

Article

Hydroisomerization of *n*-Butane over Platinum-Promoted Cesium Hydrogen Salt of 12-Tungstophosphoric Acid

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Abstract: The hydroisomerization of *n*-butane was carried out in a fixed-bed gas-flow reactor over Pt-promoted Cs_{2.5}H_{0.5}PW₁₂O₄₀ (denoted as Cs2.5). Two kinds of catalysts, a direct impregnation of Pt on Cs2.5 (denoted as Pt/Cs2.5), as well as a mechanical mixture of Pt/Al₂O₃ and Cs2.5 (denoted as Pt/Al₂O₃+Cs2.5), were used for the hydroisomerization. Pt/Al₂O₃+Cs2.5 showed a higher stationary activity than Pt/Cs2.5 because the Pt particles supported on Al₂O₃ were much smaller than those supported on Cs2.5. The initial activity decreased with increasing H₂ pressure over Pt/Al₂O₃+Cs2.5. This indicates that the hydroisomerization of *n*-butane over Pt/Al₂O₃+Cs2.5 proceeded through a bifunctional mechanism, in which *n*-butane was hydrogenated/dehydrogenated on Pt sites and was isomerized on acid sites of Cs2.5. For the hydroisomerization of *n*-butane over Pt/Al₂O₃+Cs2.5 the hydrogenation/dehydrogenation on Pt sites is a limiting step at a low Pt loading and the isomerization on solid acid sites is a limiting step at a high Pt loading. During the reaction, hydrogen molecules were dissociated to active hydrogen atoms on Pt sites, and then the formed active hydrogen atoms moved to the solid acid sites of Cs2.5 (spillover effect) to eliminate the carbonaceous deposits and suppress the catalyst deactivation. Because Cs2.5 has suitably strong and uniformly-distributed solid acid sites, Pt/Al₂O₃+Cs2.5 showed a higher stationary activity than Pt/Al₂O₃+H-ZSM-5 and Pt/Al₂O₃+SO₄/ZrO₂ for the hydroisomerization of *n*-butane at a low H₂ pressure.

Keywords: hydroisomerization; *n*-butane; platinum; heteropolyacid; bifunctional catalyst

1. Introduction

Polyoxometalates, including heteropolyoxometalates and isopolyoxometalates, can be used as excellent catalysts for both acid-catalyzed reactions and oxidation reactions [1–15]. Among them, 12-tungstophosphoric acid ($\text{H}_3\text{PW}_{12}\text{O}_{40}$), a heteropolyacid with Keggin structure, has strong acidity and is widely used for many important catalytic reactions [1–3]. However, $\text{H}_3\text{PW}_{12}\text{O}_{40}$ is limited by its low surface area ($<10 \text{ m}^2 \text{ g}^{-1}$), which hinders its application in gas-flow fixed-bed reactions. Introduction of large counter cations (such as K, NH_4 , Cs, and so on) into $\text{H}_3\text{PW}_{12}\text{O}_{40}$ greatly increases the surface area. In particular, a partial substitution of Cs^+ for H^+ of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ substantially enhances its activity for many acid-catalyzed reactions [1–3]. $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ (abbreviated as Cs2.5) is usually the most active solid acid for many reactions among the various $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$ catalysts due to its strong acidity (similar to $\text{H}_3\text{PW}_{12}\text{O}_{40}$) and large surface area ($>200 \text{ m}^2 \text{ g}^{-1}$) [1–3].

n-Butane is an important industrial chemical which can be obtained from the petroleum industry and Fischer–Tropsch synthesis process. The skeletal hydroisomerization of *n*-butane to isobutane is a large-scale industrial process. Isobutane is utilized in the butene alkylation to isooctane as well as in the produce of MTBE (methyl *tert*-butyl ether) or ETBE (ethyl *tert*-butyl ether). All of these products are well known as non-leaded high octane gasoline additives. The hydroisomerization of *n*-butane occurs through carbenium cation intermediates, which requires the presence of strong acid in the system. Bifunctional catalysts containing metals and solid acids are promising for the hydroisomerization of *n*-butane. The metal sites provide the hydrogenation-dehydrogenation function and the acid sites provide the isomerization function. In generally, Pt is the most effective metal catalyst, and thus the development of highly active solid acid catalysts is an important task for designing bifunctional catalysts in the hydroisomerization of *n*-butane.

The commercial process for the hydroisomerization of *n*-butane is performed using the Pt/Cl– Al_2O_3 catalyst [16,17]. This process requires a continuous addition of toxic and corrosive chloride additives to restore the chloride species that leached slowly during the reaction. Therefore, it is urgent to develop a solid acid catalyst without chloride for the industrial process of *n*-butane hydroisomerization. Heteropolyacids [18–23], solid superacids (SO_4/ZrO_2 , WO_x/TiO_2 , etc.) [24–32], and acidic zeolites (H-ZSM-5, H-Beta, etc.) [33–39] have been investigated for the hydroisomerization of *n*-butane.

How to combine the Pt catalyst with the solid acid catalyst is an interesting subject in catalyst design. For preparing bifunctional catalysts, although the direct support of the Pt on the solid acid by impregnation is a universal method, the mechanical mixing Pt/ Al_2O_3 or Pt/ SiO_2 with the solid acid is a unique method. As early as fifty years ago, a mechanical mixture of Pt/ SiO_2 and aluminum silicates had been used for investigating the reaction mechanism of saturated hydrocarbons isomerization over bifunctional catalysts [40]. In the recent years, mechanical mixed catalysts have been of interest for the hydroisomerization of *n*-butane because they have some advantages compared with the directly impregnated catalysts. These advantages include the strong mechanical strength, the high molding

ability, and so on [27,28,35]. We have found that the mechanically mixed catalyst Pt/Al₂O₃+Cs2.5 showed a higher activity and a higher stability than those of the directly impregnated catalyst Pt/Cs2.5 for the hydroisomerization of *n*-pentane and *n*-hexane [5–7]. In the present study, we investigated the catalytic performance of Pt-promoted Cs2.5 catalysts for the hydroisomerization of *n*-butane and also compared Pt-promoted Cs2.5 catalysts with Pt-promoted SO₄/ZrO₂ and Pt-promoted H–ZSM-5 for the hydroisomerization of *n*-butane.

2. Experimental Section

2.1. Catalyst Syntheses

H₃PW₁₂O₄₀ was purchased from Wako Pure Chemical Company. Cs_{2.5}H_{0.5}PW₁₂O₄₀ (abbreviated as Cs2.5) was prepared by titrating an aqueous solution of H₃PW₁₂O₄₀ (0.08 mol L⁻¹) with an aqueous solution of Cs₂CO₃ (0.12 mol L⁻¹), as described in detail in the literature [41,42].

Pt/Cs2.5 was prepared from aqueous solutions H₂PtCl₆, H₃PW₁₂O₄₀ and Cs₂CO₃ as reported in the literature [18]. To an aqueous solution of H₃PW₁₂O₄₀ (0.08 mol L⁻¹, 44 mL), an aqueous solution of H₂PtCl₆ (0.04 mol L⁻¹, 16 mL) was added dropwise at 323 K to obtain a yellow solution. Then the aqueous solution of Cs₂CO₃ (0.12 mol L⁻¹, 36 mL) was added dropwise to the solution at 323 K at a rate of about 0.6 mL min⁻¹. The resulting colloidal solution 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 in Pt/Cs2.5 corresponds to 1.0 wt%.

Pt/Al₂O₃ was prepared by the impregnation of Al₂O₃ (JRC-ALO-4, 167 m² g⁻¹) in an aqueous solution of H₂PtCl₆. After drying at 373 K for 24 h, the sample was calcined at 773 K for 3 h in air. The loading of Pt for Pt/Al₂O₃ was 2.0 wt%.

The mechanically mixed catalyst of Pt/Al₂O₃ with Cs2.5 (abbreviated as Pt/Al₂O₃+Cs2.5) was prepared as follows: after grinding the mixture of 2.0 wt% Pt/Al₂O₃ with Cs2.5 (mass ratio = 1:1) in a mortar for 30 min, the powder was pressed into a disk at 40 kg cm⁻² and then sieved to 24–60 mesh. Thus the Pt loading in Pt/Al₂O₃+Cs2.5 was 1.0 wt%.

SO₄/ZrO₂ (abbreviated as SZ) was prepared using a method reported in the literature [43]. Zr(OH)₄, which was obtained by the hydrolysis of ZrOCl₂ with NH₄OH, was treated with an aqueous solution of H₂SO₄ (1 N). After filtering out the liquid (H₂SO₄ solution), the resulting solid (SO₄²⁻-Zr(OH)₄) was calcined at 773 K for 3 h in air to form SO₄/ZrO₂.

H-ZSM-5 (abbreviated as HZ) was obtained from Na-ZSM-5 (Tosoh Corporation, HSZ-820 NAA, SiO₂/Al₂O₃ = 23.2, surface area: 322 m² g⁻¹) by the ion-exchange method. Na-ZSM-5 was treated with an aqueous solution of NH₄NO₃ (1 N) to form NH₄-ZSM-5, followed by drying at 373 K for 24 h. NH₄-ZSM-5 was calcined at 773 K for 3 h to form H-ZSM-5.

