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New catalytic functions of heteropoly compounds as solid acids

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Abstract

Our recent developments in catalysis of heteropoly compounds as solid acids have been described. “Water-tolerant catalysis” is one of novel catalytic functions of an acidic Cs salt, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (Cs2.5). Comparison of adsorption amounts of water and benzene led to the following order of hydrophobicity; HZSM-5 ($Si/Al = 628$) $>$ silica $>$ Cs3 $>$ H-ZSM-5 ($Si/Al = 40$) $\sim$ Cs2.5 $>$ silica-alumina $>$ alumina. Owing to the hydrophobicity, Cs2.5 was highly active for organic reactions like hydration of alkene and hydrolysis of esters and oligosugars in water. Also, Cs2.5 was efficient for the reaction of nitrile with alcohol to *N*-alkylamide even in excess water. Cs2.5 was also active for solid–solid pinacol rearrangement and Beckmann rearrangement, and was reusable by washing a small amount of solvent. In a bi-phasic reaction system, $H_3PW_{12}O_{40}$ (in liquid state) was exceptionally active for synthesis of diphenylmethane from formalin (aqueous formaldehyde) and benzene. As a bifunctional catalyst, Pt-$Cs_{2.5}H_{0.5}PW_{12}O_{40}$ showed good performance for skeletal isomerization of *n*-butane and hydroisomerization of benzene. Mechanism of *n*-butane isomerization was studied using ^{13}C-*n*-butane; the reaction proceeds mainly through monomolecular pathway over Pt-Cs2.5, while bimolecular pathway was predominant over Cs2.5. Cs2.1 and Rb2.1 possessed ultramicropores with the widths of about 0.50 and 0.60 nm, respectively, and the corresponding Pt-promoted catalysts exhibited shape selectivities for oxidation and hydrogenation. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Heteropoly compounds; Water-tolerant solids; Micropores; Shape selectivity; Skeletal isomerization

1. Introduction

Heteropoly compounds are the objective of research for a long time. Much work has been done and there are several commercial processes utilizing heteropoly compounds [1]. The reactions catalyzed by them both in heterogeneous and homogeneous systems have been reviewed by many researchers [1–9]. These reviews include mainly acid-catalyzed reactions and oxidation reactions. Our comprehensive review [1] addressed the advances in heterogeneous and homogeneous catalysis by heteropoly acids until 1995. A review by Hill and McCartha [2] focused on the oxidation reactions by polyoxometalates in homogeneous system. Mizuno and Misono [3] summarized recent progresses in heterogeneous catalysis in acid-catalyzed reactions and oxidation reactions. Kozhevnikov [4] surveyed the use of heteropoly acids in liquid-phase reaction. More recently, Okuhara and Nakato [8] discussed porous heteropoly acids as shape selective catalysts, and Barton et al. [9] reported the heteropoly salts as tailored porous materials.

As a recent industrial application, Showa Denko (Oita, Japan) performed synthesis of acetic acid by ethylene oxidation in the presence of water over Pd-$H_4SiW_{12}O_{40}/SiO_2$ with the capacity of 100,000 ton per year [10]. This reaction is suggested to proceed

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in two steps, hydration of ethylene and oxidation of ethanol. If so, this is the first example of solid heteropoly compound for acid-catalyzed reaction in industry. As a solid acid, an acidic Cs salt, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$, is much attractive, because this salt shows hydrophobicity and insolubility, and has a high surface area and unique pores as well as strong acidity. This review tried to focus on our recent research as for the acid-catalyzed reactions mainly by $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ and its derivatives.

