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Catalysis by Heterogeneous Supported Heteropoly Acid

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Catalytic performance and availability of supported heteropoly acid under vapor-phase conditions were studied through alkylation of benzene with ethylene, esterification of acetic acid with ethanol, and dehydration of 2-propanol as model reactions. These reactions differ from each other in terms of the affinity of reaction substrate for heteropoly acid. Heteropolytungstic acid exhibited high catalytic activity and selectivity when it was loaded on silica gel or on activated carbon. In every reaction, there was observed a ceiling of catalytic activity at a certain content of heteropoly acid (ca. 15–25 wt%). The results of XRD and TPD measurements on supported heteropoly acid suggest that the reactions which are operated at more than 150°C proceed principally on the surface, or at most in the surface layers, of the heteropoly acid crystallites dispersed on support. Supported heteropoly acid appears to excel silica–alumina, supported phosphoric acid, and acidic zeolites in the catalytic capability particularly for those reactions which are carried out at relatively low temperatures (less than 200°C) or involve water as a reactant or a product.

I. INTRODUCTION

Acid catalysis of Keggin-type heteropoly acid has attracted much interest, since the heteropoly acid (hereafter abbreviated as HPA) possesses strong acidity to be applicable to several acid-catalyzed reactions in the liquid phase at moderate temperatures. The authors have reported that HPA catalyzes ether cleavage (*1*, *2*), transesterification (*3*), hydration of olefin (*4*) and acetylene (*5*), and methanol addition to isobutene (*6*) much more effectively than the ordinary protonic acids such as sulfuric and *p*-toluenesulfonic acids; and even more than boron trifluoride etherate. We have proposed that such high catalyst efficiency of HPA is essentially due to those specific properties of heteropoly anion which can be characterized by very weak basicity and great softness, in addition to a large molecular size of polyhedral heteropoly anion (*2*). It is, therefore, expected that HPA, when loaded on a suitable support, will work also as an active solid acid catalyst to be comparable to, or preferable to, the typical solid acids such as silica–alumina, supported phosphoric acid, and acidic zeolites. Indeed, there have been reported a number of vapor-phase reactions over supported HPA, such as olefin hydration (*7*), alcohol dehydration (*8*), decomposition of carboxylic acid (*9*), methanol addition to isobutene (*10*), and methanol conversion (*11*). We have recently pointed out that activated carbon is an excellent support to be able to fix HPA firmly on it, and thus entrapped HPA acts as a solid acid catalyst even in water or in organic solvents without any appreciable leaching (*12*).

However, little information has been known as to how supported HPA differs from, or excels, typical solid acids in catalyst performance and availability. In addition, it seems significant to know whether not only the surface but also the interior of supported HPA crystallites takes part in catalysis, because, in contrast to typical solid acids of metal oxides, HPA readily absorb those substances which have strong affinity for HPA, for example, ammonia, amine, and alcohol, throughout the bulk of its crystal structure.

This paper aims to characterize the heter-

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ogeneous acid catalysis by supported HPA in connection with the changes in dispersion state and acid property of HPA, through the examination of a couple of reactions which are different in terms of the affinity of reaction substrate for HPA. Such characterization will be useful also when we design a certain supported HPA catalyst for the purpose of improving a conventional homogeneous process in which a soluble acid catalyst has been employed.

II. EXPERIMENTAL METHODS

Catalysts

Every supported HPA was prepared by impregnating a support with aqueous HPA and drying at room temperature *in vacuo*.

Four kinds of heteropoly acid were used. 12-Tungstophosphoric ($H_3PW_{12}O_{40} \cdot 19H_2O$), 12-tungstosilicic ($H_4SiW_{12}O_{40} \cdot 26H_2O$), 12-molybdophosphoric ($H_3PMo_{12}O_{40} \cdot 26H_2O$), and 12-molybdosilicic ($H_4SiMo_{12}O_{40} \cdot 14H_2O$) acids were of commercially available purity.

