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Skeletal isomerization of *n*-heptane and hydroisomerization of benzene over bifunctional heteropoly compounds

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Abstract

Hydroisomerization of benzene and skeletal isomerization of *n*-heptane have been studied using various 2 wt.% Pt-promoted solid acids such as Pt–$Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (Pt–$Cs_{2.5}$), SiO_2 supported Pt–$Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (Pt–$Cs_{2.5}/SiO_2$), Pt–$SO_4{}^{2-}/ZrO_2$, Pt–WO_3/ZrO_2, and Pt–H-β zeolite. The catalytic activity for the formation of methylcyclopentane in the hydroisomerization of benzene was in order of Pt–$Cs_{2.5}/SiO_2$ > Pt–$Cs_{2.5}$ > Pt–WO_3/ZrO_2 > Pt–$SO_4{}^{2-}/ZrO_2$. The highest activity of Pt–$Cs_{2.5}/SiO_2$ among these bifunctional catalysts would be due to high ability for hydrogenation of benzene and high activity for skeletal isomerization of cyclohexane. In the skeletal isomerization of *n*-heptane, it was found that Pt–$Cs_{2.5}/SiO_2$ was more selective than Pt–H-β zeolite, which is known to be the most efficient catalyst for this reaction, though it was less active than Pt–H-β zeolite.

Keywords: Heteropoly compound; Solid acid; Skeletal isomerization; Cyclohexane; Benzene; *n*-Heptane; Bifunctional catalyst

1. Introduction

Skeletal isomerization of alkanes has industrially important applications because branched alkanes are useful as clean high-octane fuel. This process is a refinery process that in fact produces significant quantities of the ideal component of reformulated gasoline: *iso*-alkanes. There are also a number of reports detailing hydroisomerization of *n*-alkanes over bifunctional catalysts [1–15]. The isomerizations of *n*-butane and *n*-pentane have been commercialized using Pt–$SO_4{}^{2-}/ZrO_2$ and Pt–zeolites [16,17].

Although hydrocarbon-oils including aromatics like benzene are efficient gasoline having a high-octane number, it is keenly desirable to reduce the content of benzene in gasoline from a viewpoint of environmental protection. One possible way to diminish benzene keeping its octane number is to transform benzene to methylcyclopentane by hydroisomerization. Research octane numbers (RON) of benzene and methylcyclopentane are 100 and 91, respectively, while those of cyclohexane and *n*-hexane are 83 and 25, respectively [18]. Thus the development of effective catalyst for the hydroisomerization of benzene is desired.

n-Heptane, of which RON is 0, is one of the fraction of naphtha. The skeletal isomerization of *n*-heptane to *iso*-heptane is effective to enhance RON to 42–112, but it is generally difficult because the cracking reaction through β-scission of C_7-carbenium ion intermediates readily takes place on acidic sites as a side reaction. So far there are many reports as for the isomerization of *n*-heptane [19–32]. While this reaction is much more important for the production of clean fuel, there is no industrial process.

In the present study, we performed the skeletal isomerization of *n*-heptane and hydroisomerization of benzene with Pt-heteropoly compounds and typical

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bifunctional catalysts and compared the catalytic activity and selectivity for these bifunctional catalysts. The differences in the activity and selectivity among them have been discussed on the basis of the acid strength, pore-structure, and state of Pt.

