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Studies of the Acidity and Ionic Conductivity of Silica-Supported Heteropoly Compounds. I. The Dehydration of *t*-Butyl Alcohol over Heteropoly Compound Catalysts

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The dehydration of *t*-butyl alcohol (TBA) using various heteropoly compound (HPC) catalysts has been studied. Taking the adsorption of water on the surface of the catalyst into consideration, it is presumed that the dehydration of liquid TBA is governed by a Langmuir-Hinshelwood-like mechanism. Also, the change in the catalytic activity with the amount of HPC supported on the silica suggests that TBA is dehydrated through a pseudo-liquid mechanism in which a few layers of the HPC supported take part in the catalytic reaction. The layer thickness, regarded as a pseudo-liquid phase, depends markedly on the kind of HPC supported. For the dehydration of gaseous TBA, on the contrary, the reaction is found to be of the zero-order; it proceeds through in outer-surface mechanism in which only the outer layer of HPC is effective.

Heteropoly compounds (HPC) e.g., 12-molybdophosphoric acid and its salts have been widely used as catalysts for various kinds of reactions since SOHIO catalysts were applied to the oxidation of α,β-unsaturated aldehydes.[1] As may be seen from the latest industrial applications of the hydration of propylene,[2] the selective oxidation of methacrylaldehyde[3] and the oxidative dehydrogenation of isobutyric acid,[4] it is apparent that heteropoly acid (HPA) catalysts are useful for the hydration, dehydration, and dehydrogenation of organic compounds.[5–9]

Some of the HPA catalysts not only behave as strong acids, but also play rôles as oxidizing agents.[10] Also, it has been reported that both surface and inner sites of solid HPC take part in some catalytic reactions, like liquid catalysts. Misono et al. have called this phenomenon the "pseudo-liquid mechanism."[11] For these reasons, there is still much controversy as to the catalytic rôle in the supported HPC for the respective reactions, despite the fact that they are widely used practically.[12] The present paper, therefore, deals with the dehydration of liquid and gaseous *t*-butyl alcohol (TBA):

$$(CH_3)_3C\text{-}OH \rightarrow (CH_3)_2C{=}CH_2 + H_2O \qquad (1)$$

in the presence of the supported HPA on the basis of the activity and the activation energy of the dehydration reaction obtained. HPC prepared by the substitution of other cations, such as sodium, potassium, and ammonium, for the hydrogen ions of HPA will be examined as well, since the control of acid and oxidizing properties is particularly important for catalytic reactions in order to get products with a high yield and selectivity.

Experimental

Preparation of Catalysts. As-received 12-molybdophosphoric acid and 12-tungstophosphoric acid from the Japan New Metals Co., Ltd., were used. The supports used AEROSIL-200, AEROSIL-OX50, AEROSIL-300, and AEROSIL-380 (Aerosil Nippon Co., Ltd.) has surface areas S of about 200, 50, 130, 300, and 380 $m^2 g^{-1}$ respectively. Solutions or emulsions of HPC were prepared as follows: Potassium salt emulsions of HPA were prepared by the slow addition of an aqueous potassium carbonate solution into a HPA solution. Sodium and ammonium salt solutions and cesium salt emulsions were obtained by the same procedures. Bismuth oxide salt solutions were prepared by using bismuth carbonate oxide in 0.10 mol dm^{-3} nitric acid. The degree of the substitution of other cations for the hydrogen ion of HPA was defined as the number of hydrogen-ion-substituted n.

The support-free catalysts were as-received HPA themselves or were prepared drying the HPC solutions or the emulsions at 383 K for 24 h, grinding them, and then calcining them at 573 K for 3 h. The supported catalysts were obtained by the following procedure. The support was calcined at 773 K for 3 h and then impregnated with a required amount of the HPC solution. The resulting solution was dried at 383 K for 24 h, ground, and then calcined at 573 K for 3 h. The supported amount of HPC was expressed as m, milimoles of HPC per gram of support; The m varied are the range of 0.05—1.50 mmol/g-supt. The IR spectra confirmed that the catalysts containing bismuth oxide ions were free from nitrate ions. The resulting support-free and supported catalysts will hereafter be abbreviated as H_3PMo-HPA and H_3PMo/SiO_2-200 respectively, where SiO_2-200 stands for AEROSIL-200.

Dehydration of *t*-Butyl Alcohol. The dehydration of liquid TBA in the heterogeneous system using supported catalyst was carried out in a batchwise reactor. The TBA of 0.212 mol (20 cm^3) was pipetted into a 300 cm^3 flask, after which the supported catalyst of 0.15 g was placed in an inner glass ampoule separated from the TBA. They were kept in a preheated oil bath. The TBA was refluxed for more than 1 h at 355.3 K. Afterwards, the ampoule was broken to cause the dehydration of TBA to start. The amount of isobutene (IB) generated as time passed was measured by the use of a gas burette.

