

ACID CATALYSIS OF HETEROPOLY COMPOUNDS FOR INDUSTRIAL ORGANIC REACTIONS

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Abstract

The acid catalysis of heteropolyacid and its acidic salts for various types of industrial organic reactions has been studied in the reaction systems of homogeneous liquid phase and heterogeneous liquid and vapor phases. Heteropolyacid was a very effective Brønsted acid catalyst for the reactions involving carbenium cations, oxonium ions, and oxocarocations: alkene hydration, ether cleavage reactions including ring opening reactions of epoxide, esterification, transesterification, and Friedel-Crafts alkylation and acylation reactions. At the same proton concentrations and the same ionic strengths, the catalytic activity of heteropolyacid was 3 to 100 times higher than those of the ordinary protonic acids such as sulfuric, nitric, perchloric, and phosphoric acids. The high catalytic activity of heteropolyacid was elucidated by a unique property of heteropoly anion to be able to stabilize the cationic intermediates. Heteropolyacid was effectively be applied as a protonic acid catalyst to several industrially important organic reactions in the forms of a homogeneous solution catalyst and a heterogeneous supported catalyst. Acidic alkali metal salts of heteropolyacid could effectively be applied as insoluble and readily separable solid acid catalysts to the Friedel-Crafts reactions in highly polar organic solvents. Tungstophosphoric acid, as well as its acidic cesium salt, was immobilized in the silica matrix by means of sol-gel technique. Silica-included heteropoly compounds efficiently worked for the hydrolysis of esters as water-insoluble solid acid catalysts.

Keywords: catalysis, heteropolyacid, solid acids, silica inclusion, industrial organic reactions

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1. Introduction

Heteropolyacid (hereafter abbreviated HPA) is defined as a condensate of different kinds of oxoacids. Among various HPA, the Keggin-type acid is most popular, being well known as "heteropoly blue" in colorimetric determination of phosphorus. It is also frequently used as an oxidizing agent for the organic compounds separated by thin layer chromatography. The chemistry of HPA has long been studied extensively,¹⁻³⁾ but its debut in the field of catalyst chemistry and technology is rather recent; the importance of the Keggin structure was first suggested in 1959 in a Sohio patent for the oxidation of methacrolein.⁴⁾ It should be noted, however, that HPA is now being commercially applied mainly in Japan as a practical catalyst material to several petrochemical processes including the direct hydration of propene for the manufacture of 2-propanol in 1972 (the first industrial application of HPA molecular catalysis),^{5,6)} the oxidation of methacrolein to methacrylic acid in 1982,⁷⁾ the chemical separation of isobutene as *t*-butanol from the spent butane-butene fraction in 1984,⁸⁾ the oligomerization of tetra-hydrofuran to polymeric diol in 1985,⁹⁾ and the hydration of *n*-butenes in 1989.¹⁰⁾ Most of the pioneering work since the 1970s has been done mainly by Russian and Japanese research groups¹¹⁻¹⁵⁾ centering on homogeneous molecular catalysis of HPA and heterogeneous catalysis with HPA crystal bulk. Their work on HPA catalysis has pointed to the essential role of the Keggin structure of HPA both in acid catalysis⁶⁾ and oxidation catalysis.¹⁶⁾ In addition to its practical usefulness, HPA is attracting much academic interest as a potential catalyst material because it possesses dual catalytic functions of strong acidity and high oxidizing ability.

We can utilize HPA as a catalyst material through the following three different approaches, as follows: 1) using the acid-base and redox properties inherent in the HPA molecule, 2) using HPA only as a starting material for a tungsten or molybdenum oxide catalyst,

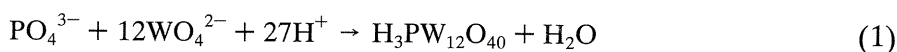
and 3) using general catalytic functions common to most of the ordinary tungsten and molybdenum compounds.

The latter two approaches do not utilize the specific advantages of HPA as a catalyst. This study has been carried out to elucidate the characteristics of HPA acid catalysis based on the first approach, emphasizing its inherent advantages over the other conventional catalyst materials for many industrially important acid-catalyzed reactions.

2. Fundamental Chemistry of Heteropolyacid

2.1. Structures

A typical HPA of 12-tungstophosphoric acid is formed when a phosphate ion is condensed with tungstate ions as shown in Eq. (1).



A heteroatom, which is located in the center of the HPA molecule (P in Eq. (1)), can be chosen from among a wide variety of I to VIII elements in the periodic table. The atoms which are bound to the central heteroatom through oxygen atoms are called polyatoms or addenda atoms (W in Eq. (1)). They are represented by the transition metals such as Mo, W, V, and Nb. A single HPA molecule which consists of different kinds of addenda atoms is often called a "mixed coordinated" species. Some examples of heteropoly molybdate anion are listed in Table 1. The structure of the typical 1:12 Keggin-type heteropoly anion was assigned by J.F. Keggin in 1933.¹⁷⁾ A structural model of the Keggin anion ($\text{PW}_{12}\text{O}_{40}^{3-}$) is illustrated in Fig. 1; four oxygen atoms forming a central tetrahedron of heteroatom P, and twelve terminal and twenty-four bridged oxygen atoms forming twelve octahedra of addenda atoms W are shown. One can imagine the form of the Keggin anion as a sphere having a diameter of approximately 1 nm. HPA that is applicable as a catalyst material is limited exclusively to the Keggin-type and Dawson-type acids owing to their availability and chemical stability.

Table 1. Typical Heteropoly Molybdate Anions.

Structure	Heteroatom (X)	Chemical formula
1:12 Keggin	P ⁵⁺ , As ⁵⁺ , Si ⁴⁺ , Ge ⁴⁺	[X ⁿ⁺ Mo ₁₂ O ₄₀] ⁽⁸⁻ⁿ⁾⁻
Silverton	Ce ⁴⁺ , Th ⁴⁺	[X ⁴⁺ Mo ₁₂ O ₄₂] ⁸⁻
1:11 Keggin (lacunate)	P ⁵⁺ , As ⁵⁺ , Si ⁴⁺ , Ge ⁴⁺	[X ⁿ⁺ Mo ₁₁ O ₃₉] ⁽¹²⁻ⁿ⁾⁻
2:18 Dawson	P ⁵⁺ , As ⁵⁺	[X ₂ ⁵⁺ Mo ₁₈ O ₆₂] ⁶⁻
1:9 Waugh	Mn ⁴⁺ , Ni ⁴⁺	[X ⁴⁺ Mo ₉ O ₃₂] ⁴⁻
1:6 Anderson (A type)	Te ⁶⁺ , I ⁷⁺	[X ⁿ⁺ Mo ₆ O ₂₄] ⁽¹²⁻ⁿ⁾⁻
(B type)	Co ³⁺ , Al ³⁺ , Cr ³⁺	[X ⁿ⁺ Mo ₆ O ₂₄ H ₆] ⁽⁶⁻ⁿ⁾⁻

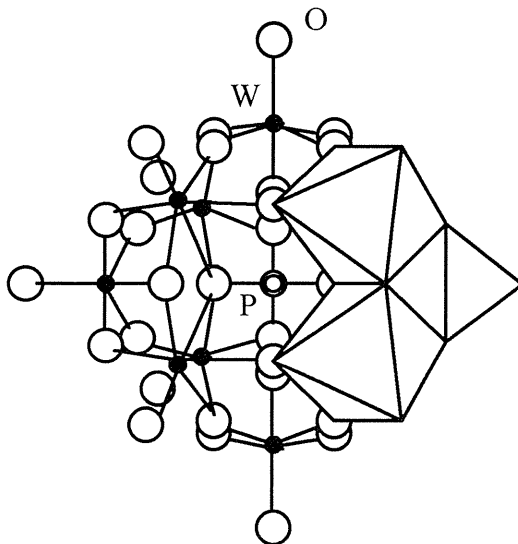


Fig. 1. A schematic Keggin structure of $PW_{12}O_{40}^{3-}$ anion.

The crystal form of HPA depends on the amount of water of crystallization. The water molecules in HPA crystal are arranged as protonated aquo cations, for example as $H_3(H_2O)_{29}^{3+}$, in the face-centered cubic lattice of $H_3PW_{12}O_{40} \cdot 29H_2O$.¹⁸⁾ This water of crystallization can be eliminated on heating as easily as the water in zeolite, whereby the proton activity in HPA crystal is increased to show higher catalytic activity in acid-catalyzed reactions. Unlike the rigid anionic zeolite framework, the Keggin anions are still mobile even in dehydrated HPA crystal, and not only water but certain kinds of polar organic molecules can also go in and out among the Keggin anions, being accompanied by a volume change of HPA crystal. Such structural flexibility of HPA crystal should be taken into account when employing HPA as a heterogeneous catalyst.¹²⁾

HPA may be a kind of mixed metal oxide compound in terms of chemical composition (Table 1), but it must be strictly distinguished from ordinary mixed metal oxides in that HPA crystal is composed of the Keggin anions which are arranged discretely. This structural feature of HPA is deeply associated with its unique properties and catalytic functions, in contrast to the other mixed metal oxides and isopoly compounds such as paramolybdate ($Mo_7O_{24}^{6-}$), whose crystals are built up from indefinite long sequences of MoO_6 octahedron.

2.2. Properties

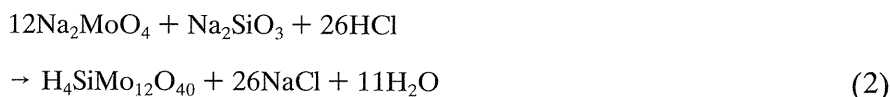
Important properties of the Keggin-type HPA relevant to catalysis are summarized in Table 2. Particular attention should be paid to the stability of HPA anion. HPA is liable to be hydrolyzed in basic aqueous media,¹⁹⁾ but it is thermally very stable, and favorably applicable to the vapor-phase reactions conducted at high temperatures up to 400–500°C.

2.3. Synthesis and Identification

The Keggin-type HPA is prepared by heating an acidic ($1 < pH < 2$) aqueous solution of molybdate or tungstate and an oxoacid of heteroatom or its salt, as exemplified by Eq. (2).²⁰⁾

Table 2. Properties of Keggin-type Heteropolyacid.

* A polymeric electrolyte (MW=1000-4000), very soluble in water.
* Soluble in alcohol, ether, ketone, carboxylic acid, ester; reacting with diethyl ether to form an etherate.
* Forming sparing soluble or insoluble salts with K ⁺ , Cs ⁺ , Ag ⁺ , Tl ⁺ , Hg ²⁺ , NH ₄ ⁺ , and organic amines.
* A polybasic strong acid, completely dissociative in water.
* High oxidizing ability of Mo and V containing HPA.
* Decomposed with alkali into the corresponding simple oxoacids.
* Durability against hydrolysis: Heteroatom: Si>Ge>P>As; addenda atom: W>Mo>V.
* Thermal stability: H ₃ PW ₁₂ O ₄₀ (610 °C) > H ₄ SiW ₁₂ O ₄₀ (540 °C) > H ₃ PMo ₁₂ O ₄₀ (495 °C) > H ₄ SiMo ₁₂ O ₄₀ (375 °C).



HPA thus prepared is isolated either as a metal salt by crystallization or as a free acid either by the acidification with mineral acid followed by extraction with ether, or by ion exchange. In the ether extraction, a heavy ether adduct of HPA is formed which is immiscible with water and ether, thus separable. 12-Molybdophosphoric acid is obtained also by heating an aqueous slurry of MoO₃ and H₃PO₄. Free acid of HPA can also be prepared by calcining ammonium salt in air at a high temperature. HPA salts are obtainable by neutralizing the corresponding free acids carefully with alkali carbonate. Mixed coordinated HPA is synthesized by reacting an oxoacid of heteroatom with more than two kinds of metal oxides or salts of addenda atoms in a given molar ratio.^{20,21)}

To identify the Keggin structure of HPA, X-ray diffraction, UV and IR spectroscopies are available in addition to chemical analysis. UV²²⁾ and IR²³⁾ data are useful particularly for the identification of the HPA of W and Mo. Qualitative identification of HPA is also possible through the observations of its extraordinarily high solubility in water or of coloring of heteropoly blue when reacted with a mild reducing agent such as ascorbic acid.

3. Acid Catalysis of Heteropolyacid

The strong acidity of HPA makes it suitable as a catalyst for many acid-catalyzed organic reactions. Table 3 lists various types of reactions catalyzed by the Keggin-type HPA and its related compounds, most of which are industrially important. HPA catalyst is expected to show advantages of high activity, high selectivity, easy recovery, and good workability over the conventional acid catalysts such as sulfuric acid, aluminum chloride, boron fluoride,

Table 3. Organic Reactions Catalyzed by Heteropolyacid.

Reactions	Substrates	References
Isomerization	1-butene, <i>m</i> -xylene, <i>p</i> -xylene	11, 25
Hydration	propene, isobutene, cyclohexene, phenylacetylene	25b, 26, 27, 28
Dehydration	2-propanol, cyclohexanol, dicyclohexyl ether, butanol	11, 25b,c,d; 29, 33c
Ether formation	methanol + isobutene(<i>t</i> -BuOH), epoxide + alcohol, ethylene oxide	30, 31, 32
Glycosidation	acetylated aldohexose + higher alcohol	74
Esterification	carboxylic acid + alcohol (alkene)	33, 34, 35
Decomposition	carboxylic acid, ester, ether	36, 37, 38
Rearrangement	cumene hydroperoxide	39
Friedel-Crafts	alkylation	40, 41, 42, 43
reactions	acylation	44, 45, 46
Prins reaction	styrene + formaldehyde, ethene + formaldehyde	27, 47
Polymerization	tetrahydrofuran	9, 73
MTG reaction ^a	methanol	48

^a Methanol conversion to gasoline.






supported phosphoric acid, and silica alumina. The reactions shown in Table 3 are classified into liquid-phase homogeneous reactions due to high miscibility of HPA with water and organic substrates, and heterogeneous reactions over supported or unsupported HPA, usually in vapor phase.

3.1. Liquid-phase Homogeneous Reactions

In homogeneous acid-catalyzed reactions, neutral salts of HPA such as $\text{Na}_4\text{SiW}_{12}\text{O}_{40}$ and $(n\text{-Bu}_4\text{N})_4\text{SiMo}_{12}\text{O}_{40}$ were quite inactive in nature. The protons of HPA therefore played a decisive role in reaction promotion. However, as will be shown below, the coexistence of heteropoly anions as conjugate bases accelerated reactions much more efficiently. In contrast the counter anions of the conventional protonic acids such as sulfate, nitrate, and perchlorate, took no part in activation of reactants. In this sense, the acid catalysis of HPA should be understood as acid and base molecular catalysis.


