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Catalysis by Heteropoly Compounds. III.† The Structure and Properties of 12-Heteropolyacids of Molybdenum and Tungsten ($H_3PMo_{12-x}W_xO_{40}$) and Their Salts Pertinent to Heterogeneous Catalysis

Makoto MISONO,* Noritaka MIZUNO, Koichi KATAMURA, Atsushi KASAI, Yasuo KONISHI, Kanji SAKATA, Toshio OKUHARA, and Yukio YONEDA
Department of Synthetic Chemistry, Faculty of Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113

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The fundamental properties of 12-heteropolyacids of Mo and W, such as the structure, the surface area, the acidity, and the reduction-oxidation mechanism, have been studied in their solid state in relation to heterogeneous catalysis. The primary structure (heteropolyanion) was rather stable, but the secondary structure was very variable according to the interaction with various molecules, like water, alcohols, ketones, and pyridine. This structural characteristic is important for the understanding of the catalysis of these compounds; it may be called the "pseudo-liquid phase." The heteropolyacids were all strong protonic acids, as revealed by the interaction with pyridine. The redox cycle was reversible within a limited extent of reduction. The redox mechanism is also discussed in this paper.

Heteropoly compounds have recently attracted much attention as catalysts for various industrial processes, such as oxidation, hydration, esterification, and etheration.[1] Considerable efforts have also been devoted to them in basic studies. It is hoped that the structure of the catalyst can be defined on a molecular scale of the heteropolyanion.[2,3]

We have studied the acidic and redox properties of several heteropoly compounds in their solid state and have attempted to correlate these properties with the catalytic actions.[2] In our opinion, the "pseudo-liquid phase" hypothesis we have proposed represents one of the very important aspects of heteropolyacid catalysis.[4] These studies are, in a sense, an extension of our early efforts at the design of catalysts based on the relationships between the acidity or the oxidizing power and the catalytic activity or selectivity.[5] Possible way of catalyst design based on heteropoly acids has also been discussed before.[6]

In the present paper, we wish to report some of the fundamental properties pertinent to the heterogeneous catalysis of heteropolyacids, such as the structure, the water content, the surface area, the pore-size distribution, and the acidic and redox properties. The heteropolyacids studied are 12-heteropolyacids of Mo and W containing P as the heteroatom.

Experimental

X-Ray Diffraction Powder Pattern. The powder pattern of X-ray diffraction was recorded on an X-ray diffractometer (Rigaku Denki, Rotaflex). When heteropoly acids or their salts were very water-soluble, samples were usually pretreated in nitrogen or helium saturated with water vapor. In the case of heat-treated samples, they were quickly set on a sample holder and covered with a Mylar film.

Infrared Spectra. About a 5-mg portion of the sample was deposited on a silicon plate or pressed into a KBr disk, and the spectra were recorded in an in situ IR cell by means of an FT-IR spectrometer (JEOL JIR-10), as has been described previously.[7,8]

Other Properties. The water content and the amount of pyridine absorption were measured by the use of a quartz spring balance. The surface area and pore-size distribution were measured by means of the absorption of nitrogen. The latter was kindly measured at the Daicel Chem. Ind. Co., Ltd., by the use of a Sorptomatic 1800 apparatus (Carlo Erba), based on the BJH equation.[24]

Materials. $H_3PW_{12}O_{40}\cdot nH_2O$ (A) was prepared according to the literature.[9] $Na_2WO_4\cdot 2H_2O$ (100 g) and $Na_2HPO_4\cdot 12H_2O$ (50 g) were added to 160 ml of decationized water, and the mixture was refluxed at 80 °C with stirring. Then, 24% HCl (150 ml) was added to the solution at 80 °C. After the solution had been concentrated to a volume of 100 ml by evaporation at 50 °C, it was cooled to room temperature. $H_3PW_{12}O_{40}$ was extracted with an equal amount of diethyl ether (with slow agitation after the addition of several drops of 35% HCl). The ether was removed by keeping the etherate at 50 °C. Then it was dissolved in water and concentrated at 50 °C. Recrystallization from an aqueous solution and drying in a KOH-desiccator for 2 d formed $H_3PW_{12}O_{40}\cdot 21$—$22H_2O$. $H_3PW_{12}O_{40}\cdot nH_2O$ (B) was prepared by extraction with ether from a 50% aqueous solution of $H_3PW_{12}O_{40}$ obtained from the Nippon Inorganic Colour and Chemical Co., Ltd. After evacuation at room temperature, the *n* value was 6 for both samples.

