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Catalysis by Heteropoly Compounds. VI. The Role of the Bulk Acid Sites in Catalytic Reactions over $Na_xH_{3-x}PW_{12}O_{40}$[1]

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Several acid-catalyzed reactions were investigated over partial Na salts of 12-tungstophosphoric acid ($Na_xH_{3-x}PW_{12}O_{40}$). Thermal desorption of pyridine absorbed in the bulk combined with infrared measurement demonstrated that the Na salts were purely protonic acids and their "bulk" acidity (strength and amount) decreased as the Na content increased. On the basis of the absorptivity of reactants into the bulk of catalysts and the activity patterns for several acid-catalyzed reactions, it has been proposed that catalytic reactions are divided into "bulk-type" and "surface-type" reactions. In the case of the "bulk-type" reactions such as dehydration of 2-propanol or conversion of methanol to hydrocarbons, the reactants were readily absorbed in the bulk and the catalytic activities for these reactions were well correlated with the bulk acidity of the Na salts measured by the thermal desorption of pyridine. It was very probable that these reactions proceeded mainly in the bulk. On the other hand, reactions of hydrocarbons like butene and cumene, which were adsorbed only on the surface, take place only on the surface ("surface-type" reactions).

INTRODUCTION

The structures of 12-heteropoly compounds in the solid state are characterized by the Keggin structure (primary structure) (*1*) and the secondary structure (three-dimensional arrangement of Keggin anion, water, cation, etc.) (*2, 3*). In the Keggin anion of 12-tungstophosphoric acid ($H_3PW_{12}O_{40}$), tungsten atom is located at the center of an oxygen octahedron. The phosphorus atom is surrounded by 12 WO_6 octahedra forming a PO_4 tetrahedron by corner sharing. The crystal structure of hydrates like $H_3PW_{12}O_{40} \cdot 29H_2O$ and $H_3PW_{12}O_{40} \cdot 6H_2O$ has been well defined (*1, 4*). This well-definable structure is suitable for fundamental studies for modification or control of catalytic properties.

One of the purposes of the present investigation is to clarify how the acidity and catalytic activity can be controlled by the partial substitution of H^+ with Na^+. In the acid-catalyzed reactions over solid acid catalysts, the control of acidity (strength and amount) is important, because each reaction requires proper acidity to proceed selectively.

A second purpose is to demonstrate the important role of the catalyst bulk. We already reported that polar molecules like water and alcohols easily penetrate into and come out of the bulk, expanding and contracting the interstitial space between the Keggin anion, while nonpolar molecules like hydrocarbons do not (*3*). Due to this variable nature of the secondary structure, some reactions proceed in the bulk at the state which may be termed "pseudo-liquid phase" (*2, 5*). Therefore, in the present work, the bulk acidity as well as the absorption properties of reactant into the bulk was measured. The reactivity of alcohols ab-

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sorbed in the bulk was evaluated by thermal desorption. Several reactions of alcohols and hydrocarbons were examined and compared with the acidity and absorptivity.

EXPERIMENTAL

Catalysts. $H_3PW_{12}O_{40}$ was synthesized from Na_2WO_4 and Na_2HPO_4 according to the literature (*6*), as described previously (*3*). The partial sodium salts of $H_3PW_{12}O_{40}$ were prepared by use of Na_2CO_3. The aqueous solution of Na_2CO_3 was added dropwise to the aqueous solution of $H_3PW_{12}O_{40}$ (abbreviated as H_3PW_{12}) with vigorous stirring at 25°C. The resultant solution was concentrated by evaporation at about 50°C, and then dried in a KOH desiccator for 2 days. The sodium salts obtained will be denoted "formally" as $Na_xH_{3-x}PW_{12}O_{40}$ (abbreviated as $Na_xH_{3-x}PW_{12}$ when necessary) on the basis of the ratio of Na to polyanion. Cesium salt was prepared by the use of Cs_2CO_3 in the same manner as in the case of the sodium salts. The solution with the precipitate was evaporated to dryness at 50°C.

