Journal of Catalysis **204,** 157–162 (2001)
doi:10.1006/jcat.2001.3341, available online at http://www.idealibrary.com on IDEAL®

Heteropolyacid Catalysts for Hydroisomerization of *n*-Hexane: Effects of Alkali Salt Modification

N. Essayem,[1] Y. Ben Taârit, P. Y. Gayraud, G. Sapaly, and C. Naccache

Institut de Recherches sur la Catalyse, CNRS, conventionné UCB-Lyon, 2, Avenue Albert Einstein, 69626 Villeurbanne cedex, France

Received April 12, 2001; revised June 28, 2001; accepted June 28, 2001

12-Tungstophosphoric acid, $H_3PW_{12}O_{40}$, and a series of its acid alkali salts associated with silica-supported platinum have been used as catalysts in the hydroisomerization of *n*-hexane and compared with platinum-supported, appropriately dealuminated mordenite. High selectivity toward isomerization was observed with both the heteropolyacid (HPA)-type catalysts and the mordenite at elevated conversions. The acid sites of the heteropolyacids/salts exhibited an efficiency higher than that of mordenite, in line with the higher acid strength of the former sites. Yet, despite their higher acid strength, heteropolyacids/salts showed a lower selectivity toward dimethylbutanes than mordenite. In addition, heteropolyacids, though more active than mordenite at low temperature, appeared to be only poor monofunctional isomerization catalysts. © 2001 Academic Press

Key Words: **hydroisomerization; acidity; heteropolyacids; alkanes; *n*-hexane.**

---

1. INTRODUCTION

Heteropolyacids like $H_3PW_{12}O_{40}$ (HPA) and their alkali or ammonium salt derivatives show interesting properties in acid-type catalyzed reactions. Among these reactions the isomerization of C_5, C_6 linear alkanes is particularly important in the refinery industry to increase the octane number of the gasoline pool. Indeed, while the octane number of *n*-hexane is only 29, those of 2,2-dimethylbutane and 2,3-dimethylbutane are respectively 92 and 104. Since thermodynamic data indicate that branched isomers are favored at low temperature it is recommended that the isomerization of *n*-C_6 occurs at low temperature. However, the reaction mechanism involves endothermic steps, and from the point of view of kinetics, high reaction temperature is required. Thus, because of the thermodynamic and kinetic limitations only strong acid catalysts are efficient. Chlorinated alumina containing platinum was found particularly efficient at 423 K in the isomerization of C_5/C_6 paraffins, a monofunctional acid mechanism being proposed. By contrast over Pt/H mordenite a significant isomerization rate was obtained at 523 K, 100 K higher than that over Pt/Al_2O_3, Cl. At 523 K the bifunctional (metal–acid) reaction mechanism prevailed. The development of novel solid acid catalysts such as heteropolyacids, sulfated zirconia, has initiated additional investigations with the aim of developing new promising catalysts for the isomerization of C_5/C_6 paraffins (1–6).

In the present study we have investigated the isomerization of *n*-hexane over $H_3PW_{12}O_{40}$ and a series of its cesium, potassium, rubidium, and ammonium derivatives. Indeed, it is now well known that the partial exchange of proton by large monovalent cations such as K^+, NH_4^+, Cs^+, and Rb^+ may lead to solids with enhanced surface area and thus enhanced superficial acidity. By using different exchange levels and different cations one can monitor both textural features and the superficial protonic densities. Therefore one can expect different catalytic behaviors as already observed (7, 8).

For comparison, H-mordenite was also included. In this work emphasis was placed on activity measurements and product distribution analysis. The bulk acid H_3P was compared with two types of porous salts (Table 1): a Cs salt ($Cs_2HPW_{12}O_{40}$) characterized by a poor S_{BET} but a high protonic density and three salts with a higher exchange level that exhibit an enhanced S_{BET} and thus a lower protonic density ($K_{2.3}H_{0.7}PW_{12}O_{40}$, $Rb_{2.4}H_{0.6}PW_{12}O_{40}$, $(NH_4)_{2.6}H_{0.4}PW_{12}O_{40}$). The porosity of all these salts showing only slight differences. Our aim was to produce a clear picture of the isomerizing properties of HPA catalysts and pinpoint the differences and analogies that may exist in the various reaction steps occurring over HPA and H-mordenite type catalysts.

