

Molecular design of solid acid catalysts. Isomerization of *n*-butane catalyzed by acidic cesium salts of 12-tungstophosphoric acid combined with platinum¹

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Abstract

Our recent efforts made for the molecular design of solid acid catalysts utilizing heteropoly compounds are described first and, then, as an example, the isomerization of *n*-butane in the presence of hydrogen catalyzed by a bifunctional catalyst consisting of Pt and Cs_{2.5}H_{0.5}PW₁₂O₄₀ was examined mostly at 573 K. Presence of Pt suppressed substantially the catalyst deactivation and gave much higher stationary activity, although the initial activity was lowered a little due to a decrease in the concentration of butenes produced. It was further demonstrated that the activity of Pt for hydrogenolysis was nearly completely suppressed by the protonic acid sites present near Pt, giving a very high selectivity for isomerization.

Keywords: Heteropolyacid catalyst; Isomerization; Butane; Platinum; Bifunctional catalysis

1. Introduction

Heteropoly compounds or polyoxometalates are ‘metal–oxygen molecules’, and have been proven to be useful catalytic materials in fundamental studies as well as in practical synthetic processes. This is mainly because their acid–base and redox properties can be controlled systematically by proper choice of constituent elements of polyanions and counter cations. This control is made possible by taking advantage of their molecular nature. In this article, our recent

efforts directed to design the acidic property and performance of solid acid catalysts are described.

We showed previously that it is important to distinguish between the primary, secondary and tertiary structure, in order to understand the catalysis of solid heteropoly compounds [1,2]. The primary structure is the structure of the heteropolyanion, and the secondary structure the three-dimensional arrangement of the polyanion and counter cation. Although the concept of tertiary structure has not been established yet, it contains crystal size, pore distribution, surface area, mode of aggregation, etc. and is also important [2]. In some cases, polar molecules are absorbed into the solid bulk, forming a ‘pseudoliquid’ phase, and react there (bulk-type catalysis). There is another type of bulk-type catalysis (bulk-type II), but this was found so

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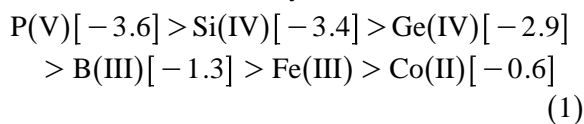
forth only for oxidation catalysis at high temperatures [1,2].

The isomerization of *n*-butane to isobutane, which is an important process to provide feedstock for methyl tert-butyl ether (MTBE) and C8 alkylates, is catalyzed by solid acids combined with noble metals. In general, isomerization of *n*-alkanes is catalyzed by this type of solid catalysts, e.g., Pt/chlorinated alumina [3], Pt/SiO₂ + zeolites [4], and Pd_xH_{3-2x}PW₁₂O₄₀ [5]. We attempted to utilize an acidic Cs salt of 12-tungstophosphoric acid, Cs_{2.5}H_{0.5}PW₁₂O₄₀ [6,7], for the acid component of the catalyst for this reaction and found that the addition of Pt or Pd to Cs_{2.5}H_{0.5}PW₁₂O₄₀ enhanced greatly the stationary catalytic activity and selectivity for *n*-butane isomerization in the presence of hydrogen [8,9]. We attributed this effect to: (i) Pt accelerates the dehydrogenation of *n*-butane to butenes which isomerize on acid sites of heteropoly compounds; (ii) the coke formation is suppressed by hydrogen supplied via Pt. In this work, we investigated in more detail the roles of Pt and acidity in the bifunctional mechanism, by varying the relative quantity of Pt to acid site and varying the method of mixing the two components.

2. Molecular design of solid acids

2.1. Acidity control by changing the primary and secondary structure

As for the Keggin-type heteropolyanions, XW₁₂O₄₀ⁿ⁻, the acid strength in solution increases with the valency of central atom, X.



where *H*₀ values of acetonitrile solution are given in brackets [10]. (The *H*₀ data are also given in Table 1 of [11], but there are typographical errors.) The catalytic activity of these heteropolyacids in the solid state followed this order [12].