2. Water-tolerant catalysis by $Cs_{2.5}H_{0.5}PW_{12}O_{40}$

Mineral acids like sulfuric acid have widely been used for chemical processes in industry, but there are problems of corrosion and production of a large amount of waste. Instead of these acids, water-tolerant solid acids are desirable for environmentally friendly catalytic processes. However, solid acids are generally poisoned by water and they loose their catalytic activities in aqueous solution. Only H-ZSM-5 zeolite has commercially been used as a water-tolerant solid acid for liquid-phase hydration of cyclohexene by Asahi Chemicals [11,12]. On the other hand, Izumi et al. [13] reported that silica-supported $H_3PW_{12}O_{40}$ catalyzed hydrolysis of ethyl acetate in water. We evaluated semi-quantitatively the hydrophobicity of Cs2.5 in comparison of the amount of adsorption between water and benzene [14]. Fig. 1 shows the ratio of the adsorption area of benzene to that of water as a function of the relative pressure of the adsorbates, where the adsorption area is defined as the product of the adsorption amount and molecular cross sectional area [14]. From the ratio in adsorption area of benzene to that of water, the hydrophobicity of solid acid surface was estimated to be in the order; H-ZSM-5 (Si/Al = 628) > $Cs_3PW_{12}O_{40}$ (Cs3) > H-ZSM-5 (Si/Al = 40) ~ $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (Cs2.5) > SiO_2-Al_2O_3 > Al_2O_3 [14]. It was thus concluded that the surface of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ has the hydrophobic nature close to that of H-ZSM-5 (Si/Al = 40) which is ordinarily used as catalyst. Catalytic activities of various solid acids for hydrolysis of ethyl acetate in excess water were compared [14]. The activity of Cs2.5 (per unit of weight) was 3 and 35 times higher than those of H-ZSM-5 (Si/Al = 40) and H-ZSM-5 (Si/Al = 628), respectively. SiO_2-Al_2O_3 and Al_2O_3 were inactive under the same reaction conditions. Furthermore, the specific activity of Cs2.5 (per acid amount) was seven times higher than those of these two H-ZSM-5. The hydrophobicity [14] and bimodal pore structure [15] as well as the strong acidity [16] are responsible for the high catalytic activity of Cs2.5 in the hydrolysis.

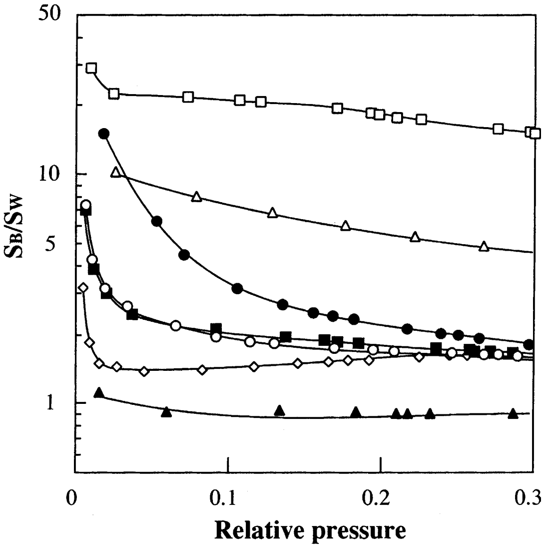


Fig. 1. Hydrophobicity of solid acids evaluated from the adsorptions of benzene and water: (○) $Cs_{2.5}H_{0.5}PW_{12}O_{40}$; (●) $Cs_3PW_{12}O_{40}$; (□) H-ZSM-5 (Si/Al = 628); (■) H-ZSM-5 (Si/Al = 40); (△) SiO_2; (▲) Al_2O_3; (◇) SiO_2-Al_2O_3. S_W and S_B are adsorption areas of H_2O and benzene, respectively. The horizontal axis shows the relative pressure of the adsorption.

The following three reactions shown in Fig. 2 (reactions (1)–(3)) were used as tests for the water-tolerant catalysts: (1) hydrolysis of 2-methylpheny acetate; (2) hydrolysis of maltose (oligosugar); and (3) hydration of 2,3-dimethyl-2-butene [17,18]. As Table 1 shows, Cs2.5 was far superior in activity in comparison with these oxide solid acids for these reactions. While Cs2.5 was less active (per catalyst weight) than the liquid acids such as H_2SO_4, and *para*-toluenesulfonic acid (PTS) for the hydrolysis of 2-methylpheny acetate, the specific activity of Cs2.5 (per acid amount) was about 15 times higher than those of the liquid acids. Protons on the hydrophobic surface of Cs2.5 are probably saved from the poisoning by water.

