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Unique catalysis of an acidic salt of heteropoly acid, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$, consisting of microcrystallites

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Abstract

Catalytic functions of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$, an acidic salt of dodecatungstophosphoric acid, were investigated for hydration of olefins in large excess water and pinacol rearrangement in a solvent-free solid–solid system. $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ worked as insoluble fine particles constructed by aggregated microcrystallites during the hydration; the particle size was determined to be 40–200 nm when dispersed in water. Hydration of 2,3-dimethyl-2-butene was efficiently catalyzed by the fine particles at 343 K. Furthermore, the heteropoly compound catalyzed solid–solid pinacol rearrangement at room temperature, the mesoporous structure of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ being retained. The catalytic activities of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ for these reactions were found to be higher than those of other conventional solid catalysts.

Keywords: Acid catalysis; Heteropoly compounds; Hydration; Solid-solid catalysis; Microcrystallites

1. Introduction

Heteropolyacids are polymeric oxoacids composed of more than two different metal ions. $H_3PW_{12}O_{40}$ is a member of heteropolyacids, and known as a strong acid which efficiently catalyzes a variety of reactions such as alkylation and acylation of hydrocarbons, hydration of olefins, and polymerization of THF [1,2]. An acidic cesium salt, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$, also exhibits strong solid acidity [3], and is present as fine particles possessing relatively high surface areas with mesopores [4,5]. This salt is insoluble in water and various organic solvents, and thus utilized as an effective solid acid catalyst in solid–liquid and solid–gas reaction systems [1–3,6–8]. Another feature of the Cs salt is the hydrophobic surface [9].

From these characteristics, we have attempted to apply the heteropoly compound to reactions in the presence of excess water [10,11]. Such ‘‘water-tolerant catalysis’’ using solid acids is important for replacing homogeneous acid-catalyzed systems where liquid acids such as H_2SO_4 and HF, having disposal or toxic problems, are used as catalysts [12]. In addition, we reported solid–solid catalysis of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ for pinacol rearrangement as another type of environmentally benign system [13].

In the present paper, we have further studied the catalysis of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ for environmentally compatible processes. We will describe high catalytic performance of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ for hydration of olefins in large excess water and solid–solid pinacol rearrangement owing to the ultrafine-particle structure.

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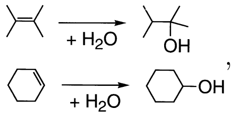
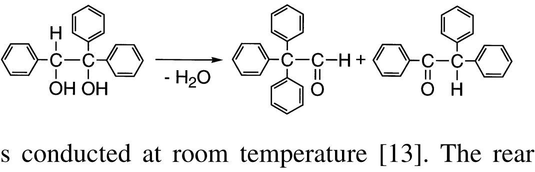
2. Experimental

$Cs_{2.5}H_{0.5}PW_{12}O_{40}$ was prepared from aqueous solutions of $H_3PW_{12}O_{40}$ and Cs_2CO_3 according to the literature [4]. The secondary particle size of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ dispersed in water was analyzed by laser diffraction method using a Shimadzu SALD-2000A analyzer. Surface area and mesopore size distribution were determined from N_2 adsorption isotherms measured with a BEL Japan BELSORP 28SA gas adsorption apparatus after evacuation of the samples at 523 K. H-ZSM-5 (Toshoh HSZ-860HOA, Si/Al=37), Nb_2O_5 (CBMM HY-340 AD/1177), Amberlyst-15 (Organo), Nafion-H (NR-50, Du Pont Japan), *p*-toluenesulfonic acid (Wako, abbreviated as PTS hereafter), $H_3PW_{12}O_{40}$ (Nippon Inorganic Color and Chemicals), and H_2SO_4 (Wako) were used as reference catalysts.

