution and the monomolecular pathway yields only ^{13}C$_2$-isobutane.

Figure 1 shows the isotopic distributions of isobutane formed over Pt–Cs2.5 and Cs2.5 at 423 K[10]~[12]. Difference isotopic distributions are obtained for Pt–Cs2.5 and Cs2.5. Pt–Cs2.5 gives exclusively ^{13}C$_2$-isobutane (**Fig. 1A**), whereas Cs2.5 gives a distribution from ^{13}C$_0$-isobutane to ^{13}C$_4$-isobutane (**Fig. 1B**). The isotopic distribution of isobutane formed over Cs2.5 (solid rectangles) is close to the binomial distribution (open rectangles). Binomial patterns of ^{13}C-isobutane were calculated by using the ^{13}C to ^{12}C ratio (r), assuming the binomial distribution, $1 : 4r : 6r^2 : 4r^3 : r^4$, where r was determined by the optimization between the observed fractions and the calculated ones for $x = 0$, 1, 3 and 4 in ^{13}C$_x$^{12}C$_{4-x}$H$_{10}$ of isobutane. It is noted that the fraction of ^{13}C$_2$-isobutane in the observed pattern over Cs2.5 (**Fig. 1B**) was slightly higher than that of the calculated binomial distribution, indicating that the isomerization mainly proceeds through the bimolecular mechanism, monomolecular mechanism being minor. The contribution of the monomolecular pathway can be estimated from the fraction of ^{13}C$_2$-isobutane which exceeded from that of the binomial distribution. It was confirmed that the *n*-butane after the reaction was exclusively ^{13}C$_2$-*n*-butane (not shown here) for all cases.
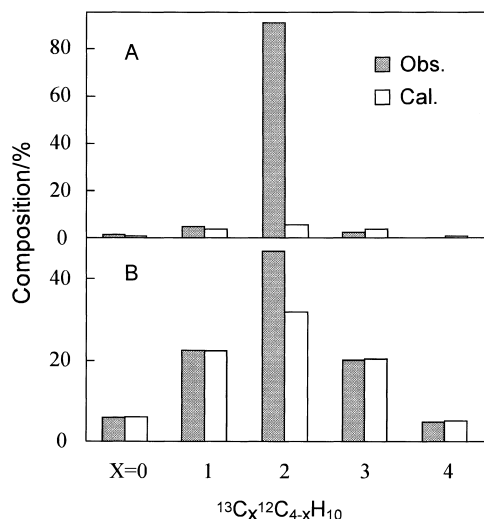
Conversions are 10% and 12% for A and B, respectively.

Fig. 1　^{13}C-Distribution of Isobutane in the Isomerization of 1,4-$^{13}C_2$-*n*-Butane over (A) 1 wt%Pt–$Cs_{2.5}H_{0.5}PW_{12}O_{40}$ and (B) $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ at 423 K

(◯): 1 wt%Pt–$Cs_{2.5}H_{0.5}PW_{12}O_{40}$,　　(△): 1 wt%Pt–$SO_4^{2-}$/$ZrO_2$,
(●): $Cs_{2.5}H_{0.5}PW_{12}O_{40}$, and (▲): sulfated ZrO_2.

Fig. 2　Contribution of Monomolecular Pathway in Skeletal Isomerization of *n*-Butane as a Function of Temperature

Figure 2 shows the contribution of the monomolecular pathway with the reaction temperature for Cs2.5, SZ and their Pt-modified catalysts. The contribution of the monomolecular pathway is low for Cs2.5 and SZ at 423 K, demonstrating that the reaction at 423 K occurs exclusively *via* the bimolecular mechanism. The contribution of the monomolecular pathway greatly increases as the reaction temperature increases, indicating that the contribution of the monomolecular mechanism becomes significant on the solid acid catalysts at the high temperature[11),12)]. In contrast, the contribution of the monomolecular mechanism was high at these reaction temperatures over their Pt-modified catalysts[11),12)].

The selectivities to isobutane at 423 K are 96.3% (10%-conversion) and 94.9% (10%-conversion) on Pt–Cs2.5 and Pt–SZ, respectively, and 86.8% (13%-conversion) and 86.4% (11%-conversion) on Cs2.5 and SZ, respectively. These differences in selectivity can be accounted for by the switching of the mechanism, depending on existence or absence of Pt. As shown in **Fig. 2**, the contribution of the monomolecular pathway is significant on the bifunctional catalysts, which are responsible for the higher selectivity of the bifunctional catalysts. The presence of Pt and H2 might greatly suppress the formation of alkenes and thus the bimolecular pathway would be blocked. On the other hand, the bimolecular pathway was dominant over the solid acid catalysts.

