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Influence of structural differences and acidic properties of phosphotungstic acids on their catalytic performance for acylation of pyruvate ester to α-acyloxyacrylate ester

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ABSTRACT

Various heteropolyacids, including Keggin-type ($H_3PW_{12}O_{40}$), Dawson-type ($H_6P_2W_{18}O_{62}$) and Preyssler-type ($H_{14}[NaP_5W_{30}O_{110}]$) phosphotungstic acids, were examined as catalysts for acylation of ethyl pyruvate with acetic anhydride to synthesize ethyl α-acetoxyacrylate in liquid phase. This compound is one of candidate monomers for bio-based polymers bearing high thermal durability and transparency. Catalytic performances correlated to the acid strength, the proton number and the stability of the phosphotungstic acids. Notably, performance of Preyssler-type phosphotungstic acid per unit mole of catalyst was higher than that of Keggin-type.

1. Introduction

Heteropolyacids (HPAs) are metal–oxygen clusters showing both strong acidity and high oxidizing ability [1]. These properties are very attractive and HPAs have been utilized as catalysts even in industrial processes, such as hydration of iso-butylene to tert-butanol, selective oxidation of ethylene to acetic acid and selective oxidation of methacrolein to methacrylic acid [2]. Many studies have been carried out over the past few decades on HPAs as catalysts for various organic reactions, and further explorations of new and significant catalyses with HPAs are still desired. In addition, from the viewpoint of green chemistry, HPA catalysts can contribute the development of more effective and greener reactions compare to that using corrosive acids such as HCl and H_2SO_4. Recently, we have reported efficient acylation of pyruvate esters with carboxylic anhydrides to α-acyloxyacrylate esters catalyzed by HPAs as shown in Scheme 1 [3]. α-Acyloxyacrylate ester is a promising candidate monomer for a bio-based polymer, being produced from biomass feedstock. Polymers of α-acyloxyacrylate esters show higher thermal durability than that of poly(methyl methacrylate) (PMMA), which is the material that widely used as sheets, displays, water cisterns, optical fibers, and coating resins because of its high transparency and high durability.

The reaction that we are interested in is the acylation of pyruvate esters with carboxylic anhydrides. This reaction typically progressed with tungsten-based Keggin-type HPAs owing to their strong acidity. Pyruvate ester as a substrate is one of the derivatives of lactic acid and can be synthesized by esterification and oxidative dehydrogenation from lactic acid. Lactic acid is mainly produced by fermentation of glucose, and it is considered as one of the most useful building block compounds of biorefinery [4]. Various types of HPAs, including Keggin-type ($H_3PW_{12}O_{40}$), Dawson-type ($H_6P_2W_{18}O_{62}$) and Preyssler-type ($H_{14}[NaP_5W_{30}O_{110}]$) phosphotungstic acids, their structures being illustrated in Fig. 1, were used as catalysts. It is well known that structural differences of HPAs are closely related to their properties, such as acidic property, redox property and stability [1].

Recently, Heravi et al. have demonstrated several efficient catalyses by $H_{14}[NaP_5W_{30}O_{110}]$ [5]. These researches are meaningful in terms of suggesting excellent catalytic performance of $H_{14}[NaP_5W_{30}O_{110}]$. Since Preyssler-type HPA, $H_{14}[NaP_5W_{30}O_{110}]$, has 14 protons per a mole of molecule, being almost five-times larger than that of Keggin-type $H_3PW_{12}O_{40}$, and it should be advantageous for utilization as an acid catalyst from the viewpoint of realizing high proton concentration with small amount of catalyst. Moreover, as $H_{14}[NaP_5W_{30}O_{110}]$ is known to show lower reduction potential than that of $H_3PW_{12}O_{40}$ [6], high stability for reductive decomposition is also implied. In addition, the excellent hydrolytic stability of this polyanion in a wide pH range (pH 0–10) was also pointed out [5]. However, the acid property of

