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# Skeletal isomerization of alkanes and hydroisomerization of benzene over solid strong acids and their bifunctional catalysts

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## Abstract

Hydroisomerization of benzene to methylcyclopentane has been studied using bifunctional catalysts consisting of Pt and an acidic Cs salt of $H_3PW_{12}O_{40}$. The hydrogenation ability of Pt and the surface acidity (the amount of acid sites) of the bifunctional catalysts were key factors in determining the yield; the former is required for complete hydrogenation of benzene and the latter is parallel with the activity for skeletal isomerization of cyclohexane. However, for Pt-promoted acidic Cs salts, the hydrogenation ability tended to be suppressed as the amount of proton (or the heteropoly anion) increased. As a result, 2 wt.%Pt–$Cs_{2.5}H_{0.5}PW_{12}O_{40}$ gave a high yield (51%) of methylcyclopentane at 473 K with 100% conversion of benzene. When 2 wt.%Pt was added to "$Cs_{2.5}H_{0.5}PW_{12}O_{40}$" which was prepared by impregnating $Cs_3PW_{12}O_{40}$ with the aqueous solution of $H_3PW_{12}O_{40}$, the higher yield of methylcyclopentane was also obtained. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Heteropoly compound; Bifunctional catalysts; Hydroisomerization; Benzene; Methylcyclopentane

## 1. Introduction

Bifunctional catalysts consisting of noble metal and solid acid are widely used for reforming processes including skeletal isomerization, dehydrocyclization, etc. These bifunctional catalysts provide both acid and hydrogenation–dehydrogenation functions which are required to be well-balanced to accelerate desirable reactions selectively.

Pt-promoted heteropoly compounds like Pt–$Cs_{2.5}H_{0.5}PW_{12}O_{40}$ were reported to be excellent catalysts for skeletal isomerization of *n*-alkanes [1–4]. Pt– or Pd–$Cs_{2.5}H_{0.5}PW_{12}O_{40}$ was highly active and selective for isomerization of *n*-butane in the presence of $H_2$ at 573 K [1]. It was suggested that protons present in proximity of Pt or Pd particles on $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ suppressed the hydrogenolysis of *n*-butane, which resulted in the increase of the selectivity to isobutane [1]. These bifunctional catalysts are thus expected to be available for various reforming reactions of hydrocarbons.

Hydrocarbon oils including aromatics like benzene are efficient gasoline having a high octane number. However, it is keenly desirable to reduce the content of benzene in gasoline from a viewpoint of environmental protection. One possible way to diminish the benzene content in gasoline retaining its high octane number is to transform benzene to methylcyclopentane by the hydroisomerization. Research octane numbers of benzene and methylcyclopentane are 98.0 and 91.3, respectively, while those of cyclohexane and *n*-hexane are 83.0 and 24.8, respectively. Practically, the hydroisomerization of benzene has been operated in two-step processes consisting of hydrogenation

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of benzene and skeletal isomerization of product cyclohexane.

In the present study, we attempted to elucidate the catalytic property of the heteropoly-bifunctional catalysts for the hydroisomerization of benzene to methylcyclopentane by comparing with Pt–sulfated $ZrO_2$ [5,6]. Furthermore, various kinds of the Pt-heteropoly compounds were prepared to improve the catalytic performance of this reaction. There are many reports about the skeletal isomerization of cyclohexane over solid acids such as zeolites [7,8], mixed oxides [9,10], $SbF_5$–$SiO_2$–$Al_2O_3$ [11], and $Mo_2C$ [12]. On the other hand, the results of the hydroisomerization of aromatics over bifunctional catalysts have appeared in some patents [13–15].

## 2. Experimental

### 2.1. Catalysts

As solid acids, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$, sulfated $ZrO_2$ and H-ZSM-5 were used. $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ was prepared from aqueous solutions of $H_3PW_{12}O_{40}$ and $Cs_2CO_3$ by a titration method [1,16]. The surface area was 110 $m^2\,g^{-1}$ after the calcination at 523 K. This salt will be abbreviated as Cs2.5. Sulfated $ZrO_2$ was prepared according to the literature [17]. The surface area was 90 $m^2\,g^{-1}$ after the calcination at 893 K in air. This catalyst will be denoted as $SO_4^{2-}/ZrO_2$. H-ZSM-5 (Tosoh, HSZ860HOA, Si/Al = 37, 381 $m^2\,g^{-1}$) was also used.

