Solid–Solid Catalysis by Inorganic Solid Acids: Pinacol Rearrangement over a Heteropoly Compound Consisting of Fine Particles

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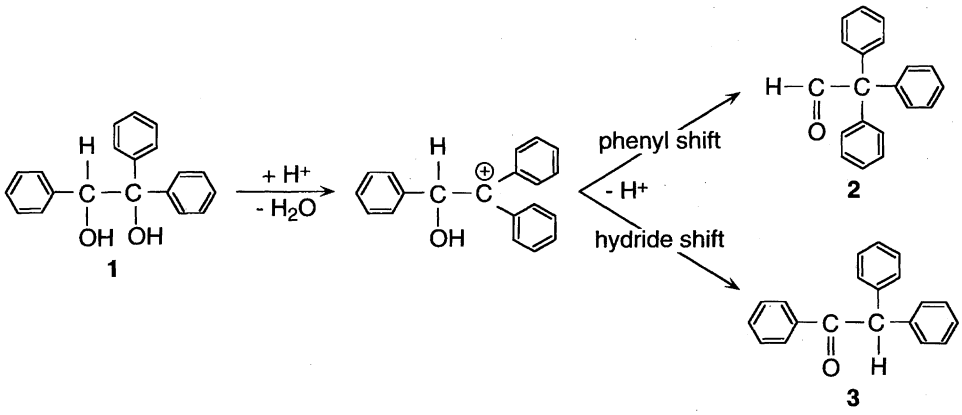
Solid-state pinacol rearrangement of 1,1,2-triphenyl-1,2-ethanediol was performed over various solid acids at room temperature. The reaction was initiated by grinding a mixture of the solid reactant and catalyst for 5 min at room temperature. Heteropoly compounds ($Cs_{2.5}H_{0.5}PW_{12}O_{40}$ and $H_3PW_{12}O_{40}$) and polymer resins (Amberlyst®-15 and Nafion®/SiO_2), all which possess strong acidities, were active, whereas H-ZSM-5, SiO_2–Al_2O_3, and *p*-toluenesulfonic acid were inactive. $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ showed the highest activity (per unit catalyst weight). The turnover number, which is defined as the number of molecules reacted divided by the number of protons on the surface, exceeded 20 for 9 h, indicating that the solid–solid reaction proceeded catalytically. This activity of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ was higher than that for the solid–liquid reaction carried out in chloroform at room temperature, demonstrating the superiority of the solid–solid catalysis. Powder X-ray diffraction measurements indicated that the reactant crystals became nearly amorphous by grinding with $Cs_{2.5}H_{0.5}PW_{12}O_{40}$, while the crystallinity of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ was unchanged. The microstructure built up from fine particles of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ would be favorable to intimate contact of the reactant with the catalyst.

Catalytic reactions by solid catalysts are ordinarily performed in solid–liquid or solid–gas reaction systems, and solid–solid catalysis is unusual. However, solid-state reactions should be useful for catalysis, because solid–solid reaction systems have several peculiarities compared with the conventional systems, e.g., unusual selectivity and the possibility to obtain products not accessible from liquid and gas phases.[1,2] Toda and co-workers have investigated various types of acid-catalyzed solid–solid organic reactions such as pinacol rearrangement,[3] dehydration, Meyer–Schuster rearrangement, and etherification of alcohols[4] by using organic solid acids, exemplified by *p*-toluenesulfonic acid (PTS) and trichloroacetic acid. However, these reactions were conducted in the presence of excess amounts of the acids. They have also reported many other solid-state organic reactions, e.g., host–guest inclusion, Baeyer–Villiger oxidation, and Grignard reactions.[5]

In contrast with these organic systems, solid-state reactions accelerated by inorganic solid acids have not been reported, to our knowledge. Solid–solid catalysis by inorganic solid acids is attractive, since they have some preferable characteristics for catalysis, e.g., high mechanical and thermal stability, high surface area, and strong acidity. In addition, solid–solid reactions between inorganic and organic compounds have been reported to give unusual product selectivities and yields; examples are oxidative coupling reactions over metal chlorides,[5] aldol condensation over NaOH,[5] reduction of ketones with $NaBH_4$,[5] and intercalation reactions of clay–organic systems.[6] It will be valuable to establish the solid–solid catalysis over inorganic solid acids for developing novel catalytic systems.

Heteropoly compounds are known as highly active catalysts.[7—12] In particular, dodecatungstophosphoric acid, $H_3PW_{12}O_{40}$, and their cesium hydrogen salts, $Cs_xH_{3-x}PW_{12}O_{40}$, efficiently work due to their strong acidity; they are classified into "superacids".[13—15] $H_3PW_{12}O_{40}$ has been used as a commercial catalyst for hydration of olefins and polymerization of tetrahydrofuran.[11a] It has been reported that various acid-catalyzed reactions such as alkylation,[16—18] ester decomposition,[19] acylation,[20] skeletal isomerization of *n*-butane,[21] and hydrolysis of esters,[22,23] effectively proceed on $Cs_{2.5}H_{0.5}PW_{12}O_{40}$. This material is built up by aggregation of very fine crystalline particles (around 10 nm); the interparticle spaces give micro- and mesopores and a high surface area (around 130 $m^2\,g^{-1}$).[11] The strong acidity and wide mesoporous surface of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ may give a new aspect of solid–solid reactions.