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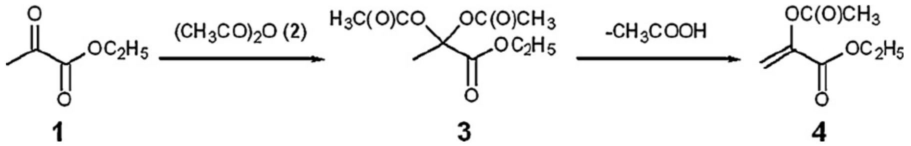

Scheme 1. Acylation of ethyl pyruvate with acetic anhydride.

this HPA is still not clear at present. In fact, there have been no reported parameters for its acidity, such as proton affinity, dissociation constants, Hammet acidity function and differential heat of adsorption.

In this study, three types of phosphotungstic acid, $H_3PW_{12}O_{40}$, $H_6P_2W_{18}O_{62}$ and $H_{14}[NaP_5W_{30}O_{110}]$, were used as catalysts, and their catalytic performances for acylation were evaluated. The acidic properties of these HPAs were also investigated by using temperature programmed desorption of ammonia (NH_3-TPD). Additionally, the stability of these HPAs was also evaluated by ^{31}P NMR and thermo gravimetric analysis (TGA). Furthermore, correlations between acidic properties, stability and catalytic performances were summarized.

2. Experimental

Keggin-type HPA, $H_3PW_{12}O_{40}$, was purchased from Nippon Inorganic Colour & Chemical and used without further purification. Preyssler-type HPA, $H_{14}[NaP_5W_{30}O_{110}]$, was prepared by following the previously described procedure [6,7]. Its cesium salts, $Cs_xH_{14-x}[NaP_5W_{30}O_{110}]$, were prepared by adding a prescribed amount of Cs_2CO_3 to the aqueous solution of $H_{14}[NaP_5W_{30}O_{110}]$. Dawson-type HPA, $H_6P_2W_{18}O_{62}$, was prepared from $Na_6P_2W_{18}O_{62}$ by extraction with ether according to the reported technique [8]. Structures of these HPA were confirmed by ^{31}P NMR (160 MHz, ECX-400, JEOL) in D_2O with respect to 85% H_3PO_4, XRD (Cu-Kα, RINT 2000, Rigaku), FT-IR (PARAGON 1000, Perkin Elmer) and elemental analysis (ICP-AES: IRIS-AP, Jarrell Ash Japan, AAS: AAnalyst 800, Perkin Elmer). Acylation of pyruvate ester with carboxylic anhydride was executed in carboxylic acid. In this paper, ethyl pyruvate (**1**), acetic anhydride (**2**) and acetic acid were used. Reactions were typically carried out at 343 K for 1 h. Products were analyzed by using FID-GC equipped with a capillary column. For NH_3-TPD measurement, Multi-Task T.P.D. (BEL Japan) was used as an instrument. Sample weight was 0.1 g, and NH_3 gas was adsorbed at 373 K. Heating rate was 10 K min^{-1} from 373 to 1173 K. Desorbed components were analyzed by a Q-mass detector (m/z = 16). Thermo gravimetric analysis (TGA, Thermo plus TG 8120, Rigaku) was carried out for the evaluation of thermal stability of each HPA. ^{31}P NMR (ECX-400, JEOL) of HPAs after reaction was measured in the same procedure described as above after dilution of reaction solution with D_2O.

Table 1
Catalytic performance of various HPAs.[a]

Entry	Catalyst	Conversion (%)	Yield (%)	
			3	**4**
1	$H_3PW_{12}O_{40}$	68	7	61
2	$H_6P_2W_{18}O_{62}$	59	0	54
3	$H_{14}[NaP_5W_{30}O_{110}]$	46	8	35
4[b]	*p*-TsOH	13	3	5
5[b]	H_2SO_4	21	12	8

[a] Reaction conditions: **1** (2 mmol), **2** (20 mmol), acetic acid (20 mmol), catalyst (entries 1–5, 2.5 mol%; entry 3, 1.25 mol%), 343 K, 1 h.
[b] See Ref. [3].