4.　Skeletal Isomerization of *n*-Heptane

Thermodynamic compositions of isomers for hep-tanes are presented in **Fig. 3**. The desired branched heptanes are thermodynamically favorable at lower temperatures[13)]. The research octane numbers of heptanes are also summarized in **Fig. 3**, which is one of the important indexes of the fuel. The research octane number of *n*-heptane is 0 and it increases to 42-52 for mono-branched, 81-98 for di-branched, and 112 for tri-branched heptanes by the isomerization.
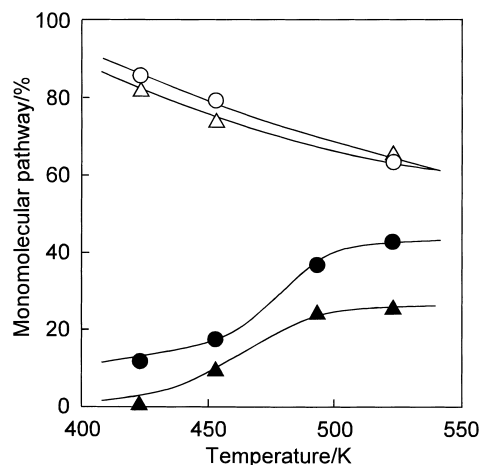
4. 1.　Reaction Pathway of *n*-Heptane Isomerization

The possible reaction pathways for the *n*-heptane isomerization are illustrated in **Scheme 3**. The carbenium cation (*s*-heptyl cation) can be formed acidic sites (Lewis and Brønsted acid sites). The *s*-heptyl cation formed transforms into *t*-carbenium cation of mono-branched heptanes (2-M$^⊕$ and 3-M$^⊕$ in **Scheme 3**). These *t*-carbenium cations turn into the corresponding mono-branched heptanes (2-M and 3-M in **Scheme 3**) by hydride-transfer reaction along with generating other carbenium cations, called as the chain reaction. In the presence of H2, the reaction of the carbenium cation with H2 will be often important.

In *n*-butane isomerization, the monomolecular mechanism is of minor importance over typical solid acid catalysts such as SO_4^{2-}/ZrO_2, Fe–Mn–SO_4^{2-}/ZrO_2, and Cs2.5[8)~11)]. The bimolecular mechanism is predominant in this reaction. On the other hand, Ono[14)] pointed out that the bimolecular mechanism becomes less important in the isomerization of *n*-heptane or *n*-octane. Isomerization *via* monomolecular mechanism is to dominate this reaction. In the bimolecular mechanism, oligomerization-cracking usually forms various byproducts rather than the isomerization products.

The β-scission becomes critical as a side reaction of the monomolecular mechanism in the isomerization of