These facts prompted us to investigate solid–solid catalysis of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ and some other solid acids. We chose solid-state pinacol rearrangement of 1,1,2-triphenyl-1,2-ethanediol (**1**) to triphenylacetoaldehyde (**2**) and diphenylacetophenone (**3**) (Scheme 1) as a model reaction of solid–solid acid catalysis. In fact, Toda and Shigemasa reported that PTS accelerated this reaction in solid state at 333 K,[3] although the reaction was carried out with the reactant to catalyst molar ratio of 1 : 3. We have preliminarily reported that $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ catalyzed the solid-state pinacol rearrangement at room temperature;[24] this acidic salt was much more active than some other solid acid catalysts including PTS, probably due to the strong acidity and finely granular



Scheme 1. Pinacol rearrangement of 1,1,2-triphenyl-1,2-ethanediol (**1**) to triphenylacetoaldehyde (**2**) and diphenylacetophenone (**3**).

form.

In the present paper, we report detailed results of the solid-state pinacol rearrangement over $Cs_{2.5}H_{0.5}PW_{12}O_{40}$. The catalytic activity of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ was compared with those of other conventional solid acids, such as PTS, Amberlyst®-15, and H-ZSM-5. Selectivities of the products were discussed in relation to the reaction temperature and the acid strength of the catalysts. Structural information by powder X-ray diffraction (XRD) indicated that the crystalline reactant became amorphous over $Cs_{2.5}H_{0.5}PW_{12}O_{40}$.

Experimental

Catalysts. $H_3PW_{12}O_{40}$ was supplied from Nippon Inorganic Colour and Chemical; it was purified by diethyl ether extraction and then dissolved into water. This material was subjected to the catalytic tests after evacuating at 318 K and storing under ambient conditions; by this pretreatment the hydration state became $H_3PW_{12}O_{40}\cdot 13H_2O$.[25] $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ was prepared from aqueous solutions of $H_3PW_{12}O_{40}$ and Cs_2CO_3 (Merck) by a titration method.[13,26] The obtained solid was pretreated at 523 K in air for 3 h, according to a procedure reported elsewhere.[13,26] $Cs_3PW_{12}O_{40}$ was prepared by the same method. H-ZSM-5 (JRC-Z5-70H, Si/Al (atomic ratio) = 40), HY (JRC-Z-HY-4.8, Si/Al = 2.4), and SiO_2–Al_2O_3 (JRC-SAL-2, Si/Al = 5.3) were supplied from the Catalysis Society of Japan as reference catalysts, and were used without pretreatments. $Nb_2O_5\cdot nH_2O$ (NIOBIA HY-340 AD/1177) was supplied from Companhia Brasileira de Metalurgia e Minoraçào (CBMM) and pretreated at 773 K in air for 3 h. Sulfated zirconia (abbreviated as SO_4^{2-}/ZrO_2) was prepared by the method in the literature,[27] and calcined at 773 K in air for 3 h. TiO_2–SiO_2 (Ti/Si = 1.0) was prepared by coprecipitation from $Si(OC_2H_5)_4$ (Tokyo Kasei Kogyo., 99.5%) and $TiCl_4$ (Wako Pure Chemical Industries, 99.0%) in aqueous ammonia, and calcined at 773 K for 3 h in air.[28] PTS monohydrate was purchased from Wako Pure Chemicals Industries, and used as received. Amberlyst®-15 was obtained from Organo, and used without pretreatments. Nafion® in silica composite catalyst, where 13 wt% of Nafion® resin was entrapped in porous silica matrix (SAC-13, designated Nafion®/SiO_2), which is a novel strong solid acid catalyst recently developed by Du Pont,[29] was obtained from Du Pont Japan and used without pretreatments.

Catalytic Reactions. The reactant **1**, 1,1,2-triphenyl-1,2-ethanediol, was synthesized according to the literature.[30] The obtained white needle-like powder was identified as **1** by ^{1}H- and ^{13}C NMR, IR, field desorption mass spectroscopy (FD-MS), and elemental analyses. The purity was determined to be > 99% by high performance liquid chromatography (HPLC).

For solid–solid reactions, powder of **1** (0.1 g, 0.34 mmol) and catalyst (0.2 g) were mechanically mixed by grinding in a glass mortar at room temperature. The mixing time was 5 min unless otherwise noted. Then, the mixture was kept at a reaction temperature under atmospheric conditions. Small portions of the mixture (ca. 0.01 g) were withdrawn at certain time intervals during the reaction, and the organic components in the mixture were separated by dissolution into 1,4-dioxane and filtration. Then the organic solution was subjected to the HPLC measurement. In some cases, powder samples during the catalytic reactions were analyzed by XRD.

For liquid phase reactions, **1** (0.1 g) was dissolved in $CHCl_3$ (20 cm^3), to which a catalyst (0.2 g) was added. The catalysts other than PTS were not dissolved. Reactions were carried out by stirring the solution at room temperature, and the products were analyzed by HPLC after filtration.

Analysis of Products. In the mixtures after the solid–solid reactions of **1** over the catalysts, two main products were detected by HPLC (retention time: 12 and 16 min) in addition to **1** (retention time: 50 min). These products were isolated by preparative thin layer chromatograpy (PLC), and identified as **2** (retention time: 12 min) and **3** (retention time: 16 min) by ^{1}H- and ^{13}C NMR, IR, and FD-MS analyses. In some cases, we observed a small amount of a by-product, which appeared on HPLC with a retention time of 14 min, in addition to the rearrangement products (**2** and **3**). This species was also isolated by PLC, and identified as benzophenone (**4**) on the basis of NMR and FD-MS analyses. HPLC analysis was carried out at room temperature by using a system composed of a JASCO BIP-I pump, a YMC-Pack SIL-06 column, and a Hitachi 638-0410 UV detector (detecting at 256 nm). A mixture of hexane and ethyl acetate (10 : 1 in volume) was used as eluent.