2. EXPERIMENTAL

2.1. *Catalysts*

$H_3PW_{12}O_{40}$ was prepared following the method described in the literature (9). Cesium, rubidium, potassium, or ammonium acid salts were obtained by reacting the HPA sample in aqueous solution with metal chloride solution

---

[1] To whom correspondence should be addressed. E-mail: essayem@catalyse.univ-lyon1.fr. Fax: 33 4 72 44 53 99.

TABLE 1

Physicochemical Features of Alkali or Ammonium Salts of $H_3PW_{12}O_{40}$

Sample	H_3P	Cs_2HP	$K_{2.3}H_{0.7}P$	$Rb_{2.4}H_{0.6}P$	$(NH_4)_{2.6}H_{0.4}P$
M/P mol. ratio	—	2	2.3	2.4	2.6
S_{BET} (m^2 g^{-1})	7	28	115	126	125
δ ^1H MAS-NMR	10.5	8.5	8.1	8.9	9.4
[H^+] 10^{17} H^+ m^{-2}	20.8	20.8	12.3	9.3	6.6

containing the stoichiometric quantity of the desired cation M^+. The resulting precipitate, $M_xH_{3-x}PW_{12}O_{40}$, was centrifuged and freeze-dried and the exact value of x was obtained from chemical analysis of M and W. For the ammonium salt, IR spectroscopy was applied to measure the NH_4^+/P molar ratio using as reference spectrum that of $(NH_4)_3PW_{12}O_{40}$. Specific areas of the samples, determined by N_2 adsorption at 77 K, are given in Table 1. All heteropolysalts exhibit pore sizes ranging from 0.5 to 1.2 nm with a high contribution of pores of 0.55 nm to the total volume. At variance with their S_{BET}, only small differences exist in the porosity features of the salts investigated in this study. Table 1 also summarizes two characteristics of the catalysts' acidity: their ^1H MAS-NMR chemical shift, measured after treatment of the samples for 2 h at 473 K, and their superficial protonic density deduced from their H/P molar ratio and their BET surface area. The protonic densities were calculated according to a model previously described where the porous acidic salt $M_{3-x}H_xPW_{12}O_{40}$ is assumed to correspond to $H_3PW_{12}O_{40}$ phase dispersed on the neutral $Cs_3PW_{12}O_{40}$ salt and the surface occupied by each heteropolyanion is taken to be equal to 1.44 nm^2 (7, 8).

The bifunctional heteropolyacid catalysts were prepared by grinding an equal quantity of HPA and Pt/SiO_2 (Pt content: 1 wt%). To obtain close contact between both components of the composite catalysts, a long grinding time was allowed. The catalysts that were prepared are denoted Pt–Cs_2HP, Pt–H_3P, Pt–$Rb_{2.4}H_{0.6}P$, Pt–$K_{2.3}H_{0.7}P$, Pt–$(NH_4)_{2.6}H_{0.4}P$.

The zeolite-type bifunctional catalyst consisted of a H-form mordenite (H-M) impregnated with a solution of Pt salt (tetraammineplatinum chloride) to incorporate 0.6 wt% Pt. H-M was partially dealuminated by hydrothermal treatment and subsequent washing with 1 N HCl treatment resulting in Si/Al = 10. Its H^+ density is equal to 24×10^{17} H^+ m^{-2}.

2.2. *Isomerization Reaction*

The reaction runs were performed using a microreactor operating at atmospheric pressure and plug-flow mode. For each reaction run 0.5 g of the composite catalyst was used. Typical conditions for the reaction were: reaction temperature 473–523 K, H_2/n-C_6 ratio 17.5, and total flow rate ranging from 8.6 to 0.2 liters h^{-1}. Prior to the reaction run the composite catalyst was treated at 473 K in flowing H_2 for a period of 2 h. The reactor effluents were analyzed with a gas chromatograph equipped with a flame ionization detector. The outlet hydrocarbon components were separated by a CP-Sil 2CB fused silica capillary column.

Preliminary experiments have shown that within 4 h time on stream, during which WHSV has been changed to vary the conversion of n-C_6, the catalytic activity of the samples remained unchanged.

