Catalysis by Heteropoly Compounds

34. Skeletal Isomerization of *n*-Butane over Pt- or Pd-Promoted Cesium Hydrogen Salts of 12-Tungstophosphoric Acid¹

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Skeletal isomerization of n-butane has been studied over bifunctional catalysts consisting of noble metals and an acidic cesium salt of 12-tungstophosphoric acid, Cs2.5H0.5PW12O40. At 473 K in the presence of 0.05 atm of H₂, 1 wt% Pt-Cs_{2.5}H_{0.5}PW₁₂O₄₀ (1% in weight of Pt impregnated to Cs2.5H0.5PW12O40) showed activity and selectivity comparable to 1 wt% Pt-sulfated zirconia, while at 573 K and 0.5 atm of H₂, 1 wt% Pt- and Pd-Cs_{2.5}H_{0.5}PW₁₂O₄₀ became much more active and selective for the formation of isobutane than 1 wt% Pt-sulfated zirconia and 1 wt% Pt-exchanged ZSM-5. Negative dependence of the initial reaction rate on H₂ pressure and little dependence on Pt loading level for Pt-Cs_{2.5}H_{0.5}PW₁₂O₄₀ indicate that the reaction proceeds through a bifunctional mechanism in which *n*-butane is rapidly dehydrogenated to *n*-butenes on Pt, n-butenes isomerize to isobutylene on acid sites, and then isobutylene is hydrogenated to isobutane on Pt. A remarkable effect of the presence of hydrogen was the repression of the catalyst deactivation. This is probably caused by the hydrogenation of coke and/or its precursor and a decrease in the butene partial pressure. Very interesting was the unique function of protons; protons present in proximity of Pt or Pd particles suppress the hydrogenolysis that takes place on Pt or Pd and greatly increase the selectivity to isobutane. © 1997 Academic Press

INTRODUCTION

Skeletal isomerization of *n*-butane to isobutane is of great importance because isobutane is a feedstock for alkylation with butenes to C8 alkylates and synthesis of methyl *tert*butyl ether (MTBE) (1). Solid acid catalysts such as sulfated zirconia (SO_4^{2-}/ZrO_2) (2–4), zeolites (5–7), chlorinated-Al₂O₃ (8), and heteropoly compounds (9, 10) have been reported to catalyze this reaction.

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Solid acid catalysts combined with noble metals are called "bifunctional catalysts" and are effective for skeletal isomerization of *n*-butane and other alkanes (11–21). Pt/chlorinated-Al₂O₃ has been used commercially for this reaction (1). The addition of Pt to chlorinated-Al₂O₃ accelerated greatly *n*-butane isomerization, while it little changed the acid strength (12, 13). Recently, Pt-promoted SO_4^{2-}/ZrO_2 was reported to be active for isomerization of alkanes in the presence of H_2 (14-20). $H_3PW_{12}O_{40}$, a popular heteropolyacid, is a strong acid and catalyzes effectively various reactions (22, 23). Ono and co-workers observed that Pd_xH_{3-2x}PW₁₂O₄₀/SiO₂ catalyzed *n*-hexane isomerization in the presence of H_2 (24). The conversion was nearly independent of the Pd content, while it was low without Pd. We reported preliminarily that Pt- or Pdpromoted $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ was active and selective for the *n*-butane isomerization (25).

The roles of the metallic component of bifunctional catalysts have been claimed to be (i) dehydrogenation of *n*-butane to butenes, which are precursors of *sec*-butyl carbenium ion intermediate and (ii) formation of hydrogen atom on the surface from a gas phase H_2 (1, 11). Roles of hydrogen atoms are possibly (i) suppression of the coke formation by hydrogenation of coke precursors (11, 20) or (ii) generation of new protonic acid sites from hydrogen atoms (18, 21).

In the present study, we investigated *n*-butane isomerization using a cesium hydrogen salt of 12-tungstophosphoric acid promoted by noble metals, that is, Pt- or Pd- $Cs_{2.5}H_{0.5}PW_{12}O_{40}$, to elucidate the roles of the metals, H₂, and protons on the activity and selectivity. The effects of H₂ pressure, the loading amount of Pt, pretreatment conditions, and reaction temperature have been examined. By comparing the catalysts with other bifunctional catalysts such as sulfated zirconia promoted by Pt, Pt-SO₄²⁻/ZrO₂, and Pt-loaded hydrogen form zeolite, Pt-HZSM-5, the catalytic features of Pt- or Pd-Cs_{2.5}H_{0.5}PW₁₂O₄₀ have been demonstrated with emphasis on the reaction mechanism.

¹ For part 33, see Einaga, H., and Misono, M., *Bull. Chem. Soc. Japan* **70**, (1997), in press.

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EXPERIMENTAL

1. Catalysts

Cesium salts, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ and $Cs_3PW_{12}O_{40}$, were prepared as described previously (26). These salts will be denoted by Cs2.5 and Cs3, respectively. Four kinds of Pt-Cs_{2.5}H_{0.5}PW₁₂O₄₀ were prepared. The first series was obtained from H₂PtCl₆ (Kojima Chem. Co.), H₃PW₁₂O₄₀ (Nippon Colour and Chemical Co.), and Cs₂CO₃ (Merck Co.). To the aqueous solution of H₃PW₁₂O₄₀ (0.08 mol · dm⁻³, 44 ml), an aqueous solution of H₂PtCl₆ (0.04 mol · dm⁻³, 15 ml) was dropped at 323 K to obtain a yellow solution. Then the aqueous solution of Cs₂CO₃ (0.12 mol · dm⁻³, 36 ml) was dropped to the solution at 323 K. The resulting milky solution was evaporated at 323 K to solid. This series of catalyst will be denoted by Pt-Cs_{2.5}H_{0.5}PW₁₂O₄₀(A) (abbreviated as Pt-Cs_{2.5}(A)). The loading amount of Pt was 1.0 wt%.

The second series was prepared from $Pt(NH_3)_4Cl_2$ (Aldrich Chem. Co.) by the same method as described above. This series will be denoted by $Pt-Cs_{2.5}H_{0.5}$ $PW_{12}O_{40}(B)$ (abbreviated as $Pt-Cs_{2.5}(B)$). The loading amounts of Pt were changed from 0.1 to 1.5 wt%.

The third series was prepared by impregnating 1 wt% Pt-Cs₃PW₁₂O₄₀(A) with the aqueous solution of H₃PW₁₂O₄₀, where 1 wt% Pt-Cs₃PW₁₂O₄₀(A) was prepared from the aqueous solution of H₂PtCl₆ and was pretreated at 573 K in a flow of O₂ for 2 h. The amount of H₃PW₁₂O₄₀ added to 1 wt% Pt-Cs₃PW₁₂O₄₀(A) was adjusted to obtain the ratio of Cs⁺ to PW₁₂O³⁻₄₀ = 2.5. After the impregnation, it was again treated at 573 K in the O₂ flow for 2 h. This series will be denoted by H3(imp)/Pt-Cs3(A). Besides Pt-Cs3(A), 1 wt% Pt-Cs₃PW₁₂O₄₀(B) (abbreviated by Pt-Cs3(B)) was obtained from Pt(NH₃)₄Cl₂ by the same method as described above. Especially 1 wt% Pt-Cs₃PW₁₂O₄₀(B) which was pretreated at 773 K in the O₂ flow for 2 h will be denoted by Pt-Cs3(β).

The forth series of Pt-Cs_{2.5}H_{0.5}PW₁₂O₄₀ was obtained by impregnation of 1 wt% Pt-Cs3(B) (after the pretreatment in the O₂ flow at 573 K for 2 h) or 1 wt% Pt-Cs3(β) with the aqueous solution of H₃PW₁₂O₄₀. The ratio of Cs⁺ to PW₁₂O³⁻₄₀ was adjusted to 2.5. This series is denoted by H3(imp)/Pt-Cs3(B) or H3(imp)/Pt-Cs3(β).