Typical acid catalysis of HPA for liquid-phase homogeneous reactions in aqueous and organic media is listed in Table 4, compared with the catalytic efficiency of several conventional acids. The activation energy of some reactions in Table 4 are presented in Table 5. As shown in Table 4, HPA was very effective particularly for reactions which proceed via the protonated cationic intermediates such as carbenium cations in alkene hydration, oxonium

Table 4. Heteropoly Acid-catalyzed Homogeneous Reactions.

Reactions (temperature/°C)	Relative reactivity/mole of acid					
	Heteropoly acid ^a				Ordinary acid	
	PW	SiW	PMo	SiMo	H ₂ SO ₄	TsOH ^b
<i>i</i> -C ₄ H ₈ + H ₂ O → <i>t</i> -BuOH (39)	1.0	0.88	1.0	0.70	0.49	—
PhC ≡ CH + H ₂ O → PhCOCH ₃ (60)	1.0	0.47	1.0	—	0.03	—
PhCH = CH ₂ + HCHO → Ph  (55)	1.0	0.93	1.2	—	0.003	0.16
ClCH ₂ CH  CH ₂ + CH ₂ = CHCH ₂ OH →	1.0	1.2	0.89	—	0.03	—
ClCH ₂ CH(OH)CH ₂ OCH ₂ CH = CH ₂ (45)						
ClCH ₂ CH  CH ₂ + AcOH →	1.0	0.68	0.65	0.21	—	4 × 10 ⁻⁴
ClCH ₂ CH(OH)CH ₂ OAc (30)						
THF ^c + AcOH → AcO(CH ₂) ₄ OAc (95)	1.0	1.0	0.53	—	—	0.009
AcOEt + BuOH → AcOBu + EtOH (49)	1.0	0.94	0.78	1.0	0.21	0.13
AcOEt + EtCO ₂ H →	1.0	1.1	0.79	0.58	0.04	0.03
AcOH + EtCO ₂ Et (71)						
O=  + HOCH ₂ CH ₂ OH →	1.0	1.3	0.80	—	—	0.4
 (27)						

^aPW: tungstophosphoric acid, SiW: tungstosilicic acid, PMo: molybdophosphoric acid, SiMo: molybdosilicic acid. ^b*p*-Toluenesulfonic acid. ^cTetrahydrofuran.

Table 5. Activation Energies of Homogeneous Reactions.

Reactions	Temp./°C	Activation energy/kcal mol ⁻¹	
		PW ₁₂ ^a	Other acids
<i>i</i> -C ₄ H ₈ + H ₂ O → <i>t</i> -BuOH	35–50	14	18 (HNO ₃)
PhC ≡ CH + H ₂ O → PhCOCH ₃	55–70	24	28 (H ₂ SO ₄)
ClCH ₂ CH  CH ₂ + AcOH →	25–35	13	16 (BF ₃ ·Et ₂ O)
ClCH ₂ CH(OH)CH ₂ Oac			
THF ^c + AcOH → AcO(CH ₂) ₄ Oac	90–100	27	29 (TsOH ^b)
AcOEt + BuOH → AcOBu + EtOH	50–80	9.3	13 (H ₂ SO ₄)
Bu ₂ O + AcOH → BuOAc	102–118	28	34 (TsOH ^b)

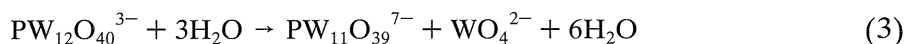
^a12-Tungstophosphoric acid. ^b*p*-Toluenesulfonic acid.

ions in ether cleavage reactions including ring opening reactions of epoxide, and oxocarboxations in transesterification.

3.1.1 Reactions in aqueous media

Alkene hydration: Izumi and Mizutani have first pointed out that HPA exhibits high catalytic activity and selectivity for the hydration of alkene, rendering it applicable as a commercial catalyst to the manufacture of 2-propanol.⁵⁾ The liquid-phase hydration of isobutene, for example, was catalyzed by an aqueous HPA under atmospheric pressure much more efficiently than nitric acid at the same proton concentrations and the same ionic strengths²⁷⁾ (Fig. 2). Other simple oxoacids such as sulfuric acid and perchloric acid showed completely the same activity as nitric acid at the same proton concentration. The rate of hydration in aqueous nitric acid is believed to be directly proportional to the proton concentration,⁴⁹⁾ but the rate of hydration in aqueous HPA showed higher order (1.5) dependence on the proton concentration. The activation energy of the hydration was lowered by about 4 kcal/mole when HPA was used (Table 5).

HPA is completely dissociated in aqueous solution.⁵⁰⁾ For instance, $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ is a tetrabasic acid whose four protons are quite equivalent.^{50a)} Although HPA is fairly susceptible to alkali,^{51,52)} $\text{H}_3\text{PW}_{12}\text{O}_{40}$ and $\text{H}_4\text{SiMo}_{12}\text{O}_{40}$ decompose even in a weakly acidic aqueous solution (Eqs. (3) and (4)).^{51b,53)}



However, according to the measurements of conductivity and pH,^{50,54,55)} even $\text{H}_3\text{PW}_{12}\text{O}_{40}$, which is somewhat sensitive to hydrolysis, can exist intact in an acidic aqueous

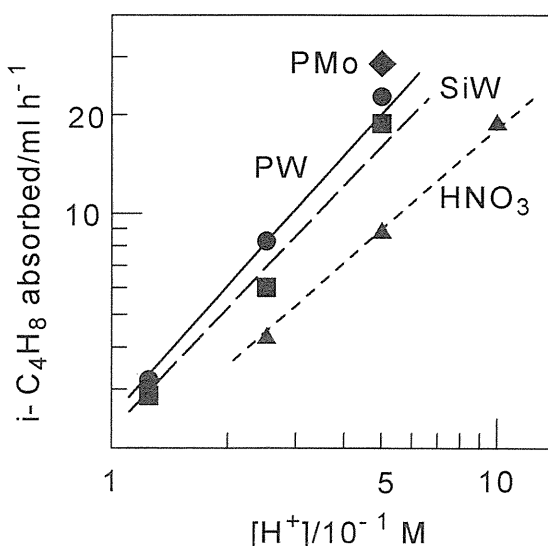
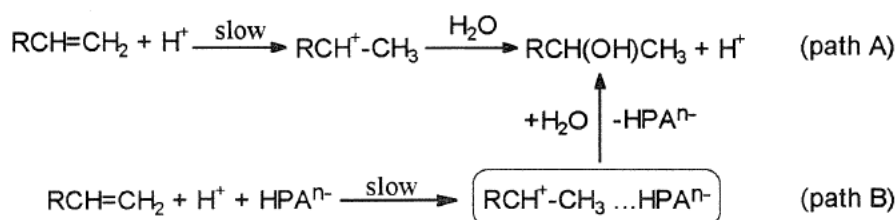


Fig. 2. Dependence of the rate of isobutene hydration on proton concentration at 39°C. Ionic strength: 1.00 M (HNO_3 , PW_{12}), 1.25 M (SiW_{12}).



Scheme 1. Alkene hydration by heteropoly acid.

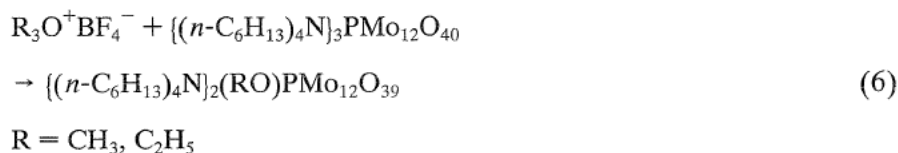
solution ($pH=1.0-1.5$), if a certain oxygen-containing organic substance such as *t*-butyl alcohol, acetone, or dioxane is added. In addition, it has also been confirmed by X-ray diffraction⁵⁶⁾ and ¹⁶O-NMR⁵⁷⁾ studies that SiW₁₂O₄₀⁴⁻ anion holds its Keggin structure in an aqueous solution. It is therefore probable that HPA dissociated completely without deterioration during the hydration of butene in acidic ($pH < 1.0$) aqueous solutions exemplified by Figs. 2. In the alkene hydration catalyzed by ordinary protonic acids, the rate depends merely on the proton concentration (specific acid catalysis),⁵⁸⁾ and the formation of a carbenium ion from H₃O⁺ and an alkene molecule controls the rate. The fact that HPA exhibited higher catalytic activity than nitric acid under the same proton concentration and the same ionic strength suggests that heteropoly anion played an important role in accelerating the reaction.

Izumi and co-workers proposed a parallel reaction mechanism as shown in Scheme 1 for the HPA-catalyzed alkene hydration, which involves path A by the specific acid catalysis and another path B via the carbenium ion being stabilized by heteropoly anion.²⁷⁾ Since the activities of proton and heteropoly anion are both regarded as constant in a dilute aqueous solution at a constant ionic strength, the overall reaction rate of the isobutene hydration according to the parallel reaction mechanism can be expressed as Eq. (5):

$$v = k_a p_b [\text{H}_3\text{O}^+] + k_b p_b [\text{H}_3\text{O}^+] [\text{HPA}^{n-}] \quad (5)$$

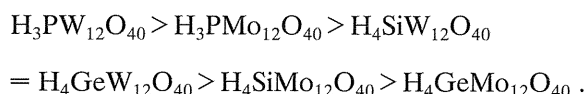
where k_a and k_b denote the rate constants of paths A and B, respectively, p_b the partial pressure of isobutene, and $[\text{HPA}^{n-}]$ the concentration of heteropoly anion. The compatibility of Eq. (5) with the experimental data was elucidated by a good linear relationship between $v/\{p_b[\text{H}_3\text{O}^+]\}$ and $[\text{HPA}^{n-}]$. The kinetic result thus suggests that heteropoly anion may stabilize the intermediate carbenium ion through mutual strong interaction to lower the activation energy, resulting in enhancement of hydration rate.

The existence of the interaction between heteropoly anion and carbenium ion may be directly supported by the studies on the structural analysis of *O*-alkylated HPA compounds and the NMR analysis of the HPA-catalyzed ethanol dehydration. Knoth and co-workers⁵⁹⁾ prepared *O*-alkylated HPA compounds according to the following reaction,



where a bridged oxygen atom of HPA was alkylated to form an *O*-alkylated HPA compound. The bond distance between the alkyl carbon and the oxygen atom of HPA was determined to be 1.64 Å, which is much longer than the ordinary C-O covalent bond of 1.43 Å. This long C-O bond distance suggests that the interaction between alkyl carbon and HPA oxygen is rather ionic. More directly, in the dehydration of ethanol inside the bulk of H₃PW₁₂O₄₀ crystal, Misono and co-workers⁶⁰⁾ confirmed the existence of ethyl cation directly bound to the bridged oxygen of PW₁₂O₄₀³⁻ anion through solid-state ¹³C MAS NMR spectroscopy.

The catalytic activity of HPA for isobutene hydration varied depending on the kind of HPA. This difference in catalytic activity was mostly associated with the difference in proton activity or acid strength of aqueous HPA. The relative acid strengths of different HPA could be estimated by measuring the relative base strengths of their conjugate bases, namely the basicities of heteropoly anions. According to Barcza and Pope,⁶¹⁾ the basicity of heteropoly anion can be successfully determined by measuring the degree of hetero-conjugation (hydrogen bonding) of chloral hydrate (Cl₃CH(OH)₂) with heteropoly anion in an organic medium by means of NMR spectroscopy: the variation of chemical shift for the chloral hydrate protons correlates with the basicity of heteropoly anion. The change in chemical shift of the hydroxy protons of chloral hydrate with the change in the concentration of heteropoly anion was measured in C₆D₅NO₂ solutions,³⁸⁾ and the result is shown in Fig. 3. Since PW₁₂O₄₀³⁻ anion was the weakest base, H₃PW₁₂O₄₀ should correspond to the strongest acid among various HPA in Fig. 3. The order of acid strength of HPA was therefore expressed as follows:



This order of acid strength for HPA explained fairly well the difference in the catalytic activity of HPA in isobutene hydration. Judging from the relative basicity of conjugate anion,

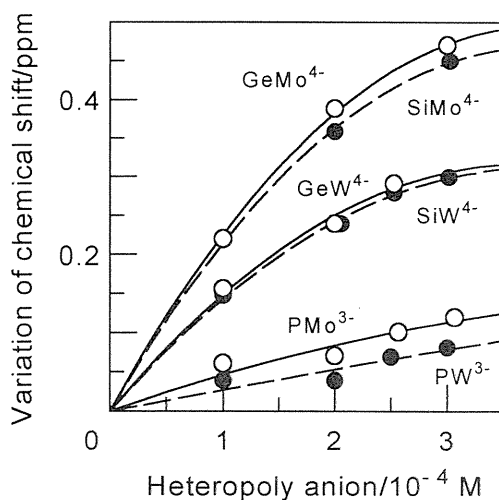


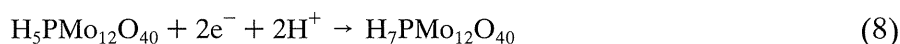
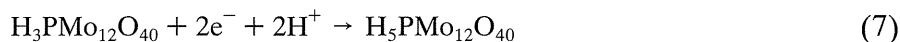
Fig. 3. Heteroconjugation of chloral hydrate protons with heteropoly anion in C₆D₅NO₂ at 30°C.

the acid strength of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ was almost comparable to that of perchloric acid, but the catalytic activity of the HPA was much higher owing to the nature of heteropoly anion as mentioned above.

A commercial technology of separating isobutene from the butane-butene fraction through direct hydration of isobutene into *t*-butyl alcohol has recently been developed using an extraordinarily concentrated aqueous solution of HPA (0.1–0.5 M).⁸⁾ In the isobutene hydration with concentrated aqueous acid, HPA also shows higher catalytic activity than nitric and perchloric acids, and the reaction rate is expressed only by the second term of Eq. (5) at a HPA concentration of more than 0.5 M, i.e. the reaction path B in Scheme 1 becomes dominant.⁸⁾ Although this hydration process can be operated at a relatively low reaction temperature (ca. 80°C) giving high conversion owing to high catalytic activity and can minimize unfavorable side reactions such as isobutene oligomerization, careful attention must be paid to suppress the deterioration of HPA because aqueous HPA at high concentrations is liable to be decomposed.^{62,63)}

3.1.2 Reactions in organic media

Remarkable acid catalysis of HPA was realized also in reactions in nonaqueous organic media. Typical reactions included ether cleavage such as nucleophilic ring opening of epoxides and tetrahydrofuran, transesterification, and Friedel-Crafts type reactions. In general, HPA used for the reactions in organic media maintained its Keggin structure in the course of reactions, which could be confirmed by examining its IR spectrum.²³⁾ HPA such as $\text{H}_3\text{PMo}_{12}\text{O}_{40}$, which possesses a high redox potential due to the addenda atoms of Mo, was readily reducible with organic substrates at relatively high temperatures (ca. >95°C), changing its color from yellow to blue (Eq. (7) and (8)). The IR spectrum of the reduced $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ showed remarkable decreases in absorbance at 1060 cm^{-1} (P-O) and 860 cm^{-1} (Mo-O-Mo).⁸⁴⁾



This reducibility of HPA caused the decrease in acid strength because of the increase in basicity of heteropoly anion. At high reaction temperatures, therefore, heteropolytungstic acids, which are not so susceptible to reduction, often worked as more efficient catalysts than heteropolymolybdc acids in organic media, but under ambient conditions the order of catalytic activity of HPA agreed fairly well with the order of the acid strength mentioned above.