The conversion X(liq) was determined as follows:

$$X(\text{liq}) = A/B_0 \times 100 \qquad (2)$$

where A and B_0 stand for the amount of IB generated (mol) and the initial amount of TBA (mol) respectively.

The eluted HPA was determined as follows. The HPA dissolved in the TBA solution was separated from the dispersed HPA on the support by means of centrifugation. The TBA solution was dried at 383 K for 24 h and then calcined at 573 K for 3 h. The residue was dissolved in a certain volume of water for analysis. An appropriate volume of the sodium hydroxide solution was added to the solution, and then the excess amount of sodium hydroxide was titrated with hydrochloric acid.

The dehydration of TBA in the presence of a support-free H_3PMo solution, in which the H_3PMo has been dissolved in TBA of 20 cm^3, was also examined. The H_3PMo concentration was adjusted to 3.00 mmol dm^{-3}. The amount of H_3PMo present in the solution of 20 cm^3 corresponds to that in 0.40 mmol/g-supt H_3PMo/SiO_2-200 of 0.15 g.

Gas-phase dehydration was performed in a conventional cylindrical continuous-flow-type quartz-reactor, 16 mmϕ× 525 mm, in the temperature range between 413 and 513 K under atmospheric pressure. The catalyst (0.15 g) was mixed with glass beads (5 g) and then placed in the fixed-bed. TBA was fed continuously into the reactor through a preheated tube at the flow rate of 0.158, 0.211, 0.317, and 0.422 mol h^{-1} using a microfeeder. After passing through the reactor, the gas was cooled by a circulation device using circulated ice-cooled water in order to remove the TBA and water. Then the IB generated was assayed by measuring the time taken to obtain 10 cm^3 of IB by the use of a gas burette.

The conversion X(gas) was estimated as:

$$X(\mathrm{gas}) = V/F \times 100 \tag{3}$$

where V is the velocity of IB generated (mol h^{-1}), and F, the velocity of TBA supplied (mol h^{-1}).

Results and Discussion

Kinetics of the Dehydration of Liquid *t*-Butyl Alcohol. Figure 1 shows the representative plots of the conversion X(liq) as a function of the time exiled. The conversion increases markedly with the amount of the supported H_3PMo at the low loadings (less than 0.6 mmol/g-supt), while it increases slightly at higher loadings (Fig. 1(a)). When the hydrogen ions of H_3PMo and H_3PW are replaced by a potassium ion, the catalytic activity decreases with the increase in the number of hydrogen ions substituted n from 1 to 3 (Fig. 1(b)). A similar trend was observed for the replacement of sodium and ammonium ions.

It seems probable that the water evolved during the dehydration of TBA is adsorbed on the surface of HPC. Assuming the formation of the TBA, HPC, TBA·HPC, and H_2O·HPC species, the following Langmuir–Hinshelwood mechanism is obtained:

$$\mathrm{TBA} + \mathrm{HPC} \overset{K_\mathrm{B}}{\rightleftarrows} \mathrm{TBA}\cdot\mathrm{HPC} \tag{4}$$

moreover

$$\mathrm{H_2O} + \mathrm{HPC} \overset{K_\mathrm{W}}{\rightleftarrows} \mathrm{H_2O}\cdot\mathrm{HPC} \tag{5}$$

$$\mathrm{TBA}\cdot\mathrm{HPC} \xrightarrow{k_1} \mathrm{IB} + \mathrm{H_2O} + \mathrm{HPC} \tag{6}$$

where K_B, and K_W are the equilibrium constants for Eqs. 4 and 5 respectively, and k_1, the rate constant for Reaction 6, which will be defined in detail in a later paragraph. Equilibria 4 and 5 lead to these relations:

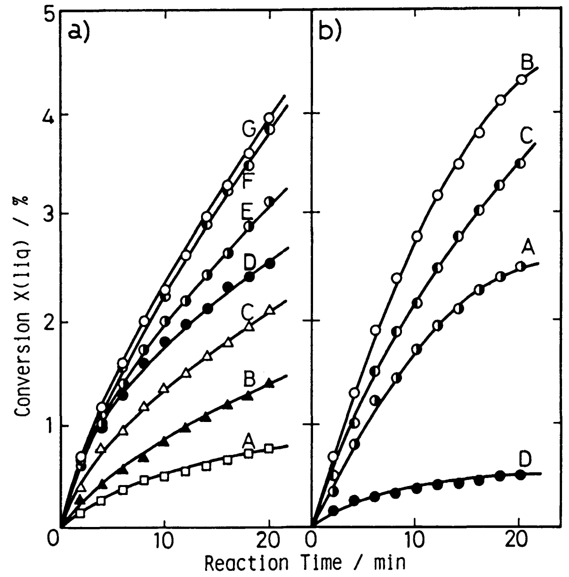

Fig. 1. Plots of the conversion vs. the exciled time for the dehydration of liquid TBA over a) H_3PMo/SiO_2-200 with various loadings of H_3PMo; A: m=0.05, B: m=0.10, C: m=0.20, D: m=0.30, E: m=0.45, F: m=0.60, G: m=0.90 mmol/g-supt H_3PMo/SiO_2-200 and b) 0.10 mmol/g-supt $K_nH_{3-n}PW/SiO_2$-200; A: n=0, B: n=1, C: n=2, D: n=3.

$$K_\mathrm{B} = \frac{[\mathrm{TBA}\cdot\mathrm{HPC}]_\mathrm{S}}{[\mathrm{TBA}]\cdot[\mathrm{HPC}]_\mathrm{S}} \tag{7}$$

and

$$K_\mathrm{W} = \frac{[\mathrm{H_2O}\cdot\mathrm{HPC}]_\mathrm{S}}{[\mathrm{H_2O}]\cdot[\mathrm{HPC}]_\mathrm{S}} \tag{8}$$

respectively, where [TBA] and [H_2O] are the equilibrium concentrations of TBA and water (mol dm^{-3}) respectively and where [HPC]$_\mathrm{S}$, [TBA·HPC]$_\mathrm{S}$, and [H_2O·HPC]$_\mathrm{S}$ are the concentrations of HPC, TBA·HPC, and H_2O·HPC at the surface of the catalyst per liter of the HPC-dispersed TBA solution (mol dm^{-3}). If K_B and K_W are big enough, the total concentration of the surface HPC, [HPC]$_\mathrm{S,t}$ (mol dm^{-3}), should be expressed as:

$$[\mathrm{HPC}]_\mathrm{S,t} = [\mathrm{TBA}\cdot\mathrm{HPC}]_\mathrm{S} + [\mathrm{H_2O}\cdot\mathrm{HPC}]_\mathrm{S} \tag{9}$$

By combining Eqs. 7, 8, and 9, the following relation is derived:

$$\frac{[\mathrm{TBA}\cdot\mathrm{HPC}]_\mathrm{S}}{[\mathrm{HPC}]_\mathrm{S,t}} = \frac{K_\mathrm{B}\cdot[\mathrm{TBA}]}{K_\mathrm{B}\cdot[\mathrm{TBA}]+K_\mathrm{W}\cdot[\mathrm{H_2O}]} \tag{10}$$

On the other hand, the rate of the reaction r (min^{-1}) for Eq. 6 is given by:

$$r = k_1\cdot[\mathrm{TBA}\cdot\mathrm{HPC}]_\mathrm{S}, \tag{11}$$

and so the relation:

$$r=\frac{k_1\cdot K_B\cdot[\mathrm{TBA}]\cdot[\mathrm{HPC}]_{s,t}}{K_B\cdot[\mathrm{TBA}]+K_W\cdot[\mathrm{H_2O}]} \qquad (12a)$$

or

$$\frac{1}{r}=\frac{K_W\cdot[\mathrm{H_2O}]}{K_B\cdot k_1\cdot[\mathrm{HPC}]_{s,t}\cdot[\mathrm{TBA}]}+\frac{1}{k_1\cdot[\mathrm{HPC}]_{s,t}} \qquad (12b)$$

is worked out. Eq. 12b implies a linear relationship between $1/r$ and $[\mathrm{H_2O}]/[\mathrm{TBA}]$.

Figure 2 shows the plots of $1/r$ as a function of $[\mathrm{H_2O}]/[\mathrm{TBA}]$, in which the value of the rate of the reaction for each point was estimated from the data in Fig. 1. It can be seen that this does indeed give a linear relation, implying that the mechanism assumed above is reasonable for the dehydration of liquid TBA with the supported HPC. The same mechanism can also be deduced for the other supported HPCs examined. For this reason, the apparent rate constant k_1' ($=k_1\cdot[\mathrm{HPC}]_{s,t}$) and the value of K_W/K_B for the dehydration of liquid TBA with the supported HPC are evaluated from the intercept and the slope of the lines in Fig. 2 respectively.

In the series of molybdophosphates examined, it was observed that the catalysts turned from yellow to blue during the dehydration of TBA, indicating that hexavalent molybdenum is reduced to a pentavalent one. However, the catalysts pre-reduced by hydrogen gas at 373 K did not show any particular catalytic activity. This proves that the dehydration of TBA proceeds via an acid catalytic reaction, not via a redox reaction.