3. RESULTS AND DISCUSSION

The results of the reaction of n-hexane at 498 K over the composite catalyst Pt–H_3P are given in Table 2. The n-hexane conversion was changed by varying the feed space velocity. Table 2 lists the selectivities toward isomerization and cracking as well as the product distribution at increasing n-C_6 conversion. It appears that the bifunctional catalyst based on $H_3PW_{12}O_{40}$ is highly selective for n-C_6 isomerization. The cracked products consisted of propane, butanes, and pentanes, C_4 alkanes predominantly being formed. In addition Table 2 shows that little change in the distribution of the cracked products occurred as the conversion increased. These observations suggest that C_3, C_4, C_5 alkanes

TABLE 2

n-C_6 Reaction over Bifunctional Pt–H_3P[a]

WHSV (h^{-1})	Conversion (%)	Selectivity cracking	Distribution of the cracked products							Selectivity isomerization	C_6 isomer distribution			
			C_1	C_2	C_3	iC_4	C_4	iC_5	C_5		2,2-DMC_4	2,3-DMC_4	2-MC_5	3-MC_5
8.9	16	1.3	—	0.8	18.7	32.8	11.6	17.9	18.2	98.7	1.2	9.0	54.6	35.2
4.5	26	1.3	—	0.6	19.0	33.3	11.4	19.7	16.1	98.7	1.6	10.0	54.1	34.3
2.2	39	1.5	—	0.7	19.1	34.2	10.8	21.6	13.6	98.5	2.4	11.0	53.3	33.9
1.1	52	2.1	0.2	0.7	18.7	35.2	10.6	23.2	11.3	97.9	4.1	11.9	51.9	32.2
0.6	67	4.1	0.2	0.6	19.1	36.6	9.9	23.7	9.8	95.9	7.7	12.1	49.5	30.7
0.3	75	6.9	0.2	0.6	19.1	37.3	10.0	23.7	9.2	93.1	12.1	12.3	46.9	28.7

[a] $T_R = 498$ K; $P_{nC_6} = 41$ Torr; $H_2/nC_6 = 17.5$; catalyst weight 0.2 g $H_3P + 0.2$ g Pt/SiO_2.

resulted from primary cracking reaction of large C_n^+ carbenium ions with $n > 6$. The direct β-scission of n-$C_6H_{11}^+$ or i-$C_6H_{11}^+$ carbenium ions is not favorable since it involves secondary → primary or tertiary → primary carbenium ions. Hence before desorption or cracking of the C_6 species, a second C_6 molecule can add to i-$C_6H_{11}^+$ to form a dimer which will crack more effectively into predominantly isobutane.

The C_6 branched isomers formed at low conversion were predominantly 2-methylpentane (2-MeC_5), 3-methylpentane (3-MeC_5), and 2,3-dimethylbutane (2,3-dMeC_4). By contrast, the 2,2-dimethylbutane containing quaternary carbons was formed in a significant amount only at high conversion, the amount always being far below that expected from thermodynamics. Skeletal rearrangement of n-hexane proceeds via a protonated cyclopropane carbenium ion intermediate. Ring opening of the CPC intermediate results in 2-methylpentyl and 3-methylpentyl species. As the branching of the molecule at the center of the hydrocarbon chain is slightly kinetically more favorable, the ratio 3-MeC_5/2-MeC_5 is slightly larger than expected from thermodynamics although isomerization via 1,2-methyl shift may occur simultaneously. At 16% n-hexane conversion the experimental value of 3-MeC_5/2-MeC_5 is 0.64 compared with the thermodynamic ratio of 0.67. Table 2 shows that within monomethylpentane isomers the distribution between 2- and 3-MeC_5 did not vary much with the conversion, which suggests that 2-MeC_5 and 3-MeC_5 are both primary isomerization products.

The formation of dibranched C_6 isomers, 2,3-dimethylbutane (2,3-dMeC_4) and 2,2-dimethybutane (2,2-dMeC_4), requires two successive "protonated cyclopropane" (PCP) events. As a result the approach to the thermodynamic value of dimethylbutanes depends on the n-hexane conversion. Table 2 shows that the ratio of 2,3-dMeC_4/2-MeC_5 increased from 0.16 to 0.26 as n-C_6 conversion increased from 16 to 75%, at thermodynamic equilibrium this ratio is 0.37. One can conclude that at high n-C_6 conversion the concentrations of 2-MeC_5, 3MeC_5, and 2,3-dMeC_4 are close to their thermodynamic values. However, that of 2,2-dMeC_4 is far below its thermodynamic value.

