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PREPARATION PROCESS AND CATALYTIC ACTIVITY OF $Cs_xH_{3-x}PW_{12}O_{40}$

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When $H_3PW_{12}O_{40}$ solution was titrated with Cs_2CO_3 solution, $Cs_2HPW_{12}O_{40}$ was precipitated at the Cs/anion ratio of 0.5-2, while $Cs_3PW_{12}O_{40}$ was formed at the ratio of 3. Based on these results, the peculiar variation with x and heat-treatment observed for catalytic activity of $Cs_xH_{3-x}PW_{12}O_{40}$ has been explained.

12-Tungstophosphoric acids are efficient catalysts for acid-catalyzed reactions like dehydration of alcohols, particularly at low temperatures. It has recently been reported that salt formation sometimes enhances the catalytic activity[1)] and that the catalytic activity depends on the stoichiometry of the salts in complicated manners.[2,3)] In order to elucidate these effects, we attempted closer examination of the preparation process of $Cs_xH_{3-x}PW_{12}O_{40}$, paying attention to the Cs to $PW_{12}O_{40}$(anion) ratio, and found novel phenomena which seem essential to understand acid-catalysis of water-insoluble salts of heteropoly acids. Cs salt is a typical water-insoluble salt and important in practical uses because of its high catalytic activity and high thermal stability.

$H_3PW_{12}O_{40}$ (abbreviated as PW_{12}) was obtained commercially. The catalysts (Cs salts) were prepared by adding slowly predetermined amounts of an aqueous solution of Cs_2CO_3 to an aqueous solution of PW_{12}, and precipitates were subsequently evaporated to dryness togehter with solution. The Cs salts obtained by this procedure will be abbreviated as $Cs_xH_{3-x}PW_{12}$, where x is the Cs/anion ratio in the catalyst. In some cases, precipitates formed during the precipitation process were separated by centrifugation (3500 rpm) for the analysis of their stoichiometry. The Cs content in the precipitates was determined by means of atomic absorption analysis after the precipitates thus separated were dissolved in an aqueous NaOH solution. The surface area, the water content and absorption of molecules were measured by the methods described previously.3) Surface area was low for $x = 0\text{-}2$, but 100-200 m^2g^{-1} for $x = 2.5$ and 3. The acidic properties of these catalysts were similar to $Cs_xH_{3-x}PMo_{12}O_{40}$.5) Amounts of absorption of alcohols and dimethyl ether decreased from $x = 0$ to 3. Dehydration of 2-propanol and conversion of dimethyl ether were carried out with a continuous flow reactor at atmospheric pressure after pretreatment of the catalysts at 110 °C or 300 °C in flowing He.

Figure 1 shows the variation of the catalytic activity for dehydration of 2-propanol and conversion of dimethyl ether to hydrocarbons as a function of the Cs content, x.4) For catalysts pretreated at 110 °C, the catalytic activity decreased linearly to almost zero as x increased from 0 to 2. Pretreatment at 300 °C decreased the activities of $x = 1$ and 2, but the activity of $x = 2.5$ significantly increased by the pretreatment. It is remarkable in Fig. 1 that the catalytic activity varied in a contrastic way between the ranges $x = 0\text{-}2$ and $x = 2\text{-}3$, and that the catalytic activity of $x = 2.5$ after treated at 300 °C was comparable or higher than that of $x = 0$.

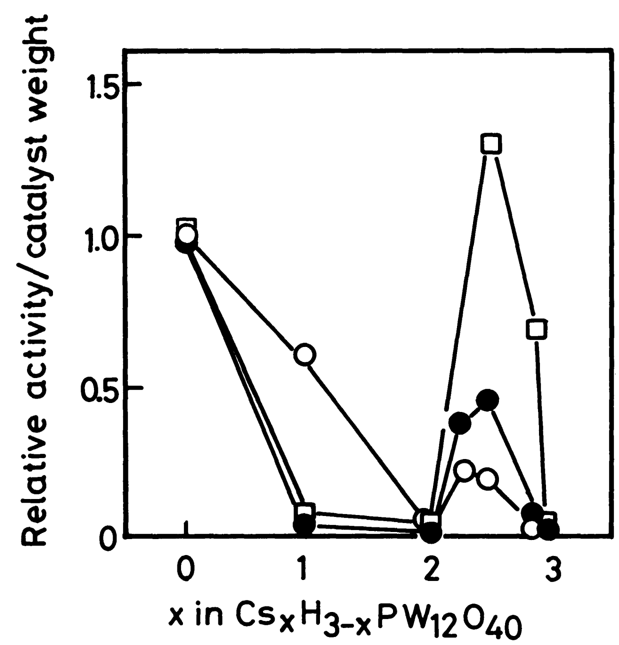

Fig. 1. Variation of catalytic activity as a function of Cs content.

○: Dehydration of 2-propanol at 110 °C after pretreatment at 110 °C.

●: Dehydration of 2-propanol at 110 °C after pretreatment at 300 °C.

□: Conversion of dimethyl ether at 290 °C after pretreatment at 300 °C.