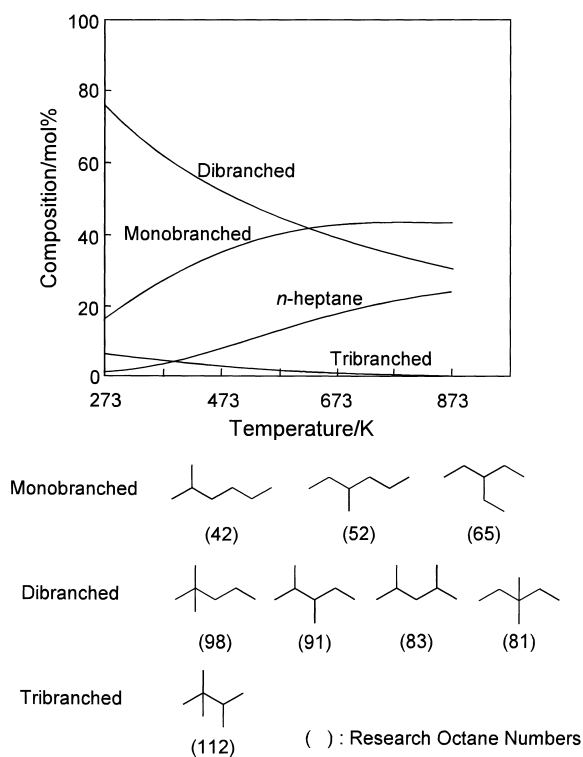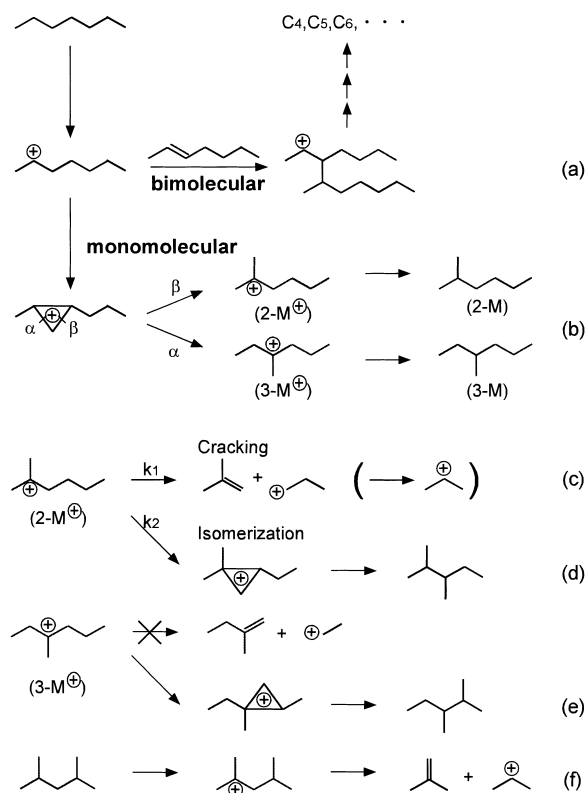Fig. 3 Equilibrium Composition of C7 Isomers as a Function of Temperature and Research Octane Numbers of C7 Isomers

Scheme 3

n-heptane. If the number of carbon atoms is 7 or more, the β-scission of the carbenium cations can take place to form alkenes and carbenium cations with less number of carbon atoms. As a result, smaller hydrocarbon chains are formed. This is one reason for the low selectivities in the isomerization of *n*-heptane. Presumably the relative rates for the isomerization through the protonated cyclopropane intermediate and for β-scission ((d) and (c) in **Scheme 3**) depends on the stability of the corresponding carbenium cation, in other words, the acid strength of catalysts. Since the difference in stability between the tertiary and secondary carbenium cations is about 54 kJ·mol^{-1} [3], the activation energy of β-scission ((c) in **Scheme 3**) would be about 63 kJ·mol^{-1} [3]. On the other hand, the activation energy for the isomerization through the protonated cyclopropane intermediate would be about 71 kJ·mol^{-1} [3].

4. 2. Recent Investigations of *n*-Heptane Isomerization

Activity and selectivity for the skeletal isomerization of *n*-heptane are summarized in **Table 3**[15]. Chao *et al.*[15a] reported that Pt/H–β was more active and selective for isomerization of *n*-heptane than Pt-mordenite due to the effect of the pore structure. H–β has 12-membered ring channels (diameter of the largest pore opening is 0.65 × 0.76 nm) and cavities (with a diame-

ter of 1.2-1.3 nm at channel intersection). For the diffusion of the related molecules, H–β has less steric hindrance than mordenite. Blomsma *et al.*[15b] also showed the high catalytic performance of Pt–Pd/H–β.

Partitz *et al.*[15d] revealed the effects of pore-size and location of the acid sites of SAPO-based catalysts on the selectivity. SAPO-31 with 12-membered oxygen rings was highly active and selective. Parlitz *et al.*[15d] claimed that Pd/SAPO-11 was selective, while it was less active. Saberi *et al.*[15f] reported that the bifunctional catalyst, Pt–Zn–HY, was highly active and selective.

Liu *et al.*[15h] reported that the mixture of Pt/Al$_2$O$_3$ and Cs$_{2.5}$H$_{0.5}$PW$_{12}$O$_{40}$ was highly selective. Matsuda *et al.*[15k,l] found a high activity and selectivity of Pt/MoO$_3$ when the catalyst was reduced with H$_2$. The Pt may enhance the formation of the H$_x$MoO$_3$ phase, which is the precursor of the active Mo$_x$H$_y$ phase.

