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Organic reactions in excess water catalyzed by solid acids

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Abstract

A solid acid, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$, efficiently catalyzed the reactions in which water participates such as hydrolysis of ester, hydration of alkene, and esterification, in excess water. This acidic salt was far superior in the activity to other oxide catalysts such as H-ZSM-5, Nb_2O_5, SO_4^{2-}/ZrO_2, and SiO_2–Al_2O_3. When $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ was separated from the reactant solution and reused five times for the hydrolysis of ethyl acetate repeatedly, the reaction rate was retained more than 90%. These results demonstrates that $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ is an efficient water-tolerant solid acid. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Acidic salts of heteropoly acid; Water-tolerant catalyst; Hydration; Hydrolysis

1. Introduction

There are many industrial processes in which water is concerned as solvent or reactant. Liquid acids such as H_2SO_4, HF and $AlCl_3$ have been utilized as catalysts in these processes. Because the liquid acids have disposal or toxicity problems, solid acids in particular environmental benign oxide-based catalysts are urgently desirable [1]. The challenges to replace them by solid catalysts have been performed. However, generally solid acids are not active in water due to poisoning, and only a few materials have been found as such water-tolerant solid acid catalysts. Being a notable example, H-ZSM-5 catalyzes hydrolysis of ester [2], and has been utilized in a commercial process for hydration of cyclohexene in excess water [3]. However, the constrained pores and not so strong acidity of H-ZSM-5 restrict its wide application. Some heteropoly compounds are strong acids, and they effectively catalyze a variety of reactions such as alkylation, decomposition, and acylation in solid–liquid reaction systems [4–6]. Among the heteropoly compounds, an insoluble acidic salt $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ exhibits very high activities for various reactions because of its superacidity and high surface area. Recently, Izumi et al. have shown versatility of heteropoly compounds as water-tolerant catalysts; $H_3PW_{12}O_{40}$ included in a silica matrix effectively catalyzes in the presence of water for esterification and hydrolysis [7,8].

In the present paper, we summarize our recent results on high catalytic performance of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (denoted as Cs2.5 hereafter) as a water-tolerant catalyst for various reactions such as hydrolysis of esters (Eq. (1)), hydration of alkene (Eq. (2)), and esterification (Eq. (3)). Supporting of Cs2.5 onto oxides was also investigated in order to improve the stability of catalyst in water.

$$\text{R-OCOCH}_3 + H_2O \rightarrow \text{R-OH} + CH_3COOH \qquad (1)$$

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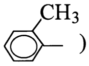
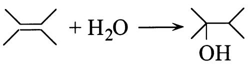
(R = C_2H_5, )



(2)

$$C{=}C\text{-}COOH + n\text{-}C_4H_9OH \rightarrow C{=}C\text{-}COOC_4H_9 + H_2O \quad (3)$$

2. Experimental

The acidic Cs salt, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$, was prepared from aqueous solutions of $H_3PW_{12}O_{40}$ and Cs_2CO_3 according to the literature [9,10]. The obtained salt is denoted as Cs2.5. Cs2.5-supported catalysts were prepared from oxides by an incipient-wetness technique. As the support, $Nb_2O_5{\cdot}nH_2O$ (NIOBIA, HY-340, CBMM, calcined at 373 K), Al_2O_3 (JRC-ALO-1, 150 $m^2\,g^{-1}$), TiO_2 (P-25, 50 $m^2\,g^{-1}$), ZrO_2 (170 $m^2\,g^{-1}$), and SiO_2 (Aerosil 200, 200 $m^2\,g^{-1}$). Various solid and liquid catalysts, H-ZSM-5 (JRC-Z5-70H, Si/Al=40), SiO_2–Al_2O_3 (JRC-SAL-2, Si/Al=5.3), SO_4^{2-}/ZrO_2, Nb_2O_5, Amberlyst-15, Nafion-H, H_2SO_4, $H_3PW_{12}O_{40}$, and *p*-toluenesulfonic acid (PTS) were used as reference catalysts. As test reactions, hydrolysis of esters, esterification, and hydration of alkenes were carried out in the presence of excess water.