Pt-promoted $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ catalysts were prepared by the titration method [1,18,19]. An aqueous solution of $H_2PtCl_6.6H_2O$ (0.04 mol $dm^{-3}$) was added to an aqueous solution of $H_3PW_{12}O_{40}$ (0.08 mol $dm^{-3}$) at room temperature. Then an aqueous solution of $Cs_2CO_3$ (0.10 mol $dm^{-3}$) was added dropwise to the mixture at the rate of 0.1 $cm^3\,min^{-1}$ with vigorous stirring at room temperature. The obtained suspension was allowed to stand overnight at room temperature, and evaporated at 318 K to obtain solid. The loading amount of Pt was changed from 0.5 to 4.0 wt.%. This catalyst will be denoted as, e.g., 0.5 wt.%Pt–Cs2.5. These heteropoly compounds were pretreated in a flow of $O_2$ for 2 h and then in a flow of $H_2$ for 1 h at 573 K.

Two other kinds of Pt-promoted heteropoly compounds were prepared. To get the first, Pt was impregnated into $Cs_3PW_{12}O_{40}$ which was prepared similarly to $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ to get 2 wt.%Pt–$Cs_3PW_{12}O_{40}$. Then the aqueous solutions of $H_3PW_{12}O_{40}$ was added to Pt–$Cs_3PW_{12}O_{40}$ in an incipient wetness method. These catalysts will be denoted as H3/2 wt.%Pt–Cs3. The second was obtained by the addition of Pt to $H_3PW_{12}O_{40}/Cs_3PW_{12}O_{40}$ having various compositions prepared by the incipient wetness impregnation of $Cs_3PW_{12}O_{40}$ with the aqueous solution of $H_3PW_{12}O_{40}$. To the $H_3PW_{12}O_{40}/Cs_3PW_{12}O_{40}$, the aqueous solution of $H_2PtCl_6$ was added after $H_3PW_{12}O_{40}/Cs_3PW_{12}O_{40}$ was calcined at 573 K in air for 5 h. The resulting catalysts were denoted as, e.g., 2 wt.%Pt–H3/Cs3. These were pretreated in a flow of $O_2$ for 2 h and then in a flow of $H_2$ for 1 h at 573 K. For these catalysts-15 wt.%$H_3PW_{12}O_{40}$-added samples correspond to the average composition of "$Cs_{2.5}H_{0.5}PW_{12}O_{40}$".

0.5 wt.%Pt–sulfated $ZrO_2$ was prepared using $H_2PtCl_6.6H_2O$ according to the literature [5,6], which is denoted as Pt–$SO_4^{2-}/ZrO_2$. Prior to use, these materials were pretreated in the flow of $H_2$ at 573 or 673 K for 1 h. 0.5 wt.%Pt–mordenite was prepared by an ion-exchange method using $NH_4$–mordenite (from Na–mordenite (JRC-Z-M-15) and $NH_4NO_3$) and $Pt(NH_3)_4(OH)_2$ (Aldrich Chem.). These Pt catalysts were calcined in air at 773 K for 4 h.

### 2.2. Catalytic reactions

Skeletal isomerization of *n*-butane or *n*-pentane was performed in a closed circulation system (about 300 $cm^3$) with 40 Torr of *n*-butane or 48 Torr of *n*-pentane. Cs2.5 and $SO_4^{2-}/ZrO_2$ (0.5 g) were pre-evacuated at 573 K for 3 h and 673 K for 5 h, respectively. The products were analyzed with an on-line TCD gas chromatograph (Shimadzu GC 8A) with a column of VZ-7.

Hydroisomerization of benzene was carried out in a continuous flow system under atmospheric pressure. The feed gas consisted of benzene, 13% and $H_2$, 87% in volume. The total flow rate was 5–10 $cm^3\,min^{-1}$. Prior to the reaction, the catalysts (2.0 g) were pretreated in an $O_2$ flow (50 $cm^3\,min^{-1}$) for 2 h, in a He (50 $cm^3\,min^{-1}$) for 10 min, and then in a $H_2$ flow (50 $cm^3\,min^{-1}$) for 1 h at 573 K. The products were analyzed with a FID GC (Shimadzu GC-14B) equipped with a capillary column (WCOT Fused Silica Squalane).