As will be demonstrated below, the catalytic activity of HPA for many acid-catalyzed reactions in organic media was much higher than that of sulfuric acid, *p*-toluenesulfonic acid, and a typical powerful Lewis acid of $\text{BF}_3 \cdot \text{Et}_2\text{O}$ on the basis of molar concentration of catalyst, or even on the basis of proton concentration, where all the protons of multi-basic acids including HPA are assumed to be equally effective in nonaqueous organic media. Hence the remarkable difference in catalytic efficiency between HPA and other acids should be attributed to certain qualitative differences in the acid property.

As an example, let us examine the differences in acid property between HPA and *p*-toluenesulfonic acid (TsOH), which is often applied as a soluble acid catalyst in organic synthesis. In organic media, as well as TsOH and sulfuric acid, HPA appears to behave as a weak electrolyte. Indeed, as shown by the dependence of molar electric conductivity of HPA on its concentration in acetic acid solution (Fig. 4),³⁸⁾ the curvature of this phoreogram indicates that each HPA existed as a weak electrolyte in acetic acid; this HPA-acetic acid system

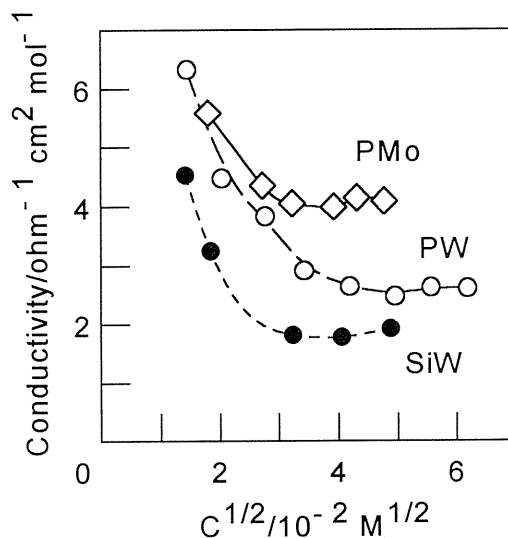
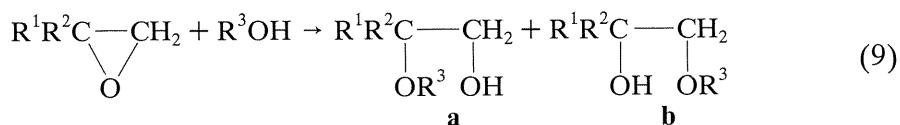


Fig. 4. Molar conductivity of acetic acid solutions of heteropoly acid at 30°C.

relates to the acetolysis of ethers, which was described below. The catalytic activity in organic media must therefore be associated with the acidity of nondissociated acid species rather than with the concentration of dissociated proton. The acidity of HPA and TsOH in acetic acid in various concentrations was qualitatively evaluated using Hammett indicators. Both $\text{H}_3\text{PW}_{12}\text{O}_{40}$ and $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ showed the acid strength between -5.6 and -3.0 in terms of H_0 function even at lower concentrations of 5.2×10^{-4} and 5.5×10^{-4} M, respectively, but TsOH could reveal the same acid strength only at high concentrations above 3.7×10^{-1} M. Such stronger acidity of HPA in organic media is probably due to low susceptibility to solvation by polar organic molecules, compared with other conventional smaller size acids. Thus the stronger acidity of HPA in organic media is probably responsible at least in part for its higher catalytic activity. However, the experimental facts that both TsOH and sulfuric acid were quite inactive for the ether cleavage reactions with acetic anhydride even at very high concentrations (vide infra) and that the activation energies for the HPA-catalyzed acetolysis of ethers were obviously lower by 2–6 kcal/mol than those when catalyzed by TsOH (Table 5) suggest that the catalytic activity of HPA may also be influenced by specific characteristics of HPA other than strong acidity. Softness of heteropoly anion may be associated with the important role of HPA in stabilizing the intermediate acetyl cation.

*Alcoholysis of epoxides*³¹⁾: HPA efficiently catalyzed the nucleophilic ring opening of epoxides with alcohol into the corresponding β -hydroxy ethers in liquid phase under relatively mild reaction conditions (Eq. (9)).



a: abnormal ring opening product, **b**: normal ring opening product

These reactions were carried out in homogeneous liquid phase at 45°C. To repress unfavorable polymerization of epoxides, excess alcohol had to be used. In the presence of HPA catalyst, epichlorohydrin (ECH) reacted with allyl alcohol in S_N2 fashion being completely converted with a high selectivity of 95–97 mole into the normal ring opening product of 1-allyloxy-3-chloro-2-propanol, which is an important precursor of allyl glycidyl ether. No polymeric by-product was formed. The crystalline water of HPA had little effect on the ECH conversion and selectivity so long as its concentration did not exceed 6×10^{-2} M. On the other hand, the reactions using sulfuric acid and perchloric acid as catalysts were very slow even when they were employed in considerably high concentrations; furthermore, rapid deactivation was observed with lapse of time. Much higher concentrations of H_2SO_4 , together with reflux condition, was required for converting ECH completely into the hydroxy ether as indicated in the conventional synthetic method.⁶⁴ The rapid deactivation observed with H_2SO_4 catalyst implies that the acid reacted either with allyl alcohol, ECH, or the product hydroxy ether to form an alkyl sulfate, resulting in loss of acidity. It is known that a half-ester is formed from the reaction of methanesulfonic acid with ethylene oxide.⁶⁵ Fig. 5 illustrates the change in specific electric conductivity as a measure of acidity change in the reaction system of ECH-allyl alcohol- H_2SO_4 . The conductivity sharply decreased with reaction time (curve a), and this change corresponded well to a rapid decline in reaction rate (curve b). The conductivity began to diminish noticeably when ECH was added to a mixture of allyl alcohol and H_2SO_4 , and the introduction of an additional amount of the product hydroxy ether to this system gave little influence on the conductivity (curve c). The decrease in catalytic activity of H_2SO_4 is therefore likely due to the reduction of acidity as a result of equilibrated formation of an ester, probably glycol monosulfate from ECH. On the other hand, no change in the conductivity was observed with HPA catalyst, which suggests that HPA barely reduced its acidity during the reaction, and HPA maintained its high catalytic activity. Considering that $HClO_4$ did not lose its acidity during the reaction so drastically as H_2SO_4 but that its catalytic efficiency was far lower than that of HPA, the high activity of HPA may be attributed to the unique ability of heteropoly anion to stabilize the intermediate oxonium ion formed from a

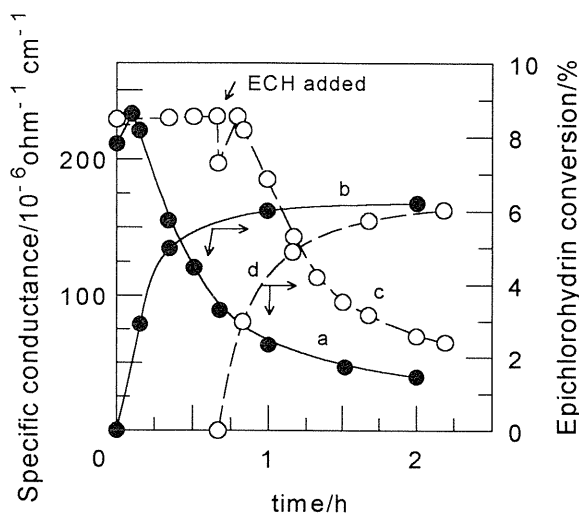


Fig. 5. Specific conductivity of H_2SO_4 (0.0127 M) system at 25.5°C. ECH (51.2 mmol) was added to allyl alcohol (588 mmol) from the start (a, b) and after 40 min (c, d).

Table 6. Alcoholysis of Epoxide Catalyzed by $\text{H}_3\text{PW}_{12}\text{O}_{40}$ and *p*-Toluenesulfonic acid at 45°C.

Epoxide	Alcohol mole ratio ^a	Catalyst (10^{-3} M)	Reaction time/h	Epoxide Conv./%	Hydroxy Yield/% ^b	ethers Selec./% ^c
1,2-Epoxybutene	PrOH (11.6)	HPA ^d (1.99)	5	100	94.5	64 (b)
		TsOH ^e (1.95)	5	0.3	100	58 (b)
	<i>t</i> -BuOH (9.2)	HPA (6.04)	5	60	88.0	66 (b)
		TsOH (6.14)	5	0.0	—	—
Isobutene oxide	PrOH (11.6)	HPA (30.6)	2.5	100	98.6	84 (a)
		TsOH (31.0)	2.5	78	100	99 (a)
	<i>t</i> -BuOH (9.41)	HPA (30.2)	3	70	96.0	99 (b)
		TsOH (36.1)	3	3	100	0 (b)
Styrene oxide	PrOH (15.2)	HPA (4.82)	2	100	100	93 (a)
		TsOH (5.30)	2	7.0	100	92 (a)
	<i>t</i> -BuOH (12.1)	HPA (61.2)	4	77	97.8	87 (a)
		TsOH (62.5)	4	8.8	100	85 (a)

^aAlcohol/epoxide. ^bCalculated from the GLC peak area of hydroxy ethers and unidentified polymeric by-product. ^cComposition of the major hydroxy ether isomer in Eq. 3.9. ^d $\text{H}_3\text{PW}_{12}\text{O}_{40}$. ^e*p*-Toluenesulfonic acid.

proton and an epoxide molecule.

Table 6 summarizes the catalytic activities of $\text{H}_4\text{PW}_{12}\text{O}_{40}$ and *p*-toluenesulfonic acid (TsOH) for the addition of 1-propanol and *t*-butyl alcohol to 1,2-epoxybutane, isobutene oxide, and styrene oxide. At a similar catalyst concentration, HPA converted each epoxide into the corresponding hydroxy ether much faster than TsOH. HPA is thus generally applicable as an effective and selective catalyst to the alcoholysis of epoxides. HPA was particularly suited to obtaining abnormal ring opening products which would not be formed by basic catalysts.

*Acetolysis of ethers*³⁸: The reactions were performed in an excess of acetic acid in homogeneous liquid phase. HPA was far more active in all cases than the comparative acid catalysts such as *p*-toluenesulfonic acid (TsOH) and $\text{BF}_3 \cdot \text{Et}_2\text{O}$. Fig. 6 shows the result of the acetolysis of epichlorohydrin (ECH). Regardless of the catalyst used, the acetolysis of ECH at 30°C gave the normal ring opening β -hydroxy ester, 1-acetoxy-3-chloro-2-propanol, selectively. It should be noted that the catalytic activity of TsOH decreased noticeably at an earlier stage of the reaction, even though the acid concentration was 10^3 times higher than that of HPA. This deactivation is probably due to acidity loss resulting from the formation of a tosyl ester of epichlorohydrin as observed in the alcoholysis of ECH. Indeed, the electric conductivity of a reaction medium containing TsOH catalyst rapidly decreased with reaction time, owing to the decrease in acidity, in contrast with no change observed for $\text{H}_4\text{PW}_{12}\text{O}_{40}$ catalyst. The decrease in catalytic activity of TsOH was closely related to the decrease in conductivity. As for the AcOH-TsOH-ECH system, the formation of a tosyl ester from ECH was confirmed by the appearance of IR absorption peaks at 1365 and 1175 cm^{-1} (tosyl ester) in place of the decrease in absorbance at 1160 and 814 cm^{-1} (TsOH). On the other hand, HPA did not form its esters with epoxides; consequently it could easily effect the cleavage reaction.

1,2-Epoxybutane and styrene oxide likewise readily underwent acetolysis at 30°C in the presence of HPA (Table 7). The normal ring opening products, 1-acetoxy-2-butanol and

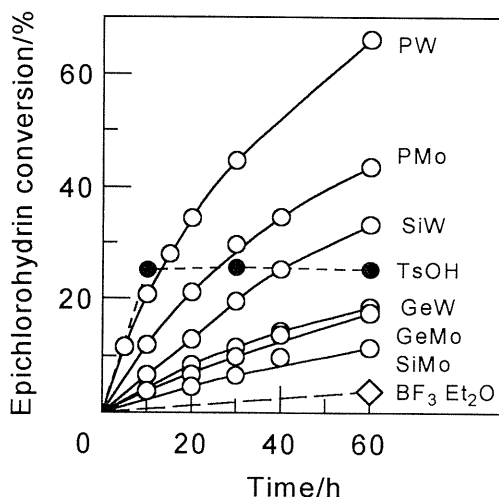


Fig. 6. Acetolysis of epichlorohydrin at 30°C. ECH: 13 mmol, AcOH: 260 mmol, $H_4PW_{12}O_{40}$ (1.9×10^{-4} M), $H_3PMo_{12}O_{40}$ (1.9×10^{-4} M), $H_4SiW_{12}O_{40}$ (1.4×10^{-4} M), TsOH (1.8×10^{-1} M), $H_4GeW_{12}O_{40}$ (1.4×10^{-4} M), $H_4GeMo_{12}O_{40}$ (1.4×10^{-4} M), $H_4SiMo_{12}O_{40}$ (1.6×10^{-4} M), $BF_3 \cdot Et_2O$ (3.6×10^{-4} M).

Table 7. Acetolysis of Epoxide^a.

Epoxide	Catalyst (10^{-4} M)	Reaction time/min	Epoxide conv./%	Select. ^b /mol%
1,2-Epoxybutane	$H_3PW_{12}O_{40}$ (1.9)	30	41	64
	$BF_3 \cdot Et_2O$ (7.3)	30	17	71
	None	240	4	80
Styrene oxide	$H_3PW_{12}O_{40}$ (0.39)	15	82	71
	$BF_3 \cdot Et_2O$ (1.9)	15	31	72
	None	15	29	69

^a1,2-Epoxybutane 15 mmol, styrene oxide 4.6 mmol, AcOH 260 mmol, 30°C.

^bNormal ring-opening products: 1-acetoxy-2-butanol from 1,2-epoxybutane, 2-acetoxy-1-phenylethanol from styrene oxide.