Mechanism of the Dehydration of Liquid *t*-Butyl Alcohol. Figure 3 shows the plots of the apparent rate constant k_1' against the amount of HPC supported on AEROSIL-200. It is noteworthy that, for all the catalysts studied, the apparent rate constant k_1' increases linearly with the amount of HPC loaded, and that it then approaches a limiting value. Also, the activity is in this order: $\mathrm{H_3PMo/SiO_2\text{-}200<H_3PW/SiO_2\text{-}200}$, while it decreases with the degree of substitution for the hydrogen ion of HPA. The limiting values of the apparent rate constant, k_L, for the respective catalysts are summarized in Table 1.

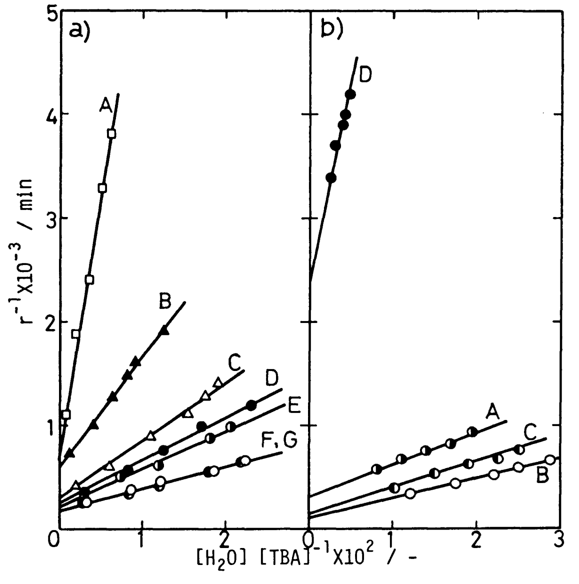

Fig. 2. Kinetics for the dehydration of liquid TBA over a) $\mathrm{H_3PMo/SiO_2\text{-}200}$ with various loadings of $\mathrm{H_3PMo}$; A: m=0.05, B: m=0.10, C: m=0.20, D: m=0.30, E: m=0.45, F: m=0.60, G: m=0.90 mmol/g-supt $\mathrm{H_3PMo/SiO_2\text{-}200}$ and b) 0.10 mmol/g-supt $\mathrm{K_nH_{3-n}PW/SiO_2\text{-}200}$; A: n=0, B: n=1, C: n=2, D: n=3.

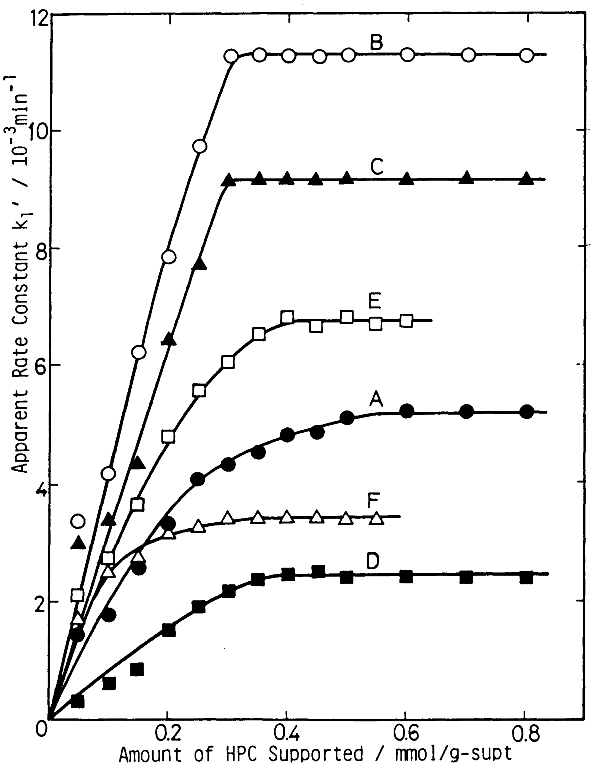

Fig. 3. The plots of the apparent rate constants for the dehydration of liquid TBA k_1' against the amount of HPC supported on silica m; A: $\mathrm{H_3PMo/SiO_2\text{-}200}$, B: $\mathrm{KH_2PMo/SiO_2\text{-}200}$, C: $\mathrm{K_2HPMo/SiO_2\text{-}200}$, D: $\mathrm{K_3PMo/SiO_2\text{-}200}$, E: $\mathrm{H_3PW/SiO_2\text{-}200}$, F: $\mathrm{H_3PMo/SiO_2\text{-}130}$.