Pd-Cs_{2.5}H_{0.5}PW₁₂O₄₀ was obtained from the aqueous solutions of Pd(NO₃)₂ (Kojima Chem. Co.), H₃PW₁₂O₄₀, and Cs₂CO₃ by the same method described above. The loading levels of Pd were 0.1–1.5 wt%. These catalysts will be abbreviated as Pd-Cs_{2.5.1} wt% Pt-HZSM-5 was prepared as described previously (27). H-ZSM-5, which was obtained from Na-ZSM-5 (Tosoh Corporation, HSZ-820NAA, SiO₂/Al₂O₃ = 23.3, 332 m² · g⁻¹) by an ion-exchange method, was added to an aqueous solution of NH₄NO₃ to form NH₄-ZSM-5 and then NH₄-ZSM-5 obtained was added to the aqueous solution of Pt(NH₃)₄Cl₂. After the

solution was stirred at 353 K for 3 h, the solid was filtered and washed with deionized water, and then dried at 373 K.

One wt% Pt-SO₄²⁻/ZrO₂ (125 m² g⁻¹) was prepared by a method as in the literature (18). Zr(OH)₄ obtained from ZrOCl₂ was treated with an aqueous solution of H₂SO₄ (1 N), and the resulting solid was calcined at 873 K for 5 h in air. Then the obtained SO₄²⁻/ZrO₂ was impregnated with the aqueous solution of H₂PtCl₆ (0.04 mol \cdot dm⁻³) and was calcined at 873 K in air. This catalyst is denoted by 1 wt% Pt-SO₄²⁻/ZrO₂. 1 wt% Pt-Al₂O₃ (N. E. Chemcat Co., Lot No. 137-90099, 154 m² g⁻¹) was also used as reference.

2. Skeletal Isomerization of n-Butane

Skeletal isomerization of *n*-butane was carried out at a temperature in the range from 473 to 573 K in a continuous flow reactor (Pyrex, 12 mm of inside diameter) under an atmospheric pressure (9, 10). The reactant mixture consisting of *n*-butane (0.05 atm), H₂ (0~0.50 atm), and N₂ balance was fed to 0.5–1.0 g of catalyst. Total flow rate was 10 cm³ · min⁻¹. Prior to the reaction, the heteropoly compounds were pretreated in the flow of O₂ or H₂ (60 cm³ · min⁻¹) at 573 K for 1 h. Pt-SO₄²⁻/ZrO₂ was pretreated in the O₂ flow (60 cm³ · min⁻¹) and then in an H₂ flow (60 cm³ · min⁻¹) at 643 K for 1 h each. Pt-ZSM-5 and Pt-Al₂O₃ were pretreated in the O₂ flow and then in the H₂ flow at 723 K for 1 h each. The reaction products were analyzed with an FID GC (Hitachi GC-163) equipped with VZ-10 and SE-30 columns (9, 10, 25).

3. Other Measurements

Infrared spectra were recorded with a Fourier transform infrared spectrometer (Shimadzu FT IR-8500) at room temperature. The sample was dispersed on a thin silicon plate and was set in an *in situ* IR cell (ca 500 cm³), which was connected to a closed circulation system (ca 250 cm³). The sample was pretreated at 573 K in H_2 (350 torr) or O_2 (350 torr) for 2 h.

The surface area was measured by BET method with an N₂ adsorption system (Micromeritics ASAP-2000) after the pretreatment in vacuum at 573 K for 0.5 h. The surface areas of Cs2.5, 1 wt% Pt-Cs2.5(A) and 1 wt% Pt-Cs2.5(B), 1 wt% Pd-Cs2.5(A) after evacuation at 573 K were 135, 115, 100, and 108 m² g⁻¹, respectively. X-ray diffraction patterns were recorded with an X-ray diffractometer (Mac Science MXP³) using CuK α radiation. The sample was mixed with Si powder as an internal standard (catalyst:Si=1:3 in weight).

Adsorption of CO on Pt-Cs2.5 and Pt-Cs3 was measured by a pulse method. After the pretreatment of the catalyst (about 1 g) in the flow of O₂ ($60 \text{ cm}^3 \cdot \text{min}^{-1}$) and then in the flow of H₂ ($60 \text{ cm}^3 \cdot \text{min}^{-1}$) at 573 K, a pulse of CO (0.71 cm³) was introduced repeatedly to the catalyst at room temperature. The concentration of CO at the outlet of the reactor was followed by a GC or mass spectrometer (Anelva AGA-100) directly connected to the pulse system. Solid-state ³¹P NMR spectra of the heteropoly compounds were taken by the same method as described previously (28). After the samples were pretreated at 573 K in a vacuum, they were enclosed into Pyrex tubes (5-mm outside diameter and 10-mm height) to avoid the rehydration by air moisture. The sample tube was directly set in a rotor for the solid-state MAS NMR (JEOL JNM-GX270).

RESULTS

Figure 1 shows the time courses of *n*-butane isomerization over 1 wt% Pt-Cs2.5(A) and bifunctional catalysts in the presence of 0.5 atm H₂ at 573 K; 1 wt% Pt-Cs2.5(A) was pretreated in the O₂ flow at 573 K for 2 h prior to the reaction. The conversion for 1 wt% Pt-Cs2.5(A) decreased initially, and reached a stationary value (43%) after about 2 h on stream. The selectivity to isobutane for 1 wt% Pt-Cs2.5(A) was 91% after 2 h. The yield obtained for 1 wt% Pt-Cs2.5(A) was about 40%, which corresponds to about 80% that in the equilibrium (29). The selectivities observed for 1 wt% Pt-SO₄²⁻/ZrO₂ and 1 wt% Pt-HZSM-5 were 49% and 34%, respectively, as shown in Fig. 1, while the activities were higher than that of 1 wt% Pt-Cs2.5(A).

The changes of the selectivity as a function of the conversion are given in Fig. 2 for 1 wt% Pt-Cs2.5(A) and 1 wt% Pt-SQ₄²⁻/ZrO₂. While the selectivity to isobutane for 1 wt% Pt-Cs2.5(A) was independent of the conversion up to 43%, the selectivity for 1 wt% Pt-SO₄²⁻/ZrO₂ decreased as the conversion increased. The selectivity for 1 wt% Pt-Cs2.5(A) was always higher than that for 1 wt% Pt-SO₄²⁻/ZrO₂ in these conversions.



FIG. 1. Time courses of *n*-butane isomerization at 573 K over Ptbifunctional catalysts: (○), 1% Pt-Cs_{2.5}H_{0.5}PW₁₂O₄₀(A); (▲), 1 wt% Pt-SO₄²⁻/ZrO₂; and (●), 1 wt% Pt-HZSM-5. Feed gas; *n*-butane: H₂: N₂ = 0.05:0.50:0.45, W/F = 40 g · h · (mol of feed gas)⁻¹ (except for Pt-ZSM-5, 20 g · h · (mol of feed gas)⁻¹).



FIG. 2. Selectivity changes as a function of conversion over 1 wt% Pt-Cs_{2.5}H_{0.5}PW₁₂O₄₀(A) (\bigcirc) and 1 wt% Pt-SO²⁻₄/ZrO₂ (\blacktriangle) at 573 K. Feed gas; *n*-butane : H₂ : N₂ = 0.05 : 0.50 : 0.45.