Other Measurements. XRD patterns were recorded on a Rigaku Geigerflex 2070 diffractometer (monochromated Cu $K\alpha$ radiation). Surface areas of the solid catalysts were measured by a BET method of N_2 adsorption at 77 K using a BEL Japan BELSORP 28SA automatic gas adsorption apparatus, after the samples were evacuated at 573 K.

Results

Solid–Solid Catalysis at Room Temperature. Figure 1 shows a typical time course of solid-state pinacol rearrangement of **1** over $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ at room temperature. In this paper, the horizontal axes of the figures for time courses

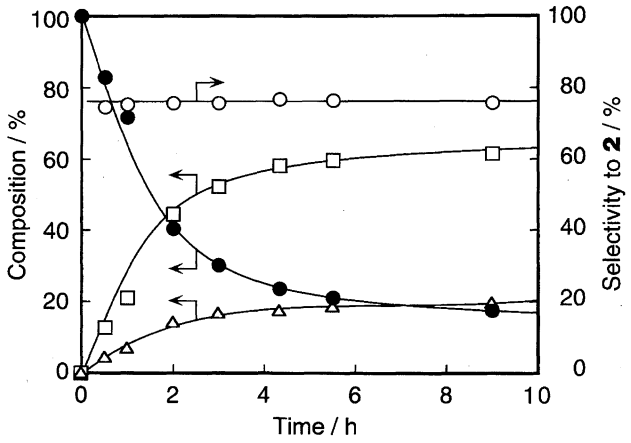


Fig. 1. Time courses of solid-state pinacol rearrangement of 1,1,2-triphenyl-1,2-ethanediol (**1**) to triphenylacetoaldehyde (**2**) and diphenylacetophenone (**3**) over $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ at room temperature. ●: **1**, □: **2**, △: **3**, ○: selectivity to **2**. The reaction was carried out using 0.1 g of **1** and 0.2 g of the catalyst with 5 min of initial grinding.

indicate the reaction time including the initial mixing time. By grinding the mixture of **1** and the catalyst for 5 min, the reaction took place to yield **2** and **3** without any further treatments such as continuous grinding of the mixture. Conversion of **1** for the pinacol rearrangement exceeded 50% at 2 h; the conversion (%) is defined as 100×(total amount of **2** and **3**)/(initial amount of **1**). The consumed **1** was balanced by yielded **2**, **3**, and a very little **4** (only 1% of conversion to **4** at 9 h, not shown in Fig. 1). Namely, pinacol rearrangement of **1** to **2** and **3** (Scheme 1) took place in the solid-state, but few side reactions occurred.

Table 1 compares the activities of various catalysts including $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ for the solid-state pinacol rearrangement at room temperature. $Cs_{2.5}H_{0.5}PW_{12}O_{40}$, $H_3PW_{12}O_{40}$, and organic resins with sulfonate groups (Amberlyst®-15 and Nafion®/SiO_2) showed activities. Although water molecules form by the reaction (Scheme 1), the reaction mixtures did not become dissolved or viscous in all cases. The selectivities to **2** were higher than 76% over the heteropoly compounds, while those over Nafion®/SiO_2 and Amberlyst®-15 were 70 and 49%, respectively. The selectivities were nearly constant during the reactions over all the catalysts.

We calculated the turnover number (TON) of the reaction as listed in Table 1. TON is defined as the number of **1** molecules converted divided by the number of protons in the catalysts (also listed in Table 1). TONs for $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ and Nafion®/SiO_2 were 9.3 and 4.0 for 9 h, respectively. For $Cs_{2.5}H_{0.5}PW_{12}O_{40}$, if we used the acid amount of the surface (0.06 mmol g^{-1})[13,31] instead of that of the catalyst bulk (0.15 mmol g^{-1}), TONs at 3 h and 9 h were estimated as 19.8 and 23.2, respectively.

Solid–Solid Catalysis at 333 K. When the reaction temperature for standing the mixture after grinding was elevated to 333 K, the reaction over the four active catalysts ($Cs_{2.5}H_{0.5}PW_{12}O_{40}$, $H_3PW_{12}O_{40}$, Amberlyst®-15, and Nafion®/SiO_2) took place more rapidly. A typical time course over $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ is shown in Fig. 2, and sim-

Table 1. Catalytic Activities of Solid Acids for Pinacol Rearrangement of **1** by Solid–Solid Reactions at Room Temperature

