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Acidic Cesium Salts of Keggin-type Heteropolytungstic Acids as Insoluble Solid Acid Catalysts for Esterification and Hydrolysis Reactions

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Acidic cesium salts of the Keggin-type heteropolyacids, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ and $Cs_{2.5}H_{1.5}SiW_{12}O_{40}$, retained their strong acidity in water-containing organic media, and worked as insoluble, efficient acid catalysts in the hydrolysis of ethyl acetate and the esterification of acetic acid with ethanol. Silica-bound $Cs_{2.5}H_{0.5}PW_{12}O_{40}$, a newly prepared composite, was an active and easily recoverable solid acid catalyst for the hydrolysis of ethyl acetate with excess water.

Liquid-phase hydrolysis, esterification, and hydration, in which water exists as a reactant or a product, are usually catalyzed by homogeneous acids such as sulfuric acid. However, insoluble solid acid catalysts are preferable to homogeneous acids to facilitate product separation and catalyst recovery. Acidic ion-exchange resins are often employed,(1,2) but their use is limited to the reactions at relatively low temperatures of less than 100 °C because of low thermal stability. Carbon-entrapped heteropolyacid previously reported by us is also applicable as a solid acid catalyst to liquid-phase dehydration of alcohol,(3) but the heteropolyacid entrapped partly dissolves out when treated with water over 100 °C. Unlike silica-alumina and Y-type zeolite, a high-silica zeolite of H-ZSM-5 keeps its strong acidity in aqueous organic media owing to hydrohobicity. H-ZSM-5 is reported to work as a solid acid catalyst for the hydrolysis of ethyl acetate,(4) but its catalytic efficiency is much lower than that of an ion-exchange resin, Amberlyst-15, because of smaller acid amount. Recently, the acid catalysis of acidic alkali metal salts of the Keggin-type heteropolyacids with large surface area has been studied,(5-9) but few works have been done on water-participating organic reactions in the liquid phase. Here we wish to report that acidic Cs salts of the Keggin-type heteropolytungstic acids are considerably durable against hydrothermal treatment, so applicable as effective and insoluble solid acid catalysts to hydrolysis and esterification reactions.

Acidic Cs salts of heteropolytungstic acids were prepared through partial neutralization of aqueous 12-tungstophosphoric and 12-tungstosilicic acids with aqueous cesium carbonate, followed by calcination at 300 °C for 3 h under a reduced pressure. The hydrolysis of ethyl acetate and the esterification of acetic acid with ethanol were performed in a Pyrex flask (30 ml) containing a suspension of catalyst powder (60 mesh pass) and reactants with vigorous agitation. The products were analyzed by gas chromatography using a PEG Unisole 30T column (2 m) and *n*-tridecane as an internal standard.

Table 1 demonstrates significant water-durability of an acidic Cs salt of 12-tungstophosphoric acid

Table 1. Effect of Hydrothermal Treatment on Catalytic Property of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$

Hydrothermal treatment	Catalytic activity for benzylation of benzene[a)]	
	$PhCH_2Cl$ conversion/%	Ph_2CH_2 yield/%
None	90	48
120 °C, 6 days[b)]	100	53

a) Benzene/$PhCH_2Cl$/catalyst = 100/5/0.02 mmol, benzene reflux 2 h.
b) Treated in an autoclave, the recovered catalyst was calcined at 300 °C for 3 h prior to reuse for benzylation.

($Cs_{2.5}H_{0.5}PW_{12}O_{40}$); its catalytic activity for the benzylation of benzene[9)] as a test reaction did not change even after hydrothermal treatment at 120 °C, and the Keggin structure was completely retained.