TABLE 4

$n$$C_6$ Conversion over Bifunctional Pt–H_3P and Its Monovalent Acidic Salts Pt–$M_xH_{3-x}P$ [a]

Catalyst	$(NH_4)_{2.6}$P-1	$K_{2.3}$P-1	$Rb_{2.4}$P-1	H_3P	Cs_2HP	Mordenite
Conversion (%)	27	20	16	16	5	3

[a] $T_R = 498$ K; $P_{nC_6} = 41$ Torr; $H_2/nC_6 = 17.5$; WHSV = 8.9 h^{-1}.

Even at high n-C_6 conversion (75%), the 2,2-dMeC_4/2-MeC_5 ratio obtained was only 0.26 compared with 1.07 for the thermodynamic ratio. Dibranched C_6 isomers formation involves ring opening of the methylcyclopropyl ion. Such ring opening generates either tertiary 2,3-dimethylbutyl ion and hence 2,3-dMeC_4 and/or secondary 2,2-dimethylbutyl ion, which gives 2,2-dMeC_4. Since thermodynamically tertiary carbenium ion is more favorable than less stable secondary carbenium ion, 2,2-dMeC_4 is kinetically less favorable than 2,3-dMeC_4. At low n-C_6 conversion Table 2 shows that the proportion of 2,2-dMeC_4 is considerably less than that of 2,3-dMeC_4, in agreement with the low rate of 2,2-dMeC_4 formation. As the residence time increased the conversion of n-C_6 increased and consequently that of 2,3-dMeC_4, approaching its thermodynamic value. The isomerization reaction, which transforms 2,3-dMeC_4 into 2,2-dMeC_4 by methyl shift, is slow since it converts *tert*-carbenium ion into *sec*-carbenium ion. Hence 2,2-dMeC_4 remains below the thermodynamic value even at high n-C_6 conversion.

Apparently the acidity of $H_3PW_{12}O_{40}$ is not strong enough so that appropriate residence times of the carbenium ion intermediates could be allowed in multistep isomerization before desorption. In conclusion, the kinetic barrier that limits the isomerization of n-hexane into 2,2-dimethylbutane is not overcome over $H_3PW_{12}O_{40}$; the concentration of the desired dimethylbutane isomers remains below the thermodynamic equilibrium value.

The results of n-hexane reaction over bifunctional Pt–H mordenite are summarized in Table 3. At 498 K and 42% conversion the isomerization selectivity was high, 97%, similarly to the behavior of $H_3PW_{12}O_{40}$. However, the

TABLE 3

$n$$C_6$ Reaction over 0.6% Pt/Mordenite [a]

WHSV (h^{-1})	Conversion (%)	Selectivity cracking	Distribution of the cracked products							Selectivity isomerization	C_6 isomer distribution			
			C_1	C_2	C_3	iC_4	C_4	iC_5	C_5		2,2-DMC_4	2,3-DMC_4	2-MC_5	3-MC_5
4.5	5	0.8	—	4.3	41.6	18.8	11.9	17.3	6.2	99.2	3.0	12.7	52.3	32.0
2.2	10	1.0	—	4.3	43.5	18.5	13.2	14.9	5.6	99.0	3.5	12.9	51.9	31.7
1.1	18	1.3	0.6	3.0	43.3	18.1	14.5	14.6	5.8	98.7	3.8	13.2	51.6	31.5
0.6	29	1.8	0.6	3.1	42.2	18.2	15.4	14.4	6.0	98.2	4.7	13.1	51.0	31.2
0.3	42	2.8	0.8	3.4	38.8	18.1	16.4	15.0	7.2	97.2	6.5	13.4	49.6	30.5

[a] $T_R = 498$ K; $P_{nC_6} = 41$ Torr; $H_2/nC_6 = 17.5$; catalyst weight = 0.2 g.