Catalytic data at stationary states at 573 K and 0.5 atm of H₂ for Pt- or Pd-promoted catalysts are summarized in Table 1. The catalytic activity estimated from the reaction rate is in the order: Pt-HZSM-5 > Pt-Al₂O₃ > Pt-SO₄²⁻/ZrO₂ > Pt-Cs2.5(A) > Pd-Cs2.5 > Pt-Cs2.5(B). The selectivity is in the order of Pt-Cs2.5(B) \approx Pd-Cs2.5 > Pt-Cs2.5(A) \gg Pt-SO₄²⁻/ZrO₂ > Pt-HZSM-5 > Pt-Al₂O₃. Consequently, the order of the rate of isobutane formation is: Pt-Cs2.5(A) \approx Pd-Cs2.5 > Pt-HZSM-5 > Pt-SO₄²⁻/ZrO₂ > Pt-HZSM-5 > Pt-SO₄²⁻/ZrO₂ > Pt-Cs2.5(B) \approx Pd-Cs2.5 > Pt-SO₄²⁻/ZrO₂ > Pt-Cs2.5(B) > Pt-Al₂O₃.

The results at 573 K under 0.05 atm of H₂ (stationary states) are shown in Table 2. Pt-Cs2.5(A), Pt-Cs2.5(B), and Pd-Cs2.5 are also more active and selective for the formation of isobutane than Pt-SO₄²⁻/ZrO₂. The conversion for Pt-SO₄²⁻/ZrO₂ decreased rapidly with the reaction time, resulting in a low conversion (3.9%) after 2 h. Pt-HZSM-5 gave the highest conversion, but the selectivity to isobutane was very low (16.4%).

Figure 3 shows the time courses of the reaction over Pt-Cs2.5(A) at 573 K under different H_2 pressures. In the



FIG. 3. Changes in the conversion of *n*-butane with time at different hydrogen pressures: (\bigcirc), 0.5 atm H₂; (\bigcirc), 0.2 atm H₂; (\triangle), 0.05 atm H₂; and (\blacktriangle), in the absence of H₂. Feed gas; *n*-butane = 0.05 atm; reaction temperature, 573 K; catalyst, 1 g, W/F = 40 g · h · mol⁻¹.

TABLE 1

Catalyst	Conversion	Reaction rate		Selectivity (mol%) ^c						
	(%)	Rate ^a	Rate ^b	C ₁	C ₂	C ₃	i-C ₄	C ₅ (+)		
1 wt% Pt-Cs2.5(A) ^d	43.0	14.5 (12.6)	13.3	2.0	1.8	3.8	90.8	1.6		
1 wt% Pt-Cs2.5(B) ^e	24.5	8.3 (8.3)	7.9	0.9	1.5	1.6	95.3	0.7		
1 wt% Pd-Cs2.5(A) f	40.0	13.6 (12.6)	12.7	0.6	0.6	2.8	94.1	1.9		
1 wt% Pt-SO $^{2-}_{4}$ /ZrO $_{2}$	64.6	22.0 (17.6)	10.6	5.8	11.3	29.4	48.6	4.9		
1 wt% Pt-HZSM-5 ^g	51.7	35.2 (10.6)	11.9	19.8	24.2	21.2	34.0	0.8		
1 wt% Pt-Al ₂ O ₃	75.8	25.8 (16.8)	2.1	21.9	51.0	18.8	8.3	0		

Activity and Selectivity for Skeletal Isomerization of *n*-Butane over Metal-Promoted Solid Acids in the Presence of 0.5 atm of H₂ at 573 K

Note. Reaction conditions: *n*-butane : $H_2 : N_2 = 0.05 : 0.50 : 0.45$; catalyst 1 g; total flow rate 10 ml min⁻¹; W/F 40 g h mol⁻¹.

^a Total reaction rate/ 10^{-8} mol g⁻¹ s⁻¹ (after 5 h). The figures in the parentheses are the rate per unit surface area/ 10^{-10} mol m⁻² s⁻¹.

^b Rate of isobutane formation/ 10^{-8} mol g⁻¹ s⁻¹ (after 5 h).

^c C₁ is CH₄, C₂ is C₂H₆, C₃ is C₃H₈, i-C₄ is isobutane, and C₅(+) is hydrocarbons containing more than five carbons.

^d From H₂PtCl₆. The catalyst was pretreated at 573 K in O₂ for 2 h.

 e From Pt(NH₃)₄Cl₂. The catalyst was pretreated at 573 K in O₂ for 2 h.

^{*f*} From Pd(NO₃)₂. The catalyst was pretreated at 573 K in O₂ for 2 h.

^g Catalyst weight 0.5 g, total flow rate 10 ml min⁻¹, W/F 20 g h mol⁻¹.

absence of H_2 , a significant catalyst deactivation was observed. In the presence of H_2 (0.05–0.5 atm), the catalyst deactivation became smaller. In the case of Pd-Cs2.5, the degree of the deactivation decreased gradually as the H_2 pressure increased, and it became nearly zero at 0.5 atm of H_2 .

In Fig. 4, the selectivities of isobutane or $C_3 + C_5$ hydrocarbons (Fig. 4A) and concentration of butenes formed during the reaction (Fig. 4B) over 1 wt% Pt-Cs2.5(A) are plotted against the H₂ pressure, where the data were collected at stationary states (after 5 h) at 573 K (see Fig. 3). In the absence of H₂, butenes appeared at the concentration of 540 ppm (corresponds to 19 mol% in total products),

which is about half that in the equilibrium (30). The selectivity to isobutane was low, 55% (conversion, 5.7%) and at the same time, an appreciable amount of $C_3 + C_5$ hydrocarbons was formed ($C_3 + C_5 = 21\%$). Contrary to this, in the presence of 0.05–0.5 atm H₂, the selectivity to isobutane reached about 90% and the concentrations of butenes were 50–5 ppm (0.3–0.03 mol% in total products).

In Fig. 5, the time courses at 473 K and 0.05 atm of H_2 are given for Pt-Cs2.5(A) and Pt-SO₄²⁻/ZrO₂. The conversion for Pt-Cs2.5(A) was nearly constant from the initial stage of the reaction, while the conversion for Pt-SO₄²⁻/ZrO₂ decreased with time. After 5 h, the conversions and selectivities for both catalysts became similar.

TABLE	2
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Activity and Selectivity for Skeletal Isomerization of *n*-Butane over Metal-Promoted Solid Acids in the Presence of 0.05 atm of H₂ at 573 K

Catalyst	Conversion (%)	Reaction rate		Selectivity (mol%) ^c						
		Rate ^a	Rate ^b	C1	C_2	C ₃	i-C ₄	$C_4^=$	C ₅ (+)	
1 wt% Pt-Cs2.5(A) d	35.7	12.7 (11.0)	11.3	1.0	0.8	5.1	89.2	<0.2 ^e	3.7	
1 wt% Pt-Cs2.5(B) f	18.8	6.4 (6.4)	5.4	1.3	0.8	7.2	85.4	0.7	4.6	
1 wt% Pd-Cs2.5 ^g	10.9	3.7 (3.4)	2.6	0.3	0.5	14.2	72.0	3.2	9.8	
1 wt% Pt-SO ₄ ²⁻ /ZrO ₂	3.9	1.3 (1.0)	0.9	0	2.1	15.7	74.4	<0.2 ^f	7.6	
1 wt% Pt-HZSM-5 ^h	72.2	49.2 (14.8)	8.0	3.9	6.5	66.6	16.4	< 0.2 ^f	6.4	

Note. Reaction conditions: *n*-butane : H_2 : $N_2 = 0.05$: 0.90; catalyst 1 g; total flow rate 10 ml min⁻¹; W/F 40 g h mol⁻¹.

^{*a*} Total reaction rate/ 10^{-8} mol g⁻¹ s⁻¹ (after 5 h). The figures in parentheses are the rate per unit surface area/ 10^{-10} mol m⁻² s⁻¹.

^{*b*} Rate of isobutane formation/ 10^{-8} mol g⁻¹ s⁻¹ (after 5 h).

 c C₁ is CH₄, C₂ is C₂H₆, C₃ is C₃H₈, i-C₄ is isobutane, C₄ is butenes, and C₅(+) is hydrocarbons containing more than five carbons. ^{*d*} From H₂PtCl₆. The catalyst was pretreated at 573 K in O₂ for 2 h.

