

Skeletal isomerization of *n*-pentane over Pt-promoted cesium hydrogen salts of 12-tungstophosphoric acid¹

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Abstract

Two kinds of Pt-promoted Cs_{2.5}H_{0.5}PW₁₂O₄₀ (Cs_{2.5}H_{0.5}PW₁₂O₄₀ will be denoted by Cs2.5), Pt directly impregnated on Cs2.5 (Pt/Cs2.5) and a physical mixture of Cs2.5 and Pt/Al₂O₃ (Pt + Cs2.5), were used to catalyze the isomerization of *n*-pentane in the presence of hydrogen at 453–573 K. Cs2.5 showed a high initial activity but deactivated rapidly. Addition of Pt greatly suppressed the deactivation and increased the selectivity to isopentane. High stationary conversion (34.8%) and selectivity (96.9%) were obtained by using Pt + Cs2.5 at a relatively low temperature (453 K) and a low hydrogen pressure (0.05 atm, hydrogen/pentane = 1). Under these reaction conditions, the stationary activity and selectivity of Pt + Cs2.5 were significantly higher than those of Pt-promoted H-ZSM-5 or SO₄²⁻/ZrO₂. It was deduced that the remarkable effect of Pt in suppressing the catalyst deactivation was brought about by activated hydrogen, which were formed on Pt, transferred to Cs2.5, and utilized to remove carbonaceous deposits or their precursors. Increase in the hydrogen pressure decreased the initial activity probably due to a decrease in the concentration of pentenes or pentyl carbenium ion. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Branched alkanes are becoming important components of gasoline to enhance the octane-number [1,2]. In this respect, the isomerization of light alkanes catalyzed by solid acids is beneficial for the production of cleaner fuels [3]. Carbenium ions formed by strong acid sites are important intermediates for this reaction [4]. We studied in this work the isomerization of *n*-pentane catalyzed by heteropolyacids.

The isomerization of *n*-pentane is performed using Friedel–Crafts type catalysts or solid acids. Friedel–Crafts type catalysts show high activity even below 373 K, but they have disadvantages in separation and corrosivity. Pt/Al₂O₃ activated by chlorine-containing compounds and Pt/zeolites are bifunctional catalysts, which are also used commercially. They are effective for the isomerizations of *n*-pentane and *n*-hexane in the presence of hydrogen usually at a high reaction temperature (> 573 K) [5,6]. As lower temperatures are favored by the equilibrium, the catalysts which consist of noble metal and various solid acids, such as Pt/SO₄²⁻/ZrO₂ [7–9], Pt/mordenites [10], Pt/beta zeolites [11], Pt/SiO₂ + H-ZSM-5 [12], and Pt

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modified clay minerals [13], have been studied. They catalyze the skeletal isomerization of *n*-pentane in a medium temperature range (473–573 K).

Heteropoly compounds are excellent solid acid catalysts for both gas–solid and liquid–solid reaction systems [14–17]. $\text{H}_3\text{PW}_{12}\text{O}_{40}$, a typical heteropolyacid, is a strong acid and effectively catalyzes various reactions [18–20]. Ono et al. [21] and Suzuki et al. [22] observed that $\text{Pd}_x\text{H}_{3-2x}\text{PW}_{12}\text{O}_{40}/\text{SiO}_2$ catalyzed *n*-hexane isomerization in the presence of hydrogen. Recently, we found that an acidic Cs salt of $\text{H}_3\text{PW}_{12}\text{O}_{40}$, namely $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$, was very active for the skeletal isomerization of *n*-butane [23,24] and the stationary activity was enhanced greatly by the addition of platinum at low hydrogen pressures [25,26].

In the present study, Pt-promoted Cs2.5 catalysts have been applied to the isomerization of *n*-pentane. By comparing the results with those of Pt-promoted $\text{SO}_4^{2-}/\text{ZrO}_2$ and Pt-promoted H–ZSM-5, the catalytic features of Pt-promoted Cs2.5 for *n*-pentane isomerization have been discussed.

2. Experimental

2.1. Catalysts

$\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ (abbreviated as Cs2.5) was prepared by the titration of the aqueous solution of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ by an aqueous solution of Cs_2CO_3 as in the previous work [27]. Pt/Cs2.5 was prepared by the following step. An aqueous solution of H_2PtCl_6 (0.04 mol dm^{-3}) was added dropwise to an aqueous solution of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (0.06 mol dm^{-3}) at 323 K, and held for 15 min at that temperature. Then, an aqueous solution of Cs_2CO_3 (0.08 mol dm^{-3}) was added to the Pt/ $\text{H}_3\text{PW}_{12}\text{O}_{40}$ solution at 323 K with a rate of about $0.6 \text{ dm}^3 \text{ min}^{-1}$, and held overnight at room temperature. The colloidal solution obtained was evaporated to dryness at 323 K. The molar ratio of Pt:Cs:PW₁₂O₄₀ was 0.18:2.5:1.0,

where the amount of Pt corresponded to 1.0 wt.%. An amount of 1 wt.% Pt/ Al_2O_3 was prepared by the impregnation of Al_2O_3 (JRC-ALO-4, $167 \text{ m}^2 \text{ g}^{-1}$) with an aqueous solution of H_2PtCl_6 at 323 K. After the sample was calcined at 773 K for 3 h in air, it was reduced at 573 K in a hydrogen flow.

