CHEMISTRY LETTERS, pp. 501 - 504, 1985.

PROTONIC CONDUCTIVITY OF ALKALINE-EARTH METAL 12-TUNGSTOPHOSPHATES IN RELATION TO THEIR CATALYTIC ACTIVITY AS SOLID ACIDS

Masamichi AKIMOTO,* Masahide OKAMOTO, and Hiroo NIIYAMA
Department of Chemical Engineering, Tokyo Institute of Technology,
Ookayama, Meguro-ku, Tokyo 152

The protonic conductivity of alkaline-earth metal 12-tungstophosphates at solid state correlated their catalytic activity as solid acids for vapor-phase dehydration of ethanol.

Recently 12-tungstophosphoric acid, $H_3PW_{12}O_{40}$ and its metal salts have attracted much attention as a novel type of solid acid catalysts. The most striking feature of the catalysis by these 12-heteropoly compounds is that the reaction of alcohols takes place not only on the surface but also in the bulk of the catalysts,[1] and the promotional effect of water for incorporation of alcohols into the bulk of the catalysts has also been reported.[2] That is, for 12-heteropoly compounds their catalytic activity as solid acids in the reaction of alcohols is great when their Brønsted acid concentration is great and when their degree of hydration is great. On the other hand, a hydrated 12-tungstophosphoric acid, $H_3PW_{12}O_{40}\cdot 29H_2O$ has well been known to be a superior proton-conductive electrolyte(σ = 0.17 mho cm^{-1}).[3] Generally the mobility of protons in the bulk of solid acids is accelerated by hydrated water molecules.[4] Hence one could expect that the protonic conductivity of 12-heteropoly compounds is great when their proton concentration is great and when their degree of hydration is great. This feature of the protonic conductivity of solid 12-heteropoly compounds is analogous to that of their catalytic activity as solid acids in the reaction of alcohols described above. In the present work, we have first studied the effects of the concentration of protons as a cation and the degree of hydration on the protonic conductivity of solid alkaline-earth metal 12-tungstophosphates and have then compared it with their catalytic activity for vapor-phase dehydration of ethanol.

Guaranteed reagent grade 12-tungstophosphoric acid was purchased from Kanto Chemical Company,Inc. Its alkaline-earth metal salts were prepared by adding their corresponding metal carbonates into the aqueous solution of 12-tungstophosphoric acid (net 40 g in 40 ml water) at room temperature. The aqueous solution of metal salt obtained was then evaporated to dryness over silica gel under vacuum at room temperature. The degree of hydration was thermogravimetrically determined in flowing dried nitrogen. Protonic conductivities were determined by d.c. four probe method in flowing hydrogen(10 (NTP)ml/min). Here the salts(10 g) had well been pulverized and were then pressed into cylindrical shape(8-mm diameter × 40 mm long) at the pressure of 1 ton/cm^2 by rubber-pressing method:the lower and upper planes of the bulk samples obtained were polished by using a sand paper. Platinum plates(8.5-mm diameter × 0.3 mm thick), platinum black(100 - 200 mesh), and platinum wires(0.2-mm diameter) were used as the electrodes, the electrode catalyst, and the connecting wires, respectively.

Table 1. Summary of the degree of hydration

Salt(25 °C)	Degree of hydration/mol H_2O mol salt^{-1}					
	100 °C	125 °C	150 °C	175 °C	200 °C	250 °C
$Ca_{1/2}H_2PW_{12}O_{40}\cdot 8.59H_2O$	5.83	5.37	4.16	2.17	1.28	0.40
$CaHPW_{12}O_{40}\cdot 9.62H_2O$	6.15	5.75	4.77	3.36	2.37	1.05
$Ca_{3/2}PW_{12}O_{40}\cdot 8.92H_2O$	6.85	6.53	6.12	5.37	4.39	2.11
$Ba_{1/2}H_2PW_{12}O_{40}\cdot 7.22H_2O$	5.81	4.57	2.73	0.97	0.38	0.09
$BaHPW_{12}O_{40}\cdot 8.83H_2O$	6.61	4.78	2.92	1.20	0.41	0.11
$Ba_{3/2}PW_{12}O_{40}\cdot 8.56H_2O$	7.44	6.78	4.92	2.04	0.41	0.16
$Mg_{1/2}H_2PW_{12}O_{40}\cdot 8.70H_2O$	5.14	4.71	3.85	2.38	0.81	0.18
$Sr_{1/2}H_2PW_{12}O_{40}\cdot 7.59H_2O$	6.15	5.62	4.10	1.72	0.84	0.11

Catalytic dehydration of ethanol was carried out using a conventional flow fixed-bed reactor and reaction products were analyzed by gas chromatography.