Hydrolysis of esters was carried out with ethyl acetate and 2-methylphenyl acetate in large excess water at 333 and 353 K, respectively [11,12]. Hydration of 2,3-dimethylbut-2-ene was conducted at 353 K with stirring a mixture of the oily reactants and excess water [13]. Esterification of acrylic acid with *n*-butanol was examined at 353 K. Products were analyzed by gas chromatography.

3. Results and discussion

Table 1 shows the relative activities of various acid catalysts for hydrolysis of ethyl acetate and 2-methylphenyl acetate [11,12]. Among inorganic solid acids, Cs2.5 was most active for both the reactants in the unit of activity per catalyst weight. While Nafion was very active per catalyst weight, Cs2.5 was comparable to Nafion-H in the catalytic activity per unit acid amount of catalysts, and much more active than H-ZSM-5, SO_4^{2-}/ZrO_2, Nb_2O_5, and Amberlyst-15. The activities

Table 1
Catalytic activities of solid and liquid acids for hydrolysis of esters

Catalyst	Acid amount ($mmol\,g^{-1}$)	Surface area ($m^2\,g^{-1}$)	Rate per weight ($\mu mol\,g^{-1}\,min^{-1}$)	
			A[a]	B[b]
Solid oxides				
$Cs_{2.5}H_{0.5}PW_{12}O_{40}$	0.15	128	30.1	10.7
H-ZSM-5	0.39	400	27.6	0.0
SO_4^{2-}/ZrO_2	0.20	125	7.0	2.0
Nb_2O_5	0.31	131	4.0	1.7
SiO_2–Al_2O_3	0.35	560	0.0	0.0
Organic resins				
Amberlyst-15	4.70	50	41.2	16.5
Nafion-H	0.80	0.02	161.9	44.5
Liquid acids				
H_2SO_4	19.8	–	46.1	55.2
PTS	5.3	–	63.2	27.7
$H_3PW_{12}O_{40}$	1.0	–	70.4	14.4

[a] Hydrolysis of ethyl acetate at 333 K; ethyl acetate 16.9 mmol and H_2O 1.6 mol.
[b] Hydrolysis of 2-methylphenyl acetate at 353 K; 2-methylphenyl acetate 4.03 mmol and H_2O 3.3 mol.

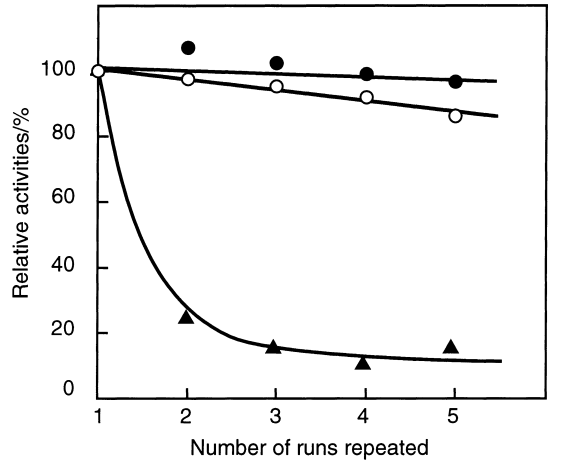


Fig. 1. Changes of the catalytic activities of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (○), H-ZSM-5 (●), and SO_4^{2-}/ZrO_2 (▲) for hydrolysis of ethyl acetate with the reusing the catalysts. Catalyst after a run was recovered from the solution by centrifugation or filtration, and dried under the ambient conditions prior to the next run.

of liquid acid catalysts, H_2SO_4, $H_3PW_{12}O_{40}$, and PTS per unit acid amount were less than that of Cs2.5, although the activities per catalyst weight of the liquid acids were higher than that of Cs2.5. The activity of Cs2.5 relative to the other catalysts was much higher for hydrolysis of bulky ester, 2-methylphenyl acetate for which H-ZSM-5 was inactive, demonstrating that Cs2.5 is a widely applicable as the water-tolerant solid acid. The stronger acidity of Cs2.5 than, e.g., that of H-ZSM-5 [10] should be a main reason for the high activity. In addition, the mesoporous structure and hydrophobic nature are probably responsible for the relative activity of Cs2.5 becoming higher for the bulky (hydrophobic) reactant [12].

