Studies of the Acidity and Ionic Conductivity of Silica-Supported Heteropoly Compounds. II. Acidity and Catalytic Activity of Supported Heteropoly Compound Catalysts

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The acidity function, H_0, of silica-supported heteropoly compounds (HPC) such as $H_3PMo_{12}O_{40}$, $H_3PW_{12}O_{40}$, and their sodium, potassium, ammonium, cesium, and bismuth oxide salts has been examined in connection with their catalytic activity for the dehydration of *t*-butyl alcohol (TBA). The values of H_0 for the respective catalysts have been determined spectrophotometrically utilizing adsorbed dicinnamylideneacetone (DCA) as a probe molecule. A linear relationship has been established between the amount of HPC supported (log *m*) and its H_0. Also, for the dehydration of TBA in the liquid-phase all plots of log k_1' vs. H_0 fall on a straight line with a slope of -1, independent of the kind of catalyst. In this case k_1' is the apparent rate constant of the dehydration of liquid TBA. On the other hand, for the gas-phase dehydration of TBA the plots yield straight lines with different slopes, depending on the type of catalyst. The dependence of the catalytic activity on the H_0 supports the previous conclusion that the dehydration of liquid and gaseous TBA proceeds through pseudo-liquid and outer-surface mechanisms, respectively.

In a previous study[1)] we proposed the dehydration mechanism of liquid and gaseous *t*-butyl alcohol (TBA) in the presence of such heteropoly compounds (HPC) as $H_3PW_{12}O_{40}$, $H_3PMo_{12}O_{40}$, and their sodium, potassium, ammonium, and bismuth oxide salts supported on silica. The dehydration of liquid TBA proceeds through a pseudo-liquid mechanism and all catalysts used are slightly poisoned by the evolved water. Regarding the dehydration of gaseous TBA the outer-surface mechanism has been confirmed, in which slight poisoning occurs during the reaction. In both cases the catalytic activity of HPC has been found to decrease with increasing number of cations substituted for hydrogen ions, implying that there should be a relation between the catalytic activity and the acid-base property of HPC.

In this paper, therefore, we present a quantitative evaluation of the acidity of HPC supported on AEROSIL-200 using the acidity function, H_0,[2,3)] and discuss the catalytic activity for the dehydration of TBA in terms of H_0 values.

Experimental

Supported HPC catalysts on AEROSIL-200 (abbreviated as SiO_2-200), such as $M_nH_{3-n}PW/SiO_2$-200 and $M_nH_{3-n}PMo/SiO_2$-200, were prepared by a previously described procedure,[1)] in which $M_nH_{3-n}PW$ and $M_nH_{3-n}PMo$ stand for $M_nH_{3-n}PW_{12}O_{40}$ and $M_nH_{3-n}PMo_{12}O_{40}$, respectively, M is sodium, potassium, cesium, ammonium, and oxobismuth ions, and *n* denotes the number of substituted hydrogen ions.

Dehydration of *t*-Butyl Alcohol. Dehydration of liquid TBA was carried out in a batch system at 355.3 K and that of gaseous TBA in a flow-system at 413—513 K. The detailed procedure for the dehydration of TBA was given in a previous paper.[1)]

Determination of Actidity. The acidity function of the supported HPC was determined spectrophotometrically using dicinnamylideneacetone (DCA) as an acid-base indicator.[4,5)] A stock solution of DCA was prepared by dissolving DCA in dry decalin, and was kept in a dark, cool place. The DCA concentration was adjusted to 2 mmol dm^{-3}. Solutions for spectrophotometry were prepared by pipetting decalin and a DCA solution of 2.0 and 0.20 cm^3, respectively, into a stoppered conical flask. Then 0.10 g catalysts are dispersed in them, and shaken for 3 h before measurement. The amount of DCA added was 4 μmol per gram catalyst, far less than the amount of acid on the surface of the catalyst (about 0.1—0.2 mmol g^{-1}). All of the procedure mentioned above was carried out in a dark place in order to avoid photodecomposition of the adsorbed DCA.

The absorption spectra of slurry containing DCA adsorbed on HPC/SiO_2-200 were recorded on a Hitachi model 340 spectrophotometer equipped with a head-on detector in quartz cells of 0.5 mm in light path length. The DCA adsorbed on H_2SO_4/SiO_2-200 of 0.02 mmol g-supt^{-1} (milimole per gram of support) and SiO_2-200 alone was referred as standards for the acid and base color, respectively. It was confirmed that the supernatant solution after adsorption of DCA had no adsorption band, indicating that all of the DCA added was adsorbed on the surface of the catalysts.

