Solid-Solid Catalysis by Ultrafine Crystallites of Heteropoly Compound for Pinacol Rearrangement

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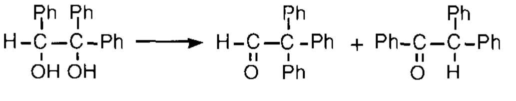
$Cs_{2.5}H_{0.5}PW_{12}O_{40}$ consisting of ultrafine crystallites efficiently catalyzes pinacol rearrangement of 1,1,2-triphenyl-1,2-ethanediol at room temperature in solid-solid reaction system, giving the corresponding aldehyde selectively, while *p*-toluenesulfonic acid, H-ZSM-5, HY, SiO_2-Al_2O_3, SO_4^{2-}/ZrO_2 and $Nb_2O_5 \cdot nH_2O$ were inactive. The activity of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ in the solid-solid reaction was higher than that in solid-liquid ($CHCl_3$) system.

Solid-solid catalysis is unusual. If solid-state organic reaction proceeds catalytically, this would be useful for organic synthesis because the solvent-free reaction system is environmentally benign. Some examples of solid-solid reactions have been reported by Toda *et al.*[1,2] The pinacol rearrangement of 1,1,2-triphenyl-1,2-ethanediol took place at 333 K over *p*-toluenesulfonic acid (PTS) in the solid state, being the yield of ketone 89% for 2.5 h.[3] Baeyer-Villiger oxidation was accelerated by solid organic peroxides.[4] However, these solid-state organic reactions were carried out in the presence of excess acids or peroxides.

The formation of host-guest complexes by mixing the components was claimed to be important for selectivity.[5] In addition, anisotropic reactivity of the crystal plane of the reactant solid was revealed by atomic force microscopy.[6] We have focused on an acidic Cs salt, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$, for solid-solid catalysis, since this salt possesses a very strong acidity which can be classified into "superacidity"[7-10] and comprises of very fine crystallites, of which the size is about 100 Å.[9,10]

$Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (abbreviated as Cs2.5, 130 m^2 g^{-1}) was prepared by the method as described previously.[10] The amount of proton on the surface of Cs2.5 was estimated to be 60 μmol g^{-1} from the composition and the surface area, being the amount of total proton 150 μmol g^{-1}.[10] As reference, $H_3PW_{12}O_{40}$, Amberlyst 15, 13wt%Nafion/SiO_2 composite catalyst (Du Pont Japan),[11] H-ZSM-5 (JRC-Z5-70H), HY (JRC-Z-HY-4.8), SiO_2-Al_2O_3 (JRC-SAL-2, Si/Al = 6.3), $Nb_2O_5 nH_2O$ (NIOBIA HY-340 AD/1177), and PTS were used. The pinacol rearrangement of 1,1,2-triphenyl-1,2-ethanediol (eq. (1)) was ordinarily performed at room temperature. After 0.1 g of the reactant **1** was mixed with 0.2 g of the solid acid (without any pretreatment) in a mortar at room temperature for 5 min, the mixture was allowed to stand at room temperature. A part of the solid mixture was sampled for HPLC analysis. Liquid phase reaction was carried out with stirring at room temperature in a flask (about 50 ml) using 0.1 g of the reactant, 0.2 g of the acid, and 20 ml of $CHCl_3$ as solvent.



$$H\text{-}\underset{OH}{\overset{Ph}{C}}\text{-}\underset{OH}{\overset{Ph}{C}}\text{-}Ph \longrightarrow H\text{-}\underset{O}{\overset{\|}{C}}\text{-}\underset{Ph}{\overset{Ph}{C}}\text{-}Ph + Ph\text{-}\underset{O}{\overset{\|}{C}}\text{-}\underset{H}{\overset{Ph}{C}}\text{-}Ph \quad (1)$$

1 **2** **3**

Figure 1 provides a typical time course of the solid-solid reaction with Cs2.5 at room temperature. As the reactant **1** decreases, triphenylacetaldehyde **2** and diphenylacetophenone **3** formed concurrently, being the former the main product. As a result, the selectivity to the aldehyde **2** was constant (76%) during the reaction, showing that the two products formed in parallel. The selectivity to aldehyde over Cs2.5 was higher than that with CCl_3COOH reported by Toda *et al.*[3]

Figure 1A shows the change of turnover number (TON) with time, where TON is defined as the amount of total products divided by the amount of protons on the surface of Cs2.5.[10] It was found that TON reached 20 at 4 h, indicating that the reaction proceeded catalytically. Even when TON was estimated by using total amount of protons through the whole bulk of Cs2.5, TON became about 8 at 4 h.

Table 1 provides the conversion and selectivity to the corresponding aldehyde **2** for various reaction systems. Cs2.5 gave a higher conversion than those of $H_3PW_{12}O_{40}$, Amberlyst 15 and Nafion/SiO_2. The higher activity of Cs2.5 than that of