When Cs2.5 was separated from the reactant solution of hydrogenolysis of ethyl acetate and reused, the reaction rate gradually decreased with the run number, and small amounts of $PW_{12}O_{40}^{3-}$ species were detected by IR and UV spectroscopies in the solution after the reactions. Fig. 1 shows changes of the catalytic activities of Cs2.5, H-ZSM-5, and SO_4^{2-}/ZrO_2 for hydrolysis of ethyl acetate [12]. The activity of Cs2.5 in the 5th run was about 90% that of the 1st run and was comparable to that of H-ZSM-5, while the activity of H-ZSM-5 remained almost unchanged after the 5th run. In contrast, the activity of SO_4^{2-}/ZrO_2 largely decreased with reusing, indicating intolerance of this solid acid to water. When Cs2.5 was treated with water (353 K for 24 h three times), the activity decreased slightly and the heteropoly species were liberated, similarly to the case of reusing.

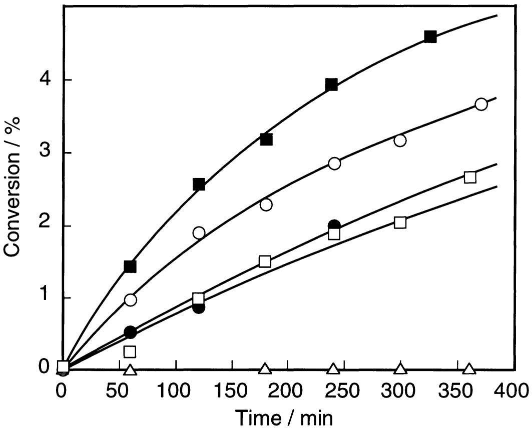


Fig. 2. Time courses of hydration of 2,3-dimethylbut-2-ene at 343 K over $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (○), H-ZSM-5 (●), Nb_2O_5 (△), $H_3PW_{12}O_{40}$ (□), and Amberlyst-15 (■). Reaction conditions; 2,3-dimethylbut-2-ene 7.8 cm^3, H_2O 43.2 cm^3, catalyst 1 g.

Fig. 2 shows time courses of hydration of 2,3-dimethylbut-2-ene over various acids [13]. Cs2.5 exhibited an appreciable activity for hydration of 2,3-dimethylbut-2-ene. Amberlyst-15 was somewhat more active than Cs2.5, while Nafion-H was much less active than Cs2.5. The order of catalytic activity per unit catalyst weight was Amberlyst-15>Cs2.5>H-ZSM-5>Nafion≫Nb_2O_5>H-Y≈SO_4^{2-}/ZrO_2≈0. We thus conclude that Cs2.5 can be used as an environmentally compatible water-tolerant catalyst for not only hydrolysis of ester but also other acid-catalyzed reactions. For hydration of cyclohexene, H-ZSM-5 was far superior in the activity to the other catalyst, as has been reported [3]. Because of the difference in molecular size (2,3-dimethylbut-2-ene>cyclohexene), mesoporous structure of Cs2.5 would largely contribute to its superiority to H-ZSM-5 for the hydration of 2,3-dimethylbut-2-ene.