H–ZSM-5 (denoted by HZ) was obtained from Na–ZSM-5 (HSZ-820NAA (Tosoh), $\text{SiO}_2/\text{Al}_2\text{O}_3 = 23.2$, surface area = $322 \text{ m}^2 \text{ g}^{-1}$) by an ion-exchange method. Na–ZSM-5 was treated with an aqueous solution of NH_4NO_3 to form NH_4 -ZSM-5, followed by drying at 383 K. NH_4 -ZSM-5 was added to an aqueous solution of H_2PtCl_6 . After the solution was stirred at 353 K for 3 h, the solid was filtrated and washed with deionized water, and then dried at 383 K and calcined at 773 K for 3 h. $\text{SO}_4^{2-}/\text{ZrO}_2$ (denoted by SZ) was prepared by a method in the literature [28]. $\text{Zr}(\text{OH})_4$, which was obtained by the hydrolysis of ZrOCl_2 solution by NH_3 , was treated with an aqueous solution of H_2SO_4 (1 N), and the resulting solid was calcined at 773 K for 5 h in air. Pt/ $\text{SO}_4^{2-}/\text{ZrO}_2$ (abbreviated as Pt/SZ) was prepared as in the literature by the impregnation of $\text{SO}_4^{2-}/\text{Zr}(\text{OH})_4$ with an H_2PtCl_6 aqueous solution followed by drying at 383 K and calcination at 773 K in air [8].

The physically mixed catalysts of Pt/ Al_2O_3 and either of Cs2.5, HZ or SZ were prepared as follows. First, 1 wt.% Pt/ Al_2O_3 was mixed with the same amount of Cs2.5, HZ or SZ, and ground in a mortar. Then the mixture was pressed to a pellet, ground to granules, and sieved to 24–60 mesh. These catalysts are denoted by Pt + Cs2.5, Pt + HZ and Pt + SZ, respectively.

2.2. Skeletal isomerization of *n*-pentane

The isomerization of *n*-pentane was performed in a flow reactor (Pyrex, 12 mm in outer diameter). The total flow rate was $10 \text{ cm}^3 \text{ min}^{-1}$ and 1 g of the catalysts were used. Prior to the reaction, Pt/Cs2.5 was treated at 573 K in a

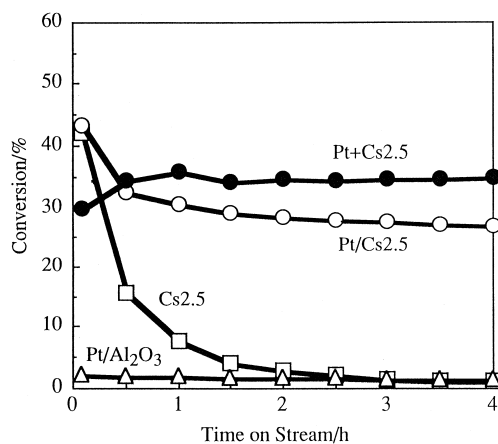


Fig. 1. Time courses of *n*-pentane isomerization at 453 K. (□) Cs2.5, (△) Pt/Al₂O₃, (○) Pt/Cs2.5, and (●) Pt + Cs2.5. Feed gas: *n*-pentane, 0.05 atm; H₂, 0.05 atm; N₂ balance. W/F, 40 g h mol⁻¹.

hydrogen flow for 2 h, and other catalysts were pretreated at the reaction temperature for 2 h in a hydrogen flow. The reaction products were analyzed with a FID GC (Hitachi GC-163) equipped with an Al₂O₃/KCl fused silica column.