Results and Discussion

Acidity Function, H_0, of Supported HPC. Figure 1 shows a representative absorption spectra of DCA adsorbed on H_3PW/SiO_2-200 catalysts. A band at 560 nm increases upon increasing the amount of supported HPC. As is evident from Fig. 1, an isosbestic point is observed at 452 nm. A band at 400 nm increases with increasing *n*, compared with $M_nH_{3-n}PW$ to H_3PW. As DCA in decalin has only band at 370 nm, the bands at 560 and 400 nm are assigned to those of the DCA adsorbed on acid and base sites, respectively. A similar trend was observed for all of the other catalysts examined. These spectral patterns do not change with the amount of DCA added, except for these absorbance.

It is well-known that H_0 is a measure of the proton-donation ability, which depends on the concentration

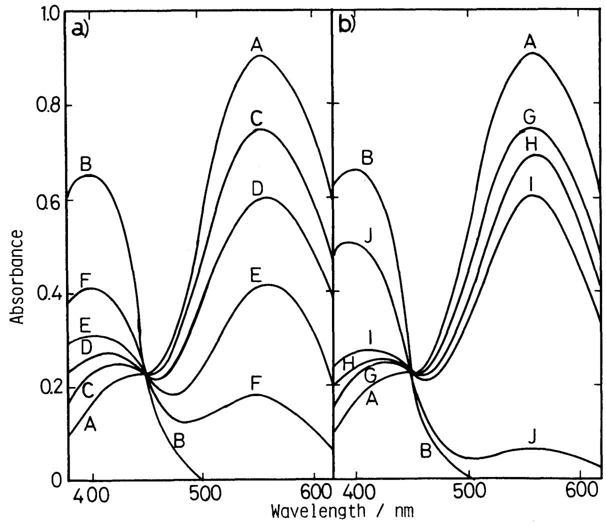

Fig. 1. Absorption Spectra of DCA adsorbed on the surface of catalysts. A: 0.02 mmol g-supt^{-1} H_2SO_4/SiO_2-200 (standard for acid color); B: SiO_2-200 alone (standard for base color); a) C: m=0.20; D: m=0.10; E: m=0.05; F: m=0.01 mmol g-supt^{-1} H_3PW/SiO_2-200; b) m=0.20 mmol g-supt^{-1}; G: H_3PW/SiO_2-200; H: KH_2PW/SiO_2-200; I: K_2HPW/SiO_2-200; J: K_3PW/SiO_2-200.

of acid. H_0 for a homogeneouus liquid H_2O–H_2SO_4 system has been defined as follows by Hammet and Deyrup:

$$H_0 \equiv (\mathrm{p}K_\mathrm{a})_\mathrm{w} - \log\,(C_\mathrm{IA}/C_\mathrm{IB}) \qquad (1a)^{2)}$$

$$= -\log\,\{a_\mathrm{H}\cdot f_\mathrm{IB}/f_\mathrm{IA}\}, \qquad (1b)^{2)}$$

where C_IA or C_IB and f_IA or f_IB stand for the concentration and activity coefficients of the indicator of an acid or base form respectively, a_H the activity of proton, and $(\mathrm{p}K_\mathrm{a})_\mathrm{w}$ the dissociation constant of an indicator in an aqueous solution.

In a heterogeneous liquid–solid system C_IA or C_IB and f_IA or f_IA in Eqs. 1a and 1b refer to the surface concentration and the activity coefficients of DCA adsorbed on acid or base site, respectively.[3] The value of $(\mathrm{p}K_\mathrm{a})_\mathrm{w}$ for DCA is −3.0.[4,6] The ratio $C_\mathrm{IA}/C_\mathrm{IB}$ is estimated spectrophotometrically utilizing the absorbance at 560 nm,

$$C_\mathrm{IA}/C_\mathrm{IB} = (d - d_\mathrm{B})/(d_\mathrm{A} - d), \qquad (2)$$

where d, d_A and d_B are the absorbance of DCA adsorbed on an HPC/SiO_2-200 catalyst, H_2SO_4/SiO_2-200, and SiO_2-200 alone, respectively. Thus, the value of H_0 for the catalyst should be determined utilizing Eqs. 1a and 2.

