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STRUCTURE AND ACIDITY OF 12-MOLYBDOPHOSPHORIC ACID AND ITS SALTS IN SOLID STATE AS CHARACTERIZED BY INFRARED SPECTROSCOPY

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Presence of water was found to be essential to maintain the Keggin structure of 12-molybdophosphoric acid (PMo_{12}). Hydronium ion was detected by IR at high water contents. PMo_{12} was almost pure Brönsted acid as seen from IR spectra of adsorbed pyridine. Dependencies of the spectra on time, temperature, and presence of water were discussed in relation to the characteristic surface properties of PMo_{12}.

Heteropoly acids and related compounds are known to be interesting catalysts, both in homogeneous and in heterogeneous systems.[2-4)] We reported previously novel surface properties of 12-molybdophosphoric acid, $H_3PMo_{12}O_{40}\cdot nH_2O$ (abbreviated hereafter as PMo_{12}).[5)] We wish to report here further findings which demonstrate the characteristic properties of PMo_{12} as a solid catalyst.

PMo_{12} samples used for the IR study were prepared as described previously.[5)] Cs, Ni, and Cu salts of PMo_{12} were prepared from PMo_{12} and corresponding metal carbonates. They were treated variously in an in situ IR cell[6)] furnished with NaCl windows and all the spectra were recorded at room temperature on a JEOL JIR-10 Fourier transform infrared spectrometer. Use of PMo_{12} and its salts supported on a thin silicon plate and NaCl windows made possible the IR measurement in the range of 600 - 1100 cm^{-1}. Deuteration of PMo_{12} was carried out by repeated D_2O-addition and evacuation cycles at 25°C. Usually about 300-times accumulation of spectra was performed to obtain sufficient S/N ratios.

Effects of Temperature and Water Vapor on the Structure of PMo_{12}. Figure 1 shows the IR spectra of PMo_{12} heated in vacuum at various temperatures. The spectrum of PMo_{12} before heat treatment (spectrum a) was essentially the same as reported.[7)] The bands at 1060 and 960 cm^{-1} are assigned to the P-O stretching and the stretching of outer Mo=O bond, respectively, following the literature.[7)] The broad bands at 890 and 790 cm^{-1} are due to the Mo-O-Mo deformation. With the rise in heating temperature to 130 - 300°C, the band at 960 cm^{-1} shifted to 980 cm^{-1}, while the other bands changed only slightly (Fig. 1, a-c). Addition of water vapor to this sample shifted the band back to 960 cm^{-1}. Reversible incorporation of water occurs in this temperature range.[5)] So this shift probably reflects the reversible change in the interaction between the outer Mo=O bonds and crystalline water. Considerable changes in IR spectra observed after 400°C-evacuation (Fig. 1, d; particularly, 1060 cm^{-1}-band) likely arise from partial or complete destruction of Keggin structure of PMo_{12}. Formation of MoO_3 structure was actually indicated from the X-ray diffraction. When water vapor

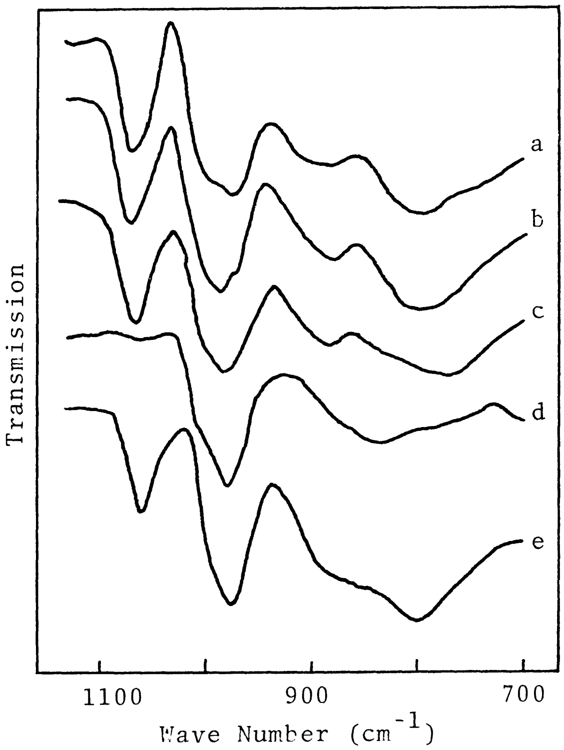

Fig. 1. IR SPECTRA OF PMo_{12}

Treated in vacuum for 30 min at (a) 25°C, (b) 130°C, (c) 300°C, and (d) 400°C. (e) H_2O added to (d) at 300°C.