The supports employed were silica gel, activated carbon, alumina, and titania. They were used as granules of 24–60 mesh. All silica gels were from Fuji Davison Chemical, and they are indicated in this study as SiO_2(A) (ID gel, surface area 319 m^2/g, pore volume 1.27 ml/g), SiO_2(B) (5D, 363 m^2/g, 1.00 ml/g), and SiO_2(C), (3A, 662 m^2/g, 0.51 ml/g). Four kinds of activated carbon were used: carbon(A), (Calgon F-300, 920 m^2/g, 0.47 ml/g), carbon(B) (Mistui SLF, 1090 m^2/g, 0.51 ml/g), carbon(C) (Kraray GC, 1656 m^2/g, 0.34 ml/g), and carbon(D) (Calgon PCB, ca. 1200 m^2/g). All carbon supports were treated beforehand with 1 *N* HNO_3 at 100°C for 2 h, then washed, and calcined at 480°C for 1 h under N_2 to remove HNO_3. Alumina (ALO-1, 160 m^2/g, 0.67 ml/g) and titania (TIO-1, 72.6 m^2/g) were the reference catalysts of the Catalysis Society of Japan (JRC) (*13*). The alumina was treated beforehand with 1 *N* HCl at 70°C for 3 h and washed with water sufficiently.

Ion-exchanged zeolites (CaY, LaY) were obtained by treating NaY with aqueous $CaCl_2$ or $La(NO_3)_3$, then washed, and calcined at 400°C for 2 h. Supported phosphoric acid was prepared according to the literature (*10*). Silica–alumina was a reference catalyst (JRC SAL-2, Al_2O_3 13.75%, 560 m^2/g). These three comparative solid acids were used as granules of 24–60 mesh.

Apparatus and Procedure

All reactions were carried out in an ordinary flow system under atmospheric pressure, using a 15-mm-i.d. Pyrex glass reactor with a fixed bed. The reaction temperature was measured by means of a thermocouple placed in the catalyst bed. The reactor effluent was cooled and trapped, and the gaseous products were collected in a gas holder.

Analysis

The liquid products were analyzed by glc using Benton 34 with DNP (a 3-m column) for the alkylation of benzene with ethylene, Porapak S (a 3-m column) for both the esterification of acetic acid with ethanol and the dehydration of 2-propanol. The gaseous products were qualitatively analyzed by glc, using Porapak Q (a 1-m column).

X-ray diffraction of supported HPA (powder) was performed by use of a Rigaku unit.

Temperature-programmed desorption spectra of ammonia on supported HPA were measured using a conventional TPD apparatus (*14*). A sample (43 mg) was preheated in a TPD cell at 500°C for 1 h in a stream of helium, exposed to ammonia at 25°C for 30 min at 1 atm, then the ammonia in the gas phase was purged with helium. TPD measurements were started from 25°C at a heating rate of 10°C/min using helium as a carrier gas (100 ml/min).

III. RESULTS

Alkylation of Benzene with Ethylene

This alkylation reaction represents a model reaction whose reactants have weak affinity for HPA, since HPA is wholly insoluble in hydrocarbon solvents. The reaction was performed at 200°C, because higher temperatures caused increasing coke formation. Most actual alkylation processes are usually operated under conditions of large excess of benzene to minimize the formation of polyalkylbenzenes, but the present experiments were done intentionally under an excess of ethylene in order to find out the selectivity of monoalkylation inherent in each catalyst.

Table 1 shows that supported heteropolytungstic acids can effectively catalyze the alkylation in the vapor phase. It is noted that heteropolymolybdic acids, such as $H_3PMo_{12}O_{40}$ and $H_4SiMo_{12}O_{40}$, were quite inactive for the alkylation. Silica gel was the most suitable among a variety of supports tested. The supported HPA was more active than the typical solid acids such as silica–alumina and supported phosphoric acid, and it was almost comparable to cation-exchanged zeolites which are known as highly active catalysts for the alkylation of benzene (*15*). In addition, the supported HPA exhibited higher selectivity for the monoalkylation than the zeolite catalysts. Probably the product ethylbenzene undergoes further ethylation more readily in the long channels of zeolite cavity than on the surface of the HPA crystallites supported on silica.