This result suggests that acidic salts of heteropolyacid may be applicable as effective solid acid catalysts to several types of water–involving organic reaction in the liquid–phase. In fact, water–insoluble acidic Cs heteropolytungstates, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$, and $Cs_{2.5}H_{1.5}SiW_{12}O_{40}$, exhibited higher catalytic activity than a comparative inorganic solid acid of H–ZSM–5 in terms of specific rate per unit catalyst weight and turnover frequency for the hydrolysis of ethyl acetate and the esterification of acetic acid with ethanol in the liquid phase (Table 2). These acidic Cs salts were stable and insoluble during the reaction. Amberlyst–15, an organic solid acid, was two or three times more active than the acidic Cs salts of heteropolytungstic acids with respect to the catalytic activity per unit weight, but its turnover frequency that denotes the specific rate per unit acid amount was much lower than those of the Cs salts. Other Cs salts with lower Cs contents, acidic potassium and ammonium salts of heteropolytungstic acids, and acidic Cs salts of heteropolymolybdic acids were all

Table 2. Catalytic Activity of Solid Acids in Water–involving Organic Reactions

Solid acid	Surface area /m^2 g^{-1}	Acid amount /mequiv. g^{-1}	Hydrolysis[a)]		Esterification[b)]	
			Activity[c)]	TF[d)]	Activity[c)]	TF[d)]
$Cs_{2.5}H_{0.5}PW_{12}O_{40}$	102	0.156[h)]	2.04	13.1	0.52	33.3
$Cs_{2.5}H_{1.5}SiW_{12}O_{40}$	49	0.468[h)]	4.56	9.7	–	–
$Cs_3HSiW_{12}O_{40}$	83	0.305[h)]	1.76	5.8	–	–
Amberlyst–15[e)]	–	4.9[i)]	7.80	1.6	1.64	3.5
H–ZSM–5[e,f)]	–	0.234[h)]	0.43	1.8	0.03	1.3
SiO_2–Al_2O_3[e,g)]	–	–	0	0	–	–

a) Ethyl acetate/water/catalyst = 1080/27.8/0.1 mmol, 60 °C. b) Acetic acid/ethanol/catalyst= 100/100/0.1 mmol, 60 °C. c) Specific rate//10^{-3} min^{-1} g^{-1} . d) Turnover frequency/min^{-1}. e) 321 mg. f) Si/Al = 70. g) Si/Al = 6.25. h) Calculated value based on chemical composition. i) Determined by titration.

ineffectual, since they partly dissolved into the liquid phase in the course of the reactions.

Table 3 indicates qualitative estimation of acid strength for the solid acids used in the liquid media relevant to the reactions listed in Table 2. Both $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ and $Cs_{2.5}H_{1.5}SiW_{12}O_{40}$ showed relatively higher acid strengths than H–ZSM–5 in each liquid medium, which corresponds well to their higher turnover frequency than that of H–ZSM–5; in a non-polar solvent $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ shows a higher acid strength of less than −13.16 in terms of H_0.[10)] Thus these two acidic Cs salts of heteropolytungstic acids may be useful as solid acid catalysts to replace ion–exchange resins for acid–catalyzed water–involving organic reactions which depend on strong acidity or high temperatures.

Table 3. Acid Strength of Solid Acid in Polar Liquid Media[a)]

Solid Acid	Water			Water–AcOEt[b)]			AcOH–EtOH[c)]		
pK_a=	+1.5	+0.8	−3.0	+1.5	+0.8	−3.0	+1.5	+0.8	−3.0
$Cs_{2.5}H_{0.5}PW_{12}O_{40}$	+	±	−	+	−	−	+	+	−
$Cs_{2.5}H_{1.5}SiW_{12}O_{40}$	+	±	−	−	−	−	+	+	−
H–ZSM–5	+	−	−	−	−	−	−	−	−

a) Qualitative estimation by Hammett indicators, +: acidic color, −: basic color, ±: border line. b) 95 wt% AcOEt. c) An equimolar mixture of AcOH and EtOH.

