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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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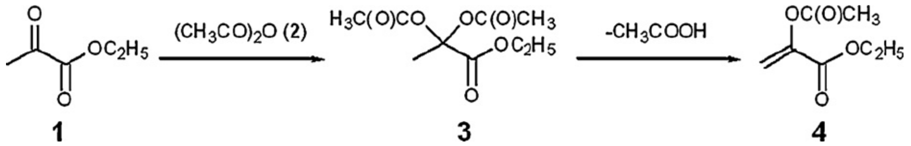

Scheme 1. Acylation of ethyl pyruvate with acetic anhydride.

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,

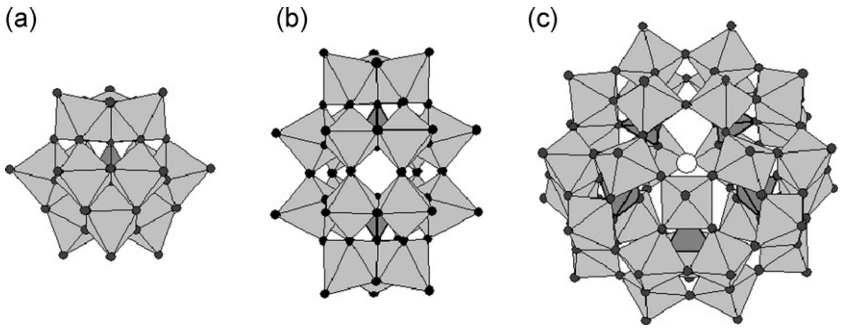

Fig. 1. Anion structures of HPAs: (a) α-Keggin-type ($[PW_{12}O_{40}]^{3-}$), (b) Dawson-type ($[P_2W_{18}O_{62}]^{6-}$), (c) Preyssler-type ($[NaP_5W_{30}O_{110}]^{14-}$), P (medium grey: P constructs PO_4 tetrahedral), W (light grey: W constructs WO_6 octahedral), O (dark grey sphere), Na^+ (white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

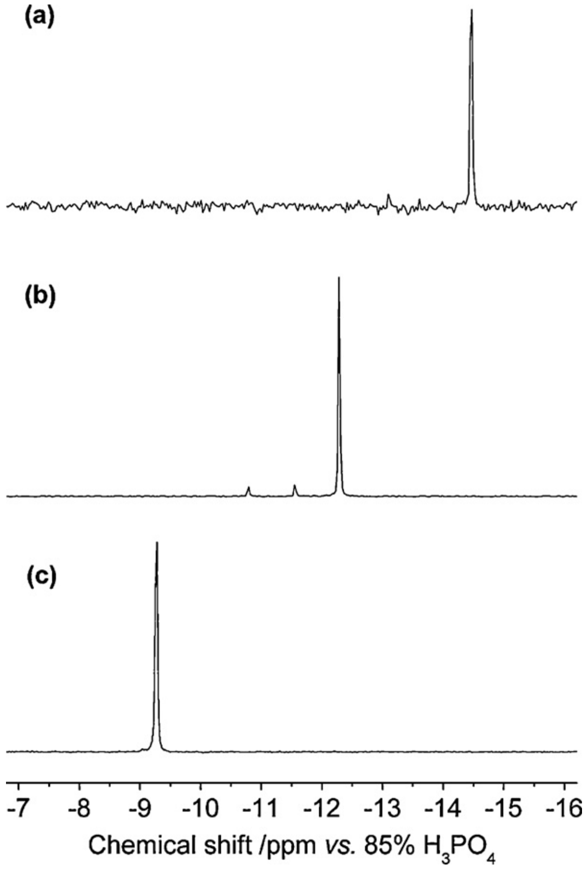

Fig. 2. ^{31}P NMR (160 MHz, in D_2O) spectra of each HPA: (a) $H_3PW_{12}O_{40}$, (b) $H_6P_2W_{18}O_{62}$ and (c) $H_{14}[NaP_5W_{30}O_{110}]$. Chemical shifts are with respect to 85% H_3PO_4.