The acidic salt, however, forms colloidal suspension in water, and recovering of the catalysts is not easy. To solve this problem, we attempted to immobilize Cs2.5 on oxide supports. The activity for supported Cs2.5 and the amount of leached heteropoly anion during hydrogenolysis of ethyl acetate are summarized in Table 2. Cs2.5-supported Nb_2O_5 was much

Table 2
Catalytic activity of supported $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ for hydrogenolysis of ethyl acetate at 343 K

Support[a]	Conversion[b]/%	Leached polyanion[c]/%	State of solution
$Nb_2O_5 \cdot nH_2O$	12.2	0	Transparency
Al_2O_3	3.7	0.1	Transparency
TiO_2	3.4	0.1	Transparency
ZrO_2	1.3	0.1	Transparency
SiO_2	3.5	1.2	Milky
SiO_2–Al_2O_3	0.1	36	Milky
$Cs_{2.5}H_{0.5}PW_{12}O_{40}$	32.0	4.0	Milky

[a] Loading amount of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ is 14 wt.%.
[b] For 2 h.
[c] Determined by UV spectroscopy.

more active among the supported catalysts and the release of the heteropoly species into water was completely suppressed. It was confirmed that the solution including Cs2.5/$Nb_2O_5 \cdot nH_2O$ was kept to be transparency during the reaction. However, the activity of Cs2.5/Nb_2O_5 was not sufficient at present. When SiO_2, TiO_2, ZrO_2 and Al_2O_3 were used as the support, the activities of Cs2.5 were poor.

Esterification of acrylic acid with *n*-butanol was examined. This reaction has been performed by using an ion-exchange resin catalyst or PTS in industries [14]. In addition, recently, Dupont et al. [15] reported that heteropolyacids supported on activated carbon were efficient solid catalysts for this reaction. In Table 3, the results for esterification of acrylic acid with *n*-butanol are summarized. Cs2.5 was comparable to SO_4^{2-}/ZrO_2 in the activity per catalyst weight and far superior to H-ZSM-5, SiO_2–Al_2O_3, and Nb_2O_5. The activity of Cs2.5 was less than those of liquid acids like $H_3PW_{12}O_{40}$, H_2SO_4, and PTS mainly because of the smaller amount of proton. It should be noted that when the reaction was performed in the presence of excess water, the activity of Cs2.5 was almost retained after addition of water to the reactants, although SO_4^{2-}/ZrO_2 lost the activity completely. These facts reveal that Cs2.5 is highly resistant to

Table 3
Activity and selectivity for esterification of acrylic acid with *n*-butanol

Catalyst	Weight (g)	Acid amount (mmol)	Conversion[a] (%)	Selectivity[a] (%)
Solid oxides				
$Cs_{2.5}H_{0.5}PW_{12}O_{40}$	1.0	0.15	19.2	99.8
			(14.5)	(91.8)
SO_4^{2-}/ZrO_2	1.0	0.20	21.2	99.7
			(0)	(–)
H-ZSM-5	0.6	0.25	4.1	95.0
Nb_2O_5	1.0	0.97	0	–
SiO_2–Al_2O_3	1.0		0	–
Organic solids				
Nafion-H	1.0	0.80	60.0	94.0
			(30.6)	(89.9)
Amberlyst-15	0.1	0.50	16.6	94.4
			(0.1)	(–)
Liquid acids				
$H_3PW_{12}O_{40}$	1.0	1.0	65.2	95.2
			(40.7)	(95.2)
H_2SO_4	0.1	2.0	69.0	93.5
			(28.5)	(93.4)
PTS	0.1	0.5	58.9	93.3
			(34.3)	(91.4)

[a] The reaction was carried out at 353 K for 4 h with acrylic acid 3 ml (43.7 mmol), *n*-butanol 4 ml (43.7 mmol), and toluene 5 ml (solvent). The results when 1 ml (55.6 mmol) of water was added to the reactant are shown in the parentheses.

water but not absolutely stable in water. As shown in Table 3, the deactivation of activity by water was observed for all of the catalysts.

4. Conclusion

The acidic Cs salt, Cs2.5, was found to be an efficient water-tolerant solid acid for hydrolysis of esters, esterification, and hydration of alkene in excess water. Cs2.5 was far superior in activity to other typical solid acid catalysts. Supporting Cs2.5 onto Nb_2O_5 suppressed the release of the heteropoly species in water, keeping the activity of Cs2.5 for the hydrolysis of ethyl acetate. The superiority of Cs2.5 in the water-tolerant catalysis is probably due to the mesoporous structure and hydrophobic nature of the surface.

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