Water content and surface area. Water content was measured by use of a quartz spring balance (sensitivity: 14.4 mg/mm) installed in a vacuum system (*3*). About 0.8 g of catalyst placed in a quartz basket was evacuated at desired temperature. One molecule of water per anion corresponded to the variation of about 5 mg. The content was calculated from the weight loss, assuming the decomposition of $H_3PW_{12}O_{40} \cdot nH_2O$ to $\frac{1}{2}P_2O_5 + 12WO_3 + (n + \frac{3}{2})H_2O$ at 450°C. Surface area was determined by the BET method using nitrogen, after heating *in vacuo* at desired temperatures for 1 h.

Other measurements. Absorption and desorption of pyridine were followed by the quartz spring balance. The catalysts were exposed to pyridine (20 mm Hg) at 25°C for 2 h after the evacuation at 130°C for 1.5 h. Then they were evacuated for 1.5 h at each temperature. The catalysts which had been used for thermal desorption were pressed into KBr disks and infrared spectra were recorded with a Fourier transform infrared spectrometer (JEOL FTIR-10) at 25°C.

Absorption of ethanol was measured by following the pressure decrease in a static system having a volume of 180 ml. The catalyst was evacuated at 130°C for 1 h, and then ethanol (30 mm Hg) was introduced at 25°C. After the amount of ethanol absorbed became about 7 molecules/anion, the catalyst was evacuated at 25°C for 1 h. Thermal desorption of ethanol, in which temperature was raised stepwise, was carried out in the same system. Gases desorbed at each temperature were collected except for methane in a trap kept at liquid nitrogen temperature and analyzed with a gas chromatograph.

Catalytic reactions. A continuous flow reactor was used for dehydration of 2-propanol, decomposition of formic acid, and alkylation of toluene with methanol. The catalyst was placed in a glass tubular reactor (5.5 mm of inside diameter) and then treated at desired temperatures in flowing helium prior to reaction. The reactants were introduced into the helium stream by an evaporator–saturator set in a thermostat.

The isomerization of *cis*-2-butene and cracking of cumene were carried out by means of a pulse method. The reactants (0.2 ml of *cis*-2-butene as gas or 2 μl of cumene as liquid) were injected with a microsyringe into a helium stream at the inlet of reactor. Dehydration of ethanol and conversion of methanol to hydrocarbons were examined in a closed circulation system connected to a gas chromatograph. The methanol conversion was carried out at 285°C with the initial methanol pressure of 80 mm Hg after the catalyst was preevacuated for 1 h at the reaction temperature. The products were collected and analyzed after the reaction period of 100 min.

Products were analyzed with gas chromatographs. The columns used were Porapak Q for propylene, 2-propanol, CO, and formic acid. VZ-7 and Benton 34 columns were used for the analysis of butenes and aromatic hydrocarbons, respectively. Ethanol, diethyl ether, and ethylene were analyzed by a Porapak Q column. C_1–C_4 hydrocarbons formed by the conversion of methanol were analyzed by using molecular sieve 5 A, Porapak Q, and VZ-7 columns.

RESULTS

Characterization of bulk properties. The water content and surface area obtained in the present study are summarized in Table 1. The salts dried at room temperature contained 13–15 molecules of water per anion and the number of water molecules tended to decrease as the Na content increased. About one molecule of water remained after the evacuation at 130°C for all catalysts and the evacuation at 300°C removed almost completely the water of crystallization. The surface areas were almost independent of the pretreatment temperature from 100 to 300°C, and decreased monotonously with the Na content.

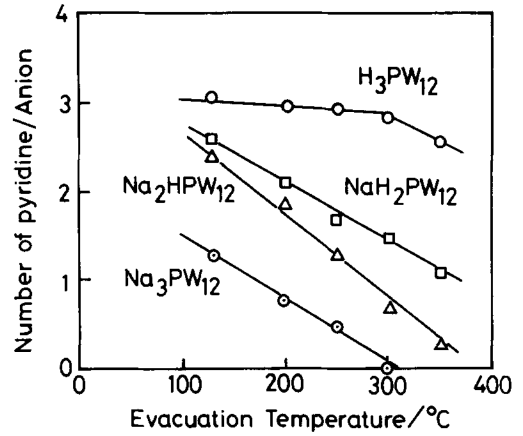


FIG. 1. Thermal desorption of pyridine from $H_3PW_{12}O_{40}$ and its Na salts. After pyridine was absorbed at 25°C, the samples were evacuated for 1.5 h at each temperature.