It was confirmed that Cs2.5 was recyclable for the hydrolysis of ethyl acetate. The reaction rate over

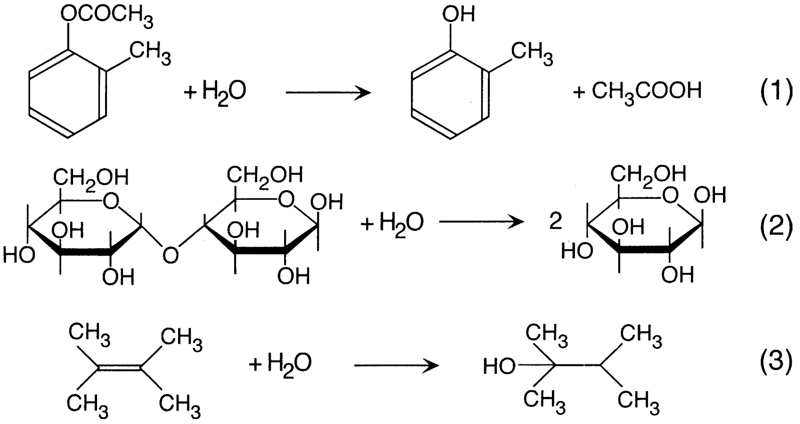


Fig. 2. Three kinds of reactions performed in water.

Cs2.5 at the fifth run was more than 90% that of the first run, whereas the rate on SO_4^{2-}/ZrO_2 decreased greatly by the repeating of run [18]. Table 2 summarizes the changes of Cs2.5 and Cs3 by the treatment with hot water. The catalytic activity was reduced to half by the treatment at 393 K, while the activity was maintained about 90% that of the untreated catalyst after the treatment at 353 K. The calorimetry of ammonia adsorption for Cs2.5 showed that the treatment with hot water decreased slightly the acid amount, whereas the acid strength was slightly changed, indicating that the decrease in the catalytic activity was due to that in the acid amount. IR confirmed that the primary structure of the Cs salt was retained in hot water [19]. A small amount of heteropoly species was released into water during the treatments, which was detected by UV spectroscopy. It was concluded that the released species were not ionically dissociated but present as heteropoly clusters [19].

Table 1
Catalytic activities of solid acids for acid-catalyzed reactions in excess water[a]

Catalyst	Reaction rate ($mmol\,g^{-1}\,h^{-1}$)		
	Reaction (1)	Reaction (2)	Reaction (3)
$Cs_{2.5}H_{0.5}PW_{12}O_{40}$	10.7	51.0	10.5
H-ZSM-5 (Si/Al = 40)	0.0	1.7	5.7
SO_4^{2-}/ZrO_2	0.4	0	0
H-mordenite	0	0	0
HY	0	0.4	0
Nb_2O_3	0.5	3.0	0.1
SiO_2-Al_2O_3	0	0	0
SiO_2-TiO_2	0	6.3	0
γ-Al_2O_3	0	4.6	0
Amberlyst-15	32.7	95.0	14.0
Nafion-H	44.5	52.0	1.8

[a] Reaction temperatures are 353, 373, and 343 K for reactions (1)–(3) in Fig. 2, respectively.

Table 2
Changes of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ by treatment with hot water

Catalyst	Surface area ($m^2\,g^{-1}$)	Rate constant[a] (min^{-1} $(H^+\text{-mol})^{-1}$)	Released heteropoly species (%)
$Cs_{2.5}H_{0.5}PW_{12}O_{40}$			
Before treatment	113	11.8	–
After treatment	141	10.8	5.2
$Cs_3PW_{12}O_{40}$			
Before treatment	145	0.0	–
After treatment	133	–	1.5

[a] Hydrolysis of ethyl acetate.

Table 3
Effects of water addition on yield of *N*-adamantylacrylamide in reaction of acrylonitrile and 1-adamantanol[a]

Catalyst	Yield of *N*-adamantylacrylamide (%)	
	Without water	With water
$Cs_{2.5}H_{0.5}PW_{12}O_{40}$	97	84
HY zeolite	79	8
Amberlyst-15	100	68
Nafion-H	97	77
Nafion-SiO_2	97	40

[a] The reaction conditions: acrylonitrile 60 mmol, 1-adamantanol 1.3 mmol, H_2O 13 mmol, catalyst 0.2 g and 373 K for 6 h.

Table 3 presents the effects of water addition on synthesis of *N*-adamantylacrylamide from acrylonitrile and 1-adamantanol. Cs2.5 gave 97% yield with the selectivity of 93%. While HY zeolite showed a certain activity, the yield and selectivity were less than those of Cs2.5. H-ZSM-5 was much less active, which is probably due to limitation of the adsorption of this bulky alcohol into the constrained pores. While the yield declined by the addition of water over all the catalysts, it was still high (84%) over Cs2.5, demonstrating that the water-tolerancy of Cs2.5 was realized in the Ritter-type reaction [20].