2-acetoxy-1-phenylethanol were primarily obtained, respectively. Tetrahydrofuran (THF), a less reactive cyclic ether, was also easily cleaved with acetic acid by the catalysis of HPA at 95°C, affording 1,4-diacetoxy-butane selectively. A possible initial intermediate product, 4-hydroxybutyl acetate, was not detected, probably because the esterification of this half-ester proceeded much faster than the preceding ring-opening of THF with acetic acid. The acetolysis of a linear ether of dibutyl ether at 118°C gave butyl acetate selectively, although the reaction was somewhat slower than the acetolysis of cyclic ethers. The order of reaction

rate in the acetolysis for different HPA catalysts reflected well their acid strengths at a low reaction temperature of 30°C (Fig. 6). At higher reaction temperatures, however, heteropolytungstic acids were always more active than the corresponding heteropolymolybdic acids, mainly because of lower susceptibility to reduction with organic substances. The activation energies of the reactions catalyzed by HPA were 2–6 kcal mol⁻¹ lower than those by BF₃ · Et₂O and TsOH. This fact again suggests the unique ability of heteropoly anion to stabilize the intermediate oxonium ions.

*Ether cleavage with acetic anhydride and butyl acetate*³⁸⁾: Reportedly, tetrahydrofuran (THF) reacts with acetic anhydride in the presence of MgBr₂, affording 4-bromobutyl acetate.⁶⁶⁾ MgBr₂ was acting there not only as a Lewis acid catalyst, but also as a brominating reagent. However, HPA, heteropolytungstic acids in particular, worked efficiently for this reaction as catalysts at 50°C (Table 8), even though HPA is a protonic acid. The major product was di(4-acetoxybutyl) ether, in contrast with the selective formation of 1,4-diacetoxybutane in the reaction of THF with acetic acid. Sulfuric acid had no activity for this cleavage reaction even at a high concentration, and BF₃ · Et₂O also was far less active than HPA.

The reaction by HPA catalyst appears to proceed via *O*-acetylation of THF. Probably HPA readily interacts with acetic anhydride producing acetyl cation which initiates the reaction. Similar catalysis by HPA, which involves the formation of acetyl cation, has been demonstrated in the Friedel-Crafts reaction of anisole with acetyl chloride.⁴³⁾ Such efficient catalysis for acetylation is one of the notable characteristics of HPA. This acetylation catalysis by HPA could be further extended to the synthesis of THF oligomers, AcO(CH₂CH₂CH₂CH₂O)_nAc, by varying the molar ratio of THF to acetic anhydride (Table 9).

The cleavage of dibutyl ether with acetic anhydride was likewise effectively catalyzed by HPA. The reaction products were butyl acetate and *s*-butyl acetate in a molar ratio of about 7:3. According to a mechanism study on the same reaction by FeCl₃,⁶⁷⁾ the reaction involves nucleophilic attack of acetate anion on an oxonium ion formed through *O*-acetylation of dibutyl ether with acetic anhydride. The formation of *s*-butyl acetate presumably assists an

Table 8. Reaction of Tetrahydrofuran with Acetic Anhydride^a.

Catalyst (/10 ⁻⁴ M)	THF conv. /%	Selectivity/mol%	
		1 ^b	2 ^c
H ₄ SiW ₁₂ O ₄₀ (3.9)	83	89	11
H ₃ PW ₁₂ O ₄₀ (3.9)	83	87	13
H ₄ GeW ₁₂ O ₄₀ (3.9)	66	95	5
H ₄ SiMo ₁₂ O ₄₀ (3.9)	15	96	4
H ₃ PMo ₁₂ O ₄₀ (3.9)	8.2	94	6
H ₄ GeMo ₁₂ O ₄₀ (3.9)	0.2	0	100
BF ₃ · Et ₂ O (20)	28	87	3
H ₂ SO ₄ (280)	0.0	-	-

^aTHF 12 mmol, Ac₂O 79 mmol, 50°C, 4 h. ^bDi(4-acetoxybutyl) ether. ^c1,4-diacetoxybutane.

Table 9. Oligomerization of Tetrahydrofuran with Acetic Anhydride^a.

Catalyst (10 ⁻⁴ M)	THF/Ac ₂ O mole ratio	Yield of oligomer/% ^b	Oligomer distribution/mol%					Molecular weight ^c
			n=1	n=2	n=3	n=4	n=5	
H ₃ PW ₁₂ O ₄₀ (1.8)	0.5	53	4.7	66.8	21.7	4.2	2.5	-
	1.0	55	3.7	53.7	22.3	6.2	1.8	-
	2.0	49	2.6	60.6	34.9	3.4	-	-
	9.0	43	-	-	-	-	-	ca. 800
BF ₃ ·Et ₂ O (49)	0.5	34	12.1	57.7	22.3	10.7	2.8	-
	1.0	15	9.7	40.9	28.7	13.1	7.5	-
	9.0	2.3	-	-	-	-	-	ca. 300

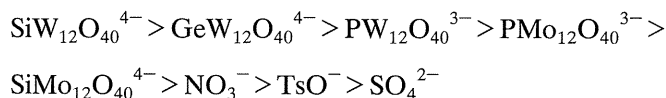
^a67°C, 4 h; oligomer: AcO(CH₂CH₂CH₂CH₂O)_nAc. ^bYield of oligomer based on THF used. ^cAverage molecular weight estimated from NMR measurement.

S_N1 mechanism, in which the transient intermediate butyl cation isomerized into *s*-butyl cation. An unsymmetrical acyclic ether, butyl methyl ether, could be similarly cleaved with acetic anhydride using HPA or BF₃·Et₂O, giving methyl acetate, butyl acetate, and *s*-butyl acetate. Heteropolymolybdc acids were less effective for these cleavage reactions of ethers with acetic anhydride because they were apt to deteriorate in the presence of acetic anhydride at higher temperatures.

It should be noted that H₄SiW₁₂O₄₀ and H₄GeW₁₂O₄₀ revealed exceptionally high activities in the cleavage of THF with acetic anhydride compared with H₄PW₁₂O₄₀, although the former two HPA were much lower than the latter with respect to acid strength. Heteropoly anion is a large cluster ion (ca. 1 nm diameter),⁶⁸⁾ and its surface charge density is very low.⁶⁹⁾ Such properties of heteropoly anion imply that it may be a soft base. This softness may explain the exceptionally high catalytic efficiency of H₄SiW₁₂O₄₀ and H₄GeW₁₂O₄₀. Table 10 summarizes the equilibrium constants (K) for the following reaction between water soluble silver salts of various anions (X) and sodium iodide measured in aqueous solutions at 25°C:



Since a soft anion is apt to interact favorably with soft silver cation(s), the smaller K values of Table 10 probably suggest increasing softness of the anions. The order of softness was therefore estimated to be as follows:



Assuming that a softer anion can stabilize and activate more effectively the oxocarbenium or acetyl cation as a transient reaction intermediate, it is easy to understand both the exceptional behavior of H₄SiW₁₂O₄₀ and H₄GeW₁₂O₄₀ and the very effective acid catalysis by HPA in comparison with other simple protonic acids.

Table 10. Equilibrium Constants for the Reactions between Silver Salts and NaI^a.

X ⁿ⁻ (10 ⁻³ M)	NaI/10 ⁻³ M	K
H ₄ SiW ₁₂ O ₄₀ ⁴⁻ (2.26)	9.04	0.001
H ₄ GeW ₁₂ O ₄₀ ⁴⁻ (2.26)	9.07	0.004
H ₄ PW ₁₂ O ₄₀ ³⁻ (3.00)	9.04	0.1
H ₃ PMo ₁₂ O ₄₀ ³⁻ (2.88)	8.97	3
H ₄ SiMo ₁₂ O ₄₀ ⁴⁻ (2.26)	9.03	4
NO ₃ ⁻ (8.98)	9.42	8
TsO ^{-b)} (9.12)	9.13	150
SO ₄ ²⁻ (4.50)	9.00	500

^a AgⁿX + nNaI → NaⁿX + nAgI, 25 °C.

*Transesterification*⁷⁰⁾: The exchange reactions of ester with alcohol and carboxylic acid (Eq. (11) and (12)) were catalyzed by HPA more effectively than by sulfuric acid and *p*-toluenesulfonic acid.

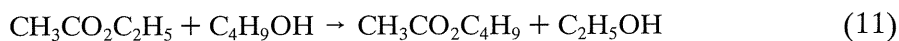


Table 11 summarizes the results of the ester exchange reactions. The activation energy of the alcohol exchange reaction by HPA (Eq. (11)) was 9.3 kcal/mol, which was about 4 kcal/mol lower than that by H₂SO₄. Dawson-type HPA⁷¹⁾ such as H₆P₂W₁₈O₆₂ and H₆P₂Mo₁₈O₆₂ was superior to the corresponding Keggin-type HPA in catalytic efficiency for transesterification. The higher activity of the Dawson-type HPA was due to its higher acid strength because in the reaction medium H₆P₂W₁₈O₆₂ changed Crystal Violet (a Hammett indicator, *p*K_a = +0.8) into its acidic color at a low molar concentration of 0.5 × 10⁻³ M, whereas the corresponding Keggin-type HPA of H₄PW₁₂O₄₀ did not even at 1.0 × 10⁻³ M. Like the Keggin-type HPA, the Dawson-type HPA maintained its original polyhedral structure in the course of the reaction, which was confirmed by examining IR spectra of H₆P₂W₁₈O₆₂ and H₆P₂Mo₁₈O₆₂.⁷²⁾ 1095 cm⁻¹ for P-O bond, 965 cm⁻¹ for W-O and Mo-O terminal bonds, 920 cm⁻¹ for W-O-W and Mo-O-Mo octahedral edge-sharing bonds, 800 cm⁻¹ for W-O-W and Mo-O-Mo octahedral corner-sharing bonds, and 850 cm⁻¹ for Mo-O-Mo octahedral corner-sharing bond.

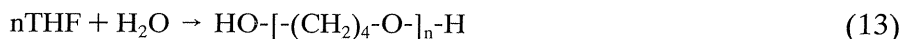
Polymerization of tetrahydrofuran: Tetrahydrofuran (THF) is polymerized giving polyoxytetramethylene glycol (PTMG). PTMG is chiefly used for the preparation of spandex fibers and thermoplastic elastomers (polyurethane), and is commercially prepared by a two-step process: (1) ring-opening polymerization of THF with FSO₃H catalyst or with acetic anhydride catalyzed by HClO₄, and (2) hydrolysis of the terminal functional groups (FSO₃- or CH₃CO₂-) of the intermediate polymers. Izumi and co-workers³⁸⁾ have found HPA was more active than HClO₄ as a catalyst for the polymerization of THF with acetic anhydride.

Table 11. Transesterification.

Catalyst	Alcohol exchange ^a		Acid exchange ^b	
	Catalyst	k ^c /10 ⁻⁵	Catalyst	k ^c /10 ⁻⁶
	concn./10 ⁻³ M	M ⁻¹ sec ⁻¹	concn./10 ⁻² M	M ⁻¹ sec ⁻¹
H ₃ PW ₁₂ O ₄₀	1.47	1.8	1.12	9.6
H ₄ SiW ₁₂ O ₄₀	1.63	1.7	1.29	11
H ₃ PMo ₁₂ O ₄₀	1.19	1.4	1.27	7.6
H ₄ SiMo ₁₂ O ₄₀	1.49	1.8	1.19	5.6
H ₂ SO ₄	12.5	0.38	14.6	0.43
<i>p</i> -TsOH ^d	9.5	0.23	2.52	0.32

^aAcOEt/n-BuOH=1, 49°C. ^bAcOEt/EtCO₂H=1, 71°C. ^cSecond-order rate constant per unit concentration of catalyst. ^d*p*-toluenesulfonic acid.

Aoshima and co-workers^{9,73)} extended such effective catalysis of HPA, and have developed a one-step process for the polymerization of THF directly to give PTMG.



3.2. Liquid-phase Heterogeneous Reactions

Since HPA is insoluble in non-polar solvents such as hydrocarbons, it is applicable as a solid acid catalyst in non-polar liquid media. In order to realize effective heterogeneous liquid-phase reactions, supported HPA, namely the HPA that is highly dispersed on a support with a large surface area, was the preferred catalyst. Acidic or neutral substances such as silica gel, diatomaceous earth, and active carbon were suitable as supports. As will be discussed in section 3.3., the liquid-phase reactions of polar reactants over solid HPA catalysts appeared to occur not only on the surface but also inside the HPA crystallites whether they existed as bulk or on a support. In order to facilitate the diffusion of the reactants throughout the pores of solid in liquid media, solid HPA catalysts whose particle sizes are less than 100 mesh should be employed.

Friedel-Crafts reactions with bulk and supported HPA: Several types of insoluble heterogeneous acid catalysts have recently been proposed for liquid-phase Friedel-Crafts reactions, to replace the conventional homogeneous catalysts such as AlCl₃ and sulfuric acid which often pose difficult operational problems of corrosion, catalyst removal from the product, and requirement of stoichiometric amount of catalyst. These heterogeneous catalyst systems include metal ion-exchanged aluminosilicates⁷⁵⁾ and sulfate-doped metal oxides.⁴⁵⁾ Regarding acylation with acyl halides, however, heterogeneous catalysts that can endure long-term use have not yet been developed.

Keggin-type HPA, which is known to catalyze several acid-catalyzed organic reactions much more effectively than the ordinary protonic acids, was also explored as an insoluble catalyst for liquid-phase Friedel-Crafts reactions in supported and non-supported states.⁴⁶⁾

Among various silica-supported HPA catalysts, $\text{H}_3\text{PW}_{12}\text{O}_{40}$ was the most active for the alkylation of benzene with 1-octene. Less than 5 mol % of a by-product dioctylbenzene was formed even at the complete conversion of alkene, provided that an excess of benzene was used at a low reaction temperature of 35°C. The isomers of 3- and 4-phenyloctanes were formed in addition to the major product of 2-phenyloctane (50–80 mol %). Fig. 7 demonstrates the remarkable effect of pretreatment temperature of catalyst on the catalytic activity of silica-supported $\text{H}_3\text{PW}_{12}\text{O}_{40}$. The maximum conversion of 1-octene was attained when the catalyst was treated at 150°C. Pretreatment at 100°C gives only meager activity. This is probably due to the remains of the crystal water of HPA which might reduce the acid strength of HPA. Indeed, according to measurement by Hammett indicators, a hydrous HPA of $\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 25\text{H}_2\text{O}$ showed acid strength of $\text{H}_0 > -3.0$, but it became more acidic ($\text{H}_0 > -8.2$) when dehydrated by calcination at above 150°C. Since it was confirmed by IR measurement that the Keggin structure of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ was completely retained even after treatment at 300°C, the reduction in catalytic activity of supported HPA calcined at 300°C was probably caused by a decrease in effective surface area of the deposited crystallites of HPA through aggregation. In this context, it was observed that the surface area of non-supported $\text{H}_3\text{PW}_{12}\text{O}_{40}$ was decreased on heating from 8.3 m²/g (150°C) to 4.2 m²/g (300°C), though the activity decreased more drastically (Fig. 7). A similar decrease in surface area on heating has already been pointed out by Misono and co-workers about non-supported $\text{H}_3\text{PMo}_{12}\text{O}_{40}$.^{25a)}

The catalytic activity of silica-supported HPA also depended greatly on the physical property of silica (Fig. 7). Lower dispersion of HPA on silica B, which had a relatively small surface area of 105 m²/g, brought about lower catalytic activity in comparison with high surface area silica A (585 m²/g). $\text{H}_3\text{PW}_{12}\text{O}_{40}$, even in non-supported state, reasonably catalyzed the reaction, but its efficiency could be enhanced markedly when supported on silica. The catalytic activity increased monotonically with the loading of HPA even beyond high levels of

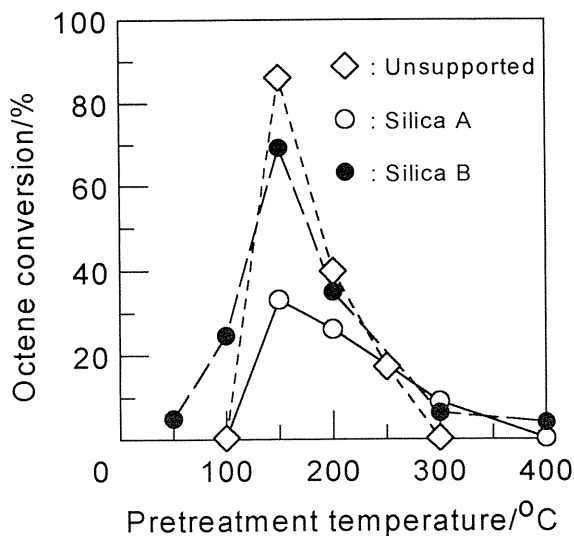


Fig. 7. Alkylation of benzene with 1-octene with $\text{H}_4\text{PW}_{12}\text{O}_{40}$ (30°C, 2 h), benzene 30 ml, 1-octene 3 mmol. Supported on silica A (15 wt%, 0.01 mmol), supported on silica B (15 wt%, 0.01 mmol), unsupported (0.03 mmol).