2. Experimental

2.1. Catalysts

Pt-promoted $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ ($Pt–Cs_{2.5}$) was prepared by a titration method [5,33]. An aqueous solution of $H_2PtCl_6{\cdot}6H_2O$ ($0.04\,mol\,dm^{-3}$) was added to an aqueous solution of $H_3PW_{12}O_{40}$ ($0.08\,mol\,dm^{-3}$) at room temperature. Then an aqueous solution of Cs_2CO_3 ($0.10\,mol\,dm^{-3}$) was added dropwise to the mixture at a rate of $0.1\,cm^3\,min^{-1}$ with vigorous stirring at room temperature. The obtained suspension was allowed to stand overnight at room temperature, and evaporated at 318 K to obtain solid. The loading amount of Pt was 2.0 wt.%. This catalyst will be denoted to $Pt–Cs_{2.5}$. Silica-supported $Pt–Cs_{2.5}$ was prepared from the aqueous solutions of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (abbreviated as $Cs_{2.5}$) and $H_2PtCl_6{\cdot}6H_2O$ using SiO_2 (Aerosil 300, $274\,m^2\,g^{-1}$), while $Cs_{2.5}$ was prepared from the aqueous solutions of $H_3PW_{12}O_{40}$ and Cs_2CO_3 [7]. The loading amounts of Pt and $Cs_{2.5}$ were adjusted to 2 and 20 wt.%, respectively. This is denoted as $Pt–Cs_{2.5}/SiO_2$. These heteropoly compounds were pretreated in a flow of O_2 for 2 h and then in a flow of H_2 for 1 h at 573 K.

The Pt-promoted $SO_4{}^{2-}/ZrO_2$ was prepared by an incipient wetness impregnation with $SO_4{}^{2-}/ZrO_2$ and the aqueous solution of H_2PtCl_6. $SO_4{}^{2-}/ZrO_2$ was obtained from H_2SO_4 and Zr hydroxide by the calcination at 893 K for 5 h according to the literature [34]. The surface area was $90\,m^2\,g^{-1}$ after the calcination at 893 K in air. The obtained 2 wt.% $Pt–SO_4{}^{2-}/ZrO_2$ has a surface area of $85\,m^2\,g^{-1}$ after the calcination at 573 K for 2 h. WO_3/ZrO_2 (W/Zr atomic ratio = 0.09) was prepared by an impregnation method using Zr hydroxide (Nippon Kigennso) and an aqueous solution of para-tungstate ammonium, $(NH_4)_6W_7O_{24}$ (Wako Pure Chemical Industries) [35]. The resulting solid was calcined at 1073 K (surface area, $47\,m^2\,g^{-1}$). The 2 wt.% $Pt–WO_3/ZrO_2$ was prepared similarly with the aqueous solution of $H_2PtCl_6{\cdot}6H_2O$ ($0.04\,mol\,dm^{-3}$) by the impregnation method. The 2 wt.% Pt–H-β zeolite was prepared from H-β zeolite (Süd-Chemie, $SiO_2/Al_2O_3 = 25$) by an ion-exchange using an aqueous solution of $[Pt(NH_3)_4]Cl_2$ (Wako Pure Chemical Industries) [36].

2.2. Catalytic reactions

Skeletal isomerization of *n*-heptane and hydroisomerization of benzene were carried out using a continuous flow system under an atmospheric pressure. The feed gas consisted of benzene 12.0% and H_2 88.0% or *n*-heptane 4.8% and H_2 95.2% in volume, respectively. Prior to the reaction, the catalysts were pretreated in an O_2 flow ($50\,cm^3\,min^{-1}$) for 2 h, in a He flow ($50\,cm^3\,min^{-1}$) for 10 min, and then in an H_2 flow ($50\,cm^3\,min^{-1}$) for 1 h at 573 K. The products were analyzed with an FID GC (Shimadzu GC-14B) equipped with a capillary column (WCOT Fused Silica Squalane).

3. Results and discussion

3.1. Hydroisomerization of benzene

As reported previously [37], the hydroisomerization of benzene proceeds sequentially through the hydrogenation of benzene to cyclohexane and isomerization of cyclohexane to methylcyclopentane. The isomerization of cyclohexane is a slow step, and the acidic property (acid strength and acid amount) is critical for this reaction. Fig. 1 shows the time courses of hydroisomerization of benzene over these bifunctional catalysts. In all the catalysts, the stationary conversions were obtained after at least 2 h. $Pt–Cs_{2.5}/SiO_2$ and $Pt–WO_3/ZrO_2$ gave higher conversions of benzene than $Pt–Cs_{2.5}$ and $Pt–SO_4{}^{2-}/ZrO_2$. The contact time (*W*/*F*) dependencies of the conversion of benzene and the yield of methylcyclopentane are shown in Fig. 2. It was found that the conversions were very high even at low *W*/*F* regions over $Pt–Cs_{2.5}/SiO_2$ and $Pt–WO_3/ZrO_2$. On the other hand, the conversions increased slowly over $Pt–Cs_{2.5}$ and $Pt–SO_4{}^{2-}/ZrO_2$ as the contact time increased. Contrary to the conversion, the yields of methylcyclopentane over these catalysts increased similarly with the contact time.