Blomsma *et al.*[16] evaluated the contributions of two mechanisms, the monomolecular mechanism (classical bifunctional mechanism) and the bimolecular mechanism (dimerization-cracking mechanism) using the product distribution. Blomsma *et al.*[17] further studied the reaction mechanism from the product distribution over Pd/H–β with various Pd loadings. They referred that the monomolecular mechanism predominates at high loadings and the bimolecular mechanism is oper-

Table 3 Activity and Selectivity for Skeletal Isomerization of *n*-Heptane

Catalyst	Temperature [K]	Conversion [%]	Selectivity[a] [mol%]	Rate [mmol·g⁻¹·h⁻¹]	Remarks	Refs.
Pt/H–β	483	84	86	8.4	$C_7/H_2 = 0.056$, $SV = 1$ h⁻¹	15a
Pt/H–β	498	83	84	9.5	$C_7/H_2 = 0.017$, 3.1 atm	15b
PtPd/H–β	498	83	91	13.6	$C_7/H_2 = 0.017$, 3.1 atm	15b
Pd–H–β	453	66	97	3.1	$C_7/H_2 = 0.05$, $SV = 1.3$ h⁻¹	15c
Pd/SAPO-11	603	74	93	0.07	$C_7/H_2 = 0.15$, $SV = 0.01$ h⁻¹	15d
Pd/SAPO-31	603	72	94	0.07	$C_7/H_2 = 0.15$, $SV = 0.01$ h⁻¹	15d
Pt/H–Y	498	63	75	15.1	$SV = 2.4$ h⁻¹	15e
Pt/Al–H–Y	498	82	72	7.9	$SV = 0.96$ h⁻¹	15e
Pt/Zn–H–Y	483	85	80	2.7	$SV = 0.32$ h⁻¹	15f
Pt/H–MOR	503	64	90	6.4	$C_7/H_2 = 0.067$, $SV = 1$ h⁻¹	15a
Pt/H–MCM-22	573	34	13	0.8	$C_7/H_2 = 0.014$, 20 atm	15g
Pt/H–ZSM-5	423	24	72	0.3	$C_7/(H_2 + N_2) = 0.05$, $SV = 1.3$ h⁻¹	15h
Pt/H–USY	508	83	86	2.1	$C_7/H_2 = 0.017$, 3.1 atm	15b
PtPd/H–USY	508	83	89	2.5	$C_7/H_2 = 0.017$, 3.1 atm	15b
Pt–Cs2.5	453	80	87	2.0	$C_7/H_2 = 0.05$, $SV = 1.3$ h⁻¹	15i
Pt–Cs2.5/SiO₂	453	74	97	0.6	$C_7/H_2 = 0.05$, $SV = 0.2$ h⁻¹	15i
Pd–$H_4SiW_{12}O_{40}$/SiO₂	453	69	93	7.4	$C_7/H_2 = 0.05$, $SV = 2.5$ h⁻¹	15c
Pt–SO_4^{2-}/ZrO₂	473	44	35	1.0	$C_7/H_2 = 0.16$, $SV = 8.4$ h⁻¹, 7.7 atm	15j
Pt–SO_4^{2-}/ZrO₂	423	29	52	0.4	$C_7/(H_2 + N_2) = 0.05$, $SV = 1.3$ h⁻¹	15h
Pd–WO_3/ZrO₂	453	68	96	1.4	$C_7/H_2 = 0.05$, $SV = 1.3$ h⁻¹	15c
MoO_3	523	81	89	4.6	$C_7/H_2 = 0.025$	15k
Pt/MoO_3	523	43	97		$C_7/H_2 = 0.025$	15l

a) Selectivity to total branched heptanes.

Table 4 Catalytic Data for Skeletal Isomerization of *n*-Heptane

Catalyst[a]	Rate[b] [mmol·g⁻¹·h⁻¹]	Selectivity[c),d] [mol%]				Conversion [%]
		Monobranched C_7[e]	Multibranched C_7[f]	i-C_7[g]	$C_3 + i$-C_4[h]	
Pt–$Cs_{2.5}H_{0.5}PW_{12}O_{40}$	2.0	59.7	27.0	86.7	13.3	80.3
Pt–Cs2.5/SiO₂	0.6	69.7	27.4	97.1	2.9	73.8
Pt–SO_4^{2-}/ZrO₂	1.7	10.7	4.4	15.1	84.9	80.5
Pt–WO_3/ZrO₂	1.4	58.7	32.0	90.7	9.3	82.7
Pt–H–β	3.4	66.8	26.0	92.8	7.2	76.4

Reaction temperature: 453 K.

a) The loading amount of Pt was 2 wt%.

b) Estimated from the conversion-*W/F* dependence.