Catalyst	Acid amount	Surface area	Conversion (%)[a]				Selectivity to **2** (%)[b]	
	mmol g^{-1}	m^2 g^{-1}	3 h		9 h		3 h	9 h
			2+3	**4**	**2+3**	**4**		
$Cs_{2.5}H_{0.5}PW_{12}O_{40}$	0.15[c]	140	69 (7.9)	1	81 (9.3)	1	76	76
$H_3PW_{12}O_{40}$	0.96[d]	7.6	21 (0.4)	tr	42 (0.8)	tr	84	84
H-ZSM-5	0.39[e]	400	nd	tr	tr	tr	—	—
H-Y	2.6[e]	740	tr	tr	tr	tr	—	—
SiO_2–Al_2O_3	0.35[f]	560	tr	tr	tr	tr	—	—
SO_4^{2-}/ZrO_2	0.20[g]	125	tr	tr	tr	tr	—	—
Nb_2O_5	0.31[h]	131	tr	tr	tr	tr	—	—
TiO_2–SiO_2	0.50[i]	370	tr	tr	tr	tr	—	—
Amberlyst®-15	4.7[j]	50[j]	4 (0.01)	tr	15 (0.05)	tr	49	49
Nafion®/SiO_2	0.10[k]	344[l]	12 (2.1)	tr	23 (4.0)	1	69	70
PTS	5.3[m]	—[n]	nd	nd	nd	nd	—	—

a) Ratio of the amount the indicated products to the initial amount of **1**. The values in the parentheses indicate TON (number of **1** molecules reacted divided by the number of protons) for the formation of **2** and **3**. The letters of "tr" and "nd" mean the amount of the products being trace (less than 0.5% of conversion) and less than the detection limit of HPLC, respectively. b) Ratio of the amount of **2** to the total amount of **2** and **3**. c) Total amount protons in the bulk calculated from the composition. The amount of acids sites on the surface has been estimated to be 0.06 mmol g^{-1}.[11,13,31] d) Total amount of protons calculated from the composition being assumed as $H_3PW_{12}O_{40}\cdot 13H_2O$. e) Ion-exchange capacity calculated on the basis of the Si/Al atomic ratio. f) Measured by pyridine adsorption.[13] g) Measured by temperature-programmed desorption of ammonia.[13] h) Acid amount with acid strength of $H_0 \leq -5.8$, from the analysis report of CBMM. i) Acid amount with acid strength of $H_0 \leq -3.0$.[28] j) From a technical description of Organo. The acid amount corresponds to the ion-exchange capacity. k) Calculated from the loaded amount of Nafion® which has 0.8 mmol g^{-1} of acid amount according to a technical description of Du Pont. The acid amount corresponds to the ion-exchange capacity of the Nafion® resin. l) From Ref. 29. m) Total amount of protons in the bulk calculated from the composition. n) Not measured.

ilar time courses were observed for the other catalysts. The results are summarized in Table 2. The conversion to **2** and **3** was found to exceed 85% within 3 h of the reactions for these catalysts. The selectivities to **2** gradually decreased during the reaction periods. In particular, the selectivities were only 1% after 9 h of the reactions over $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ and Amberlyst®-15.

Some solid acids which were inactive at room temperature showed activities at 333 K. PTS was moderately active at this temperature. H-ZSM-5 and SiO_2–Al_2O_3 were still less active at 333 K. The reactions over these less active catalysts slightly preferentially yielded **2**, and the selectivities were unchanged during the reactions. Toda and Shigemasa reported that PTS effectively accelerated the reaction at 333 K under both reduced and atmospheric pressures to yield almost 100% of the conversion and selective formation of **3** with the catalyst to reactant molar ratio of **3**.[3] We confirmed that the conversion over PTS reached 100% at 3 h with 99.6% of selectivity to **3** when the reaction was carried out at 333 K under reduced pressure using a vacuum desiccator, although 50% of conversion at 3 h and nonselective formation of the products were obtained under atmospheric pressure.

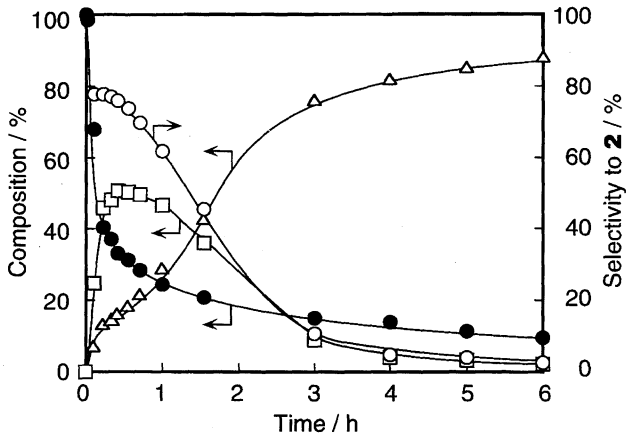


Fig. 2. Time courses of solid-state pinacol rearrangement of 1,1,2-triphenyl-1,2-ethanediol (**1**) to triphenylacetoaldehyde (**2**) and diphenylacetophenone (**3**) over $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ at 333 K. ●: **1**, □: **2**, △: **3**, ○: selectivity to **2**. The reaction was carried out using 0.1 g of **1** and 0.2 g of the catalyst with 5 min of initial grinding at room temperature.

Solid–Liquid Reaction System. We also carried out the pinacol rearrangement of **1** in liquid phase at room temperature, where the reactant was dissolved in $CHCl_3$, in order to compare with the solid–solid reactions. The results are summarized in Table 3. The solid–liquid reaction over $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ proceeded slower than the solid–solid reaction, and $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ was present as fine powder in the solvent. $H_3PW_{12}O_{40}$ was more active in the liquid-phase than in the solid-state, while $H_3PW_{12}O_{40}$ was apparently present as a solid in the liquid-phase reaction. The selectivities to **2** on both the heteropoly compounds were unchanged during the reaction, and as high as those in the solid-state reactions at room temperature. Amberlyst®-15, Nafion®/SiO_2, H-ZSM-5, and SiO_2–Al_2O_3 were inactive under the present conditions while the former two were highly active in the solid–solid reactions.