The mechanically mixed catalysts of Pt/Al₂O₃ with SZ (abbreviated as Pt/Al₂O₃+SZ) and Pt/Al₂O₃ with HZ (abbreviated as Pt/Al₂O₃+HZ) were prepared using a method similar to that of Pt+Cs2.5. After grinding the mixture of 2.0 wt% Pt/Al₂O₃ with SZ or HZ (mass ratio = 1:1) in a mortar for 30 min, the powder was pressed into a disk at 40 kg cm⁻² and then sieved to 24–60 mesh. Thus the Pt loadings in either Pt/Al₂O₃+SZ or Pt/Al₂O₃+HZ were 1.0 wt%.

2.2. Characterization

Scanning electron microscope (SEM) observations were carried out using a Hitachi S-3400N instrument with an EDX. Pt metal surface and Pt particle size were measured by a H₂ adsorption method. The H₂ uptake was estimated by the extrapolation to zero pressure of the linear part of the isotherms. The difference between the total amount of adsorbed hydrogen (H_{tot}) and the reversible part of adsorbed hydrogen (H_{rev}) gave the irreversible part of adsorbed hydrogen (H_{irr}), which was used for calculating the Pt metal surface and Pt particle size. Temperature-programmed desorption of ammonia (NH₃-TPD) was observed using a BELCAT-B automatic monitor equipped with a TCD and a mass spectrometer for ammonia species detection. A part of a 0.05 g aliquot of the sample was pretreated at 673 K for 1 h under He flow (50 mL min⁻¹). After the temperature was decreased to 373 K, ammonia was adsorbed onto the surface, followed by evacuation for 1 h at 373 K to eliminate the weakly adsorbed ammonia. Then, NH₃-TPD was carried out from 373 K to 973 K (8 K min⁻¹).

2.3. Catalytic Reaction

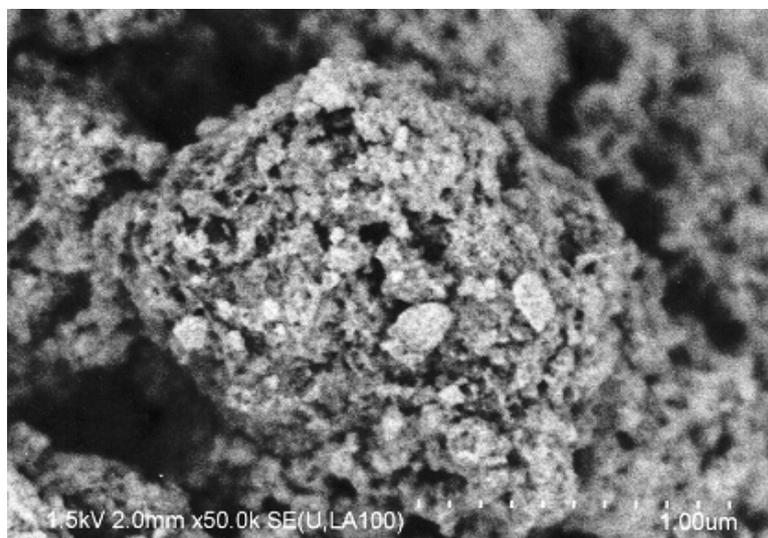
The hydroisomerizations of *n*-butane was performed in a fixed-bed quartz tubular reactor (ϕ : 8 mm) at 573 K under atmospheric pressure. In a typical reaction conditions, the total flow rate was 20 mL min⁻¹, the catalyst amount was 1 g, and the feed gas contained 10% *n*-C₄H₁₀, 10% H₂, and 80% N₂. The catalysts were pretreated in a flow of H₂ (60 mL min⁻¹) at 573 K for 1 h before reaction. During reaction, the products were analyzed with an on-line FID GC (Hitachi GC-163) equipped with an Al₂O₃/KCl fused silica capillary column.

3. Results and Discussion

3.1. Hydroisomerization of *n*-Butane over Various Catalysts

Figure 1 shows the SEM picture of the mixture of Pt/Al₂O₃ with Cs2.5 (mass ratio = 1:1) after grinding in a mortar for 30 min.

Figure 1. SEM picture of Pt/Al₂O₃+Cs2.5 (mass ratio = 1:1) after grinding for 30 min.



The size of Pt/Al₂O₃ particles was about 0.5 μm. The Cs2.5 became small powder particles adhered to the Pt/Al₂O₃ particles due to the low mechanical strength of Cs2.5. The Pt/Al₂O₃ particles and the Cs2.5 particles contacted closely with each other. Moreover, the mechanical strength was greatly strengthened after pressing the mixture into a disk at 40 kg cm⁻² for use as a catalyst.

Table 1 lists conversion and selectivity for the hydroisomerization of *n*-butane at 573 K over various catalysts. The data at 5 min could be regarded as the initial catalytic performance and the data at 5 h could be regarded as the stable catalytic performance over each catalyst.

Table 1. Catalytic hydroisomerization of *n*-butane over various catalysts at 573 K.

Catalyst	Time on stream	Conv. (%)	Selectivity (%)					
			C ₁	C ₂	C ₃	<i>i</i> -C ₄	C ₄ [≡]	C ₅₊
Pt/Al ₂ O ₃	5 min	4.2	9.7	12.6	9.3	66.2	0	2.2
	5 h	2.8	8.6	9.2	8.1	71.3	0	2.8
Cs2.5	5 min	23.5	2.6	6.8	9.6	76.5	0.8	3.7
	5 h	9.2	1.8	5.1	7.3	82.3	0.7	2.8
Pt/Cs2.5	5 min	66.1	1.9	3.2	4.7	88.4	0.7	1.0
	5 h	42.2	1.6	2.5	4.1	90.3	0.6	0.9
Pt/Al ₂ O ₃ +Cs2.5	5 min	70.3	1.2	2.4	3.9	91.2	0.6	0.6
	5 h	64.8	0.8	2.0	3.3	92.5	0.5	0.8

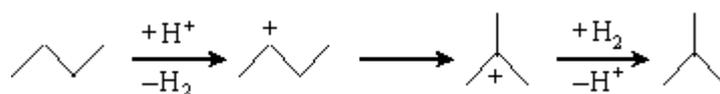
n-Butane: 0.1 atm; H₂: 0.1 atm; N₂: 0.8 atm; total flow rate: 20 mL min⁻¹.

Pt/Al₂O₃ showed a low conversion (2.8%) after 5 h on stream, which indicates that catalyst acidity is indispensable for the hydroisomerization of *n*-butane. Cs2.5 showed an initial conversion of 23.5% and an initial selectivity to isobutane of 76.5%. The solid acid Cs2.5 could catalyze the hydroisomerization of *n*-butane even without Pt [44]. However, the conversion after 5 h on stream over Cs2.5 was low (9.2%), due to the severe deactivation. The initially white Cs2.5 catalyst became black after reaction at 573 K for 5 h, indicating that carbonaceous deposits were formed on the catalyst surface, covering the acid sites of Cs2.5. This is the reason for the deactivation of the Cs2.5 catalyst. On the other hand, Pt/Cs2.5 showed an initial conversion of 66.1% and a stable conversion of 42.2%. The synergy between Pt and Cs2.5 was great, because both the initial conversion and the stable conversion were remarkably improved by introducing Pt in the solid catalyst Cs2.5. Moreover, Pt/Al₂O₃+Cs2.5 exhibited a higher stable conversion (64.8%) and a higher stable selectivity to isobutane (92.5%) than those over Pt/Cs2.5 for the hydroisomerization of *n*-butane after 5 h on stream. On the other hand, the mixture of Pt/Cs2.5 and Al₂O₃ just showed a similar performance (not shown in Table 1) to that of Pt/Cs2.5 for the hydroisomerization of *n*-butane. Thus the method for combining Pt with Cs2.5 is important for increasing the catalytic activity of bifunctional catalysts in the hydroisomerization of *n*-butane.

Scheme 1 shows the mechanism of *n*-butane hydroisomerization over a Brønsted acid catalyst. Since a heteropolyacid is a kind of typical Brønsted acid [1], it is very probable that the hydroisomerization of *n*-butane over Cs2.5 also takes place *via* this mechanism [44]. At first, a *sec*-butyl carbenium cation was formed by a step of proton addition, followed by a step of H₂

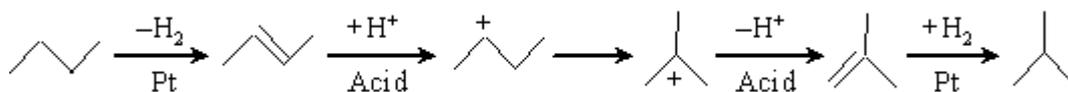
elimination. Then, the *sec*-butyl carbenium cation was transformed to a *tert*-carbenium cation by a shift of the methyl group. Finally, the *tert*-carbenium cation captured a H₂ molecule and eliminated a proton to form an isobutane molecule. All of these steps were carried out on the Brønsted acid sites.

Scheme 1. Mechanism of *n*-butane hydroisomerization over a Brønsted acid catalyst.