TABLE 5

nC_6 Reaction over Bifunctional Pt–Cs_2HP[a]

WHSV (h^{-1})	Conversion (%)	Selectivity cracking	Distribution of the cracked products							Isomerization	C_6 isomer distribution			
			C_1	C_2	C_3	iC_4	C_4	iC_5	C_5		2,2-DMC$_4$	2,3-DMC$_4$	2-MC$_5$	3-MC$_5$
8.9	5	4.3	0.5	0.5	17.7	30.2	17.0	13.6	20.5	95.7	0.4	4.0	56.8	38.8
1.1	23	5.1	0.2	0.5	17.6	31.4	17.3	15.4	17.6	94.9	1.7	7.3	55.6	35.1
0.3	48	6.5	0.2	0.3	15.9	34.6	15.7	19.4	13.8	93.5	6.0	9.8	51.9	32.3

[a] $T_R = 498$ K; $P_{rC_6} = 41$ Torr; $H_2/nC_6 = 17.5$; catalyst weight 0.2 g $Cs_2HP + 0.2$ g Pt/SiO_2.

distribution of the cracking products revealed some difference. While over Pt–H_3P, predominantly C_4 alkanes were formed, over Pt/H mordenite C_3 was preferentially formed; this is particularly true at low conversion where one should expect that almost only primary cracking is occurring. In addition the ratio i-C_4/C_4 was close to 1 over H-mordenite and 3.5 over $H_3PW_{12}O_{40}$. Therefore, cracking reactions involve *n*-hexane dimers which are less branched when the catalyst was H-mordenite; multibranched oligomers which contain quaternary carbons favor the formation of i-C_4 by β-scission.

On H-mordenite, the dimerization reaction of C_6 carbenium ions occurs within the narrow zeolite channels. The steric constraint imposed on the oligomer prevents the formation of multibranched C_{12} carbenium ions, thus limiting the cracking into iC_4. By contrast, over $H_3PW_{12}O_{40}$, the reaction occurs at the grain external surface; multibranched C_{12} intermediates form easily, favoring the cracking into i-C_4.

In conclusion, the propensity for cracking of hexane into propane and *n*-butane increases over H-mordenite as compared with $H_3PW_{12}O_{40}$.

Tables 2 and 3 give the conversion of *n*-hexane at 498 K over Pt–H_3P and Pt–H-mordenite at identical WHSV. The activity of $H_3PW_{12}O_{40}$ catalyst was about four times higher than that of H-mordenite. Since the isomerization selectivity was comparable over the two catalysts it is clear that the yield of C_6 isomers will be four times higher over $H_3PW_{12}O_{40}$. More likely, the catalytic differences between these two bifunctional catalysts should be ascribed to the highest acid strength of the heteropolyacid. Several spectroscopic data and other experiments argue for this statement:

1. ^1H MAS NMR chemical shift as large than 10.5 ppm was measured on $H_3PW_{12}O_{40}$ treated at 473 K (10).
2. As recently demonstrated by IR spectroscopy, 12-phosphotungtic acid and its porous salts were able to protonate water molecules, which can be considered as a weak base (11).
3. NH_3 TPD experiments showed the lack of NH_3 release at temperature below 773 K (13).

However, the performance of the catalysts in *n*-hexane isomerization is represented not only by the yields of total C_6 isomers but particularly by the yields of dMeC$_4$ isomers, which have a high octane number. Table 3 shows the distribution of C_6 isomers at increasing conversion over H-mordenite. It appears that at high conversion the isomer distribution ressembles that found over $H_3PW_{12}O_{40}$. In Fig. 1 the dMeC$_4$/MeC$_5$ ratios are plotted versus *n*-hexane conversion for various composite HPA catalysts and for H-mordenite. At a conversion of *n*-hexane less than 40%, the yield of dimethylbutanes, for a given conversion, apparently was slightly higher over H-mordenite. However, as *n*-C_6 conversion increased to reach the expected thermodynamic value the ratio tended to 0.40 for all catalysts which is considerably less than that expected from thermodynamics. Although clear indications were given in the literature that $H_3PW_{12}O_{40}$ is more acidic than H-mordenite (10–12), apparently the acidity of $H_3PW_{12}O_{40}$ is not enough to increase substantially the mean lifetime of the carbenium ion intermediates, as multiisomerization events can occur before desorption, such multiisomerization events being required to approach the equilibrium value of dMeC$_4$/MeC$_5$.