### 2.3. Other measurements

Dispersion of Pt on the catalyst was determined from temperature programmed desorption (TPD) of adsorbed CO, using the desorption amounts of CO and $CO_2$. It was assumed that $CO_2$ was formed due to the reaction between the adsorbed CO, and OH group of the surface and CO was adsorbed on the surface metal atom at 1:1 stoichiometry [20]. The TPD spectra were obtained by using a TPD system (Multi-task TPD, BEL, Japan) equipped with a mass spectrometer. After the catalyst was pretreated at 573 K in the flow of $O_2$ (2 h), He (10 min), and then $H_2$ (1 h). CO (100 Torr) was introduced at 298 K for 10 min. The surface area of catalyst was measured by a BET method of $N_2$ at 77 K using an automatic gas adsorption apparatus (BELSORP 28SA, BEL, Japan).

## 3. Results and discussion

Fig. 1 shows the time courses of skeletal isomerization of *n*-butane over Cs2.5 and $SO_4^{2-}/ZrO_2$ at various temperatures. As shown in Fig. 1A, the reaction proceeded with little deactivation at least for 300 min on Cs2.5. For Cs2.5, the conversion of *n*-butane increased as the reaction temperature increased from 423 to 523 K, the conversions being less than 25%. The selectivity to isobutane was in the range of 85–95% under these reaction conditions. Although $SO_4^{2-}/ZrO_2$ was more active than Cs2.5 at lower temperatures (Fig. 1B), the deactivation of $SO_4^{2-}/ZrO_2$ was significant at 523 K. The selectivity on $SO_4^{2-}/ZrO_2$ was in the range of 67–92% under these conditions.

The catalytic data of Cs2.5 and $SO_4^{2-}/ZrO_2$ for the skeletal isomerization of *n*-butane and *n*-pentane were summarized in Table 1. Both Cs2.5 and $SO_4^{2-}/ZrO_2$ gave propane and pentane as byproducts of isomerization of *n*-butane. On the other hand, isobutane as well as isopentane was mainly produced in the isomerization of *n*-pentane. The product distribution from

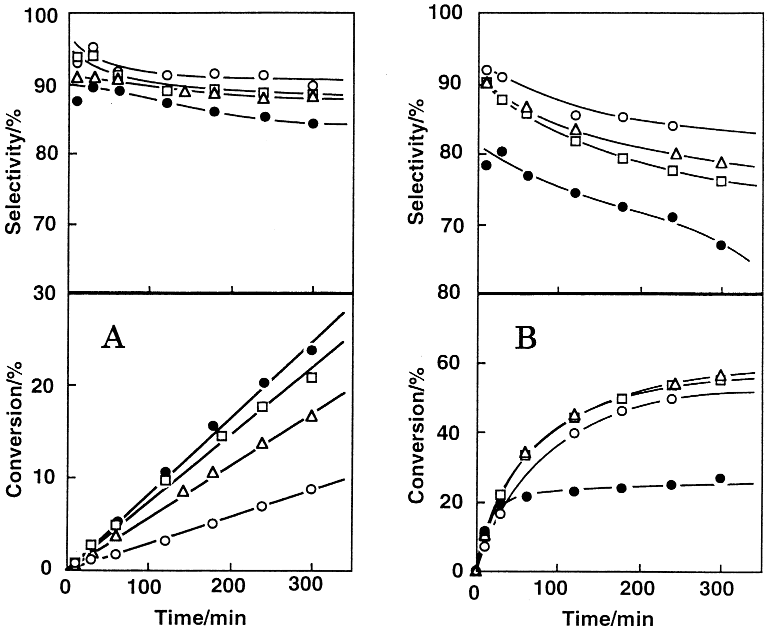

Fig. 1. Time courses of skeletal isomerization of *n*-butane on (A) $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ and (B) sulfated $ZrO_2$. Reaction temperature: (○) 423 K; (△) 453 K; (□) 493 K; (●) 523 K. Catalyst weight 0.5 g. The top is the selectivity to isobutane and the bottom is the conversion of *n*-butane.