The acidity measured by thermal desorption of pyridine is shown in Fig. 1. The uptake of pyridine was 8–10 molecules per heteropoly anion at 25°C within 2 h. In the case of H_3PW_{12}, three molecules of pyridine were held after the evacuation at 130°C. The three pyridine molecules in H_3PW_{12} were strongly held even at 300°C, and prolonged evacuation for 2.5 h at the same temperature changes very little the number of pyridine. In the case of $Na_xH_{3-x}PW_{12}$, the number of pyridine molecules which remained at 130°C exceeded those expected from the formula, e.g., 1.2 molecules of pyridine were still held in Na_3PW_{12} as shown in Fig. 1. Nonetheless, the number tended to decrease with increasing Na content. It was further noted that pyridine was desorbed at lower temperature as the Na content increased. The number of pyridine molecules held after the 300°C evacuation was 1.5, 0.7, and 0 for NaH_2PW_{12}, Na_2HPW_{12}, and Na_3PW_{12}. This thermal behavior of pyridine may be considered to reflect the "bulk" acidity.

The infrared spectra of pyridine held in H_3PW_{12} and Na_3PW_{12} are shown in Fig. 2. The spectra of pyridine held in H_3PW_{12}

TABLE 1

Surface Area and Water Content of $Na_xH_{3-x}PW_{12}O_{40}$

Catalyst	Surface area (m²/g)			Water content (molecules/anion)	
	Evacuation temperature (°C)			Before treatment	After evacuated at 130°C
	100	200	300		
$H_3PW_{12}O_{40}$	4.8	5.2	5.3	21.5	1.0
$NaH_2PW_{12}O_{40}$	3.7	3.8	3.7	14.5	1.1
$Na_2HPW_{12}O_{40}$	2.3	2.6	2.8	13.5	1.2
$Na_3PW_{12}O_{40}$	0.6	1.0	0.8	13.0	1.1

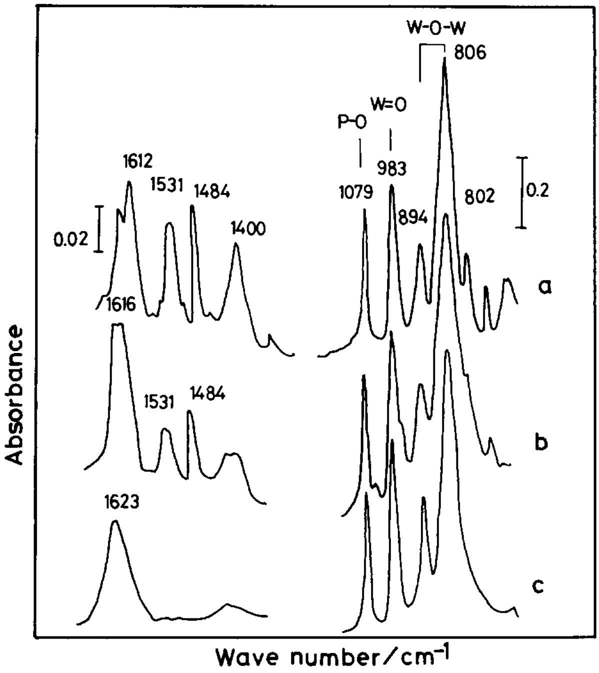


FIG. 2. Infrared spectra of pyridine held in (a) $H_3PW_{12}O_{40}$ after evacuation at 300°C, (b) $Na_3PW_{12}O_{40}$ after evacuation at 130°C, and (c) $Na_3PW_{12}O_{40}$ after evacuation at 300°C.

were essentially the same as that of the authentic pyridinium ion (*7*, *8*). The band at 1620 cm^{-1} observed in spectrum c is due to H_2O which was absorbed during the preparation of the KBr disk. Significant portion of the band at 1616 cm^{-1} in spectrum b is also due to absorbed water. When infrared spectra of ammonia absorbed in $Na_xH_{3-x}PW_{12}$ were taken in an *in situ* cell, only a band at about 1415 cm^{-1} (NH_4^+) appeared. These results show that these catalysts are purely protonic acids. As for the characteristic band of pyridinium ion, the intensity of the band observed over Na_3PW_{12} after evacuated at 130°C was about one-third that over H_3PW_{12}, which was consistent with the result of the thermal desorption (Fig. 1). The band due to pyridinium ion on Na_3PW_{12} disappeared completely after the evacuation at 300°C. The spectra of all the Na salts in the region of 800–1100 cm^{-1} were identical to that of H_3PW_{12}, indicating that the Keggin structure was mostly retained after the formation of Na salts and thermal desorption up to 300°C.