25 and 30 wt% over silica B and silica A supports, respectively, without any dissolution or deterioration of HPA. According to our study on the vapor-phase alkylation of benzene with ethene over a silica (319 m²/g)-supported H₃PW₁₂O₄₀ catalyst,³⁵⁾ a ceiling of activity increase was observed at a lower loading of 15–20 wt%. Since the vapor-phase alkylation proceeded exclusively on the outer surface of the supported HPA, a loading of more than 15 wt% did not bring about a substantial increase in activity because of crystal growth of supported HPA. Therefore, the activity increase beyond 25 wt% loading observed even with a smaller surface area silica B support (105 m²/g) in the liquid-phase alkylation reaction suggests that the reaction involves a 'bulk-type reaction', namely, the reaction occurred not only on the surface but also inside the bulk of the crystallites of HPA on the support.

In contrast to the case of alkylation with alkene, silica-supported H₃PMo₁₂O₄₀ catalyzed the alkylation of benzene with benzyl chloride most efficiently (Table 12). Neither dissolution nor deterioration of the supported heteropolyacid was observed during the reaction. Since the acid strength of H₃PMo₁₂O₄₀ is weaker than that of H₃PW₁₂O₄₀, higher catalytic efficiency of the former HPA in this alkylation reflects its stronger affinity to benzyl chloride compared with other HPA. *p*-Toluenesulfonic acid, a typical conventional protonic acid, was quite inactive for this reaction. It is therefore suggested that HPA exhibits a Lewis acid-like catalytic function through the stabilizing effect by heteropoly anion on the benzyl cation as a reaction intermediate, although HPA itself is really a protonic acid in nature.

The catalytic activity of supported H₃PMo₁₂O₄₀ for the benzylation of toluene was greatly affected by catalyst pretreatment. The maximum conversion appeared when the catalyst was preheated at 300°C, but deactivation of catalyst occurred at a higher pretreatment temperature above 300°C mainly because of decomposition of the HPA. The benzylation activity increased by increasing loading of HPA beyond 25 wt% on silica support without any dissolution or deterioration of HPA, indicating that benzylation also involved a bulk-type reaction. Other active alkyl halides such as bromocyclohexane could also be favorably applied as an alkylating agent in the presence of supported H₃PMo₁₂O₄₀ catalyst, but the catalyst was almost inactive for the alkylation reactions using primary alkyl chloride.

Silica-supported H₃PMo₁₂O₄₀ catalyst was active also for the acylation of *p*-xylene with benzoyl chloride, but the reaction proceeded further even after the catalyst was removed from the reaction medium. In addition, H₃PMo₁₂O₄₀ was found almost decomposed after the reaction. These results clearly indicate that the real active catalyst species was not the HPA on the support, but any other soluble species which might be formed by the reaction between

Table 12. Benzylation of Benzene with Silica-supported Acid Catalysts^a.

Acid	Benzyl chloride conversion/%
H ₃ PMo ₁₂ O ₄₀	72.2
H ₃ PW ₁₂ O ₄₀	27.2
H ₄ SiW ₁₂ O ₄₀	17.3
<i>p</i> -TsOH ^b	0.0

^a80°C, 2 h; support: silica B; acid: 0.02 mmol; acid loading: 15 wt%; pretreatment: 300°C, 3 h; benzene: 100 mmol, benzyl chloride: 5 mmol.

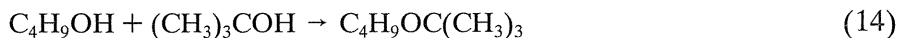
^b*p*-Toluenesulfonic acid.

HPA and benzoyl chloride. Yamaguchi and co-workers have also reported a similar possibility of deterioration of non-supported $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ employed as a catalyst in the liquid-phase acylation of chlorobenzene with *o*-chlorobenzoyl chloride.⁴⁴⁾

In contrast to $\text{H}_3\text{PMo}_{12}\text{O}_{40}$, $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ and $\text{H}_3\text{PW}_{12}\text{O}_{40}$ were both barely soluble and remain unchanged in the reaction medium of the acylation of *p*-xylene with benzoyl chloride, still holding their Keggin structures. Thus they proved to effectively catalyze the acylation as heterogeneous or insoluble catalysts, particularly when calcined at between 200–500°C. In these cases, the acylation reactions proceeded no further, if each solid catalyst was filtered off from the reaction medium. The benzoylation activity was enhanced by increasing loading of $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ beyond 30 wt% on silica support without any appreciable dissolution or deterioration of HPA, indicating that the benzoylation also involved a bulk-type reaction. In a polar reaction medium as met in the acylation of chlorobenzene, however, even silica-supported $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ gradually migrated and deteriorated in the course of the reaction, as was the case with supported $\text{H}_3\text{PMo}_{12}\text{O}_{40}$. Thus the silica-supported $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ appears to be effectively applicable as an insoluble acid catalyst for an acylation reaction in which a large excess of less polar aromatic hydrocarbon was applied, as exemplified by a reaction medium which consisted of benzene and benzoyl chloride in a molar ratio of between 10:1 and 3:1.

Benzoic anhydride was also favorably employed as an acylating agent over silica-supported $\text{H}_4\text{SiW}_{12}\text{O}_{40}$, but the acylation with benzoic acid does not proceed over this catalyst. *p*-Toluenesulfonic acid was quite inactive also for this acylation reaction. This fact again indicates the peculiar ability of heteropoly anion to stabilize the intermediate acyl cation.

Ether-forming reactions with carbon-supported HPA^{33c)}: Active carbon could tightly immobilize or entrap a certain amount of HPA, and carbon-supported HPA thus obtained catalyzed liquid-phase organic reactions in polar media, e.g. the intermolecular dehydration between butanol and *t*-butyl alcohol into butyl *t*-butyl ether (Eq. (14)).



The carbon-entrapped HPA was prepared by impregnating a carbon support of 0.4–0.7 mm particle size with a methanol solution of HPA, followed by removing methanol under evacuation at 40°C. The non-entrapped HPA could be removed by extracting with water or methanol. As shown in Fig. 8, the fraction of the HPA dissolved out of the carbon support changed with the initial HPA loading and with the kind of solvent served for extraction. The migration of HPA ceased after a certain period of extraction and the entrapped HPA with a maximum loading of 7.2–13.9 wt% was obtained. The maximum HPA loading varied moderately with the physical properties of carbon support, but chemical pretreatment of carbon had little influence on its entrapping ability. Diatomaceous earth and silica, which are often employed as supports for HPA in vapor-phase reactions, were both incapable of immobilizing HPA in polar liquid media because the HPA supported on them was almost completely removed by solvent extraction.

Table 13 demonstrates an application of the carbon-entrapped $\text{H}_4\text{PW}_{12}\text{O}_{40}$ catalyst to the reaction of Eq. (14). Under these reaction conditions, neither the homocondensation product (dibutyl ether) nor the intramolecular dehydration product (isobutene) was formed. When the reaction was repeated several times using the recovered catalyst by renewing the reactants, no leakage of HPA from the carbon support was observed, and the catalytic activity remained unchanged. Heteropoly molybdic acids such as $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ and $\text{H}_4\text{SiMo}_{12}\text{O}_{40}$ were inadequate to be trapped in carbon because these HPA were susceptible to reduction with carbon, resulting in decrease in acid strength. Misono and co-workers have recently

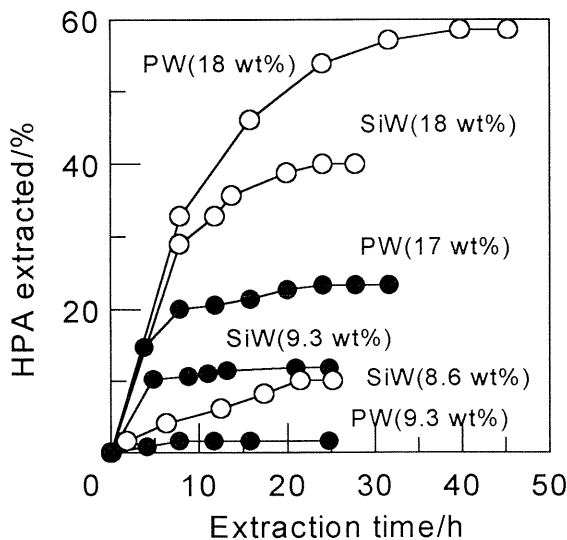


Fig. 8. Extraction of heteropoly acid supported on carbon with water (open circle) and methanol (filled circle). The values in parentheses denote the initial HPA loadings (wt%) before extraction.

Table 13. Dehydration between Butanol and *t*-Butyl Alcohol into Butyl *t*-Butyl Ether Catalyzed by Carbon-entrapped HPA^a.

Reaction repeated	<i>t</i> -BuOH conversion (%)			
	30min	60min	90min	120min
1	12	22	29	35
2	14	24	31	36
3	13	23	30	36
4	14	22	29	36

^aCarbon-entrapped $H_3PW_{12}O_{40}$ catalyst (0.58 g) with an HPA loading of 13.9 wt%, butanol 5 ml, *t*-butyl alcohol 2 ml, 106°C.

demonstrated that an insoluble acidic Cs salt, $H_{0.5}Cs_{2.5}PW_{12}O_{40}$, which has a large surface area of $136\text{ m}^2/\text{g}$, revealed good catalytic activity for the decomposition of cyclohexyl acetate at 100°C in liquid phase.⁷⁶⁾ Such insoluble acidic salts of HPA may be another effective solid acid catalyst candidate for heterogeneous liquid-phase reactions.⁸⁶⁻⁸⁷⁾

Esterification with carbon-supported HPA: HPA supported on active carbon worked as an insoluble solid acid catalyst also in liquid-phase esterification.⁷⁷⁾ The catalytic efficiency of $H_4PW_{12}O_{40}/C$ (particle size < 115 mesh path) was compared with a cation-exchange resin and *p*-toluenesulfonic acid for the reaction of acetic acid with butanol (Table 14). Non-polar

Table 14. Liquid-phase Esterification of Acetic Acid with Butanol Catalyzed by Carbon-entrapped HPA^a.

Catalyst	AcOBu yield/%	
	1.0 ^b	3.0 ^b
H ₄ PW ₁₂ O ₄₀ /C ^c	57	89
Amberlyst 15	92	-
<i>p</i> -TsOH ^d	91	-

^aAcid amount: 0.1 mmol, AcOH: 1 mmol, hexane: 5 ml, 60°C, 6 h. ^bBuOH/AcOH mole ratio. ^cActive carbon: Kuraray GC (1656 m²/g). ^d*p*-toluenesulfonic acid.

solvents such as hexane and benzene were used to minimize the leakage of HPA from carbon support. Since active carbon strongly adsorbs polar organic substances, a work-up procedure of extraction with an appropriate solvent such as methanol was necessary to recover the product completely from the catalyst. The catalytic activity of H₄PW₁₂O₄₀/C was not so high because the water that was formed by the reaction was adsorbed and remains inside the catalyst, lowering the acid strength of HPA and retarding ester formation. Carbon-supported HPA, which is heat-durable, may be applicable to esterification processes operated at relatively higher temperatures, where the product water can be continuously removed from the reactor.

3.3. Vapor-phase Heterogeneous Reactions

HPA has moderately high thermal stability. The Keggin-type H₄PW₁₂O₄₀, H₄SiW₁₂O₄₀, H₃PMo₁₂O₄₀, and H₄SiMo₁₂O₄₀ begin to decompose irreversibly at high temperatures of 610, 540, 495, and 375°C, respectively. HPA, usually on a support, could hence be employed as a solid acid catalyst in the vapor-phase reactions operated at relatively high temperatures. The features of acid catalysis by HPA in the solid state were deeply associated with its crystalline structure.

HPA crystal is formed by the secondary structure in which the Keggin anions as the primary structure are arranged with hydronium ions keeping the charge balance.¹⁸⁾ The water coordinating to the protons is zeolitic,^{1a)} so it is readily removable and can be re-absorbed even under ambient conditions. The crystal structure of HPA is flexible so that not only water molecules but also polar organic substances can be incorporated inside the crystal of HPA even in vapor phase at relatively high temperatures. Consequently the protons not only on the surface but also inside the bulk of HPA crystal are often responsible for catalyzing the reactions as in homogeneous liquid phase.¹²⁾ Such unique behavior in acid catalysis of HPA solid is never observed with ordinary mixed metal oxide catalysts that work only through surface acid sites.

According to an NMR study,⁷⁸⁾ the protons exist as hydronium ions in HPA crystal. It is also confirmed from an IR study⁷⁹⁾ that HPA crystal has only Brønsted acid sites. The acid strength of H₄PW₁₂O₄₀ is less than -8.2 in terms of H₀,¹¹⁾ and both H₄PW₁₂O₄₀ and H₄SiW₁₂O₄₀ in the solid states are more acidic than silica-alumina.²⁵⁾ No appreciable distribution of acid strength was observed with the H₄PW₁₂O₄₀ supported on diatomaceous earth at less than +1.5 in terms of H₀, beyond which weak solid acidity of the support itself begins to

appear.¹¹⁾ This fact implies that HPA has uniform acid sites in its crystal holding the molecular specificity of the Keggin unit, i.e. its protons are all equivalent.