We considered that the contrast in behavior between the ranges $x = 0\text{-}2$ and $x = 2\text{-}3$ was related to their preparation processes. Precipitates were separated at the Cs titrated/anion ratio (α) = 0.5, 1.0, 1.5, 2.0, 2.5, and 3.0, and the Cs/anion ratios of the precipitates were determined as given in Table 1. Data in Table 1 indicate that precipitates were mostly $Cs_2HPW_{12}O_{40}$ for $\alpha = 0.5\text{-}2$, and $Cs_3PW_{12}O_{40}$ for $\alpha = 3$. It was confirmed that the treatment of $Cs_2HPW_{12}O_{40}$ (the

Table 1. Content of Cs in the Precipitates Formed during the Preparation Process of the Cs Salts

Cs titrated/ anion ratio α	Aging time/h	Cs/anion ratio in precipitates a) A	B	Surface area b) $m^2 g^{-1}$
0	-	-	-	5.3
0.5	20	2.0	-	0.1
1.0	2	1.8	2.1	-
1.0	20	2.0	2.1	0.6
1.5	20	2.2	-	36
2.0	2	2.0	1.9	-
2.0	20	2.1	2.2	28
2.5	20	2.5	-	104
3.0	20	2.9	2.9	118

a) The content of phosphorus in the precipitates was confirmed in some cases by the absorptiometry. A: Atomic absorption analysis, B: Gravimetric analysis (The Cs/anion ratio was estimated from the weight of precipitates separated, where the amount of Cs in the solution was negligible. The values are less accurate.).

b) After pretreatment at 300 °C.

precipitates formed at α = 0.5-2) with a solution containing Cs_2CO_3, the amount of which was equivalent to form stoichiometric salt (Cs_3PW_{12}), transformed the precipitates to the $Cs_3PW_{12}O_{40}$ having high surface areas. Note that the catalysts used for experiments shown in Fig. 1 were prepared by drying together the precipitates and solution, and are different from the precipitates themselves.

Based on these results the precipitation processes are speculated as follows. Although this speculation has not been fully confirmed, it can explain the peculiar behavior shown in Fig. 1. Therefore, we believe that the results in Table 1 and the speculation based on them are important for the understanding of the acid catalysis of heteropoly compounds.

(1) In the range of $0 < x \leq 2$, precipitates are $Cs_2HPW_{12}O_{40}$. Therefore, the catalysts obtained after drying the precipitates and solution are mixtures of $H_3PW_{12}O_{40}$ and $Cs_2HPW_{12}O_{40}$. The fraction of $H_3PW_{12}O_{40}$ in the catalyst decreases from unity to zero as x changes from 0 to 2. If the catalytic activity of $Cs_2HPW_{12}O_{40}$ is assumed to be very low (as x = 2 was so), the catalytic activity decreases nearly to zero as x increases from 0 to 2. This trend is in good agreement with the catalytic activity obtained after 110 °C-treatment (Fig. 1). Thus in this range the reaction proceeds in the bulk of $H_3PW_{12}O_{40}$.6) Heat treatment at 300 °C makes possible the diffusion of Cs^+ and H^+, and probably transforms the

mixture into more nearly homogeneous acidic salts. The homogenization was indicated in the case of the mixture of organic salts and acid.[1c)] If one assumes again that these acidic salts are much less active, the lowered activities for 300 °C-treated catalysts (x = 1, 2) are well understood.

(2) In the range of $2 < x \leq 3$, the precipitate ($Cs_2HPW_{12}O_{40}$) reacts with Cs ion in solution. Partial dissolution and re-precipitation, accompanied by ion-exchange of Cs^+ for H^+, transforms the precipitate into $Cs_3PW_{12}O_{40}$ having high surface area. Therefore, the catalyst with x = 2.5 after drying is probably a mixture of $Cs_3PW_{12}O_{40}$ and $Cs_2HPW_{12}O_{40}$. Since Cs ion likely reacts with the precipitate ($Cs_2HPW_{12}O_{40}$) at the surface of precipitate, the surface of particle after above reactions may be richer in Cs content (lower in H^+ content). The heat treatment at 300 °C possibly homogenizes the mixture, resulting in the increase of the proton concentration near the surface. The acidic salt may not be very active, but owing to its high surface area it shows high catalytic activity. If the catalytic activity is normalized to the surface area, x = 2 and 2.5 have the activity of the comparable order. Decrease of the catalytic activity from x = 2.5 to 3 may be attributed to the decrease in the proton concentration.

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References

1) a) T. Baba and Y. Ono, Bull. Chem. Soc. Jpn., 55, 2657 (1982); b) T. Hibi, T. Okuhara, M. Misono, and Y. Yoneda, Chem. Lett., 1982, 1275; c) T. Hibi, T. Okuhara, M. Misono, and Y. Yoneda, Shokubai, 25, 118 (1983).
2) M. Ai, Appl. Catal., 4, 245 (1982); Shokubai, 23, 287 (1981); H. Niiyama, Y. Saito, S. Yoshida, and E. Echigoya, Nippon Kagaku Kaishi, 1982, 569.
3) T. Okuhara, N. Hayakawa, A. Kasai, M. Misono, and Y. Yoneda, Shokubai, 22, 226 (1980); T. Okuhara, A. Kasai, N. Hayakawa, Y. Yoneda, and M. Misono, J. Catal., 121 (1983); M. Misono, K. Sakata, Y. Yoneda, and W. Y. Lee, "Proc. 7th Intern. Congr. Catal., Tokyo, 1980," Kodansha-Elsevier (1981), p. 1047.
4) These results were preliminary presented at the meeting of the catalysis Society of Japan, Sapporo, Aug. 1983.
5) T. Komaya and M. Misono, Chem. Lett., 1983, 1177.
6) T. Okuhara, T. Hashimoto, M. Misono, Y. Yoneda, H. Niiyama, Y. Saito, and E. Echigoya, Chem. Lett., 1983, 573, and references cited therein.

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