Microporous Heteropoly Compound as a Shape Selective Catalyst : $Cs_{2.2}H_{0.8}PW_{12}O_{40}$

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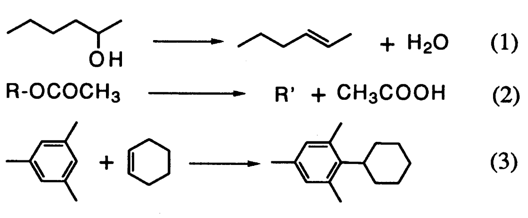
The pore size of acidic Cs salts ($Cs_xH_{3-x}PW_{12}O_{40}$) was precisely controlled by the Cs content. $Cs_{2.2}H_{0.8}PW_{12}O_{40}$ possesses micropores in the range from 6.2 to 7.5 Å (in diameter) and exhibits efficient shape selective catalysis toward decomposition of ester, dehydration of alcohol, and alkylation of aromatics in liquid-solid system. This is the first example of shape-selective solid superacid.

Heteropolyacids are known to be excellent catalysts for acid-catalyzed reactions and are already used in large-scale catalytic processes.[1-5] We reported previously that $H_3PW_{12}O_{40}$ and its acidic Cs salts possess superacidity and among them $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ showed very high activities in the liquid-solid reaction system, compared with other typical solid acid catalysts such as SO_4^{2-}/ZrO_2, Nafion-H, zeolites, etc.[6-9] Microcalorimetric studies also showed the strong acidity of $H_3PW_{12}O_{40}$.[10] The present study demonstrates that the pore structure of the superacidic Cs salts can be modified by careful control of preparation procedure, and that $Cs_{2.2}H_{0.8}PW_{12}O_{40}$ has a unique microporous structure and exhibits shape selective catalysis by its constrained pore size.

We prepared cesium hydrogen salts, $Cs_xH_{3-x}PW_{12}O_{40}$ (abbreviated as Csx), by titration of an aqueous solution of $H_3PW_{12}O_{40}$ with an aqueous solution of Cs_2CO_3.[6,11] To the solution of $H_3PW_{12}O_{40}$ (0.08 mol dm^{-3}), an appropriate amount of the aqueous solution of Cs_2CO_3 (Cs; 0.2 mol dm^{-3}) was added dropwise at a rate of about 1 cm^3 min^{-1} controlled automatically at room temperature. The resulting white colloidal solution was allowed to stand overnight at room temperature and then evaporated at 318 K to a solid. Surface area was measured by N_2 adsorption. The pore sizes of these salts were estimated from the adsorption of molecules having different molecular sizes as in the literatures,[12-15] where the adsorption was mainly measured by a microbalance connected directly to a high vacuum system[16] after the pretreatment at 573 K.

Catalytic reactions (eqs. 1-3) were performed in a three-neck flask (about 100 cm^3) after the catalysts (about 100 mg) were pretreated in a He flow at 573 K. The reactions were carried out with 7.9 mmol (in 142 mmol of nonane) of 2-hexanol at 373 K, 216 mmol of 1,3,5-trimethylbenzene and 10 mmol of cyclohexene at 343 K, isopropyl acetate (17 mmol in 142 mmol of undecane) at 373 K, *sec*-butyl acetate (15 mmol in 142 mmol of undecane) at 373 K, and cyclohexyl acetate (14 mmol in 112 mmol of nonane) at 373 K, respectively.



As shown in Figure 1, the change of the surface area as a function of the Cs content is remarkable. It was already reported that the salts of large cations such as Cs^+ and NH_4^+ have high surface areas and microporous structures.[1,17-19] The present result reproduced the known high surface area and microporosity of Cs2.5 and Cs3. The surface area increased significantly when the Cs content, x, changed from x=2 (1 m^2 g^{-1}) to x=3 (156 m^2 g^{-1}), although it decreased slightly from x=0 (6 m^2 g^{-1}) to x=2. Cs2.1, Cs2.2 and Cs2.5 gave the surface areas of 55, 72 and 135 m^2 g^{-1}, respectively.

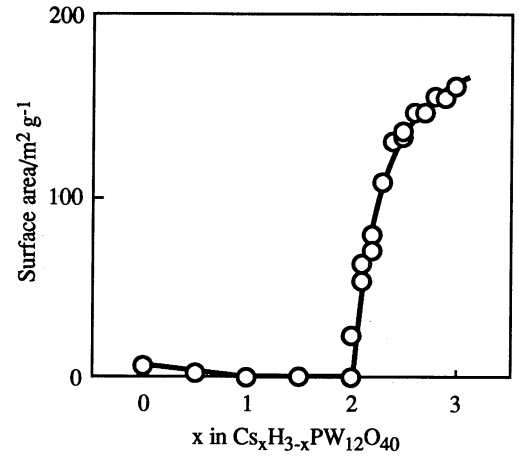


Figure 1. Surface area of $Cs_xH_{3-x}PW_{12}O_{40}$. The surface area was measured by N_2 adsorption at 77 K after the treatment in a vacuum at 573 K.

Table 1 compares the adsorption capacities of these Cs salts for various molecules. Benzene (kinetic diameter = 5.9 Å)[12] and neopentane (6.2 Å)[12] are adsorbed on Cs2.2 and Cs2.5, and the ratios of the adsorption capacity between Cs2.2 and Cs2.5 are similar to the ratio for N_2 adsorption. On the other hand, both are little adsorbed on Cs2.1, indicating that the pore size of Cs2.1 is less than 5.9 Å. Of particular interest are the results of 1,3,5-trimethylbenzene (7.5 Å) and 1,3,5-triisopropylbenzene (8.5 Å).[12-15] Both are adsorbed significantly on Cs2.5, but little on Cs2.2, indicating that the pore size of Cs2.2 is in the range of 6.2~7.5 Å and that of Cs2.5 is larger than 8.5 Å in diameter. This result demonstrates that the pore structure can be changed by the substitution of H^+ to Cs^+.