Table 1 summarizes the degree of hydration for a series of alkaline-earth metal salts at 100 - 250 °C. For three types of calcium salts, the degree of hydration at 100 - 250 °C always follows the order $Ca_{1/2}H_2PW_{12}O_{40} < CaHPW_{12}O_{40} < Ca_{3/2}PW_{12}O_{40}$. A similar order of the degree of hydration is seen for barium salts. Thus the degree of hydration increased as the protons in $H_3PW_{12}O_{40}$ were replaced step by step by alkaline-earth metal ions. In addition, with the exception of some values at 100 and 125 °C the degree of hydration for these three types of calcium salts is always greater than that for the corresponding barium salts. Similarly, for a series of $M_{1/2}H_2PW_{12}O_{40}$ type salts(M = alkaline-earth metal) the degree of hydration at 150 - 200 °C increases in the order $Ba^{2+} < Sr^{2+} \leqq Ca^{2+} \cong Mg^{2+}$(Table 1). Although this order is not clear at 100 and 125 °C, it is undoubtedly an increasing order of the electronegativity of cations. The degree of hydration for solid alkaline-earth metal 12-tungstophosphates seems to be decisively affected by the electronegativity of alkaline-earth metal ions as cations on which water molecules are coordinated.

The protonic conductivities of solid alkaline-earth metal salts measured at 125 - 175 °C are summarized in Table 2. The results of previous experiments indicated that the reactions at platinum electrodes($H_2 \rightarrow 2H^+ + 2e$ at anode and $2H^+ + 2e \rightarrow H_2$ at cathode) are not rate-determining and that only charge carriers are protons. However, the protonic conductivity of 12-tungstophosphates showed a complicated behavior: it usually increased with rising temperature from 25 to 75 °C but it then rapidly decreased with further rise in temperature from 100 to 150 °C and it again increased above 150 °C. The observed increase in protonic conductivity with rising temperature is due to the effect of the activation energy on the mobility of protons whereas the observed decrease in protonic conductivity with rising temperature is caused by the evaporation of hydrated water. These two effects on the protonic conductivity compete each other at various temperatures. At any rate, the protonic conductivity of alkaline-earth metal 12-tungstophosphates varied from 10^{-6} to 10^{-4} mho cm^{-1} between 125 and 175 °C, and the protonic conductivity of $M_{1/2}H_2PW_{12}O_{40}$ and $MHPW_{12}O_{40}$ type salts was

Table 2. Summary of the protonic conductivity

Salt(25 °C)	Protonic conductivity/10^{-4}mho cm^{-1}		
	125 °C	150 °C	175 °C
$Ca_{1/2}H_2PW_{12}O_{40}\cdot 8.59H_2O$	0.209	0.187	0.633
$CaHPW_{12}O_{40}\cdot 9.62H_2O$	0.429	0.583	0.694
$Ca_{3/2}PW_{12}O_{40}\cdot 8.92H_2O$	0.174	0.030	0.015
$Ba_{1/2}H_2PW_{12}O_{40}\cdot 7.22H_2O$	1.10	2.58	6.35
$BaHPW_{12}O_{40}\cdot 8.83H_2O$	2.01	2.34	0.797
$Ba_{3/2}PW_{12}O_{40}\cdot 8.56H_2O$	0.426	0.352	0.215
$Mg_{1/2}H_2PW_{12}O_{40}\cdot 8.70H_2O$	0.184	0.194	1.19
$Sr_{1/2}H_2PW_{12}O_{40}\cdot 7.59H_2O$	0.282	0.277	1.19

always greater than that of $M_{3/2}PW_{12}O_{40}$ type salts(Table 2), as had been expected. However, the protonic conductivity of $CaHPW_{12}O_{40}$ is always greater than that of $Ca_{1/2}H_2PW_{12}O_{40}$ at 125 - 175 °C although the proton concentration follows the order $CaHPW_{12}O_{40} < Ca_{1/2}H_2PW_{12}O_{40}$(Table 2). This result is caused by the greater degrees of hydration for the former salt than for the latter salt at these temperatures(Table 1). The most interesting finding is that $M_{3/2}PW_{12}O_{40}$ type salts had also protonic conductivities of 10^{-6}- 10^{-5} mho cm^{-1} although these salts were neutral ones. This finding supports the previously reported mechanism of the generation of Brønsted acids in which these acids are generated by adsorption of water on metal ions as cations.[5] It is to be noted that $Ca_{3/2}PW_{12}O_{40}$ had the lowest value of protonic conductivity at 175 °C(1.48×10^{-6} mho cm^{-1}) in these 12-tungstophosphates whereas $Ba_{1/2}H_2PW_{12}O_{40}$ had the greatest value at 175 °C(6.35×10^{-4} mho cm^{-1}).

