Hydration of Olefins in Excess Water Catalyzed by an Insoluble Cesium Hydrogen Salt of Dodecatungstophosphoric Acid

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A solid acid, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$, efficiently catalyzed hydration of 2,3-dimethylbut-2-ene in excess water at 343 K, while typical oxide-based catalysts such as Nb_2O_5, SiO_2-Al_2O_3, TiO_2-SiO_2, and SO_4^{2-} / ZrO_2 were almost inactive. The activity (per unit weight) of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ was found to be higher than those of liquid acids like $H_3PW_{12}O_{40}$ and H_2SO_4, and of a commercial solid acid, H-ZSM-5, for hydration of cyclohexene.

Clean chemical processes using solid acids are desirable in place of the processes by liquid acids such as sulfuric acid, hydrofluoric acid, and aluminum chloride which present disposal or toxicity problems.[1] Among solid acids, environmentally compatible oxide-based solid acids are required, but they generally lose their activities in water due to poisoning of water.

As far as we know, a notable finding as for water-tolerant catalysis by solid acid is hydrolysis of ester catalyzed by H-ZSM-5.[2] After that, hydration of butenes by H-mordenite,[3] hydration of epoxide to diol by Nb_2O_5,[4] hydrolysis of ethyl acetate by supported heteropoly compounds,[5] unsupported ones,[6] and zirconium phosphonates[7] have been reported. Asahi Chemical Ind. has developed a commercial process for hydration of cyclohexene using H-ZSM-5 in water.[8] Ishida *et al.*[9] inferred that the hydration of cyclohexene proceeded in the pores of H-ZSM-5 and the formation of dicylohexyl ether was greatly suppressed by the shape-selectivity.[9] Due to the constrained pores, however, there are some restrictions for general application; *e.g.*, H-ZSM-5 is unfavorable for hydration of bulky olefins.

Here we wish to report that an acidic Cs salt of $H_3PW_{12}O_{40}$, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$, is an efficient water-tolerant solid acid for hydration of 2,3-dimethylbut-2-ene in excess water.

$Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (abbreviated as Cs2.5) was prepared from aqueous solutions of $H_3PW_{12}O_{40}$ (0.08 mol dm^{-3}) and Cs_2CO_3 (0.10 mol dm^{-3}).[10] The surface area was 130 m^2 g^{-1} after the evacuation at 523 K. SO_4^{2-} / ZrO_2 (125 m^2 g^{-1})[11] and TiO_2-SiO_2 (370 m^2 g^{-1})[12] were prepared according to the literature. Prior to use, SO_4^{2-}/ZrO_2 was washed with water at 343 K for 1 h. Nb_2O_5 (NIOBIA HY-340, CBMM Co., 131 m^2 g^{-1}), H-ZSM-5 (Tosoh HSZ-860HOA, Si/Al = 37), H-mordenite (JRC-Z-HM10, Si/Al = 5.0), HY (JRC-Z-HY 4.8, Si/Al = 2.4), Nafion-H (NR-50, Du Pont), and Amberlyst-15 (Organo Co.) were used as references. Hydration of 2,3-dimethylbut-2-ene was performed at 343 K in a three-neck Pyrex reactor (100 cm^3) and that of cyclohexene was carried out at 373 K in a glass-made autoclave (200 cm^3). The reactants were 2,3-dimethylbut-2-ene / water / catalyst = 7.8 cm^3 (0.065 mol) / 43.2 cm^3 (2.4 mol) / 1 g and cyclohexene / water / catalyst = 7.8 cm^3 (0.077 mol) / 43.2 cm^3 (2.4 mol) / 1 g. Products in both oil and water phases were analyzed by GC (Shimadzu 8A) with a column of PEG-20M Uniport B.