Table 1
Conversion and selectivity of skeletal isomerization of *n*-butane and *n*-pentane over $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ and sulfated $ZrO_2$ at 423 K (reaction conditions: *n*-butane, 40 Torr or *n*-pentane, 48 Torr; catalyst weight 0.5 g; at 473 K)

| Catalyst | Conversion/% [h] | Selectivity/mol%[a] | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | C1 | C2 | C3 | *i*-C4 | C5 | | |
| *n-Butane isomerization* | | | | | | | | |
| Cs2.5 | 6.6 [4] | 0 | 0 | 4.4 | 91.3 | 3.5 | | |
| SZ | 19.6 [2] | 0 | 0 | 10.1 | 83.1 | 5.1 | | |
| H-ZSM-5 | 6.9 [10] | 0 | 0.2 | 63.5 | 36.3 | 0 | | |
| | | C1 | C2 | C3 | *i*-C4 | *n*-C4 | *i*-C5 | C6 |
| *n-Pentane isomerization* | | | | | | | | |
| Cs2.5 | 15.5 [6] | 0 | 0 | 4.5 | 45.5 | 0 | 46.5 | 4.5 |
| SZ | 13.5 [4] | 0 | 0 | 5.3 | 43.3 | 1.3 | 43.3 | 6.7 |
| H-ZSM-5[b] | 13.2 [1] | 0 | 0 | 14.4 | 41.1 | 17.4 | 16.7 | 10.3 |

[a] C1, methane; C2, ethane; C3, propane; *i*-C4, isobutane; *n*-C4, *n*-butane; C5, pentanes; *i*-C5, isopentane; and C6, hexanes.

[b] Catalyst weight 0.32 g.

*n*-pentane over $SO_4^{2-}/ZrO_2$ was similar to the literature [21]. Conclusively, Cs2.5 and $SO_4^{2-}/ZrO_2$ catalyzed efficiently the skeletal isomerization of these alkanes. Hence, we used Cs2.5 and $SO_4^{2-}/ZrO_2$ as a component of bifunctional catalyst for hydroisomerization of benzene.

It is considered that the hydroisomerization of benzene consists of hydrogenation of benzene to cyclohexane and the skeletal isomerization of cyclohexane to methylcyclopentane. The former reaction rate is necessarily governed by the hydrogenation ability of Pt of the bifunctional catalyst, and the latter is determined by the acidic property. Thus catalyst design for optimization of both functions is indispensable to prepare a prominent catalyst. As was not shown here, the skeletal isomerization of cyclohexane proceeded with a rate similar to that of the formation of methylcyclopentane from benzene over 2 wt.%Pt–Cs2.5, when the conversion of benzene was near 100%.

In order to determine the reaction temperature at which the highest yield is achieved, the influence of the reaction temperature on the yield of methylcyclopentane in hydroisomerization of benzene was examined using 0.5 wt.%Pt–Cs2.5. The results are shown in Fig. 2, in which the broken line corresponds to the equilibrium yield of methylcyclopentane among benzene, cyclohexane, and methylcyclopentane. It is expected that maximum yield (73.8%) is obtained at 500 K under these conditions. As shown in Fig. 2, the yield of methylcyclopentane increased and then decreased through a maximum at 473 K when the reaction was performed successively from 423 to 573 K for about each 2 h. The decrease in the yield is observed at the reaction temperatures higher than 473 K, probably attributed to the catalyst deactivation, and the significant drop of the yield at 573 K is due to the equilibrium limitation. From the results of Fig. 2, we chose 473 K as the reaction temperature.