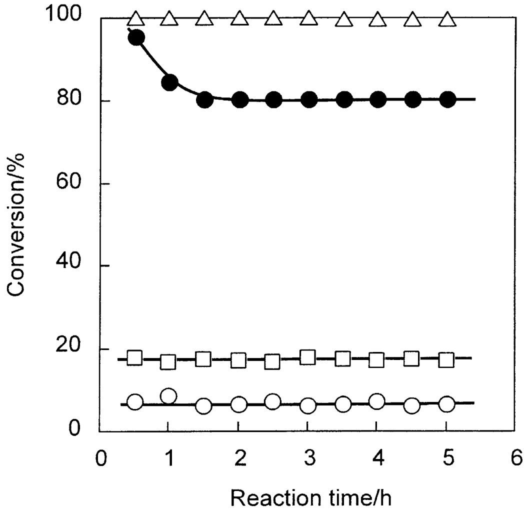

Fig. 1. Time courses of hydroisomerization of benzene: (○) Pt–$Cs_{2.5}$, (△) Pt–$Cs_{2.5}/SiO_2$, (□) Pt–SO_4^{2-}/ZrO_2, and (●) Pt–WO_3/ZrO_2. Reaction temperature: 473 K; benzene:H_2 = 12.0:88.0; $W/F = 5.1$ g h (mol of feed gas)$^{-1}$.

The selectivity and the yield of methylcyclopentane are summarized in Table 1. The yield of methylcyclopentane was in order of Pt–$Cs_{2.5}/SiO_2$ > Pt–$Cs_{2.5}$ > Pt–WO_3/ZrO_2 > Pt–SO_4^{2-}/ZrO_2. The highest activity of Pt–$Cs_{2.5}/SiO_2$ for the formation of methylcyclopentane would be brought about by the high ability for hydrogenation and the strong acid sites.

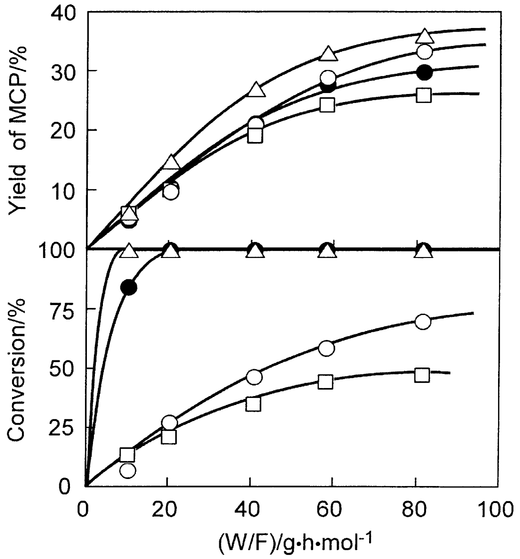

Fig. 2. W/F dependence of the conversion of benzene and yield of methylcyclopentane (MCP): (○) Pt–$Cs_{2.5}$, (△) Pt–$Cs_{2.5}/SiO_2$, (□) Pt–SO_4^{2-}/ZrO_2, and (●) Pt–WO_3/ZrO_2. Reaction temperature: 473 K.