Figure 1 shows the time courses of hydration of 2,3-dimethylbut-2-ene over various acids. It was found that Cs2.5 catalyzed efficiently this reaction, and the activity was higher than those of H-ZSM-5 and the parent $H_3PW_{12}O_{40}$ which worked as the homogeneous acid. Amberlyst-15 was somewhat more active than Cs2.5. Nb_2O_5 was much less active under the reaction conditions, whereas Nb_2O_5 was reported to be active for hydration of epoxide in water.[4] At the latter stage of the reaction over Cs2.5, the reaction became slightly slow (Figure 1). This is due to the limitation of equilibrium, at which the conversion was experimentally determined to be about 6% by the reaction for 10 h using 5 g of Amberlyst-15.

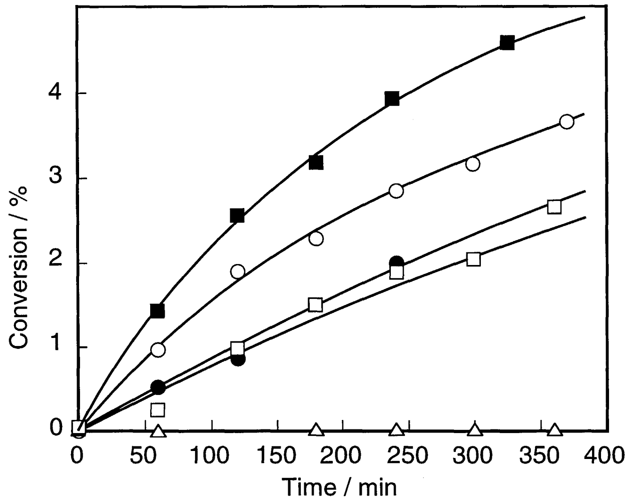

Figure 1. Time courses of hydration of 2,3-dimethylbut-2-ene at 343 K. ○: $Cs_{2.5}H_{0.5}PW_{12}O_{40}$, ●: H-ZSM-5, △: Nb_2O_5, ■: Amberlyst-15, □: $H_3PW_{12}O_{40}$ (homogeneous). 2,3-Dimethybut-2-ene / water / catalyst = 7.8 cm^3 (0.065 mol) / 43.2 cm^3 (2.4 mol) / 1 g.

In Table 1, the catalytic activity and selectivity for the hydration of 2,3-dimethylbut-2-ene catalyzed by various acids are summarized. Among the oxide-based solid acids, the order of the catalytic activity (per unit weight) was Cs2.5 > H-ZSM-5 >> Nb_2O_5 > mordenite ≈ HY ≈ SO_4^{2-}/ZrO_2 ≈ SiO_2-Al_2O_3 ≈ SiO_2-TiO_2 ≈ 0. It is noted that the selectivities for Cs2.5 and H-ZSM-5 to 2,3-dimethylbutan-2-ol were more than 99%. The catalytic activity of $H_3PW_{12}O_{40}$ (homogeneous) was less than Cs2.5 in spite of the larger amount of acid sites, indicating that the surface of Cs2.5 is a very efficient reaction field.

Nafion-H was active, but the activity was much less than that of Cs2.5. H_2SO_4 showed an activity, but was less selective. As shown in Table 1, the specific activity per acid site was exclusively high for Cs2.5, where the acid amounts in the literature[10] were used. These results clearly demonstrate that Cs2.5 is a promising candidate for environmentally compatible water-tolerant solid acid. In order to make clear the deactivation

Table 1. Activity and selectivity for hydration of 2,3-dimethylbut-2-ene

Catalyst	Rate[a]		Selectivity /mol%		
			2,3-DMB[b]	ether[c]	dimer
Solid oxides					
$Cs_{2.5}H_{0.5}PW_{12}O_{40}$	10.5	[70]	99.5	0.5	0
H-ZSM-5	5.7	[15]	99.2	0.8	0
Nb_2O_5	0.1	[0.3]	100	0	0
H-mordenite	0		-	-	-
HY	0		-	-	-
SO_4^{2-}/ZrO_2	0		-	-	-
SiO_2-Al_2O_3	0		-	-	-
SiO_2-TiO_2	0		-	-	-
Liquid acids					
$H_3PW_{12}O_{40}$	4.7	[5]	99.0	0.5	0.5
H_2SO_4	7.0	[0.4]	84.5	15.1	0.4
Polymer resins					
Amberlyst-15	14.0	[3]	99.5	0.5	0
Nafin-H	1.8	[2]	100	0	0