$H_3PMo_{12}O_{40}\cdot nH_2O$(A) was prepared by extraction with ether from a 50% aqueous solution of $H_3PMo_{12}O_{40}$ obtained from the Nippon Inorganic Colour and Chemical Co., Ltd. The $H_3PMo_{12}O_{40}\cdot nH_2O$(B) was kindly donated by the Climax Molybdenum Co. (Japan), Ltd. Two samples different in source, (A) and (B), behaved very similarly, so that, unless otherwise stated, no distinction of the two samples will be made in the following description.

$H_3PW_6Mo_6O_{40}\cdot nH_2O$ was prepared as follows. $Na_2WO_4\cdot 2H_2O$ (45.1 g), $Na_2MoO_4\cdot 2H_2O$ (33.0 g) and $Na_2HPO_4\cdot 2H_2O$ (8.15 g) were dissolved in 200 ml of decationized water. The solution was kept at 80 °C for 3 h with agitation and then concentrated to 80 ml by the use of an evaporator. Then, 100 ml of 24% HCl was added (the solution was yellow). After extraction with ether at room temperature, the crystal

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† Part I: *Proc. 7th Intern. Congr. Catal., Tokyo 1980*, Kodansha, Tokyo, and Elsevier, Amsterdam (1981), p. 1047; Part II: *Nippon Kagaku Kaishi*, accepted for publication.

was obtained in the same way as $H_3PMo_{12}O_{40}\cdot nH_2O$. The other $H_3PW_{12-x}Mo_xO_{40}$'s were similarly prepared.

The alkali salts were prepared by slowly adding equivalent amounts of alkali carbonates (aqueous solution) to the aqueous solutions of heteropolyacids following the methods in the literature.[10] The Na salt was obtained by removing water at 50—60 °C. The K and Cs salts were precipitated from a solution and evaporated to dryness.

Results

XRD and IR. Figure 1 shows the IR spectra and XRD of $H_3PMo_{12}O_{40}$ and some of its salts. These results were briefly reported before.[2] Figure 1 demonstrates that the pattern changed markedly depending on the kind of metal species. The XRD pattern of $H_3PMo_{12}O_{40}$ varied significantly also upon dehydration and rehydration. On the other hand, the IR spectra in the range of 600—1100 cm^{-1} characteristic of the heteropolyanion were quite similar with one another, indicating that the Keggin structure of the heteropolyanion (primary structure) remained unchanged. The changes in the secondary structures upon the dehydration of $H_3PMo_{12}O_{40}$ and its salts have recently been reported by Eguchi *et al.*[11] Their results and conclusion are in general agreement with ours. The IR band at *ca.* 1610 cm^{-1}, which is the bending mode of the water of crystallization, was observed for all salts, the intensity being smaller for K and Cs salts. The band at *ca.* 1720 cm^{-1}, which was presumably to be assigned to $H^+(H_2O)_n$, disappeared upon the salt formation.[8]

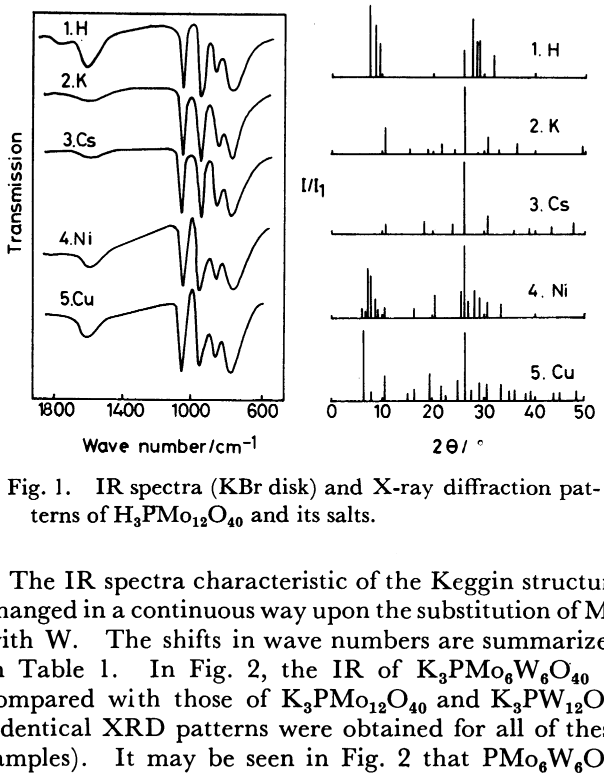

Fig. 1. IR spectra (KBr disk) and X-ray diffraction patterns of $H_3PMo_{12}O_{40}$ and its salts.

