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High Catalytic Activities of Pseudoliquid Phase of Dodecatungstophosphoric Acid for Reactions of Polar Molecules

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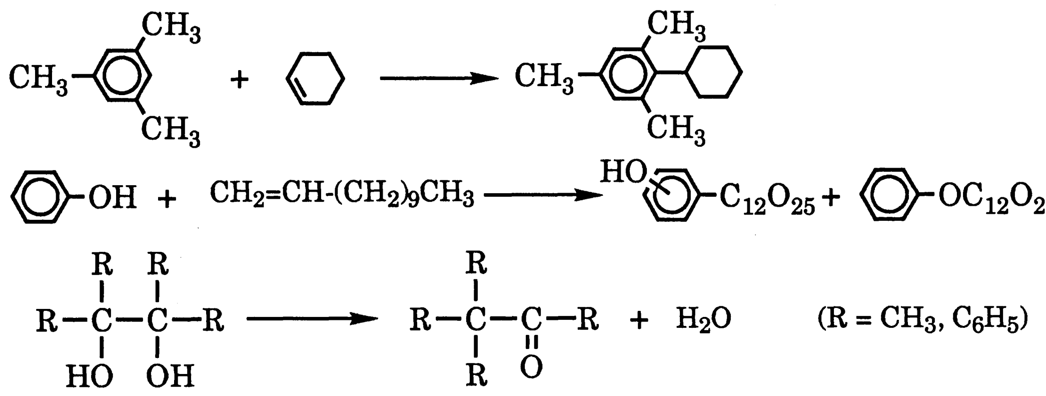
A solid $H_3PW_{12}O_{40}$ exhibited very high catalytic activities for the reactions of polar molecules in the liquid phase, while it was much less active for the reactions of nonpolar molecules. It was confirmed that the pseudoliquid phase behavior of $H_3PW_{12}O_{40}$ is responsible for the high activities.

Solid heteropoly compounds are good catalysts for a variety of reactions in both gas-solid and liquid-solid reaction systems.[1)] It has been reported that $H_3PW_{12}O_{40}$ has a unique ability to discriminate molecules by the difference in their polarity.[2,3)] That is, polar molecules like alcohol and ether are readily absorbed from the gas phase into the solid bulk, while nonpolar molecules are adsorbed only on the surface. Owing to this nature, the bulk phase takes part in the catalytic reaction (pseudoliquid phase), which was confirmed by a transient response method for a model gas-solid reaction like dehydration of alcohols.[1a,4)] In liquid phase reactions with silica-supported $H_3PW_{12}O_{40}$, Izumi et al. have suggested from dependence of the catalytic activity on the amount of loaded heteropoly acids that the bulk phase of $H_3PW_{12}O_{40}$ took part in the reactions.[1c)] Here we wish to report that the pseudoliquid phase played a significant role in catalytic synthetic reactions in the liquid-solid system.

$H_3PW_{12}O_{40}$ was purchased from Nippon Inorganic Color and Chemical Co., Ltd. The surface area was 6 $m^2\ g^{-1}$ after 573 K-evacuation. $H_{0.5}Cs_{2.5}PW_{12}O_{40}$ (abbreviated as $Cs_{2.5}$-salt, 157 $m^2\ g^{-1}$) was obtained as a precipitate by the titration of the aqueous solution of $H_3PW_{12}O_{40}$ (0.08 mol dm^{-3}) with an aqueous solution of Cs_2CO_3 (Cs^+; 0.25 mol dm^{-3}) as described previously.[5)] As references, Nafion-H (NR-50, Mitsui Toatsu Fine Chemicals

Inc., 0.02 $m^2\ g^{-1}$), HY-zeolite (prepared from SK-40, Linde, 660 $m^2\ g^{-1}$), H_2SO_4-treated ZrO_2 (abbreviated as SO_4^{2-}/ZrO_2, 85 $m^2\ g^{-1}$),[6] SiO_2-Al_2O_3 (SA-1, Catalysts and Chemical Industries Co., Ltd., Al_2O_3:13 wt%, 546 $m^2\ g^{-1}$) and H_2SO_4 (Nacalai Tesque, Inc., ultra fine grade) were used.