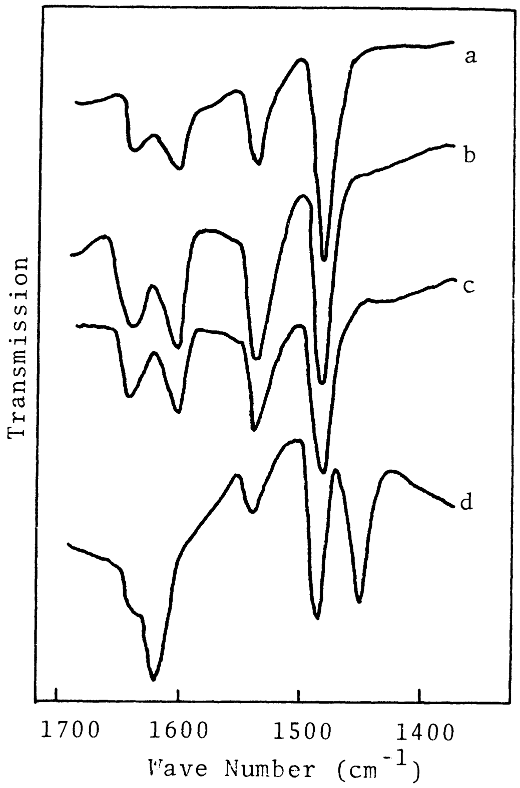

Fig. 2. IR SPECTRA OF PYRIDINE

Adsorbed on PMo_{12} preheated at (a) 130°C and (b) 300°C.
(c) Pyridinium ion[10].
(d) Adsorbed on silica-alumina[6].

was directed onto this sample and kept at 300°C for 30 min, the bands characeristic of the Keggin structure of PMo_{12} re-appeared to a considerable extent as shown in spectrum e in Fig. 1 (note the 1060 cm^{-1} band). These results demonstrate that water plays an important role in maintaining the Keggin structure particularly at high temperatures. In conformity with this idea, the IR bands of PMo_{12} heated at 400°C in the presence of water vapor closely resemble the spectrum e in Fig. 1, showing retention of the Keggin structure. Spectra very similar to spectra a-c in Fig. 1 were obtained for the salts of PMo_{12}. The structure of Keggin unit is also retained after salt formation. However, the powder patterns of X-ray diffraction changed considerably by the salt formation. The arrangement of the Keggin units probably differs among PMo_{12} and its salts.

IR spectrum of PMo_{12} pre-evacuated at 25°C for 1 min gave rise to broad bands at 3600-3200, ca. 1720, and ca. 1610 cm^{-1}. These bands became much weaker and apparently broader after severer evacuation at 130°C. Similar changes were observed for deuterated PMo_{12} in the 2700-2400 cm^{-1} range and at ca. 1200 cm^{-1}. A weak band at ca. 1290 cm^{-1}, which seems to correspond to the 1720 cm^{-1}-band of undeuterated PMo_{12}, was also observed. Bands at 3600-3200 and ca. 1610 cm^{-1}, which showed deuterium isotope shift, are assigned to the O-H stretching and the H_2O bending modes of crystalline water, respectively. NMR study on heteropoly acids showed the existence of hydronium ion in cation sites,[8] and hydronium ion in H_3OCl, H_3OBr, H_3OF, and H_3OI has a band at about 1700 cm^{-1}.[9] Based on these reports and our finding, the 1720 cm^{-1}-band for PMo_{12} (1290 cm^{-1} for deuterated PMo_{12}) can be assigned to hydronium ion. This band was absent with the salts of PMo_{12}.