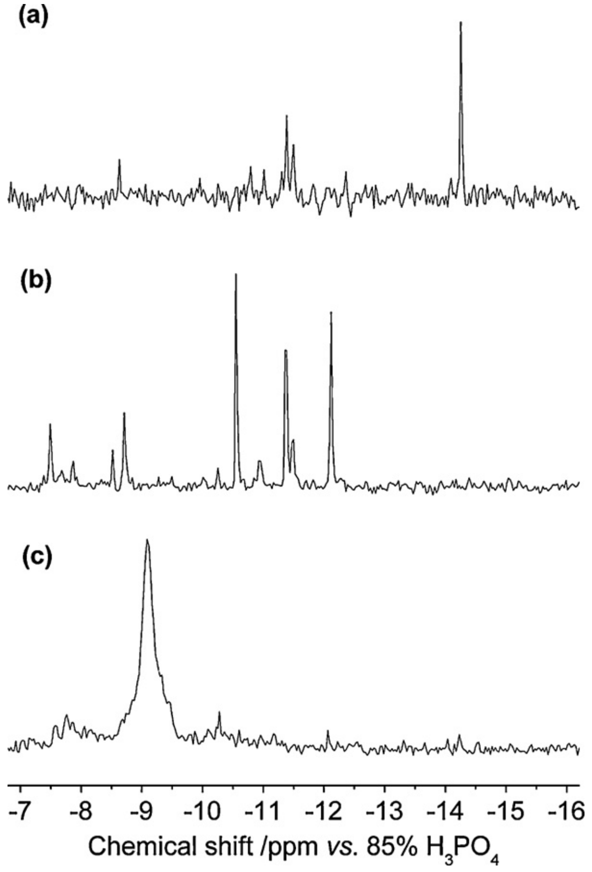

Fig. 4. ^{31}P NMR (160 MHz) spectra of each HPA solution after 1 h reaction diluted with D_2O: (a) $H_3PW_{12}O_{40}$, (b) $H_6P_2W_{18}O_{62}$ and (c) $H_{14}[NaP_5W_{30}O_{110}]$. Chemical shifts are with respect to 85% H_3PO_4.

$H_{14}[NaP_5W_{30}O_{110}]$ showed lower activity than the activities of the other two types of HPAs. The order of performance is as follows: $H_3PW_{12}O_{40} > H_6P_2W_{18}O_{62} > H_{14}[NaP_5W_{30}O_{110}]$. These results imply correlations between acidic properties of these HPAs.

To clarify this point, NH_3-TPD was carried out for the evaluation of the acidic properties of the HPAs. NH_3-TPD profiles are shown in Fig. 3. $H_3PW_{12}O_{40}$ showed the highest desorption temperature of NH_3. The peak in the range of 750–900 K is attributed to the decomposition of $(NH_4)_3PW_{12}O_{40}$. In contrast, the profiles of $H_6P_2W_{18}O_{62}$ and $H_{14}[NaP_5W_{30}O_{110}]$ are expressed with broad shapes in the range of 400–800 K. In the case of $H_6P_2W_{18}O_{62}$, the peak in the range of 650–850 K suggests the decomposition of $(NH_4)_6P_2W_{18}O_{62}$. However, in the case of $H_{14}[NaP_5W_{30}O_{110}]$, peaks are not so clear in the whole temperature range of NH_3 desorption. This profile suggests following two points: The former is that the acid strength of $H_{14}[NaP_5W_{30}O_{110}]$ would be weaker than those of the other HPAs and the latter is that the thermal stability of $H_{14}[NaP_5W_{30}O_{110}]$ is supposed to be lower than $H_3PW_{12}O_{40}$. At present, we cannot conclude whether the acidity of $H_{14}[NaP_5W_{30}O_{110}]$ is higher than that of $H_6P_2W_{18}O_{62}$ or not. Therefore, further investigations are required such as ^{31}P NMR analysis and indicator method to clarify this point. However, it is still noteworthy that even $H_{14}[NaP_5W_{30}O_{110}]$ showed much higher performance than that of *p*-toluenesulfonic acid (*p*-TsOH) and sulfuric acid (H_2SO_4). This means that acidity of $H_{14}[NaP_5W_{30}O_{110}]$ is still stronger than that of other typical acids and that it has sufficient ability to catalyze the acylation of pyruvate ester into α-acyloxyacrylate ester.

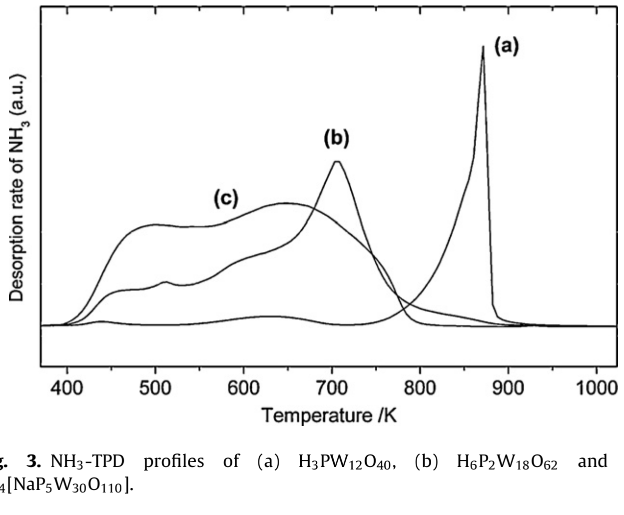

Fig. 3. NH_3-TPD profiles of (a) $H_3PW_{12}O_{40}$, (b) $H_6P_2W_{18}O_{62}$ and (c) $H_{14}[NaP_5W_{30}O_{110}]$.