TABLE 6

nC_6 Reaction over Bifunctional Pt–$K_{2.3}H_{0.7}P$[a]

WHSV (h^{-1})	Conversion (%)	Selectivity cracking	Distribution of the cracked products							Isomerization	C_6 isomer distribution			
			C_1	C_2	C_3	iC_4	C_4	iC_5	C_5		2,2-DMC$_4$	2,3-DMC$_4$	2-MC$_5$	3-MC$_5$
8.9	20	1.7	—	0.4	14.9	38.4	8.2	26.3	11.7	98.3	2.0	11.6	53.3	33.1
2.2	45	2.9	0.1	0.3	16.1	40.0	7.1	28.1	8.2	97.1	3.9	12.4	51.9	31.8
0.3	79	14.2	0.1	0.3	17.8	41.6	7.2	25.0	8.0	85.8	14.8	12.5	45.0	27.7

[a] $T_R = 498$ K; $P_{rC_6} = 41$ Torr; $H_2/nC_6 = 17.5$; catalyst weight 0.2 g $K_{2.3}H_{0.7}P + 0.2$ g Pt/SiO_2.

TABLE 7

$n\mathrm{C}_6$ Reaction over Bifunctional Pt–$\mathrm{Rb}_{2.4}\mathrm{H}_{0.6}\mathrm{HP}$[a]

WHSV (h^{-1})	Conversion (%)	Selectivity cracking	Distribution of the cracked products							Isomerization	C_6 isomer distribution			
			C_1	C_2	C_3	iC_4	C_4	iC_5	C_5		2,2-DMC_4	2,3-DMC_4	2-MC_5	3-MC_5
8.9	17	1.2	—	0.6	18.7	38.2	6.0	31.0	5.4	98.8	2.9	11.9	52.7	32.6
2.2	44	2.0	0.2	0.5	18.9	39.5	5.7	30.4	4.9	98.0	4.5	12.7	51.2	31.6
0.3	79	9.3	0.1	0.3	20.3	40.9	6.0	24.5	7.8	90.7	15.2	12.5	44.8	27.5

[a] $T_R = 498$ K; $P_{rC_6} = 41$ Torr; $H_2/nC_6 = 17.5$; catalyst weight 0.2 g $Rb_{2.4}H_{0.6}P + 0.2$ g Pt/SiO_2.

Nevertheless $H_3PW_{12}O_{40}$, although it has a low surface area resulting in low accessibility of the acid sites to the reactant, showed considerably higher activity than H-mordenite. It is clear that the isomerization reaction could be carried out at lower temperature than over H-mordenite, which is thermodynamically better for reaching a high yield of dimethylbutanes. Moreover, at laboratory scale, under the experimental conditions employed, the catalytic stabilities of H-mordenite and HPA were similar. Within 4 h on stream the loss of activity was less than 2–5% for both samples.

The present results clearly demonstrate that heteropolyacid catalysts are better candidates for isomerization of *n*-hexane, not in terms of their better selectivity to form dimethylbutanes or their stability, but rather in terms of their efficiency even at relativity low temperature of reaction.

As the number of acid sites accessible to *n*-hexane is small on bulk $H_3PW_{12}O_{40}$, partially exchanged porous salts have been used for n-C_6 isomerization, namely, $Cs_2HPW_{12}O_{40}$, $K_{2.3}H_{0.7}PW_{12}O_{40}$, $Rb_{2.4}H_{0.6}PW_{12}O_{40}$, and $(NH_4)_{2.6}H_{0.4}PW_{12}O_{40}$. The first sample is characterized by a low BET surface area, 28 $m^2\ g^{-1}$, and a protonic density equivalent to that of the bulk acid (Table 1). This Cs salt corresponds to more than one-monolayer coverage of H_3P over the Cs_3P, assuming that these samples correspond to nonacidic high-surface-area salt $Cs_3PW_{12}O_{40}$ (or K, Rb, NH_4) over which highly dispersed $H_3PW_{12}O_{40}$ is supported (7–13). The latter three samples, with a higher exchange level, exhibit a higher BET surface area and therefore a lower protonic density (Table 1). However, all these salts exhibit quite equivalent porosity; they are mainly microporous with pore apertures centered at 0.55 nm.