The alkylation of 1,3,5-trimethylbenzene with cyclohexene (Eq. 1), alkylation of phenol with 1-dodecene (Eq. 2), and rearrangements of pinacol (R = CH_3) and benzopinacol (R = C_6H_5) (Eq. 3) were carried out under an atmospheric pressure of N_2 in a three necked-flask (Pyrex glass) with a magnetic stirrer. Prior to the reaction, the catalysts (200 - 500 mg) were treated at elevated temperatures[7] in a stream of He for 2 h. The products were analyzed by gas chromatography using Silicone OV-17 and PEG 20M columns.



(1)

(2)

(3)

Figure 1 provides the catalytic activities for the reactions 1-3. $Cs_{2.5}$-salt exhibited a catalytic activity much higher than the other solid and liquid acids for the reaction 1, while the acid amount was not high as compared with zeolites, Nafion, and SiO_2-Al_2O_3.[7,8] On the other hand, the activity of $H_3PW_{12}O_{40}$ was low for this reaction; 1/20 that of $Cs_{2.5}$-salt. On the contrary, $H_3PW_{12}O_{40}$ showed greater activities for the alkylation of phenol (Eq. 2) and rearrangement of benzopinacol (Eq. 3 in toluene) than $Cs_{2.5}$-salt, and much greater activities than the other solid acids and H_2SO_4. It was confirmed that none of these reactions (Eqs. 1-3) took place in the filtrates that were obtained from the reaction mixture. Therefore, the active component was not dissolved in the liquid phase. Over $H_3PW_{12}O_{40}$ (0.2 g, 3 h), the yield of dodecylphenol was about 70% (conversion; 84%, selectivity; 82%).

The high activity of $H_3PW_{12}O_{40}$ for polar molecules (Eqs. 2 and 3) and the very low activity for nonpolar molecules (Eq. 1) indicate the action of the pseudoliquid phase behavior that was previously demonstrated in the case of gas-solid phase systems and explained the high activity of $H_3PW_{12}O_{40}$.[1a,4] Because of the high absorptivity of $H_3PW_{12}O_{40}$ for polar molecules,[3] it is possible that phenol and pinacols are absorbed into the bulk or surface layers of $H_3PW_{12}O_{40}$ and react there.

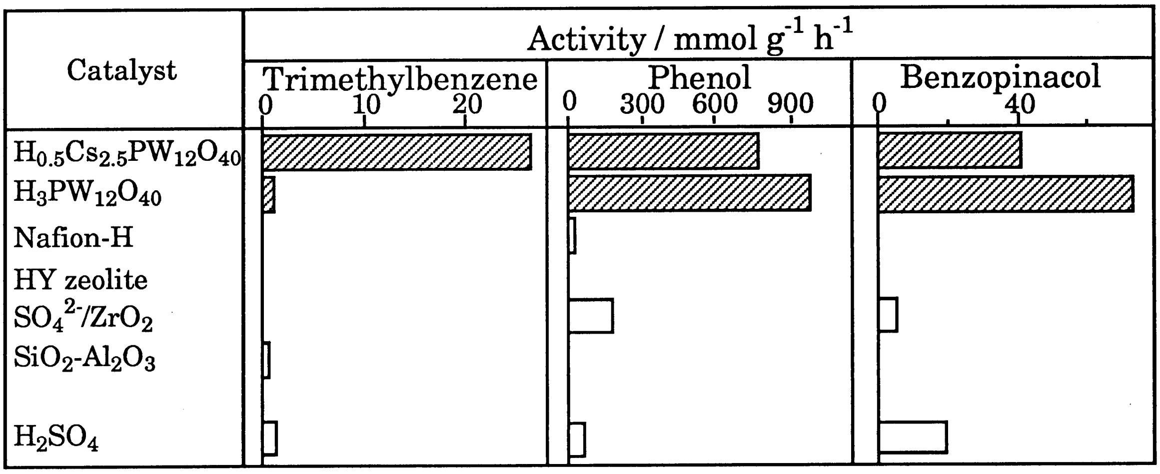


Fig. 1. Catalytic activities of solid acids for liquid-phase reactions. 1,3,5-Trimethylbenzene alkylation (373 K); trimethylbenzene 216 mmol, cyclohexene 10 mmol, phenol alkylation (373 K); phenol 63 mmol, 1-dodecene 45 mmol, benzopinacol rearrangement (298 K); benzopinacol 1 mmol.