^e Less than 2 ppm.

^f From Pt(NH₃)₄Cl₂. The catalyst was pretreated at 573 K in O₂ for 2 h.

^g From Pd(NO₃)₂. The catalyst was pretreated at 573 K in O₂ for 2 h.

^{*h*} Catalyst 0.5 g; total flow rate 10 ml min⁻¹; W/F 20 g h mol⁻¹.

100

50

0 50

40

30

20

10

0 4

23

523

Temp./K

573

Selectivity to isobutane(mol%)

Conversion to isobutane or C₁~C3(%)

FIG. 4. Selectivities and concentration of butenes as a function of H₂ pressure over 1 wt% Pt-Cs_{2.5}H_{0.5}PW₁₂O₄₀ at 573 K. (A) Selectivities to isobutane and C₃ + C₅ hydrocarbons. (B) Concentration of butenes formed at the stationary states.

Detailed data at the stationary states at 473 K for 1 wt% Pt-Cs2.5(A) and 1 wt% Pt-SO₄²⁻/ZrO₂ are summarized in Table 3. The conversions at 0.05 atm of H₂ for both catalysts were higher than those at 0.5 atm of H₂ in contrast to those at 573 K (Tables 1 and 2). The selectivity for 1 wt% Pt-SO₄²⁻/ZrO₂ was more than 90% at both H₂ pressures. On the other hand, the selectivity to isobutane for Pt-Cs2.5(A) was only 32% under 0.5 atm of H₂, the main products being C₁–C₃ hydrocarbons, whereas it was about 90% under 0.05 atm of H₂.

Figure 6 provides the dependencies in the stationary conversion and selectivity upon the reaction temperature

FIG. 5. Changes in the conversion and selectivity of *n*-butane isomerization at 473 K: (\bigcirc), 1% Pt-Cs_{2.5}H_{0.5}PW₁₂O₄₀(A); (\blacktriangle), 1 wt% Pt-SO₄²⁻/ZrO₂. Feed gas; *n*-butane:H₂:N₂=0.05:0.05:0.90, W/F = 40 g · h · mol⁻¹.



473

523

Temp./K

573

а

С

523

Temp./K

473

573

h

over Pt-SO₄²⁻/ZrO₂, Pt-Cs2.5(A), and Pt-Cs3(A). In the case of $Pt-SO_4^{2-}/ZrO_2$ (Fig. 6a), the conversion to isobutane increased once, and then it decreased as the reaction temperature increased. On the other hand, the conversion to C_1 - C_3 hydrocarbons continued to increase. The selectivities to isobutane were 96 and 49% at 473 and 573 K, respectively. Similar trends of the conversion and selectivity for Pt-SO₄²⁻/ZrO₂ have been reported by Chao *et al.* (31). On the other hand, it is remarkable for Pt-Cs2.5(A) that the conversion to C_1 - C_3 hydrocarbons was nearly independent of the reaction temperature, while the conversion to isobutane continued to increase with increasing the reaction temperature (Fig. 6b). Consequently, the selectivity for Pt-Cs2.5(A) was improved by the rise in the temperature. In the case of Pt-Cs3(A) (Fig. 6c), the hydrogenolysis occurred exclusively and the conversion for the hydrogenolysis increased monotonically with the reaction temperature.

 H_2 pressure dependencies of the reaction rates for Pt-Cs2.5(A) at 473 K are given in Fig. 7. It was found that the initial conversion decreased as the H_2 pressure increased, while the conversion at the stationary state increased once and decreased slightly. The selectivities to isobutane (at the stationary state) became slightly higher (85% to 90%) when the H_2 pressure was increased from 0 to 0.05 atm, and then decreased to 32% by the further increase to 0.5 atm. On the other hand, as shown in Fig. 8, at 573 K, although the initial conversion also tended to decrease with the H_2 pressure, the stationary conversion was greatly enhanced even by the introduction of 0.05, atm of H_2 . The selectivities to isobutane were 55, 89, 90, and 91% at 0, 0.05, 0.2, and 0.5 atm of H_2 , respectively.

Figure 9 shows the dependencies of the rates on H_2 pressure for 1 wt% Pd-Cs2.5 at 573 K. The dependencies are essentially the same as those for Pt-Cs2.5 at 573 K,





Catalyst	Н	Conversion	Reaction rate			Selectivity (mol%) ^c					
	(atm)	(%)	Rate ^a	Rate ^b	C ₁	C ₂	C ₃	i-C ₄	C ₅ (+)		
$1 \text{ wt\% Pt-Cs2.5(A)}^d$	0.05	17.1	5.2 (4.5)	0.6	1.8	1.2	4.5	89.9	2.6		
	0.5	5.4	0.6 (0.5)	1.3	27.1	12.2	28.1	31.9	0.7		
1 wt% Pt-SO ₄ ²⁻ /ZrO ₂	0.05	21.1	6.5 (5.2)	0.7	0.1	0.2	5.0	90.5	4.2		
	0.5	10.7	3.5 (2.8)	0.01	0.6	2.4	0.9	96.1	0		

Activity and Selectivity for Skeletal Isomerization of *n*-Butane at 473 K

Note. Reaction conditions: n-butane 0.05 atm; catalyst 1 g; total flow rate 10 ml min⁻¹; W/F 40 g h mol⁻¹.

^{*a*} Rate of isobutane formation/ 10^{-8} mol g⁻¹ s⁻¹ (after 5 h). The figures in parentheses are the rate per unit surface area/ 10^{-10} mol m⁻² s⁻¹. ^{*b*} Rate for the hydrogenolysis/ 10^{-8} mol g⁻¹ s⁻¹.

 $^{c}C_{1}$ is CH₄, C₂ is C₂H₆, C₃ is C₃H₈, i-C₄ is isobutane, and C₅(+) is hydrocarbons containing more than five carbons.

^d From H₂PtCl₆. The catalyst was pretreated at 573 K in O₂ for 2 h.

except that the initial conversion decreased more in the presence of H_2 . The selectivities of isobutane (after 5 h) were 13, 78, 87, and 96% for 0, 0.05, 0.2, and 0.5 atm of H_2 , respectively.

The changes in the activity and selectivity at the stationary state with Pt loading level for Pt-Cs2.5(B) are given in Fig. 10. The reaction was accelerated by a factor of about 4 only by the addition of 0.1 wt% Pt. The rate and selectivity were found to be nearly independent of the loading levels above 0.1 wt%. The activities of 1 wt% Pt-Cs2.5(A) and 1 wt% Pt-Cs2.5(B) were about 6 and 4 times as high as Cs2.5 (10). In Fig. 11, the effects of Pd loading level are shown. Also in this case, the reaction rate and selectivity were almost unchanged upon the variation of the Pd loading level.

In Table 4, the influence of the ambient gas used for the pretreatment of Pt-Cs2.5 and Pt-Cs3 is summarized. Both the activity and selectivity for Pt-Cs2.5(A) were little affected by the ambient gas. In contrast, significant changes were observed for Pt-Cs2.5(B) which was prepared from Pt(NH₃)₄Cl₂. The O₂-pretreatment of Pt-Cs2.5(B) brought

about significantly higher conversion and selectivity than the H_2 -pretreatment. Similar to Pt-Cs2.5(B), the activity of Pt-Cs3(B) was enhanced by the O₂-treatment, but, regardless of the pretreatment conditions, Pt-Cs3(A) and Pt-Cs3(B) were not selective to isobutane.