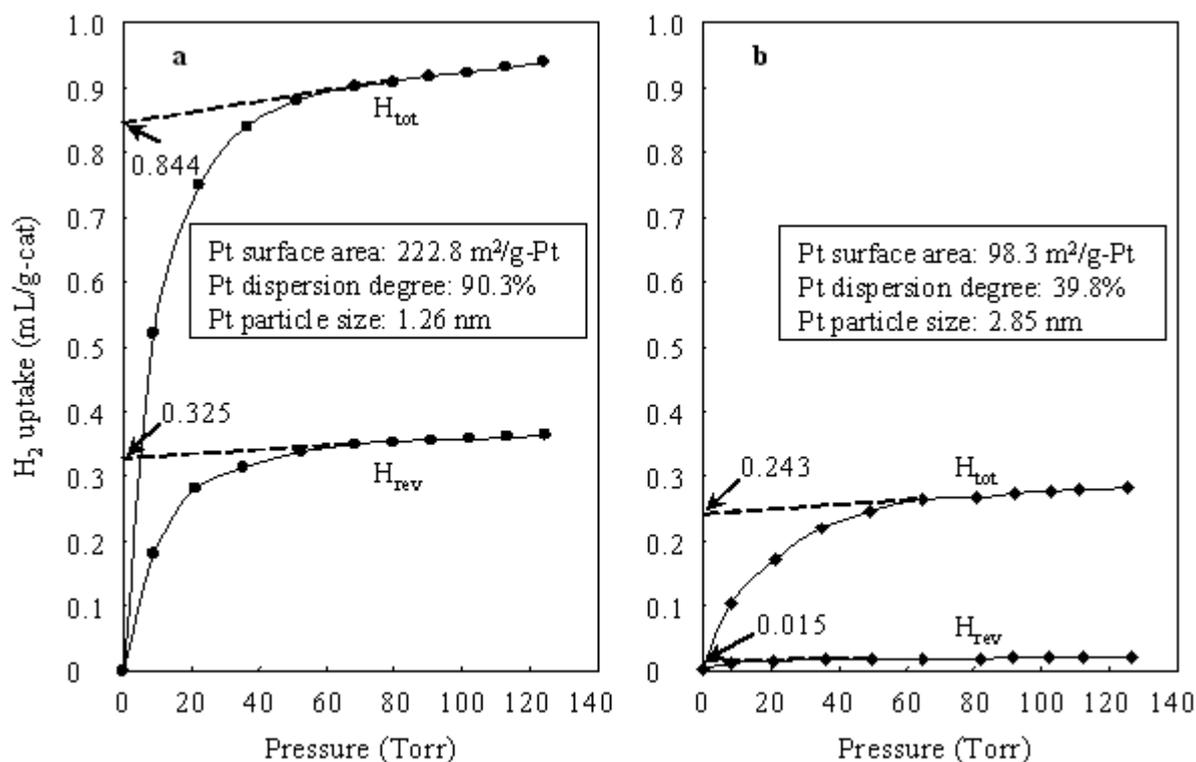


Scheme 2 shows the mechanism of *n*-butane hydroisomerization over a bifunctional catalyst containing metal and heteropolyacid [18,19]. At first, the *n*-butane molecule eliminated a H₂ molecule to form a *n*-butene molecule on the Pt sites. Then, the formed *n*-butene molecule moved to the solid acid sites to form a *sec*-butyl carbenium cation by obtaining a proton. Then, the *sec*-butyl carbenium cation was transformed to a *tert*-carbenium cation by a shift of the methyl group on the acid sites. Then, the *tert*-carbenium cation eliminated a proton to form an isobutene molecule. Finally, the isobutene molecule moved to the Pt sites to form an isobutane molecule by a process of H₂ addition.

Scheme 2. Mechanism of *n*-butane hydroisomerization over a bifunctional catalyst.



As a result, although the carbenium cation is a key intermediate in the hydroisomerization of *n*-butane over either a heteropolyacid catalyst or a bifunctional catalyst containing Pt and heteropolyacid, the path for forming the carbenium intermediate over a bifunctional catalyst is different from that over a heteropolyacid catalyst. Because the rate of formation of a carbenium species by adding proton to *n*-butene is much faster than that by adding proton to *n*-butane, in the hydroisomerization of *n*-butane the bifunctional catalysts (Pt/Cs2.5 and Pt/Al₂O₃+Cs2.5) showed much higher conversions than those observed over the monofunctional heteropolyacid catalyst Cs2.5 (Table 1). Figure 2 shows H₂ uptake by Pt/Al₂O₃+Cs2.5 and Pt/Cs2.5 at 298 K. The H₂ uptake was used as for calculating the Pt surface area, Pt dispersion degree, and Pt particle size for the samples. The total H₂ uptake contains the reversible H₂ uptake (physical absorption) and the irreversible H₂ uptake (chemical absorption). The irreversible H₂ uptake at 0 torr could be obtained from the total H₂ uptake at 0 torr and the reversible H₂ uptake at 0 torr. The obtained irreversible H₂ uptake at 0 torr was used for calculating Pt surface area and Pt dispersion degree of each sample. As shown in Figure 2, the Pt surface area and Pt dispersion degree over Pt/Al₂O₃+Cs2.5 were much larger than those over Pt/Cs2.5. Thus Al₂O₃ is a good support for Pt as comparison with Cs2.5. The high Pt dispersion degree gave Pt/Al₂O₃+Cs2.5 a higher selectivity for isobutane than that over Pt/Cs2.5 in the hydroisomerization of *n*-butane (Table 1).

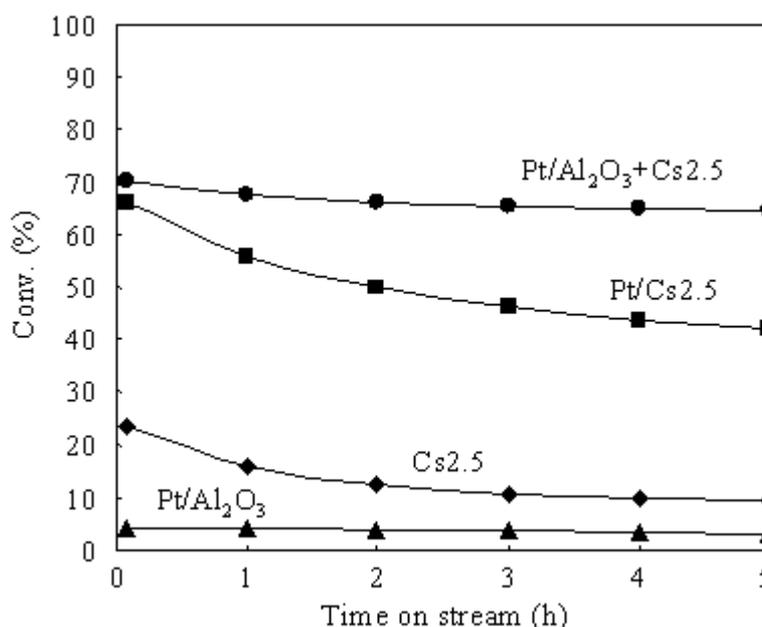
Figure 2. (a) H₂ uptake by Pt/Al₂O₃+Cs_{2.5} at 298 K. (b) H₂ uptake by Pt/Cs_{2.5} at 298 K.

Although the catalysts prepared by directly supporting Pt on solid acids (using the impregnation method) are usually used for the hydroisomerization of *n*-alkanes, the mechanical mixtures of solid acids with Pt/SiO₂ or Pt/Al₂O₃ have also been applied for the hydroisomerization of *n*-alkanes for several purposes. Firstly, a mechanical mixture of Pt/SiO₂ with aluminum silicates had been used for investigating the mechanism of *n*-alkanes hydroisomerization over Pt-promoted acid catalysts [40]. Because Pt sites and solid acid sites achieved their functions independently, the mechanical mixed catalyst showed a catalytic activity similar to that seen over the directly impregnated catalysts [40]. Secondly, because the Pt-supported zeolites have low mechanical strength and poor molding properties, the mechanical mixtures of acidic zeolites with Pt/SiO₂ or Pt/Al₂O₃ have been used to increase the mechanical strength and the molding ability of the bifunctional catalysts [33,35,45]. Thirdly, in the case of solid superacid SO₄²⁻-ZrO₂, the directly supported Pt/SO₄²⁻-ZrO₂ catalyst is not a bifunctional catalyst due to the interaction of Pt with the sulfur on the SO₄²⁻-ZrO₂ surface, while the mechanical mixed catalyst Pt/Al₂O₃+SO₄²⁻-ZrO₂ is a bifunctional catalyst [27]. Therefore, the mechanical mixed catalysts Pt/SiO₂+SO₄²⁻-ZrO₂ and Pt/Al₂O₃+SO₄²⁻-ZrO₂ showed high catalytic performances for the hydroisomerization of *n*-butane [27,28,46]. Fourthly, in the case of the heteropolyacid Cs_{2.5}H_{0.5}PW₁₂O₄₀, the mechanical mixed catalyst Pt/Al₂O₃+Cs_{2.5} showed a higher activity than that of the impregnated catalyst Pt/Cs_{2.5} for the hydroisomerization of *n*-pentane and *n*-hexane [5–7]. In the present study, we found that Pt/Al₂O₃+Cs_{2.5} showed a higher catalytic performance for the hydroisomerization of *n*-butane in comparison with Pt/Cs_{2.5}. The directly supported catalyst Pt/Cs_{2.5} had a low Pt surface area and a low Pt dispersion degree, probably because Pt²⁺ interacted with PW₁₂O₄₀³⁻ during the impregnation process.