In contrast to solution, the counter cations play very important roles for heteropoly compounds in the solid state. With increasing degree of the neutralization or the substitution by Na for protons, the catalytic activity in the pseudoliquid phase decreases in parallel with the amount of strong acid sites [1]. On the other hand, the surface-type catalysis is more sensitive to the nature of the surface and the control is not so straightforward. Cs_xH_{3-x}PW₁₂O₄₀ (denoted by CsX hereafter) which will be described below belongs to this category (surface-type).

In the way as described above the counter cation controls not only the acidic property but also the bulk-type behavior; dehydration of alcohols proceeds in pseudoliquid of Na_xH_{3-x}PW₁₂O₄₀ (bulk-type), while it takes place on the surface with Cs and K salts (surface-type).

The structure of the polyanion (primary structure) controls the acidity and bulk-type behavior as well. A Dawson-type heteropolyacid, H₆P₂W₁₈O₆₂, exhibits much greater catalytic activity for MTBE synthesis from methanol and isobutene due to the easier formation of the active pseudoliquid phase, although its acid strength (*H*₀ = -2.9) is lower than H₃PW₁₂O₄₀ [10,11].

2.2. Acidity control by changing the tertiary structure - (Cs, K, NH₄)_xH_{3-x}PW₁₂O₄₀

Acidic cesium salts of 12-tungstophosphoric acid, Cs_xH_{3-x}PW₁₂O₄₀, exhibit peculiar phenomena [6]. When the catalytic activity is plotted against the extent of the Cs substitution, the catalytic activity decreases first, but increases sharply when *x* = 2 - 2.5, and Cs_{2.5}H_{0.5}PW₁₂O₄₀ (Cs2.5) shows a very high activity which is sometimes even greater than that of the original hydrogen form. Here, careful control of conditions for titration is necessary to obtain clear-cut results. The high activity of Cs2.5 is more remarkable in liquid-phase organic reactions as shown in Fig. 1 [7].

Table 1

Activity and selectivity for skeletal isomerization of *n*-butane catalyzed by bifunctional and mixed catalysts

Catalyst	H ⁺ /anion	Conversion (%)	Selectivity (mol%)				
			C1	C2	C3	<i>i</i> -C4	C5
1 wt% Pt–Cs2.5 (1 g)	0.5	43	2.0	1.8	3.8	90.8	1.6
1 wt% Pt–Cs3 (1 g)	0	44	30.7	46.7	20.6	2.0	0
H3(imp)/1 wt% Pt–Cs3 (1 g)	0.5	39	1.1	0.7	2.6	94.0	1.6
0.1 wt% Pt–Cs3 (1 g)	0	8	40.8	14.7	41.6	2.90	0
H3(imp)/0.1 wt% Pt–Cs3 (1 g)	0.3	15	0.7	0.5	1.3	97.5	0
H3(imp)/0.1 wt% Pt–Cs3 (1 g)	0.5	20	0.9	1.2	6.1	88.1	3.7
H ₃ PW ₁₂ O ₄₀ (0.11 g) + 1 wt% Pt–Cs3 (0.6 g) ^a	0.5	15	23.5	11.6	23.6	41.3	0
3 wt% Pt/SiO ₂ (0.2 g)	0	32	25.9	33.6	21.9	18.6	0
Cs _{2.5} H _{0.5} PW ₁₂ O ₄₀ (0.8 g) + 3 wt% Pt/SiO ₂ (0.2 g) ^a	0.5	54	14.6	17.1	14.3	52.3	1.7

^a Physical mixture.Feed gas: *n*-butane:H₂:N₂ = 0.05:0.50:0.45; reaction temperature 573 K.

A nearly uniform distribution of protons and Cs in the solid bulk (or the formation of solid solutions of the hydrogen form and Cs3) after heat treatment was demonstrated by P-NMR for various values of *x* [13]. (These results were published in part in [2] and [14].) If one considers that the surface area increases considerably to about 130 m² g⁻¹ at Cs2.5 (compare with a few m² g⁻¹ for the hydrogen form and nearly null at *x* = 2) and that average proton content decreases linearly with *x*, the surface acidity (or the number of surface protons) can be estimated. The surface acidity very well parallels the catalytic activity, as shown in Fig. 1.