We surveyed water-tolerant solid acids, besides Cs2.5 and H-ZSM-5. Among many mixed oxides, MoO_3-ZrO_2 and WO_3-ZrO_2, which were calcined at temperatures higher than 973 K, were found to be highly active for hydrolysis of ester in water [21]. More recently, we also found that the some kinds of reactions were accelerated by water over MoO_3-ZrO_2 [22].

3. Bi-phasic reaction system

Bi-phasic reaction system is worthy of note as an environmentally benign process, if the product and catalyst can be separated spontaneously into the different phases. Phase transfer polymerization of tetrahydrofuran (THF) has practically been operated in bi-phasic system consisting of THF and THF-heteropoly acid phase [23]. In addition, cyclotrimerization of propionaldehyde was catalyzed efficiently by heteropoly acids in a bi-phasic system [24]. We recently found that heteropoly acids such as $H_3PW_{12}O_{40}$ were exceptionally active for synthesis of diphenylmethane from benzene and formalin (aqueous HCHO) in the bi-phasic system and could be recycled by simple dryness of the aqueous phase at room temperature [25].

Synthesis of diphenylmethane ($C_6H_5CH_2C_6H_5$, DPM) from benzene and formalin (Eq. (1)) is favorable, since the direct use of formalin is economical and the by-product is only water ideally.

$$2C_6H_6 + \text{HCHO (in water)} \rightarrow C_6H_5CH_2C_6H_5 + H_2O \tag{1}$$

There are several reports about the reaction between aromatic compounds and paraformaldehyde (water-free oligomers of HCHO) using mineral acids and solid acids like HY zeolite and SiO_2-composites of polymer resins [26]. However, when formalin was used instead of paraformaldehyde, the reaction was very slow under the same conditions [26], indicating the serious inhibition by water.

Table 4
Conversion and selectivity of diphenylmethane synthesis from benzene and formalin with solid acids[a]

Catalyst	Catalyst (mmol)	Conversion (mol%)	Yield (mol%)	Selectivity (mol%)[b]	
				MF	DPM
$H_3PW_{12}O_{40}$	4.2	93.2	35.3	34.3	37.9
$Sc(CF_3SO_3)_3$	2.1	95.1	0	83.0	0
PTS	12.6	82.2	4.1	71.8	0
HNO_3	12.6	24.4	0	90.0	0
H_3PO_4	4.2	18.7	0	68.8	0
H_2SO_4	6.3	33.7	0	92.0	0

[a] Benzene 450 mmol, HCHO 90 mmol, H_2O 222 mmol, CH_3OH 18.2 mmol, 433 K, 2 h.
[b] Based on HCHO.

The aromatic compounds accumulated in the benzene phase. While the remaining HCHO was exclusively present in the aqueous phase, methyl formate (MF) existed mainly in the benzene phase. As shown in Table 4, the conversions of HCHO were higher than 93% over $H_3PW_{12}O_{40}$ and $Sc(CF_3SO_3)_3$ [25]. It should be emphasized that only $H_3PW_{12}O_{40}$ gave DPM (the yield was 35.3% under these conditions). $Sc(CF_3SO_3)_3$ catalyzed efficiently dimerization of HCHO to MF, but was inactive for the formation of DPM. PTS was also active for the dimerization of HCHO, but did not produce DPM. Mineral acids like H_2SO_4, H_3PO_4, HNO_3, and CF_3COOH were also inactive for the formation of DPM.

The $H_3PW_{12}O_{40}$ recovered by drying the aqueous phase showed the activity, while the conversion of HCHO and yield of aromatics were somewhat reduced with the repeating of run. These changes would be due to the remaining carbonaceous species on the heteropoly acid. IR spectroscopy of $H_3PW_{12}O_{40}$ confirmed that the Keggin structure was completely retained at least after the repeated runs for five runs. While Aciplex (polymer resin)-SiO_2 showed a high activity for the reaction of pure HCHO and benzene, but it was inactive in the bi-phasic system consisting of benzene and aqueous HCHO phases [25].

