Zirconium phosphate with a high surface area as a water-tolerant solid acid

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High surface area zirconium phosphate in an amorphous phase exhibits high activities for water-related reactions such as hydrolysis of ethyl acetate and esterification of acetic acid with ethanol. The zirconium phosphate is insoluble during the reaction, is recoverable by simple filtration, and can be reused at least five times without any treatment.

KEY WORDS: zirconium phosphate; water-tolerant catalyst; hydrolysis; esterification.

1. Introduction

Solid acid catalysts are environmentally friendly with respect to corrosiveness, safety, waste generation, and ease of separation and recovery [1]. Oxides and phosphates [1] are solid acids that are attractive for reactions in which water participates as a reactant or product, such as esterification, dehydration, and hydrolysis; however, few solid acids exhibit acceptable activity [2]. An additional problem is raised if the solid acid dissolves in water, causing contamination of the reaction mixture. For practical purposes, solid acids with high sedimentation also increase the ease of separating the catalyst from the reaction suspension.

Some ion-exchange resins, such as Nafion, exhibit high activity for water-related reactions [3]; however, the low thermal stability of these resins is a disadvantage. A high-silica H-ZSM-5 zeolite is the only commercial water-tolerant solid acid, but it is limited to applications involving large-size reactants or products due to its small uniform pores [3]. An acidic Cs salt of 12-tungustophosphoric acid, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$, is highly active in acid-catalyzed reactions, even in the presence of water [3], but has the disadvantage of being difficult to separate from the reaction suspension because of low sedimentation. Therefore, development of a new water-tolerant solid acid, which possesses high activity, is stable in the presence of excess water, and is easily separated from the reaction suspension, is needed.

We report that zirconium phosphate with a high surface area shows high activities for hydrolysis and esterification, is insoluble in the reaction mixture, and is recoverable by simple filtration. Furthermore, this catalyst is reusable without any treatments such as calcination or washing.

2. Experimental

Zirconium phosphate with a high surface area (Zr–P-*amorp*) was obtained by precipitation of $ZrCl_2O \cdot 8H_2O$ (Wako Chemical, Co., 1.0 mol dm^{-3}, 31.9 cm^3) and $NH_4H_2PO_4$ (Wako Chemical, Co., 1.0 mol dm^{-3}, 63.8 cm^3) at a molar ratio of $P/Zr = 2.0$. The precipitate was filtered, washed with water, and dried at 373 K. This zirconium phosphate was confirmed to be amorphous by XRD. As references, two crystalline zirconium phosphates, α-$Zr(H_2PO_4)_2$ and ζ-$Zr(H_2PO_4)_2$, were prepared according to the literature [4]. Before the reaction, they were calcined at 673 K in air. Amorphous niobium phosphate (Nb–P-*amorp*) and amorphous titanium phosphate (Ti–P-*amorp*) were obtained by methods described in the literature [5]. $Nb_2O_5 \cdot nH_2O$ (NIOBIA HY-340 AD/2322) was supplied from CBMM and treated at 373 K in air before the reaction. $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ [6] and sulfated zirconia [7] were prepared as described previously. H-ZSM-5 (JRC-Z5-70H, $Si/Al = 40$), H–Y (JRC-Z-HY-4.8, $Si/Al = 2.4$), H-mordenite (JRC-HM-20, $Si/Al = 10$), and SiO_2–Al_2O_3 (JRC-SAL-2, $Si/Al = 5.3$) were supplied from the Catalysis Society of Japan as reference catalysts.

The hydrolysis of ethyl acetate and the esterification of acetic acid with ethanol were performed in a 3-neck Pyrex flask (ca. 120 cm^3) at 343 K with stirring. An aqueous solution of 5 mass% ethyl acetate (Wako Chemical, Co., 30 cm^3, ethyl acetate 16.9 mmol) was used for the hydrolysis. In the esterification, a mixture of acetic acid (Wako Chemical, Co., 1 cm^3, 17 mmol), ethanol (Wako Chemical, Co., 1 cm^3, 17 mmol), and toluene (Wako Chemical, Co., 5 cm^3) as solvent was

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used. The products were analyzed with a gas chromatograph (FID-GC, Shimadzu GC-8A) using a column of Carbowax 300 M Chromosorb WAW (4 mm × 2 m). The amount of dissolved catalyst was estimated by ICP-AES (Shimadzu ICPS-8000) using the reaction mixture after the reaction. The adsorption isotherm of water was measured at 298 K by an automatic adsorption apparatus (BEL Japan Inc., BELSORP 18) after evacuation at 473 K for 2 h.