TPD of NH_3 showed that the acid strength of WO_3/ZrO_2 was low [38]. Pt–SO_4^{2-}/ZrO_2 had the low activity for the hydrogenation of benzene (Table 1). As reported previously [1], C_7 and C_8 hydrocarbons were included as the by-products, together with *iso*-C_4 and C_3, in the isomerization of cyclohexane over Pt–$Cs_{2.5}$ and Pt–SO_4^{2-}/ZrO_2. Probably, the oligomerization of

Table 1
Catalytic data for hydroisomerization of benzene[a]

Catalyst[b]	Conversion (%)	Selectivity[c] (mol%)				Yield[d] (%)
		C_4–C_6	MCP[e]	CH[f]	C_7–C_8	
Pt–$Cs_{2.5}$[g]	69.9	0.6	47.4	51.0	1.0	33.2
Pt–$Cs_{2.5}/SiO_2$[h]	100	0.3	36.0	63.7	0	36.0
Pt–WO_3/ZrO_2	100	0.3	29.2	70.5	0	29.2
Pt–SO_4^{2-}/ZrO_2	44.5	0.3	60.6	37.4	0.7	27.0

[a] Reaction temperature: 473 K; $W/F = 81.2$ g h (mol of total feed gas)$^{-1}$.

[b] The loading amount of Pt was 2 wt.%.

[c] $100 \times n[C_n]$/[total carbon atom], where $[C_n]$ and [total carbon atom] mean the concentrations of hydrocarbons having n carbon atoms and 1 to n carbon atoms, respectively.

[d] For methylcyclopentane.

[e] Methylcyclohexane.

[f] Cyclohexane.

[g] 2 wt.% Pt–$Cs_{2.5}$.

[h] 2 wt.% Pt–20 wt.% $Cs_{2.5}$.

cyclohexene took place and cracking of the oligomer resulted in these by-products. These by-products were also observed for the hydroisomerization of benzene over Pt–$Cs_{2.5}$ and Pt–SO_4^{2-}/ZrO_2 (Table 1). The lower hydrogenation abilities and strong acidities of these catalysts (Pt–$Cs_{2.5}$ and Pt–SO_4^{2-}/ZrO_2) will be responsible for the formation of by-products. If the hydrogenation ability of Pt on these catalysts is not enough, cyclohexene formed from cyclohexyl cation or by dehydrogenation of cyclohexane will be accumulated to some extent. Thus the corresponding dimer will be formed on the surface, and it will occur on the strong acid sites.

3.2. Skeletal isomerization of n-heptane

Fig. 3 presents the time courses of skeletal isomerization of *n*-heptane over these bifunctional catalysts. The changes in the conversion with time were small for all cases. The stationary conversions were obtained after about 5 h, and thus the data were collected at 5 h. Fig. 4 shows the contact time (*W/F*) dependencies of the conversion for the isomerization of *n*-heptane. The conversion increased linearly with low *W/F* regions, and the reaction rates were estimated from the initial slopes of the curves.

Table 2 gives the reaction rate and the selectivity at 74–83% conversions. The catalytic activity obtained from the reaction rate was in the order of Pt-H-β > Pt–$Cs_{2.5}$ > Pt–SO_4^{2-}/ZrO_2 > Pt–WO_3/ZrO_2 > Pt–$Cs_{2.5}/SiO_2$, which is different from that for cyclohexane isomerization [1]. In the case of Pt–SO_4^{2-}/ZrO_2, the selectivity to *iso*-heptane, which involves monobranched and multibranched *iso*-heptane, was very low because of the cracking to propane and *iso*-butane. It is worthy to note that the selectivity to *iso*-heptane was higher over Pt–$Cs_{2.5}/SiO_2$ and Pt-H-β zeolite than over Pt–SO_4^{2-}/ZrO_2 (Table 2).

In Table 3, the detailed product distributions are compared between Pt–$Cs_{2.5}/SiO_2$ and Pt-H-β zeolite. The cracking products were exclusively C_3 and *iso*-C_4, which are formed by the β-scission of C_7-carbenium ion intermediates. The selectivity to *iso*-heptane (mono- and multibranched) is plotted against the conversion of *n*-heptane in Fig. 5. It was observed that the selectivities were very high up to about 60% conversion over the catalysts except Pt–SO_4^{2-}/ZrO_2. The selectivity started to decrease greatly at the conversion of about 80%. Fig. 5 demonstrated that Pt–$Cs_{2.5}/SiO_2$ is most selective among these catalysts.