c) $100 \times n[C_n]$/[total carbon atom], where $[C_n]$ and [total carbon atom] mean the concentrations of hydrocarbon having *n* carbon atom and total carbon, respectively.

d) At about 80% conversion.

e) 2-Methylhexane (2-MH) + 3-MH + ethylpentane.

f) 2,2-Dimethylpentane (2,2-DMP) + 2,3-DMP + 2,4-DMP + 3,3-DMP + 2,2,3-trimethylbutane.

g) i-C_7 = Total branched C_7 alkanes = Monobranched C_7 + Multibranched C_7.

h) i-C_4 = isobutane.

ated at low loadings. Philippou and Anderson[18] studied the reaction mechanism using ¹³C-*n*-heptane as a reactant and the location of ¹³C was analyzed with ¹³C-NMR. They concluded that the isomerization proceeded through a protonated cyclopropane intermediate and cracking through classical β-scission.

5. Our Recent Results

5. 1. Pt–$Cs_{2.5}H_{0.5}PW_{12}O_{40}$

Table 4 gives the reaction rate and the selectivity at 74-83% conversions. The catalytic activity is in order of Pt–H–β > Pt–Cs2.5 > Pt–SO_4^{2-}/ZrO₂ > Pt–WO_3/ZrO₂ > Pt–Cs2.5/SiO₂[15i]. In the case of Pt–SO_4^{2-}/ZrO₂, the selectivity to total branched heptanes, including monobranched and multi-branched heptanes, is very low because of the formation of propane and isobutane by β-scission. It is worthy to note that the selectivity to total branched heptanes is higher over Pt–Cs2.5/SiO₂ and Pt–H–β (**Table 4**).

Table 5 compares the detailed product distributions for Pt–Cs2.5/SiO₂ and Pt–H–β. The cracking products are exclusively propane and isobutane, which are formed by the β-scission of C7-carbenium cation. It

Table 5 Product Distributions of Skeletal Isomerization of *n*-Heptane

Catalyst[a]		Pt–Cs2.5/SiO$_2$	Pt–H–β
Conversion	[%]	73.8[b]	76.4[c]
Rate[d]	[mmol·g^{-1}·h^{-1}]	0.6	3.4
Yield of total *i*-C$_7$[e]		71.7	70.9
Selectivity[f]	[mol%]		
C$_1$ + C$_2$		0	0
C$_3$ + *i*-C$_4$		2.9	7.2
C$_5$ + C$_6$		0	0
Monobranched C$_7$[g]			
2-MH	(42)	34.9	33.3
3-MH	(52)	32.8	31.6
3-EP	(65)	2.0	1.9
Multibranched C$_7$[h]			
2,2-DMP	(98)	7.7	7.8
2,3-DMP	(91)	8.7	7.5
2,4-DMP	(83)	8.6	7.4
3,3-DMP	(81)	2.4	3.0
2,2,3-DMP	(112)	0	0.3
Total *i*-C$_7$[e]		97.1	92.8

Reaction temperature: 453 K, C$_7$: H$_2$ = 4.8 : 95.2.
a) The loading amount of Pt was 2 wt%.
b) Total flow rate (*F*): 10 m*l* (*W/F* = 244 g·h·mol^{-1}).
c) Total flow rate (*F*): 10 m*l* (*W/F* = 40 g·h·mol^{-1}).
d) Estimated from the conversion-*W/F* dependence.
e) Total *i*-C$_7$ = monobranched C$_7$ + multibranched C$_7$.
f) $100 \times n[C_n]$/[total carbon atom], where [C$_n$] and [total carbon atom] mean the concentrations of hydrocarbon having *n* carbon atom and total carbon, respectively.
g) 2-Methylhexane (2-MH) + 3-MH + ethylpentane. The figure in the parenthesis is the research octane number.
h) 2,2-Dimethylpentane (2,2-DMP) + 2,3-DMP + 2,4-DMP + 3,3-DMP + 2,2,3-trimethylbutane. The figure in the parenthesis is the research octane number.

Fig. 4 Conversion and Selectivity for Isomerization of *n*-Heptane over H$_4$SiW$_{12}$O$_{40}$ Supported on SiO$_2$

should be emphasized that the selectivity of Pt–Cs2.5/SiO$_2$ is comparable to that of Pt–H–β, which is known to be efficient for this reaction[15a~c]. On the other hand, the activity of Pt–Cs2.5/SiO$_2$ is less than those of Pt–Cs2.5 and Pt–H–β (**Table 4**).