The IR spectra characteristic of the Keggin structure changed in a continuous way upon the substitution of Mo with W. The shifts in wave numbers are summarized in Table 1. In Fig. 2, the IR of $K_3PMo_6W_6O_{40}$ is compared with those of $K_3PMo_{12}O_{40}$ and $K_3PW_{12}O_{40}$ (identical XRD patterns were obtained for all of these samples). It may be seen in Fig. 2 that $PMo_6W_6O_{40}$ was not a mixture of $PMo_{12}O_{40}$ and $PW_{12}O_{40}$. Similar changes with the Mo/W ratio were also found for acid forms. However, since the bands were broader for acid forms, the distinction of $PMo_6W_6O_{40}$ from the mixture of $PMo_{12}O_{40}$ and $PW_{12}O_{40}$ was not possible by IR.

Table 1. Infrared bands of $K_3PMo_{12-x}W_xO_{40}$

x in $K_3PMo_{12-x}W_xO_{40}$	IR Band $\tilde{\nu}$/cm^{-1} [a]			
	P–O	M=O	M–O–M	
0	1064	964	867	794
2	1068	968	871	802
6	1072	971	877	800
10	1079	983	887±2	811±2
12	1079	983	890	813±4

Measured by FT-IR (resolution: 4 cm^{-1}), KBr disk.
a) Assignment after C. Rochioccioli-Deltcheff *et al.*, *Spectrochim. Acta, Part A*, **32**, 587 (1976).

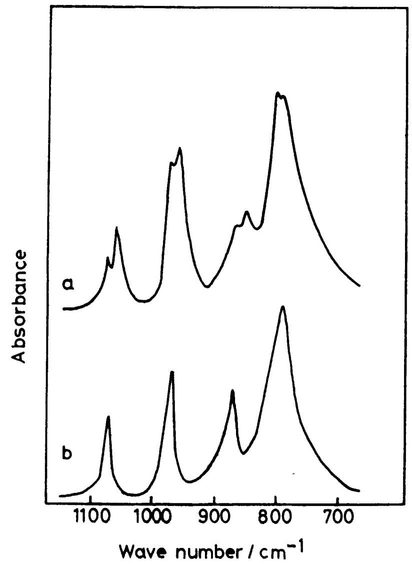

Fig. 2. IR spectra of the mixture of $K_3PMo_{12}O_{40}$ and $K_3PW_{12}O_{40}$ (a) and $K_3PMo_6W_6O_{40}$ (b) (KBr disk).

Water Content, Surface Area, and Pore-size Distribution. The changes in the water content and the surface area are shown in Table 2 for $H_3PMo_{12}O_{40}$ and $H_3PW_{12}O_{40}$. The surface area and water content were measured after the samples had been heated in a dry helium stream and after evacuation, respectively, at given temperatures. As we have reported before,[7] the dehydration of $H_3PMo_{12}O_{40}$ proceeded at low temperatures, and the surface area, showing a maximum value when treated at about 100 °C, decreased upon treatment at higher temperatures. The pore-size distribution of $H_3PMo_{12}O_{40}$ (B) is given in Fig. 3a. The surface area as estimated from the pore-size distribution was close to that obtained by the BET method. In the case of $H_3PW_{12}O_{40}$, dehydration proceeded at somewhat higher temperatures, and the change in the surface area was smaller. Two samples different in source gave similar results.