The catalytic activity per unit acid amount in the vapor-phase dehydration of 2-propanol is a measure of acid strength for solid acids. The order of acid strength is estimated as follows based on the literature.⁸⁰⁾ The difference in acid strength between supported $\text{H}_4\text{PW}_{12}\text{O}_{40}$ and $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ is consistent with that observed in homogeneous liquid phase (section 3.1).



The reaction patterns over solid HPA are conveniently divided into the bulk-type and the surface-type reactions¹²⁾ depending on the affinity of reactant to HPA. The bulk-type reactions that often reflect the total acidity of bulk HPA include dehydration of 2-propanol, decomposition of carboxylic acid, synthesis of *t*-butyl methyl ether, and methanol conversion to gasoline. Since alcohol, carboxylic acid, and ether have strong affinity to HPA and can readily dissolve it, they are incorporated inside the HPA bulk or at least into the surface layers of HPA crystal even under vapor-phase reaction conditions. The bulk-type reactions are hence termed "pseudo-liquid phase" reactions as proposed by Misono and co-workers.⁸¹⁾ On the other hand, the alkylation of toluene, decomposition of cumene, and isomerization of 1-butene all proceed almost exclusively on the surface of HPA crystal because these hydrocarbon substrates have little affinity to HPA, and they cannot enter the HPA bulk. Such surface-type reactions therefore should be effected over supported HPA catalysts that are loaded with highly dispersed HPA microcrystals.

The water content of solid HPA often influences catalytic activity. According to ¹H-NMR measurements, the activities of the protons in HPA crystal change with the number of water molecule coordinating to each proton, and the maximum activity appears at 4–5 water molecules per unit Keggin structure.^{78a)} Indeed, the maximum conversion in the vapor-phase isomerization of 1-butene at 60°C over $\text{H}_4\text{PW}_{12}\text{O}_{40}$ is obtained when the HPA was dehydrated beforehand at 100–150°C.¹¹⁾

A part of the addenda atoms of the Keggin anion can be replaced by other kinds of elements forming a "mixed-coordinated" heteropoly anion. This mixed coordination was one of the important procedures in designing HPA catalysts with different acid properties. The effect of the mixed coordination is not so conspicuous in acid catalysis as demonstrated by a monotonous change in catalytic activity for the dehydration of 2-propanol over a mixed-coordinated HPA system of $\text{H}_4\text{PW}_{12-x}\text{Mo}_x\text{O}_{40}$.⁸⁰⁾ In redox catalysis, however, a remarkable synergistic effect by mixed coordination is manifested in the catalytic behavior of HPA.

*Friedel-Crafts alkylation reactions*³⁵⁾: The alkylation of benzene with ethene is a representative surface-type reaction in which the reactants have weak affinity for HPA because HPA is wholly insoluble in hydrocarbon substrates. The reaction was performed at less than 200°C because higher temperature increased coke formation. Most alkylation processes in actual use are usually conducted under a large excess of benzene to suppress the formation of polyalkylbenzenes, but here an example carried out intentionally under an excess of ethylene was demonstrated to compare the selectivity of monoalkylation by supported HPA with those by zeolite catalysts such as CaY and LaY (Table 15).

Supported heteropolytungstic acids catalyzed alkylation in vapor phase more effectively than typical solid acids such as silica-alumina and supported phosphoric acid, and their activity was almost comparable to cation-exchanged zeolites, which are known as highly active catalysts for the alkylation of benzene.⁸²⁾ Heteropolymolybdic acids such as $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ and $\text{H}_4\text{SiMo}_{12}\text{O}_{40}$, however, were quite inactive for this reaction. Silica gel was the most suitable

Table 15. Alkylation of Benzene with Ethene over Various Solid Acid^a.

Catalyst	Reaction temp./°C	Benzene conv./%	Selectivity/mole% ^b			
			EB	DEB	SBB	Others
H ₄ PW ₁₂ O ₄₀ /SiO ₂ (A) ^c	200	3.8	85	7	4	4
H ₄ SiW ₁₂ O ₄₀ /SiO ₂ (B) ^d	200	3.9	80	8	6	6
CaY	200	4.5	66	10	9	15
LaY	200	3.6	45	27	2	26
SiO ₂ -Al ₂ O ₃	250	0.6	100	-	-	-
H ₃ PO ₄ /SiO ₂ (A)	300	0.3	100	-	-	-

^aReaction conditions: 1 atm, C₆H₆/C₂H₄ = 0.5, GHSV = 380 h⁻¹. ^bEB: ethylbenzene, DEB: diethylbenzenes, SBB: sec-butylbenzene, others: triethylbenzenes, styrene, and cumene. Selectivity is based on the converted benzene. ^cHPA loading: 23 wt% on SiO₂ (319 m²/g). ^dHPA loading: 23 wt% on SiO₂(B) (363 m²/g).

among a variety of supports tested. In addition, supported heteropolytungstic acids exhibited higher selectivity for monoalkylation than zeolite catalysts. The product ethylbenzene probably underwent further ethylation more readily in the long channels of zeolite cavities than on the surface of the HPA crystallites supported on silica.

The alkylation activity was greatly affected by the loading of HPA on support. A ceiling of the catalytic activity was observed at a loading of about 15 and 20 wt% for the silica-supported H₄SiW₁₂O₄₀ and H₃PW₁₂O₄₀, respectively. Since the equilibrium conversion of benzene was nearly 100% at 200°C, the equilibrium limitation was not the cause of the activity leveling. According to the XRD analysis of the silica-supported HPA, no distinct diffraction peaks due to HPA crystallites were observed if HPA loading remains below 9 wt%, but when the loading exceeded about 20 wt%, broad diffraction peaks appeared at 2θ=10 and 8 degrees; this is characteristic of solid state H₃PW₁₂O₄₀ and H₄SiW₁₂O₄₀ crystals, respectively. On the other hand, a simple mechanical mixture of silica gel and each solid state HPA exhibited sharp diffraction lines even when HPA content was only 5 wt%. These results indicate that HPA, at a lower content, was very finely dispersed as micro-crystals on the surface of silica gel (monolayer coverage), but the crystallites grew larger with increase in HPA loading.

Fig. 9 shows the TPD (temperature programmed desorption) spectra of the ammonia adsorbed on supported HPA. With all HPA loadings, the desorption maximum of the strongly chemisorbed ammonia appeared at 480 and 460°C for H₃PW₁₂O₄₀ and H₄SiW₁₂O₄₀, respectively. Since the desorption temperature reflects acid strength, it was concluded that the acid strength of supported HPA did not vary with HPA loading. But the area of the ammonia desorption peak, which represents the total acidity of each HPA, increased monotonically with HPA loading, because, like pyridine,⁸³⁾ ammonia was readily absorbed through the interior of HPA crystallites to neutralize all the protons of HPA.

Considering the fact that the acid strength of HPA on silica gel remained constant independent of HPA loading, the activity ceiling observed in this alkylation of benzene before equilibrium limitation could be reasonably interpreted by the idea that the reaction proceeded principally on the surface of HPA crystallites, because the increase in the effective surface

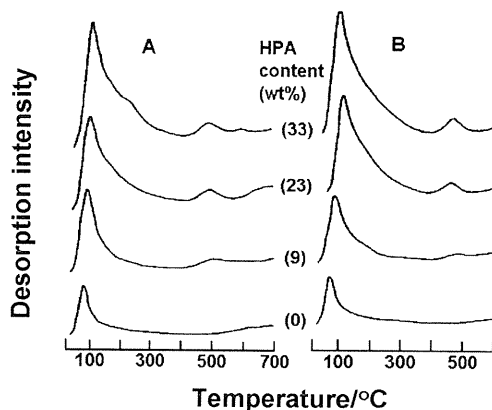


Fig. 9. Temperature programmed desorption spectra of ammonia on supported HPA. A: $\text{H}_4\text{PW}_{12}\text{O}_{40}/\text{SiO}_2$, B: $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{SiO}_2$. Each sample was treated at 500°C for 1 h prior to adsorption of ammonia.

protons of HPA with increasing HPA loading subsided through the growth of HPA crystallites. The critical HPA loadings from which the activity leveling corresponded well to those at which the X-ray diffraction peaks of large HPA crystallites became clearly discernible.

*Esterification*³⁵⁾: HPA is highly soluble in alcohol and moderately soluble in carboxylic acid and ester. Therefore, esterification may be designated as a model reaction of bulk-type reaction in vapor phase due to the strong affinity of the reactants to HPA. In contrast to the previous surface-type alkylation reaction, esterification is expected to proceed not only on the surface but also in the interior of supported HPA crystals; thus catalytic activity may increase with HPA loading. However, the leveling of catalytic activity was also observed with the increase in HPA loading in the vapor-phase esterification of acetic acid with ethanol at 150°C and at a short contact time. The HPA loading from which esterification activity began to level was somewhat higher (ca. 25–30 wt% for each of supported $\text{H}_4\text{PW}_{12}\text{O}_{40}$ and $\text{H}_4\text{SiW}_{12}\text{O}_{40}$), compared with the alkylation of benzene. It is suggested therefore that not only the surface protons but also a part of the interior protons of HPA bulk near the surface or in the surface layers took part in the reaction.

Table 16 lists the esterification activities of several supported HPA and unsupported neat HPA (an aggregate of large HPA crystals). No appreciable decline in activity was observed with any catalysts during a reaction period of 7 h. In the esterification, as well as in the alkylation, both supported and unsupported heteropolytungstic acids were more active than the corresponding heteropolymolybdic acids. The esterification activities of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalysts were examined on various supports. The HPA supported on silica gel and carbon was far more active than silica-alumina. Particularly, the HPA on a coconut-derived carbon revealed the highest activity and selectivity. The catalyst efficiency of the HPA on silica gel and carbon depended on both their surface areas and pore volumes. Preferable average pore size of support lay between 30 and 5 nm. Considering the large molecular size of HPA (ca. 1 nm), it is likely that HPA was highly dispersed on these supports. Alumina was not preferable as a support, because alumina readily decomposed HPA even if it was treated beforehand with aqueous HCl to remove alkaline impurities. Titania showed remarkable activity *per se*, but

Table 16. Esterification of Acetic Acid with Ethanol over Various Solid State HPA^a.

HPA catalyst	AcOH conversion/% ^b	Selectivity of converted EtOH/mol%		
		AcOEt	Et ₂ O	Alkenes ^c
Supported on SiO ₂ (A) ^d				
H ₄ PW ₁₂ O ₄₀	90.1	91	9	0
H ₄ SiW ₁₂ O ₄₀	96.2	88	12	0
H ₃ PMo ₁₂ O ₄₀	55.4	91	9	0
H ₄ SiMo ₁₂ O ₄₀	60.7	91	9	0
Unsupported ^e				
H ₄ PW ₁₂ O ₄₀	57.0	72	27	1
H ₄ SiW ₁₂ O ₄₀	60.7	69	30	1
H ₃ PMo ₁₂ O ₄₀	26.9	86	14	0
H ₄ SiMo ₁₂ O ₄₀	44.6	85	15	0

^aReaction conditions: 150°C, 1 atm, EtOH/AcOH = 2.5, W/F = 2.9 gs/ml. ^bAcetic acid was selectively converted to ethyl acetate.

^cA mixture of ethylene and butenes. ^dHPA loading = 5 wt%.

^eNeat HPA in the solid state.

produced considerable amounts of by-products (diethyl ether and alkenes). Accordingly, the catalytic effect inherent in HPA was not clear for titania support.

4. Acid Catalysis of Insoluble Acidic Salts of Heteropolyacid

Acidic Cs salt of 12-tungstophosphoric acid was found to work efficiently as an insoluble and readily recoverable solid acid catalyst for the alkylation of benzene and the acylation of *p*-xylene using benzyl chloride and benzoyl chloride, respectively, owing to its strong acidity and highly porous character.⁸⁵⁾

4.1. Preparation of Heteropolyacid Salts

Alkali metal salt and ammonium salt of heteropolyacid were prepared by adding dropwise a required amount of the corresponding aqueous alkali metal carbonate or ammonium carbonate (0.47 M) to aqueous heteropolyacid (0.75 M) at room temperature. Lithium and sodium salts were all water soluble with all the sorts of heteropoly anions employed, but the other metal salts were obtained as precipitates, except for some potassium salts of 12-tungstosilicic acid. The reaction mixture was aged for 20 h at room temperature, followed by evaporation, drying *in vacuo* (25 Torr) at 45°C, and finally calcination at 300°C for 3 h under a reduced pressure (25 Torr).

4.2. Acidic Alkali Metal Salt of Heteropolyacid

According to qualitative estimation by Hammett indicators, all the acidic alkali metal salts of 12-tungstophosphoric acid were strong solid acids having acid strength of less than -8.2 in terms of H_0 function. Fig. 10 illustrates the change in catalytic activity of the alkali metal salt ($M_xH_{3-x}PW_{12}O_{40}$) for the benzylation of benzene and the benzylation of *p*-xylene with the cation content denoted by x . The catalytic activity of Na salt decreased monotonously with increasing Na content for both the benzylation and the benzylation because of the decrease in acidity. For K, Rb, and Cs salts, however, the activity first decreased with increasing x between 0 and 2, then jumped to attain the maximum at $x=2.5$, except for the benzylation activity observed with K salt. Such a characteristic pattern of activity change with the cation content was first reported by Misono *et al.* concerning the dehydration of 2-propanol and the conversion of dimethyl ether in the vapor phase over Cs salt of 12-tungstophosphoric acid.⁸⁶⁾ The turnover numbers of the salt catalysts for the benzylation and the benzylation ranged from 100 to 320 mol.⁻¹

The change in surface area for alkali metal salt of $H_3PW_{12}O_{40}$ with the cation content x is shown in Fig. 11. As for Li and Na salts, their surface areas were as small as less than $10\text{ m}^2\text{ g}^{-1}$ with all values of x . It should be noted that on the whole surface area of alkali metal salt of $H_3PW_{12}O_{40}$ increases with the ionic radii of the metal cation. Sharp increase in surface area observed with K, Rb, and Cs salts beyond $x=2.0$ corresponds with the increase in catalytic activity depicted in Fig. 10. Such peculiar pattern of the activity change with the cation content x could be interpreted by the change in the surface acidity of catalyst which means the amount of the acid sites on catalyst surface, as Misono and Okuhara pointed out concerning the vapor-phase conversion of dimethyl ether⁸⁶⁾ and the liquid-phase decomposition of cyclohexyl acetate⁸⁷⁾ over Cs salt of $H_3PW_{12}O_{40}$. Indeed, the change in the relative surface acidity well reproduced the change in catalytic activity with the cation content, where the relative surface acidity was calculated as the product of the specific surface area and the bulk acidity of salt, assuming that the composition of salt was uniform throughout the surface and

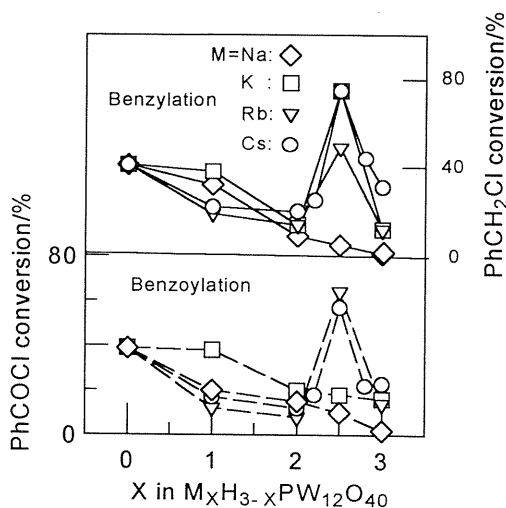


Fig. 10. Catalytic activity of 12-tungstophosphates for benzylation of benzene and benzylation of *p*-xylene. Benzene/ $PhCH_2C$ /catalyst=100/5/0.02 mmol, reflux 2 h; *p*-xylene/ $PhCOCl$ /catalyst=100/5/0.01 mmol, reflux 2 h.