Considering the effective cross section per molecule σ of HPC:

$$\sigma=1.09\,(M/L\cdot D)^{2/3} \qquad (13)$$

the surface coverage θ is expressed as:

$$\theta=m\cdot\sigma\cdot(L/S)\times10^{-4} \qquad (14)$$

where M and D are the molecular weight and the density of HPC respectively, and L, the Avogadro number.

Assuming that HPC molecules adsorb both on the HPC monolayer deposited on the support and on the surface of the support, critical values of m=0.30 or 0.60 can be expected if one or two layers are available respectively. The value of m at the limiting value of the apparent rate constant m_L for $\mathrm{H_3PMo/SiO_2\text{-}200}$ in

Table 1. Limiting Activity for the Dehydration of Liquid TBA

HPC$^{a)}$	$m_L$$^{b)}$	$\theta_L$$^{c)}$	k_L×$10^3$$^{d)}$
	mmol/g-supt		min^{-1}
H_3PMo	0.55	1.82	5.30
KH_2PMo	0.30	1.01	11.25
K_2HPMo	0.30	1.02	9.15
K_3PMo	0.35	1.20	2.40
Na_3PMo	0.60	1.01	2.00
Cs_3PMo	0.35	1.20	2.25
$(BiO)_3PMo$	0.30	1.22	1.40
H_3PW	0.40	1.79	8.50
K_3PW	0.25	1.15	1.25
$(NH_4)_3PW$	0.25	1.13	1.75

a) The support used is AEROSIL-200 (S=200 m^{2}g^{-1}). b) m_L means the amount of HPC supported reached at the limiting activity. c) θ_L means the surface coverage given by Eq. 15 at m_L. d) k_L is the limiting activity.

Table 1 agrees well with the latter one. For the other catalysts studied, the values of m_L are in harmony with either critical one.

The number of layers of HPC available for the dehydration of TBA θ_L is, estimated as:

$$\theta_L = m_L/m_1 \qquad (15)$$

where m_1 represents the amount of HPC required for the formation of a monolayer on a support. As θ_L=1.82 for H_3PMo/SiO_2-200 is obtained, it is presumed that two layers at the surface of H_3PMo take part in the dehydration of liquid TBA. For the cation-substituted catalyst KH_2PMo/SiO_2-200, on the contrary, the value of θ_L is estimated to be 1.01, implying that only one layer takes part in the catalytic reaction. The difference in the thickness of the pseudo-liquid phase between HPA and its salts may be attributable to the difference in their hydrophilic/hydrophobic properties. Consequently, it is presumed that the dehydration of liquid TBA using the supported HPC proceeds through a pseudo-liquid mechanism.

Effect of Water. Figure 4 shows the plots of the K_W/K_B ratio against the amount of H_3PW and its potassium salts supported on AEROSIL-200. It is apparent that the K_w/K_B ratio decreases with the increase in the number of hydrogen ions substituted n from 1 to 3, this is consistent with the magnitude of the k_1' value. There is no doubt that the anomalously low activity of HPA for the dehydration of TBA compared with those of its salts is attributable to the adsorption of water: the greater the number of hydrogen ions substituted, the more hydrophobic the resulting catalyst is. The cause is the decrease in the affinity of HPC for alcohol. Similar results were also obtained for H_3PMo and its potassium salts (Table 1). It is, therefore, concluded that the hydrophobic/hydrophilic properties of the surface for the supported catalyst are a primary factor affecting their catalytic activity for the dehydration of liquid TBA.

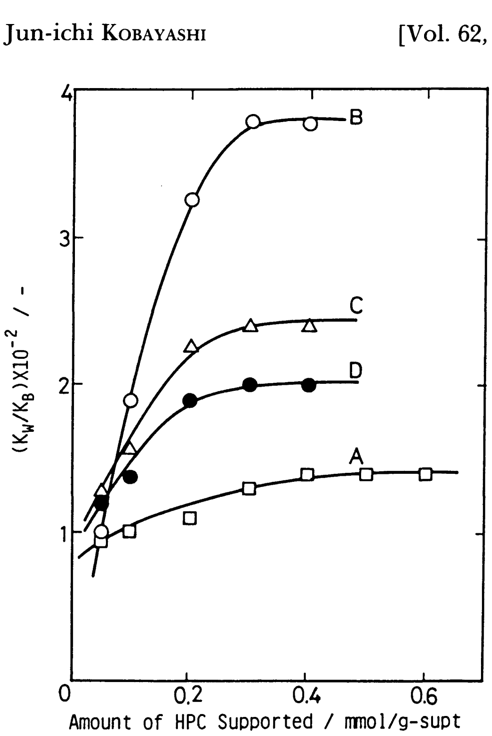

Fig. 4. The plots of K_W/K_B as a function of the amount of $K_nH_{3-n}PW$ supported on AEROSIL-200 m; A: n=0, B: n=1, C: n=2, D: n=3.