The IR bands of ν_{OH} ($\approx$3600 cm^{-1}) and δ_{H_2O} ($\approx$1610 cm^{-1} for Mo; $\approx$1700 cm^{-1} for W) due to the water of crystallization disappeared upon evacuation at 25 °C for $H_3PMo_{12}O_{40}$ and at 100 °C for $H_3PW_{12}O_{40}$. The

TABLE 2. WATER CONTENT AND SURFACE AREA (IN PARENTHESES) OF 12-TUNGSTO- AND 12-MOLYBDOPHOSPHORIC ACID AFTER HEAT TREATMENT

	Surface area (m^2 g^{-1}) and Water content (molecule/anion)[a]				
	Before treatment	Temperature of heat treatment (°C)			
		25	100	200	300
$H_3PW_{12}O_{40}$					
A	10	6.0 (—)	1.0 (4.8)	0.8 (—)	0.2 (4.7)
B	21	6.0 (3)	1.3 (4)	1.0 (8)	≈0 (5.5)
$H_3PMo_{12}O_{40}$					
A	22	5 (<0.1)	1.2 (13)	0.8 (8)	≈0 (3)
B	19	≈5 (<1)	1.2 (14)	1 (10)	≈0 (2)

a) It is assumed that heat treatment at 450°C causes $H_3PM_{12}O_{40} \rightarrow 1/2P_2O_5 + 12MoO_3 + 3/2H_2O$

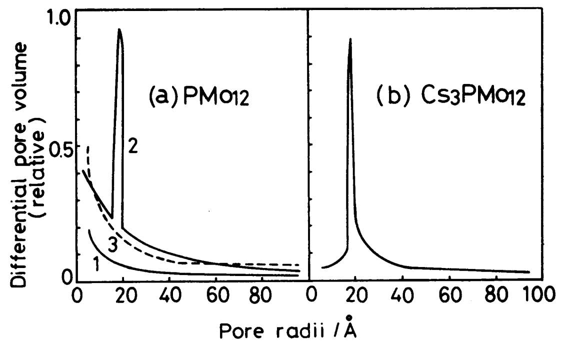

Fig. 3. Pore-size distibution.
(a) $H_3PMo_{12}O_{40}$, 1: treated at 25 °C, 2: at 110 °C, 3: at 300 °C. (b) $Cs_3PMo_{12}O_{40}$, treated at 110 °C.

bands at ≈3200 cm^{-1} of $H_3PMo_{12}O_{40}$, presumably attributable to $H^+(H_2O)_n$, remained below 200 °C, but the 1720 cm^{-1}-band became very small upon 25 °C-evacuation. The ν_{OH} band of $H_3PW_{12}O_{40}$ (3200 cm^{-1}) also decreased, but remained after the evacuation at 200—250 °C, while the bending modes of H_2O and $H^+(H_2O)_n$, which were not clearly separated into two peaks, almost disappeared upon 100 °C-evacuation. The Cs salt exhibited a very high surface area, which decreased upon heat treatment above about 300 °C. An example of the pore-size distribution is given in Fig. 3b.

The observation, by means of a microscope (×100) and a scanning-electron microscope (SEM) (×1000—5000), of the change in the appearance of $H_3PMo_{12}O_{40}$ upon heat treatment is summarized as follows. A sample was, before treatment, constituted of large lustrous particles whose surfaces were covered by fine particles *ca.* 10 μm in diameter. According to SEM, the surface of the particles was irregular (roughness in the order of 1—5 μm: probably primary particles) and had crevices of *ca.* 1 μm. After 100 °C-treatment, SEM indicated that the particles had grown (*ca.* 5 μm), possibly by experiencing partial melting. The surface had become less irregular, but the number and length of crevices (≈1 μm) had increased. After 450 °C-treatment, only aggregated fine particles (≈1 μm) were observed by SEM.

Acidic Properties. We reported previously that a considerable amount of pyridine was absorbed in the bulk of $H_3PMo_{12}O_{40}$.[8)] According to the weight measurement,[2,12)] $H_3PMo_{12}O_{40}$ and $H_3PW_{12}O_{40}$ absorbed several molecules of pyridine per heteropolyanion when they were brought in contact with pyridine vapor, and after evacuation at 100—150 °C, three molecules per anion, equivalent to the number of protons, remained in the bulk. The IR spectra showed that pyridine was present exclusively in the form of the pyridinium ion, indicating the formation of pyridinium salts. Broad bands which could be assigned to the ν_{N-H} of the pyridinium ion appeared in some cases at 2500—3000 cm^{-1}, but so far we have not been able to obtain sufficient reproducibility to confirm this band, although it would be good evidence to demonstrate the uniformity of the acid strength.