3. Results and discussion

Table 1 summarizes the catalytic data for the hydrolysis of ethyl acetate and esterification of acetic acid with ethanol over various solid acids. H-ZSM-5 and $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ showed high activities for both reactions [3]. In contrast, $LaPO_4$, SiO_2–Al_2O_3, H–Y, and H-mordenite were much less active. Although sulfated zirconia, Nb–P-*amorp*, and Ti–P-*amorp* gave moderate conversions, these catalysts were soluble in the reaction mixture and strongly deactivated upon repeated reactions. $Nb_2O_5 \cdot nH_2O$ showed activity comparable to Ti–P-*amorp* for both reactions, but this catalyst became inactivated after treatment with water at 353 K (table 1), probably due to dissolution of the active component.

Table 1
Catalytic data for hydrolysis of ethyl acetate and esterification of acetic acid with ethanol over various solid acids

Catalyst	Surface area ($m^2\ g^{-1}$)	Conversion (%)	
		Hydrolysis[a]	Esterification[b]
H-ZSM-5 (Si/Al = 40)	400	29	43
$Cs_{2.5}H_{0.5}PW_{12}O_{40}$[c]	128	29	67
SO_4^{2-}/ZrO_2[d]	227	22	12
Nb–P-*amorp*[d]	88	12	9
Ti–P-*amorp*[d]	174	11	6
Zr–P-*amorp*	130	8	20
$LaPO_4$	106	6	2
$Nb_2O_5 . nH_2O$[e]	131	3	11
SiO_2–Al_2O_3	539	0	2
H–Y (Si/Al = 2.4)	740	0	4
H-mordenite (Si/Al = 5.0)	500	0	4

[a] Reaction conditions: ethyl acetate 16.9 mmol, water 30 cm^3, catalyst weight: 0.8 g, 343 K and 2 h.
[b] Reaction conditions: ethanol 17.1 mmol, acetic acid 17.4 mmol, toluene 5 cm^3, catalyst weight 0.8 g, 343 K and 2 h.
[c] Catalyst powder could not be recovered by filtration.
[d] Catalyst was soluble in the hydrolysis reaction mixture, and strongly deactivated with repeated reactions.
[e] Treated with water at 353 K for 24 h before the reactions.

Table 2
Catalytic data for hydrolysis of ethyl acetate over various zirconium phosphates[a]

Catalyst	Surface area ($m^2\ g^{-1}$)	Conv. (%)	Dissolved amount[b] (%)	
			Zr	P
Zr-P-*amorp* 1st run	130	8.0	0.0	1.0
3rd run		7.1	0.0	0.9
5th run		7.4	0.0	0.7
α-$Zr(HPO_4)_2$	26	4.9	0.0	2.7
ζ-$Zr(HPO_4)_2$	10	4.7	0.0	0.9

[a] Reaction conditions: ethyl acetate 16.9 mmol, water 30 cm^3, catalyst weight: 0.8 g, 343 K and 2 h.
[b] Dissolved amount was estimated by ICP-AES using the reaction mixture after the reaction.