Figure 1 illustrates the effect of HPA content (i.e., supported amount of HPA) on the alkylation activity. This result is necessary to identify a critical amount of HPA which actually works on the support. A ceiling of the catalytic activity was observed at HPA contents of about 15 and 20 wt% for the supported $H_4SiW_{12}O_{40}$ and $H_3PW_{12}O_{40}$, respectively. Since the equilibrium conversion of benzene is nearly 100% at 200°C, the equilibrium limitation is not the cause of the activity leveling.

Esterification of Acetic Acid with Ethanol

HPA is highly soluble in alcohol and moderately soluble in carboxylic acid and ester. Therefore, esterification can be designated as a model reaction whose reaction substrates have good affinity for HPA even in the vapor phase. It is expected that, in contrast to the alkylation reaction, the esterification proceeds not only on the surface but also in the interior of supported HPA crystallites thereby increasing catalytic activity with HPA content. Such catalytic behavior working throughout the bulk of HPA has recently been reported about the dehydration of 2-propanol at 80°C over unsupported solid state HPA by Misono *et*

TABLE 1

Alkylation of Benzene with Ethylene over Various Solid Acids[a]

Catalyst	Reaction temp. (°C)	Benzene conversion (%)	Selectivity (%)[b]			
			EB	DEB	SBB	Others
$H_3PW_{12}O_{40}/SiO_2$(A)[c]	200	3.8	85	7	4	4
$H_4SiW_{12}O_{40}/SiO_2$(B)[c]	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_2O_3	250	0.6	100	—	—	—
H_3PO_4/SiO_2(A)	300	0.3	100	—	—	—

[a] Reaction conditions: 1 atm, $C_6H_6/C_2H_4 = 0.5$, GHSV = 380 h^{-1}.

[b] EB: ethylbenzene, DEB: diethylbenzene, SBB: *sec*-butylbenzene, others: triethylbenzenes, styrene, and cumene. Selectivity is based on the converted benzene.

[c] HPA content = 23 wt%.

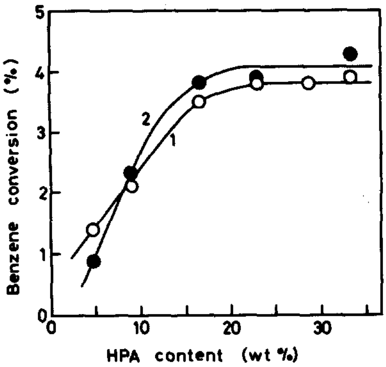

FIG. 1. Effect of HPA content in benzene alkylation. 1: $H_3PW_{12}O_{40}/SiO_2$ (A), 2: $H_4SiW_{12}O_{40}/SiO_2$ (A); reaction conditions: 200°C, 1 atm, $C_6H_6/C_2H_4 = 0.5$, GHSV $= 380\ h^{-1}$.

al., and this type of reaction is called "pseudo-liquid phase reaction" (*16*).

However, as shown in Fig. 2, there was observed a leveling of the activity with the increase in HPA content in the vapor-phase esterification of acetic acid with ethanol at 150°C. The observed maximum conversion of acetic acid was far below the equilibrium value, because much higher conversions (86–89%) were obtained at a longer contact time at the same reaction temperature. Table 2 lists the esterification activities of several supported HPA and unsupported neat HPA (an aggregate of large HPA crystallites). No appreciable decline in activity was observed with any catalysts during a reaction period of 7 h. In the esterification, as in the alkylation, both supported and unsupported heteropolytungstic acids were more active than the corresponding heteropolymolybdic acids. The amount of HPA in each supported catalyst used was only $\frac{1}{20}$ of the unsupported counterparts, but the activity of the supported HPA was much higher.