PTS was dissolved in the solvent to give a homogeneous solution, and showed some activity in this system. Contrary to the solid–solid reaction, PTS in the liquid–liquid reaction preferentially gave **3** (Table 3).

We additionally note that 1,4-dioxane was also examined as a solvent of the liquid phase reaction. However, no reaction occurred over any of the catalysts investigated.

Effects of the Grinding Conditions. Figure 3 shows time courses of the solid-state pinacol rearrangement at room temperature over $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ conducted under different mixing conditions. We found that the product yield became high by lengthening the grinding time. Conversion to the rearrangement products exceeded 90% at 9 h by grinding for 30 min with maintaining the amounts of **1** (0.1 g) and the catalyst (0.2 g), whereas it leveled off at about 80% when the mixing time was 5 min. On the other hand, the apparent catalytic activity decreased when we used a larger amount of the reaction mixture. Conversion to the rearrangement products was 55% after 9 h of the reaction by using 0.25 g and 0.5 g of **1** and the catalyst, respectively, with 5 min of

Table 2. Catalytic Activities of Solid Acids for Pinacol Rearrangement of **1** by Solid–Solid Reactions at 333 K

Catalyst	Conversion (%)[a]					Selectivity to **2** (%)[b]	
	3 h			9 h		3 h	9 h
	2+**3**		**4**	**2**+**3**	**4**		
$Cs_{2.5}H_{0.5}PW_{12}O_{40}$	85	(9.7)	tr	92	(10.5)	tr	11	1
$H_3PW_{12}O_{40}$	92	(1.6)	tr	94	(1.6)	tr	51	20
H-ZSM-5	10	(0.4)	tr	18	(0.8)	tr	63	63
SiO_2-Al_2O_3	2	(0.1)	1	5	(0.2)	3	53	53
Amberlyst®-15	95	(0.3)	tr	96	(0.4)	tr	37	1
Nafion®/SiO_2	86	(14.8)	1	90	(15.5)	2	62	53
PTS	46	(0.1)	tr	65	(0.2)	tr	56	56

a) Ratio of the amount the indicated products to the initial amount of **1**. The values in the parentheses indicate TON (number of **1** molecules reacted devided by the number of protons) for the formation of **2** and **3**. The letters of "tr" mean trace amount (less than 0.5% of conversion) of the products. b) Ratio of the amount of **2** to the total amount of **2** and **3**.

Table 3. Catalytic Activities of Solid Acids for Pinacol Rearrangement of **1** by Liquid Phase Reactions at Room Temperature

Catalyst	Conversion (%)[a]				Selectivity to **2** (%)[b]	
	3 h		9 h		3 h	9 h
	2+3	**4**	**2+3**	**4**		
(Solid–liquid system)						
$Cs_{2.5}H_{0.5}PW_{12}O_{40}$	35 (4.0)	tr	63 (7.2)	tr	87	88
$H_3PW_{12}O_{40}$	88 (1.6)	tr	97 (1.7)	tr	80	80
H-ZSM-5	tr	tr	tr	3	—	—
SiO_2–Al_2O_3	nd	tr	nd	tr	—	—
Amberlyst®-15	tr	tr	tr	tr	—	—
Nafion®/SiO_2	tr	tr	tr	tr	—	—
(Homogeneous liquid system)						
PTS	39 (0.1)	tr	75 (0.2)	1	19	19

a) Ratio of the amount the indicated products to the initial amount of **1**. The values in the parentheses indicate TON (number of **1** molecules reacted devided by the number of protons) for the formation of **2** and **3**. The letters of "tr" and "nd" mean the amount of the products being trace (less than 0.5% of conversion) and less than the detection limit of HPLC, respectively. b) Ratio of the amount of **2** to the total amount of **2** and **3**.

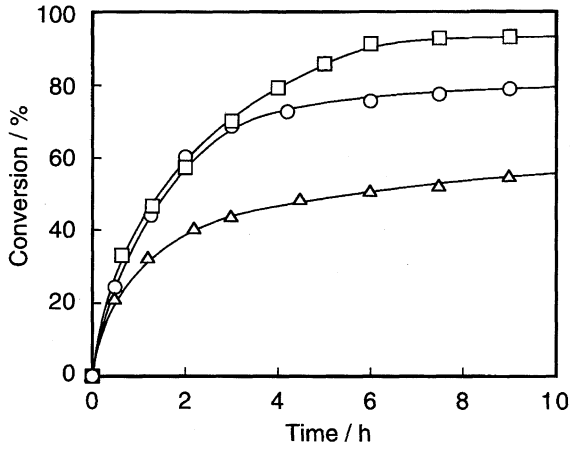


Fig. 3. Time courses of solid-state pinacol rearrangement of 1,1,2-triphenyl-1,2-ethanediol (**1**) to triphenylacetoaldehyde (**2**) and diphenylacetophenone (**3**) over $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ at room temperature with different mixing conditions of ○: 0.1 g of **1** and 0.2 g of the catalyst with 30 min of initial grinding, ○: 0.1 g of **1** and 0.2 g of the catalyst with 5 min of initial grinding, △: 0.25 g of **1** and 0.5 g of the catalyst with 5 min of initial grinding.

grinding time. The selectivity of the reaction did not change with the grinding conditions.