As for the adsorption or absorption of molecules, hydrocarbons like ethylene and benzene were adsorbed only on the surface of H_3PW_{12} (*3*) and $Na_xH_{3-x}PW_{12}$. The amount of ethylene which was irreversible held was less than 0.03 molecules of ethylene per anion for all the catalysts at 25°C. On the other hand, alcohols such as methanol, ethanol, and propanol were readily absorbed in the bulk of $Na_xH_{3-x}PW_{12}$ at 25°C. The amounts of ethanol absorbed at 30 mm Hg within 10 min were 8, 7.5, 6, and 3.5 per anion for $Na_xH_{3-x}PW_{12}O_{40}$ (x = 0, 1, 2, and 3: preevacuated at 130°C).

Figure 3 shows the desorption products in the stepwise thermal desorption of ethanol. Desorption as ethanol from H_3PW_{12} was observed below 100°C as shown in Fig. 3A. The evolution as ethylene started above 75°C, and the amount of desorbed ethylene reached maximum at 75–100°C. Above 150°C, ethane, propane, and methane were mainly detected in the desorbed gases (*9*). Over the sodium salts, desorbed gases were mostly ethylene and ethanol. As shown in Fig. 3B, peak of ethylene desorp-

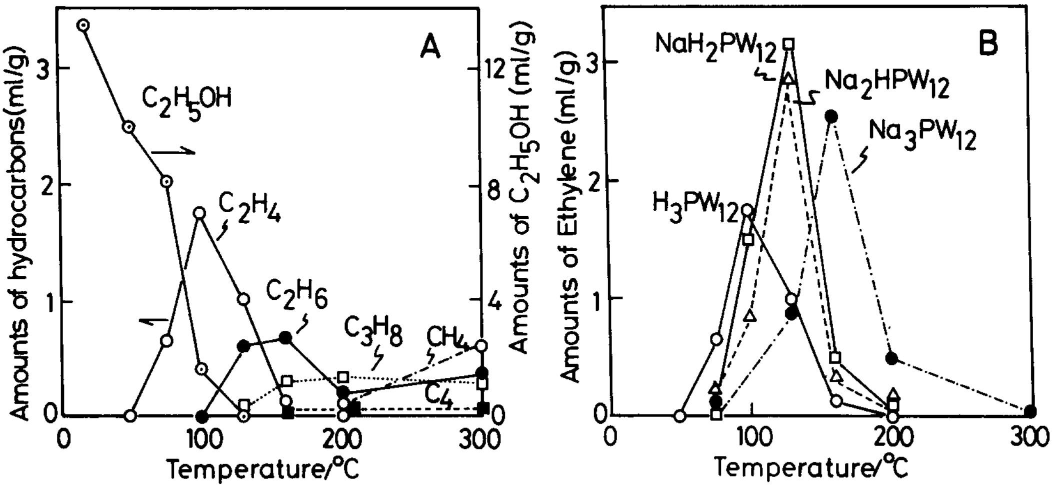


FIG. 3. Thermal desorption of ethanol absorbed in the bulk. (A) Variation of products as a function of temperature over $H_3PW_{12}O_{40}$. (B) Ethylene formation as a function of temperature over $Na_xH_{3-x}PW_{12}O_{40}$.

tion shifted to higher temperatures as the Na content increased, that is, 100–130°C for NaH_2PW_{12} and Na_2HPW_{12}, and 130–160°C for Na_3PW_{12}. Diethyl ether was not detected for all the catalysts upon thermal desorption of ethanol.

Catalytic reactions. The dehydration of 2-propanol and the decomposition of formic acid proceeded without deactivation over all the catalyst producing only propylene and water from 2-propanol, and only CO and water from formic acid, respectively. In addition, the rates were almost independent of the pretreatment temperature in the range from 100 to 300°C over H_3PW_{12}. As shown in Fig. 4, the catalytic activities for these reactions decreased monotonously as the Na content of the salts increased.