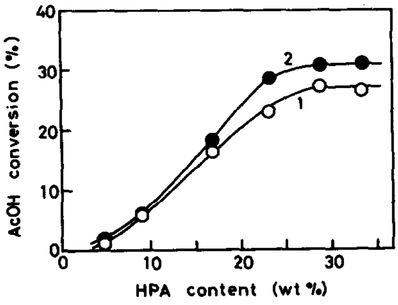

FIG. 2. Effect of HPA content in esterification of acetic acid. 1: $H_3PW_{12}O_{40}/SiO_2$ (A), 2: $H_4SiW_{12}O_{40}/SiO_2$ (A); reaction conditions: 150°C, 1 atm (N_2 0.3 atm, EtOH/AcOH = 1), $W/F = 2.2 \times 10^{-2}$ g s/ml.

The esterification activities of $H_3PW_{12}O_{40}$ loaded on various supports are shown in Table 3, together with the data of silica–alumina, a comparative solid acid catalyst. It should be noted that the HPA supported on silica gel or carbon was evidently far more efficient than silica–alumina. Particularly, the HPA on a coconut-derived carbon (carbon(C) and (D) in Table 3) revealed the highest activity and selectivity. The catalyst efficiency of the HPA on silica gel or carbon seems to relate to both surface area and pore volume of each support. Preferable average pore size of support is between 30 and 50 Å. Considering a large molecular size of HPA (ca. 10 Å), it is likely that HPA is highly dispersed on these supports. Alumina was not suitable as a support, because alumina readily decomposed HPA even if it was treated beforehand with aqueous HCl to remove alkaline impurities. Titania showed a remarkable activity *per se*, while producing a considerable amount of byproducts (diethyl ether and olefins). Accordingly, the catalytic effect inherent in HPA was not obvious in the case of titania support.

Dehydration of 2-Propanol

Figure 3 shows the change of catalytic activity with HPA content in the dehydration of 2-propanol affording propene at 150°C. Alcohol is the most intimate with HPA among many neutral organic substrates, but the dehydration activity leveled when HPA content exceeded about 25 wt% just as observed in the esterification reaction. In this dehydration, unsupported HPA was far less effective than supported HPA in terms of the activity per a unit amount of HPA.

TABLE 2

Esterification of Acetic Acid with Ethanol over Various Solid State HPA[a]

HPA catalyst	AcOH conversion (%)[b]	Selectivity (mol%) of converted EtOH		
		AcOEt	Et_2O	Olefins[c]
Supported on SiO_2(A)[d]				
$H_3PW_{12}O_{40}$	90.1	91	9	0
$H_4SiW_{12}O_{40}$	96.2	88	12	0
$H_3PMo_{12}O_{40}$	55.4	91	9	0
$H_4SiMo_{12}O_{40}$	60.7	91	9	0
Unsupported[e]				
$H_3PW_{12}O_{40}$	57.0	72	27	1
$H_4SiW_{12}O_{40}$	60.7	69	30	1
$H_3PMo_{12}O_{40}$	26.9	86	14	0
$H_4SiMo_{12}O_{40}$	44.6	85	15	0

[a] Reaction conditions: 150°C, 1 atm, EtOH/AcOH = 2.5, W/F = 2.9 g s/ml.

[b] Acetic acid was selectively converted to ethyl acetate.

[c] A mixture of ethylene and butenes.

[d] HPA content = 5 wt%.

[e] Neat HPA in the solid state was used.