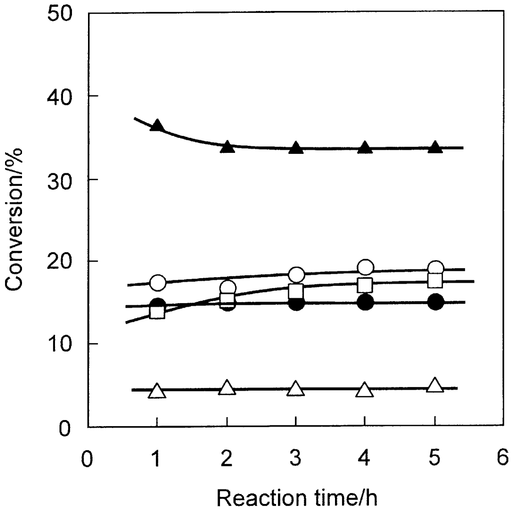

Fig. 3. Time course of skeletal isomerization of *n*-heptane: (○) Pt–$Cs_{2.5}$, (△) Pt–$Cs_{2.5}/SiO_2$, (□) Pt–SO_4^{2-}/ZrO_2, (●) Pt–WO_3/ZrO_2, and (▲) Pt–H-β zeolite. Reaction temperature: 453 K; *n*-heptane:H_2 = 4.8:95.2; *W/F* = 5.1 g h (mol of feed gas)$^{-1}$.

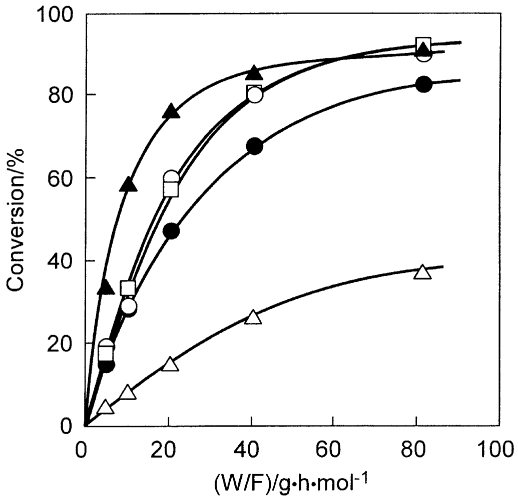

Fig. 4. *W/F* dependence of the conversion of *n*-heptane isomerization: (○) Pt–$Cs_{2.5}$, (△) Pt–$Cs_{2.5}/SiO_2$, (□) Pt–SO_4^{2-}/ZrO_2, (●) Pt–WO_3/ZrO_2, and (▲) Pt–H-β zeolite. Reaction temperature: 453 K.

Table 2
Catalytic data for skeletal isomerization of *n*-heptane[a]

Catalyst[b]	Rate[c] (mmol g^{-1} h^{-1})	Selectivity[d,e] (mol%)				Conversion (%)
		Monobranched *iso*-C_7[f]	Multibranched *iso*-C_7[g]	*iso*-C_7[h]	C_3 + *iso*-C_4	
Pt–$Cs_{2.5}$	2.0	59.7	27.0	86.7	13.3	80.3
Pt–$Cs_{2.5}$/SiO_2	0.6	69.7	27.4	97.1	2.9	73.8
Pt–SO_4^{2-}/ZrO_2	1.7	10.7	4.4	15.1	84.9	80.5
Pt–WO_3/ZrO_2	1.4	58.7	32.0	90.7	9.3	82.7
Pt-H-β zeolite	3.4	66.8	26.0	92.8	7.2	76.4

[a] Reaction temperature: 453 K.

[b] The loading amount of Pt was 2 wt.%.