Changes in the catalysts with the pretreatment conditions were examined by using IR spectroscopy. The intensities and wavenumbers of the IR bands due to the Keggin structure were independent of the ambient gas for the pretreatment. What is remarkable for Pt-Cs2.5(B) is the presence of a band at 1415 cm⁻¹ due to NH₄⁺ after the N₂ and H₂ pretreatments, in addition to the bands due to the Keggin anion. This band was much smaller after the O₂-pretreatment. In Table 5, the amounts of NH₄⁺ which remained after the pretreatments are summarized. The amounts of NH₄⁺ in the table were estimated from the relative peak intensities of NH₄⁺ and ν (W=O) (985 cm⁻¹) by comparing with those of the stoichiometric salt, (NH₄)₃PW₁₂O₄₀, and were expressed by the ratios of NH₄⁺/polyanion. The ratio NH₄⁺/polyanion for Pt-Cs2.5(B) was 0.20 after the



FIG. 7. Effects of H₂ pressure on initial and stationary activities for isomerization of *n*-butane at 473 K over 1 wt% Pt-Cs_{2.5}H_{0.5}PW₁₂O₄₀(A). (\bigcirc), initial conversion (after 5 min); (\bullet), stationary conversion (after 5 h). Feed gas; *n*-butane: 0.05 atm, W/F = 40 g · h · mol⁻¹.



FIG. 8. Effects of H₂ pressure on initial and stationary activities for isomerization of *n*-butane at 573 K over 1 wt% Pt-Cs_{2.5}H_{0.5}PW₁₂O₄₀(A). (\bigcirc), initial conversion (after 5 min); (\bullet), stationary conversion (after 5 h). Feed gas; *n*-butane: 0.05 atm, W/F = 40 g \cdot h \cdot mol⁻¹.



FIG. 9. Effects of H₂ pressure on initial and stationary activities for isomerization of *n*-butane at 573 K over 1.5 wt% Pd-Cs_{2.5}H_{0.5}PW₁₂O₄₀. (\bigcirc), initial conversion (after 5 min); (\bullet), stationary conversion (after 5 h). Feed gas; *n*-butane: 0.05 atm, W/F = 40 g · h · mol⁻¹.

 O_2 -treatment, while these ratios were 0.47 and 0.46 after the N_2 and H_2 pretreatments, respectively. No peak due to NH_4^+ was detected for 1 wt% Pt-Cs2.5(A) and Pt-Cs3(A), which were prepared from H_2PtCl_6 .

Effects of the addition of $H_3PW_{12}O_{40}$ to 1 wt% Pt-Cs3(B) and 1 wt% Pt-Cs3(β) on the activities and selectivities are given in Table 6; 1 wt% Pt-Cs3(B) and 1 wt% Pt-Cs3(β) were those after the O₂ pretreatment at 573 and 773 K, respectively. The Pt particle sizes of Pt-Cs3(B) and Pt-Cs3(β) estimated from the CO adsorption were 27 and 180 A, respectively. As shown in Table 6, both Pt-Cs3(B) and Pt-Cs3(β) produced mainly C₁–C₃ hydrocarbons. Pt-Cs3(β) was more active for the hydrogenolysis than Pt-Cs3(β). When H₃PW₁₂O₄₀ was added to Pt-Cs3(B) by the impregnation method, the isomerization was greatly accelerated, while the hydrogenolysis was nearly completely suppressed. Consequently, the selectivity to isobutane was significantly enhanced by the addition of H₃PW₁₂O₄₀. The



FIG. 10. Dependencies of the loading amount of Pt of Pt-Cs_{2.5}H_{0.5} PW₁₂O₄₀(B) on the activity and selectivity (5 h) in *n*-butane isomerization: (•), conversion of *n*-butane; (\bigcirc), selectivity to isobutane. Catalyst: Pt-Cs_{2.5}H_{0.5}PW₁₂O₄₀(B) (from Pt(NH₃)₄Cl₂). Feed gas; *n*-butane: H₂:N₂ = 0.05:0.50:0.45; reaction temperature, 573 K; W/F = 40 g · h · mol⁻¹.



FIG. 11. Dependencies of the loading amount of Pd of Pd-Cs_{2.5}H_{0.5} PW₁₂O₄₀ on the activity and selectivity in *n*-butane isomerization: (\bullet), stationary conversion of *n*-butane; (\bigcirc), selectivity to isobutane. Feed gas; *n*-butane : H₂ : N₂ = 0.05 : 0.50 : 0.45; reaction temperature, 573 K; W/F = 40 g · h · mol⁻¹.

effect of the addition of $H_3PW_{12}O_{40}$ to Pt-Cs3(β) was essentially the same as Pt-Cs3(B), except that the rate of hydrogenolysis on Pt-Cs3(β) changed little, resulting in a lower selectivity than $H_3(imp)/Pt$ -Cs3(B).

Figure 12 shows the solid-state ³¹P NMR spectra of these heteropoly compounds. Pt-Cs3(A) gave a single peak at -15.0 ppm (Fig. 12d). H3(imp)/Pt-Cs3(A) and Pt-Cs2.5(A) showed similar patterns, in which two peaks were detected mainly at about -15.0 ppm (-15.1 and -15.0 ppm for Figs. 12b and 12c, respectively) and -13.4 ppm. Besides these two peaks, a small peak at -12.2 ppm was also observed for H3(imp)/Pt-Cs3(A). In the case of Cs2.5, three main peaks were detected at -14.8, -13.3, and -12.0 ppm. H3(imp)/Cs3, which was prepared by impregnation by using Cs3 instead of Pt-Cs3(A) and pretreated at 573 K in

TABLE 4

Effects of Ambient Gas at Pretreatment on Activity and Selectivity for Skeletal Isomerization of *n*-Butane at 573 K

	Pretreatment	Conver-	Selectivity (mol%) ^a					
Catalyst	atmosphere	(%)	C_1	C_2	C_3	i-C ₄	C ₅	
1% Pt-Cs2.5(A) ^b	O_2	43.0	2.0	1.8	3.8	90.8	1.6	
	H_2	38.0	1.7	2.2	3.5	91.0	1.6	
1% Pt-Cs2.5(B) ^c	O_2	24.5	0.9	1.5	1.6	95.3	0.7	
	H_2	13.2	32.8	34.9	30.5	1.8	0	
1% Pt-Cs3(A) ^b	O_2	44.0	30.7	46.7	20.6	2.0	0	
	H_2	35.9	30.4	46.6	21.9	1.1	0	
1% Pt-Cs3(B) ^c	O_2	31.0	39.1	20.3	37.8	2.6	0.2	
	H_2	4.0	33.7	31.9	30.8	3.6	0	

 aC_1 is $CH_4,\ C_2$ is $C_2H_6,\ C_3$ is $C_3H_8,\ i\text{-}C_4$ is isobutane, and $C_5(+)$ is hydrocarbons containing more than five carbons.

^b Pt-Cs2.5(A) and Pt-Cs3(A): from H₂PtCl₆.

 c Pt-Cs2.5(B) and Pt-Cs3(B): from Pt(NH_3)_4Cl_2. Feed gas; *n*-butane : H_2 : N_2 = 0.05 : 0.45; catalyst 1 g; W/F 40 g h mol^{-1}.

Amount of NH₄⁺ Remained on 1 wt% Pt-Cs2.5(B) after the Pretreatments at 573 K

Ambient gas at treatment	$\mathrm{NH}_4^+/\mathrm{polyanion}^a$	H ⁺ /polyanion ^b
N_2	0.47	0.03
H_2	0.46	0.04
O_2	0.20	0.30

 a NH₄⁺/PW₁₂O₄₀³⁻ determined by infrared spectroscopy. b The amount of protons after the pretreatment in the unit of $H^+/PW_{12}O_{40}^{3-}$ (see text).

vacuum, gave a similar spectrum to that of Cs2.5, as reported previously (32).