First, it is important to recall that $Cs_2HPW_{12}O_{40}$ salt, with this precise composition, was observed to be more active than the bulk acid for n-C_4 isomerization, a reaction that requires a high density of strong acid sites (7, 8, 13). The highest activity of $Cs_2HPW_{12}O_{40}$ was simply ascribed to its highest superficial acidity with respect to the acid H_3P. On the other hand, the almost totally exchanged porous salts exhibit only poor activity in n-C_4 isomerization due to their low protonic density compared with bulk H_3P and $Cs_2HPW_{12}O_{40}$ (7, 8, 13).

Partial exchange of $H_3PW_{12}O_{40}$ with Cs ions, to form $Cs_2HPW_{12}O_{40}$, has no beneficial effects either on activity or on the yield of dimethylbutane. By contrast, partial exchange with K^+, Rb^+, and NH_4^+ to reach a composition near $M_{2.5}H_{0.5}P$ considerably increased not only the specific surface area of the solids but also the catalytic activity for *n*-hexane isomerization (Table 4), the highest promoting effect being obtained with NH_4^+. Apparently, a high protonic density does not favor the activity of HPA in n-C_6 isomerization (Table 4). However, this observation is not coherent with the activity level of bulk H_3P. That is why it is believed that a dispersion of H_3P over Pt/SiO_2 might have occurred through the mechanical mixing applied to obtain the composite bifunctional catalyst. Indeed it has previously been shown that dispersed H_3P over neutral Cs_3P can be prepared by grinding (14). The isomerization selectivity and the isomer product distribution at identical n-C_6 conversion were close to those observed with pure $H_3PW_{12}O_{40}$ catalyst (Table 5 and Fig. 1). In Tables 5–8 are reported the product distributions for the cracking reaction as well as the C_6 isomer distribution. One can observe that Cs_2HP salt shows a slightly higher

TABLE 8

$n\mathrm{C}_6$ Reaction over Bifunctional Pt–$(\mathrm{NH}_4)_{2.6}\mathrm{H}_{0.4}\mathrm{P}$[a]

WHSV (h^{-1})	Conversion (%)	Selectivity cracking	Distribution of the cracked products							Isomerization	C_6 isomer distribution			
			C_1	C_2	C_3	iC_4	C_4	iC_5	C_5		2,2-DMC_4	2,3-DMC_4	2-MC_5	3-MC_5
8.9	27	0.9	0.5	1.0	17.8	37.0	6.5	31.9	5.3	99.1	2.0	11.5	53.5	33.0
2.2	61	2.2	0.2	0.5	19.0	39.0	5.9	30.5	4.9	97.8	4.7	13.0	50.9	31.4
0.3	82	12.4	0.1	0.3	20.5	41.1	6.2	24.4		87.6	17.3	11.9	44.0	26.8

[a] $T_R = 498$ K; $P_{nC_6} = 41$ Torr; $H_2/nC_6 = 17.5$; catalyst weight 0.2 g $(NH_4)_{2.6}H_{0.4}HP + 0.2$ g Pt/SiO_2.

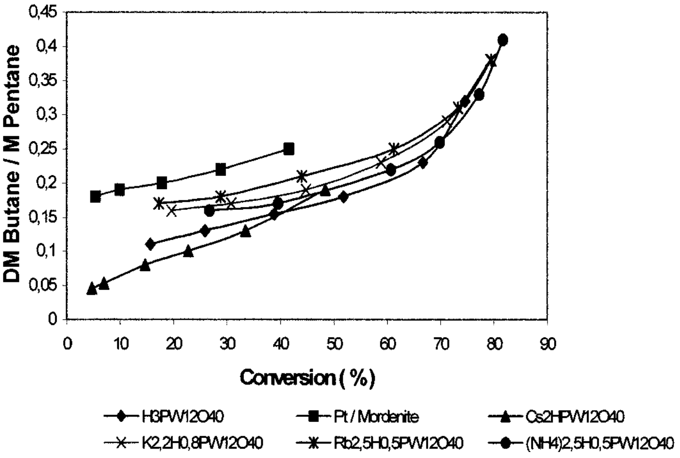

FIGURE 1

selectivity to cracked products than the other salts, caused, more likely, by its higher protonic density. The comparison with the results observed on pure $H_3PW_{12}O_{40}$ indicates clearly that little difference exists when the comparison is made at the same hexane conversion. However, one can observe a slightly higher formation of dibranched alkanes over the exchanged monovalent salts $Rb_{2.4}$, $(NH_4)_{2.6}$, and $K_{2.3}$. We do not believe that the acidic features of the salts are at the origin of this result since spectroscopic data are rather in favor of sites of higher strength over the bulk acid. It is more reasonable to refer to the microporosity of these salts which can favor the formation of dibranched alkanes, which are secondary products. This reinforces the idea that the reaction occurs over *quite* identical acid sites whatever the nature of the exchange.