Pyridine adsorbed or absorbed by PMo_{12}. Typical spectra of pyridine are shown in Fig 2. Spectra a and b were obtained for PMo_{12} samples, which were preheated respectively at 130°C and 300°C, after pyridine introduction and subsequent pumping off at 130°C for 1 hr. Bands at 1480 cm^{-1}, 1540 cm^{-1}, 1600 cm^{-1}, and 1630 cm^{-1} are exhibited. It is notable that the 1450 cm^{-1}-band indicative of both Lewis acid and hydrogen-bonded pyridine was very small or absent for PMo_{12}. These spectra more closely resemble that of pyridinium ion in chloroform (Fig. 2,c)[10] than that of pyridine adsorbed on silica-alumina in the range of 1600-1630 cm^{-1} (Fig 2,d). The close resemblance of adsorbed pyridine on PMo_{12} to liquid-phase pyridinium ion indicates that acid sites of PMo_{12} are protonic and that pyridinium ions (probably also protons before pyridine adsorption) are only loosely bound in the solid lattice.

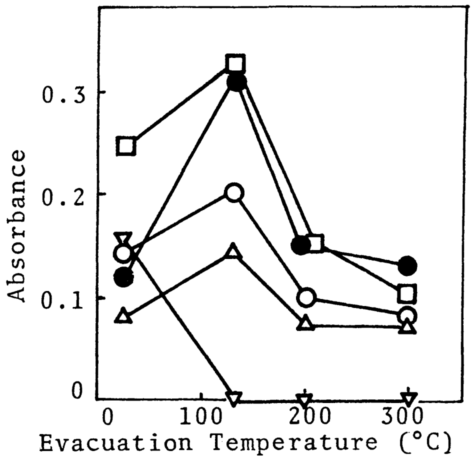

Fig. 3. EFFECTS OF EVACUATION TEMPERATURE UPON IR BANDS OF PYRIDINE ON PMo_{12}
(PMo_{12} was preevacuated at 300°C. Evacuation at each temperature was for 30 min.)
△ 1630cm^{-1}, ○ 1600cm^{-1}, ● 1540cm^{-1}
□ 1480cm^{-1}, ▽ 1450cm^{-1}

Figure 3 shows the changes in the absorbance of each pyridine band with increase in the evacuation temperature after adsorption. The 1450 cm^{-1}-band almost disappeared after 130°C-evacuation (see also Fig. 1,a). On the other hand, the bands at 1480, 1540, 1600, and 1630 cm^{-1} increased in intensity by the 130°C-evacuation. Then these four bands gradually decreased by further increase in the evacuation temperature, but they still remained considerably even at 300°C. It was reported that pyridine adsorbed on Brönsted sites of silica-alumina was very small after 300°C - evacuation and completely disappeared by 350°C-evacuation.[6] Therefore, PMo_{12} is probably a stronger Brönsted acid than silica-alumina. Naturally, pyridine remained little on the salts of PMo_{12} after evacuation, although the surface area was much higher in the case of Cs salt.

It was found further by careful study that the IR bands of pyridine on 200°C-preheated PMo_{12}, especially the band indicative of Brönsted acid, increased gradually with time in the presence of pyridine at room temperature (IR bands due to gas-phase pyridine were substracted by computer manipulation).[11] The band intensity was remarkably enhanced by the introduction of water vapor to the system (about three times). Since number of Lewis acids sites was very small, this increase is not due to the conversion of Lewis sites to Brönsted sites. Moreover, this high level of band intensity was also obtained, when the adsorption temperature was raised to 200°C, regardless of the presence of water vapor (the bands changed slightly by evacuation). In the case of silica-alumina, the formation of pyridinium ion on the surface is believed to be instantaneous and almost independent of the adsorption temperature. Therefore, the findings in the present study may demonstrate the characteristic feature of the surface properties of PMo_{12}, i. e., easy structural rearrangement of surface layer and rapid penetration of pyridine into the bulk in the presence of water vapor or at high temperatures. Weight increase caused by pyridine absorption suggests that the ratio of pyridine to Keggin unit can be more than unity.

In conclusion, water vapor stabilizes the Keggin units (primary structure) and at the same time makes the arrangement (secondary structure) of the Keggin units easily rearrangeable. Since heteropoly compounds are usually used as catalysts in the presence of steam, these roles of water may be very important in understanding the catalytic actions of heteropoly compounds.

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