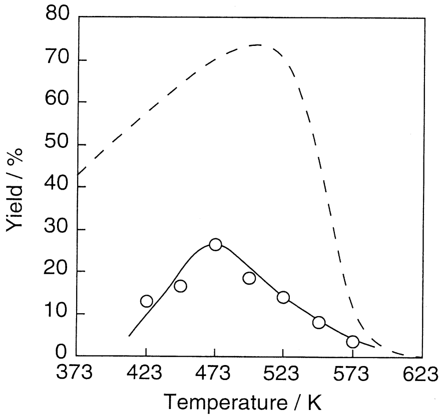

Fig. 2. Change of yield of methylcyclopentane in hydroisomerization of benzene over 0.5 wt.%Pt–$Cs_{2.5}H_{0.5}PW_{12}O_{40}$ upon reaction temperature. Reaction conditions: benzene:$H_2$ = 13:87 in volume, total flow rate 10 $cm^3$ $min^{-1}$, and catalyst weight 2.0 g.

Fig. 3 shows the time courses of hydroisomerization of benzene over Pt–Cs2.5 having different amounts of Pt loading. Decrease in the conversion with time

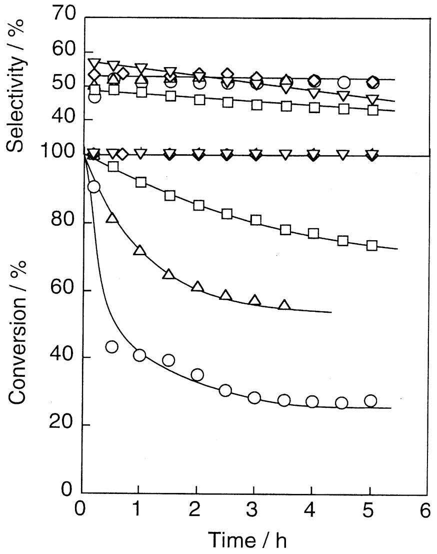

Fig. 3. Time courses of hydroisomerization of benzene at 473 K over Pt–$Cs_{2.5}H_{0.5}PW_{12}O_{40}$ having different amount of Pt: (○) 0.25 wt.%; (△) 0.5 wt.%; (□) 1.0 wt.%; (◇) 2.0 wt.%; and (▽) 4.0 wt.%. Reaction conditions: benzene:$H_2$ = 13:87 in volume, total flow rate 10 $cm^3$ $min^{-1}$, and catalyst weight 2.0 g.

was significant at the lower levels of the Pt loadings, but no decrease was observed when the Pt loading exceeded to 2 wt.%. Stationary conversions were obtained at least after ca. 5 h over these catalysts. It is clear that the stationary conversions became higher as the amount of Pt increased. It is noted that both 2 and 4 wt.%Pt–Cs2.5 gave 100% conversion in this reaction period. The selectivity to methylcyclopentane was around 50% over these catalysts. The results of Fig. 3 demonstrates that the hydrogenation ability of Pt of Pt–Cs2.5 would be sufficient when the Pt loadings were higher than 2 wt.%.

Fig. 4 gives the conversion of the hydroisomerization of benzene as a function of the surface area of Pt on Pt–Cs2.5. The surface area of Pt was calculated from the dispersion of Pt and the loading amount, assuming the density of Pt atom, $1.25 \times 10^{19}$ $m^{-2}$ [22]. The conversion increased linearly as the surface area of Pt increased up to about 0.20 $m^2$ $g^{-1}$, and the change became smaller at higher levels of surface area, which is due to the approaching upper limitation (100%) of the conversion. On the other hand, the yield of methylcyclopentane increased as the surface area of Pt (up to 0.2 $m^2$ $g^{-1}$), but changed only slightly at higher levels of the Pt surface area. The different behavior between the conversion and yield indicates that the increase of the Pt surface area is effective for the hydrogenation, but not for the skeletal isomerization of cyclohexane. Since Pt itself little possesses the activity for the skeletal isomerization, it is reasonable that the rate of skeletal isomerization of cyclohexane depends on the amount of acid sites. Thus the slight change of the yield of methylcylopentane with the Pt surface area above 0.2 $m^2$ $g^{-1}$ (Fig. 4) means that the acid amounts remained almost unchanged.