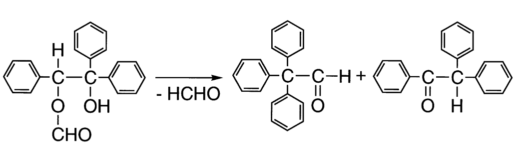
Catalysis of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ was investigated for two types of reactions. Hydration of olefins, 2,3-dimethyl-2-butene and cyclohexene



in a solid–liquid system was carried out by stirring catalyst in a mixture of the oily reactants and excess water [11]. Products were analyzed by gas chromatography. Solid–solid pinacol rearrangement of 1,1,2-triphenyl-1,2-ethanediol to triphenylacetoaldehyde and diphenylacetophenone



was conducted at room temperature [13]. The rearrangement reaction of 1,1,2-triphenyl-1,2-ethanediol-2-formate



was also examined. The reactions were initiated by grinding a mixture of the solid reactant and catalyst for 5 min at room temperature, and the mixture was then kept under the ambient conditions. Products were analyzed by HPLC.

3. Results and discussion

3.1. *Particle size distribution of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ in water*

$Cs_{2.5}H_{0.5}PW_{12}O_{40}$ consists of fine particles constructed by aggregation of microcrystallites in which Keggin-type $PW_{12}O_{40}^{3-}$ clusters are arranged in a body-centered cubic manner, and has a high surface area (around 130 $m^2\,g^{-1}$) [2]. Each crystallite corresponds to a primary particle, and an aggregate of the crystallites is regarded as a secondary particle. Interstices between the primary particles correspond to mesopores [2,5], which are defined as pores with widths between 2 and 50 nm [14]. The size of the primary particles has been estimated to be around 10 nm by the BET surface area and the line width of the X-ray diffraction peak [5,9].

A laser diffraction technique afforded the size of the secondary particles of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$. Fig. 1 shows the secondary particle size distribution of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ dispersed in water analyzed by this method. The particles were distributed from 40 to 200 nm. $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ forms a colloidal suspension in water, and we have already reported that the surface area and pore size, i.e., aggregated state of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ was somewhat altered after treatments with water [9]. However, the secondary particle

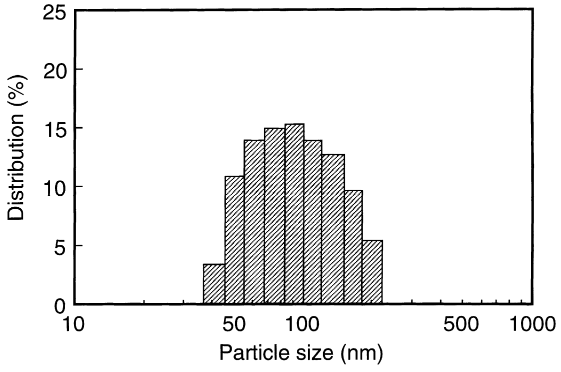


Fig. 1. Particle size distribution of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ dispersed in water measured by laser diffraction method.

size obtained by the laser diffraction is consistent with that of $Cs_3PW_{12}O_{40}$ estimated by transmission electron microscopy [4]. This fact suggests that the secondary particles, and thus the mesoporous structure, of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ are almost retained in water. We have already shown weak interactions between water molecules and the surface of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ by water adsorption measurement [9]. The less hydrophilic nature would prevent the $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ secondary particles from disaggregating in water.

3.2. *Water-tolerant catalysis of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ – hydration of olefins*

Table 1 summarizes the activities and selectivities of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ and some other acids for hydration of 2,3-dimethyl-2-butene in the presence of a large excess of water. The data were collected at 343 K after the reaction for 2 h. $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ was most active among these acid catalysts in the unit of the activity per acid amount. The activity of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ was comparable to those of Amberlyst-15, PTS and H_2SO_4 even if compared on the basis of the catalyst weight. We also examined reusability of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ recovered after a catalytic run by centrifugation and dried in air, and found that the high catalytic activity was retained in the second and third runs. These facts reveal the high catalytic potential of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ for solid–liquid hydration of olefins in water.

Table 2 provides the catalytic performance of these acids for hydration of cyclohexene. In contrast with the reaction of 2,3-dimethyl-2-butene, the activity of H-ZSM-5 was much more active than those of all the

Table 1
Activity and selectivity of acid catalysts for hydration of 2,3-dimethyl-2-butene[a]