[a] Initial rate/μmol·g^{-1}·min^{-1}. The figures in the brackets are the rates per acid site/mmol·$(acid\text{-}mol)^{-1}$·min^{-1}.
[b] 2,3-dimethylbutan-2-ol. [c] 2,3-dimethylbutyl ether.

of catalyst, Cs2.5 was reused after it was separated by centrifugation from the solution. It was confirmed that the activity (per unit weight of the catalyst) at the first run remained almost unchanged at the second and third runs.

The activation energy of the hydration of 2,3-dimethylbut-2-ene over Cs2.5 was determined to be 14±1 kcal mol^{-1} in the temperature range 323 - 373 K. This value is close to that for hydration of isobutylene catalyzed by $H_3PW_{12}O_{40}$,[13] which is reasonable because both the reactions would proceed *via tert*-carbenium ion intermediates.

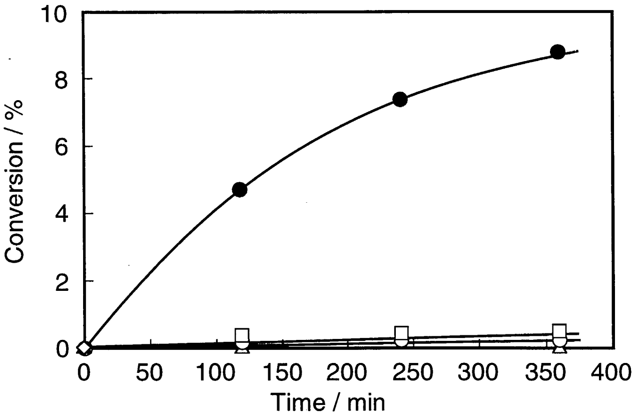

Figure 2. Time courses of hydration of cyclohexene at 373 K. ○: $Cs_{2.5}H_{0.5}PW_{12}O_{40}$, ●: H-ZSM-5, △: Nb_2O_5, □: $H_3PW_{12}O_{40}$ (homogeneous). Cyclohexene / water / catalyst = 7.8 cm_3 (0.077 mol) / 43.2 cm_3 (2.4 mol) / 1 g.

As has already been reported by Ishida *et al.*,[9] H-ZSM-5 was excellent catalyst for hydration of cyclohexene. We also examined the hydration of cyclohexene over a variety of acids under similar reaction conditions.[8] Figure 2 showed that H-ZSM-5 was far superior in the activity to Cs2.5, $H_3PW_{12}O_{40}$, and Nb_2O_5. Additionally the activity (per unit weight) was 7, 5 and 3 times higher than those of Nafin-H, H_2SO_4 and Amberlyst-15, respectively. This remarkable catalytic function of H-ZSM-5 for cyclohexene may be brought about by specific interaction between cyclohexene and the wall of pores to draw it into the pores. The poor activity of H-ZSM-5 for 2,3-dimethylbut-2-ene would be due to the limitation of the adsorption or diffusion of the molecule in pores, since the critical size of 2,3-dimethylbut-2-ene is slightly larger than that of cyclohexene in molecular model by MM2.

The combination of very strong acidity[14] and hydrophobic nature of the surface of the Cs salt[15] is responsible for the pronounced activity of Cs2.5 for 2,3-dimethylbut-2-ene. The mesoporous structure of Cs2.5[14,16] is favorable for the access of the bulky molecule to the acid sites, which is another reason for the high activity.

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