Zr–P-*amorp* exhibited activity in these reactions; for the hydrolysis, the catalytic activity was much higher than that of $LaPO_4$, SiO_2–Al_2O_3, H–Y, and H-mordenite, but was lower than H-ZSM-5 and $Cs_{2.5}H_{0.5}PW_{12}O_{40}$. For the esterification, the activity of Zr–P-*amorp* was second only to that of H-ZSM-5 and $Cs_{2.5}H_{0.5}PW_{12}O_{40}$. No dissolution of zirconium was observed after hydrolysis, and the dissolution of phosphorus was negligibly small (table 2), almost within the measurement error level. It should be emphasized that the Zr–P-*amorp* catalyst powder settled rapidly after the stirring stopped, allowing easy recovery of the catalyst by filtration. After filtration, a transparent solution was obtained, a result quite different from that found for $Cs_{2.5}H_{0.5}PW_{12}O_{40}$, which yielded a milky solution.

Figure 1 shows the changes in catalytic activity of Zr–P-*amorp* upon repeated reactions, along with the results of Nb–P-*amorp* and Ti–P-*amorp* for comparison. Between the runs, the catalyst was separated by filtration and dried at 373 K. The activities of Nb–P-*amorp* and Ti–P-*amorp* in the hydrolysis reaction greatly decreased after the first run. In contrast, the activity of Zr–P-*amorp* was unchanged for at least five runs, and dissolution of the catalysts was not observed (table 2). These results demonstrate that Zr–P-*amorp* is reusable for hydrolysis reactions without special treatment such as calcination or acid washing.

Table 2 displays a comparison of catalytic activity for hydrolysis of ethyl acetate over Zr–P-*amorp* and crystalline zirconium phosphates. The surface area and amount of dissolved catalyst are also presented. The crystalline zirconium phosphates (α-$Zr(HPO_4)_2$ and $10 m^2 g^{-1}$ ζ-$Zr(HPO_4)_2$ also possessed catalytic activity for the hydrolysis, but these activities were lower than that of Zr–P-*amorp*. Zr–P-*amorp* had a high surface area (130 $m^2\ g^{-1}$) in comparison with the crystalline zirconium phosphates (26 $m^2\ g^{-1}$ for α-$Zr(HPO_4)_2$ and 10 $m^2\ g^{-1}$ for ζ-$Zr(HPO_4)_2$. Thus, the high catalytic activity of Zr–P-*amorp* is due to its high surface area.

Zirconium phosphate and niobium phosphate are known to catalyze various acid-catalyzed reactions in organic media [8], but only a few reports exist concerning catalysis in the presence of excess water. Segawa *et al.* [9] reported that one zirconium phosphonate, $Zr[(O_3PCH_2.SO_3H)_x(O_3PC_{12}H_{25})_{1-x}]$, exhibited high activity for the

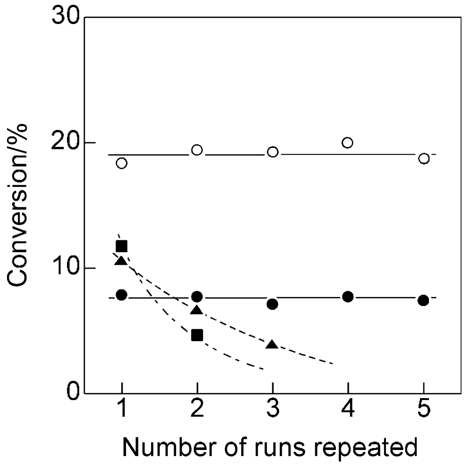

Figure 1. Change in conversion with repeated hydrolysis of ethyl acetate and esterification of acetic acid with ethanol over zirconium phosphate (Zr–P-*amorp*), niobium phosphate (Nb–P-*amorp*) and titanium phosphate (Ti–P-*amorp*). (●) hydrolysis and (○) esterification over Zr–P-*amorp*, (■) hydrolysis over Nb–P-*amorp*, and (▲) hydrolysis over Ti–P-*amorp*. Reaction conditions: hydrolysis; ethyl acetate 16.9 mmol, water 30 cm^3, catalyst weight 0.8 g, 343 K and 2 h, esterification; ethanol 17.1 mmol, acetic acid 17.4 mmol, toluene 5 cm^3, catalyst weight 0.8 g, 343 K and 2 h.

hydrolysis of ethyl acetate and esterification of acetic acid with ethanol, but zirconium phosphate was essentially inactive for these reactions. They proposed that the $–CH_2SO_4H$ and $–C_{12}H_{25}$ groups adopted acidic and hydrophobic functions, respectively, for $Zr[(O_3PCH_2\text{-}SO_3H)_x(O_3PC_{12}H_{25})_{1-x}]$, resulting in the high activity [9]. Although the reasons for the phenomenon are not well understood, the difference between their data and the data obtained by our group for zirconium phosphate is probably due to differences in the preparation procedures of the catalysts.