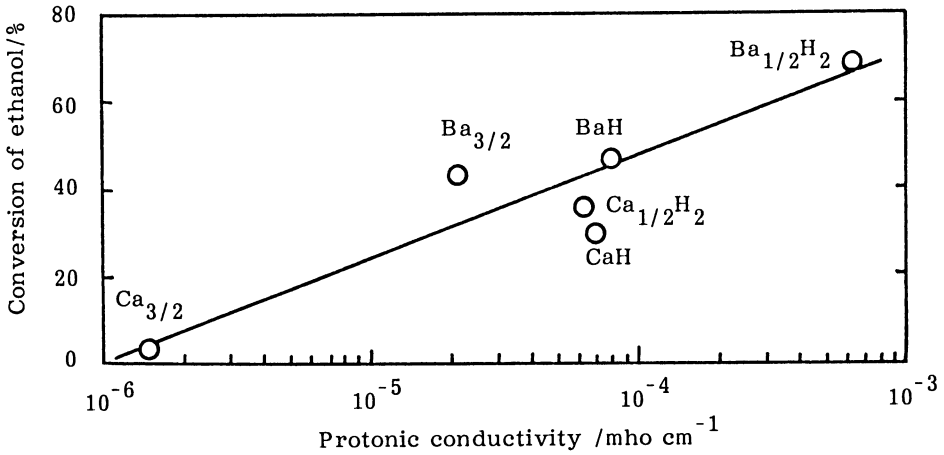

Fig.1. Correlation between the protonic conductivity and the steady-state catalytic activity for dehydration of ethanol at 175 °C. Catalyst : 0.50 g. Feed : C_2H_5OH + He 50 (NTP)ml/min(C_2H_5OH 40 vol%).

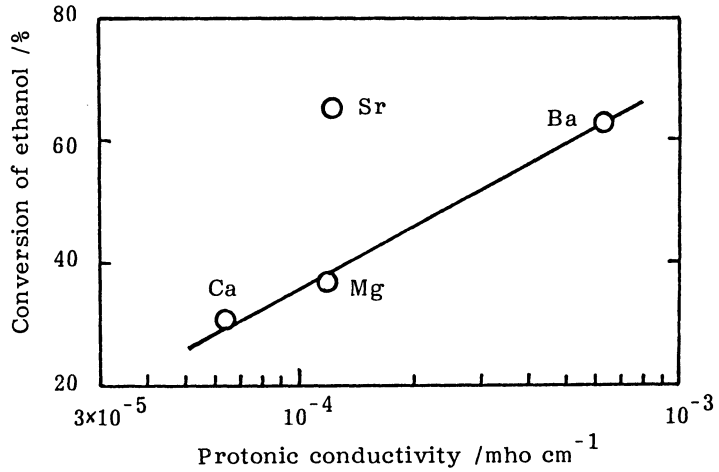

Fig.2. Correlation between the protonic conductivity of $M_{1/2}H_2PW_{12}O_{40}$ type salts (M = Mg, Ca, Sr, and Ba) and their steady-state catalytic activity for dehydration of ethanol at 175 °C. Catalyst: 0.50 g. Feed: C_2H_5OH + He 39 (NTP)ml/min(C_2H_5OH 23 vol%).

The catalytic activity of alkaline-earth metal salts for dehydration of ethanol was determined at 175 °C. The catalytic activity was low at the initial stages of the reaction, but it increased rapidly with elapsed time of the reaction and then nearly levelled off after 3 h. The values of conversion of ethanol thus obtained at 175 °C are compared with those of protonic conductivity at 175 °C (Figs.1 and 2). As had been expected, the conversion of ethanol was the lowest, 1.8%, over $Ca_{3/2}PW_{12}O_{40}$ whereas the conversion was the greatest, 69.0%, over $Ba_{1/2}H_2PW_{12}O_{40}$, and the values of conversion of ethanol at 175 °C for each three types of calcium and barium salts reasonably correlated those of protonic conductivity for the salts at 175 °C(Fig. 1). With the exception of strontium salt, a similar correlation was obtained for $M_{1/2}H_2PW_{12}O_{40}$ type salts at 175 °C(Fig.2). Water was produced in the catalytic dehydration of ethanol at 175 °C. Hence, we do not always believe that the degree of hydration for these alkaline-earth metal salts during the catalytic reaction was equal to the value at 175 °C in Table 1. However, it is not unreasonable to consider that the order of protonic conductivity at 175 °C shown in Table 2 was preserved during the catalytic reaction of ethanol although the yield of water and hence the degree of hydration increased as the catalytic activity increased. The reason for the deviation of strontium salt from the correlation(Fig.2) remains unknown.

Thus, the above finding made in the present work indicates that the protonic conductivity of 12-heteropoly compound catalysts at solid state can be employed as a measure of their catalytic activity as solid acid catalysts. We believe that the use of protonic conductivity as a measure of catalytic activity is limited to the acid-catalyzed reactions over 12-heteropoly compound catalysts in which such polar compounds as alcohols and amines are reactants.

References

1) M.Misono, K.Sakata, Y.Yoneda, and W.Y.Lee, Proc. 7th Intern.Congr.Catal., 1980, 1047; T.Okuhara, T.Hashimoto, M.Misono, Y.Yoneda, H.Niiyama, Y.Saito, and E.Echigoya, Chem.Lett., 1983, 573.
2) Y.Saito, N.Yoneda, H.Niiyama, and E.Echigoya, 46th Symposium on Catalysis, 3P07, Sendai(1980).
3) O.Nakamura, T.Kodama,I.Ogino, and Y.Miyake, Chem.Lett., 1979, 17.
4) Y.Ozawa, N.Miura, N.Yamazoe, and T.Seiyama, Denki Kagaku, 51, 207(1983).
5) H.Niiyama, Y.Saito, S.Yoshida, and E.Echigoya, Nippon Kagaku Kaishi, 1982, 569.

(Received January 16, 1985)