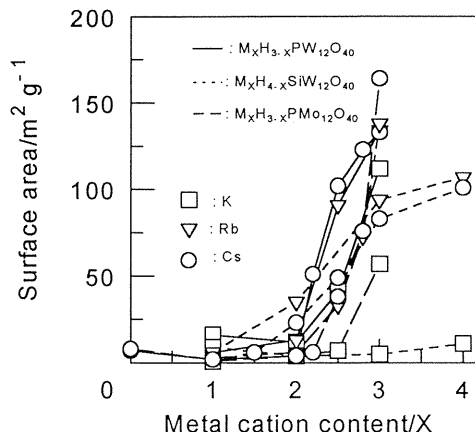


Fig. 11. Relative surface acidity of 12-tungstophosphates.

the bulk. The uniformity of the bulk composition for $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ has recently been shown by Okuhara *et al.* through NMR measurement.⁸⁸⁾

No dissolution of catalytically active species from the salt was observed in the course of the benzylation and the benzoylation, since both reactions ceased completely if the salt was removed from the reactor on the way of the reaction. It was confirmed by IR measurement that the Keggin structure of the salt was completely retained during the reaction showing no changes in the absorption bands characteristic of the Keggin structure (P-O: 1080 cm^{-1} , W=O: 985 cm^{-1} , W-O- W_{corner} : 887 cm^{-1} , W-O- W_{edge} : 807 cm^{-1}).

The pore size distribution of the most active salts ($\text{M}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$, M=K, Rb, and Cs) is illustrated in Fig. 12. Particularly, $\text{Rb}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ and $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ are highly porous materials with mesopores of 2–7 nm diameter in average. The surface areas of the salts were consistent with their mesopore structures, since their nitrogen adsorption isotherms were very close to BET type. The mesopore structure is probably formed by the arrangement of fine primary particles of salt crystallites. The SEM picture of $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ indicated that the salt consisted of fine particles of 10 nm diameter in average. The other salts with a cation content of less than 2 in terms of x in $\text{M}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$, as well as the parent acid (x=0), showed smaller surface area and smaller pore volume owing to large size of crystallites (20–200 nm). The efficient catalytic performance observed with $\text{Rb}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ and $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ is, therefore, deeply associated with their mesoporous structures being built of fine primary particles to afford large pore volume and large surface area.

In the DTA profile of $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$, a small exothermic change and a sharp endothermic peak were observed at around 600°C and 1013°C , respectively, in addition to a broad endothermic peak until around 200°C due to dehydration of crystalline water. The latter peak denotes melting of $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$.⁸⁹⁾ $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$ with an x value of more than 1.5 including neutral salt (x=3) showed almost the same melting point, and the Keggin structure was retained still after melting, whereas $\text{H}_3\text{PW}_{12}\text{O}_{40}$ and $\text{CsH}_2\text{PW}_{12}\text{O}_{40}$ decomposed at around 600°C showing a sharp exothermic DTA peak. The small exothermic peak of $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ at 600°C may be due to partial decomposition of the acid sites, since the catalytic activity drastically reduced when the salt was calcined at high temperatures beyond 500°C . $\text{K}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ and $\text{Rb}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ showed almost the same thermal durability as $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$; their melting points were 898 and 976°C , respectively.

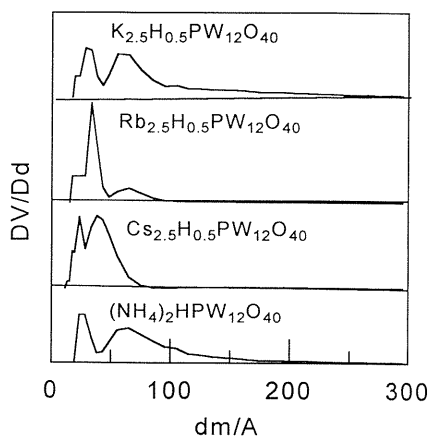


Fig. 12. Pore-size distribution of 12-tungstophosphates.

Li and Na salts of 12-tungstosilicic and 12-molybdophosphoric acids were all water soluble. K salt of 12-tungstosilicic acid ($K_xH_{4-x}SiW_{12}O_{40}$) became water soluble when x is less than 2. These water-soluble salts were catalytically inactive because of small surface area as less than $10\text{ m}^2\text{ g}^{-1}$. All of insoluble acidic salts were strong solid acids having acid strength of less than -8.2 in terms of H_0 function. In Fig. 2, the change in surface area with the cation content is depicted. Regarding the benzylation, the maximum activity was obtained at a cation content of $x=2$ for K and Cs salts of 12-tungstosilicic acid, and $x=2.8$ for Cs salt of 12-molybdophosphoric acid. Catalytically active $Cs_3HSiW_{12}O_{40}$ salt was a porous material with pore sizes between 2–5 nm and a pore volume of 0.33 ml g^{-1} . The salts of 12-tungstosilicic and 12-molybdophosphoric acids were less active for the benzylation than the corresponding salt of 12-tungstophosphoric acid. The salt of 12-molybdophosphoric acid, as well as the parent free acid, decomposed and completely dissolved in the reaction medium in the course of the benzylation reaction, in contrast to the salts of 12-tungstophosphoric and 12-tungstosilicic acids which remained insoluble holding the Keggin structure.

Among different kinds of insoluble acidic salt of the Keggin-type heteropolyacid, K, Rb, Cs, and ammonium salts were mesoporous materials with large surface area, strong acidity, and large pore volume. Particularly, $K_{2.5}H_{0.5}PW_{12}O_{40}$, $Rb_{2.5}H_{0.5}PW_{12}O_{40}$, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$, $Cs_{2.5}H_{0.5}PMo_{12}O_{40}$, $K_2H_2SiW_{12}O_{40}$, $Cs_2H_2SiW_{12}O_{40}$, and $(NH_4)_2HPW_{12}O_{40}$ worked as efficient solid acid catalysts for the liquid-phase Friedel-Crafts alkylation of benzene with benzyl chloride, and some of them could also effectively be applied to the acylation of *p*-xylene with benzoyl chloride or benzoic anhydride. The efficiency of some active salt catalysts for the benzylation and the benzoylation is summarized in Table 17, comparing with several representative solid acids reported to be effective for liquid-phase Friedel-Crafts alkylation reactions. The salt catalysts were much more active than HY, LaY and Nafion-H in terms of the activity per unit weight. The clay catalyst, Zn-promoted montmorillonite, showed high activity for the benzylation, but was less effective for the benzoylation than the salt catalysts because considerable deactivation occurred due to dissolution of the active metal components. Similar deactivation was observed also with LaY. The insoluble acidic heteropolyacid salts examined in this study appear to be applicable to several types of liquid-phase acid-catalyzed reactions in relatively polar organic media as efficient and environmentally friendly solid acid catalysts.

Table 17. Activity Comparison with Other Solid Acids.

Solid acid	Benzylaiton of benzene ^a	Benzoylation of <i>p</i> -xylene ^b
	PhCH ₂ Cl conv./%	PhCOCl conv./%
H ₃ PW ₁₂ O ₄₀	41	39
Cs _{2.5} H _{0.5} PW ₁₂ O ₄₀	75	57
Cs _{2.5} H _{0.5} PMo ₁₂ O ₄₀	93	-
Cs ₂ H ₂ SiW ₁₂ O ₄₀	99	12
(NH ₄) ₂ HPW ₁₂ O ₄₀ ^c	100	77
HY	36	9
LaY	50	9
Nafion-H	24	48
Zn-montmorillonite ^d	100	35 ^e

^aBenzene/benzyl chloride=100/5 mmol, catalyst 65 mg, reflux, 2 h. ^b*p*-Xylene/benzoyl chloride=100/5 mmol, catalyst 35 mg, reflux, 2 h. ^cCalcined at 450°C, catalyst 30 mg. ^dZn²⁺-ion exchanged montmorillonite. ^eCatalyst 140 mg.

4.3. Acidic Ammonium Salts of Heteropolyacid

The catalysis of neutral ammonium and alkylammonium salts of heteropolyacid have extensively been studied on methanol conversion to hydrocarbons,⁹⁰⁾ disproportionation of alkylbenzene,⁹¹⁾ and the conversion of dimethyl ether to alkenes⁹²⁾ in the vapor phase. There is, however, little information about the application of acidic ammonium salt of heteropolyacid to liquid-phase acid-catalyzed reactions.

Acidic ammonium salt was obtained either directly by adjusting the amount of ammonium carbonate to be reacted with heteropolyacid, or indirectly by managing the degree of decomposition of neutral ammonium salt prepared beforehand. As for (NH₄)₃PW₁₂O₄₀, the reduction in weight on heating followed two stages: the first weight loss occurred below 200°C was due to dehydration of crystalline water, and the second observed above 300°C was caused by the decomposition of ammonium ions to liberate ammonia. The decomposition of the Keggin structure took place at 600°C.

The acidic ammonium salt was an insoluble and porous material having a relatively large surface area and strong acidity ($H_0 < -8.2$). It was more active than the corresponding Cs and Rb salts for the benzylation, but less active for the benzoylation. In order to obtain active acidic ammonium salt having higher acidity and larger surface area, calcination at 450°C was most preferable and easily to manage. The change in catalytic activity for acidic ammonium salt with the time of calcination at 450°C was shown in Fig. 13. The most active acidic ammonium salt (NH₄)₂HPW₁₂O₄₀ was obtained after 2 hours' calcination of (NH₄)₃PW₁₂O₄₀. It was a porous material with a surface area of 63 m² g⁻¹ and a pore volume of 0.52 ml g⁻¹, and catalytically more active than the corresponding salt obtained directly. (NH₄)₂HPW₁₂O₄₀ did not deteriorate in the benzylation, but gradually reduced its activity in the benzoylation using benzoyl chloride owing to partial dissolution. The benzoylation of *p*-xylene with benzoic anhydride was efficiently catalyzed over (NH₄)₂HPW₁₂O₄₀ with no deactivation to give a conversion of 53% under the same reaction condition.

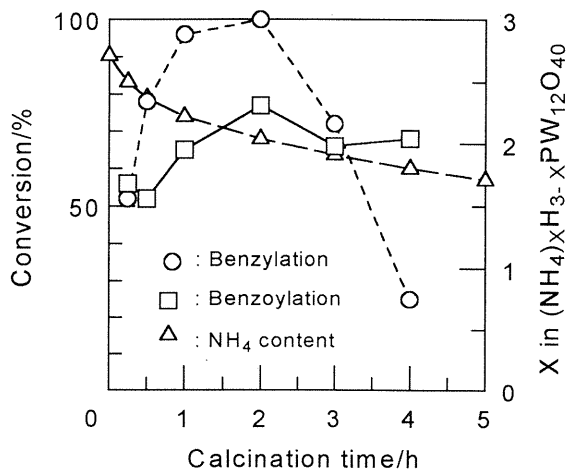


Fig. 13. Changes in catalytic activity and NH_4 content of ammonium 12-tungstophosphate during calcination at 450°C . Benzene/ PhCH_2Cl /catalyst=100/5/0.02 mmol, reflux 2 h; *p*-xylene/ PhCOCl /catalyst=00/5/0.01 mmol, reflux 2 h.

5. Immobilization of Heteropoly Compounds by Silica Inclusion

Insoluble acidic alkali metal salts of the Keggin-type heteropoly-acids, such as $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$, worked as efficient acid catalysts not only for Friedel-Crafts alkylation and acylation reactions, but also for esterification and hydrolysis in the liquid phase.^{93a)} $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ was much more active than H-ZSM-5 for the hydrolysis of ethyl acetate and the esterification of acetic acid with ethanol, since it showed higher acid strength ($H_0 > 0.8$) than H-ZSM-5 ($H_0 > 1.5$) in both water and alcohol. However unfortunately, $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ readily disperses in water or in alcohol forming a colloidal solution because it consists of very fine crystal particles (ca. 10 nm in average), consequently the salt becomes inseparable by means of simple filtration. We showed that the cesium salt could be transformed into a readily separable solid acid, a new type of mesoporous material, by including it into the silica network through a sol-gel technique which involved the hydrolysis of ethyl orthosilicate.^{93b)} Moreover, we found that even 12-tungstophosphoric acid itself, which is freely soluble in water, could also be entrapped effectively in silica matrix to be a water-insoluble and readily separable microporous solid acid catalyst.

5.1. Inclusion of Heteropoly Compounds with Silica

Silica-included heteropoly compounds were prepared through the hydrolysis of ethyl orthosilicate conducted at 40°C for 1 h and then 80°C for 3 h in the presence of $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ or $\text{H}_3\text{PW}_{12}\text{O}_{40}$ dispersed or dissolved in ethanol. The hydrogel obtained was dehydrated slowly at 45°C in vacuo (25 Torr), followed by grinding into 60 mesh-pass particles. In the case of salt inclusion, the dried gel was extracted with water at 80°C for 10 h to remove the non-trapped salt and organics, and finally calcined at 300°C for 3 h in vacuo (25 Torr). As for acid inclusion, the dried gel was once calcined at 150°C for 3 h in vacuo (25 Torr) to fasten the silica network, then extracted with water at 80°C for 3 h, and finally calcined at 150°C for 3 h in vacuo (25 Torr).