Effect of the Amount of HPC Supported on the Acidity Function, H_0. In Fig. 2, plots of H_0 vs. log m are given, in which m (mmol g-supt^{-1}) is the amount of H_3PW, KH_2PW, K_2HPW, K_3PW or H_3PMo supported on SiO_2-200. Taking into account the definition of H_0 in Eqs. 1a and 1b, showing that H_0 corresponds to pH (=−log[H^+]) in dilute solution,[2] it is noticed that a linear relationship obtained between H_0 and log m is reasonable (Fig. 2). The slope of the lines for H_3PW/SiO_2-200 and H_3PMo/SiO_2-200 is approximately −1, and those for their salts on SiO_2-200 give the same results as shown in Table 1.

Concerning the kind of heteropoly compound, the acidity is found to decrease in the order H_3PW/SiO_2-200>H_3PMo/SiO_2-200>H_3P/SiO_2-200 (where H_3P denotes the phosphoric acid, H_3PO_4) and H_3PW/SiO_2-200>KH_2PW/SiO_2-200>K_2HPW/SiO_2-200>K_3PW/SiO_2-200. The former order of acidity corresponds to that of acid strength measured in acetone,[7] and is estimated from the formation constant for polyanions with chloral hydrate.[8,9] Also, Misono has reported that the amount of strong acid decreases with increasing cation content, in parallel with a change in catalytic activity.[10]

It is natural that the acidity function depends on

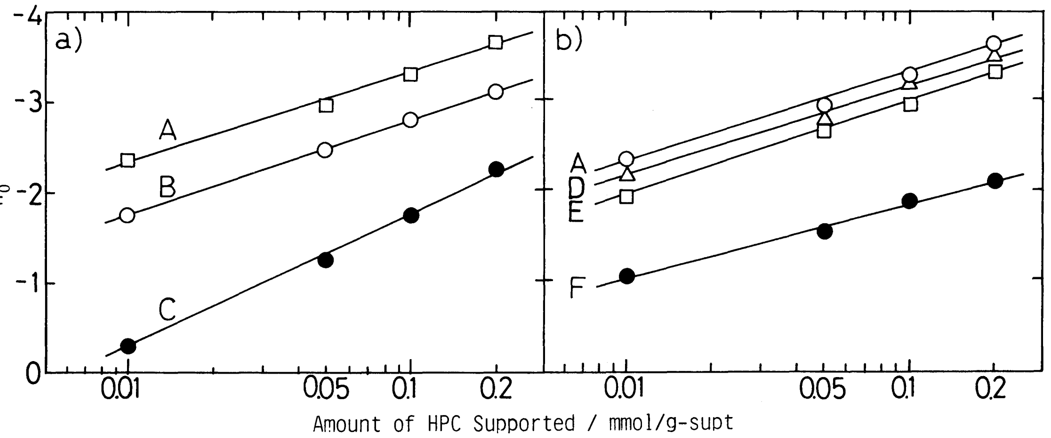

Fig. 2. The plots of acidity function H_0 against amount of HPC supported on SiO_2-200. a) A: H_3PW/SiO_2-200; B: H_3PMo/SiO_2-200; C: H_3P/SiO_2-200; b) A: H_3PW/SiO_2-200; D: KH_2PW/SiO_2-200; E: K_2HPW/SiO_2-200; F: K_3PW/SiO_2-200.

Table 1. The Value of the Acidity Function H_0 for HPC Supported on AEROSIL-200 and Their Slope against the Amount of HPC Supported

HPC[a)]	Acidity function H_0				Slope[c)]
	m=0.01[b)]	m=0.05[b)]	m=0.10[b)]	m=0.20[b)]	
H_3PW	−2.40	−2.94	−3.31	−3.66	−1.10
H_3PMo	−1.78	−2.52	−2.90	−3.20	−1.07
H_3P	−0.30	−1.25	−1.75	−2.25	−1.45
KH_2PW	−2.17	−2.89	−3.22	−3.51	−1.08
K_2HPW	−1.94	−2.71	−2.96	−3.30	−1.06
K_3PW	−1.05	−1.54	−1.89	−2.14	−0.93
$(NH_4)H_2PW$	−2.27	−3.04	−3.20	−3.57	−1.07
$(NH_4)_2HPW$	−2.10	−2.85	−3.10	−3.44	−1.05
$(NH_4)_3PW$	−1.27	−1.80	−2.13	−2.38	−0.95
KH_2PMo	−1.75	−2.44	−2.70	−2.95	−0.95
K_2HPMo	−1.50	−2.18	−2.48	−2.80	−0.98
K_3PMo	−1.40	−2.00	−2.25	−2.53	−0.86
NaH_2PMo	−1.76	−2.53	−2.65	−3.22	−1.10
Na_2HPMo	−1.57	−2.26	−2.60	−2.92	−1.08
Na_3PMo	−1.20	−1.98	−2.25	−2.56	−1.06
$(BiO)H_2PMo$	−1.72	−2.31	−2.80	−2.96	−1.06
$(BiO)_2HPMo$	−1.47	−2.10	−2.45	−2.67	−0.91
$(BiO)_3PMo$	−1.26	−1.92	−2.11	−2.40	−0.86

a) The support used is AEROSIL-200 (S=200 m^2 g^{-1}). b) m (mmol g-supt^{-1}) means the amount of HPC supported on AEROSIL-200. c) "Slope" means the slope of the plots for the acidity function H_0 against the amount of HPC supported log m.