Dispersion State and Acid Property of HPA on Silica Gel

Figure 4 illustrates the XRD patterns of silica-supported HPA. No distinct diffraction peaks were observed if HPA content remained below 9 wt%, but when the content exceeded about 20 wt%, broad diffraction peaks appeared at $2\theta = 10$ and 8°, which are characteristic to solid state $H_3PW_{12}O_{40}$ and $H_4SiW_{12}O_{40}$, respectively. On the other hand, as shown in Fig. 5, 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

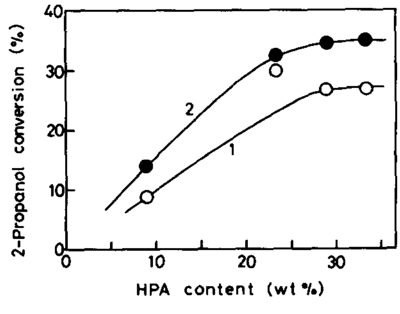

FIG. 3. Effect of HPA content in 2-propanol dehydration. 1: $H_3PW_{12}O_{40}/SiO_2$ (A), 2: $H_4SiW_{12}O_{40}/SiO_2$ (A); reaction conditions: 150°C, 1 atm (C_3H_7OH/N_2 = 1), W/F = 3.8×10^{-2} g s/ml.

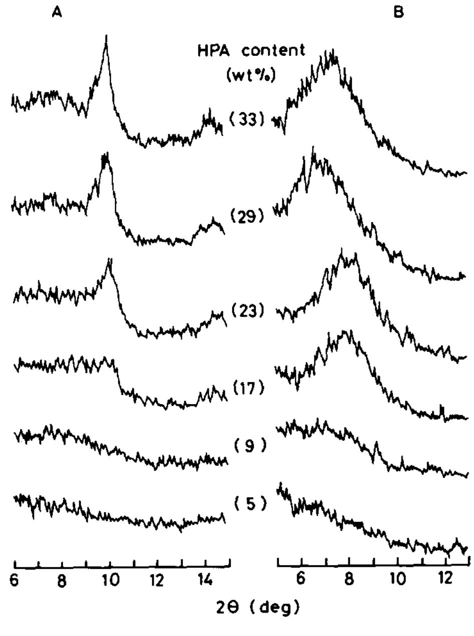

FIG. 4. X-ray diffraction of supported HPA. A: $H_3PW_{12}O_{40}/SiO_2$ (A), B: $H_4SiW_{12}O_{40}/SiO_2$ (A); supported $H_3PW_{12}O_{40}$ samples were treated at 60°C for 2 h before measurement (4×10^2 cps).

HPA, at a lower content, was very finely dispersed as small crystallites on the surface of silica gel, but the crystallites grew larger with the increase in HPA content.

Figure 6 shows the TPD spectra of ammonia on supported HPA. With all HPA contents, the desorption maximum of the strongly chemisorbed ammonia appeared at 480 and 460°C for $H_3PW_{12}O_{40}$ and $H_4SiW_{12}O_{40}$, respectively. Since the desorption temperature reflects acid strength, it can be said that the acid strength of each supported HPA does not vary with the HPA content. But the area of desorption peak, which represents the total acidity of each HPA, increased monotonously with the HPA content, because ammonia, as well as pyridine (*17*), was readily absorbed through the interior of HPA crystallites to neutralize all the protons of HPA.

TABLE 3

Esterification of Acetic Acid with Ethanol over Various Solid Acids[a]

Catalyst	AcOH conversion (%)[b]	Selectivity (mol%) of converted EtOH		
		AcOEt	Et_2O	Olefins[c]
Supported $H_3PW_{12}O_{40}$ on[d]				
SiO_2(A)	90.1	91	9	0
SiO_2(B)	86.2	91	6	3
SiO_2(C)	97.8	84	16	trace
Carbon(A)	46.3	98	trace	2
Carbon(B)	48.0	100	0	0
Carbon(C)	98.2	94	6	0
Carbon(D)	99.2	93	7	0
Al_2O_3	9.0	89	3	8
TiO_2	97.0	74	26	trace
Support only				
SiO_2(A)	4.5	89	0	11
Carbon(B)	30.8	100	0	0
Carbon(C)	37.7	100	0	0
Al_2O_3	17.1	93	4	3
TiO_2	95.1	86	10	4
Comparative solid acid				
SiO_2–Al_2O_3	24.3	99	trace	1

[a] Reaction conditions: 150°C, 1 atm, EtOH/AcOH = 2.5, W/F = 2.9 g s/ml.
[b] Acetic acid was selectively converted to ethyl acetate.
[c] A mixture of ethylene and butenes.
[d] HPA content = 5 wt%.