XRD Measurements. Figure 4 shows XRD patterns of the mixture of **1** (0.1 g) and $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (0.2 g) collected during the solid-state reaction at room temperature. Intense diffraction peaks due to **1** were observed after grinding (5 min) the reactant without the catalyst (Fig. 4a). However, the peaks became very weak after grinding with $Cs_{2.5}H_{0.5}PW_{12}O_{40}$. Intensities of the peaks due to **1** in the mixture at 15 min of the reaction (Fig. 4c), where conversion to the rearrangement products was 15%, were less than 1/200 those before grinding with the catalyst (Fig. 4a). The crystallinity of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ was unchanged, however, after the grinding (Fig. 4c). The XRD pattern of the reaction mixture changed little during the reaction period of 9 h (Fig. 4d); thus the difference in the XRD patterns did not directly reflect progress of the reaction. Diffraction peaks due to **2** and **3**, i.e., the species other than **1** and $Cs_{2.5}H_{0.5}PW_{12}O_{40}$, were not observed in these diagrams.

These XRD patterns of the reaction mixture were similar to that of a mixture of **1** and $Cs_3PW_{12}O_{40}$ (Fig. 4e). $Cs_3PW_{12}O_{40}$ is structurally almost the same as $Cs_{2.5}H_{0.5}PW_{12}O_{40}$, consisting of fine crystallites (ca. 10 nm), but it is catalytically inactive because of the absence of protons. We confirmed that the rearrangement reaction did not proceed over $Cs_3PW_{12}O_{40}$. Intensities of the XRD peaks due to **1** greatly decreased by grinding with $Cs_3PW_{12}O_{40}$, as observed for the mixture of **1** and $Cs_{2.5}H_{0.5}PW_{12}O_{40}$. Thus, the decrease in the intensities of XRD peaks due to **1** caused by mixing with the solid heteropoly compounds does not mean disappearance of **1**, but a great decrease in the crystallinity of the reactant **1**.

Discussion

Solid–Solid Catalysis by Various Solid Acids. The present study clarifies that solid-state pinacol rearrangement of **1** proceeds over various solid acids, and the results expand the field of solid-state acid-catalyzed reactions developed by Toda et al.[3—5] Among the catalysts examined, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$, $H_3PW_{12}O_{40}$, Amberlyst®-15, and Nafion®/SiO_2 can be regarded as active ones, because they exhibited activities at room temperature (Table 1). The differences in the activity of the catalysts would be related to their acid strengths. $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ and $H_3PW_{12}O_{40}$ are known as very strong acids.[11,13—15,32] Amberlyst®-15 and Nafion®/SiO_2 also have strong acidities,[29,30] but their acidities are somewhat weaker than those of the heteropoly compounds.[11] Acid strengths of H-ZSM-5 and SiO_2–Al_2O_3 are lower than those of the heteropoly compounds.[13,33,34] Acidity of an acetonitrile solution of PTS is weaker than that of $H_3PW_{12}O_{40}$.[35] Our results reveal that the four catalysts

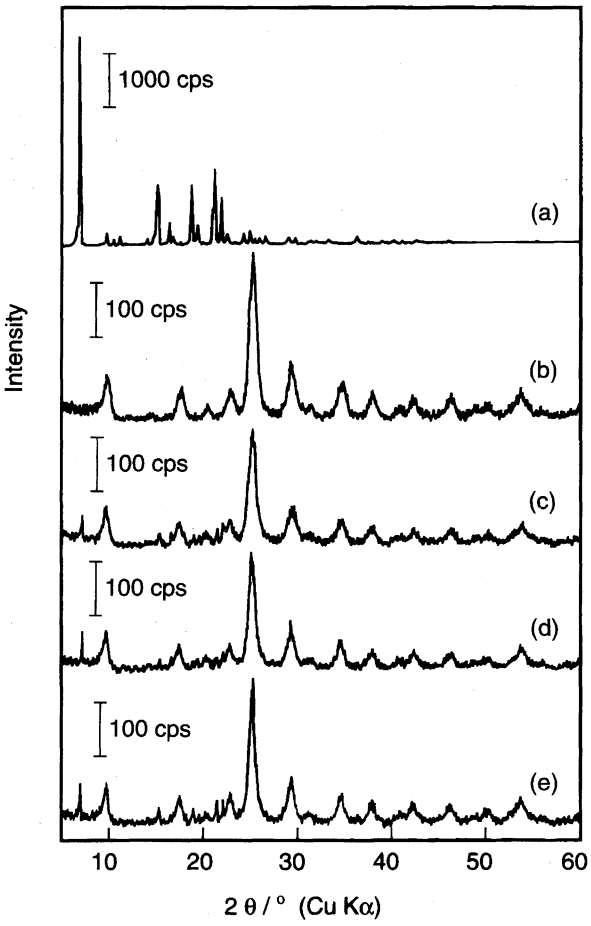


Fig. 4. XRD patterns of (a) 1,1,2-triphenyl-1,2-ethanediol (**1**) (after grinding for 5 min), (b) $Cs_{2.5}H_{0.5}PW_{12}O_{40}$, (c) mixture of **1** and $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ being allowed to react for 15 min, (d) mixture of **1** and $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ being allowed to react for 9 h, and (e) mixture of **1** and $Cs_3PW_{12}O_{40}$. Reactions were carried out at room temperature using 0.1 g of **1** and 0.25 g of the catalyst with 5 min of initial grinding. Grinding of **1** and $Cs_3PW_{12}O_{40}$ was conducted with the same manner.

active at room temperature ($Cs_{2.5}H_{0.5}PW_{12}O_{40}$, $H_3PW_{12}O_{40}$, Amberlyst®-15, and Nafion®/SiO_2) are distinguished by the strong acidities, while that the other weaker solid acids become slightly active only at the elevated temperature (Tables 1 and 2).