The acidity was measured by means of the thermal desorption of pyridine from the pyridinium salts. The results are given in Fig. 4. Only a small amount of pyridine was desorbed by the evacuation below about 300 °C in the case of $H_3PW_{12}O_{40}$. An increase in the evacuation period from 1 h to 4 h at 300 °C changed the results little. At 350 °C, the pyridine was removed gradually. In the case of $H_3PMo_{12}O_{40}$, the removal was not significant at 250 °C, but a considerable amount was desorbed above 300 °C. Examination by means of IR revealed that this removal was accompanied by

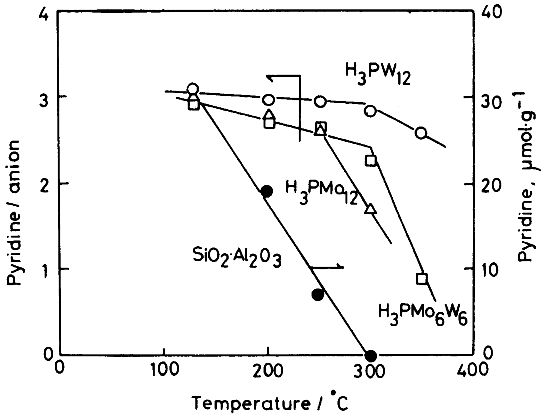

Fig. 4. Thermal desorption of pyridine.
Evacuated for 1 h at each temperature by increasing the temperature stepwise.

a partial degradation of the Keggin structure. The result for $H_3PMo_6W_6O_{40}$ was intermediate.

Redox Properties. The stoichiometry of the reduction by H_2 and re-oxidation by O_2 of $H_3PMo_{12}O_{40}$ has previously been reported.[2,4c] At 200—300 °C, reduction-oxidation by 2 electrons per polyanion proceeded reversibly in a stoichiometric manner. By this redox cycle, the intensity of the IR bands assigned to P–O (1060 cm^{-1}) and Mo–O–Mo (880 and 790 cm^{-1}) changed reversibly. However, when $H_3PMo_{12}O_{40}$ was reduced by 4 electrons per anion, the O_2-uptake was only 36% of the preceding H_2-uptake (72% of the amount required to re-oxidize to the original oxidation state). In this case, the IR spectrum after re-oxidation resembles that before reduction, but it was not identical. The sample pre-reduced by 8 electrons was re-oxidized only to 56%, and the IR spectrum after re-oxidation was significantly different. Reduction at 350 °C by 30 electrons per anion resulted in the formation of a mixture of MoO_3 and MoO_2, as revealed by XRD. Reduction by 3 electrons in the presence of water vapor was nearly reversible.

In the case of the reversible redox cycle, water (collected for 1—2 h by a trap kept at the temperature of liquid N_2) was evolved in both the reduction and re-oxidation steps. In the reduction step at 300 °C, only a half of the H_2 absorbed was collected as water. The rest was collected in the subsequent re-oxidation step, satisfying the stoichiometry, $H_2+1/2O_2 \rightarrow H_2O$. As the temperature increased, the water evolved in the first step increased. The fact that only a part of the H_2 observed was collected as water in the reduction step is not likely to be the result of the incomplete desorption of water which had already been formed in this step, because only a negligible amount of water was collected by pumping after the reduction. Therefore, the water collected in the re-oxidation step was probably formed by the reaction with O_2. This idea was confirmed further by the temperature-programmed desorption (TPD) and reduction (TPR).[13] According to TPR, $H_3PW_{12}O_{40}$ was much less reducible than $H_3PMo_{12}O_{40}$.

The reduction processes of other heteropolyacids and the correlation with the catalytic activity were previously reported briefly.[2,14] The details will be reported in forthcoming papers.

Interaction of Heteropolyacids with Inorganic and Organic Molecules. *Water*: A large amount of water was absorbed or desorbed rapidly in the case of acid forms. When D_2O was brought into contact with $H_3PW_{12}O_{40}$ at 25 °C after evacuation, the IR bands due to the water of crystallization (δ_{H_2O}) exhibited a very rapid shift (in 1 min) from the 1700 cm^{-1}-region to 1272 cm^{-1}.[12] A similar rapid exchange was also found in the case of $H_3PMo_{12}O_{40}$. According to the absorption isotherm of water, about one molecule of water was absorbed per anion at 300 °C for $H_3PMo_{12}O_{40}$ at 10—30 Torr**.