In Fig. 5, the rate constant k_1 is plotted as a function of the amount of H_3PW and its potassium salts supported on AEROSIL-200. The value of k_1 increases with the HPC loadings until it reaches a maximum at m=0.20; thereafter decreases. At the maximum, θ_L=1, so that the increase in the rate constant at low loadings may be ascribed to the two-dimensional network formation of H_3PW molecules, while the decrease at higher loadings seems due to the stacking effect of HPC molecules on each other. Also, it is presumed that the cluster of HPC in the two-dimensional network works more effectively as a catalyst than does the HPC molecule distributed separately.

Effect of Surface Area of Support. Concerning the surface area of the support, the relative activity of HPC is found to be enhanced as the surface area decreases (Table 2). This may come from the fact that the smaller the surface area is, the easier the two-dimensional network formation of HPC should be.

Comparison of Heterogeneous and Homoeneous Catalysts. The elution of HPA in the heterogeneous system mentioned above has been examined. The kinetics of the dehydration of TBA in the homogeneous systems with the H_3PMo and H_3PW solutions confirms that the reaction proceeds through the same mechanism as does that of the heterogeneous system. H_3PW was found to be more active than H_3PMo, which is the same in the heterogeneous system. A comparison between the heterogeneous and the homogeneous systems indicates that the apparent rate constant of the heterogeneous one is much larger than

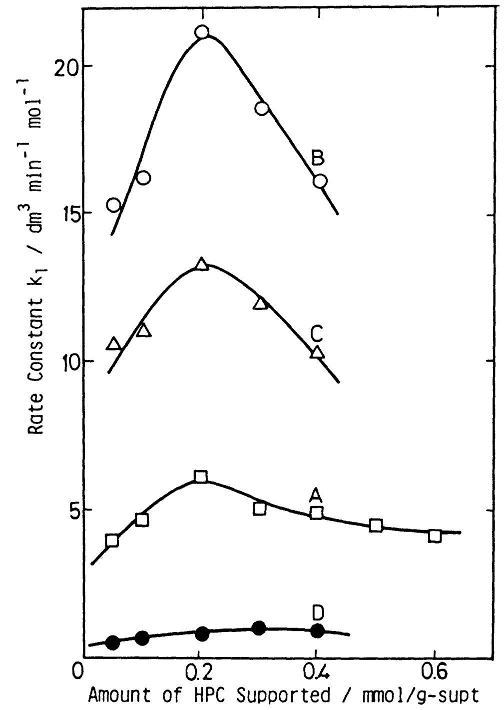

Fig. 5. The plots of rate constant k_1 as a function of the amount of $K_nH_{3-n}PW$ with supported on AEROSIL-200 m; A: n=0, B: n=1, C: n=2, D: n=3.

that of the homogeneous one by a factor of 10. The HPA (6.2, 7.2, and 10.5%) was eluted into the solution in 20 min in the heterogeneous system with H_3PMo, with m=0.20, 0.40, and 0.80 respectively. Hence, under these conditions, the elution of H_3PMo is not considered to affect the activity significantly, especially the initial activity.

Kineties of the Dehydration of Gaseous *t*-Butyl Alcohol. For the dehydration of gaseous TBA, the conversion become constant in 10 min, whatever the catalyst examined. Figure 6 shows plots of the conversion X(gas) as a function of the contact time W/F, in which W denotes the weight of the catalyst (g). There is no doubt that the dehydration of gaseous TBA proceeds through a zero-order reaction.

Assuming the reaction:

$$\text{TBA}\cdot\text{Catalyst} \xrightarrow{k_0} \text{IB} + H_2O + \text{Catalyst} \qquad (6')$$

where k_0 is the rate constant for Reaction 6′ per gram of the catalyst (mol g^{-1} h^{-1}), the rate for Reaction 6′ V (mol h^{-1}) is given by:

$$V = k_0 \cdot [\text{TBA}\cdot\text{Catalyst}] \qquad (16)$$

where [TBA·Catalyst] is the weight of the species TBA·Catalyst (g). If K_B is big enough, and if K_W is small enough to neglect, Eq. 16 should be expressed as:

$$V = k_0 \cdot [\text{Catalyst}] = k_0 \cdot W \qquad (17)$$

where [Catalyst] is the weight of the catalyst (g). By combining Eqs. 2 and 17, the following relation is derived:

$$X(\text{gas}) = k_0 \cdot W/F \times 100 \qquad (18)$$

The rate constant k_0 was obtained from the slopes given in Fig. 6 at a constant temperature. It is noticeable that the activity of the catalyst was decreased markedly after the feed had been stopped once or when the reaction temperature was raised over 473 K. However, it was re-activated by calcination at 573 K for 3 h. Further investigations of this point are in progress.