Figure 2 shows the relative catalytic activities of Cs2.1 and Cs2.2 for each reaction to those of Cs2.5. Cs2.5 catalyzed all the reactions with considerable activities (the reaction rates are shown in the parentheses in Figure 2). On the other hand, although Cs2.2 was as active as Cs2.5 for the dehydration of 2-hexanol and decomposition of isopropyl acetate, it was much less active for the decomposition of cyclohexyl acetate and alkylation of 1,3,5-trimethylbenzene. Critical sizes of molecules are estimated to be as follows;[12] 2-hexanol (~ 5.0 Å) ≈ isopropyl

Table 1. Adsorption Data for $Cs_xH_{3-x}PW_{12}O_{40}$ (x=2.1, 2.2, and 2.5)

Molecule (C.S.[a] /Å^2)	Kinetic diameter[b] /Å	Pressure /Torr (P/P$_0$)[c]	Temp. /K	Adsorption amount /μmol g^{-1} Cs2.1	Cs2.2	Cs2.5	Ratio[d]
N_2 (16.2)	3.6	137 (0.18)	77	487	861	1648	0.52
Benzene (30.5)	5.9	21 (0.20)	300	10	124	232	0.53
Neopentane (37.2)	6.2	99 (0.19)	273	5	179	390	0.46
1,3,5-TMB[e] (41.1)	7.5	0.6 (0.20)	300	–	11	237	0.05
1,3,5-TIPB[f] (59.4)	8.5	9×10^{-3} (0.20)	300	–	15	236	0.06

[a] Cross section calculated from the molecular weight and density of liquid. [b] See refs. 12-15. [c] The ratio of the partial pressure introduced (P) to the saturated vapor pressure (P_0). [d] Adsorption amount on Cs2.2 divided by that on Cs2.5. [e] 1,3,5-Trimethylbenzene. [f] 1,3,5-Triisopropylbenzene.

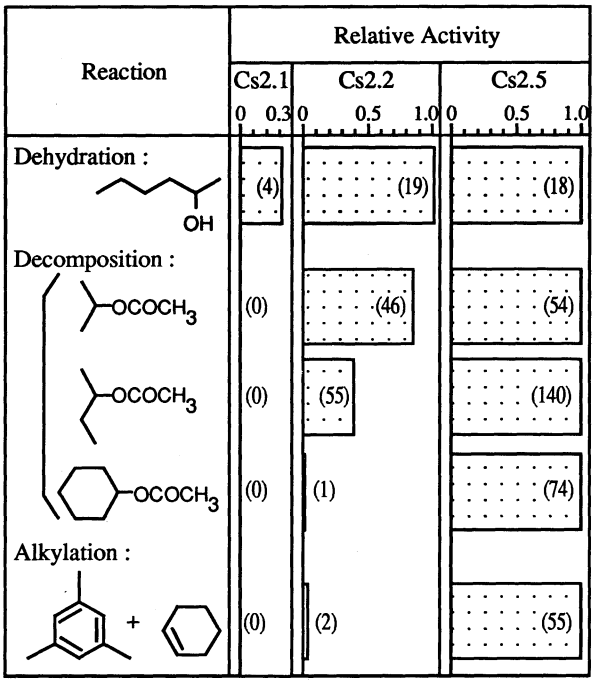


Figure 2. Relative activities of $Cs_xH_{3-x}PW_{12}O_{40}$ (x= 2.1, 2.2, 2.5) for various kinds of reactions in liquid-solid reaction system. Catalytic activity was estimated from the initial rate of the reaction. The activity of Cs2.5 for each reaction is to be unity. The figures in the parentheses are the reaction rates in the unit of mmol g^{-1} h^{-1}.

acetate (~ 5.0 Å) < *sec*-butyl acetate (~ 5.7 Å) < cyclohexyl acetate (~ 6.0 Å) < 1,3,5-trimethylbenzene (7.5 Å), where the figures in the parentheses for the former four are the critical sizes estimated from Pauling's atomic radius and molecular model by MM2. Therefore, the unique catalysis of Cs2.2 is understood if one assumes that it is active only for smaller molecules; that is, the "reactant shape selectivity", where the catalyst differentiates the reactant according to its size.

Results of Cs2.1 shown in Figure 2 demonstrate further that the catalytic functions are controlled by the Cs content. In accordance with the smaller pore, Cs2.1 had an activity for the dehydration of 2-hexanol, but was inactive for other reactions, irrespective of its considerably high surface area (55 m^2 g^{-1}).

It was confirmed that the typical zeolites such as H-Y and H-ZSM-5 were inactive for the decomposition of the esters and the alkylation of 1,3,5-trimethylbenzene with cyclohexene under the same reaction conditions. This is probably due to the weaker acidity for H-Y and the smaller pores for H-ZSM-5. The superacidity (and probably the organophilicity of the pore wall) makes the salt active in liquid-solid organic reaction systems. We wish to emphasize that this is the first example for the shape selective catalysis of heteropolyacids and believe that the shape selectivity of the heteropolyacids open up a way to the development of new types of solid superacid catalysts.

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