The oxygen exchange between water vapor and the heteropoly anion was also very rapid.[15] The oxygen of the heteropoly anion in the whole bulk (except for PO_4) of $H_3PMo_{12}O_{40}$ and $Cu_{3/2}PMo_{12}O_{40}$ exchanged at 150—250 °C, as was revealed by the IR isotope shifts (10—15 cm^{-1}).

CO_2 and O_2: The ^{18}O-exchange of $H_3PMo_{12}O_{40}$ with CO_2 was much slower than with H_2O. The rate was represented by a first-order rate equation where the whole bulk oxygen atoms participate equally. The exchange with O_2 was still slower, the rate being $H_2O \gg CO_2 \gg O_2$.

Other Molecules: The rate and amount of absorption varied from molecule to molecule. The pretreatment temperature also had an influence on the rate of absorption. For example, the absorption process of acetone was as follows (as monitored by IR bands). Over $H_3PMo_{12}O_{40}$ having about 5 molecules of crystal water (pre-evacuated at 25 °C), the amount of acetone which was absorbed within 30 min at 25 °C increased linearly with the pressure of acetone. However, in the case of $H_3PMo_{12}O_{40} \cdot H_2O$, there was a critical pressure for absorption. Acetone suddenly started to be absorbed when its partial pressure reached 60 Torr. The critical pressure was also observed for acrolein.

TABLE 3. ABSORPTION (AND ADSORPTION) OF VARIOUS MOLECULES BY $H_3PW_{12}O_{40}$ AT ROOM TEMPERATURE (MOLECULE/HETEROPOLY ANION)

Molecule	Irreversible	Total
Pyridine	6.0	>9
NH_3	3.2	4.3
2-Propanol	6.3	∞
Ethanol	6.2	∞
Methanol	2.2	∞
Benzene	0.1 (0.8)[a]	0.5
Toluene	0.04 (0.4)	0.4
1-Butene	0.2 (1.1)	0.25
Ethylene	0.03 (0.05)	0.04

a) Figures in parentheses are surface coverage.

The amounts of reversible and irreversible adsorption (or absorption) by $H_3PW_{12}O_{40}$ at 25 °C are given in Table 3. The uptake of hydrocarbons was very small. Probably adsorption took place only on the surface. In support of this idea, no change in the IR spectrum was found by contact with butene at 25 °C. On the other hand, polar molecules containing oxygen or nitrogen (O-base and N-base) were adsorbed rapidly, and 2—6 molecules per anion were retained in $H_3PW_{12}O_{40}$ after evacuation. Most of the O-bases were desorbed when evacuated at a slightly higher temperature. For example, changes upon heat treatment in the IR spectra of $H_3PMo_{12}O_{40}$ and $H_3PW_{12}O_{40}$ which had absorbed acetone are shown in Fig. 5. A large portion of the acetone observed for $H_3PMo_{12}O_{40}$ (1100—600 cm^{-1}) were changed to the reduced state after evacuation at 130 °C. When $H_3PMo_{12}O_{40}$ was evacuated at 130 °C in the absence of acetone, such a great change was not observed. In the case of $H_3PW_{12}O_{40}$ pre-evacuated at 25 °C, acetone was more easily absorbed into the bulk at a low pressure. This absorbed acetone was held in the bulk more tightly than in $H_3PMo_{12}O_{40}$. New peaks (1461, 1538, and

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** 1 Torr≈133.322 Pa.

1592 cm^{-1}) began to appear at 80 °C, accompanied by a decrease in the bands corresponding to acetone. Then, these new peaks increased with the increase in the evacuation temperature up to 130 °C. Their intensities were reduced at 160 °C.