4. Solid–solid catalysis

While solid–solid catalysis is unusual, it is attractive. Solid acids have some preferable characteristics such as high mechanical and thermal stability, high surface area, and strong acidity for this catalysis. When solid state pinacol rearrangement of 1,1,2-triphenyl-1,2-ethandiol was initiated by grinding a mixture of the solid reactant and solid acid for 5 min at room temperature, Cs2.5 showed the highest activity (per unit catalyst weight) among the solid acids (Fig. 3) [27,28]. The turnover number, which is defined as the number of reacted molecules divided by the number of protons on the surface, exceeded 20 for 9 h, indicating that the solid–solid reaction proceeded catalytically. This activity of Cs2.5 was higher than that for the solid–liquid reaction carried out in $CHCl_3$, demonstrating the superiority of the solid–solid catalysis. Reusability of Cs2.5 was confirmed. XRD and SEM revealed that by grinding with Cs2.5, the reactant crystallites changed into very fine amorphous particles to stick to the catalyst, the crystallinity of Cs2.5 being unchanged [29]. We found that Beckmann rearrangement for cyclododecanone oxime took place on Cs2.5 in solid–solid reaction system at 373 K. Powder (0.1 g) of cyclododecanone oxime and solid acid (0.2 g) was physically mixed in a sealed tube, and then the mixture was heated at 373 K for 3 h. As shown in Table 5, the reaction took place catalytically over Cs2.5; and Cs2.5 showed the highest activity among various solid acids [30].

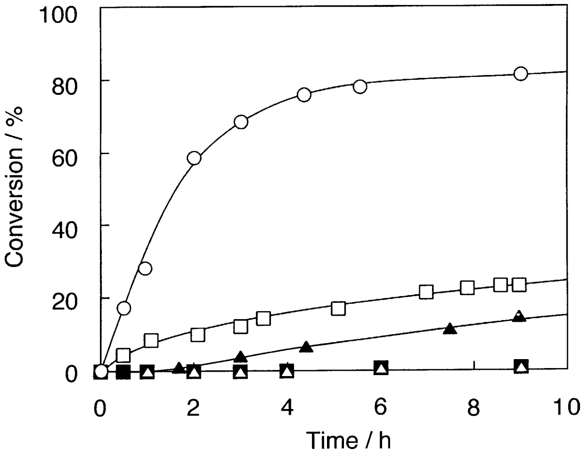


Fig. 3. Time courses of solid–solid pinacol rearrangement over solid acids at room temperature. The reaction was carried out with catalyst 0.1 g and 1,1,2-triphenyl-1,2-ethandiol 0.5 g after grinding for initial 5 min.

Table 5
Solid–solid Beckmann rearrangement of cyclododecanone oxime over various solid acids[a]

Catalyst	Acid amount ($mmol\,g^{-1}$)	Yield (%)	Selectivity (%)	TON
$Cs_{2.5}H_{0.5}PW_{12}O_{40}$	0.06	24.3	100	10.3
H-ZSM-5	0.39	3.3	100	0.2
HY	2.60	1.8	100	0
H-mordenite	1.40	0.8	100	0
SiO_2-Al_2O_3	0.35	0.9	100	0
Nafion-SiO_2	0.12	11.1	77	2.2
Amberlyst-15	4.70	0.7	100	0

[a] Cyclododecanone oxime 0.1 g (507 mmol) and catalyst 0.2 g, 373 K in a vacuum after mixing for initial 5 min.

5. Alkane isomerization by bifunctional heteropoly compounds

Skeletal isomerizations of *n*-alkanes are practically important because the branched alkanes are useful as clean fuel. The addition of Pt (that is, formation of bifunctional catalysts) enhanced the activity and selectivity in the presence of H_2. Cs2.5 is a promising candidate of the solid acid for the bifunctional catalyst. The activity and selectivity for the *n*-butane isomerization in the presence of H_2 were enhanced by the addition of Pt to Cs2.5 [31]. To reveal the reasons for enhancement in the selectivity, we tried to elucidate the reaction mechanism for the reaction [32,33].

Recent mechanistic studies of *n*-butane isomerization using ^{13}C-*n*-butane [34,35] pointed out that there are two possible pathways, that is, bimolecular pathway which is accompanied with intermolecular rearrangement and monomolecular one with intramolecular rearrangement. As illustrated in Scheme 1, if the reaction proceeds through the monomolecular pathway involving a protonated cyclopropane intermediate, the product isobutane would be $^{13}C_2$-isobutane, if 1,4-$^{13}C_2$-*n*-butane was used as reactant. In addition, the high selectivity (100%) to isobutane is expected in this mechanism. On the other hand, it is considered that the bimolecular mechanism proceeds with intermolecular rearrangement. In this case, a variety of isobutane having different numbers of ^{13}C would be formed from 1,4-$^{13}C_2$-*n*-butane (Scheme 1), because octyl cations readily undergo various rearrangements containing methyl shifts to give *tert*-carbenium ions.