The results of the methanol conversion to hydrocarbons are given in Table 2. The main products were C_1 through C_4 hydrocarbons over these catalysts. Ono *et al.* reported similar products over the salts of Cu and Ag (*10*). The rate of the formation of C_1 through C_4 hydrocarbons also decreased monotonously with the Na content. The distribution of product hydrocarbons varied little with the Na content of the salts, suggesting the same reaction pathway. This is

TABLE 2

Conversion of Methanol to Hydrocarbons over Sodium Salts at 285°C

Catalyst	Rate[a] (ml (STP)/g h)	Product distribution (%)[b]							
		C_1	C_2	$C_2^=$	C_3	$C_3^=$	i-C_4	n-C_4	$C_4^=$
$H_3PW_{12}O_{40}$	19.2	14.5	1.0	11.3	14.1	17.4	23.4	4.6	13.7
$NaH_2PW_{12}O_{40}$	16.6	15.5	1.0	11.0	15.3	17.1	21.3	5.5	13.3
$Na_2HPW_{12}O_{40}$	4.5	20.9	1.1	10.9	14.0	18.1	17.5	4.4	13.1
$Na_3PW_{12}O_{40}$	2.2	16.3	tr	9.0	15.2	16.9	25.8	5.6	11.2

[a] The rate was calculated from the amount of methanol consumed to hydrocarbons in the gas phase.
[b] The product distribution was calculated based on carbon: C_n, paraffin; $C_n^=$, olefin.

in contrast to the same reaction over organic salts (*11*).

Figure 4 shows the relationships between the activity for these reactions and the acidity of the bulk estimated from the number of pyridine molecules which remained after the evacuation at 300°C. Good correlations were found between the rates and the bulk acidity. The variation in the catalytic activity for the isomerization of *cis*-2-butene as a function of the Na content is shown in Fig. 5. Decrease in the conversion with the pulse number was small in this reaction. In contrast to the reactions given in Fig. 4, the activity patterns for the butene isomerization greatly changed depending on the pretreatment temperature and were not monotonous: $H_3PW_{12} > Na_2HPW_{12} \gtrsim NaH_2PW_{12} \gg Na_3PW_{12}$ after treatment at 150°C, and $Na_2HPW_{12} > Na_3PW_{12} \gtrsim NaH_2PW_{12} \gtrsim H_3PW_{12}$ after treatment at 300°C. It was noted that the activity itself changed significantly by the pretreatment temperature; the activity of H_3PW_{12} measured at 50°C increased by a factor of 7 as the pretreatment temperature was reduced from 300 to 50°C.

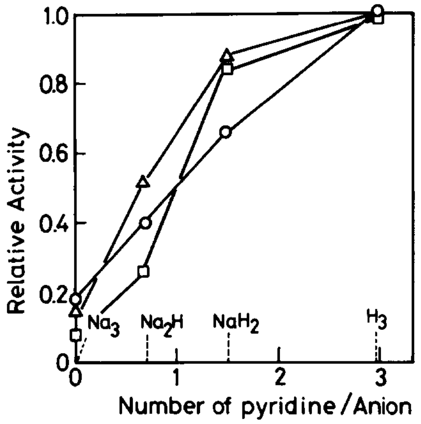


FIG. 4. Relationships between catalytic activity and bulk acidity. (○) Dehydration of 2-propanol (0.1 g, 100°C, 2-propanol: 4%, total flow rate: 200 ml/min). The conversion was 9.5% over $H_3PW_{12}O_{40}$. (△) Decomposition of formic acid (0.2 g, 150°C, formic acid: 5.4%, total flow rate: 100 ml/min). The conversion was 54.6% over $H_3PW_{12}O_{40}$. (□) Conversion of methanol to hydrocarbons (0.25 g, 285°C). The abscissa represents the number of pyridine which were not desorbed by evacuation at 300°C.

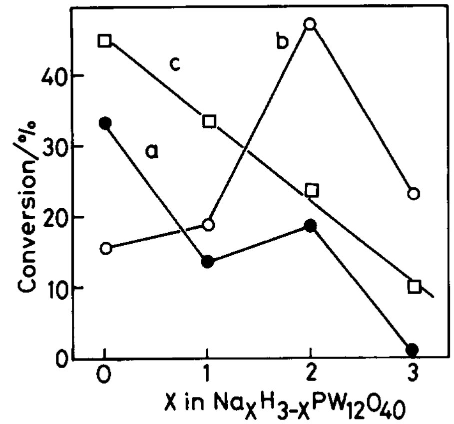


FIG. 5. Activity pattern for the isomerization of *cis*-2-butene. The reaction was carried out at: (a) 25°C after treatment at 150°C, (b) 50°C after treatment at 300°C, (c) at 100°C in the presence of water (3.2%) after treatment at 300°C.