The crystal sizes of acidic Cs salts of heteropolyacids, however, are very small (less than 1 μm), and the salts disperse in water forming colloidal solutions, so become inseparable by filtration. $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ could be supported on silica gel, but the $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ supported was easily removed from silica when put into water or alcohol. We tried to make a solid acid containing $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ that forms no colloid, consequently being readily recoverable from aqueous media, and found a preferable composite in which $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ was tightly bound with silica sol. This silica–bound composite was prepared through hydrolysis of ethyl orthosilicate with its 5 molar equivalents of water at 80 °C in the presence of colloidal $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ dispersed in ethanol, followed by evaporation, extraction with water at 80 °C, and calcination at 300 °C. The weight ratios of Si/Cs and W/Cs of the resultant composite observed by XRF analysis agreed with the values calculated from the amounts of orthosilicate and $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ initially fed.

Table 4 denotes the catalytic efficiency of the silica–bound $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ for the hydrolysis of ethyl acetate with excess water, comparing with the results by Amberlyst–15 and H–ZSM–5. Silica itself was inactive for the hydrolysis, but the silica–bound $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ catalysts were active and thermally stable up to 450 °C. They are catalytically more efficient than Amberlyst–15 and H–ZSM–5 with respect to the turnover frequency based on the unit acid site. No migration of colloidal $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ was observed during the reaction provided the weight ratio of silica matrix exceeded 0.8. Such favorable catalytic behavior of silica–bound $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ was never obtained for the other composites prepared from alumina sol, titania sol, and zirconia sol as matrix materials.

The silica-bound $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ found through the present study may be preferable as an insoluble solid acid catalyst particularly to the reactions conducted at relatively higher temperatures in highly polar liquid media such as esterification, hydrolysis, and hydration.

Table 4. Hydrolysis of Ethyl Acetate Catalyzed by Silica-bound $Cs_{2.5}H_{0.5}PW_{12}O_{40}$[a)]

Weight ratio of SiO_2 to $Cs_{2.5}H_{0.5}PW_{12}O_{40}$	Surface area /m^2 g^{-1}	Catalytic activity		
		k_1[b)]x10^3	k_2[c)]x10^3	TF[d)]
0.2	139	1.87	2.25	14.4
0.4	194	1.98	2.76	17.7
0.8	418	1.67	3.06	19.6
1.2	520	1.38	3.10	19.9
1.6[e)]	714	0.66	1.75	11.2
SiO_2[e,f,g)]	-	0.0	-	0.0
Amberlyst-15[e,h)]	-	19.13	-	3.9
H-ZSM-5[e,f)]	-	1.90	-	8.1

a) Ethyl acetate/water/$Cs_{2.5}H_{0.5}PW_{12}O_{40}$ = 9500/500/353 mg, 60 °C.
b) Specific rate/min^{-1} g^{-1}. c) Specific rate per unit weight of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ included/min^{-1} g^{-1}. d) Turnover frequency/min^{-1}. e) Catalyst 160 mg.
f) Calcined at 300 °C. g) Prepared by hydrolysis of ethyl orthosilicate. h) Dried at 100 °C.

References

1) S. A. Bernard and L. P. Hammett, *J. Am. Chem. Soc.*, **75**, 1798, 5834 (1953).
2) S. Sussman, *Ind. Eng. Chem.*, **38**, 1228 (1946).
3) Y. Izumi and K. Urabe, *Chem. Lett.*, **1981**, 663.
4) S. Namba, N. Hosonuma, and T. Yashima, *J. Catal.*, **72**, 16 (1981).
5) T. Nishimura, T. Okuhara, and M. Misono, *Chem. Lett.*, **1991**, 1695.
6) T. Nishimura, T. Okuhara, and M. Misono, *Appl. Catal.*, **73**, L7 (1991).
7) S. Tatematsu, T. Hibi, T. Okuhara, and M. Misono, *Chem. Lett.*, **1984**, 865.
8) T. Hibi, K. Takahashi, T. Okuhara, and M. Misono, *Appl. Catal.*, **24**, 69 (1986).
9) Y. Izumi, M. Ogawa, W. Nohara, and K. Urabe, *Chem. Lett.*, **1992**, 1987.
10) T. Okuhara, T. Nishimura, H. Watanabe, and M. Misono, *J. Mol. Catal.*, **74**, 247 (1992).

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