Fig. 4 shows the isotopic distributions of isobutane formed over Pt-Cs2.5 and Cs2.5 at 423 K [32,33]. Contrastive distributions were obtained between Pt-Cs2.5 and Cs2.5. Pt-Cs2.5 gave exclusively $^{13}C_2$-isobutane (Fig. 4A), indicating that the contribution of monomolecular pathway was significant over the bifunctional catalysts. On the other hand,

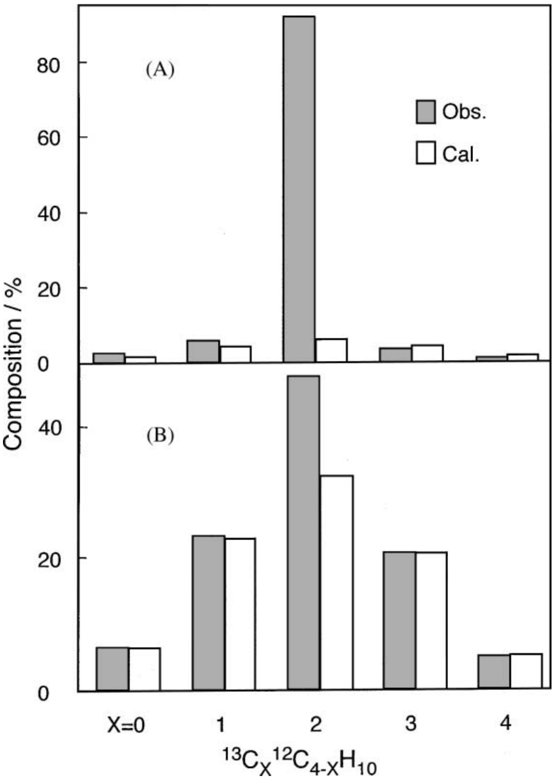
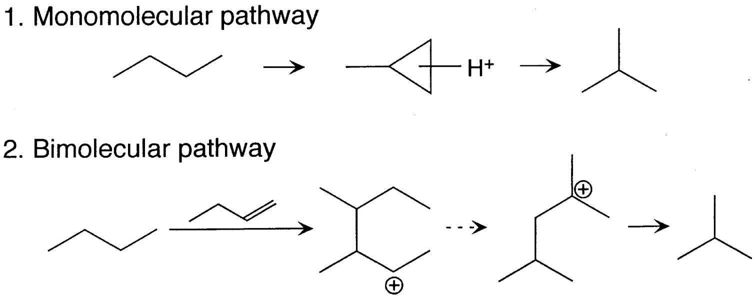


Fig. 4. Distribution of ^{13}C in isobutane formed by skeletal isomerization of 1,4-$^{13}C_2$-*n*-butane over (A) Pt-$Cs_{2.5}PW_{12}O_{40}$ and (B) $Cs_{2.5}PW_{12}O_{40}$ at 423 K.



Scheme 1. Reaction pathways for skeletal isomerization of *n*-butane.

Cs2.5 brought about a spread distribution close to the binomial distribution (open rectangles), showing that the bimolecular pathway would be predominant over Cs2.5. The contributions of monomolecular pathway over these catalysts and SO_4^{2-}/ZrO_2 were estimated quantitatively against the reaction temperature [33]. The contribution of the monomolecular pathway was low at 423 K over the non-promoted solid acids and increased gradually as the temperature increased. On the other hand, the contribution of monomolecular pathway was significant over the bifunctional catalysts. The preferable operation of the monomolecular mechanism on Pt-Cs2.5 is responsible for the high selectivity.