3. Results

Fig. 1 shows typical time courses of the conversion of *n*-pentane over Cs2.5, Pt/Cs2.5, Pt/Al₂O₃, and Pt + Cs2.5 at 453 K with 0.05 atm of hydrogen. The selectivities are summarized in Table 1. The initial activity of Cs2.5 was very high (more than 40% conversion), but the conversion decreased considerably at the

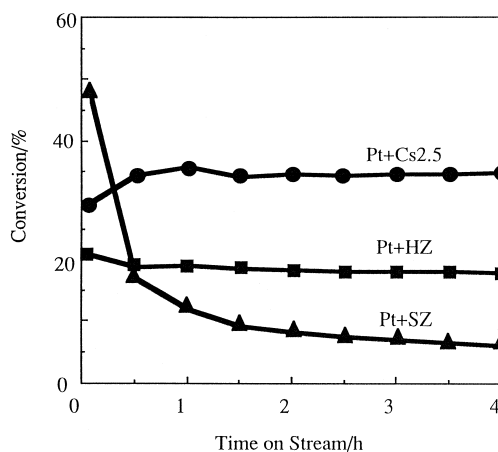


Fig. 2. Conversions of *n*-pentane with time at 453 K. (●) Pt + Cs2.5, (■) Pt + HZ, (▲) Pt + SZ. Feed gas: *n*-pentane, 0.05 atm; H₂, 0.05 atm; N₂ balance. W/F, 40 g h mol⁻¹.

initial stage of the reaction. The selectivity increased with the reaction time from the initial selectivity of 20.2 to 100% after 4 h. The catalytic activity of Pt/Al₂O₃ was very low under these reaction conditions. When Pt was added to Cs2.5, high conversions were maintained (Pt/Cs2.5: 27.1%, Pt + Cs2.5: 34.8%), and high selectivities were observed at the stationary state. Pt + Cs2.5 showed the highest stationary conversion among the four catalysts.

Pt + Cs2.5 is compared with Pt + HZ and Pt + SZ in Fig. 2. The initial activity of Pt + SZ was higher than Pt + Cs2.5, but it deactivated rapidly. Pt + Cs2.5 gave the highest stationary conversion. In Table 2, the catalytic activities

Table 1
Conversions and selectivities of isomerization of *n*-pentane at 453 K

Catalyst	Time on stream	Conversion (%)	Selectivity (%)			
			C ₃	C ₄	<i>i</i> -C ₅	C ₆₊
Cs2.5	5 min	42.1	9.4	67.4	20.2	2.4
	4 h	1.1	0	0	100	0
Pt/Al ₂ O ₃	5 min	2.1	6.2	37.4	45.7	7.0
	4 h	1.4	3.3	25.9	62.3	4.9
Pt/Cs2.5	5 min	43.2	0.5	8.3	87.0	4.2
	4 h	27.1	0.3	2.1	96.4	1.1
Pt/Al ₂ O ₃ + Cs2.5	5 min	29.9	0	0	100	0
	4 h	34.8	0	1.7	96.9	1.4

Feed gas: *n*-pentane, 0.05 atm; H₂, 0.05 atm; and N₂ balance. W/F, 40 g h mol⁻¹; catalyst, 1 g.

Table 2

Conversions and selectivities of skeletal isomerization of *n*-pentane at 453 K

Catalyst	Conversion (%)	Selectivity (%)			
		C ₃	C ₄	<i>i</i> -C ₅	C ₆₊
Pt/Al ₂ O ₃ + Cs2.5	34.8	0.0	1.7	96.9	1.4
Pt/Al ₂ O ₃ + HZSM-5	19.2	0.2	3.9	93.3	2.6
Pt/Al ₂ O ₃ + SO ₄ ²⁻ /ZrO ₂	9.4	3.7	9.1	79.4	7.8
Pt/SO ₄ ²⁻ /ZrO ₂	5.2	2.3	6.8	81.8	3.1
Pt/Al ₂ O ₃ + HZSM-5 ^a	64.7	0.0	1.8	97.6	0.8
Pt/SO ₄ ²⁻ /ZrO ₂ ^b	6.3	0.0	0.4	99.6	0.0

Feed gas: *n*-pentane, 0.05 atm; H₂, 0.05 atm; and N₂ balance; W/F, 40 g h mol⁻¹.

^aReaction temperature, 523 K. *n*-Pentane, 0.1 atm; H₂, 0.9 atm; W/F, 10 g h mol⁻¹; Pt (2.5%)/Al₂O₃, 0.2 g; and H-ZSM-5, 0.8 g. Compare with the data in Ref. [29].

^bReaction temperature: 523 K. *n*-Pentane, 0.3 atm; H₂, 0.7 atm; WHSV, 17.3 h⁻¹; and Pt, 0.5 wt.%. Compare with the data in Ref. [8].

and the product distributions of Pt-promoted solid acid catalysts are summarized. The selectivity to isopentane of Pt + Cs2.5 was comparable to that of Pt + HZ and higher than that of Pt + SZ. Pt/SZ was less active than Pt + SZ, as in the case of *n*-butane isomerization [30]. Thus Pt + Cs2.5 is an excellent catalyst for skeletal isomerization of *n*-pentane even under a low pressure of hydrogen and at a relatively low temperature. Data in Table 2 (last two lines in the table) also demonstrate that Pt + HZ and Pt/SZ used in the present study were very similar to those reported in the literature [8,12], since they showed almost the same activities and selectivities as those in the literature under the same reaction conditions.