3.2. Deactivation of Various Catalysts in the Hydroisomerization of *n*-Butane

Figure 3 shows the time courses of *n*-butane hydroisomerization over various catalysts at 573 K. Pt/Al₂O₃ showed a very low conversion due to the lack of strong acid sites. Thus Pt/Al₂O₃ can barely be used as an independent catalyst for the hydroisomerization of *n*-butane. The presence of strong acid sites in the catalyst is indispensable for the hydroisomerization of *n*-butane. Cs2.5 showed an initial conversion (after 5 min on stream) of 23.5%, but the conversion decreased to 9.2% after 5 h on stream. The carbonaceous deposits which formed by the polymerization of alkene intermediates and by-products (such as *n*-butene, *iso*-butene, and so on) covered the solid acid sites and caused a serious deactivation of the Cs2.5 catalyst. The carbonaceous deposits are hydrocarbons with large molecular weights and high ratios of C to H. When Pt was introduced into Cs2.5 (*i.e.*, Pt/Cs2.5 and Pt/Al₂O₃+Cs2.5), the deactivation was greatly repressed in the hydroisomerization of *n*-butane. Pt catalyzes the hydrogenation of the carbonaceous deposits (covered acid sites) by supplying hydrogen. In concrete, the remarkable effect of Pt in suppressing the catalyst deactivation was brought about by the activated hydrogen, which were formed on Pt, transferred to Cs2.5, and utilized to remove the carbonaceous deposits [5,6]. Pt/Al₂O₃+Cs2.5 showed a higher catalytic stability than that of Pt/Cs2.5 for the hydroisomerization of *n*-butane because the Pt dispersion degree in Pt/Al₂O₃+Cs2.5 was much higher than that in Pt/Cs2.5 (Figure 2).

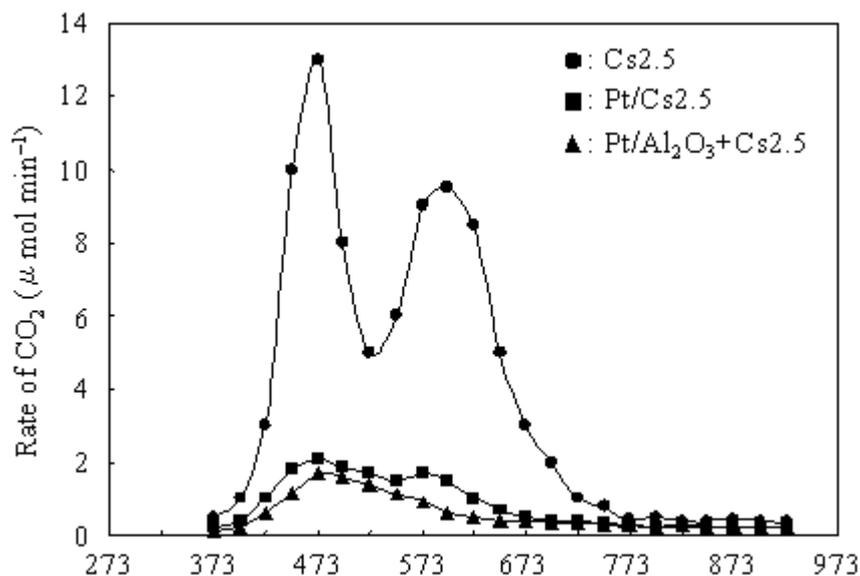
Figure 3. Time courses of the hydroisomerization of *n*-butane over various catalysts at 573 K.



The amount of the carbonaceous deposits on the used catalyst could be calculated by a temperature-programmed oxidation (TPO) method [47–49]. After the reaction was carried out over each catalyst for 5 h at 573 K, the reactor was cooled to room temperature in flowing N₂ gas. The catalyst was then treated in air flow (1.5 L h⁻¹) by increasing the temperature at 2.5 K min⁻¹ to change the carbonaceous deposits to CO₂. The formed CO₂ could be detected by a TCD GC.

Figure 4 shows the dependence of the rate of CO₂ (formed from carbonaceous deposits) on the calcination temperature over various catalysts after 5 h on stream at 573 K.

Figure 4. Dependence of the rate of CO₂ (formed from carbonaceous deposits) on the calcination temperature over various catalysts after 5 h on stream at 573 K.



An integration of the rate of CO₂ formation gave the amount of total CO₂, from which the amount of the carbonaceous deposits (after 5 h on stream at 573 K) were calculated as 4.5, 0.6, and 0.4 wt% on Cs 2.5, Pt/Cs2.5, and Pt/Al₂O₃+Cs2.5, respectively. Moreover, according to the amount of CO₂ and H₂O formed in the TPO measurement for various catalysts after 5 h on stream at 573 K, the H/C ratios were calculated as about 0.3, 0.6, and 0.7 for the carbonaceous deposits on Cs 2.5, Pt/Cs2.5, and Pt/Al₂O₃+Cs2.5, respectively. Two peaks with the highest rate at around 473 and 598 K were observed from the plot of Cs2.5. In general, the peak at lower temperature could be regarded as “soft coke” and the peak at the higher temperature could be regarded as “hard coke” [50,51]. Pt/Cs2.5 deposited both “soft coke” and “hard coke” on the surface, but the amount deposited on the Pt/Cs2.5 surface was much lower than that on the Cs2.5 surface. Thus Pt/Cs2.5 showed a much higher stability than that over Cs2.5 at 573 K (Figure 3). Further, the amount of carbonaceous deposit on Pt/Al₂O₃+Cs2.5 (0.4 wt.%) was lower than that on Pt/Cs2.5 (0.6 wt.%) after 5 h on stream. In the TPO profile of Pt/Al₂O₃+Cs2.5, the peak of “hard coke” at 573–598 K was very small and just became a shoulder peak for the peak of “soft coke” at low temperature. Therefore, Pt/Al₂O₃+Cs2.5 showed a very high stability for the hydroisomerization of *n*-butane (Figure 3).

3.3. Hydroisomerization of *n*-Butane over the Pt/Al₂O₃+Cs2.5 Catalyst

Figure 5 shows the effect of Pt amount in the Pt/Al₂O₃+Cs2.5 catalyst for the hydroisomerization of *n*-butane at 573 K. Either the pressure of *n*-butane or the pressure of H₂ was 0.1 atm. The initial conversion greatly increased when a small amount of 2 wt.% Pt/Al₂O₃ was added to Cs2.5, but it almost remained at a constant value when the amount of 2 wt.% Pt/Al₂O₃ was more than 0.1 g. On the other hand, 0.5 g of 2 wt.% Pt/Al₂O₃ was necessary for suppressing the deactivation to make the

stationary conversion close to the initial conversion. Thus Pt has two effects in the hydroisomerization of *n*-butane. Firstly, Pt achieves a hydrogenation-dehydrogenation function, which greatly improves the initial conversion over Pt/Al₂O₃+Cs2.5. It seems that 0.1 g of 2 wt.% Pt/Al₂O₃ is enough for increasing the initial conversion. Therefore, the hydrogenation-dehydrogenation on Pt sites is a limiting step when the amount of Pt/Al₂O₃ is less than 0.1 g in Pt/Al₂O₃+Cs2.5, and the isomerization on Cs2.5 sites is a limiting step when the amount of Pt/Al₂O₃ is more than 0.1 g in Pt/Al₂O₃+Cs2.5. Therefore, the speed of hydrogenation-dehydrogenation on Pt is very fast and a small amount of Pt can achieve the hydrogenation-dehydrogenation function. Secondly, Pt plays an important role for suppressing the catalyst deactivation and for maintaining the catalytic stability for the hydroisomerization of *n*-butane. The deactivation can not be completely suppressed with a small amount of Pt/Al₂O₃ (Figure 5). It needs a relatively large amount of 2 wt.% Pt/Al₂O₃ (about 0.5 g) to eliminate the catalyst deactivation over Pt/Al₂O₃+Cs2.5 for the hydroisomerization of *n*-butane.

Figure 5. Effect of Pt amount in the Pt/Al₂O₃+Cs2.5 catalyst for the hydroisomerization of *n*-butane at 573 K. (■) Initial conversion. (●) Stationary conversion. Cs2.5: 0.5 g. Reaction conditions: *n*-butane: 0.1 atm; H₂: 0.1 atm; N₂: 0.8 atm; total flow rate: 20 mL min⁻¹.