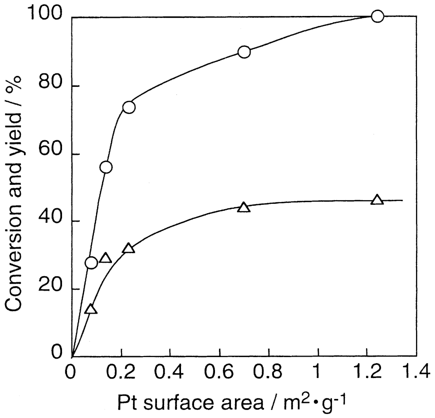

Fig. 4. Conversion of benzene (○) and yield of methylcyclopentane (△) as a function of Pt surface area of Pt–$Cs_{2.5}H_{0.5}PW_{12}O_{40}$. Reaction conditions: benzene:$H_2$ = 13:87 in volume, total flow rate 10 $cm^3$ $min^{-1}$, 473 K, and catalyst weight 2.0 g.

Fig. 5 provides the influence of amounts of $H_3PW_{12}O_{40}$ in the H3/2 wt.%Pt–Cs3 on the conversion and yield, where H3/2 wt.%Pt–Cs3 correspond to the catalysts prepared by the impregnation of 2 wt.%Pt–$Cs_3PW_{12}O_{40}$ with the $H_3PW_{12}O_{40}$ solution. It was observed that 2 wt.%Pt–Cs3 itself was highly active for the hydrogenation of benzene, but was inactive for the skeletal isomerization. Up to 9 wt.% of $H_3PW_{12}O_{40}$, the conversion of benzene was retained to be 100% and the yield increased with the amount of $H_3PW_{12}O_{40}$. However, the amount of $H_3PW_{12}O_{40}$ exceeded to 15 wt.%, the conversion of benzene became less than 100% and the yield decreased with the increase in the amount of $H_3PW_{12}O_{40}$. Consequently, the addition of 21 wt.% $H_3PW_{12}O_{40}$ to 2 wt.%Pt–Cs3 lowered greatly both

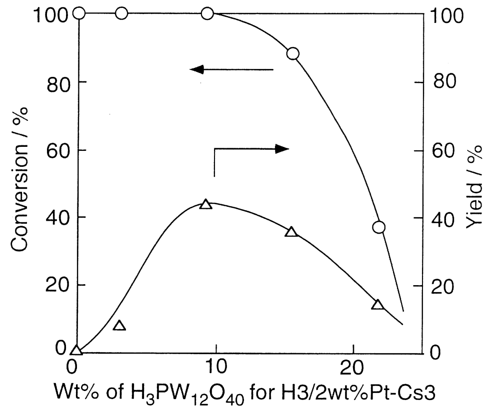

Fig. 5. Conversion of benzene (○) and yield of methylcyclopentane (△) as a function of the amount of $H_3PW_{12}O_{40}$ of $H_3PW_{12}O_{40}$/2 wt.%Pt–$Cs_3PW_{12}O_{40}$. Reaction conditions: benzene:$H_2$ = 13:87 in volume, catalyst weight 2.0 g, total flow rate 10 cm$^3$ min$^{-1}$, and 473 K.

the conversion and yield. These results clearly indicate that the addition of $H_3PW_{12}O_{40}$ suppressed appreciably the hydrogenation ability.

Fig. 6 gives the changes of the Pt surface area and surface acidity as a function of the amount of $H_3PW_{12}O_{40}$ and of H3/2 wt.%Pt–Cs3. The surface acidity corresponds to the amount of the acid sites on the surface [22–24] as described above. The BET surface areas were 104, 91, 76, 76, and 75 m$^2$ g$^{-1}$ for H3/2 wt.%Pt–Cs3 with the amounts of $H_3PW_{12}O_{40}$ added to 2 wt.%Pt–Cs3, 0, 3, 9, 15 and 21 wt.%, respectively. As shown in Fig. 6, the surface acidity increased linearly as the amount of $H_3PW_{12}O_{40}$ increased. Contrary to this, the Pt dispersion was reduced from 22 (2 wt.%Pt–Cs3) to 21, 16, 10 and 8% with the addition of 3, 9,15, and 21 wt.% of $H_3PW_{12}O_{40}$. Therefore, the depression of yield by the addition of large amount of $H_3PW_{12}O_{40}$ in spite of the increase in the surface acidity (Fig. 5) is attributed to the decrease in the hydrogenation ability brought about by lowering the Pt dispersion. Probably, $H_3PW_{12}O_{40}$ covered partly the particle of Pt. For enhancement of yield, not only the surface acidity, but also the Pt surface area should be retained high.

