CHEMISTRY LETTERS, pp. 709-712, 1978. Published by the Chemical Society of Japan

SURFACE PROPERTIES OF 12-MOLYBDOPHOSPHORIC ACID CATALYST

Makoto MISONO, Yasuo KONISHI, Motonobu FURUTA,1) and Yukio YONEDA
Department of Synthetic Chemistry, Faculty of Engineering,
The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113

Surface properties and catalytic activity for butene isomerization have been investigated for 12-molybdophosphoric acid. The surface area changed reversibly by dehydration and hydration below 300°C, but irreversible destruction was caused at 400°C. The catalytic activities per unit surface area were nearly constant. From these results and infrared spectra of pyridine adsorbed, strong protonic acidity probably of nearly uniform acid strength was concluded.

Heteropoly acids and related compounds function not only as acidic catalysts but also as selective and active catalysts in oxidation reactions like formation of methacrylic acid from methacrolein.2) Although the bulk structures of heteropoly acids have been subjects of several investigations,3) the surface properties such as acidity and surface structure have been investigated to much lesser extent. We studied these properties of 12-molybdophosphoric acid, a heteropoly acid. This compound may be considered to be a model compound for solid acid catalyst, of which the bulk structure is relatively well known.

12-Molybdophosphoric acid ($H_3PMo_{12}O_{40}\cdot xH_2O$, abbreviated hereafter as PMo_{12}) was obtained from Climax Molybdenum Co.(Japan) Ltd. It contained 19-20 water molecules per $PMo_{12}O_{40}$ unit (Keggin structure) as determined by weight decrease on heating at 450°C. Catalytic activity for butene isomerization was measured by pulse technique. About 100 mg of PMo_{12} loaded in a microreactor (6 mm o.d.) was preheated for 1 hr at a temperature between 50 - 450°C in a dry helium stream, where the temperature was raised slowly to a predetermined temperature. After the temperature was lowered to 50°C, cis-2-butene (100 μl) was pulsed. Surface area was measured by a gas chromatographic method by use of Yanagimoto GSA-10 at the nitrogen pressure of 230 Torr. PMo_{12} samples (about 100 mg each) were submitted to surface area measurement, after they were preheated in a U tube (6 mm o. d.) at several temperatures in a dry helium stream and weighed. During this procedure the influence of humidity was carefully avoided. Infrared spectra were recorded at room temperature on a Fourier transform infrared spectrometer (JEOL JIR-10) with the aid of an in situ cell as was described elsewhere.4) The samples for the infrared study were prepared by dipping thin silicon plates in PMo_{12} aqueous solution and subsequent drying.

The surface area and the extent of dehydration varied by heat treatment as shown in Fig. 1. Water molecules of crystallization were mostly removed by heating at 50 - 100°C, and only one or two water molecules were removed at 100 - 400°C. This is in general agreement with the TGA results.5) It was reported that PMo_{12} decomposes to P_2O_5 and MoO_3 above 350°C, losing ca. 1.5 molecules of water.[5] Surface area which was less than 0.1 m^2/g increased to more than 10 m^2/g (> 100 times) by the treatment between 100 - 150°C, and then declined by heating at higher temperatures. Prolonged treatment at each temperature had relatively small effects on the surface area and the water content. Rehydration in the stream of helium saturated with water vapor and subsequent heat treatment reproduced the changes in the surface area shown in Fig. 1, when the heat treatment was not higher than 300°C. The changes were not reversible when treated above 400°C, indicating the destruction of the Keggin structure between 300 and 400°C. These results are in accordance with the changes in the infrared absorption bands of PMo_{12} in 1100 - 700 cm^{-1} region.[6]

Pore distributions measured by nitrogen adsorption are given in Fig. 2. It is noteworthy that a very sharp distribution of pore size at about 20 Å in radius developed by the 110°C - treatment, in addition to pores having broad distribution which was observed commonly for three samples. This sharp distribution of pore size was formed reproducibly and seems to be related to the structural change between $H_3PMo_{12}O_{40} \cdot 19 - 20\ H_2O$ and $H_3PMo_{12}O_{40} \cdot 1 - 2\ H_2O$ caused by reversible hydration and dehydration.[7]

Catalytic activity of PMo_{12} for butene isomerization was high when treated at 100 - 150°C and declined by heating at higher temperatures, as the surface area did. The activity of PMo_{12} supported on silica gel also changed similarly by heat treatment.