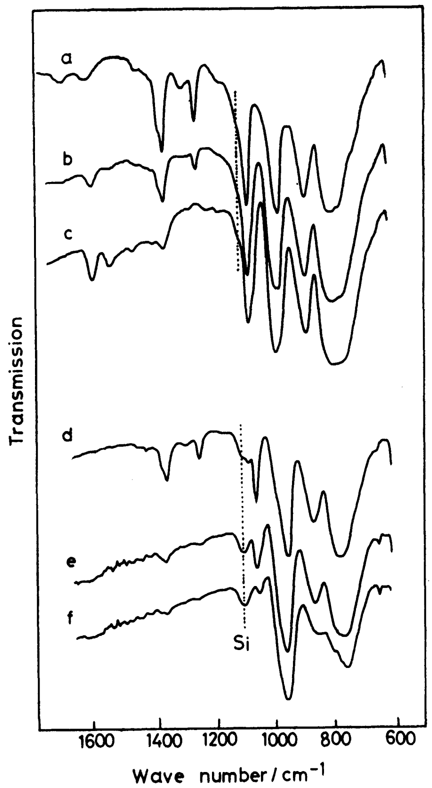


Fig. 5. Thermal desorption of acetone from $H_3PW_{12}O_{40}$ and $H_3PMo_{12}O_{40}$.
$H_3PW_{12}O_{40}$; a: Acetone (60 Torr) and evacuated at 25 °C, b: evacuated at 80 °C, c: evacuated at 130 °C. $H_3PMo_{12}O_{40}$; d: Acetone (120 Torr) and evacuated at 25 °C, e: evacuated at 80 °C, f: evacuated at 130 °C. Samples were pre-evacuated at 25 °C.

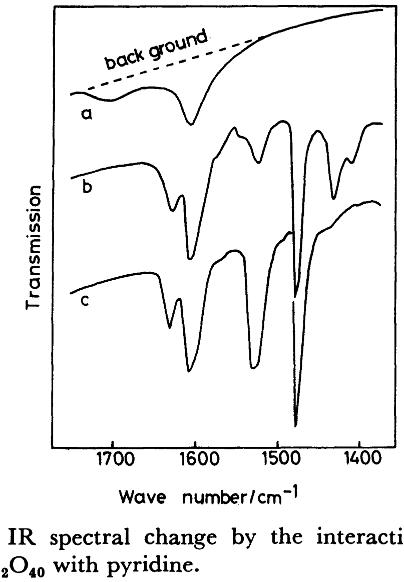


Fig. 6. IR spectral change by the interaction of $H_3PMo_{12}O_{40}$ with pyridine.
a: Evacuated for 30 s at 25° C, b: 1 h after the introduction of pyridine vapor (4 Torr), c: evaculated for 1 h at 130 °C after b.

The absorption of pyridine was followed by means of the IR, as is shown in Fig. 6. As the 1720 cm^{-1}-band and probably also the 1620 cm^{-1}-band disappeared, the 1540 cm^{-1}-band, characteristic of the pyridinium ion, appeared, together with the other bands of absorbed pyridine. Upon evacuation at 130 °C, the bands at 1400—1700 cm^{-1} became identical with that of the authentic pyridinium ion (Fig. 6c).[16] The re-addition of pyridine at 25 °C and evacuation at 130 °C reversibly changed the spectrum between b and c.

Discussion

Primary and Secondary Structure. As is shown by the IR spectra in Fig. 1, the Keggin structure is retained upon salt formation and dehydration (or rehydration). However, the XRD patterns which reflect a three-dimensional regularity vary tremendously. These facts led us to conclude that the "primary structure" (the Keggin unit) of heteropoly acids ($PMo_{12}O_{40}{}^{3-}$, in this case) is stable, but that the "secondary structure" (the three-dimensional arrangement of the heteropolyanion, water, and the counter cation) is subject to easy rearrangement.[2,4] We consider that a clear distinction between the primary and secondary structures is important for understanding the catalytic action of heteropoly acids. These characteristics make heteropoly acids behave like a solution, and in some cases the catalytic reactions proceed in the interstitial space of the bulk. This is the hypothesis of the "pseudo-liquid phase."[2,4] In this respect, water in the bulk and in the gas phase often plays an important role. Evidence to support the reactions in the bulk has previously been reported.[17,18]