The support of Pt and Cs2.5 on silica probably results in (a) decreased acid strength and (b) change in the pore-structure of the active phase of Cs2.5. Since it is considered that the cracking proceeds through β-scission of C7 carbenium cations to propyl cation and isobutene, and the isomerization takes place *via* protonated cyclopropane intermediate, the relative rates of these two reactions probably depend on the acid strength. If the latter reaction takes place on weaker acid sites, the increase in the selectivity by supporting Pt and Cs2.5 on SiO$_2$ is reasonable. It is well known that the pores of Cs2.5 have a bimodal distribution consisting of micropores and mesopores[19),20)]. In the case of skeletal isomerization of *n*-butane, the micropore-size of porous Pt-solid acids greatly influences the product distribution; Pt-solid acids having the smaller pores tended to form cracking products[6]. The micropores of Pt–Cs2.5 contributed largely to the surface
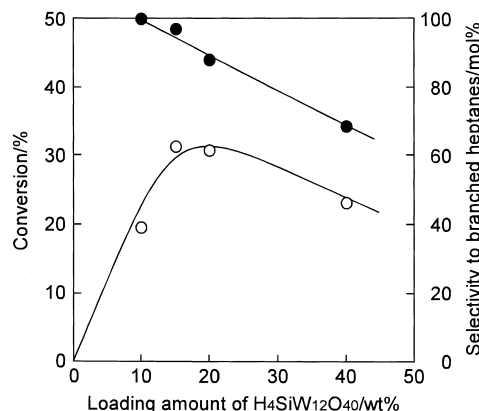
area and so affect the selectivity. Due to the dispersion, the length of the pores will become smaller. This would reduce the cracking and enhance the selectivity to all branched heptanes in the skeletal isomerization of *n*-heptane.

5. 2 . Pd–H$_4$SiW$_{12}$O$_{40}$/SiO$_2$

Effects of the loading amount of H$_4$SiW$_{12}$O$_{40}$ on the conversion and selectivity to branched heptanes over 2 wt%Pd–H$_4$SiW$_{12}$O$_{40}$/SiO$_2$ are shown in **Fig. 4**. The stationary conversion peaked at around 15 wt% of the loading amount. It is noted that the selectivity to branched heptanes increased with decreasing the loading amount of H$_4$SiW$_{12}$O$_{40}$, the maximum occurring at 10 wt%H$_4$SiW$_{12}$O$_{40}$. The acid strength on the loading amount was examined by temperature-programmed desorption (TPD) of NH$_3$ to identify the factor influencing the selectivity.

Figure 5 shows the NH$_3$-TPD spectra for H$_4$SiW$_{12}$O$_{40}$/SiO$_2$[21]. A sharp peak at around 800 K is observed for bulk H$_4$SiW$_{12}$O$_{40}$. H$_4$SiW$_{12}$O$_{40}$ supported on SiO$_2$ showed a lower temperature of NH$_3$ desorption, indicating that the acid strength was reduced. It is reported that H$_3$PW$_{12}$O$_{40}$ interacts with the surface of SiO$_2$, where protons of H$_3$PW$_{12}$O$_{40}$ react with OH groups on SiO$_2$ to form $-OH_2^+$ --- H$_2$PW$_{12}$O$_{40}^{-}$[22]. It is reasonable to consider that the protons of H$_4$SiW$_{12}$O$_{40}$ also react with OH groups on SiO$_2$ to form $-OH_2^+$ --- H$_3$SiW$_{12}$O$_{40}^{-}$. This interactions would reduce the acid strength. If the interaction between H$_4$SiW$_{12}$O$_{40}$ and OH groups on SiO$_2$ is essential, the degree of dispersion will influence the acid strength.

Since Pd-free H$_4$SiW$_{12}$O$_{40}$/SiO$_2$ was much less active, the critical role of Pd is clear. As was previously discussed[4d], Pd activates alkanes to form the corresponding alkene, which is readily transformed to carbenium cation intermediates. In the absence of Pd, acid (proton) is required to directly attack the alkane to form carbenium ion intermediates.
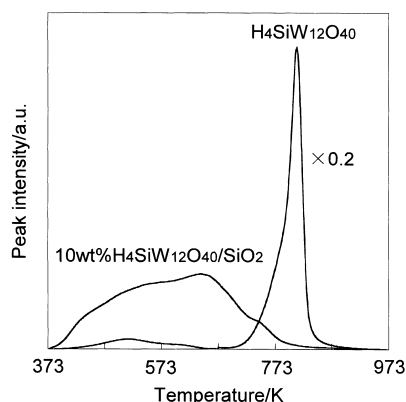
Fig. 5 NH₃-TPD Spectra from $H_4SiW_{12}O_{40}$ and 10 wt%$H_4SiW_{12}O_{40}$/SiO$_2$