In Fig. 3, it was confirmed that the stationary conversion for Pt + Cs2.5 increased linearly with W/F, the ratio of the catalyst weight to the flow rate of pentane. The effects of the pretreatment temperature on stationary conversion and selectivity are shown in Fig. 4. In the range of 453–573 K, the conversion and selectivity were nearly constant. The conversion decreased greatly with the pretreatment temperature above 573 K and the selectivity increased from 97 to 100%. Fig. 5 shows the effects of the Cs content of the heteropolyacid component in Pt + Cs_x

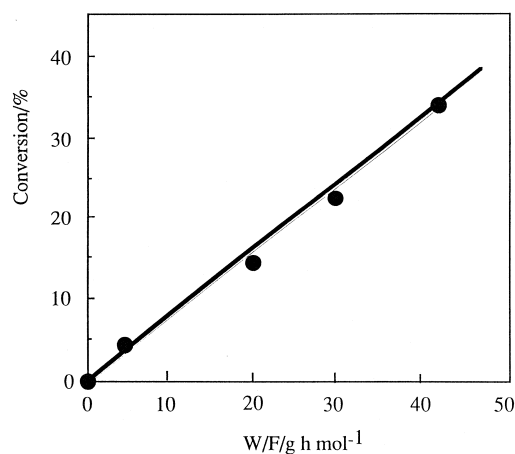


Fig. 3. Effect of W/F on conversion for *n*-pentane isomerization over Pt + Cs2.5 at 453 K. Feed gas: *n*-pentane, 0.05 atm; H₂, 0.05 atm; N₂ balance.

(*x* is defined by Cs_{*x*}H_{3-*x*}PW₁₂O₄₀). The stationary activity showed a maximum at *x* = 2.5, and the selectivity was almost constant except for a significant decrease for *x* = 3.

Results for a series of Pt + Cs2.5 catalysts having different mixing ratios, where the amount of Cs2.5 was kept constant and the partial pressure of *n*-pentane and hydrogen were 0.05 atm, are plotted in Fig. 6. With an increase in the content of Pt/Al₂O₃, the deactivation was remarkably suppressed. The effects are further demonstrated in Fig. 7. When a small amount of

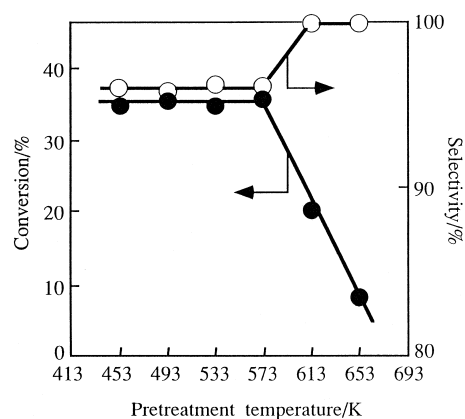


Fig. 4. Effects of pretreatment temperature on conversion and selectivity for *n*-pentane isomerization at 453 K over Pt + Cs2.5. (●) Conversion, (○) selectivity. Feed gas: *n*-pentane, 0.05 atm; H₂, 0.05 atm; N₂ balance. W/F, 40 g h mol⁻¹.

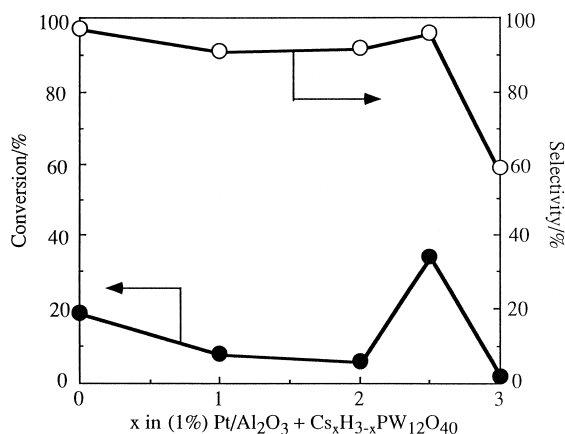


Fig. 5. Effect of Cs content of *n*-pentane isomerization over (1%) Pt/Al₂O₃ + Cs_xH_{3-x}PW₁₂O₄₀. (●) Conversion, (○) selectivity. Feed gas: *n*-pentane, 0.05 atm; H₂, 0.05 atm; N₂ balance. W/F, 40 g h mol⁻¹; reaction temperature, 453 K.

Pt/Al₂O₃ was added to Cs2.5, the stationary conversion and selectivity increased greatly, but for the amount of Pt/Al₂O₃ greater than 0.2 g, the conversion and selectivity remained constant. As for the initial stage (not shown in Fig. 7), the conversion remained almost constant but the selectivity increased greatly with increasing of Pt/Al₂O₃.