Very probable preparation processes for CsX's are schematically illustrated in Fig. 2. When the amount of Cs is low, ultrafine precipitate particles (probably Cs3, 8–10 nm in diame-

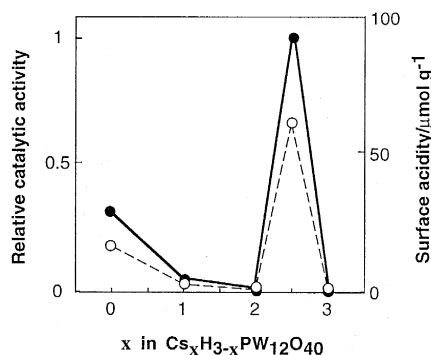


Fig. 1. Catalytic activity and surface acidity of Cs_xH_{3-x}PW₁₂O₄₀, CsX. (●) Relative catalytic activity for alkylation of 1,3,5-trimethylbenzene with cyclohexene, (○) surface acidity.

ter as estimated from the XRD line width) are thickly covered by H₃PW₁₂O₄₀, which is deposited upon evaporation of water, and form large aggregates, whereby the hydrogen form is possibly acting as cement. After heat treatment they are converted to particles having a similar size as before heat treatment and nearly uniform composition. This homogenization process confirmed by P-NMR and XRD proceeds through the diffusion of protons and Cs ions. At *x* = 2.5, the amount of Cs3 is greater and the hydrogen form deposited on Cs3 is smaller, so that the hydrogen form may form very thin films or small islands on Cs3. Hence, a high surface area

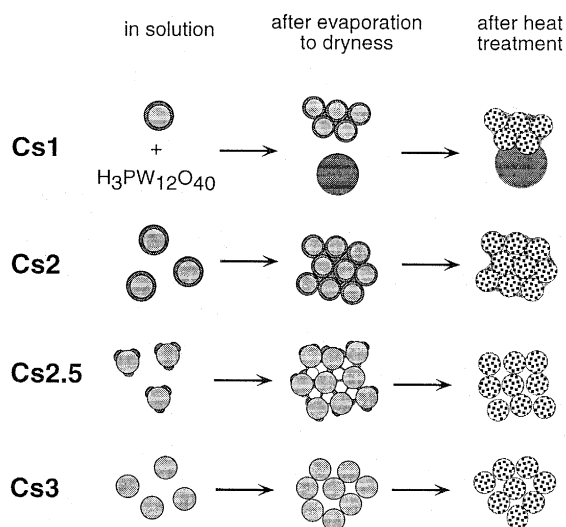


Fig. 2. Conceptual illustration of the preparation processes of Cs_xH_{3-x}PW₁₂O₄₀.

of the ultrafine particles can be maintained. Heat treatment produces fine particles having a uniform composition of $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$. Similar behavior is also observed for K and NH_4 salts, although the change is less distinct.

It was demonstrated that their micropore structure can be precisely controlled by the Cs content and shape selective adsorption and catalysis can be revealed [15].

3. Isomerization of *n*-butane catalyzed by Pt + CsX

Cs2.5 is an excellent solid acid which was developed as described above from our attempts to understand and control the heteropoly catalysts at the molecular level. In the extension of this line of research, we found that a catalyst consisting of Cs2.5 and Pt or Pd was an efficient catalyst for isomerization of *n*-butane [8,9]. Here, we attempted to make clear the roles of Cs2.5 and noble metals.

3.1. Experimental

Cs2.5, Cs3 [6,7] and Pt– $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ (Pt: 0.1–1.5 wt%) [8,9] were prepared as described before. Pt– $\text{Cs}_3\text{PW}_{12}\text{O}_{40}$ (Pt: 0.1 and 1 wt%, denoted by Pt(0.1)–Cs3 and Pt(1)–Cs3, respectively) were prepared similarly from H_2PtCl_6 and Cs3. Part of Pt–Cs3 was impregnated with aqueous solutions of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ to controlled loading levels after treatment in an N_2 flow at 573 K. The dried solids were calcined at 573 K in air. These are denoted by H(imp)/Pt(0.1) or Pt(1)–Cs3. 3 wt% Pt/ SiO_2 was prepared by impregnation of SiO_2 (JRC-SIO-4, $347 \text{ m}^2 \text{ g}^{-1}$) with an aqueous solution of $\text{Pt}(\text{OH})_2(\text{NH}_3)_4$. After the sample was calcined at 773 K for 5 h in air, it was reduced at 723 K in an H_2 flow.