Table 6 summarizes the activity and selectivity to branched heptanes over Pd–$H_4SiW_{12}O_{40}$/SiO$_2$ and Pd–H-β. It should be emphasized that the activity of Pd–$H_4SiW_{12}O_{40}$/SiO$_2$ is higher than that of Pd–H–β, whereas the selectivity to branced heptanes is comparable to or slightly lower than that over Pd–H–β. These results indicate that bifunctional heteropolyacid catalysts have great potentials for production of clean gasoline by the skeletal isomerization of n-heptane.

Acknowledgments

Table 6 Product Distributions of Skeletal Isomerization of n-Heptane

Catalyst[a]		Pd–15 wt%$H_4SiW_{12}O_{40}$/SiO$_2$	Pt–H–β
Conversion	[%]	66.7[b]	66.0[c]
Rate[d] [mmol·g⁻¹·h⁻¹]		7.4	3.1
Yield of total i-C$_7$[e]		61.7	63.8
Selectivity[f] [mol%]			
C$_1$ + C$_2$		0	0
C$_3$ + i-C$_4$		7.5	3.4
C$_5$ + C$_6$		0	0
Monobranched C$_7$[g]			
2-MH	(42)	34.2	37.7
3-MH	(52)	32.5	36.0
3-EP	(65)	2.0	2.3
Multibranched C$_7$[h]			
2,2-DMP	(98)	4.8	5.5
2,3-DMP	(91)	8.7	6.8
2,4-DMP	(83)	8.6	6.1
3,3-DMP	(81)	1.2	2.2
2,2,3-DMP	(112)	0.5	0
Total i-C$_7$[e]		92.5	96.6

Reaction temperature: 453 K, C$_7$: H$_2$ = 4.8 : 95.2.
a) The loading amount of Pd was 2 wt%.
b) Total flow rate (F): 10 ml (W/F = 20 g·h·mol⁻¹).
c) Total flow rate (F): 10 ml (W/F = 40 g·h·mol⁻¹).
d) Estimated from the conversion-W/F dependence.
e) Total i-C$_7$ = monobranched C$_7$ + multibranched C$_7$.
f) $100 \times n[C_n]$/[total carbon atom], where [C$_n$] and [total carbon atom] mean the concentrations of hydrocarbon having n carbon atom and total carbon, respectively.
g) 2-Methylhexane (2-MH) + 3-MH + ethylpentane. The figure in the parenthesis is the research octane number.
h) 2,2-Dimethylpentane (2,2-DMP) + 2,3-DMP + 2,4-DMP + 3,3-DMP + 2,2,3-trimethylbutane. The figure in the parenthesis is the research octane number.