Fig. 8 shows the dependences of the reaction rates on the partial pressure of *n*-pentane. The initial rate (solid circles) was proportional to the

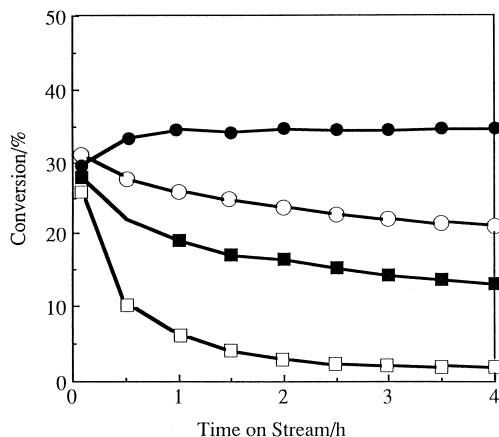


Fig. 6. Time courses of *n*-pentane isomerization over (1%) Pt/Al₂O₃ + Cs2.5. Cs2.5, 0.5 g; Pt/Al₂O₃: (□) 0 g, (■) 0.05 g, (○) 0.1 g, (●) 0.5 g. Feed gas: *n*-pentane, 0.05 atm; H₂, 0.05 atm; N₂ balance. Total flow rate, 10 cm³ min⁻¹; reaction temperature, 453 K.

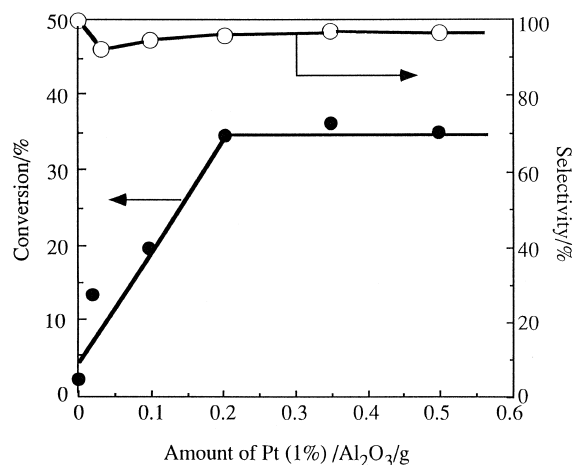


Fig. 7. Effect of Pt loading on *n*-pentane isomerization over Pt + Cs2.5 at 453 K. Feed gas: *n*-pentane, 0.05 atm; H₂, 0.05 atm; N₂ balance. Cs2.5: 0.5 g, total flow rate: 10 cm³ min⁻¹. (●) Stationary conversion (after 4 h), (○) stationary selectivity (after 4 h).

n-pentane pressure (i.e., first order in *n*-pentane) at 453 K at 0.05 atm of hydrogen pressure. However, the rate at the stationary state (solid squares) tended to level off at higher pressures of *n*-pentane (> 0.2 atm).

Fig. 9 shows the time courses of conversion of the *n*-pentane catalyzed by Pt + Cs2.5 at 453 K at various hydrogen pressures. The initial activity was very high in nitrogen, but the deac-

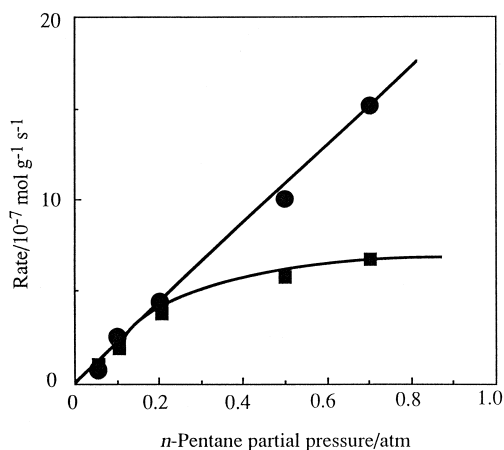


Fig. 8. Pressure dependence of *n*-pentane isomerization over Pt + Cs2.5 at 453 K. (●) Initial rate (5 min); (■) stationary rate (4 h); partial pressure of H₂, 0.05 atm; N₂ balance; catalyst, 1 g; W/F, 40 g h mol⁻¹.