Initial and stationary activities expressed by %conversion over 100 mg of PMo_{12} was nearly constant as shown in Fig. 3, when they are normalized to specific surface

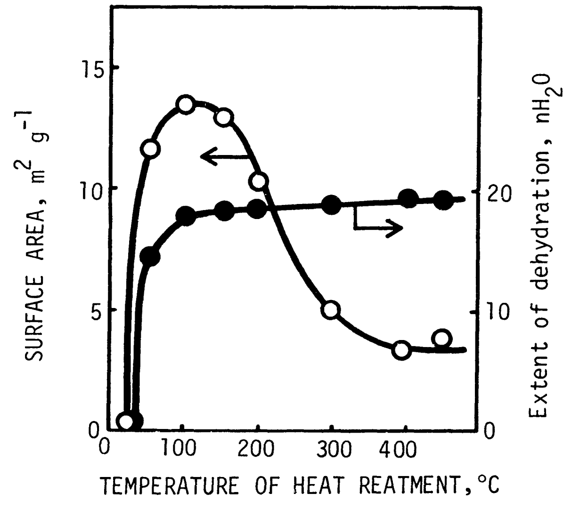

Fig. 1. SURFACE AREA AND EXTENT OF DEHYDRATION OF 12-MOLYBDO-PHOSPHORIC ACID TREATED AT VARIOUS TEMPERATURES

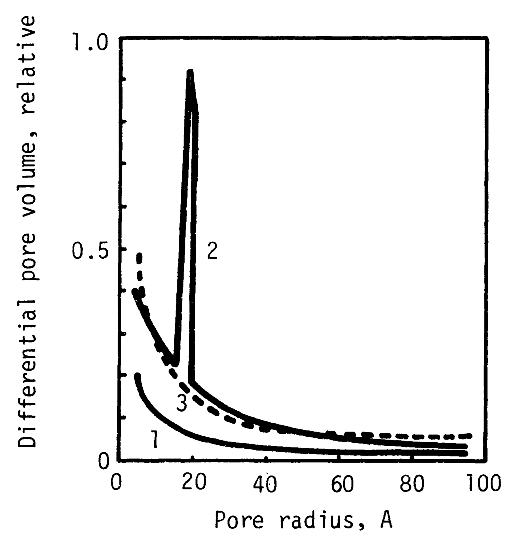

Fig. 2. Pore size distribution of 12-molybdophosphoric acid
1. Treated at 25°C (pore volume:0.026 cm^3/g), 2. treated at 110°C (0.027), 3. treated at 450°C (0.066).

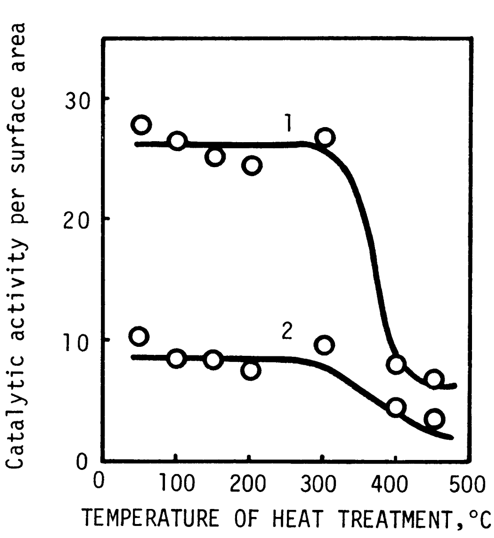

Fig. 3. CATALYTIC ACTIVITY FOR BUTENE ISOMERIZATION PER UNIT SURFACE AREA OF 12-MOLYBDOPHOSPHORIC ACID TREATED AT VARIOUS TEMPERATURES.