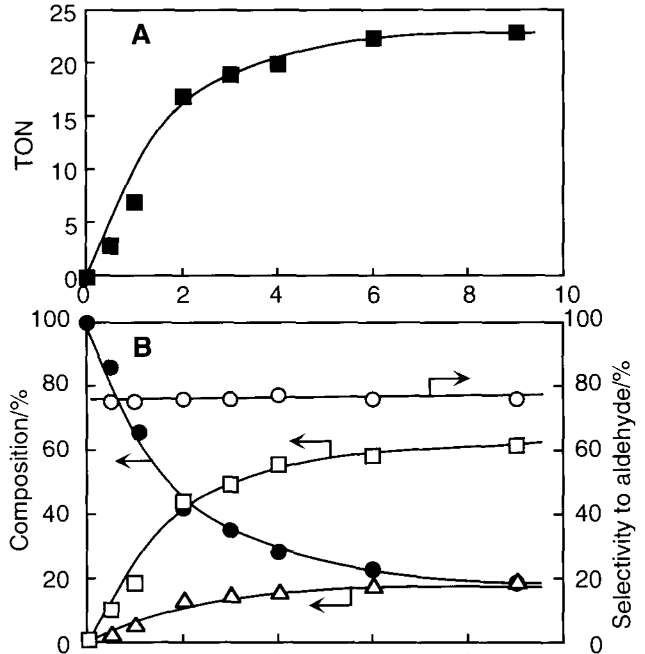


Figure 1. Time courses of solid-state pinacol rearrangement of 1,1,2-triphenyl-1,2-ethanediol over $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ at room temperature. ●: 1,1,2-triphenyl-1,2-ethanediol, □: triphenylacetaldehyde, △: diphenylacetophenone, ○: Selectivity to triphenylacetaldehyde, ■: Turnover number (see text). The reaction was performed with 0.1 g of 1,1,2-triphenyl-1,2-ethanediol (0.35 mmol) and 0.2 g of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (0.06 mmol).

$H_3PW_{12}O_{40}$ is probably due to the larger amount of proton on the surface.[9] PTS, zeolites (H-ZSM-5 and HY), SO_4^{2-}/ZrO_2, and SiO_2-Al_2O_3 were inactive for the solid-solid reaction. As for the selectivity, these heteropoly compounds ($H_3PW_{12}O_{40}$ and Cs2.5) as well as Nafion/SiO_2 gave aldehyde **2** selectively. It was confirmed that PTS was active at 333 K to gave mainly the ketone **3** as reported by Toda *et al.*,[3] while TON was only 0.33.

When the reaction was carried out in solvent ($CHCl_3$) with PTS (0.2 g, 1.05 mmol) and 1,1,2-triphenyl-1,2-ethanediol (0.1 g, 0.35 mmol), PTS worked as homogeneous acid and showed an activity (Table 1) even at room temperature, yielding the ketone **3** selectively. The selectivity was nearly independent of the conversion, indicating that the reaction by PTS also proceeds by the parallel mechanism in this system. On the other hand, Cs2.5 was present in the solid state and gave also aldehyde mainly, of which the selectivity was unchanged during the reaction. However, the activities of PTS and Cs2.5 in the solvent system were less than that of Cs2.5 in the solid-solid reaction. Thus these results demonstrate that Cs2.5 exhibits efficient solid-solid catalysis. It should be emphasized that in solid-solid reaction, the solid acid, Cs2.5, is reusable without the treatment of neutralization, which is another advantage of the solid acid.

Table 1. Conversion and selectivity for pinacol rearrangement of 1,1,2-triphenyl-1,2-ethanediol at room temperature

Catalyst	Conversion/%		Selectivity to aldehyde /%	
	3 h	9 h	3 h	9 h
Solid-solid system[a]				
$Cs_{2.5}H_{0.5}PW_{12}O_{40}$	65	81	76	76
$H_3PW_{12}O_{40}$	17	35	84	84
Nafion/SiO_2[b]	9	26	69	70
Amberlyst 15	7	19	49	49
H-ZSM-5	0	0	–	–
SiO_2-Al_2O_3	0	0	–	–
HY	0	0	–	–
SO_4^{2-}/ZrO_2	0	0	–	–
PTS	0	0	–	–
$Nb_2O_5 \cdot nH_2O$	0	0	–	–
Solid-liquid system[c]				
$Cs_{2.5}H_{0.5}PW_{12}O_{40}$	42	63	87	88
Amberlyst 15	0	0	–	–
Nafion/SiO_2[b]	0	0	–	–
SiO_2-Al_2O_3	0	0	–	–
HY	0	0	–	–
Liquid-liquid system[c]				
PTS	45	72	19	19
CCl_3COOH	0	0	0	0

[a] 1,1,2-triphenyl-1,2-ethanediol 0.1 g and solid acid 0.2 g was mixed at room temperature.

[b] Nafion-SiO_2 composite catalyst (reference 11).

[c] The reaction was performed at room temperature with 1,1,2-triphenyl-1,2-ethanediol 0.1g, acid 0.2 g, and $CHCl_3$ 20 ml.

The different selectivities among these acids were probably brought about from the difference in the acid strength, since these heteropoly compounds as well as Nafion/SiO_2 have very strong acidities[10,11] and their acid strengths are far higher than that of PTS.[12] The reason for the selectivity change by the acid strength is, however, unclear at present.

Toda *et al.*[5] claimed that host-guest complexes were formed by mixing the organic components in the solid state. On the other hand, since Cs2.5 consists of the fine rigid crystallites, the surface of the Cs2.5 crystallites would be the reaction field. The migration of the reactant and product molecules would make proceed the reaction catalytically through the replacement each other around the surface of the crystallites. It is also possible that the fine crystallites themselves migrate to accelerate the reaction in this system.

In conclusion, Cs2.5 is prominent in activity and selectivity in the solid-state pinacol rearrangement. The unique character of Cs2.5 may open the new type of the reaction control for many other organic reactions which have long been carried out in solution.

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