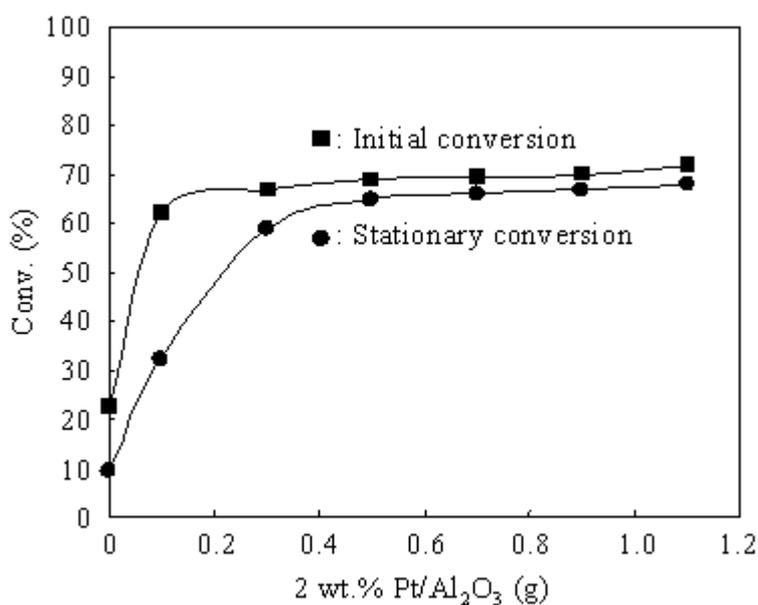


Figure 6 shows the time courses of the hydroisomerization of *n*-butane over Pt/Al₂O₃+Cs2.5 at 573 K under various H₂ pressures. The partial pressure of *n*-butane was 0.1 atm and the partial pressure of H₂ was changed from 0 to 0.5 atm. Under a N₂ atmosphere (P_{H₂} = 0), the initial conversion was very high, but the deactivation was serious. With increasing H₂ pressure, the deactivation was gradually suppressed, but the initial conversion decreased. Thus H₂ has two effects in the hydroisomerization of *n*-butane: decreasing the initial conversion and suppressing the catalyst deactivation. Actually, H₂ plays two roles in the hydroisomerization of *n*-butane over bifunctional catalysts. One role of H₂ is the hydrogenation of isobutene to isobutane on Pt sites (the last step in Scheme 2). According to Scheme 2, the first step is the dehydrogenation of *n*-butane to *n*-butene for the hydroisomerization of *n*-butane over a bifunctional catalyst. Under a high H₂ partial pressure, the

equilibrium of the dehydrogenation step shifts to *n*-butane, which causes the decrease of the concentration of *n*-butene intermediates in the reaction system. As a result, because the presence of H₂ is not favorable for the dehydrogenation step in the hydroisomerization of *n*-butane (the first step in Scheme 2), the initial conversion decreases with increasing H₂ pressure over Pt/Al₂O₃+Cs2.5. Another role of H₂ in the hydroisomerization of *n*-butane over bifunctional catalysts is the suppression of catalyst deactivation. As discussed above, the carbonaceous deposits that formed on the catalyst surface cause the catalyst deactivation. H₂ molecules can form active H atoms on Pt sites during the reaction. The formed active H atoms shift (spillover) to the acid sites and hydrogenate the carbonaceous deposits on the acid sites of Cs2.5. Therefore, the catalyst deactivation can be suppressed by increasing H₂ pressure in the hydroisomerization of *n*-butane over Pt/Al₂O₃+Cs2.5.

Figure 6. Time courses of the hydroisomerization of *n*-butane over Pt/Al₂O₃+Cs2.5 at 573 K under various H₂ pressures. *N*-butane: 0.1 atm; N₂: balance; total flow rate: 20 mL min⁻¹.

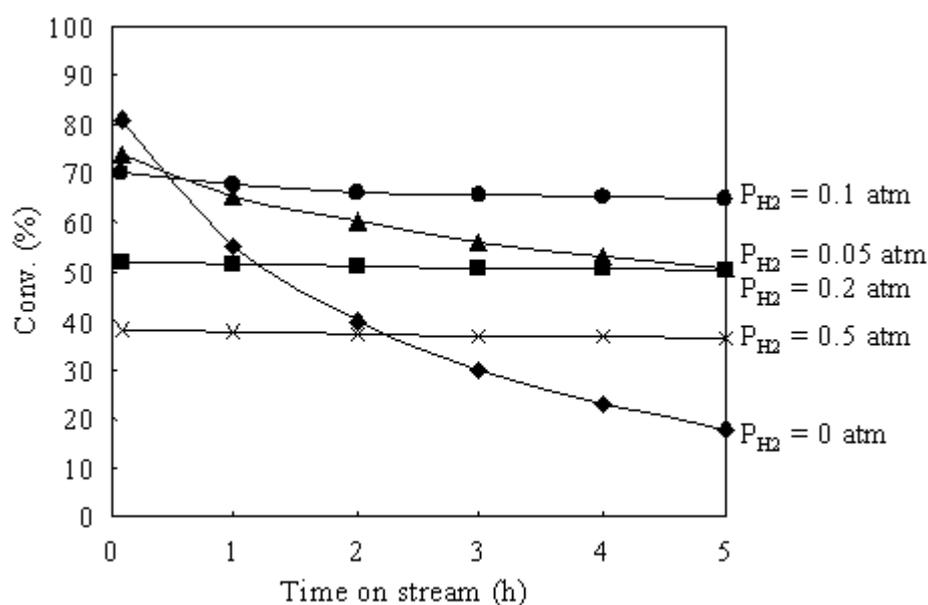
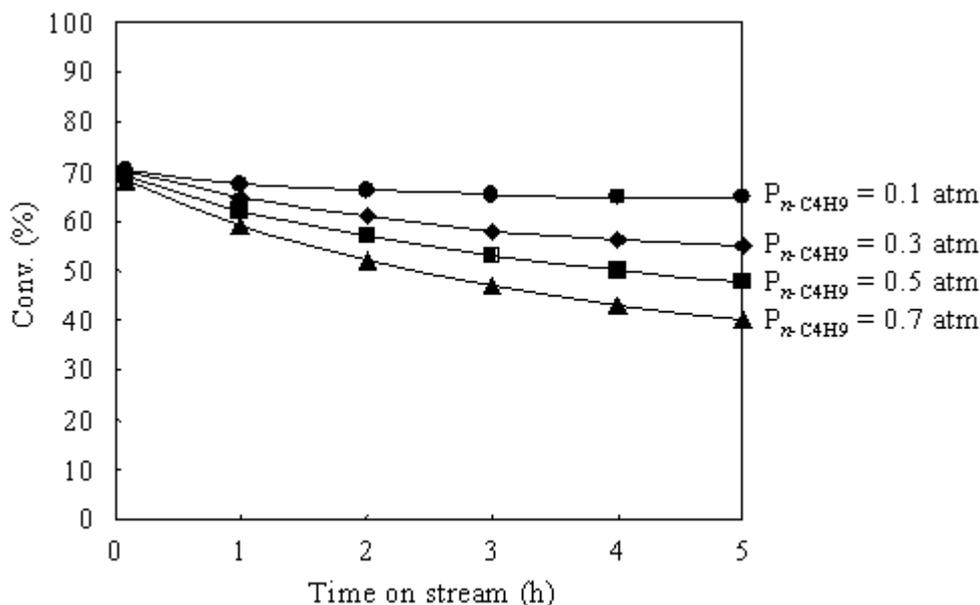


Figure 7 shows the time courses of the *n*-butane hydroisomerization over Pt/Al₂O₃+Cs2.5 at 573 K under various *n*-butane pressures. The partial pressure of H₂ was 0.1 atm and the partial pressure of *n*-butane was changed from 0.1 to 0.7 atm.

The initial conversions over Pt/Al₂O₃+Cs2.5 showed almost the same values under various *n*-butane pressures. This implies that the initial rate is proportional to the *n*-butane pressure (*i.e.*, first order in *n*-butane). Thus the “bimolecular mechanism” (by alkylation-cracking a C₈ intermediate) is not important for the hydroisomerization of *n*-butane over Pt/Al₂O₃+Cs2.5 [6,43]. On the other hand, the conversion after 5 h on stream decreased with increasing the *n*-butane pressure. The increase of *n*-butane pressure means the decrease in the ratio of H₂ to *n*-butane in the feed gas, which caused the catalyst deactivation during the reaction. Therefore, it needs a high H₂ pressure to maintain the catalyst stability for the *n*-butane hydroisomerization over Pt/Al₂O₃+Cs2.5 under a high partial pressure of *n*-butane.

Figure 7. Time courses of the *n*-butane hydroisomerization over Pt/Al₂O₃+Cs2.5 at 573 K under various *n*-butane pressures. H₂: 0.1 atm; N₂ balance; total flow rate: 20 mL min⁻¹.



3.4. Comparison of Various Bifunctional Catalysts for the Hydroisomerization of *n*-Butane

Table 2 lists the results obtained in the hydroisomerization of *n*-butane with various bifunctional catalysts. We compared the Pt/Al₂O₃+Cs2.5 catalyst with the catalysts of Pt/Al₂O₃+SZ and Pt/Al₂O₃+HZ in this study because both Pt-promoted solid super acid SZ (SO₄²⁻-ZrO₂) and Pt-promoted acidic zeolite HZ (H-ZSM-5) have been reported as effective catalysts for the hydroisomerization of *n*-butane [24–35].

Table 2. Comparison of various bifunctional catalysts for the hydroisomerization of *n*-butane.