References

1) Weyda, H., Koehler, E., *Catal. Today*, **81**, 51 (2003).
2) Kimura, T., *Catal. Today*, **81**, 57 (2003); Kimura, T., *PETROTECH*, **25**, (2), 111 (2002).
3) Gates, B. C., "Catalytic Chemistry," John Wiley & Sons, Inc., New York (1992).
4) (a) Na, K., Okuhara, T., Misono, M., *J. Chem. Soc., Faraday Trans. 1*, **91**, 367 (1995); (b) Yori, J. C., Pieck, C. L., Parera, J. M., *Appl. Catal. A: General*, **181**, 5 (1999); (c) Unpublished data; (d) Na, K., Okuhara, T., Misono, M., *J. Catal.*, **170**, 96 (1997); (e) Santesteban, J. G., Calbro, D. C., Borgard, W. S., Chang, C. D., Vartuli, J. C., Tsao, Y. P., Natal-Santiago, M. A., Bastian, R. D., *J. Catal.*, **183**, 314 (1999).
5) (a) Unpublished data; (b) Risch, M., Wolf, E. E., *Catal. Today*, **62**, 255 (2000); (c) Scheithauer, M., Jentoft, R. E., Gates, B. C., Knozinger, H., *J. Catal.*, **191**, 271 (2000); (d) Fujimoto, K., Maeda, K., Aimoto, K., *Appl. Catal. A: General*, **91**, 81 (1992).
6) Okuhara, T., Yoshinaga, Y., Watanabe, R., *Am. Chem. Soc. Book*, **738**, 369 (1999).
7) Hattori, H., Ebitani, K., *Hyomen*, **32**, 32 (1994).
8) Garin, F., Seyfried, L., Gitard, P., Maire, G., Abdulsamad, A., Sommer, J., *J. Catal.*, **151**, 26 (1995).
9) Adeeva, V., Lei, G. D., Sachtler, W. M. H., *Catal. Lett.*, **33**, 135 (1995).
10) Suzuki, T., Okuhara, T., *Chem. Lett.*, **2000**, 470.
11) Suzuki, T., Okuhara, T., *Catal. Lett.*, **72**, 111 (2001).
12) Okuhara, T., Echizen, T., *PETROTECH*, **25**, (2) 98 (2002).
13) Chica, A., Corma, A., *J. Catal.*, **187**, 167 (1999).
14) Ono, Y., *PETROTECH*, **25**, (2), 92 (2002); Ono, Y., *Catal. Today*, **81**, 2 (2003).
15) (a) Chao, K.-J., Wu, H.-C., Leu, L.-J., *Appl. Catal. A: General*, **143**, 223 (1996); (b) Blomsma, E., Martens, J. A., Jacobs, P. A., *J. Catal.*, **165**, 241 (1997); (c) Unpublished data; (d) Parlitz, B., Schreier, E., Zubowa, H.-L., Eckelt, R., Lieske, E., Lischke, G., Fricke, R., *J. Catal.*, **155**, 1 (1995); (e) Mao, R. L. V., Saberi, M. A., *Appl. Catal. A: General*, **199**, 99 (2000); (f) Saberi, M. A., Mao, R. L. V., Martiu, M., Mak, A. W. H., *Appl. Catal. A: General*, **214**, 229 (2001); (g) Kinger, G., Majda, D., Vinek, H., *Appl. Catal. A: General*, **225**, 301 (2002); (h) Liu, Y., Koyano, G., Misono, M., *Top. Catal.*, **11/12**, 239 (2000); (i) Miyaji, A., Okuhara, T., *Catal. Today*, **81**, 43 (2003); (j) Iglesia, E., Soled, S. L., Kramer, G. M., *J. Catal.*, **144**, 238 (1993); (k) Matsuda, T., Hirata, Y., Suga, S., Sakagami, H., Takahashi, H., *Appl. Catal. A: General*, **193**, 185 (2000); (l) Uchijima, F., Takagi, T., Itoh, H., Matsuda, T., Takahashi, N., *Phys. Chem. Chem. Phys.*, **2**, 1077 (2000).
16) Blomsma, E., Martens, J. A., Jacobs, P. A., *J. Catal.*, **155**, 141 (1995).
17) Blomsma, E., Martens, J. A., Jacobs, P. A., *J. Catal.*, **159**, 323 (1996).
18) Philippou, A., Anderson, M. W., *J. Catal.*, **158**, 385 (1996).

19) Okuhara, T., Watanabe, H., Nishimura, R., Inumaru, K., Misono, M., *Chem. Mater*., **12**, 253 (2000).
20) Yoshinaga, Y., Suzuki, T., Yoshimune, M., Okuhara, T., *Top.* *Catal*., **19**, 179 (2002).
21) Miyaji, A., Echizen, T., Nagata, K., Yoshinaga, Y., Okuhara, T., *J. Mol. Catal. A*, **201**, 145 (2003).

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要　　旨

ヘプタンの骨格異性化によるクリーンガソリン合成

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種々の固体酸およびそれらを貴金属で修飾した二元機能固体酸を触媒とするヘプタンの骨格異性化によるクリーンガソリンの合成の報告をまとめた。前半ではブタンとペンタンの異性化を例に触媒の特性を述べた。アルカンの活性化のステップや選択性支配因子について触れ，同位体法による骨格異性化の反応機構を解説した。固体酸では二分子反応が主であるが，二元機能触媒上では単分子機構で反応が進行する。後半ではヘプタン異性化経路とヘプタン異性化の特異性を指摘した後，最近のこの反応についての報告をまとめた。Pt–Cs$_{2.5}$H$_{0.5}$PW$_{12}$O$_{40}$/SiO$_2$ とPd–H$_4$SiW$_{12}$O$_{40}$/SiO$_2$ は Pt–H–β と選択性は類似していたが，後者のヘテロポリ触媒は活性に優れていた。

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