Catalyst	Acid amount (mmol g^{-1})	Surface area (m^2 g^{-1})	Rate[b]		Selectivity (%)		
			(μ mol g^{-1} min^{-1})	(mmol (acid-mol)$^{-1}$ min^{-1})	Alcohol[c]	Ether[d]	Dimer[e]
Inorganic solid acid							
$Cs_{2.5}H_{0.5}PW_{12}O_{40}$							
Run 1	0.15[f]	130	10.4	69.3	99.2	0.8	0
Run 2[g]			11.1	74.0	97.0	2.0	1.0
Run 3[g]			8.3	55.5	98.4	1.6	0
H-ZSM-5	0.44[h]	440	4.8	10.9	96.7	3.3	0
Nb_2O_5	0.31[i]	130	0.1	0.3	100	0	0
Polymer catalyst							
Amberlyst-15	4.70[j]	50[j]	13.2	2.8	100	0	0
Nafion	0.80[j]	0.02[j]	4.4	5.5	100	0	0
Homogeneous acid							
$H_3PW_{12}O_{40}$	1.0[k]		4.7	4.7	98.2	1.8	0
PTS	5.3[k]		13.7	2.6	100	0	0
H_2SO_4	19.8[k]		9.7	0.5	84.1	15.2	0

[a] Reaction conditions: 2,3-dimethyl-2-butene/water/catalyst=7.8 cm^{-3} (0.065 mol)/43.2 cm^{-3} (2.4 mol)/1 g, 343 K, under atmospheric pressure in a glass flask attached with a refluxing condenser.

[b] Estimated from the results obtained after the reaction for 2 h.

[c] 2.3-Dimethyl-2-butanol.

[d] 2,3,-Dimethylbutyl ether.

[e] Dimer of 2,3-dimethyl-2-butene.

[f] Amount of protons calculated from the composition.

[g] Catalytic run using the catalyst employed in the previous run after recovering by centrifugation and drying in air.

[h] Ion-exchange capacity calculated from the Si/Al atomic ratio.

[i] Acid amount with acid strength of $H_0 \leq -5.8$ [10].

[j] From Ref. [10]. Acid amount corresponds to the ion-exchange capacity.

[k] Amount of protons calculated from the composition.

Table 2
Activity and selectivity of acid catalysts for hydration of cyclohexene[a]

Catalyst	Rate[b]		Selectivity (%)	
	(μmol g^{-1} min^{-1})	(mmol (acid-mol)$^{-1}$ min^{-1})	Cyclohexanol	Dicyclohexylether
Inorganic solid acid				
$Cs_{2.5}H_{0.5}PW_{12}O_{40}$	0.8	5.3	81.3	18.7
H-ZSM-5	30.7	69.8	99.8	0.2
Nb_2O_5	0	0	–	–
Polymer catalyst				
Amberlyst-15	7.2	1.5	98.7	1.3
Nafion	3.4	4.3	96.7	3.3
Homogeneous acid				
$H_3PW_{12}O_{40}$	0.3	0.3	64.0	36.0
PTS	3.5	0.7	95.7	4.3
H_2SO_4	12.8	0.7	99.4	0.6

[a] Reaction conditions: cyclohexene/water/catalyst=7.8 cm^{-3} (0.077 mol)/43.2 cm^3 (2.4 mol)/43.2 cm^{-3} (2.4 mol)/1 g, 373 K, under autogenous pressure in an autoclave.

[b] Estimated from the results obtained after the reaction for 2 h.

other catalysts. The high activity of H-ZSM-5 for this reaction has already been reported, and in fact, applied to a commercial process by Asahi [15]. This has been explained by the hydrophobic property of the pores of H-ZSM-5 and the shape selectivity due to peculiar fitting of the reactant molecules to the pores in size, being a special case. If the activity was compared among the catalyst other than H-ZSM-5, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ was most active per acid amount (Table 2).

Hence, it should be emphasized that $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ is a widely applicable active catalyst for various acid-catalyzed reactions in the presence of large excess water. Such water-tolerant catalysis of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ in aqueous media has already been reported for hydrolysis of esters [10].