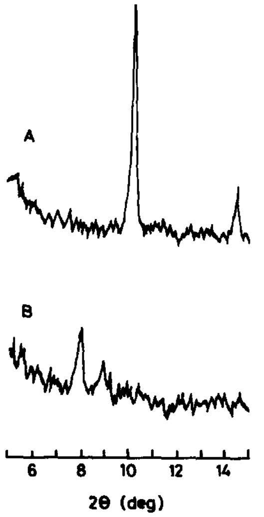

FIG. 5. X-ray diffraction of mechanical mixtures of HPA and silica gel. A: $H_3PW_{12}O_{40}$ + SiO_2 (A), B: $H_4SiW_{12}O_{40}$ + SiO_2 (A); HPA content = 5 wt%; the mixture of $H_3PW_{12}O_{40}$ and silica gel was treated at 60°C for 2 h before measurement (4 × 10^2 cps).

IV. DISCUSSION

Considering the fact that the acid strength of HPA on silica gel remains constant independent of HPA content, the activity ceiling observed in all test reactions under nonequilibrium conditions can be reasonably interpreted by an idea that every reaction proceeds principally on the surface of HPA crystallites, because the increase in the effective surface protons of HPA with increasing HPA content subsides through the growth of crystallite size. For example, the activity ceiling in the alkylation of benzene with ethylene becomes perceptible at HPA contents of about 15 and 20 wt% for supported $H_4SiW_{12}O_{40}$ and $H_3PW_{12}O_{40}$, respectively. These critical HPA contents correspond well to those at which the diffraction peaks of large HPA crystallites become clearly discernible (Fig. 4). The HPA contents from which esterification and dehydration activities begin to level are somewhat higher (ca. 25 wt%). It is suggested that, in these cases, not only the surface protons but also a part of the protons in the surface layers of HPA crys-

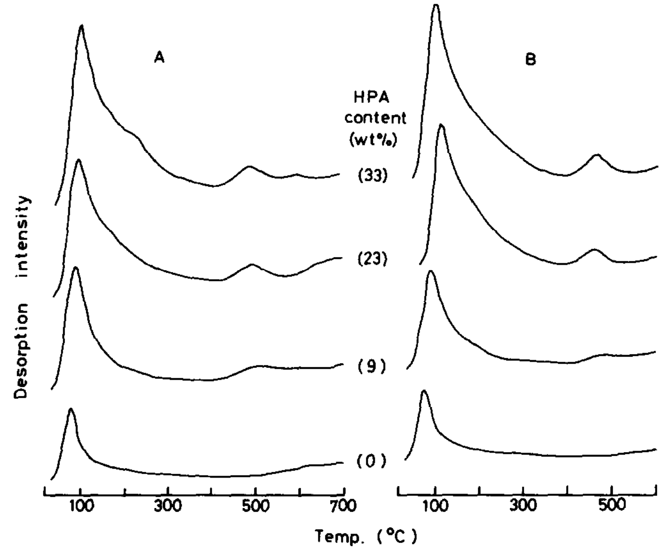

FIG. 6. TPD spectra of ammonia on supported HPA. A:$H_3PW_{12}O_{40}/SiO_2$(A), B:$H_4SiW_{12}O_{40}/SiO_2$(A); every sample was treated at 500°C for 1 h prior to adsorption of ammonia.

tallites take part in the reactions. In addition, the fact that at higher HPA contents the catalytic activities of supported HPA do not correlate with the total acidity of bulk HPA on support offers another basis to the interpretation that the present vapor-phase reactions are catalyzed mainly by the surface protons of HPA crystallites.