It is remarkable that when the reaction was carried out in flowing helium containing H_2O (3.2%) at 100°C, the activity decreased linearly with the content of Na in a similar manner as in Fig. 4.

Table 3 shows the results of dealkylation of cumene and alkylation of toluene. The conversion of the cumene cracking (based on benzene) greatly decreased with the pulse number. About 10% of cumene injected remained on the catalysts for each pulse and the ratio of propylene to benzene in the product was 0.5–0.6. The deactivation tended to decrease as x in $Na_xH_{3-x}PW_{12}$ increased. Irregular activity pattern was found also for this reaction: $Na_3PW_{12} > H_3PW_{12} > Na_2HPW_{12} > NaH_2PW_{12}$. In the case of alkylation of toluene, the catalytic activity based on toluene conversion was almost the same among the catalysts at the initial stage (1 h), but the activity decreased greatly with the reaction time, and Na_3PW_{12} became most active at a later stage because of its smaller deactivation. The selectivity was almost independent of the Na content, *o*-xylene being the main product.

The variation of the gas phase composition and the amount of ethanol absorbed were measured during the course of the de-

TABLE 3

Cracking of Cumene and Alkylation of Toluene with Methanol over $Na_xH_{3-x}PW_{12}O_{40}$

Catalyst	Cracking of cumene[a]			Alkylation of toluene[b]				
	Conversion (%) Pulse number			Conversion (%) Time (h)		Selectivity (%)[c]		
	1	2	3	0–1	1–2	*p*	*m*	*o*
$H_3PW_{12}O_{40}$	14.5	3.9	2.3	3.6	0.7	29.6	24.0	46.2
$NaH_2PW_{12}O_{40}$	0.5	0.2	0.1	3.3	0.9	31.0	26.5	42.5
$Na_2HPW_{12}O_{40}$	6.3	2.9	1.9	3.2	0.3	39.4	3.0	57.6
$Na_3PW_{12}O_{40}$	16.5	10.5	7.5	3.4	1.5	25.2	17.8	57.0

[a] The reaction was carried out at 250°C after the catalysts (0.2 g) were pretreated at 300°C for 1 h (pulse size: 2 μl, flow rate: 30 ml/min).

[b] The reaction was carried out at 300°C after the catalyst (0.5 g) was pretreated at 300°C for 1 h (toluene: 2.8%, methanol: 8.4%, total flow rate: 50 ml/min).

[c] In the product at the later stage of reaction (1–2 h); *p*: *p*ara-xylene, *m*: *meta*-xylene, *o*: *ortho*-xylene.

hydration of ethanol over H_3PW_{12}. Results are shown in Fig. 6. Rapid absorption corresponding to about one molecule of ethanol per anion was observed at the beginning of the reaction (dotted line in Fig. 6). The amount of ethanol absorbed corresponds to about 10 surface layers, if one assumes that the surface area of H_3PW_{12} is 5 m^2/g and the cross section of ethanol is 26 Å^2, which is estimated from the density of liquid ethanol. When the pressure of ethanol was increased abruptly (broken line A in Fig. 6), the rate of diethyl ether formation was accelerated approximately in proportion to the second order of the ethanol pressure. On the other hand, the rate of ethylene formation did not change and the amount of absorbed ethanol changed only slightly upon the pressure jump. After 80 min, the circulating gases were collected by a trap kept at liquid nitrogen temperature (broken line B in Fig. 6). The amount of diethyl ether recovered was equal to that in the gas phase, indicating that no diethyl ether came out from the bulk. The amounts of ethylene and ethanol recovered exceeded those in the gas phase owing to the desorption from the bulk.