3.3. *Solid–solid catalysis of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ – pinacol rearrangement*

Table 3 summarizes the catalytic activities of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ and some other solid acids for solid–solid pinacol rearrangement of 1,1,2-triphenyl-1-2-ethanediol and 1,2,2-triphenyl-1,2-ethanediol-2-formate at room temperature. For comparison, we also show the results of a conventional liquid phase reaction. $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ exhibited the highest activities for the solid–solid reactions of both the reactants. PTS did not catalyze the solid–solid reactions at room temperature, although Toda et al. [16] reported that it accelerated the solid–solid pinacol rearrangement at 333 K. The strong acidity of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ will contribute to its high activity at room temperature. The high surface area of the heteropoly compound due to the fine-particle structure should also be another factor for the activity because $H_3PW_{12}O_{40}$, having low surface area (6 m^2 g^{-1}), was less active than $Cs_{2.5}H_{0.5}PW_{12}O_{40}$. We also note that the activity of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ in the solid–solid system was higher than that for the conventional solid–liquid reaction. Since the solid–solid reaction proceeds in the absence of solvent molecules, the reactant molecules can interact directly and easily with the acid sites on the catalyst; the intimate contact is responsible for the high activity of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ in the solid–solid reaction. In contrast, superiority of $H_3PW_{12}O_{40}$ or PTS in the liquid phase reaction would be due to “pseudo-liquid” behavior [1,2] of the heteropolyacid in the reactant solution or dissolution of PTS in $CHCl_3$.

A typical time course of the solid–solid reaction over $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ is illustrated in Fig. 2. The solid–solid reaction gradually proceeded for several hours only after the initiation by grinding a solvent-free mixture of the solid catalyst and reactant. The turnover number of the reaction of 1,1,2-triphenyl-1,2-

Table 3
Activity and selectivity of acid catalyst for pinacol rearrangement of 1,1,2-triphenyl-1,2-ethanediol and 1,1,2-triphenyl-1,2-ethanediol-2-formate by solid–solid reactions[a]

Catalyst	Surface area (m2 g^{-1})	Reaction of 1,1,2-triphenyl-1,2-ethanediol			Reaction of 1,1,2-triphenyl-1,2-ethanediol-2-formate		
		Conversion at 3 h (%)[b]		Selectivity to aldehyde (%)[c]	Conversion at 3 h (%)[b]		Selectivity to aldehyde (%)[c]
$Cs_{2.5}H_{0.5}PW_{12}O_{40}$	130	69	[7.9]	76	38	[4.2]	64
		35	[4.0]	87[d]			
$H_3PW_{12}O_{40}$	7.6	21	[0.4]	84	32	[0.5]	80
		88	[1.6]	97[d]			
H-ZSM-5	400	nd	[–]	–	tr	[–]	–
		tr	[–]	–[d]			
Amberlyst-15	4.7[e]	4	[0.01]	49	17	[0.06]	49
		tr	[–]	–[d]			
PTS	–[f]	nd	[–]	–	tr	[–]	–
		39	[0.1]	19[d,g]			

[a] Reaction conditions: reactant/catalyst=0.1 g/0.2 g, room temperature.

[b] Ratio of the total amount of triphenylacetoaldehyde and diphenylacetophenone to the initial amount of the reactant. The values in the brackets indicate turnover number (number of the converted reactant molecules divided by the number of protons on the catalyst) for pinacol rearrangement. 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.

[c] Ratio of the amount of triphenylacetoaldehyde to the total amount of the aldehyde and diphenylacetophenone.

[d] The data obtained from liquid phase reaction. Reaction conditions: reactant/catalyst=0.1/0.2 g, in $CHCl_3$ (20 cm^3) as solvent, room temperature.

[e] From a technical description of Organo, Japan.

[f] Not measured.

[g] The reaction was carried out in a homogeneous liquid phase because PTS was dissolved in $CHCl_3$.

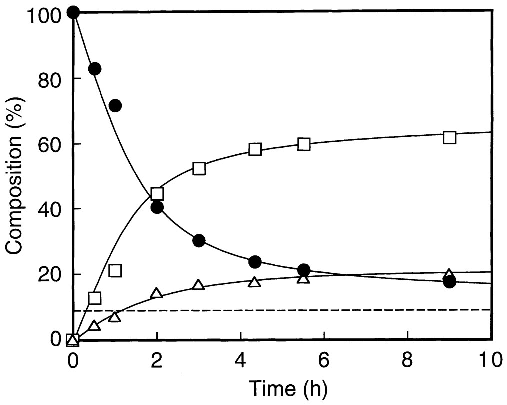


Fig. 2. Time course of solid–solid pinacol rearrangement of 1,1,2-triphenyl-1,2-ethanediol to triphenylacetoaldehyde and diphenylacetophenone over $Cs_{2.5}H_{0.5}PW_{12}O_{40}$. Reaction was initiated by grinding a mixture of the reactant (0.1 g) and the catalyst (0.2 g) for 5 min and conducted at room temperature by standing the ground mixture in air. (●) 1,1,2-triphenyl-1,2-ethanediol, (□) triphenylacetoaldehyde, (△) diphenylacetophenone. Dashed line indicated the fraction of each product at when the number of each product molecule formed was equal to the acid amount of the catalyst.