Reports have suggested that hydrophobicity of the catalyst surface as well as acidic properties dominate the catalytic activity of acid-catalyzed reactions in the presence of water, because acid sites surrounded by hydrophilic surface tend to be poisoned by water [2,10]. As shown in figure 2, the amount of water adsorbed at low relative pressure on H-ZSM-5 (Si/Al = 40), which is a commercial water-tolerant solid acid [11], was small, indicating that the surface of this catalyst is hydrophobic [12]. In contrast, a large amount of water was adsorbed on Zr–P-*amorp*, indicating the surface of this catalyst is relatively hydrophilic, although this catalyst showed activity for the water-related reactions. This novel feature of the high surface area zirconium phosphate is likely because only limited acid sites surrounded by a local hydrophobic surface work in the presence of excess water, or because acid sites of the zirconium phosphate have a specific structure that avoids excessive attacks of water, but these need further investigation.

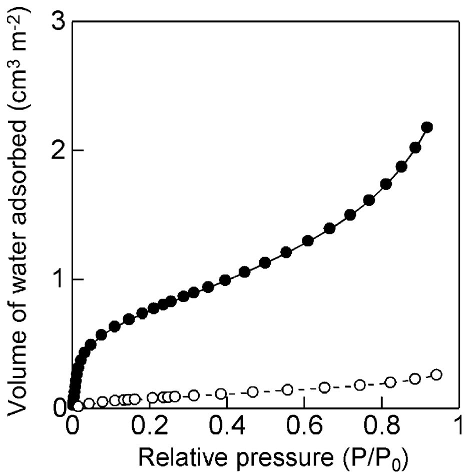

Figure 2. Adsorption isotherm of water on (●) high surface area zirconium phosphate (Zr–P-*amorp*) and (○) H-ZSM-5 (Si/Al = 40).

4. Conclusion

Zirconium phosphate with a high surface area had catalytic activity for water-related reactions such as hydrolysis and esterification, was insoluble in the presence of excess water, and possessed high sedimentation. In addition, this catalyst was reusable without any special treatment. Thus, we conclude that zirconium phosphate with a high surface area is a new candidate for water-tolerant solid acid catalysts.

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References

[1] K. Tanabe and W.F. Hoelderich, Appl. Catal. A 181 (1999) 399.
[2] T. Okuhara, Chem. Rev. 102 (2002) 3641.
[3] M. Kimura, T. Nakato and T. Okuhara, Appl. Catal. A 165 (1997) 227.
[4] R.C.T. Slade, J.A. Knowles, D.J. Jones and J. Roziere, Solid State Ionics 96 (1997) 9.
[5] S. Roca and C. Airoldi, Thermochim. Acta 284 (1996) 289.
[6] T. Okuhara, T. Nishimura, H. Watanabe and M. Misono, J. Mol. Catal. 74 (1992) 247.
[7] M. Hino, S. Kobayashi and K. Arata, J. Am. Chem. Soc. 101 (1979) 6439.
[8] K. Tanabe, M. Misono and Y. Ono, in: *New Solid Acids and Bases*, (Kodansha-Elsevier, Tokyo, 1989), pp.188.
[9] K. Segawa, A. Sugiyama and Y. Kurusu, Stud. Surf. Sci. Catal. 60 (1991) 73.
[10] L. Li, Y. Yoshinaga and T. Okuhara, Phys. Chem. Chem. Phys. 1 (1999) 4913.
[11] H. Ishida, Catal. Surv. Jpn. 1 (1997) 241.
[12] H. Nakamoto and H. Takehashi, Zeolites 2 (1982) 67.