the number of cations substituted for hydrogen ions. A similar trend, in which the acidity decreases with hydrogen-ion substitution, was observed in case of other cations.

Correlation between the Catalytic Activity and the Acidity Function, H_0. Acid catalysis activity has been related to the strength and/or the amount of acid.[10–12)] Figures 3 and 4 show plots of the apparent rate constants, k_1' (min^{-1}), and the rate constants, k_0 (mol g^{-1} h^{-1}), for the dehydration of liquid and gaseous TBA[1)] against H_0, respectively. It is apparent that they are empirically formulated as follows for the dehydration of liquid TBA:

$$\log k_1' = -H_0 + \text{const.} \tag{3}$$

For gaseous TBA,

$$\log k_0 = -(1-\delta)\cdot H_0 + \text{const.} \tag{4}$$

As can be seen from the dehydration of liquid TBA in Fig. 3, a large majority of the plots of log k_1' vs. H_0 are on the same line with a slope of −1. These results support the idea that the apparent rate constant k_1' in the dehydration of liquid TBA is an available measure for the surface acidity of the catalyst. Other lines with a slope of −1 for H_3PMo/SiO_2-200, H_3PW/SiO_2-200, $Na_nH_{3-n}PMo/SiO_2$-200 (n=1—3) and $(NH_4)H_2PW/SiO_2$-200 are considered to be due to a strong interaction of the acid site and the alcohol.

For the dehydration of gaseous TBA, however, it is found that the slope of log k_0 vs. H_0 varies with the kind of catalyst (Fig. 4); plots for H_3PW/SiO_2-200, H_3PMo/SiO_2-200, and KH_2PMo/SiO_2-200 are on the same line, with a slope of −0.63. Those for K_2HPMo/SiO_2-200 and K_3PMo/SiO_2-200 are on the other line, with a slope of −1.50.

Therefore, H_0 affects the activity for the dehydration of TBA. A similar correlation between the acidity and

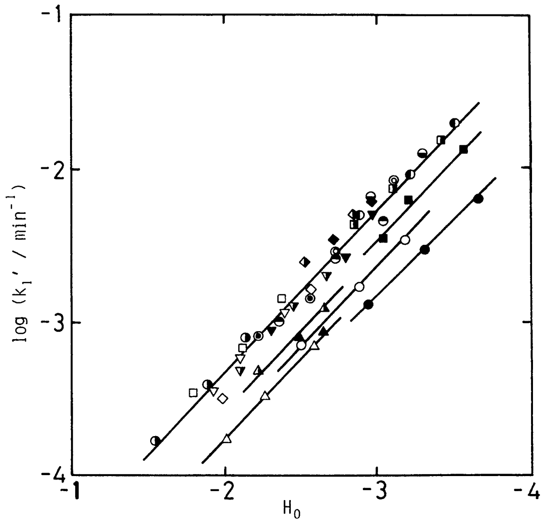

Fig. 3. The relation between the apparent rate constants k_1' for the dehydration of liquid TBA at 355.3 K and the acidity function H_0. ●: H_3PW, ◐: KH_2PW, ◒: K_2HPW, ◑: K_3PW, ■: $(NH_4)H_2PW$, ◧: $(NH_4)_2HPW$, □: $(NH_4)_3PW$, ○: H_3PMo, ◆: KH_2PW, ⬖: K_2HPMo, ⬗: K_3PMo, ▲: NaH_2PMo, ◭: Na_2HPMo, △: Na_3PMo, ◎: CsH_2PMo, ◓: Cs_2HPMo, ⊙: Cs_3PMo, ▼: $(BiO)H_2PMo$, ⧩: $(BiO)_2HPMo$, and ▽: $(BiO)_3PMo$ supported on SiO_2-200.