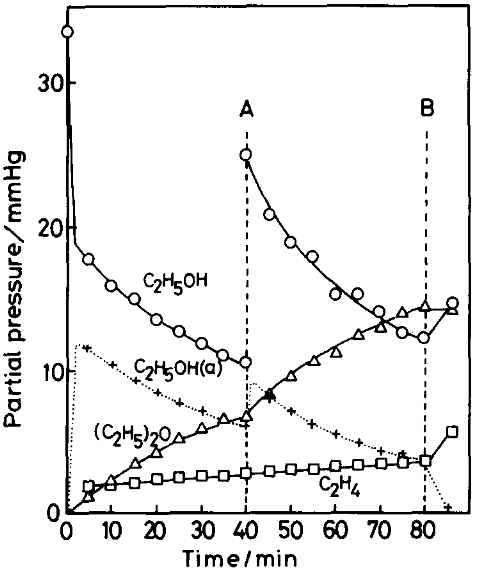


FIG. 6. Time course of the dehydration of ethanol over $H_3PW_{12}O_{40}$. The reaction was carried out at 100°C after the catalyst (0.3 g) was preevacuated at 130°C for 1 h. The pressure of ethanol was increased abruptly (A), and the gases were trapped (B). $C_2H_5OH(a)$ represents the ethanol in the bulk (calculated from material balance).

DISCUSSION

Bulk acidity. The Na salts of H_3PW_{12} as well as H_3PW_{12} itself are very soluble in water, while K and Cs salts are water insoluble. The decrease in the surface area by the formation of Na salts was in contrast to the case of Cs salts, of which the surface area was 170 m^2/g.

The acidity of $Na_xH_{3-x}PW_{12}$ may be similarly estimated as was done previously (*2, 3*), since pyridine was easily absorbed in the bulk of the Na salts to form pyridinium ion, and the Keggin structure was retained during thermal desorption. The amount of protons present in the bulk can be estimated from the amount of pyridine which are protonated and the acid strength is reflected in the desorption temperature. It may be stated, therefore, on the basis of the trend in Fig. 1 that the formation of Na salts decreased both the acid amount and the acid strength.

The acid amount of the sodium salts estimated from the number of pyridinium ion exceeded the number of protons expected from the formula. It is known that $PW_{12}O_{40}^{3-}$ undergoes hydrolysis which produces protons in aqueous solution when pH increases slightly (*1, 12*): $PW_{12}O_{40}^{3-}$ + $3H_2O \rightarrow PW_{11}O_{39}^{7-} + WO_4^{2-} + 6H^+$. Indeed, upon titration of $H_3PW_{12}O_{40}$ with NaOH, pH was almost unchanged even when the ratio of OH^-/heteropoly anion exceeded 3. Therefore, probably partial degradation by hydrolysis had taken place during the preparation of the salts. In contrast, the stoichiometric salts of Cs exhibited very low protonic acidity. In this case, the salt was water insoluble and formed precipitate instantaneously, so that the degradation by hydrolysis was likely much suppressed during the preparation.

"Bulk-type" and "surface-type" reactions. The presence of two types of the activity patterns (Figs. 4 and 5) in the catalytic reactions over the partial Na salts seems closely related to the difference in absorptivity of reactants; polar molecules readily penetrate into the bulk of $Na_xH_{3-x}PW_{12}$, while nonpolar molecules are adsorbed only on the surface. The catalytic activity for the dehydration of 2-propanol, the decomposition of formic acid, and the conversion of methanol decreased monotonously with the increase of Na content and was correlated well with the *bulk* acidity (Fig. 4). This activity pattern is naturally understood if one assumes that these reactions proceed mainly in the *bulk*. It will be indicated in the following section that dehydration of alcohol actually proceeds in the bulk. Therefore, this type of reaction may be called "bulk-type" reactions.

The bulk acidity is also reflected in the thermal desorption of ethanol absorbed in the bulk (Fig. 3B). In this case, formation of ethylene from ethanol requires the fission of the C–O bond on the Brønsted acid site, so that the ease of the dehydration depends likely on the acidity of the catalysts. Therefore, in the thermal desorption of ethanol, desorption temperature of ethylene will shift to higher temperature as the acid strength decreases. Actually, desorption as ethylene occurred at higher temperature over the Na salts than H_3PW_{12} (Fig. 3), which was consistent with the decrease in the acid strength by the formation of the Na salts.

The catalytic activity for the "bulk-type" reactions was little dependent on the pretreatment temperature (*13*). It is likely that although the secondary structure changes during pretreatments by the removal of the water of crystallization, the secondary structure becomes very similar by its rearrangement under the reaction conditions. Probably water formed by the reaction made this rearrangement easier (*2*).