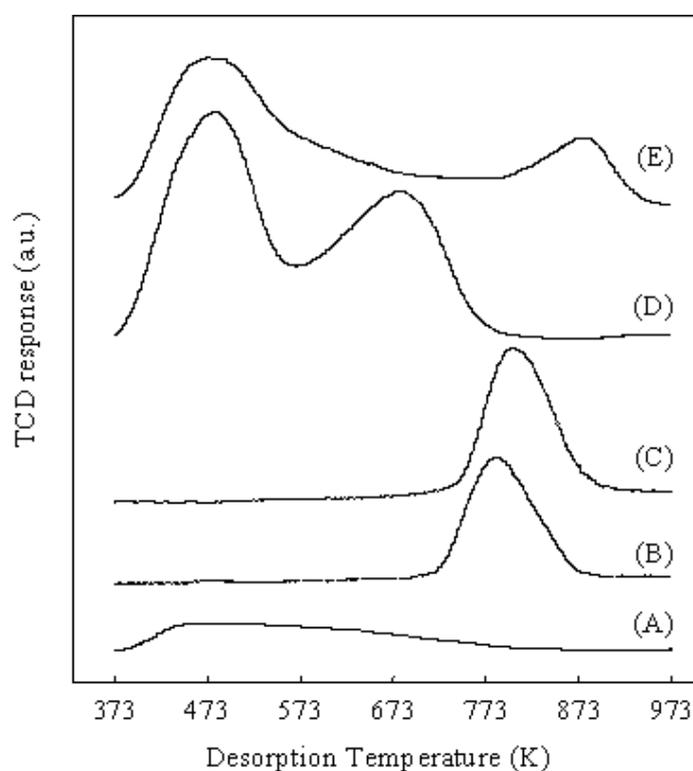
Catalyst	Time on stream	Conv. (%)	Selectivity (%)					
			C ₁	C ₂	C ₃	<i>i</i> -C ₄	C ₄ ⁼	C ₅₊
Pt/Al ₂ O ₃ +Cs2.5	5 min	70.3	1.2	2.4	3.9	91.2	0.6	0.6
	5 h	64.8	0.8	2.0	3.3	92.5	0.5	0.8
Pt/Al ₂ O ₃ +SZ	5 min	77.6	7.7	10.6	14.3	61.2	1.3	4.8
	5 h	20.5	4.6	7.2	10.1	71.7	1.0	5.2
Pt/Al ₂ O ₃ +HZ	5 min	39.7	2.7	3.1	5.7	87.1	0.9	0.5
	5 h	32.2	1.8	3.3	4.6	88.7	1.1	0.4

Reaction temperature: 573 K; *n*-butane: 0.1 atm; H₂: 0.1 atm; N₂: 0.8 atm; catalyst: 1 g; total flow rate: 20 mL min⁻¹.

Pt/Al₂O₃+Cs2.5, Pt/Al₂O₃+SZ and Pt/Al₂O₃+HZ had the same Pt dispersion because the Pt metal was supported on Al₂O₃ for all three catalysts. Therefore, the difference of solid acids (Cs2.5, SZ, and HZ) determined the difference of catalytic performances for the hydroisomerization of *n*-butane over various catalysts. As shown in Table 2, Pt/Al₂O₃+Cs2.5 showed the highest conversion (64.8%) and

the highest selectivity for isobutane (92.5%) among the various catalysts after 5 h on stream. Pt/Al₂O₃+SZ showed the highest initial conversion (77.6%), but the conversion rapidly decreased to 20.5% after 5 h on stream. Moreover, the selectivity for isobutane over Pt/Al₂O₃+SZ was low. Pt/Al₂O₃+HZ showed lower conversion and selectivity than those over Pt/Al₂O₃+Cs2.5. As a result, Pt/Al₂O₃+Cs2.5 is the best catalyst for the hydroisomerization of *n*-butane at a low H₂ pressure (0.1 atm). Brønsted acid sites in Cs2.5 contributed to the acid function of Pt/Al₂O₃+Cs2.5 for the hydroisomerization of *n*-butane since heteropolyacids are pure Brønsted acids without Lewis acid sites [1]. Figure 8 shows the NH₃-TPD profiles of various catalysts. The NH₃-TPD is a powerful tool for measuring the acidic strength of a solid acid. The NH₃ molecules desorbed from the weak acid sites at low temperatures and desorbed from the strong acid sites at high temperatures.

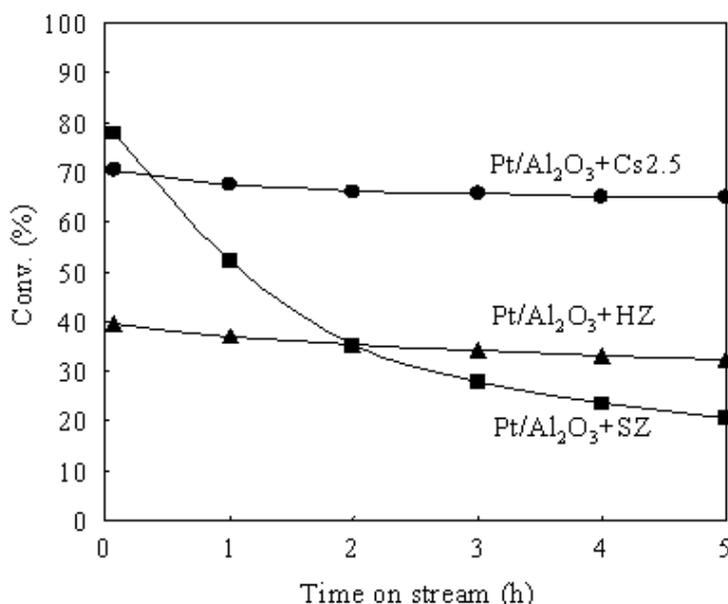
Figure 8. NH₃-TPD profiles of various catalysts. (A): Pt/Al₂O₃; (B): Pt/Cs2.5; (C): Pt/Al₂O₃+Cs2.5; (D): Pt/Al₂O₃+HZ; (E): Pt/Al₂O₃+SZ.



Pt/Al₂O₃ showed a weak and broad peak at about 473 K in the NH₃-TPD profile, indicating that the acid sites in Pt/Al₂O₃ are very weak. Although Pt/Cs2.5 and Pt/Al₂O₃+Cs2.5 showed the peaks with similar shape in the NH₃-TPD profiles, the maximum temperature of NH₃ desorption from Pt/Cs2.5 was slightly lower than that from Pt/Al₂O₃+Cs2.5. Thus the acidic strength of Pt/Cs2.5 was slightly weaker than that of Pt/Al₂O₃+Cs2.5. This is the reason that Pt/Al₂O₃+Cs2.5 showed a higher initial conversion than that over Pt/Cs2.5 (Figure 3). The decrease of the acid strength of Pt/Cs2.5 probably because the ion exchange of Pt²⁺ with H⁺ in Cs_{2.5}H_{0.5}PW₁₂O₄₀ occurred in the impregnation stage of the synthesis of Pt/Cs2.5. For a solid acid, the strongest acid sites provide its main character for the acid-catalyzed reactions. The peak at the maximum temperature in the NH₃-TPD profile corresponds to the strongest acid sites and thus it determines the acidic strength of a solid acid. According to the

peak position at the maximum temperature in the NH_3 -TPD profile of various samples (Figure 8), the acidic strength of various catalysts was in an order of $\text{Pt}/\text{Al}_2\text{O}_3+\text{SZ} > \text{Pt}/\text{Al}_2\text{O}_3+\text{Cs}2.5 > \text{Pt}/\text{Cs}2.5 > \text{Pt}/\text{Al}_2\text{O}_3+\text{HZ} > \text{Pt}/\text{Al}_2\text{O}_3$. $\text{Pt}/\text{Al}_2\text{O}_3+\text{HZ}$ showed two peaks at around 473 K and 673 K in the NH_3 -TPD profile, while $\text{Pt}/\text{Al}_2\text{O}_3+\text{SZ}$ showed two peaks at around 473 K and 873 K in the NH_3 -TPD profile. These results indicate that both $\text{Pt}/\text{Al}_2\text{O}_3+\text{HZ}$ and $\text{Pt}/\text{Al}_2\text{O}_3+\text{SZ}$ have two types of acid sites: weak acid sites and strong acid sites. The hydroisomerization of *n*-butane occurs through carbenium cation intermediates which are easy to be formed on the strong acid sites. Thus the strong acid sites provide the main effect for the catalytic performances over $\text{Pt}/\text{Al}_2\text{O}_3+\text{HZ}$ and $\text{Pt}/\text{Al}_2\text{O}_3+\text{SZ}$. However, the weak acid sites also catalyze the reaction although the reaction rate is low. Because the products formed from the strong acid sites and the weak acid sites are different, the broadly distributed acid sites caused the decrease of the selectivity for isobutane over $\text{Pt}/\text{Al}_2\text{O}_3+\text{HZ}$ and $\text{Pt}/\text{Al}_2\text{O}_3+\text{SZ}$ (Table 2). On the other hand, either $\text{Pt}/\text{Cs}2.5$ or $\text{Pt}/\text{Al}_2\text{O}_3+\text{Cs}2.5$ showed only one peak in the NH_3 -TPD profile, implying that the strength of the acid sites were distributed uniformly on the surfaces of $\text{Pt}/\text{Cs}2.5$ and $\text{Pt}/\text{Al}_2\text{O}_3+\text{Cs}2.5$. The uniform acid strength gave $\text{Pt}/\text{Cs}2.5$ and $\text{Pt}/\text{Al}_2\text{O}_3+\text{Cs}2.5$ high selectivity for isobutane in the hydroisomerization of *n*-butane (Table 1). Figure 9 shows the time courses of various bifunctional catalysts for the hydroisomerization of *n*-butane at 573 K. Either the pressure of *n*-butane or the pressure of H_2 was 0.1 atm.