The catalytic results indicate another feature of the present system. The inorganic solid catalysts except $H_3PW_{12}O_{40}$ were more active in the solid–solid reaction than in the solid–liquid reaction (in $CHCl_3$), although mass transport in the solid sate seems to be rather more restricted than that in the liquid phase. This would be ascribed to the absence of solvent in the solid-state reaction; reactant molecules can interact with the acid sites without poisoning by solvent molecules. As a matter of fact, 1,4-dioxane completely hindered the reaction, as mentioned in the Results. In contrast, the higher activity of $H_3PW_{12}O_{40}$ for the solid–liquid reaction is probably explained by formation of "pseudoliquid phase":[11a] internal surfaces of $H_3PW_{12}O_{40}$ become available for reactions through adsorption of the reactant molecules. In fact, $H_3PW_{12}O_{40}$ has been reported to show a high catalytic activity for rearrangement of benzopinacol in liquid phase due to the formation of a "pseudoliquid phase".[36]

Characteristics of the Solid–Solid Reaction over $Cs_{2.5}H_{0.5}PW_{12}O_{40}$. The present results demonstrate that $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ is the most active acid catalyst for the solid–solid pinacol rearrangement, in particular at room temperature. The TON of the reaction over $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ was much larger than those over the other catalysts (Table 1). We note that TON over $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ at room temperature is calculated to be 23.2 for 9 h of the reaction, if we use the amount of acid sites present on the surface;[13,31] $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ is *catalytically* active for the solid–solid pinacol rearrangement.

We suppose that the pore structure of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ greatly contributes to the high catalytic activity, in addition to the strong acidity. Since $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ consists of aggregated fine particles which give the relatively high surface area, the reactant should be effectively dispersed on the surface of the catalyst. Interstices between the aggregated particles form mesopores characteristic to $Cs_{2.5}H_{0.5}PW_{12}O_{40}$, and the mesoporosity of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ should be important to catalyze the reaction of bulky molecules such as **1**. We note that H-ZSM-5, characterized by the microporosity of the zeolite structure, exhibits very low activity; bulky reactant molecules will be excluded from the intrapore acid sites.

We can estimate the number of "surface reactant layers" on $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ from the molecular size of **1** and the surface area of the catalyst, by assuming that the reactant molecules were present as stacked layers which fully covered the surface after grinding. The area occupied by one molecule of **1** projected onto its (100) plane is calculated to be 0.648 nm^2 with 0.6 nm of thickness from the results of XRD structural analysis.[37] Since 0.1 g (0.34 mmol) of **1** was present on 0.2 g of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (140 $m^2\,g^{-1}$), the number of the surface reactant layers is estimated to be $(0.648\times10^{-18}\times N_A\times0.34\times10^{-3})/(140\times0.2) = 4.7$ layers, where N_A is Avogadro's number. Namely, about 5 monolayers of **1** were present on the surface of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$, and the catalytic tests showed that more than 80% of the reactant molecules underwent the reaction (see Table 1). The reactant molecules present in the second to fifth layers, which do not contact the catalyst surface at first, must have been diffused to undergo the reaction on the catalyst surface. Hence, we conclude that the solid-state reactant molecules are not immobilized during the reaction but diffuse to undergo the reaction catalytically over $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ even at room temperature; the solid phase provides an environment where the organic molecules are rather mobile.

We infer that a key to accelerating the reaction is grinding finely the solid crystalline reactant to prepare an intimate mixture with the catalyst. Insufficient mixing would result in low conversion to the products, because coarsely ground large particles of **1** do not closely contact the catalyst surface. This is supported by the results in Fig. 3; a high yield of the products was achieved by long time grinding, and it

decreased under the less sufficient mixing conditions where the amount of the reaction mixture was enlarged under the constant mixing time. On the other hand, the XRD results indicate that the grinding of **1** with the Cs salts of $H_3PW_{12}O_{40}$ causes a drastic decrease in its crystallinity but not in that of the catalyst, regardless of the occurrence of the catalytic reactions. Namely, the grinding process collapses the crystallites of **1** to produce nearly X-ray amorphous fine particles. We infer that the reactant molecules become mobile in the amorphous particles to undergo the reaction, because the molecules in the amorphous state should no longer be strictly immobilized as in the crystalline state. The residual large crystalline particles detected by XRD would remain during the reaction to limit the final conversion below 100%.

We propose a model of the reaction at the solid–solid interface as schematically drawn in Fig. 5. The first step of the reaction is close contact of the fine particles of **1** with the catalyst surface. The grinding process collapses the crystallites of the reactant to prepare such a state. The reaction proceeds at the contacted solid–solid interface. The products separate from the surface and diffuse into the organic solid phase to fill the positions of reactant molecules in the bulk without formation of large and less mobile crystalline particles. In fact, XRD did not detect any peaks due to the products. Then the replaced reactant molecules become able to contact the catalyst surface to undergo the rearrangement.