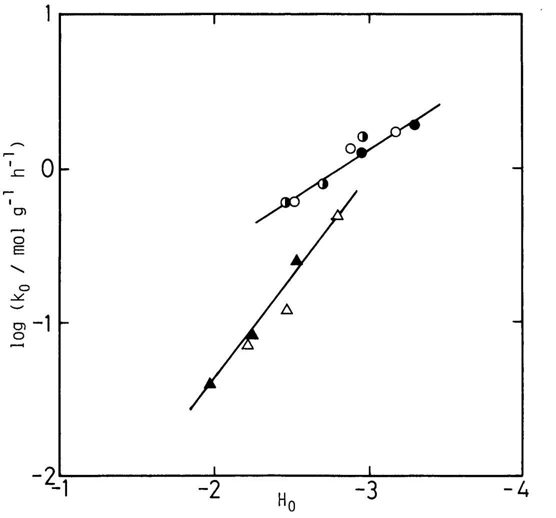

Fig. 4. The relation between the rate constants k_0 for the dehydration of gaseous TBA at 453 K and the acidity function H_0. ●: H_3PW, ○: H_3PMo, ◑: KH_2PMo, △: K_2HPMo, ▲: K_3PMo supported on SiO_2-200.

the catalytic activity in a homogeneous system was proposed by Paul and Long.[13,14]

Mechanisms of the Dehydration of *t*-Butyl Alcohol. In conformity to the theoretical procedure proposed by Paul and Long,[13,14] the following mechanisms are postulated regarding the present system:

$$R + A \underset{}{\overset{K_R}{\rightleftarrows}} R\cdot A \tag{5}$$

and

$$R\cdot A \xrightarrow{r} P + H_2O + A, \tag{6}$$

where A is an active acid site on the catalysts and R, R·A, and P denote the reactant TBA, adsorbed species with TBA, and isobutene produced, respectively. Eq. 6 is assumed to be the rate determining step.

Taking the activated complex (transition state) theory into consideration, the rate, r, is expressed as

$$r = k'\cdot[(R\cdot A)^{\neq}] = k'\cdot K^{\neq}\cdot K_R\cdot[R]\cdot f_R\cdot a_H'/f^{\neq}, \tag{7}$$

where f_R and $f^{\neq}$ stand for the activity coefficients for the reactant, R, and the activated complex, $R\cdot A^{\neq}$, respectively. a_H' is the proton activity, and k' the rate constant of Eq. 6, and $K^{\neq}$ $(=[(R\cdot A)^{\neq}]/[(R\cdot A)])$ the equilibrium constant between the activated complex $(R\cdot A)^{\neq}$ and the adsorbed species $(R\cdot A)$.

Taking into consideration the kinetics of the dehydrations of TBA,[1] the experimental apparent rate constant, k, which corresponds to k_1' or k_0 in the dehydration of liquid and gaseous TBA, may generally be related to k' as

$$\log k = \log k' + \text{const.} \tag{8}$$

If the value of a_H' in a catalytic reaction experiment is proportional to a_H in indicator adsorption type, the relation for a heterogeneous catalysis can be written as follows from Eqs. 7 and 1b:

$$\log k = -H_0 + \log\{(f_{IA}/f_{IB})(f_R/f^{\neq})\} + \text{const.} \tag{9}$$

If the value of $(f_{IA}/f_{IR})(f_R/f^{\neq})$ is approximately unity, the second term Eq. 9 becomes negligible; therefore,

$$\log k = -H_0 + \text{const.} \tag{10}$$

$f_{IA}/f_{IB} = f^{\neq}/f_R$ implies that the protonation behavior of TBA as a reactant is similar to that of DCA. This formula satisfies Eq. 3, which is an empirical one for the dehydration of liquid TBA.

In a homogeneous acid catalysis the slope of the correlation between the catalytic activity and the acidity function has been verified to be -1.[13,14] Therefore, the results in Fig. 3 prove that liquid TBA is dehydrated through a pseudo-liquid mechanism.[15] This is consistent with our previous conclusion based on kinetic data.[1]

In the case that the value of $(f_{IA}/f_{IB})(f_R/f^{\neq})$ is different from unity (Eq. 11), on the basis of Eq. 1b, assuming the second term of Eq. 9 is proportional to H_0,

$$\log k = -(1-\delta)\cdot H_0 + \text{const.} \tag{11}$$

Here, δ is a parameter which depends on the activity coefficients of the reactant and the activated complex formed on the surface of the catalyst. This also agrees with an empirical formula (Eq. 4) for the dehydration of gaseous TBA.

In contrast to the dehydration of liquid TBA, any deviation from -1 of the slope supports the idea that the dehydration of gaseous TBA proceeds through an outer-surface mechanism.[1]

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