Effect of the Amount of HPC Supported for the Gas-Phase Dehydration of *t*-Butyl Alcohol. Figure 7 shows the plot of the rate constant k_0 as a function of the amounts of various HPCs supported on AEROSIL-200. It is obvious that the rate constant k_0 increases with the increase in the amount of HPC supported at the low loadings and is in the order of: $H_3PW \fallingdotseq H_3PMo > KH_2PMo > K_2HPMo > K_3PMo$, in harmony with the increase in the number of hydrogen ions replaced by potassium. For the H_3PMo/SiO_2-200 and H_3PW/SiO_2-200, the values of m_L at the maximum rate constant were 0.25—0.30 (θ_L=0.83—0.99) and 0.20 (θ_L=0.90) respectively. These values are remarkably different from those for the dehydration of liquid TBA, supporting the idea that only the first layer of HPC in contact with reaction gases takes part in the dehydration of gaseous TBA. It is, therefore, concluded that the dehydration proceeds through the outer-surface mechanism.

Table 2. Limiting Activity for the Dehydration of Liquid TBA

Catalyst	m_L[a)] mmol/g-supt	θ_L[b)]	$k_L \times 10^3$[c)] min^{-1}	$k_L/S \times 10^5$[d)] min^{-1} m^{-2} g
H_3PMo/AEROSIL-OX50[e)]	0.15	1.98	3.00	6.00
H_3PMo/AEROSIL-130[f)]	0.35	1.78	3.45	2.65
H_3PMo/AEROSIL-200[g)]	0.55	1.82	5.30	2.65
H_3PMo/AEROSIL-300[h)]	0.75	1.62	7.20	2.40
H_3PMo/AEROSIL-380[i)]	1.00	1.74	8.35	2.20

a) m_L means the amount of HPC supported reached at the limiting activity. b) θ_L means the surface coverage given by Eq. 15 at m_L. c) k_L is the limiting activity. d) k_L/S means the relative activity per unit of surface area. d—h) The supports used have the surface areas S of e) 50, f) 130, g) 200, h) 300, and i) 380 m^2 g^{-1}.

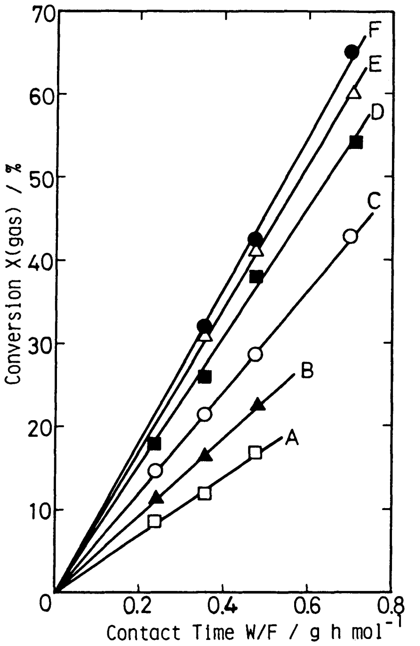

Fig. 6. Kinetics for the dehydration of gaseous TBA over 0.05 mmol/g-supt H_3PMo/SiO_2-200 at various temperature T; A: T=413 K, B: T=433 K, C: T=453 K, D: T=473 K, E: T=493 K, F: T=513 K.

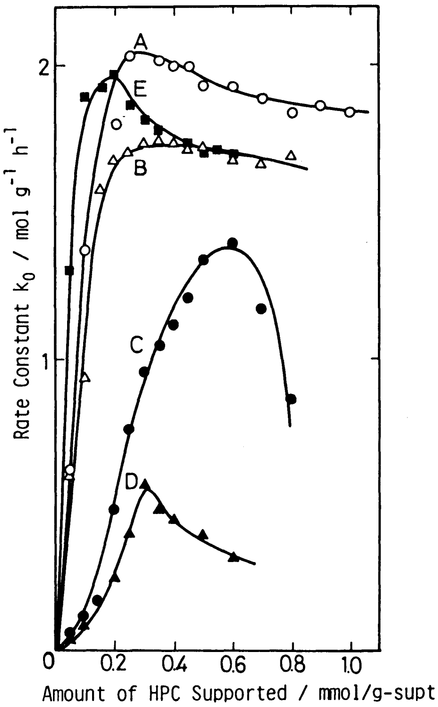

Fig. 7. The plots of the rate constants for the dehydration of gaseous TBA k_0 at 453 K against the amount of HPC supported on AEROSIL-200 *m*; *A*: H_3PMo/SiO_2-200, B: KH_2PMo/SiO_2-200, C: K_2HPMo/SiO_2-200, D: K_3PMo/SiO-200, E: H_3PW/SiO_2-200.