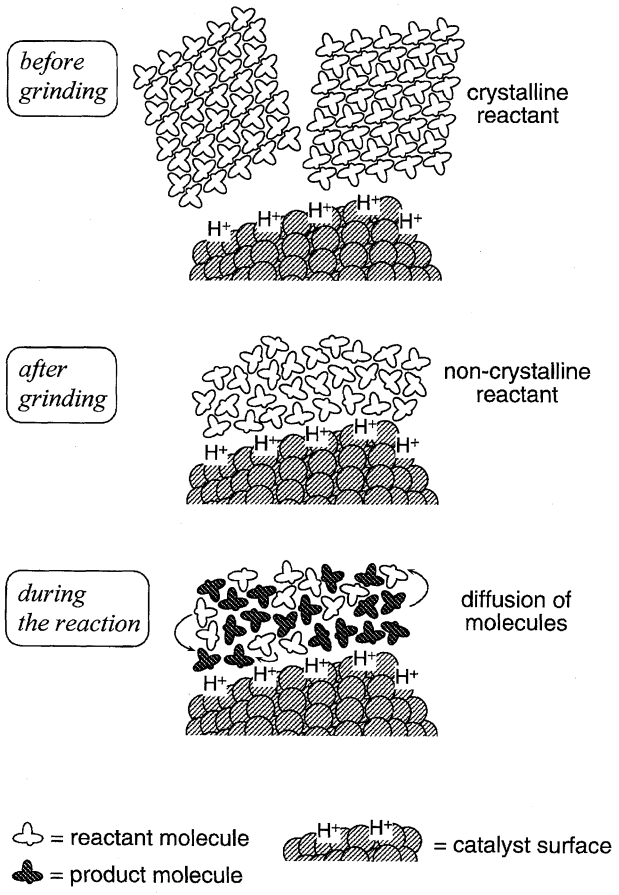


Fig. 5. Schematic model of how the solid–solid catalytic reaction occurs over $Cs_{2.5}H_{0.5}PW_{12}O_{40}$.

The reaction proceeds through reoccurrence of the diffusion and replacement of the molecules in the amorphous organic phase.

Selectivity of the Rearrangement Products. Toda and Shigemasa reported that solid–solid pinacol rearrangement of **1** over PTS gave **3** selectively with almost 100% of conversion at 333 K under both atmospheric and reduced pressures.[3] They presumed that hydride ion more easily migrates to give **3** than the bulky phenyl anion (see Scheme 1), because the solid-state reaction takes place under sterically crowded and less mobile conditions.

However, the present study confirmed that selectivity of the solid–solid pinacol rearrangement varied with the reaction temperature (Tables 2 and 3). The reactions at room temperature over the heteropoly compounds and Nafion®/SiO_2 preferentially gave **2**, whereas the selectivity to **3** increased at 333 K. Thus, the solid-state reaction cannot be simply characterized by the tendency toward selective formation of **3**. Our results showed that **2** and **3** formed in parallel at room temperature over these catalysts, the selectivities being constant during the reaction (Table 1 and Fig. 1). On the contrary, the reactions at 333 K gave **3** with nearly 100% of the selectivities; the amount of **2** increased at the initial stage but decreased with the reaction time after passing a maximum amount (Table 2 and Fig. 2). Hence, we suppose that pinacol rearrangement of **1** itself essentially forms **2** and **3** in parallel, and isomerization of **2** to **3** occurs independently on the rearrangement reaction in some cases. Toda and Shigemasa mentioned that **3** is thermodynamically more stable than **2**.[3]

We can rationalize the time courses that differ with the reaction temperatures by assuming that the isomerization reaction requires a temperature higher than that for the rearrangement reaction. When the reaction is conducted at low temperatures (such as room temperature), the selectivity is constant during the reaction because the isomerization does not occur. In contrast, the reaction at elevated temperatures causes isomerization of **2** to **3**, and thus selectively gives **3**. The results of high selectivity to **3** at 333 K obtained by Toda and Shigemasa[3] are consistent with this assumption (their results involve selective formation of **2** at lower temperature (298 K) over CCl_3COOH).

By comparing the selectivity to **2** over various catalysts carried out at temperatures where the isomerization did not proceed, we found that it decreased in the order of $H_3PW_{12}O_{40} > Cs_{2.5}H_{0.5}PW_{12}O_{40} >$ Nafion®/SiO_2 > H-ZSM-5 > PTS > SiO_2–Al_2O_3 > Amberlyst®-15. This ordering appears to correspond more or less to the acid strengths of the catalyst; strong acids such as $Cs_{2.5}H_{0.5}PW_{12}O_{40}$, $H_3PW_{12}O_{40}$, and Nafion®/SiO_2 gave higher selectivities to **2**. Although the mobility of phenyl anion is restricted more than that of hydride ion because of steric effects, phenyl anion itself has a higher migratory aptitude than hydride ion due to large electron density on aryl group. This can explain the selective formation of **2**; however effects of acid strength on the selectivity change is unclear at present. Anyway, we conclude that selectivity of the solid-state pinacol rearrangement of **1** is not defined as preferential formation of **3**, as inferred

by Toda and Shigemasa,[3] but depends on the catalysts used.

Conclusions

This study clarified that $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ can work as an active solid acid catalyst for solid–solid reactions as well as for conventional solid–liquid and solid–gas reactions. The solid-state pinacol rearrangement proceeds over $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ much more effectively than on PTS, which is a typical solid acid catalyst for solid–solid organic reactions. The strong acidity of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ should be a reason for such high activity. A key to the solid–solid reactions over $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ is crushing organic crystals through mixing with the catalyst powders into very fine nearly amorphous organic particles. The ground reactant particles are highly dispersed on the catalyst to undergo the reaction effectively. This feature indicates that the mechanism of solid-state reactions of organic species on inorganic macromolecular catalysts differs from those between organic crystals, where the host–guest inclusion phenomena have been reported to be a key to promoting the reaction.[3,5]

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