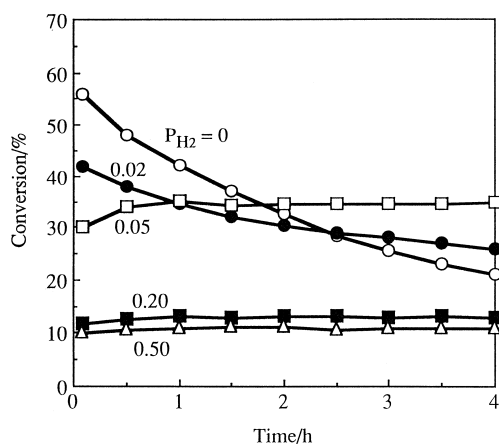


Fig. 9. Time courses of the isomerization of *n*-pentane over Pt + Cs2.5 at 453 K. Feed gas: H₂: (○) 0 atm, (●) 0.02 atm, (□) 0.05 atm, (■) 0.20 atm, (△) 0.50 atm; *n*-pentane, 0.05 atm; N₂ balance. W/F, 40 g h mol⁻¹.

tivation was serious. When the hydrogen pressure increased, the deactivation was suppressed gradually, while the initial conversion decreased. Pressure dependences of the reaction rate on hydrogen for Pt + Cs2.5 at 423, 453 and 493 K are given in Fig. 10. It was found that both the initial (after 5 min) and stationary (after 4 h) selectivities increased with the hydrogen pressure. The initial conversions decreased

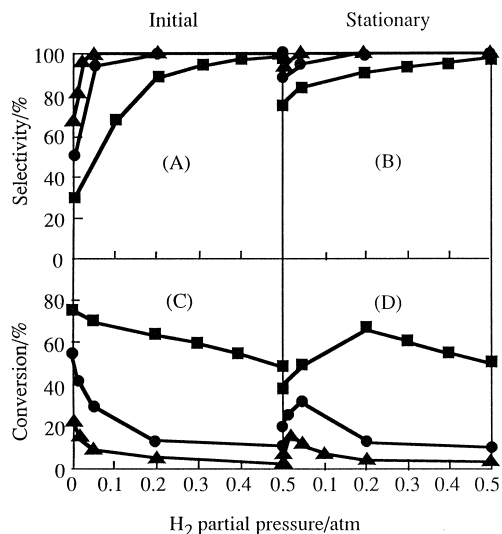


Fig. 10. Effect of H₂ partial pressure on *n*-pentane isomerization over Pt + Cs2.5. (▲) 423 K, (●) 453 K, (■) 493 K. (A) initial selectivity (after 5 min); (B) stationary selectivity (after 4 h); (C) initial conversion (after 5 min); (D) stationary conversion (after 4 h); *n*-pentane, 0.05 atm; N₂ balance; W/F, 40 g h mol⁻¹.

with the hydrogen partial pressure at each temperature, but the conversions at the stationary state showed maxima at certain hydrogen partial pressures. The maxima were observed at higher hydrogen pressures as the reaction temperature increased (Fig. 10D). The highest stationary yield was obtained at 493 K in 0.2 atm of hydrogen pressure; the conversion was 62% and the selectivity 91%. In the case of Cs2.5 (without Pt), hydrogen pressure (0–0.5 atm) little influenced the reaction. Under high hydrogen pressure (0.5 atm) at 493 K, stationary conversion was higher for Pt + SZ (63%) than Pt + Cs2.5 (52%), but the selectivity was lower for Pt + SZ (92%) than Pt + Cs2.5 (98%).

Fig. 11 shows the temperature dependence of *n*-pentane isomerization over Pt + Cs2.5. Comparison of the conversions at 5 min (open circles) and 4 h (solid circles) show that the deactivation took place above 493 K with 0.05 atm hydrogen pressure, while there was little deactivation even at 573 K when 0.5 atm hydrogen was present. By-products were C₃, C₄, C₆ and C₇ below 493 K. C₁ and C₂ were observed at 493 K and increased significantly above 533 K.

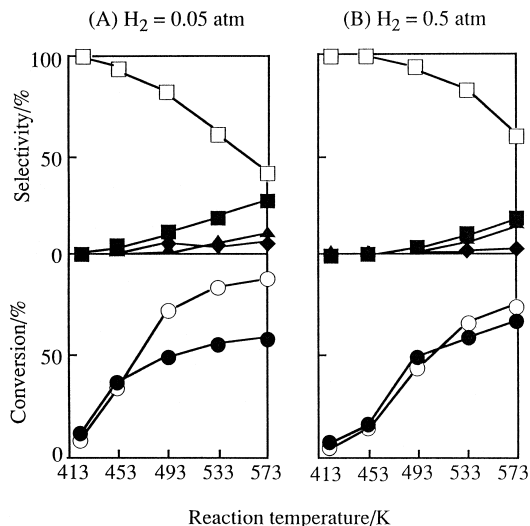


Fig. 11. Effect of reaction temperature on *n*-pentane isomerization over Pt + Cs2.5 in the H₂ pressure of: (A) 0.05 atm, (B) 0.5 atm. *n*-Pentane, 0.05 atm; W/F, 40 g h mol⁻¹. (○) Initial conversion (5 min), (●) stationary conversion (4 h), (□) selectivity to *i*-C₅ (5 min), (■) selectivity to (C₃ + C₄) (5 min), (▲) selectivity to (C₁ + C₂) (5 min), (◆) selectivity to (C₆ + C₇) (5 min).