At higher loadings of HPC, X-ray diffraction confirmed that they were crystallized. If the diffusion of TBA in the crystal of HPC plays a significantly important rôle in its dehydration rate, the activation energy should depend on the amount of the supported HPC. However, as may be seen in Table 3, the activation energies for the gas-phase dehydration using H_3PMo/SiO_2-200 are independent of the amounts loaded. It is, therefore, presumed that the reaction at the surface is the rate-determining step for the dehydration of gaseous TBA. These results also supported the outer-surface mechanism.

In the dehydration of gaseous TBA using HPA and its potassium salts, the order for the activity with respect to the substitution of hydrogen ions of HPA can reasonable interpreted in terms of the acidity. In the dehydration of liquid TBA, on the contrary, the activity of HPA is not consistent with the order of the acidity. It is conceivable that the extremely low activity of HPA is due to the adsorption of water at the surface of the catalyst.

Concerning the species formed by the replacement of the hydrogen ion by the potassium ion, it has been reported that only one species, $K_3PMo_{12}O_{40}$, is formed, while the $H_3PMo_{12}O_{40}$ species grows epitaxially on its surface.[13] Taking this into consideration, the species with the compositions of K_2HPMo and KH_2PMo are considered to be mixtures of the $H_3PMo_{12}O_{40}$ and $K_3PMo_{12}O_{40}$ species, with K/HPC molar ratios of 2

Table 3. Activation Energy for the Dehydration of Gaseous TBA over HPC Supported on AEROSIL-200

m[a]	Activation energy/kJ mol^{-1}				
mmol/g-supt	H_3PMo[b]	KH_2PMo[b]	K_2HPMo[b]	K_3PMo[b]	H_3PW[b]
0.05	27.2	38.2	39.0	38.2	17.4
0.10	26.6	34.9	35.2	35.8	15.4
0.25	26.8	19.1	20.8	50.7	10.0
0.40	26.2	18.3	18.3	25.7	10.4
0.70	27.0	10.0	17.4	36.6	—
1.00	27.0	—	—	—	—
Free[d]	1.9	—	—	—	—

a) *m* means the amount of HPC supported on AEROSIL-200. b) The support used is AEROSIL-200 (S=200 m^2 g^{-1}). d) "Free"the support-free H_3PMo-HPA.

and 1 respectively. It can, therefore, be speculated that, at low loadings of HPC, the two species are formed simultaneously on the silica support, while at higher loadings the $H_3PMo_{12}O_{40}$ species is stacked on the $K_3PMo_{12}O_{40}$.

As may be seen from Fig. 7, the values of m_L are 0.30—0.40 (θ_L=1.01—1.34), 0.60 (θ_L=2.04), and 0.30 (θ_L=1.03), for KH_2PMo/SiO_2-200, K_2HPMo/SiO_2-200, and K_3PMo/SiO_2-200 respectively. The dehydration of gaseous TBA with potassium-substituted HPA is thought to proceed through the outer-surface mechanism. If $H_3PMo_{12}O_{40}$ and $K_3PMo_{12}O_{40}$ are distributed homogeneously, the value of θ_L is expected to be approximately unity. Taking the heterogeneous distribution of $H_3PMo_{12}O_{40}$ and $K_3PMo_{12}O_{40}$ (the growth of the $H_3PMo_{12}O_{40}$ species on the surface of the $K_3PMo_{12}O_{40}$ species) into consideration, however, the theoretically estimated values of θ_L are 1.50 and 3.00 for KH_2PMo/SiO_2-200 and K_2HPMo/SiO_2-200 respectively. The experimental results support the latter distribution (Fig. 7).

The activation energies for K_3PMo/SiO_2-200 are about 37 $kJ\,mol^{-1}$, regardless of the amount of HPC supported. As may be seen in Table 3, the activation energies for the gas-phase dehydration using partially potassium-substituted HPA decrease with an increase in the amount of HPC supported: at low loading of HPC supported, the activation energy is similar to the value for K_3PMo/SiO_2-200, while at higher loadings of HPC, it is similar to that for H_3PMo/SiO_2-200. It is, therefore, reasonable to speculate that the $H_3PMo_{12}O_{40}$ and $K_3PMo_{12}O_{40}$ species are distributed heterogeneously on the surface of the catalyst.

In conclusion, it is deduced that, for the partially potassium-substituted catalysts, mixtures of $H_3PMo_{12}O_{40}$ and $K_3PMo_{12}O_{40}$ with different mole ratios are formed and that the surfaces of the catalysts are covered with $H_3PMo_{12}O_{40}$ predominantly.

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