Skeletal isomerization of *n*-butane was carried out at 473–573 K in a continuous flow reactor. A reactant gas mixture consisting of *n*-butane (0.05 atm), H_2 (0–0.5 atm), and N_2 (balance) was fed to 0.2–1 g of catalyst. The

total flow rate was 10 ml min^{-1} . Prior to the reaction, the catalysts were treated usually in an N_2 flow at 573 K for 2 h. Products were analyzed by gas chromatography.

3.2. Results

Figs. 3 and 4 show the effects of the amount of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ added by impregnation to Pt(0.1)–Cs3 and Pt(1)–Cs3. In both cases the hydrogenolysis (or hydrocracking) of *n*-butane prevailed when the hydrogen form was not added. The rate was greater for Pt(1)–Cs3. As the protons were introduced by the addition of the hydrogen form, hydrogenolysis decreased and isomerization to isobutane gradually increased. It is remarkable in Fig. 3 that hydrogenolysis almost disappeared at 0.09 g $\text{H}_3\text{PW}_{12}\text{O}_{40}$ with a total of 1 g catalyst ($\text{H}^+/\text{anion} = 0.3$). The cracking products beyond $\text{H}^+/\text{anion} = 0.3$ are mainly produced by acid-catalyzed cracking, as discussed below.

Results obtained for the physical mixture of Pt(1)–Cs3 (1 g) and $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (variable amount) are shown in Fig. 5. Powder samples were mixed only by shaking in a small bottle. General trends similar to those in Figs. 3 and 4 may be noted.

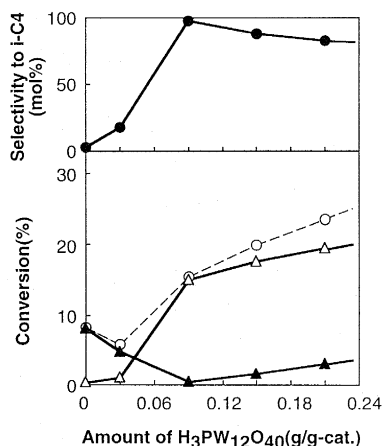


Fig. 3. Effects of the amount of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ impregnated on 0.1 wt% Pt–Cs3 for the isomerization of *n*-butane. (○) total conversion of *n*-butane, (●) selectivity to isobutane, (△) conversion to isobutane, (▲) conversion to C1–C3. Feed gas: *n*-butane: H_2 : N_2 = 0.05:0.50:0.45, reaction temperature: 573 K, catalyst weight ($\text{H}_3\text{PW}_{12}\text{O}_{40}$ + Pt–Cs3); 1 g, W/F = $40 \text{ g h (mol } n\text{-butane)}^{-1}$.

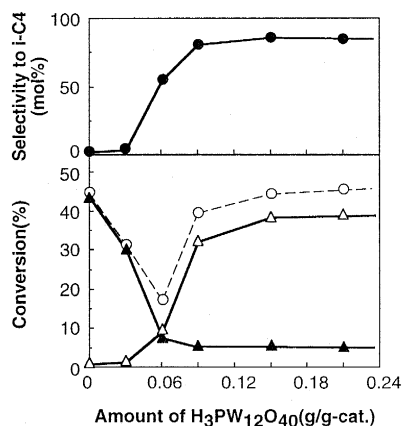


Fig. 4. Effects of the amount of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ impregnated on 1 wt% Pt-Cs3 for the isomerization of *n*-butane. Legends and the reaction conditions are the same as those of Fig. 3.

The effects of mixing Cs2.5 and Pt/SiO₂ are shown in Figs. 6 and 7. Mixing was performed only by shaking as in the previous systems. In Fig. 6 are shown the results obtained by varying the amount of Cs2.5 and in Fig. 7 those by varying the amount of Pt/SiO₂. Pt/SiO₂ showed a total conversion of *n*-butane of 32% with selectivity to isobutane of about 20% (Fig. 6). When Cs2.5 was added, isomerization to isobutane increased, while the hydrogenolysis remained almost constant.