1. Initial activity, 2. stationary activity.

areas which are given in Fig. 1. Since the catalytic activity is strongly dependent on the acid strength,[9)] this result probably indicates that the acidity of PMo_{12} is nearly constant at least for PMo_{12} treated at temperatures not higher than 300°C. The trans-2-/1-butene ratio was 5 - 10, indicating that PMo_{12} is a strong acid.[9)] Corresponding to the reversible changes caused by hydration and dehydration described above, the stationary activity of PMo_{12} treated at 300°C increased to that of PMo_{12} preheated at 100 - 150°C, 10 - 15 min after a H_2O pulse. The recovery was only partial for PMo_{12} treated at 400°C.

Infrared spectra of pyridine which remained after evacuation at 200°C on PMo_{12} preevacuated at 200 or 300°C exhibited strong absorption bands at 1480, 1530, 1600, and 1630 cm.$^{-1}$ More than half of the intensity remained after evacuation at 300°C. These four bands show a close resemblance to those observed with pyridinium ion in chloroform and pyridinium ion-salts (1480 - 1490, 1525 - 1540, 1600 - 1610, and 1630 - 1640 cm^{-1}).[10)] Pyridinium ion reported for silica-alumina has bands at 1485 - 1500, 1540 - 1550, 1620 - 1630, 1630 - 1640 cm^{-1},[11)] difference in 1600 - 1630 cm^{-1} being noted.

Absorption band at 1450 - 1460 cm^{-1} which is characteristic of pyridine coordinated with metal ion (Lewis acid site)[10)] was very small or absent for PMo_{12}. Therefore, acidic sites of PMo_{12} are essentially of Brönsted (protonic) type after evacuation at temperatures not higher than 300°C.

Present findings are summarized as follows.

i) The number of water molecules of crystallization changes little at 100 - 300°C.
ii) The structure of $PMo_{12}O_{40}$ unit remains almost unchanged below 300°C. For PMo_{12} treated at temperatures not higher than 300°C, iii) water adds and leaves reversibly, iV) acidity per unit surface area is almost constant and v) it is protonic.

On the basis of these findings, it may be concluded that protons (three for one $PMo_{12}O_{40}$ unit) which exist on the surface of the $PMo_{12}O_{40}$ unit together with one or two molecules of water are the origin of the acidity and the catalytic activity for butene isomerization and that the acid strength is probably uniform.

The authors acknowledge Central Research Laboratory of Daicel Co. Ltd. for the measurement of pore size distribution.

References

1. On leave from Sumitomo Chemical Industry Co. Ltd.
2. M. Otake, T. Onoda, Shokubai, 18, 169(1976); T. Ohara, ibid., 19, 157(1977).
3. G.A. Tsigdinos, Molybdenum Chemicals Bulletin, cdb-12a (revised), Climax

Molybdenum Co., 1969; Y. Sasaki, K. Matsumoto, Kagaku no Ryoiki, 29, 853(1975).

4. K. Mizuno, M. Ikeda, T. Imokawa, J. Take, and Y. Yoneda, Bull. Chem. Soc. Jpn., 49, 1788(1976).

5. G.A. Tsigdinos, IEC, Prod. Res. Develop., 13, 267(1974).

6. M. Furuta, Y. Konishi, M. Misono, and Y. Yoneda, The 37th National Meeting of the Chemical Society of Japan, 3Q14, Yokohama, 1978.

7. Lattice constant of $H_3PWO_{40}\cdot 29H_2O$, in which $PW_{12}O_{40}$ unit (Keggin structure) and $H_3\cdot 29H_2O$ unit form a diamond-like lattice, is 23.3 Å, while that of $5H_2O$ crystal is 12.1 Å, $PW_{12}O_{40}$ units becoming closer with each other.[7] It is probable that careful removal of water molecules of crystallization under mild conditions causes the aggregation of $PW_{12}O_{40}$ units, leaving narrow open space between the aggregated particles (pores of 20 Å in radius). Treatments at higher temperatures likely result in extensive aggregation.

8. A.J. Bradley, J.W. Illingworth, Proc. Roy. Soc. (London), A157, 113(1936).

9. e.g., M. Misono and Y. Yoneda, J. Phys. Chem., 76, 44(1972).

10. D. Cook, Can. J. Chem., 39, 2009(1961).

11. L. Forni, Catal. Rev., 8, 65(1972); M. Ikeda, Bachelor's Thesis. Univ. of Tokyo, 1975.

(Received May 8, 1978)