Pt-Cs2.5 was used for hydroisomerization of benzene to methylcyclopentane. Both the hydrogenation ability of Pt and the amount of acid sites were key factors in determining the yield; the former is required for complete hydrogenation of benzene and

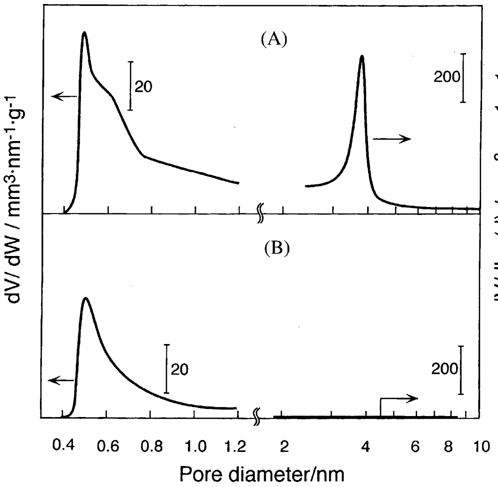


Fig. 5. Pore size distributions for (A) Pt-$Cs_{2.5}H_{0.5}PW_{12}O_{40}$ and (B) Pt-$Cs_{2.1}H_{0.9}PW_{12}O_{40}$. Micropores (<2 nm) and mesopores (2–50 nm) were analyzed with Ar and N_2 adsorption isotherms, respectively.

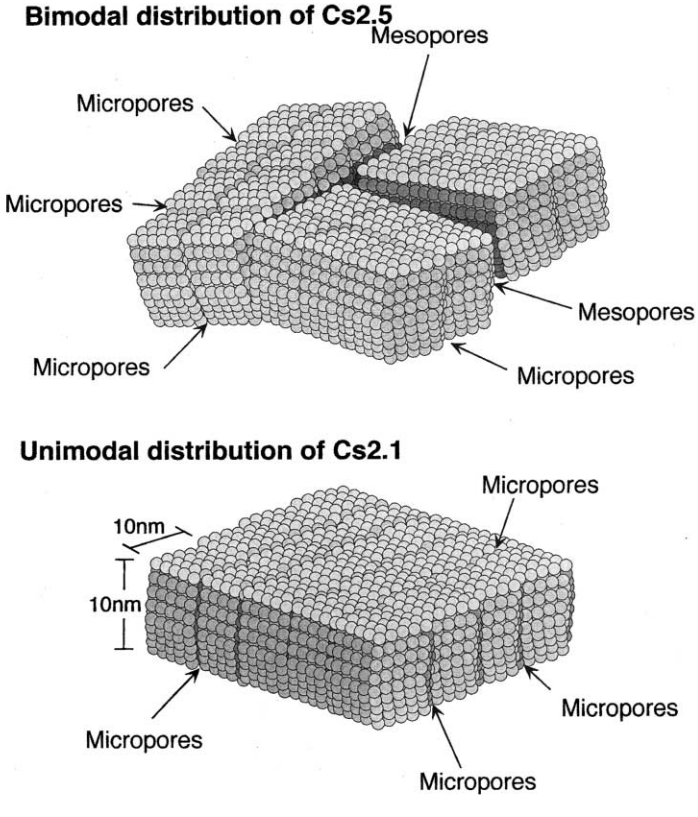


Fig. 6. Proposed models for pores of the acidic Cs salts.

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, in the presence of 2 wt.% Pt-$Cs_{2.5}H_{0.5}PW_{12}O_{40}$, high yield (51%) of methylcyclopentane can be obtained at 473 K with 100% conversion of benzene [36]. The thermodynamic equilibrium yield is 70%.

6. Shape-selective microporous heteropoly compounds

Microporous heteropoly compounds such as $Cs_{2.1}H_{0.9}PW_{12}O_{40}$ have recently been synthesized [37–42]. These have attracted much attention, because they have pores similar to those of zeolites and strong acidities [37–45]. The addition of Pt brought about shape selective bifunctional catalysts [38–45]. As shown in Fig. 5, the pores of Pt-$Cs_{2.5}H_{0.5}PW_{12}O_{40}$ showed bimodal distributions in the range from micropore to mesopore [44]. On the other hand, Pt-$Cs_{2.1}H_{0.9}PW_{12}O_{40}$ possessed only ultramicropores. Adsorption of various molecules such as N_2 (molecular size (MS) = 0.36 nm), *n*-butane (MS = 0.43 nm), isobutane (MS = 0.50 nm), benzene (MS = 0.59 nm), 2,2-dimethylpropane (MS = 0.62 nm), and 1,3,5-trimethylbenzene (MS = 0.75 nm) revealed that the pore-width of 0.5 wt.% Pt-$Cs_{2.1}H_{0.9}PW_{12}O_{40}$ was in the range of 0.43–0.50 nm. The fraction of external surface area in the total surface area of Pt-$Cs_{2.1}H_{0.9}PW_{12}O_{40}$ was estimated to only 0.06 from the adsorption of 1,3,5-trimethylbenzene and *t*-plot of N_2 adsorption [44]. It is presumed that the mesopores are voids between the primary particles (crystallites) with the size of about 10 nm and the micropores correspond to the spaces of crystal planes between the crystal planes formed by misfits [39,41]. Proposed models for the porous heteropoly compounds are illustrated in Fig. 6.