As a result, the yield of isobutane increased

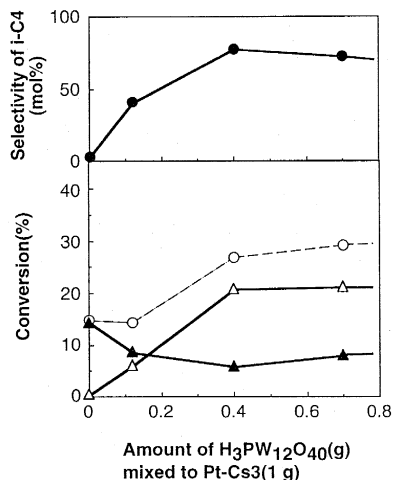


Fig. 5. Effects of the amounts of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ in the physical mixtures with 1 wt% Pt-Cs3 for the isomerization of *n*-butane. Legends and the reaction conditions are the same as those of Fig. 3. Catalyst weight: 1 wt% Pt-Cs3 (1 g) + $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (variable).

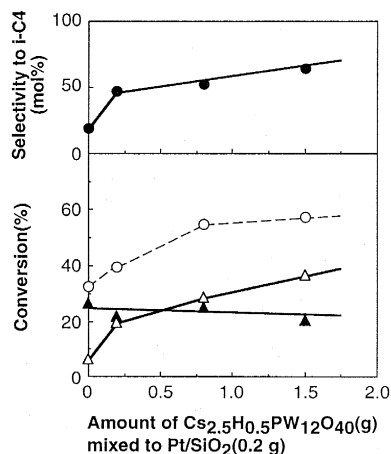


Fig. 6. Effects of the amount of $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ in the physical mixtures with Pt/SiO₂ for the isomerization of *n*-butane. Legends and the reaction conditions are the same as those of Fig. 3. Catalyst weight: Pt/SiO₂ (0.2 g) + $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ (variable).

with the addition of Cs2.5, but the selectivity was less than 70%.

When a small amount of Pt/SiO₂ was added to Cs2.5 which alone exhibited a high selectivity for isomerization, the rate increased sharply maintaining the high selectivity, but the rate of isomerization showed saturation with a further increase in the amount of Pt/SiO₂. On the other hand, the hydrogenolysis increased gradually and continued to increase with the amount of Pt/SiO₂ added. Consequently, the selectivity to

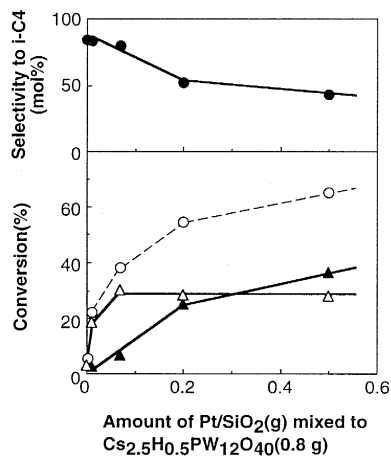


Fig. 7. Effects of the amount of Pt/SiO₂ in the physical mixtures with $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ for the isomerization of *n*-butane. Legends and the reaction conditions are the same as those of Fig. 3. Catalyst weight: $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ (0.8 g) + Pt/SiO₂ (variable).

isobutane declined at higher contents of Pt/SiO₂. Representative data are also given in Table 1.

3.3. Discussion

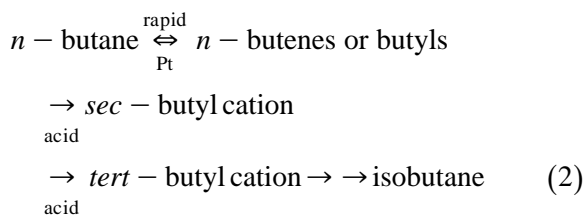
3.3.1. Structure of catalysts

IR indicated that the polyanion structure was maintained for H(imp)/Pt–Cs₃ catalysts. After heat treatment of the impregnated catalysts, a nearly uniform solid solution was probably formed by the migration of proton and Cs ions as observed previously for CsX. The migration might have taken place to some extent for the physical mixtures of hydrogen form and Pt–Cs₃, but the migration was rather limited as judged from the reaction data in Fig. 5. The migration seems to be still smaller for the physical mixtures of Pt/SiO₂ (Figs. 6 and 7).