4. Discussion

4.1. Roles of surface acidity

$\text{H}_3\text{PW}_{12}\text{O}_{40}$ is so far the strongest acid among heteropoly compounds [31]. Cs2.5 is usually the most active catalyst for the surface-type catalysis among the Cs salts of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ [16,17]. This is because the acid strength of the Cs2.5 is approximately the same as $\text{H}_3\text{PW}_{12}\text{O}_{40}$ and its surface area is very high. In consequence, the amount of surface proton of Cs2.5 for unit weight is much higher than that of $\text{H}_3\text{PW}_{12}\text{O}_{40}$. The activity change of Pt + Cs x shown in Fig. 5 correlates well with the amount of surface acid sites reported previously [16,17], indicating that the activity is primarily determined by the surface acidity.

The structure of Cs2.5 is stable and the amount of the water of crystallization is approximately null in the range of 373–573 K. But the lattice oxygens are removed with protons in the form of water above 613 K resulting in the loss of acidity [24]. This explains the results shown in Fig. 4; the activity of Pt + Cs2.5 was constant when the pretreatment temperature was below 573 K, and decreased greatly when the temperature was above 613 K.

4.2. Roles of Pt and H_2

The addition of Pt/ Al_2O_3 , which was almost inactive, to Cs2.5 did not enhance the initial activity but the stability was significantly improved (Fig. 1). When the amount of Pt/ Al_2O_3 mixed was low, the deactivation was not suppressed completely, but with a sufficient amount of Pt/ Al_2O_3 the activity rather increased in the initial stage and a high stationary activity was maintained (Fig. 6). Fig. 7 shows that 0.2 g of Pt/ Al_2O_3 was sufficient to eliminate the deactivation. The selectivity was high and nearly constant even when the amount of Pt/ Al_2O_3 was high, which shows the hydrogenolysis on Pt/ Al_2O_3 is not significant in this case under these reaction conditions. Note that the hy-

drogenolysis was not negligible in the case of *n*-butane isomerization [25,26]. Therefore, it may be stated that the remarkable effects of Pt are to increase the selectivity to isopentane and suppress the deactivation. Pt catalyzes the hydrogenation of coke or coke precursor covering acid sites by supplying hydrogen [32]. This may explain the suppression of deactivation.

As shown in Fig. 1, although the initial activity of Pt/Cs2.5 was higher than that of Pt + Cs2.5 because the content of Cs2.5 was higher (ca. 2:1). The deactivation was greater for Pt/Cs2.5 possibly due to the dispersion of Pt was lower for Pt/Cs2.5. The amount of hydrogen adsorbed per Pt for Pt/ Al_2O_3 was more than twice that for Pt/Cs2.5. Little deactivation results in the high activity of Pt + Cs2.5 after 4 h.

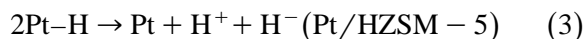
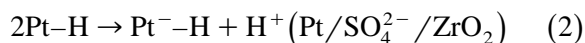
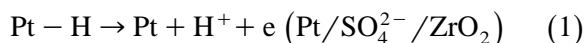
As shown in Figs. 9 and 10, the partial pressure of hydrogen showed a great influence on the reaction in the presence of both Pt/ Al_2O_3 and Cs2.5. As discussed above, hydrogen suppressed the deactivation probably by hydrogenating the coke precursor or coke which causes the deactivation of catalysts. The negative dependence of the initial rate and deactivation on the hydrogen pressure (Fig. 9) may be explained by the decrease in the concentration of pentenes in bifunctional catalysis (see below). The hydrogen pressure for the highest stationary conversion increased with the reaction temperature (Fig. 10D). This is explained in a similar way. Since the pentene concentration would increase at high temperature, a higher hydrogen pressure is required to suppress the coke formation.

4.3. Reaction mechanism

As high performance of pentane isomerization was obtained by using Pt-promoted Cs2.5 (Pt + Cs2.5 and Pt/Cs2.5), the mechanism of the reaction is an interesting subject. The main aim of the present study is to make clear the catalytic feature of the heteropoly catalysts and there is not sufficient experimental evidence to

conclude the mechanism unambiguously. However, the following discussion may be made to understand the present results. It is certain as discussed above that the acidity of Cs2.5 plays an important role and pentyl carbenium ions formed on acid sites are the key intermediates. There are several possible mechanisms for the formation of 2-pentyl cation and the conversion of isomerized 2-methylbutyl cation to isopentane. As for the formation of carbenium ions, there are three possible routes: (i) protonation to form carbonium ion followed by its transformation to carbenium ion and hydrogen; (ii) hydride abstraction of pentane by Lewis acid site; and (iii) dehydrogenation of pentane to pentene and subsequent protonation. After the isomerization of 2-pentyl cation to 2-methylbutyl cation, hydride transfer to it from *n*-pentane or hydrogen produces isopentane, or deprotonation of the cation to isopentene followed by its hydrogenation on Pt forms isopentane. Bimolecular mechanism is another possible path, and this also proceeds via carbenium ions.