[c] Estimated from the conversion-*W*/*F* dependence.

[d] $100 \times n[C_n]$/[total carbon atom], where $[C_n]$ and [total carbon atom] mean the concentrations of hydrocarbons having *n* carbon atom and 1 to *n* carbon atoms, respectively.

[e] At about 80% conversion.

[f] 2-Methylhexane (MH) + 3-MH + 3-ethylpentane.

[g] 2,2-Dimethylpentane (DMP) + 2,3-DMP + 2,4-DMP + 3,3-DMP + 2,2,3-trimethylbutane.

[h] Total C_7 = monobranched + multibranched heptanes.

Fig. 6 shows the yields of monobranched and multibranched heptanes as a function of the conversion over Pt–$Cs_{2.5}$/SiO_2 and Pt–H-β zeolite. Both the catalysts gave the similar changes of the yields. Monobranched heptanes increased up to about 70% conversion and then decreased with the conversion. Multibranched heptanes showed maxima at about 80% conversion.

One of the characteristics of Pt–$Cs_{2.5}$/SiO_2 in the *n*-heptane isomerization is the high selectivity to *iso*-heptane. It should be emphasized that the selectivity of Pt–$Cs_{2.5}$/SiO_2 was comparable to that of Pt–H-β zeolite, which is known to be efficient for this reaction [39]. On the other hand, the activity of Pt–$Cs_{2.5}$/SiO_2 was less than those of Pt–$Cs_{2.5}$ and Pt–H-β zeolite.

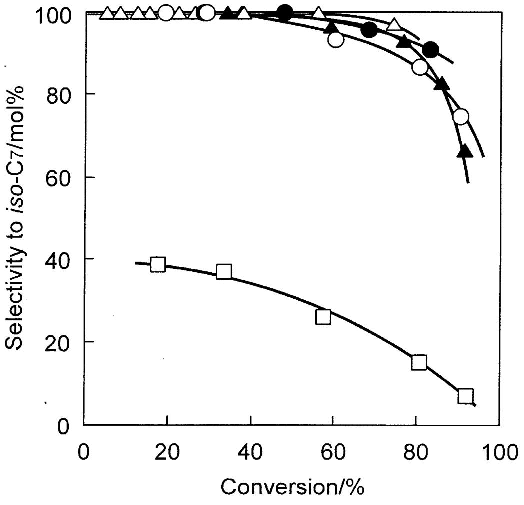

Fig. 5. Selectivity to *iso*-heptane as a function of conversion for isomerization of *n*-heptane: (○) Pt–$Cs_{2.5}$, (△) Pt–$Cs_{2.5}$/SiO_2, (□) Pt–SO_4^{2-}/ZrO_2, (●) Pt–WO_3/ZrO_2, and (▲) Pt-H-β zeolite. Reaction temperature: 453 K.

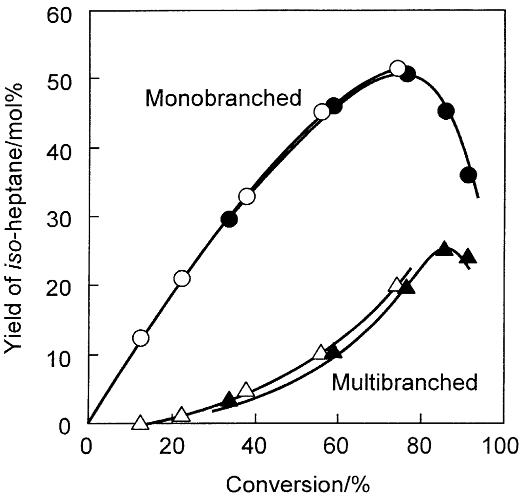

Fig. 6. Yields of *iso*-heptane on skeletal isomerization of *n*-heptane: (○) and (△) Pt–$Cs_{2.5}$/SiO_2, and (●) and (▲) Pt–H-β zeolite. Reaction temperature: 453 K.