The dispersion of Pt measured by CO adsorption changed only slightly (from 33 to 20%) after impregnation in the case of H(imp)/Pt(1)–Cs₃ [9]. Further, the catalytic performance at the stationary state was almost the same between the O₂-pretreatment and the H₂-pretreatment after the O₂-treatment, indicating that the oxidation state of Pt before use had little influence.

3.3.2. Roles of Pt

The reaction proceeds essentially by a bifunctional mechanism [8,9]. Pt promotes dehydrogenation of *n*-butane and the acid isomerizes butenes or butyls via *sec*-butyl cation. Since only a small amount of Pt was sufficient to accelerate the isomerization as in the previous work [9] and as shown by the results in Fig. 7, the dehydrogenation–hydrogenation of *n*-butane must be a rapid process.



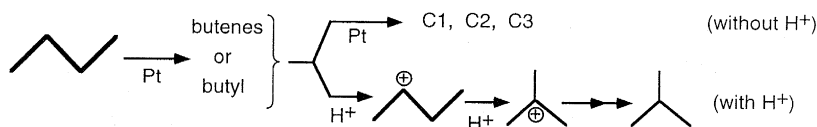
The last step of Eq. (2) can proceed by hydrogenation of isobutylene or by hydride transfer from *n*-butane.

Another significant effect of Pt is the suppression of catalyst deactivation in the presence of hydrogen. When the hydrogen partial pressure increased, both the initial rate and deactivation decreased. This indicates that the deactivation is due to coke deposition from butenes of which the concentration is inversely related to the hydrogen pressure. Pt probably suppresses the concentration of coke precursors by supplying hydrogen atoms to them.

3.3.3. Role of protonic acidity

The role of proton to isomerize *n*-butane via *sec*-butyl cation may be obvious. What is very remarkable in addition to this is that the activity of Pt for hydrogenolysis (or hydrocracking) of butane was nearly completely suppressed by the presence of protonic acid of heteropolyacid. As clearly seen in Figs. 3 and 4, when the protons were introduced to Pt–Cs₃ or the amount of H₃PW₁₂O₄₀ impregnated increased, the hydrogenolysis decreased and the isomerization gradually rose. This fact demonstrates that protons modified the catalytic performance of Pt. Since dehydrogenation is rapid as discussed above, the supply of butenes would not be rate-limiting and hence the evolution of the isomerization path should not affect the path for hydrogenolysis as far as Pt portion was intact. In fact, in the case of mixtures of Pt/SiO₂ and Cs_{2.5} where Pt must be little affected by the presence of Cs_{2.5}, the activity for hydrogenolysis remained nearly constant (Fig. 6).

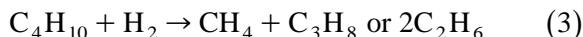
This indicates that the function of Pt was substantially modified and that close contact between Pt and proton is required to cause this modification. The necessity of close contact for this effect is inferred also from the following results. (i) The effect of proton impregnation was greater when the Pt dispersion was higher [9]. (ii) The effect was in the order H(imp)/Pt(0.1)–Cs₃ > H(imp)/Pt(1)–Cs₃ ≫ physical mixture of hydrogen form and Pt–Cs₃



Scheme 1. Reaction scheme of isomerization and hydrogenolysis of *n*-butane catalyzed by heteropolyacids combined with Pt.

> physical mixture of Pt/SiO₂ and Cs2.5. Since the higher dispersion of Pt favors intimate interaction between Pt and support, and physical mixing would bring about only loose contact, this order is the plausible order of the closeness of the contact between proton and Pt. A probable reaction mechanism is illustrated in Scheme 1.

Cracking products increased again when a large amount of hydrogen form was added to Pt–Cs3 (Fig. 3). This cracking is not the hydrogenolysis catalyzed by Pt, but is acid-catalyzed cracking of oligomerized butenes. In the cases of Pt–Cs3 and Pt/SiO₂, the concentrations of C1 and C3 were nearly the same, indicating the reaction of Eq. (3). This is probably the nature of ‘ordinary’ Pt. On the other hand, C3 ≫ C1 and C2 for acid-catalyzed cracking:



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