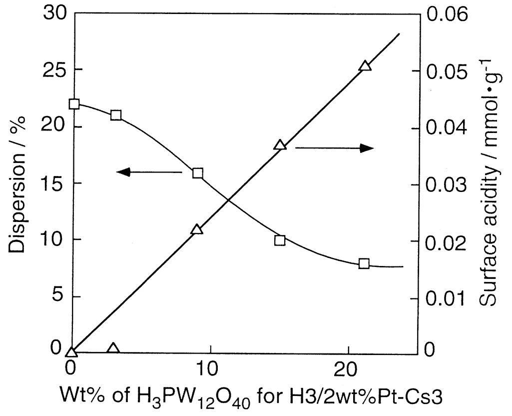

Fig. 6. Effects of amount of $H_3PW_{12}O_{40}$ of $H_3PW_{12}O_{40}$/2 wt.%Pt–$Cs_3PW_{12}O_{40}$ on the dispersion of Pt and surface acidity.

In order to keep the high dispersion of Pt at the higher surface acidity, we attempted to prepare a different type of bifunctional catalysts. That is, $H_3PW_{12}O_{40}$ was first added to Cs3 by the incipient wetness technique and the obtained solids were calcined at 573 K in air (this is denoted as H3/Cs3). As was reported previously [23], nearly uniform acidic salts were obtained by this treatment. Finally, the aqueous solution of $H_2PtCl_6.6H_2O$ was added to the H3/Cs3 (incipient wetness impregnation), and the resultant solid was pretreated in the $O_2$ flow and then in the $H_2$ flow as described in experimental section. As a matter of fact (Table 2), we obtained 25% dispersion of Pt for 2 wt.%Pt–H3/Cs3 having 15 wt.%$H_3PW_{12}O_{40}$, which is higher than that (10%) of H3/2 wt.%Pt–Cs3 with 15 wt.% of $H_3PW_{12}O_{40}$. In this preparation, the covering of Pt particles with $H_3PW_{12}O_{40}$ was probably prevented.

In Fig. 7, the influence of wt.% of $H_3PW_{12}O_{40}$ in 2 wt.%Pt–H3/Cs3 on conversion of benzene and yield is shown. Changes similar to those of Fig. 5 were found, but the maximum yield (51%) was obtained at 15 wt.% of $H_3PW_{12}O_{40}$. In these catalysts, the Pt dispersions were 33, 28, 25 and 7 for the 2 wt.%Pt–H3/Cs3 with 3, 9, 15, and 21 wt.% of $H_3PW_{12}O_{40}$. In addition, the catalyst surface areas were 104, 96, 85, and 40 m$^2$ g$^{-1}$ for the 2 wt.%Pt–H3/Cs3 with 3, 9, 15, and 21 wt.% of $H_3PW_{12}O_{40}$.

The catalytic data for the hydroisomerization of benzene over these heteropoly compounds are listed in Table 2, together with the other bifunctional catalysts. When the Pt loading amount was 0.5 wt.%, Pt–Cs2.5 exhibited about 30% yield of methylcyclopentane

Table 2
Activity and selectivity for skeletal isomerization of benzene at 473 K over bifunctional catalysts (reaction conditions: benzene:$H_2$ = 13:87 in volume; total flow rate = 10 $cm^3 min^{-1}$; and catalyst weight 2.0 g)