5.2. Silica-included Acidic Cesium Salt of 12-Tungstophosphoric Acid

The catalytic behavior of acidic cesium salt of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ was first examined through the hydrolysis of ethyl acetate with a small amount of water ($\text{AcOEt}/\text{H}_2\text{O}=3.88$ mole ratio) in order to avoid colloidal dispersion of the salt. Fig. 14 illustrates the changes in catalytic activity and surface area of the salt with the Cs content in terms of x in the formula of $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$. The hydrolysis activity decreased monotonously with increasing Cs content or decreasing acidity, whereas the surface area increased abruptly from less than 10 to $130\text{ m}^2\text{ g}^{-1}$ at above $x=2.0$. $\text{CsH}_2\text{PW}_{12}\text{O}_{40}$, as well as the parent free acid $\text{H}_3\text{PW}_{12}\text{O}_{40}$, dissolved during the hydrolysis reaction, and $\text{Cs}_2\text{HPW}_{12}\text{O}_{40}$ partly dissolved. $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$, however, remained as an insoluble solid without forming a colloidal solution. The activity was related directly to the bulk acidity of the salt. This catalytic behavior in the hydrolysis was quite different from that observed with the $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$ ($x=0$ to 3) catalyst in the liquid-phase Friedel-Crafts reactions whose catalytic efficiency was greatly dependent on surface area because the reactions proceeded exclusively on the surface owing to low polarity of the reaction media (Fig. 10). Other acidic salts of heteropolyacid such as $(\text{NH}_4)_2\text{HPW}_{12}\text{O}_{40}$, $\text{Cs}_2\text{H}_2\text{SiW}_{12}\text{O}_{40}$, and $\text{Cs}_{2.5}\text{H}_{0.5}\text{PMo}_{12}\text{O}_{40}$, which worked as efficient and insoluble solid acid catalysts for the liquid-phase Friedel-Crafts reactions, were unfavorable for the hydrolysis of ethyl acetate because they partly dissolved in the course of the reaction.

The salt of $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ consists of relatively uniform very fine crystal particles with ca. 10 nm diameter in average as described above. In the hydrolysis of ethyl acetate with a low concentration of water, the salt particles could be separated by filtration as large-size aggregates from the liquid medium. However, if applied to the hydrolysis under the commonly employed reaction condition using a large excess of water, i.e. in a highly polar reaction medium, the salt particles formed a colloidal solution, and so became inseparable. In order to make the salt recoverable from water, we tried to include the salt with silica matrix into a composite by means of a sol-gel technique which involved the hydrolysis of ethyl orthosilicate according to the preparative method described in the experimental section. The ratios of

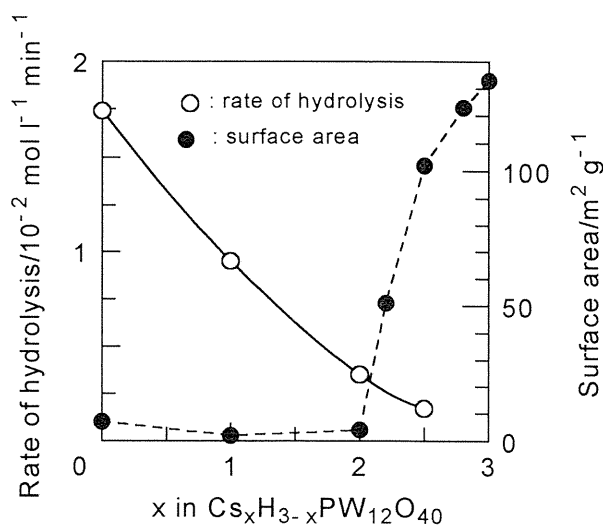


Fig. 14. Changes in catalytic activity of AcOEt hydrolysis and surface area with Cs content of $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$. AcOEt=9.5 g, $\text{H}_2\text{O}=0.5$ g, catalyst=0.1 mmol, 60°C .

$\text{SiO}_2/\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$, $\text{H}_2\text{O}/(\text{EtO})_4\text{Si}$, and $\text{EtOH}/(\text{EtO})_4\text{Si}$ were the most important criteria to effect better inclusion. Higher SiO_2 content brought about smaller leakage of the salt. Higher water content accelerated much the hydrolysis of $(\text{EtO})_4\text{Si}$ to cause more leakage of the salt, probably due to the formation of a rough silica network.⁹⁴⁾ Ethanol was necessary to make ethyl orthosilicate and water miscible each other. In the present preparative method for silica inclusion, the salt to be included promoted the hydrolysis of ethyl orthosilicate by its own acid catalysis. According to SEM measurement, in the silica-included $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ sample with a silica content of 1.2 in terms of the calculated weight ratio, the fine crystal particles of the salt appeared to be included in a silica matrix with the original morphology. The composite was a porous material with mesopores and a large surface area of $364 \text{ m}^2 \text{ g}^{-1}$.

Table 18 lists the catalytic efficiency of silica-included $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ for the hydrolysis of ethyl acetate with excess water; the activity of non-modified $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ is given for comparison. Silica itself was inactive for the hydrolysis. At a silica weight ratio of less than 1.2, considerable leakage of $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ as colloid from the silica composite was observed during the reaction, but the leakage could be effectively suppressed when the ratio was increased to 8. The silica composites were comparable with the non-modified salt in catalytic activity. They were less active than Amberlyst-15, and more active than H-ZSM-5 on the basis of the rate per unit catalyst weight. However the values of their turnover frequency were larger than those of Amberlyst-15 and H-ZSM-5. This means that the silica-included $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ shows higher acid strength in water than the resin and the zeolite. A

Table 18. Hydrolysis of Ethyl Acetate Catalyzed by Silica-included $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ ^a.

$\text{SiO}_2/\text{Cs}_{2.5}\text{PW}$ ^b	Surface area ($\text{m}^2 \text{ g}^{-1}$)	Catalytic activity		Leakage ^e (%)
		Rate ^c	TOF ^d	
0.0 ^f	105	2.80	17.9	-
1.2	598	3.06	17.7	>1
2.0	-	1.94	12.4	0.77
4.0	-	2.78	17.8	0.62
8.0	364	2.07	13.2	0.20
SiO_2 ^g	865	0.0	0.0	-
Amberlyst-15 ^h	-	4.9 ⁱ	3.9	-
H-ZSM-5 ⁱ	-	0.23 ^j	8.1	-

^a $\text{H}_2\text{O}=9.5 \text{ g}$, $\text{AcOEt}=0.5 \text{ g}$, catalyst=0.05 mmol on the basis of $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$, 60°C . Catalyst was prepared under the conditions of $\text{H}_2\text{O}/(\text{EtO})_4\text{Si}=5$, $\text{EtOH}/(\text{EtO})_4\text{Si}=1.3$ (mole ratio), and calcined at 300°C for 3 h. ^bWeight ratio of SiO_2 to $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ calculated from the amounts of reagents charged at the preparation. ^cFirst-order specific rate per unit weight of $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ ($10^{-3} \text{ min}^{-1} \text{ g}^{-1}$). ^dTurnover frequency (min^{-1}). ^eLeakage of $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ during the hydrolysis reaction (3 h), estimated by UV spectrometry. ^fNon-modified $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$. ^gPrepared by hydrolysis of $(\text{EtO})_4\text{Si}$. ^h160 mg, dried at 100°C . ⁱ160 mg, calcined at 300°C . ^jFirst-order specific rate per unit weight.

silica composite with a silica weight ratio of 8 was readily recoverable by simple filtration, and it could be reused for the hydrolysis reaction repeatedly (4 times) without deactivation. The composite was less stable than the salt itself, but it worked as a solid acid catalyst even after being treated at 450°C, although there was a gradual deactivation due to the reduction in surface area. IR spectroscopy indicated that the Keggin structure of $\text{PW}_{12}\text{O}_{40}^{3-}$ anion was retained completely in the composite until 450°C, showing its characteristic absorption bands. No IR absorption bands characteristic of $\text{SiW}_{12}\text{O}_{40}^{4-}$ anion were observed, which suggests that the exchange between P and Si in the Keggin anion did not occur in the course of the procedure for silica inclusion.

5.3. Silica-included 12-Tungstophosphoric Acid

In place of silica inclusion of $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$, we next tried to immobilize $\text{H}_3\text{PW}_{12}\text{O}_{40}$ itself into the silica matrix for the purpose of obtaining an insoluble and recoverable solid acid more readily. The method of immobilization was almost the same as for silica inclusion of the cesium salt, except for pre-calcination before extraction with hot water and the final calcination temperature. Compared with the salt inclusion, a higher weight ratio of silica to $\text{H}_3\text{PW}_{12}\text{O}_{40}$ was necessary to effect better inclusion, since $\text{H}_3\text{PW}_{12}\text{O}_{40}$ is freely soluble in water. As for the composites with silica to acid weight ratios of less than 5, considerable leakage of the acid was observed after the extraction with hot water, but the acid leakage could be somewhat reduced when the ratio was increased to 8. $\text{H}_3\text{PW}_{12}\text{O}_{40}$ included in silica formed relatively uniform crystallites with 10 nm diameter in average. Silica-included $\text{H}_3\text{PW}_{12}\text{O}_{40}$ was also a porous composite with mesopores and a large surface area of more than $500\text{ m}^2\text{ g}^{-1}$.

Table 19 summarizes the catalytic efficiency of silica-included $\text{H}_3\text{PW}_{12}\text{O}_{40}$ with different silica contents for the hydrolysis of ethyl acetate. As expected, the activity of silica-included

Table 19. Hydrolysis of Ethyl Acetate Catalyzed by Silica-included $\text{H}_3\text{PW}_{12}\text{O}_{40}$ ^a.

$\text{SiO}_2/\text{HPW}^b$	Surface area ($\text{m}^2\text{ g}^{-1}$)	Catalytic activity		Leakage ^e (%)
		Rate ^c	TOF ^d	
3.0 ^f	-	2.5	24	2.13
5.0 ^f	623	3.5	34	1.79
8.0 ^g	581	1.9	18	0.62
12 ^{g,h}	869	2.1	20	0.32

^a $\text{H}_2\text{O}=9.5\text{ g}$, $\text{AcOEt}=0.5\text{ g}$, catalyst=0.05 mmol on the basis of $\text{H}_3\text{PW}_{12}\text{O}_{40}$, 60°C. Catalyst was calcined at 150°C for 3 h prior to use. ^bWeight ratio of SiO_2 to $\text{H}_3\text{PW}_{12}\text{O}_{40}$ calculated from the amounts of reagents charged at the preparation. ^cFirst-order specific rate per unit weight of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ ($10^{-2}\text{ min}^{-1}\text{ g}^{-1}$). ^dTurnover frequency (min^{-1}). ^eLeakage of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ during the hydrolysis reaction (3 h), estimated by UV spectrometry. ^fCatalyst was prepared under the conditions of $\text{H}_2\text{O}/(\text{EtO})_4\text{Si}=3$ and $\text{EtOH}/(\text{EtO})_4\text{Si}=0.2$ (mole ratio). ^gCatalyst was prepared under the conditions of $\text{H}_2\text{O}/(\text{EtO})_4\text{Si}=5$ and $\text{EtOH}/(\text{EtO})_4\text{Si}=0.7$ (mole ratio). ^hRe-inclusion of a composite with a silica to acid weight ratio of 8.

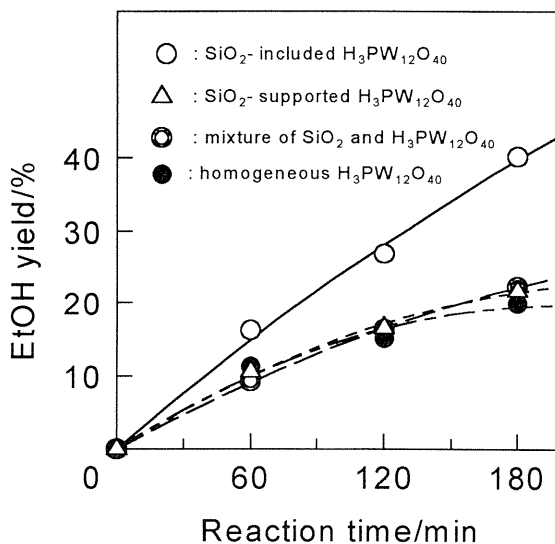


Fig. 15. Effect of silica inclusion on catalytic activity of H₃PW₁₂O₄₀. SiO₂/acid=8.0 wt ratio, net weight of the acid introduced=0.05 mmol, AcOEt=0.5 g, H₂O=9.5 g, 60°C.

H₃PW₁₂O₄₀ was much higher than silica-included Cs₂₅H_{0.5}PW₁₂O₄₀ on the basis of unit weight of composite, when compared at the same silica content. Leakage of H₃PW₁₂O₄₀ during the hydrolysis reaction could be suppressed as low as 0.3%, if the silica to acid weight ratio was increased to 12 by repeating silica inclusion for a composite having a silica weight ratio of 8.

Fig. 15 shows the hydrolysis activities of four different H₃PW₁₂O₄₀ catalyst systems; a silica-included H₃PW₁₂O₄₀ with a silica weight ratio of 8, silica-supported H₃PW₁₂O₄₀, a physical mixture of silica and H₃PW₁₂O₄₀, and homogeneous H₃PW₁₂O₄₀, where the net amount of H₃PW₁₂O₄₀ charged in the reactor was kept the same for all catalyst systems. The catalytic activities of the supported and the mixed systems were almost the same as for homogeneous acid, because all the H₃PW₁₂O₄₀ supported or mixed completely dissolved into the reaction medium. Interestingly, the catalytic activity of the silica-included acid was much higher than the homogeneous acid. Probably H₃PW₁₂O₄₀ was entrapped in the silica network as a highly concentrated aqueous solution: the silica network appeared to be narrow enough to prevent the Keggin anion (ca. 1 nm diameter) from migrating outside the silica network.

6. Summary

The acid catalysis of heteropolyacid and its acidic salts for various types of industrial organic reactions has been studied in the reaction systems of homogeneous liquid phase and heterogeneous liquid and vapor phases. Heteropolyacid was a very effective Brønsted acid catalyst for the reactions involving carbenium cations, oxonium ions, and oxocarocations: alkene hydration, ether cleavage reactions including ring opening reactions of epoxide, esterification, transesterification, and Friedel-Crafts alkylation and acylation reactions. At the same

proton concentrations and the same ionic strengths, the catalytic activity of heteropolyacid was 3 to 100 times higher than those of the ordinary protonic acids such as sulfuric, nitric, perchloric, and phosphoric acids at acid. The higher catalytic activity of heteropolyacid was elucidated by the unique ability of heteropoly anion to strongly stabilize the cationic intermediates to reduce activation energy. Heteropolyacid was effectively be applied as a protonic acid catalyst to several industrially important organic reactions both in the forms of a homogeneous solution catalyst and a heterogeneous supported catalyst. Acidic alkali metal salts of heteropolyacid could effectively be applied as insoluble and readily separable solid acid catalysts to the Friedel-Crafts reactions in highly polar organic solvents. Tungstophosphoric acid, as well as its acidic cesium salt, was immobilized in the silica matrix by means of sol-gel technique. Silica-included heteropoly compounds could be applicable to the hydrolysis of esters as water-insoluble solid acid catalysts.

Heteropolyacid and its acidic salts are catalytically highly active, less toxic, thermally much stable, so they can be expected as environmentally benign acid catalysts to be able to replace the conventional problematic acid catalysts such as sulfuric acid, aluminum chloride, and boron trifluoride.

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