DISCUSSION

1. Reaction Paths of Skeletal Isomerization of n-Butane

It is generally accepted that skeletal isomerization of n-butane over bifunctional catalysts proceeds according to the following steps as shown by Eqs. [1]-[3] (1, 11): (i) dehydrogenation of *n*-butane to butenes on metal sites; (ii) isomerization of butenes to isobutylene at acid sites via sec- and tert-butyl carbenium ions; and (iii) hydrogenation of isobutylene to isobutane on metal sites. As another possible step for the formation of isobutane from *tert*-butyl carbenium ion, hydride transfer from H₂ or *n*-butane has been proposed (19).

$$\underset{\text{Metal}}{\longleftarrow} \quad \underset{+}{\overset{+}{\underset{+}{\longleftarrow}}} \quad + H_2 \qquad [1]$$

$$\left(\begin{array}{c} & & \\ & & \\ & & \\ & & \end{array}\right) \xrightarrow{H^+} & \underset{\oplus}{\circledast} & \underset{\oplus}{\Longrightarrow} & \underset{\oplus}{\longleftarrow} & \underset{H^+ H^+}{\coprod} & [2]$$

"Bimolecular mechanism" is also possible. Although the elucidation of the mechanism is not the primary purpose of the present study, the mechanism will be discussed briefly to make clear the characteristics of the present catalytic system.

Promoting effects of Pt or Pd (Figs. 10 and 11), as well as the negative dependency of the initial rate on H₂ pressure (Figs. 7–9) support the important roles of metals in the step of Eq. [1]. Little dependencies of the loading amount of Pt and Pd (Figs. 10 and 11) indicate that the step of Eq. [1] is in equilibrium as in the case of Pt/chlorinated- Al_2O_3 (12). In contrast to the initial rate, the stationary rate depended positively on the H_2 pressure (Figs. 8 and 9). This is most



FIG. 12. Solid-state ³¹P NMR spectra of heteropoly compounds: (a) Cs2.5H0.5PW12O40; (b) 1 wt% Pt-Cs2.5H0.5PW12O40(A); (c) H3(imp)/1 wt% Pt-Cs₃PW₁₂O₄₀(A); and (d) 1 wt% Pt-Cs₃PW₁₂O₄₀(A). The samples were pretreated at 573 K in vacuum.

probably due to the catalyst deactivation by coke. Actually the deactivation was significant in the absence of H₂ and was appreciable at low H_2 pressure range. By this, the stationary conversions at low H_2 pressures became low. In the high H_2 pressure range, the coke formation was possibly suppressed by the rapid hydrogenation of the coke and/or its precursor and the low concentrations of butenes.

As another possible role of H₂, the generation of acidic protons has been proposed (18, 21, 33). Hattori and co-workers claimed for Pt-SO $_4^2$ /ZrO $_2$ that protons are generated from hydrogen atom formed on Pt, releasing electron to Lewis acid site (18). Fujimoto and co-workers presumed that protons are produced on the surface of ZSM-5 via the spillover of hydrogen atom from the surface of Pt in a hybrid catalyst consisting of Pt/SiO₂ and H-ZSM-5 (21). Indeed, the effect of H₂ was significant as shown in Fig. 3 in the case of Pt-Cs2.5(A). However, Pt-Cs3(A), which has no inherent acid sites, was still inactive for the isomerization even in the presence of H₂ (Table 4). This shows that protons were not formed on Pt-Cs3(A). Probably, new protons were not generated also in the case of Pt-Cs2.5.

If the dehydrogenation-hydrogenation steps are in equilibrium, the slow step would be in Eq. [2]. Since the protonation of butenes and the deprotonation are postulated to be rapid, the rate-determining step is probably the transformation from sec-butyl carbenium ion to tert-butyl carbenium ion. When HF-SbF₅ was used as a catalyst, the isomerization of *n*-butane to isobutane was very slow, while *n*-butane-1-¹³C was rapidly isomerized to *n*-butane-2-¹³C and skeletal isomerization of *n*-pentane was also fast (11). These results

	Pretreatment			Conversion	Selectivity $(mol\%)^d$					
Catalyst	(K)	\mathbf{D}^{b}	(d) <i>^c</i>	(%)	C1	C_2	C_3	i-C ₄	C ₅	
Pt-Cs3(B)	573	0.33	(27)	31.0	39.1	20.3	37.8	2.6	0.2	
Pt-Cs3(β)	773	0.05	(180)	7.1	32.9	39.8	17.4	9.9	0	
H3(imp)/Pt-Cs3(B) ^e H3(imp)/Pt-Cs3(β) ^e	573 573	0.20 0.05	(45) (180)	39.0 32.3	1.1 0.9	0.7 1.6	2.6 12.2	94.0 80.1	1.6 5.2	

 TABLE 6

 Effects of H₃PW₁₂O₄₀ Addition to 1 wt% Pt-Cs₃PW₁₂O₄₀(B)

^a Pretreatment temperature.

^b Dispersion of Pt by CO adsorption.

^c The figures in the parentheses are particle sizes estimated from the dispersion in Å.

 $^{d}C_{1}$ is CH₄, C₂ is C₂H₆, C₃ is C₃H₈, i-C₄ is isobutane, and C₅(+) is hydrocarbons containing more than five carbons.

 e H₃PW₁₂O₄₀ was impregnated with Pt-Cs3(B); Final Pt loading: 0.85 wt%. Feed gas: *n*-butane : H₂ : N₂ = 0.05 : 0.50 : 0.45;

catalyst 1 g; W/F 40 g h mol⁻¹; reaction temperature 573 K.

were explained by the monomolecular mechanism through protonated cyclopropane intermediates (11), in which only the *n*-butane isomerization to isobutane is required to proceed through the primary carbenium ion.

It should be emphasized that the selectivity to isobutane reached 91–95% on Pt-Cs2.5(A), (B) and Pd-Cs2.5 at 573 K. As can be seen in Table 1, C₁, C₂, and C₃ hydrocarbons are formed as byproducts for these catalysts, showing that the hydrogenolysis of *n*-butane slightly took place as the side reaction. Contrary to this, the byproducts on Cs2.5 (without Pt) were mainly C_3 and C_5 as reported previously (10). According to "bimolecular mechanism" (3, 34-37), it is possible that C₈ and C₁₂ hydrocarbons are formed as intermediate products from sec-butyl carbenium ion and butenes which were produced by deprotonation of sec-butyl carbenium ion and are cracked into smaller hydrocarbons such as C_3 , isobutane, and C_5 . Whether the reaction proceeds via monomolecular or bimolecular mechanism is likely dependent on the reaction conditions. As a matter of fact, whereas the fractions of $C_3 + C_5$ hydrocarbons in total products were small (less than 2%) over 1 wt% Pt-Cs2.5 and 1 wt% Pd-Cs2.5 at 573 K and 0.5 atm H₂ (Table 1), the amounts of $C_3 + C_5$ hydrocarbons were not slight at 0.05 atm H₂ at both 573 and 473 K (Tables 2 and 3). These results suggest that at 573 K and 0.5 atm of H₂, monomolecular mechanism is preferable over these catalysts, but the bimolecular mechanism cannot be ignored at lower H₂ pressures. The C₃ and C₅ hydrocarbons are considered to be formed by cracking of C₈ species produced via bimolecular mechanism. As is demonstrated in Fig. 4, the fraction of $C_3 + C_5$ hydrocarbons correlated with the concentration of butenes formed during the reaction. This is reasonable because the contribution of the bimolecular mechanism increases as the concentration of butenes increases.

If the bimolecular mechanism operates, various kinds of C_8 species are formed from *sec*-butyl carbenium ion and butenes. These C_8 species are likely to give disproportion-

ated products such as C_3 and C_5 hydrocarbons, as well as isobutane. High selectivities obtained over 1 wt% Pt-Cs2.5(B) and 1 wt% Pd-Cs2.5(A) (Table 1) suggest that the bimolecular mechanism may be less important over these catalysts under these reaction conditions. Skeletal isomerization of butenes to isobutylene proceeded at 573 K on H-ZSM-5 (38). Since the acid strength of Cs2.5 was higher than that of H-ZSM-5 (26), it is probable that the step shown by Eq. [2] is facile on Pt-Cs2.5 at 573 K, if the reaction took place via monomolecular mechanism. In order to determine the contribution of each mechanism, the experiment using isotopic labeled molecules is necessary.