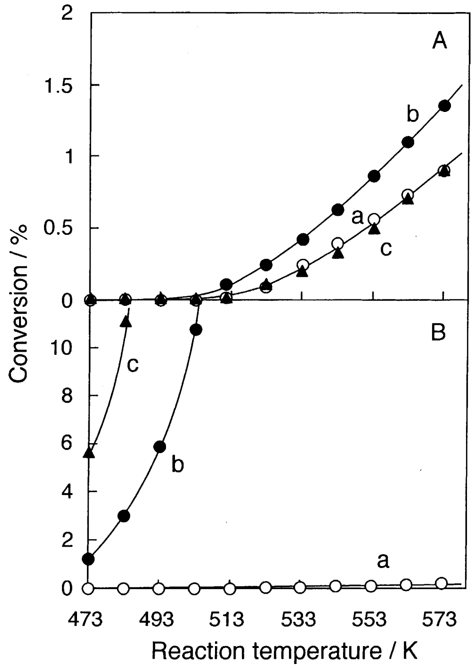


Fig. 7. Temperature dependencies of conversions for oxidations of (A) methane and (B) benzene: (a) 0.5 wt.% Pt-$Cs_{2.1}H_{0.9}PW_{12}O_{40}$; (b) 0.5 wt.% Pt-$Cs_{2.5}H_{0.5}PW_{12}O_{40}$ and (c) 0.5 wt.% Pt/SiO_2.

Due to the constrained pores, 0.5 wt.% Pt-$Cs_{2.1}H_{0.9}PW_{12}O_{40}$ exhibited an efficient reactant shape selectivity for catalytic oxidations; smaller molecules like methane (MS = 0.38 nm) and CO (MS = 0.38 nm) were readily oxidized, while benzene (MS = 0.59 nm) was not oxidized [37,38]. The typical examples are demonstrated in Fig. 7. Furthermore this catalyst discriminated between *n*-butane and isobutane in oxidation reaction [44]. This efficient shape selectivity indicates that Pt is exclusively present in the pores, but not on the external surface.

By substitution for Cs^+ to Rb^+, K^+, and $NH_4{}^+$, the pore size expanded to more than 0.59 nm (benzene). Rb2.1 salt had the micropores having the width close to the size of benzene (0.59 nm), and the formation of the stoichiometric salts of $NH_4{}^+$ brought about the uniform supermicropores having the width above 0.75 nm (1,3,5-trimethylbenzene) [45].

The width of pores of Pt-promoted heteropoly compounds and zeolites influenced greatly the selectivity in skeletal isomerization of *n*-butane [43]. With 0.5 wt.% Pt-$Cs_{2.5}H_{0.5}PW_{12}O_{40}$, which possesses mesopores with the width of about 5 nm, about 94% selectivity was obtained in the presence of H_2 at 573 K. On the other hand, the ultramicroporous heteropoly compound, 0.5 wt.% Pt-$Cs_{2.1}H_{0.9}PW_{12}O_{40}$, gave mainly propane as well as isobutane. In addition, Pt-H-ZSM-5 and H-ZSM-5 produced mainly small molecules such as ethane and propane, while Pt-HY gave isobutane with 80% selectivity. These results demonstrated that the pore width of the microporous materials is a crucial factor influencing the selectivity of skeletal isomerization of *n*-butane due to the product shape selectivity by the constrained pores [43].

7. Conclusions

Novel functions of heteropoly compounds are demonstrated. A unique salt, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ was highly active for organic reactions in water, which is brought about from the hydrophobicity, strong acidity, mesoporosity and insolubility. Pt-promoted $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ was effective for skeletal isomerization of alkanes. The reaction mechanism of this reaction was elucidated using ^{13}C-butane. The pore structure of these heteropoly compounds was changed by the control of the content of Cs. Pt-$Cs_{2.1}H_{0.9}PW_{12}O_{40}$ has ultramicropores with the width of about 0.50 nm and exhibited shape selectivity for oxidation of hydrocarbons.

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