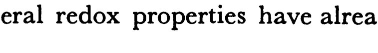
Since the lattice constant of $H_3PW_{12}O_{40}\cdot 29H_2O$ is 23.3 Å,[19a] and since the $H_3PW_{12}O_{40}\cdot 6H_2O$ which is formed by dehydration has the lattice constant of 12.5 Å,[19b] dehydration obviously causes a shrinkage of the unit cell. Adjacent heteropolyanions come much closer when water molecules between the anions are removed. Therefore, the water of crystallization is not zeolitic in this case. The pore-size distribution also supports this idea as has been discussed before.[7] Since the size of the Keggin unit is about 10 Å or a little greater in diameter, the pore size which would be expected from the zeolitic desorption of water should be 5—7 Å in radius for 29-hydrate and 1—2 Å for 6-hydrate. This does not agree with the pore-size distribution observed. Therefore, the pore actually measured must have been formed between fine primary particles which had been shrunk by dehydration. The apparent expansion of the volume by the absorption of water, pyridine, *etc.* also supports the idea that water is not zeolitic. These molecules penetrate into the bulk by expanding the interstitial space. A similar explanation may be applied to water-soluble metal salts. The dehydration-rehydration of 0—2 hydrates probably proceeds in essentially the same way, although no direct evidence has been obtained.

In the case of water-insoluble salts, like K, Cs, and NH_4 salts, almost the same XRD patterns, which were close to the ASTM card of K or NH_4 salt (9-408, 412), were reproducibly obtained, indicating that the secondary structures of these salts are rather stable. Recently, Eguchi, Yamazoe, and Seiyama reported that water is zeolitic for these salts.[11)]

Acidic and Redox Properties. The acidic properties (amount, strength, and type (Brønsted or Lewis)) of ordinary solid acids can be determined most reliably when the thermal desorption of pyridine is measured by IR spectroscopy. Therefore, the thermal desorption of pyridine (or the thermal decomposition of pyridinium salt) given in Fig. 4 reasonably reflects the acidic properties of these compounds. The amount of pyridine which remained after evacuation represents the amount of acidic protons, and the change in this amount by the evacuation temperature is related to the acid-strength distribution. Although the number of pyridine did not change by a prolonged period of evacuation, we are still uncertain whether or not these data reflect the true equilibrium. Therefore, we will discuss here only the number of acidic protons and the qualitative trend of the acid strength.

The quantity of pyridine which was not removed by 100—250 °C-evacuation agreed with the total number of protons for three heteropoly acids. Thus, uniform pyridinium salts were formed after this procedure. This uniformity enables us to estimate the number of acidic protons on or near the surface. If one assumes the surface area to be 10 m^2 g^{-1}, and the number of Keggin units on the surface to be 1/100 $Å^2$, the number of the surface acidic proton becomes 50 μeq g^{-1}, which is comparable with the value of 30—50 μeq g^{-1} of Brønsted sites for SiO_2–Al_2O_3.[21)] As for the acid strength, we may conclude qualitatively that heteropolyacids are stronger than SiO_2–Al_2O_3, since the pyridinium ion on SiO_2–Al_2O_3 almost disappears upon evacuation above 300 °C, as is shown in Fig. 4. Pyridine started to be removed at about 250 °C in the case of heteropolyacids containing Mo. However, a partial degradation was indicated by the IR in this case, so that the desorption at lower temperatures does not necessarily mean that their acid strength is weaker than $H_3PW_{12}O_{40}$.

The IR spectra of pyridine absorbed changed by evacuation at 130 °C and the readdition of pyridine at 25 °C, as is shown in Fig. 5. This process was reversible, and the spectrum after evacution (Spectrum d) was identical with the authentic pyridinium salt given in the literature.[16)] It was suggested that the 1540-cm^{-1}-band characteristic of the pyridinium ion becomes weak when a dimer ion is formed.[20)] Therefore, the change taking place between Spectra b and c in Fig. 5 may be as follows, if one takes into account the fact that the pyridine/proton ratio was about two after evacuation at 25 °C:



The general redox properties have already been discussed by several investigators.[2,4,13,22,23)] We will discuss here only the spectral changes in the IR spectra given in Fig. 5. The spectral change in $H_3PMo_{12}O_{40}$ in the 600—1100 cm^{-1} region may be due to the reduction of $H_3PMo_{12}O_{40}$ by acetone, since it is much more reducible than $H_3PW_{12}O_{40}$ and the spectral change resembles that found upon reduction by H_2.[2,13)] The new peaks which appeared at 1400—1600 cm^{-1} for $H_3PW_{12}O_{40}$ may be attributed to the mesityl oxide formed from acetone, since mesityl oxide absorbed by $H_3PW_{12}O_{40}$ gave IR bands at 1619, 1442, and 1376 cm^{-1}.

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