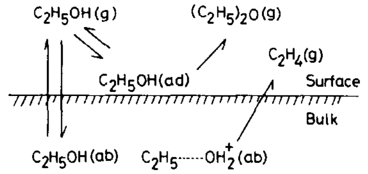
On the other hand, the activity patterns for the second type reactions (Fig. 5 and Table 3) were complicated and were quite different from those of the "bulk-type" reactions. For example, the most active catalyst was Na_2HPW_{12} for the isomerization of *cis*-2-butene, and Na_3PW_{12} for the cracking of cumene and alkylation of toluene. These reactants were not absorbed into the bulk, but were adsorbed only on the surface. Therefore, these reactions must proceed only on the surface. The anomalous activity patterns of these reactions may be caused by the difference between the *surface* acidity and the *bulk* acidity. It is understandable that the surface acidity is sensitive to pretreatments. Actually, the catalytic activity for butene isomerization greatly depended on the pretreatment temperature (Fig. 5). These reactions may be called "surface-type" reactions.

It is of interest to note that the activity pattern for the isomerization of butene changed to that of "bulk-type" reactions in the presence of water vapor (Fig. 5c). Since butene was not absorbed into the bulk even in the presence of water vapor under the reaction conditions, this change might not be due to the change from "surface-type" to "bulk-type" reaction. The rearrangement of the secondary structure have probably been accelerated by the presence of water, and the surface acidity became close to that of the bulk. Probably, the water content, which influences significantly the catalytic activity, also became stationary in the presence of water vapor. This may be the reason why the "surface-type" reaction apparently reflected the bulk acidity in this case as in the "bulk-type" reactions.

Role of the bulk in the dehydration of ethanol. Followings are noted in the results given in Fig. 6. (1) Considerable amount of ethanol is present in the bulk during the reaction. (2) Distinct difference in the pressure dependence exists between diethyl ether and ethylene formation: little pressure dependence of the ethylene formation and nearly second-order dependence of diethyl ether were observed. (3) The amount of ethanol absorbed did not change much during the reaction and upon the pressure jump of ethanol. The difference in the pressure dependence for the two reactions indicates that the reactions take place on different sites. Little dependence of both the formation of ethylene and the absorbed amount of ethanol on the pressure of ethanol suggests that ethylene is formed from the absorbed ethanol. On the other hand, the second-order dependence of diethyl ether formation is understood by the reaction between the two molecules adsorbed on the surface.

The absence of diethyl ether in the bulk during the reaction is confirmed by the following results. (1) The amount of diethyl ether recovered after the run (Fig. 6) was almost equal to that present in the gas phase, so that the amount of diethyl ether in the bulk was negligible. (2) Diethyl ether was not absorbed in the bulk at low pressure (30 mm Hg) at 25°C. (3) Diethyl ether which was absorbed by raising the pressure (100 mm Hg) was easily expelled from the bulk by the ethanol vapor.

All of these results are understood if one assumes that ethylene is produced from ethanol absorbed in the bulk and diethyl ether is formed from ethanol adsorbed on the surface. The fact observed in the thermal desorption of ethanol that ethanol absorbed in the bulk was dehydrated to ethylene but not to diethyl ether supports the above idea. On the basis of these results, we propose the following scheme (Scheme 1) for the dehydration of ethanol (*9*).



SCHEME 1. Reaction model for the dehydration of ethanol.

As for the dehydration of 2-propanol, we measured directly the amount of 2-propanol in the bulk at the stationary state of flow reaction (*5*, *14*). The amount of 2-propanol held in the bulk of H_3PW_{12} was 4–8 molecules/anion at 80–90°C. Details will be reported in the forthcoming paper.

We proposed to call the state of heteropoly acids under these reaction conditions "pseudo-liquid phase" (*2*). We regard this as an important feature of heteropoly compounds, which distinguishes them from the ordinary solid acids. This concept well explains some characteristic catalysis of heteropoly acids, e.g., very high catalytic activity of heteropoly acid particularly at low temperatures for the dehydration of 2-propanol despite its low surface area (*15*). Another possible reason for the high activity is the formation of a complex between alcohols and heteropoly anion, which may be accelerated in the "pseudo-liquid phase". A complex of this kind has recently been reported (*16*).

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