Figure 9. Time courses various bifunctional catalysts for the hydroisomerization of *n*-butane at 573 K. (●) $\text{Pt}/\text{Al}_2\text{O}_3+\text{Cs}2.5$, (■) $\text{Pt}/\text{Al}_2\text{O}_3+\text{SZ}$, (▲) $\text{Pt}/\text{Al}_2\text{O}_3+\text{HZ}$.



For a bifunctional catalyst in the hydroisomerization of *n*-alkanes, the balance between acid and metal is very important for obtaining the optimum performance [52,53]. The acid strength is an important factor for controlling the activity and the selectivity in the hydroisomerization of *n*-alkanes. Strong acids usually exhibit high activity but also usually show low selectivity and serious deactivation.

As shown in Figure 9, the initial conversion was in the order $\text{Pt}/\text{Al}_2\text{O}_3+\text{SZ} > \text{Pt}/\text{Al}_2\text{O}_3+\text{Cs}2.5 > \text{Pt}/\text{Al}_2\text{O}_3+\text{HZ}$. This order coincided with the order of the acid strength of the various catalysts.

Moreover, Pt/Al₂O₃+SZ showed a serious deactivation under a low H₂ pressure (0.1 atm) and the activity after 5 h on stream was low. A high H₂ pressure is need for the hydroisomerization of *n*-butane over the Pt-promoted SZ (SO₄²⁻-ZrO₂) catalysts [25–31]. Actually, the deactivation of Pt/Al₂O₃+SZ could be suppressed under a high H₂ pressure of 0.7 atm. Moreover, because the conversion over Pt/Al₂O₃+Cs2.5 decreased with increasing H₂ pressure (Figure 6), Pt/Al₂O₃+SZ showed a higher stationary conversion than that over Pt/Al₂O₃+Cs2.5 under a high H₂ pressure of 0.7 atm. On the contrary, Pt/Al₂O₃+Cs2.5 showed a higher stationary conversion than that over Pt/Al₂O₃+SZ under a low H₂ pressure of 0.1 atm (Figure 9). Thus Pt/Al₂O₃+Cs2.5 is a good catalyst under low H₂ pressures and Pt/Al₂O₃+SZ is a good catalyst under high H₂ pressures for the hydroisomerization of *n*-butane. In comparison with Pt/Al₂O₃+SZ, using Pt/Al₂O₃+Cs2.5 as a catalyst for the hydroisomerization of *n*-butane decreases the cost of the process (because H₂ is much more expensive than N₂) and improves the safety of the operation (because a gas stream containing a large amount of H₂ is very dangerous).

4. Conclusions

By introducing Pt in Cs_{2.5}H_{0.5}PW₁₂O₄₀, the activity and the selectivity for isobutane in the hydroisomerization of *n*-butane were greatly increased. Because the Pt surface area and Pt dispersion degree of Pt/Al₂O₃ are much larger than those of Pt/Cs2.5, the mechanical mixed catalyst Pt/Al₂O₃+Cs2.5 showed a higher stationary conversion than that over the directly supported catalyst Pt/Cs2.5. Moreover, Pt/Al₂O₃+Cs2.5 showed a higher initial conversion than that over Pt/Cs2.5 because the acid strength of Pt/Cs2.5 was lower than that of Pt/Al₂O₃+Cs2.5 (due to the ion exchange of Pt²⁺ with H⁺ in the stage of impregnation). Comparing with Pt/Al₂O₃+HZ, Pt/Al₂O₃+Cs2.5 showed a higher activity (due to the stronger acid strength of Cs2.5) and a higher selectivity for isobutane (due to the uniformly-distributed acid sites on Cs2.5). Pt/Al₂O₃+SZ showed the highest initial conversion among various catalysts, but the activity decreased rapidly under a low H₂ pressure (due to the excessively strong acidity of SO₄²⁻-ZrO₂). As a result, Pt/Al₂O₃+Cs2.5 is an excellent catalyst for the hydroisomerization of *n*-butane under a low H₂ pressure because Pt/Al₂O₃ has highly dispersed Pt particles and Cs_{2.5}H_{0.5}PW₁₂O₄₀ has properly strong and uniformed distributed solid acid sites.

References

1. Okuhara, T.; Mizuno, N.; Misono, M. Catalytic chemistry of heteropoly compounds. *Adv. Catal.* **1996**, *41*, 113–252.
2. Okuhara, T.; Mizuno, N.; Misono, M. Catalysis by heteropoly compounds—Recent developments. *Appl. Catal. A: Gen.* **2001**, *222*, 63–77.
3. Misono, M. Unique acid catalysis of heteropoly compounds (heteropolyoxometalates) in the solid state. *Chem. Commun.* **2001**, *13*, 1141–1152.
4. Guo, Y.; Hu, C. Heterogeneous photocatalysis by solid polyoxometalates. *J. Mol. Catal. A: Chem.* **2007**, *262*, 136–148.
5. Liu, Y.; Koyano, G.; Misono, M. Hydroisomerization of *n*-hexane and *n*-heptane over platinum-promoted Cs_{2.5}H_{0.5}PW₁₂O₄₀ (Cs2.5) studied in comparison with several other solid acids. *Top. Catal.* **2000**, *11*, 239–246.
6. Liu, Y.; Na, K.; Misono, M. Skeletal isomerization of *n*-pentane over Pt-promoted cesium hydrogen salts of 12-tungstophosphoric acid. *J. Mol. Catal. A: Chem.* **1999**, *141*, 145–153.

7. Liu, Y.; Koyano, G.; Na, K.; Misono, M. Isomerization of *n*-pentane and *n*-hexane over cesium hydrogen salt of 12-tungstophosphoric acid promoted by platinum. *Appl. Catal. A: Gen.* **1998**, *166*, 263–265.
8. Liu, Y.; Murata, K.; Hanaoka, T.; Inaba, M.; Sakanishi, K. Syntheses of new peroxopolyoxometalates intercalated layered double hydroxides for propene epoxidation by molecular oxygen in methanol. *J. Catal.* **2007**, *248*, 277–287.
9. Liu, Y.; Murata, K.; Inaba, M. Direct oxidation of benzene to phenol by molecular oxygen over catalytic systems containing Pd(OAc)₂ and heteropolyacid immobilized on HMS or PIM. *J. Mol. Catal. A: Chem.* **2006**, *256*, 247–255.
10. Liu, Y.; Murata, K.; Inaba, M.; Mimura, N. Direct epoxidation of propylene by molecular oxygen over Pd(OAc)₂-[(C₆H₁₃)₄N]₃{PO₄[W(O)(O₂)₂]₄}-CH₃OH catalytic system, *Appl. Catal. B: Environ.* **2005**, *58*, 51–59.
11. Liu, Y.; Murata, K.; Inaba, M. Liquid-phase oxidation of benzene to phenol by molecular oxygen over transition metal substituted polyoxometalate compounds. *Catal. Commun.* **2005**, *6*, 679–683.
12. Liu, Y.; Murata, K.; Inaba, M. Direct epoxidation of propylene by molecular oxygen over catalyst system containing palladium and peroxo-heteropoly compound in methanol. *Chem. Commun.* **2004**, 582–583.
13. Liu, Y.; Murata, K.; Inaba, M.; Mimura, N. Selective oxidation of propylene to acetone by molecular oxygen over M_{x/2}H_{5-x}[PMo₁₀V₂O₄₀]/HMS (M = Cu²⁺, Co²⁺, Ni²⁺). *Catal. Commun.* **2003**, *4*, 281–285.
14. Liu, Y.; Murata, K.; Inaba, M.; Nakajima, H.; Koya, M.; Tomokuni, K. Catalytic oxidation of cyclohexene by molecular oxygen over isopolyoxometalates. *Chem. Lett.* **2004**, *33*, 200–201.
15. Liu, Y.; Murata, K.; Inaba, M. Epoxidation of propylene with molecular oxygen in methanol over a peroxo-heteropoly compound immobilized on palladium exchanged HMS. *Green Chem.* **2004**, *6*, 510–515.
16. Adeeva, V.; Sachtler, W.M.H. Mechanism of butane isomerization over industrial isomerization catalysts. *Appl. Catal. A: Gen.* **1997**, *163*, 237–243.
17. Behaviour, S. Influence of hydrogen chloride addition on the catalytic isomerization activity of chlorinated alumina and chlorinated platinum-alumina solids. *J. Chem. Soc. Faraday Trans.* **1990**, *86*, 567–570.
18. Na, K.; Okuhara, T.; Misono, M. Catalysis by heteropoly compounds. 34. Skeletal isomerization of *n*-butane over Pt- or Pd-promoted cesium hydrogen salts of 12-tungstophosphoric acid. *J. Catal.* **1997**, *170*, 96–107.
19. Na, K.; Iizaki, T.; Okuhara, T.; Misono, M. Molecular design of solid acid catalysts. Isomerization of *n*-butane catalyzed by acidic cesium salts of 12-tungstophosphoric acid combined with platinum. *J. Mol. Catal. A: Chem.* **1997**, *115*, 449–455.
20. Ma, Z.; Hua, W.; Ren, Y.; He, H.; Gao, Z. *n*-Butane isomerization over Cs-salts of H₃PW₁₂O₄₀: A mechanistic study by ¹³C MAS NMR. *Appl. Catal. A: Gen.* **2003**, *256*, 243–250.
21. Zou, Y.; Yue, B.; Zhang, B.; He, H. Solid synthesis of Cs_xH_{3-x}PW₁₂O₄₀ salts and their catalytic activity for the isomerization of *n*-butane. *Chem. Lett.* **2006**, *35*, 202–203.