| Catalyst | Conversion/% | Selectivity[a]/% | | | | | | | | | Yield[b]/% |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | C1–C2 | C3 | C4 | C5 | C6 | MCP | CH | C7 | C8 | |
| 0.5 wt.%Pt–Cs2.5[c] | 56.0 | 0 | 0 | 0.6 | 0.2 | 0.1 | 52.1 | 46.0 | 0 | 1.0 | 29.2 |
| 2 wt.%Pt–Cs2.5[d] | 99.9 | 0 | 0.1 | 2.1 | 1.1 | 0.1 | 51.5 | 42.7 | 0.3 | 2.1 | 51.3 |
| H3/2 wt.%Pt–Cs3[e] | 100 | 0 | 0 | 1.0 | 0.3 | 0.2 | 44.0 | 53.1 | 0.3 | 1.1 | 44.0 |
| 2 wt.%Pt/H3–Cs3[f] | 100 | 0 | 0.1 | 2.4 | 0.9 | 0.6 | 51.4 | 41.8 | 0.4 | 2.4 | 51.3 |
| 0.5 wt.%Pt–SZ[g] | 54.5 | 0 | 0 | 1.1 | 1.0 | 0.2 | 56.2 | 40.4 | 0 | 1.1 | 30.7 |
| 0.5 wt.%Pt–SZ[h] | 98.5 | 0 | 0 | 0 | 0.1 | 0 | 16.4 | 83.5 | 0 | 0 | 16.2 |
| 0.5 wt.%Pt–mor[i] | 5.8 | 0 | 2.2 | 2.6 | 0 | 0 | 39.5 | 55.7 | 0 | 0 | 2.3 |

[a] Cn, hydrocarbons having *n* carbon atoms; C6, hydrocarbons having 6 carbon atoms except for methylcyclopentane and cyclohexane; MCP, methylcyclopentane; CH, cyclohexane; Selectivity/% = 100 × $n\,[C_n]$/[total carbon atom], where$[C_n]$ means the concentration of hydrocarbons having *n* carbon atoms at the outlet of the reactor.

[b] For methylcyclopentane.

[c] 0.5 wt.%Pt–$Cs_{2.5}H_{0.5}PW_{12}O_{40}$; Pt dispersion = 11%.

[d] 2 wt.%Pt–$Cs_{2.5}H_{0.5}PW_{12}O_{40}$; Pt dispersion = 14%.

[e] $H_3PW_{12}O_{40}$/2 wt.%Pt–$Cs_3PW_{12}O_{40}$ with 9 wt.%$H_3PW_{12}O_{40}$; Pt dispersion = 16%.

[f] 2 wt.%Pt/$H_3PW_{12}O_{40}$–$Cs_3PW_{12}O_{40}$ with 15 wt.%$H_3PW_{12}O_{40}$; Pt dispersion = 25%.

[g] 0.5 wt.%Pt–sulfated $ZrO_2$ pretreated in $H_2$ at 573 K for 1 h.

[h] 0.5 wt.%Pt–sulfated $ZrO_2$ pretreated in $H_2$ at 673 K for 1 h.

[i] 0.5 wt.%Pt–mordenite.

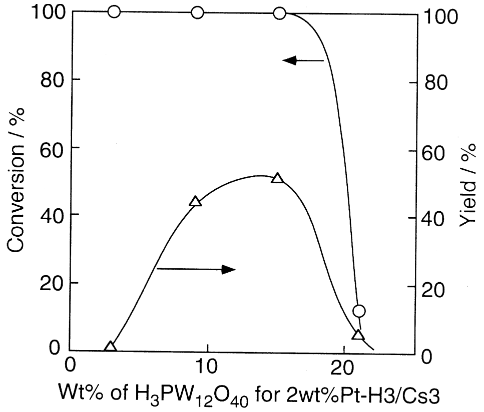

Fig. 7. Conversion of benzene (○) and yield of methylcyclopentane (△) as a function of the amount of $H_3PW_{12}O_{40}$ of 2 wt.%Pt–$H_3PW_{12}O_{40}$/$Cs_3PW_{12}O_{40}$. Reaction conditions: benzene:$H_2$ = 13:87 in volume, catalyst 2.0 g, total flow rate 10 $cm^3 min^{-1}$, and 473 K.

which is comparable to that on Pt–$SO_4^{2-}/ZrO_2$. The increase of Pt loading to 2 wt.% on Pt–Cs2.5 led to the yield being enhanced to 51%. For the bifunctional catalysts prepared from $Cs_3PW_{12}O_{40}$, the order of the addition of Pt or $H_3PW_{12}O_{40}$ significantly influenced the catalytic performance. Supporting Pt to H3/Cs3 containing 15 wt.%$H_3PW_{12}O_{40}$ brought about the high Pt dispersion and the highest yield of methylcyclopentane.

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