ethanediol over $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ reached 8 at 3 h of the reaction, where the turnover number is defined as the number of total products divided by that of all protons involved in the catalyst. Hence, we deduce that the reactant and product molecules diffuse in the solid phase without continuous grinding to catalytically undergo the reaction.

Fig. 3 shows N_2 adsorption–desorption isotherms of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ before and after the solid–solid reaction. The catalyst after the reaction with 1,1,2-triphenyl-1,2-ethanediol for 3 h was dispersed into 1,4-dioxane to dissolve the organic compounds on the surface. Then the catalyst was separated by centrifugation prior to the N_2 adsorption–desorption measurement. As shown in Fig. 3, both the isotherms before and after the reaction are classified into type IV isotherms with type H2 hysteresis loops, according to the IUPAC definition [17], whereas the BET surface area after the reaction (62 m^2 g^{-1}) was about half that of the untreated catalyst. Pore size distribution curves of both the samples estimated from the desorption branch of the isotherms with the Dollimore–Heal

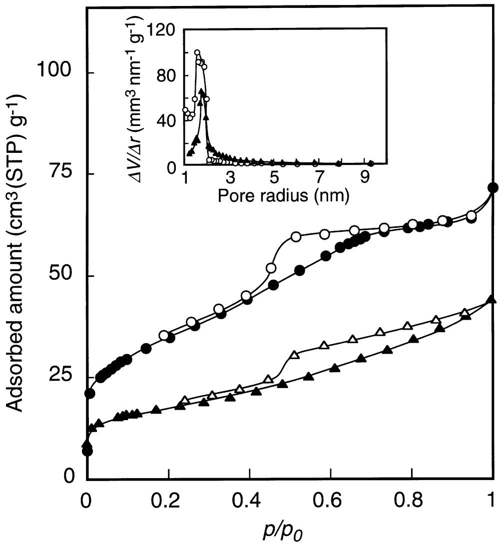


Fig. 3. Nitrogen adsorption–desorption isotherms of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ before (●,○) and after (▲,△) the solid–solid reaction of 1,1,2-triphenyl-1,2-ethanediol at room temperature for 3 h initiated by grinding a solid reaction mixture for 5 min. Inset: pore size distribution curves of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ before (○) and after (▲) the solid–solid reaction estimated by the Dollimore–Heal method.

method (Fig. 3, inset) [18] exhibited peaks at around 2 nm of pore radius. These facts demonstrate that the mesopore structure of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ was essentially retained after the solid–solid reactions, although the decrease in the surface area suggests that some organics were stuffed to be insufficiently removed in the pores. If the decrease in the surface area had been accompanied by a change of the pore structure, the shape of the hysteresis loop and pore size distribution curve would have been altered. The structural stability of the catalyst surface in the solid–solid system is in contrast with the behavior of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ in aqueous media, where the pore structure and acid amount of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ somewhat changed due to partial liberation of small heteropoly clusters [9], being an advantage of the solid–solid catalysis conducted under moderate conditions without poisoning by solvent molecules.

4. Conclusions

Acidic heteropoly compound $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ is mesoporous fine particles with a relatively high surface area. The structural features are regarded as an advantage for its catalytic applications, which has been exemplified in the present study by several environmentally compatible reactions, hydration in large excess water and pinacol rearrangement in a solvent-free system. The mesopores of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ are present on its secondary particles constructed by aggregated microcrystallites, and the secondary particles are little disaggregated in water. In addition, the mesopore structure of the heteropoly compound does not essentially change during the solid–solid catalysis. The fineness of the catalyst particles is important for the solid–solid catalysis because the reactants can easily be mixed with the catalyst to intimately contact the acid sites.

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