22. He, S.; Liu, X.; Xie, S.; Wang, Q.; Xu, Y.; Xu, L. Effect of steam on the acid strength of $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{SiO}_2 \cdot n\text{H}_2\text{O}$ and its application in skeletal isomerization of *n*-butane. *Catal. Commun.* **2003**, *4*, 585–590.
23. Yang, W.; Billy, J.; Taarit, Y.; Vadrine, J.; Essayem, N. $\text{H}_3\text{PW}_{12}\text{O}_{40}$ supported on Cs modified mesoporous silica: catalytic activity in *n*-butane isomerisation and *in situ* FTIR study. Comparison with microporous $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$. *Catal. Today* **2002**, *73*, 153–165.
24. Ebitani, K.; Konishi, J.; Hattori, H. Skeletal isomerization of hydrocarbons over zirconium oxide promoted by platinum and sulfate ion. *J. Catal.* **1991**, *130*, 257–267.
25. Matsushashi, H.; Shibata, H.; Nakamura, H.; Arata, K. Skeletal isomerization mechanism of alkanes over solid superacid of sulfated zirconia. *Appl. Catal. A: Gen.* **1999**, *187*, 99–106.
26. Funamoto, T.; Nakagawa, T.; Segawa, K. Isomerization of *n*-butane over sulfated zirconia catalyst under supercritical conditions. *Appl. Catal. A: Gen.* **2005**, *286*, 79–84.
27. Yori, J.C.; D'Amato, M.D.; Costa, G.; Parera, J.M. Isomerization of *n*-butane on $\text{Pt}/\text{SO}_4^{2-}\text{-ZrO}_2$ and mechanical mixtures of $\text{Pt}/\text{Al}_2\text{O}_3+\text{SO}_4^{2-}\text{-ZrO}_2$. *J. Catal.* **1995**, *153*, 218–223.
28. Tomishige, K.; Okabe, A.; Fujimoto, K. Effect of hydrogen on *n*-butane isomerization over $\text{Pt}/\text{SO}_4^{2-}\text{-ZrO}_2$ and $\text{Pt}/\text{SiO}_2+\text{SO}_4^{2-}\text{-ZrO}_2$. *Appl. Catal. A: Gen.* **2000**, *194–195*, 383–393.
29. Lei, T.; Xu, J.S.; Tang, Y.; Hua, W.M.; Gao, Z. New solid superacid catalysts for *n*-butane isomerization: $\gamma\text{-Al}_2\text{O}_3$ or SiO_2 supported sulfated zirconia. *Appl. Catal. A: Gen.* **2000**, *192*, 181–188.
30. Grau, J.A.; Yori, J.C.; Vera, C.R.; Lovey, F.C.; Condo, A.A.; Parera, J.A. Crystal phase dependent metal-support interactions in $\text{Pt}/\text{SO}_4^{2-}\text{-ZrO}_2$ catalysts for hydroconversion of *n*-alkanes. *Appl. Catal. A: Gen.* **2004**, *265*, 141–152.
31. Hua, W.M.; Sommer, J. Hydroisomerization of *n*-butane over sulfated zirconia catalysts promoted by alumina and platinum. *Appl. Catal. A: Gen.* **2002**, *227*, 279–286.
32. Eibl, S.; Jentoft, R.E.; Gates, B.C.; Knozinger, H. Conversion of *n*-pentane and of *n*-butane catalyzed by platinum-containing WO_x/TiO_2 . *Phys. Chem. Chem. Phys.* **2000**, *2*, 2565–2573.
33. Dorado, F.; Romero, R.; Canizares, P.; Romero, A. Hydroisomerization of *n*-butane over $\text{Pd}/\text{HZSM-5}$ and Pd/H beta with and without binder. *Appl. Catal. A: Gen.* **2002**, *236*, 235–243.
34. Dorado, F.; Romero, R.; Canizares, P.; Romero, A. Influence of palladium incorporation technique on *n*-butane hydroisomerization over $\text{HZSM-5}/\text{bentonite}$ catalysts. *Appl. Catal. A: Gen.* **2004**, *274*, 79–85.
35. Canizares, P.; Dorado, F.; Sanchez-Herrera. Hydroisomerization of *n*-butane over hybrid catalysts. *Appl. Catal. A: Gen.* **2001**, *217*, 69–78.
36. Canizares, P.; Lucas, A.; Dorado, F.; Perez, D. Effect of zeolite pore geometry on isomerization of *n*-butane. *Appl. Catal. A: Gen.* **2000**, *190*, 233–239.
37. Kumar, N.; Villegas, J.I.; Salmi, T.; Murzin, D.Y.; Heikkila, T. Isomerization of *n*-butane to isobutane over Pt-SAPO-5 , SAPO-5 , Pt-H-mordenite and H-mordenite catalysts. *Catal. Today* **2005**, *100*, 355–361.
38. Baburek, E.; Novakova, J. Effect of platinum in bifunctional isomerization of butane over acid zeolites. *Appl. Catal. A: Gen.* **2000**, *190*, 241–251.
39. Pieterse, J.A.Z.; Seshan, K.; Lercher, J.A. Structure-activity correlations for TON, FER, and MOR in the hydroisomerization of *n*-butane. *J. Catal.* **2000**, *195*, 326–335.

40. Malogolowkin, C.; Poulson, D.F. Stepwise reaction on separate catalytic centers: isomerization of saturated hydrocarbons. *Science* **1957**, *126*, 31–32.
41. Okuhara, T.; Nishimura, T.; Watanabe, H.; Misono, M. Insoluble heteropoly compounds as highly active catalysts for liquid-phase reactions. *J. Mol. Catal.* **1992**, *74*, 247–256.
42. Okuhara, T.; Watanabe, H.; Nishimura, T.; Inumaru, K.; Misono, M. Microstructure of cesium hydrogen salts of 12-tungstophosphoric acid relevant to novel acid catalysis. *Chem. Mater.* **2000**, *12*, 2230–2238.
43. Hino, M.; Arata, K. Synthesis of solid superacid catalyst with acid strength of $H_0 \leq -16.04$. *J. Chem. Soc. Chem. Commun.* **1980**, 851–852.
44. Na, K.; Okuhara, T.; Misono, M. Skeletal isomerization of *n*-butane over caesium hydrogen salts of 12-tungstophosphoric acid. *J. Chem. Soc. Faraday Trans.* **1995**, *91*, 367–373.
45. Zhang, A.; Nakamura, I.; Aimoto, K.; Fujimoto, K. Isomerization of *n*-pentane and other light hydrocarbons on hybrid catalyst. Effect of hydrogen spillover. *Ind. Eng. Chem. Res.* **1995**, *34*, 1074–1080.
46. Grau, J.M.; Vera, C.R.; Parera, J.M. Preventing self-poisoning in $[Pt/Al_2O_3+SO_4^{2-}-ZrO_2]$ mixed catalysts for isomerization-cracking of heavy alkanes by prereduction of the acid function. *Appl. Catal. A: Gen.* **2002**, *227*, 217–230.
47. Liu, Y.; Hayakawa, T.; Ishii, T.; Kumagai, M.; Yasuda, H.; Suzuki, K.; Hamakawa, S.; Murata, K. Methanol decomposition to synthesis gas at low temperature over palladium support on ceria-zirconia solid solutions. *Appl. Catal. A: Gen.* **2001**, *210*, 301–314.
48. Liu, Y.; Hayakawa, T.; Suzuki, K.; Hamakawa, S.; Tsunoda, T.; Ishii, T.; Kumagai, M. High active copper/ceria catalysts for the steam reforming of methanol. *Appl. Catal. A: Gen.* **2002**, *223*, 137–145.
49. Liu, Y.; Hayakawa, T.; Tsunoda, T.; Suzuki, K.; Hamakawa, S.; Murata, K.; Shiozaki, R.; Ishii, T.; Kumagai, M. Steam reforming of methanol over Cu/CeO₂ catalysts studied in comparison with Cu/ZnO and Cu/Zn(Al)O catalysts. *Top. Catal.* **2003**, *22*, 205–213.
50. Siddiqui, M.R.H.; Holmes, S.; He, H.; Smith, W.; Coker, E.N.; Atkins, M.P.; Kozhevnikov, I.V. Coking and regeneration of palladium-doped H₃PW₁₂O₄₀/SiO₂ catalysts. *Catal. Lett.* **2000**, *66*, 53–57.
51. Kozhevnikov, I.V.; Holmes, S.; Siddiqui, M.R.H. Coking and regeneration of H₃PW₁₂O₄₀/SiO₂ catalysts. *Appl. Catal. A: Gen.* **2001**, *214*, 47–58.
52. Degnan, T.F.; Kennedy, C.R. Impact of catalyst acid/metal balance in hydroisomerization of normal paraffins. *AIChE J.* **1993**, *39*, 607–614.
53. Essayem, N.; Taarit, Y.B.; Feche, C.; Gayraud, P.Y.; Sapaly, G.; Naccache, C. Comparative study of *n*-pentane isomerization over solid acid catalysts, heteropolyacid, sulfated zirconia, and mordenite: dependence on hydrogen and platinum addition. *J. Catal.* **2003**, *219*, 97–106.