2. State of Pt Particle and Selectivity

Whereas Pt-Cs3(A) was active for the hydrogenolysis of n-butane, Pt-Cs2.5(A) was very effective for the skeletal isomerization, being less active for the hydrogenolysis (Table 4). The rate of hydrogenolysis on Pt-Cs2.5(A) is about one-tenth that on Pt-Cs3(A). In order to elucidate the reason for the different catalysis, the states of Pt will be discussed first. It was reported that the particle size of Pt influenced greatly the activity for hydrogenolysis (39-42). Indeed, highly dispersed Pt-Cs3(B) was more active for the hydrogenolysis than Pt-Cs3(β) (Table 6). The particle size determined by the CO adsorption was about 30 Å both for 1 wt% Pt-Cs2.5(A) and 1 wt% Pt-Cs3(A). In addition, neither Pt-Cs2.5(A) nor Pt-Cs3(A) gave the XRD peak due to Pt crystallites. Therefore, the different catalytic activity for hydrogenolysis between Pt-Cs2.5(A) and Pt-Cs3(A) is not due to the difference in the particle size.

The oxidation state of Pt may be influential in the activity and selectivity. But as shown in Table 4, the selectivity for Pt-Cs2.5(A) or Pt-Cs3(A) was independent of the ambient gas for the pretreatment (H_2 or O_2). Thus the difference in the selectivity between Pt-Cs2.5(A) and Pt-Cs3(A) may not be due to the difference in the oxidation state of Pt.

3. Roles of Protons in Selective Isomerization

It should be noted that the O₂-treatment regenerated the protons on the surface of Pt-Cs2.5(B) (Table 5) and enhanced greatly the selectivity to isobutane (Table 5). Contrary to this, the H₂-pretreatment did not regenerate protons by NH₄⁺ decomposition and did not improve the selectivity to isobutane (Tables 4 and 5). Therefore, it can be concluded that the remarkable effect of the O₂pretreatment on the selectivity is attributed to the regeneration of protons. The NH₄⁺ observed on Pt-Cs2.5(B) is likely to form from protons of H₃PW₁₂O₄₀ and NH₃ in Pt(NH₃)₄Cl₂ and the regeneration of protons by the O₂pretreatment can be described as in Eq. [4] (43). Contrary to Pt-Cs2.5(B), the O₂-pretreatment of Pt-Cs2.5(A) changed the selectivity little, which is reasonable because Pt-Cs2.5(A) is NH₃-free:

$$NH_4^+ + 3/4O_2 \rightarrow H^+ + 1/2N_2 + 3/2H_2O.$$
 [4]

As shown in Table 6, the addition of $H_3PW_{12}O_{40}$ to Pt-Cs3(A) greatly accelerated the skeletal isomerization, but suppressed the hydrogenolysis. The remarkable change in the selectivity may be due to the endowment of acid sites.

We propose a mechanism for the selective formation of isobutane over Pt-Cs2.5 and H3(imp)/Pt-Cs3 in Scheme 1. In this mechanism, *n*-butane is dehydrogenated

In the absence of protons





SCHEME 1. A proposed reaction scheme.

to π -bonded butenes (**I**) or σ -bonded C₄ species (**I**') on the Pt surface (11, 42, 44). In the absence of proton, the hydrogenolysis proceeds on Pt through the intermediates (**I**) or (**I**'). According to Anderson *et al.* (44), *n*-butane is partially dehydrogenated to form multiply σ -bonded species such as 1,3-diadsorbed species (Scheme 1) on metal surfaces, which is considered to be a common intermediate for the hydrogenolysis and the skeletal isomerization on it. In the presence of protons, intermediate (**I**) and/or (**I**') would interact with protons and transform to *sec*-butyl carbenium ion (**II**). If so, the hydrogenolysis on Pt may be suppressed, because *sec*-butyl carbenium ion is unlikely the intermediate for the hydrogenolysis. By this unique function of protons, the selective isomerization may be attained over these heteropoly bifunctional catalysts.

It should be emphasized that the activity of Pt-Cs2.5(A) for hydrogenolysis was higher than that of Pt-Cs3(A) at 473 K and 0.5 atm of H₂ (Table 3 and Fig. 6), indicating that Pt on Pt-Cs2.5(A) has a high inherent activity for the hydrogenolysis. The fact that the rate of the hydrogenolysis over Pt-Cs3(A) increased by a factor of about 20 with the rise in the temperature from 473 to 573 K (Fig. 6) resembles the results of Pt catalysts (42, 44). Thus the little temperature dependencies of the rate of hydrogenolysis over Pt-Cs2.5(A) (Fig. 6a) is unique and can be explained by the mechanism in Scheme 1; as the reaction temperature increased, the hydrogenolysis is more effectively suppressed due to the rapid migration of protons. Baba et al. (33, 45) claimed from ¹H solid-state NMR that the mobility of protons was enhanced by the presence of Ag. Although the mobility of protons was not measured in the present case, Pt may accelerate the migration of proton, similarly to Ag(33, 45).

Information on protons on Pt-Cs2.5 and H3(imp)/Pt-Cs3 was given by solid-state ³¹P NMR. As already reported by us (32), the chemical shift of ³¹P of $PW_{12}O_{40}^{3-}$ is determined by the number of the protons which are directly interacting with the bridging oxygen atoms of the Keggin anion; the peaks observed for Cs2.5 at -14.9, -13.5, -12.1, and -10.9 ppm can be assigned to the Keggin anion having 0, 1, 2, and 3 protons, respectively. The spectrum of Fig. 12a is essentially consistent with the previous one (32). Vedrine *et al.* (46) observed a similar ³¹P spectrum of Cs2.5 and claimed that Cs2.5 consists of Cs3 and H₃PW₁₂O₄₀. However, since the peak at -10.9 ppm due to H₃PW₁₂O₄₀ (anhydrous) was not detected for Cs2.5 (32, 46), Cs2.5 is not a mixture of Cs3 and H₃PW₁₂O₄₀.

The single peak at -14.9 ppm observed for Cs3 (Fig. 12d) was in agreement with that previously reported for Cs3 (32). The appearance of the peak at -13.5 ppm for Pt-Cs2.5(A) and H3(imp)/Pt-Cs3(A) is evidence for the presence of protons. The lower intensities of the peak at -13.5 ppm than that of Cs2.5 suggest that the amounts of protons on Pt-Cs2.5(A) and H3(imp)/Pt-Cs3(A) were smaller than that

of Cs2.5. The decrease in protons by the introduction Pt can be described in Eq. [5]; protons react with chloride ion, which contains the starting material, H_2PtCl_6 to form HCl during the preparation processes:

$$nH^+ + PtCl_6^{2-} \rightarrow [PtCl_{6-n}]^{(2-n)-} + nHCl.$$
 [5]

4. Effect of Pt Particle Size on the Role of Protons and Selectivity

The fact that the rate of hydrogenolysis increased as the Pt particle size of Pt-Cs3 decreased is consistent with the general trend of metallic catalysts (42). The selectivity to isobutane also depended on the particle size of Pt of H3(imp)/Pt-Cs3 (Table 6). By the addition of $H_3PW_{12}O_{40}$ to Pt-Cs3, the hydrogenolysis was more effectively suppressed for smaller Pt particle (H3(imp)/Pt-Cs3), resulting in the higher selectivity for the smaller Pt particle. This is probably due to that the smaller particles (the higher dispersion) are favorable to intimate interaction between Pt and protons. As reported elsewhere (47), when Pt/SiO_2 was physically mixed with Cs2.5, the reaction rate increased greatly, but the selectivity decreased. This suggests that close proximity between the metal site and the acid site as in the case of Pt-Cs2.5 is required for the selective isomerization of *n*-butane.