CONCLUSIONS

Consistent with other studies the results presented here show that the protons in heteropolyacid bifunctional catalysts are more efficient that those of zeolites such as mordenite probably because they are more acidic but also because the reaction is less affected by diffusion since, on heteropolyacid materials only, nonconstraint surface protons intervene in the reaction. During *n*-hexane conversion the selectivity toward isomerization is similar when the reaction is carried out over heteropolyacid catalysts and over H-mordenite. The partial exchange of H^+ with cations such as K^+, Rb^+, and NH_4^+ to form porous salts near the composition $M_{2.5}H_{0.5}PW_{12}O_{40}$ has some beneficial effect on the activity due more likely to their enhanced specific surface area and, consequently, enhanced H^+ dispersion. The HPA-based catalysts apparently are not active enough to be employed for monofunctional acid-catalyzed isomerization of *n*-hexane. Addition of a dehydrogenating function, Pt for example, is still needed to obtain significant conversion levels at relatively low temperature. As a result the isomer product distributions depend mainly on the conversion level at a given reaction temperature. The formation of dibranched alkanes, i.e., dimethylbutanes, required to improve the fuel octane number, apparently is not more effectively obtained over HPA than over H-mordenite. The reason is that the formation of 2,2-dimethylbutane which contains a quartenary carbon is kinetically limited even over HPA. The low reaction rate for the conversion of 2,3-dimethylbutane into 2,2-dimethylbutane accounts for the limited amounts of dibranched isomers. On this aspect heteropolyacids and H-mordenite behave similarly. Finally although there are some advantages, higher activity, in carrying out the isomerization of C_5/C_6 alkanes over heteropolyacid catalysts, one needs to involve bifunctional mechanisms to obtain subtantial isomer yields, and as such the benefit and/or interest with respect to chlorinated alumina remain questionable.

REFERENCES

1. Suzuki, S., Kogai, K., and Ono, Y., *Chem. Lett.*, 699 (1984).
2. Baba, T., Nomura, M., and Ono, Y., *Stud. Surf. Sci. Catal.* **90**, 117 (1994).
3. Liu, Y., Koyano, G., and Misono, M., *Top. Catal.* **11/12**, 239 (2000).
4. Iglesia, E., Soled, S. L., and Kramer, G. M., *J. Catal.* **144**, 238 (1993).
5. Vaudagna, S. R., Comelli, R. A., Canavese, S. A., and Figoli, N. S., *J. Catal.* **169**, 389 (1997).
6. Travers, C., Delage, M., Queulen, S., and Essayem, N., *Catal. Today* **65**, 355 (2001).
7. Gayraud, P. Y., Essayem, N., and Védrine, J. C., *Stud. Surf. Sci. Catal.* **130**, 2549 (2000).
8. Guisnet, M., Bichon, Ph., Gnep, N. S., and Essayem, N., *Top. Catal.* **11/12**, 247 (2000).
9. Pope, M. T., "Heteropoly- and Isopolyoxometallates," Inorganic Chemistry Concepts, Vol. 8, Springer-Verlag, Berlin, 1983.
10. Essayem, N., Tong, Y. Y., Jobic, H., and Védrine, J. C., *Appl. Catal. A: General* **194/195**, 109 (2000).
11. Essayem, N., Holmqvist, A., Gayraud, P. Y., Védrine, J. C., and Ben Tâarit, Y., *J. Catal.* **197**, 273 (2001).
12. Essayem, N., Frety, R., Coudurier, G., and Vedrine, J. C., *J. Chem. Soc. Faraday Trans.* **93**, 3243 (1997).
13. Essayem, N., Coudurier, G., Fournier, M., and Védrine, J. C., *Catal. Lett.* **34**, 223 (1995).
14. Gayraud, P. Y., Essayem, N., and Védrine, J. C., *Catal. Lett.* **56**, 35 (1998).