There are two possible roles of Pt. One is the formation of pentene by dehydrogenation of pentane. Once pentene is formed, its isomerization to isopentene can proceed via pentyl cations on acid sites and the isomerized 2-methylbutene is easily hydrogenated to isopentane. This is the well-known bifunctional mechanism [33,34]. Negative effect of hydrogen on the initial activity favors this mechanism (Fig. 9). Another possibility is the spill-over of hydrogen atoms from Pt to the surface of solid acid and forms protons there. Hattori assumes that protons and electrons formed are trapped on solid acid in the case of Pt/SO₄²⁻/ZrO₂ (Eq. (1)) [35]. Iglesia et al. [7] and Zhang et al. [29] suggested the following mechanisms, Eqs. (2) and (3), respectively.



Rather small influence of the presence of Pt on the initial activity (Fig. 6) may not favor the classical bifunctional mechanism, in which an increase in the activity is expected, and hence favors the spill-over mechanism. In either case, the presence of Pt and hydrogen must increase the stationary activity and selectivity, by the suppression of olefin concentration by hydrogenation. This prevents the polymerization or coke formation. Another important effect is that the spilled-over active hydrogen (in any form) hydrogenates the coke or coke precursors on the solid acids and prevent deactivation.

4.4. Side reactions

The main side reactions of isomerization of *n*-pentane are usually disproportionation and hydrogenolysis. Disproportionation reaction is alkylation-cracking via a C₁₀ intermediate and is a part of 'bimolecular mechanism' [36,37], where the main by-products are C₃ + C₇ or C₄ + C₆. C₆ and C₇ are more reactive and may be cracked to smaller fragments. The hydrogenolysis converts C₅ to C₁ + C₄ or C₂ + C₃. This type of side reactions is likely dependent on the catalysts and reaction conditions. The formation of C₆ over Cs2.5 alone (Table 1) suggests the presence of disproportionation reaction by the bimolecular mechanism. The high selectivity to isopentane of Pt/Cs2.5 and Pt + Cs2.5 in the presence of sufficient hydrogen (Table 1) indicates that the disproportionation reaction or the bimolecular mechanism is not important under these reaction conditions.

The contribution of the two side reactions may be evaluated by product distributions. For Pt + Cs2.5, C₆ and C₇ were observed at 0.05 atm of hydrogen above 493 K, but not observed at 0.5 atm of hydrogen (Fig. 11). This indicates that the disproportionation reaction is suppressed by hydrogen. Hydrogenolysis reaction occurs in the high temperature region, as C₁ and C₂ were observed above 533 K both with 0.05 and 0.5 atm of hydrogen.

4.5. Comparison of various solid acid catalysts

It may be accepted that the skeletal isomerization of *n*-pentane over solid acids and Pt-promoted solid acids proceeds via carbenium ions present on acid sites and the acidic property is an important factor in controlling the reaction.

When a noble metal is added to a solid acid, the balance between acidity (strength and amount), metal amount and hydrogen partial pressure must be important for the optimum performance of the isomerization. Strong acid site would exhibit a high activity, but it tends to be deactivated easily by carbonaceous deposits. The titration by Hammett's indicators showed that acid sites stronger than -16 in H_0 function are present on the surface of SZ [28]. NH_3 TPD also indicated its strong acidity [31,38]. Accordingly, SZ is very active, but deactivates fast [39]. Hence, a high hydrogen pressure is needed to suppress the deactivation.

According to the temperature-programmed desorption of NH_3 , the acid strength of $H_3PW_{12}O_{40}$ was lower than that of SZ, but higher than that of HZ [31,38]. Another interesting feature of Cs2.5 is that the acid strength is nearly uniform [31,38]. It is therefore probable that the coke formation is not so fast as in the case of SZ and the deactivation due to coke is more easily suppressed than the case of Pt + SZ or Pt/SZ. The deactivation was smaller also for Pt + HZ, but the activity was low. The lower activity of Pt + HZ is explained by the weaker acid strength of HZ than Cs2.5. Thus the uniformity and moderate strength of the acid sites of Cs2.5 are most probably the reasons why Pt-promoted Cs2.5 showed high activity and good stability.

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