CONCLUSION

A new bifunctional catalyst, Pt or Pd-promoted $Cs_{2.5}H_{0.5}PW_{12}O_{40}$, was found to be efficient catalyst for the skeletal isomerization of *n*-butane. At 573 K in the presence of H₂, these heteropoly compounds were superior to Pt-SO₄²⁻/ZrO₂ and Pt-HZSM-5 with respect to the selectivity. Over these heteropoly compounds, the bifunctional mechanism has been proposed, on the basis of the little dependence of metal loading level and the negative dependence of the H₂ pressure on the reaction rate. A unique role of proton in the selective formation of isobutane has been demonstrated. A probable interpretation is that protons present near the metal particles interact with the intermediates for hydrogenolysis and direct them to isomerization. By this, the selective isomerization proceeds over the bifunctional heteropoly compounds.

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REFERENCES

- Frischkorn, G. L., Kuchar, P. J., and Olson, R. K., *Energy Prog.* 8, 154 (1988).
- Hino, M., Kobayashi, S., and Arata, K., J. Am. Chem. Soc. 101, 6439 (1979); Arata, K., Adv. Catal. 37, 165 (1990).

- Adeeva, V., de Haan, J. W., Janchen, J., Schunemann, V., van de Ven, L. T. M., Sachtler, W. M. H., and van Santen, R. A., *J. Catal.* **151**, 364 (1995); Adeeva, V., Lei, G. D., and Sachtler, W. M. H., *Catal. Lett.* **33**, 135 (1995).
- Yaluris, G., Larson, R. B., Kobe, J. M., Gonzalez, M. R., Fogash, K. B., and Dumesic, J. A., *J. Catal.* **158**, 336 (1996).
- Stocker, M., Hemmerbach, P., Rader, J. H., and Grepstad, J. K., *Appl. Catal.* 25, 223 (1986).
- 6. Yori, J. C., Luy, J. C., and Parera, J. M., Appl. Catal. 46, 103 (1989).
- Shigeishi, R., Garforth, A., Harris, I., and Dwyer, J., J. Catal. 130, 423 (1991).
- 8. Mechlor, A., Garbowski, E., Mathieu, M. V., and Primet, M., *J. Chem. Soc. Faraday Trans. I* 82, 1893 (1986).
- 9. Na, K., Okuhara, T., and Misono, M., Chem. Lett., p. 1141 (1993).
- Na, K., Okuhara, T., and Misono, M., J. Chem. Soc. Faraday Trans. 91, 367 (1995).
- Gates, B. C., Katzer, J. R., and Schuit, G. C. A., *in* "Chemistry of Catalytic Processes." McGraw-Hill, New York, 1979.
- Melchor, A., Garbowski, E., Mathieu, M. V., and Primet, M., J. Chem. Soc. Faraday Trans. 182, 1893 (1986).
- Bernard, P., and Primet, M., J. Chem. Soc. Faraday Trans. 86, 3667 (1990).
- Garin, F., Andriamasinoro, D., Abdulsamad, A., and Sommer, J., J. Catal. 131, 199 (1991).
- 15. Hino, M., and Arata, K., Catal. Lett. 30, 25 (1995).
- Coelho, M. A., Resasco, D. E., Sikabwe, E. C., and White, R. L., *Catal. Lett.* 32, 253 (1995).
- Jatia, A., Chang, C., Macleod, J. D., Okubo, T., and Davis, M. E., *Catal. Lett.* 25, 21 (1994).
- 18. Ebitani, K., Konishi, J., and Hattori, H., J. Catal. 131, 257 (1991).
- 19. Iglesia, E., Soled, S. L., and Kramer, G. M., J. Catal. 144, 238 (1993).
- Tanabe, K., and Yamaguchi, T., *in* "Successful Design of Catalysts," p. 99. Elsevier, Amsterdam, 1989.
- 21. Fujimoto, K., Maeda, K., and Aimoto, K., Appl. Catal. A 91, 81 (1992).
- 22. Misono, M., Catal. Rev. Sci-Eng. 29, 269 (1987); 30, 339 (1988).
- 23. Okuhara, T., Mizuno, N., and Misono, M., Advan. Catal. 41, 113 (1996).
- Suzuki, S., Kogai, K., and Ono, Y., *Chem. Lett.*, p. 699 (1984); Ono, Y., Taguchi, M., Gerile, Suzuki, S., and Baba, T., *in* "Catalysis by Acids and Bases" (B. Imelik, C. Naccache, G. Coudurier, Y. Ben Taarit, and J. C. Vedrine, Eds.), p. 167. Elsevier, Amsterdam, 1985.
- Na, K., Okuhara, T., and Misono, M., J. Chem. Soc. Chem. Commun., p. 1422 (1993).
- Okuhara, T., Nishimura, T., Watanabe, H., and Misono, M., J. Mol. Catal. 74, 247 (1992).
- Inui, T., Makino, Y., Okazaki, F., Nagano, S., and Miyamoto, A., *Ind. Eng. Chem. Res.* 26, 647 (1987).
- Lee, K. Y., Arai, T., Nakata, S., Asaoka, S., Okuhara, T., and Misono, M., J. Am. Chem. Soc. 114, 2836 (1992).
- Pines, H., *in* "The Chemistry of Catalytic Hydrocarbon Conversions." Academic Press, New York, 1981.
- 30. Aston, J. G., and Szasy, G., J. Chem. Phys. 14, 67 (1946).
- 31. Chao, K., Wu, H., and Leu, L., J. Catal. 157, 289 (1995).
- Okuhara, T., Nishimura, T., Na, K., and Misono, M., *in* "Acid-Base Catalysis-II" (H. Hattori, M. Misono, and Y. Ono, Eds.), p. 419. Elsevier/Kodansha, Amsterdam/Tokyo, 1994.
- 33. Baba, T., and Ono, Y., Zeolite 7, 292 (1987).
- 34. Wan, K. T., Khouw, C. B., and Davis, M. E., J. Catal. 158, 311 (1996).
- Adeeva, V., Lei, G. D., and Sachlter, W. M. H., *Appl. Catal. A: General* 118, L11 (1994).
- 36. Zarkalis, A. S., Hsu, C.-Y., and Gates, B. C., Catal. Lett. 29, 235 (1994).
- 37. Cheung, T., D'Itri, J. L., and Gates, B. C., J. Catal. 151, 464 (1995).
- 38. Butler, A. C., and Nicolaides, C. P., Catal. Today 18, 443 (1993).
- 39. Moreno-Castilla, C., Porcel-Jiménez, A., Carrasco-Marín, F., and Utrera-Hidalgo, E., *J. Mol. Catal.* **66**, 329 (1991).

- 40. Bond, G. C., and Yide, X., J. Chem. Soc. Faraday Trans. 180, 969 (1984).
- Mills, G. A., Heinemann, H., Milliken, T. A., and Oblad, A. G., *Ind. Eng. Chem.* 45, 134 (1953); Weisz, P. B., and Swegler, E. W., *Science* 126, 31 (1957).
- 42. Boudart, M., Advan. Catal. 20, 153 (1969).
- Okuhara, T., Na, K., and Misono, M., *in* "Science and Technology in Catalysis 1994" (Y. Izumi, H. Arai, and M. Iwamoto, Eds.), p. 245. Kodansha, Tokyo, 1995.
- 44. Anderson, J. R., and Avery, N. R., J. Catal. 5, 446 (1996).
- Baba, T., Nomura, M., and Ono, Y., *in* "Acid-Base Catalysis II" (H. Hattori, M. Misono, and Y. Ono, Eds.), p. 419. Elsevier/Kodansha, Amsterdam/Tokyo, 1994.
- Essayem, N., Coudurier, Fournier, G. M., and Vedrine, J. C., *Catal. Lett.* 34, 223 (1995).
- Na, K., Iizaki, T., Okuhara, T., and Misono, M., J. Mol. Catal. A 115, 449 (1997).