As for the catalysis by unsupported HPA (Table 2), it is also probable that only the surface or surface-layer protons of HPA crystal work under the present reaction conditions leading low catalyst efficiency. Alternatively, the low catalyst efficiency observed with both the unsupported HPA and the supported catalysts of higher HPA contents may be explained by assuming that the reactions proceed in the interior of HPA crystallites but the reaction rates are controlled by the diffusion of organic substrates through HPA bulk. Such diffusion control is, however, unlikely, because the activation energies of the esterification and the dehydration over the unsupported HPA ($H_3PW_{12}O_{40}$) were 18.1 and 28 kcal/mol, respectively, in a temperature range between 150 and 168°C; these values appear too large to be attributed to the diffusion control. It has been reported that the catalytic activity of the dehydration of 2-propanol at 80°C with unsupported solid state HPA correlates well with the total acidity of the bulk of HPA, and the reaction proceeds in the interior of HPA crystal (*16*). This result is inconsistent with the present experiments performed at a higher temperature of 150°C. This disagreement can be rationalized by thinking that at 80°C a considerable amount of water is still included in the interior of HPA crystal as a form of aquocations, and this water can feasibly exchange with 2-propanol, whereas at 150°C little water can exist in the bulk of HPA, so that the crystal structure of HPA becomes too rigid to accept 2-propanol within it. Indeed, hydrous HPA (i.e., $H_4SiW_{12}O_{40} \cdot 26H_2O$) is extraordinarily soluble in alcohol, but anhydrous HPA prepared by drying at more than 150°C becomes almost insoluble, namely alcohol molecules can hardly enter the interior of anhydrous HPA crystal.

It is, therefore, generally inferred that the reactions catalyzed by supported HPA, when operated at more than about 150°C in the vapor phase, proceed principally on the surface, or at most in the surface layers, of

HPA crystallites, unless the reaction substrates are as strongly basic as ammonia or amine.

The difference in catalytic activity observed with a variety of supported HPA can be elucidated with respect to acid strength. As for the esterification, for example, the desorption temperature of chemisorbed ammonia for each unsupported HPA, which is shown in Table 4, correlates well with the specific activity per unit proton of each supported HPA that was estimated from the AcOH conversion given in Table 3 taking account of molecular weight and acid equivalence of each HPA. Thus the order in catalytic activity of supported HPA is expressed as follows:

$H_3PW_{12}O_{40} > H_4SiW_{12}O_{40} > H_3PMo_{12}O_{40} > H_4SiMo_{12}O_{40}$. The acid strength of $H_3PMo_{12}O_{40}$ is, in essence, larger than that of $H_4SiW_{12}O_{40}$ as previously pointed out by the authors (*2*). The above order, however, is in reverse. Moreover as for the alkylation of benzene with ethylene, $H_3PMo_{12}O_{40}$ is almost inactive. Probably $H_3PMo_{12}O_{40}$ is more liable to undergo reduction with organic substrates or ammonia at high temperatures, and its acid strength decreases owing to the increase in basicity of the conjugate base, molybdophosphate anion. Indeed, after the alkylation reaction, the ir spectrum of $H_3PMo_{12}O_{40}$ on silica gel showed significant decreases in absorbance at 1060 (P–O) and 860 (Mo–O–Mo) cm^{-1}; these decreases in absorbance are characteristic to a reduced form of $H_3PMo_{12}O_{40}$ (*18*).

In conclusion, supported HPA, especially heteropolytungstic acid loaded on silica gel or activated carbon, works as an efficient solid acid catalyst. Supported HPA appears to excel ordinary solid acids in the capability of catalyzing those vapor-phase reactions which are operated at relatively low temperatures (less than 200°C) or involve water as a reactant or a product.

TABLE 4

TPD of Ammonia on Unsupported HPA[a]

HPA	$H_3PW_{12}O_{40}$	$H_4SiW_{12}O_{40}$	$H_3PMo_{12}O_{40}$	$H_4SiMo_{12}O_{40}$
Desorption temp. (°C)	592	532	463	423

[a] Every HPA was treated at 150°C for 1 h prior to adsorption of ammonia.

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