$H_{14}[NaP_5W_{30}O_{110}]\cdot 27H_2O$: ^{31}P NMR (ppm *vs.* 85% H_3PO_4, 160 MHz, D_2O): −9.4, FT-IR (cm^{-1}, KBr): 778 (υ(W–O_c–W)), 912 (υ(W–O_b–W)), 1018 (υ(W–O_t)), 1090, 1164 (υ(P–O)). Elemental analysis calculated (found) for $H_{14}[NaP_5W_{30}O_{110}]\cdot 27H_2O$ (%): Na 0.29 (0.31), P 1.95 (1.59), W 69.3 (69.6).

$H_6P_2W_{18}O_{62}\cdot 43H_2O$: ^{31}P NMR (ppm *vs.* 85% H_3PO_4, 160 MHz, D_2O): −12.3, FT-IR (cm^{-1}, KBr): 782 (υ(W–O_c–W)), 912 (υ(W–O_b–W)), 960 (υ(W–O_t)), 1091 (υ(P–O)). Elemental analysis calculated (found) for $H_6P_2W_{18}O_{62}\cdot 43H_2O$ (%): P 1.20 (1.23), W 64.3 (64.4).

3. Results and discussion

3.1. Acidic properties and catalytic performances of phosphotungstic acids

From the spectra of ^{31}P NMR, as shown in Fig. 2, HPAs were successfully synthesized with high purity, and chemical shifts of the peaks correspond to the values in the literature [3,9]. Small peaks of β-isomer were observed in the spectrum of $H_6P_2W_{18}O_{62}$, it being generated during the ether extraction with sulfuric acid (Fig. 2(b)).

Catalytic performances of the HPAs are summarized in Table 1. It has been confirmed that this reaction was a consecutive reaction from **1** to ethyl α-acetoxyacrylate (**4**) *via* ethyl 2,2-diacetoxypropionate (**3**) with $H_3PW_{12}O_{40}$ catalyst [3]. Since the solubility of $H_{14}[NaP_5W_{30}O_{110}]$ was low, the amount of the catalyst was decreased compared to those of $H_3PW_{12}O_{40}$ and $H_6P_2W_{18}O_{62}$. As shown in Table 1,

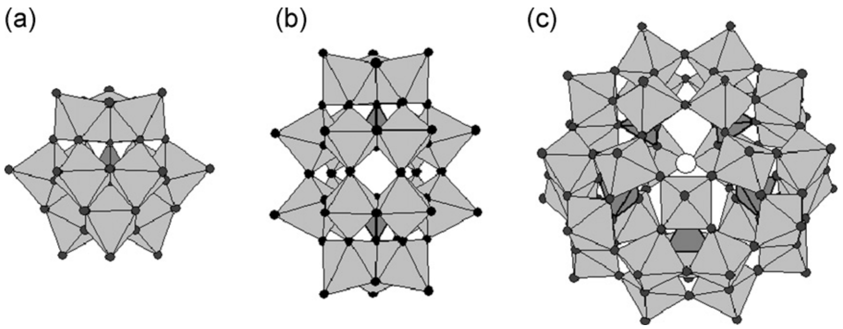

Fig. 1. Anion structures of HPAs: (a) α-Keggin-type ($[PW_{12}O_{40}]^{3-}$), (b) Dawson-type ($[P_2W_{18}O_{62}]^{6-}$), (c) Preyssler-type ($[NaP_5W_{30}O_{110}]^{14-}$), P (medium grey: P constructs PO_4 tetrahedral), W (light grey: W constructs WO_6 octahedral), O (dark grey sphere), Na^+ (white sphere in (c)).