Table 3
Product distributions of skeletal isomerization of *n*-heptane[a]

	Catalyst[b]	
	Pt–$Cs_{2.5}/SiO_2$	Pt–H-β zeolite
Conversion (%)	73.8	76.4
Rate[c] ($mmol\,g^{-1}\,h^{-1}$)	0.6	3.4
Yield of total *iso*-C_7[d]	71.7	70.9
Selectivity[e] (mol%)		
$C_1 + C_2$	0	0
C_3 + *iso*-C_4	2.9	7.2
$C_5 + C_6$	0	0
Monobranched[f] *iso*-C_7		
2-MH (42)	34.9	33.3
3-MH (52)	32.8	31.6
3-EP (65)	2.0	1.9
Multibranched[g] *iso*-C_7		
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 *iso*-C_7[d]	97.1	92.8
Octane number of products	57.6	55.0

[a] Reaction temperature: 453 K, total flow rate: $10\,ml\,min^{-1}$, $C_7:H_2 = 4.8:95.2$.

[b] The loading amount of Pt was 2 wt.%.

[c] Estimated from the conversion-*W*/*F* dependence.

[d] Total C_7 = monobranched + multibranched.

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

[f] 2-MH + 3-MH + 3-ethylpentane. The figure in the parenthesis is the RON.

[g] 2,2-DMP + 2,3-DMP + 2,4-DMP + 3,3-DMP + 2,2,3-trimethylbutane. The figure in the parenthesis is the RON.

By the supporting of Pt–$Cs_{2.5}$ on silica, the selectivity to *iso*-heptane was enhanced with the suppression of the cracking (Table 2). We presume the following three possibilities for the increase in the selectivity by the supporting of Pt and $Cs_{2.5}$ on SiO_2. The first one is decreasing in the acid strength. The change in the acid strength of $Cs_{2.5}$ by the supporting was already reported [1], though the change was not significant. Since it is considered that the cracking proceeds through β-scission of C_7-carbenium ions to propyl cation and *iso*-butene [30–32,40] and the isomerization takes place via protonated cyclopropane intermediate [40], the relative rates of these two reactions must depend on the acid strength. If the latter reaction is catalyzed by weaker acid sites, the increase in the selectivity by the supporting $Cs_{2.5}$ on SiO_2 is expected.

The second factor is the hydrogenation ability of Pt. As was demonstrated in Table 1, the hydrogenation ability of Pt–$Cs_{2.5}/SiO_2$ is higher than Pt–$Cs_{2.5}$. As was reported already [37], Pt strongly interacted with the Keggin anion, resulted in the decreasing of its hydrogenation ability. When both Pt and $Cs_{2.5}$ were supported on SiO_2, it is considered that the interaction between Pt and $Cs_{2.5}$ is weak because of the dispersion of each component. Thus it is expected that the hydrogenation ability of Pt is retained to be high on SiO_2. The high hydrogenation ability of the catalyst would decrease the content of olefins on the surface, which is the reason for suppressing the cracking reaction over Pt–$Cs_{2.5}/SiO_2$.

The third one may be the change in the pore-structure of active phase of $Cs_{2.5}$ on the catalyst. It is well known that the pores of $Cs_{2.5}$ have bimodal distribution consisting of micropores and mesopores [41,42]. In the case of skeletal isomerization of *n*-butane, the micropore-size of porous Pt-solid acids influenced greatly on the product distribution; the smaller pores tended to give cracking products [43]. Since the micropores of Pt–$Cs_{2.5}$ contributed largely to the surface area [41], these would affect the selectivity. $Cs_{2.5}$ consists of small crystallites having the size of 10 nm and forms the secondary particles of the micrometer size [41]. When Pt–$Cs_{2.5}$ was dispersed on SiO_2, the secondary particles must be smaller, although there is no evidence at present. Owing to the dispersion, the length of the pores will become shorter. This would lower the cracking to enhance the selectivity to *iso*-pentane in the skeletal isomerization of *n*-heptane.

Acknowledgements

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