In order to elucidate the pseudoliquid phase behavior in the present system, the rearrangement of pinacol was examined in more detail at 323 K in 1,2-dichloroethane. The amounts of molecules held by the catalysts were determined from the mass balance in the reaction solution by using 1,2-dichloroethane as an internal standard. 1,2-Dichloroethane was chosen because of its negligibly small absorption.[3] Here the amounts of molecules held by the catalysts are expressed in the unit of the number of surface layer, i.e., the amount divided by that corresponding to the surface monolayer.[5] In the case that the molecules are absorbed in the bulk phase during the reaction, the amounts held by the catalysts may exceed those of the surface monolayer. The results are shown in Fig. 2. It was found that the number of the surface layer was about 20 for $H_3PW_{12}O_{40}$, while it was less than unity for the others. The uptake for $H_3PW_{12}O_{40}$ was the largest even when it was compared per unit weight of catalysts. It was confirmed that $H_3PW_{12}O_{40}$ collected by the filtration of the reaction solution contained a large amount of molecules (pinacol and methyl *tert*-butyl ketone) in agreement with the uptake shown in Fig. 2.

It has been pointed out that the presence of water of crystallization accelerates the absorption of polar molecules into the bulk and dissolution of $H_3PW_{12}O_{40}$ into a solution.[1b,9] In accordance with this idea, when

$H_3PW_{12}O_{40}\cdot6H_2O$ was used as a catalyst instead of anhydrous one for the pinacol rearrangement (298 K), both the rates of the catalytic reaction and of the uptake of molecules were enhanced. These facts demonstrate that the pseudoliquid phase behavior exists in the present liquid-solid system and, owing to this behavior, the catalytic activity of $H_3PW_{12}O_{40}$ is enhanced.

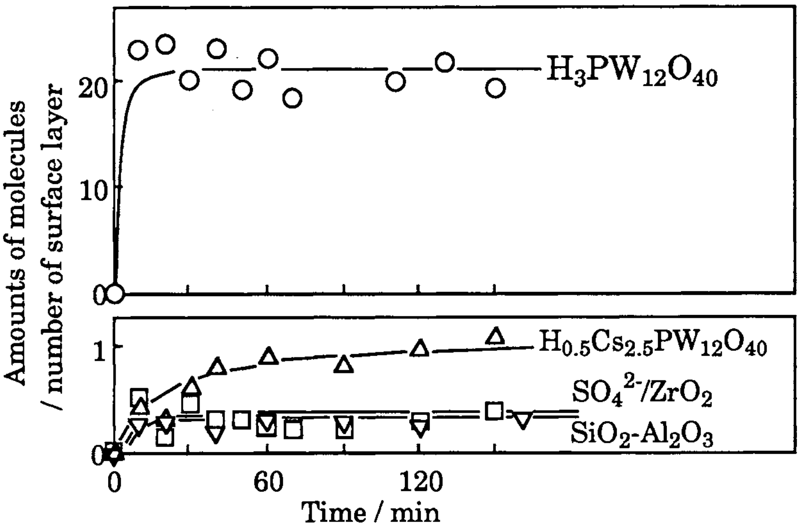


Fig. 2. Amounts of molecules held by the catalysts during the rearrangement of pinacol at 323 K.
Pinacol; 1 mmol (in 1,2-dichloroethane), catalyst weight; 0.20 g.
The vertical axis shows the number of molecules held by the catalysts divided by that corresponding to the surface monolayer.

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