In addition, as shown in Fig. 4, reaction mixture after 1 h was analyzed by ^{31}P NMR diluted with D_2O. Comparing these spectra, that of $H_6P_2W_{18}O_{62}$ was dramatically changed after reaction, forming lots of de-shielded species. On the other hand, those of $H_3PW_{12}O_{40}$ and $H_{14}[NaP_5W_{30}O_{110}]$ were similar to those in Fig. 2. This means that the stability of $H_{14}[NaP_5W_{30}O_{110}]$ in the solution should be clearly higher than that of $H_6P_2W_{18}O_{62}$.

Catalytic performances of these HPAs in the initial period were compared as shown in Table 2. We have previously reported that the reaction order of the acylation was determined to be of first order with respect to both concentrations of **1** and **2** [3]. Therefore, the reaction constant was estimated by the following equation, where t, x, k and $C_0(\mathbf{A})$ are reaction time, total concentration of **3**

Table 2
Rate constants of various HPAs.[a]

Entry	Catalyst	k^{b}/L mol^{-1} s^{-1} (mol-H^{+})$^{-1}$	k^{c}/L mol^{-1} s^{-1} (mol-cat.)$^{-1}$
1	$H_3PW_{12}O_{40}$	0.67	2.0
2	$H_6P_2W_{18}O_{62}$	0.24	1.5
3	$H_{14}[NaP_5W_{30}O_{110}]$	0.28	3.9

[a] Reaction conditions: entries 1 and 2, **1** (2 mmol), **2** (20 mmol), catalyst (2.5 mol% as HPA vs. **1**); entry 3, **1** (3.8 mmol), **2** (38 mmol), catalyst (0.18 mol% as HPA vs. **1**); 343 K, 360 s (entries 1 and 3) and 240 s (entry 2).

[b,c] The reaction constant calculated by using the equation in the text.

and **4** at *t*, rate constant and initial concentration of **A**, respectively:

$$\ln\frac{C_0(\mathbf{2})\{C_0(\mathbf{1})-x\}}{C_0(\mathbf{1})\{C_0(\mathbf{2})-x\}}=\{C_0(\mathbf{1})-C_0(\mathbf{2})\}kt$$

The rate constants per unit mole of proton being compared, $H_3PW_{12}O_{40}$ showed the highest rate and the order was as follows: $H_3PW_{12}O_{40} > H_{14}[NaP_5W_{30}O_{110}] > H_6P_2W_{18}O_{62}$. However, in contrast, the order of the rate constants per unit mole of catalyst was quite different from that per unit mole of proton: $H_{14}[NaP_5W_{30}O_{110}] > H_3PW_{12}O_{40} > H_6P_2W_{18}O_{62}$. This significantly suggests that large numbers of protons in $H_{14}[NaP_5W_{30}O_{110}]$ is the great advantage for progressing the reaction effectively with small amount of catalyst. On the contrast, in spite of higher desorption temperature of NH_3 in $H_6P_2W_{18}O_{62}$ than $H_{14}[NaP_5W_{30}O_{110}]$, the rate constants of $H_6P_2W_{18}O_{62}$ resulted in the lowest value. As mentioned above, the results of ^{31}P NMR indicated that $H_6P_2W_{18}O_{62}$ was easily decomposed in the reaction mixture. Due to this low stability in the solution, $H_6P_2W_{18}O_{62}$ probably showed the lowest rate constant.

In addition, remarkably, the solubility of $H_{14}[NaP_5W_{30}O_{110}]$ into acetic acid was lower than those of other HPAs. For the comparison of performances under homogeneous conditions, its amount should be decreased. Nevertheless, it showed the highest performances per unit mole of catalyst among other phosphotungstic acids, being the advantage of large numbers of protons.

3.2. Thermal stability of phosphotungstic acids

Curves of TGA were demonstrated in Fig. 5. $H_3PW_{12}O_{40}$ showed small loss of weight in its TG curve, and two separated peaks deriving from dehydration of physically adsorbed and crystal water were observed at temperatures below 373 K and around 423–473 K in DTG curves [10]. In the case of $H_6P_2W_{18}O_{62}$, physisorbed and crystal water were released in three steps. For $H_6P_2W_{18}O_{62}$, it has been observed that isolated acid sites trapped between Dawson units are formed as a result of the degradation of large water clusters $H^{+}(H_2O)_n$, and that its structure remains unaltered up to 873 K [11]. The DTG curve of $H_{14}[NaP_5W_{30}O_{110}]$ is rather broad with almost no clear peak except for a peak at around 343 K. This result implies that the thermal stability of $H_{14}[NaP_5W_{30}O_{110}]$ is lower than that of $H_6P_2W_{18}O_{62}$. On the other hand, it should be emphasized that partial decomposition of phosphotungstic acids occurs at higher temperature such as above 450 K. This obviously means that the estimation of acidic properties of phosphotungstic acids by NH_3-TPD includes the influence of decomposition. Therefore, more accurate evaluations of acidic properties, such as measurements of differential heat of NH_3 adsorption [12], proton affinity [13] and deprotonation enthalpy [14], should be required for further discussion. However, the higher stability of $H_{14}[NaP_5W_{30}O_{110}]$ in the solution than that of $H_6P_2W_{18}O_{62}$ was emphasized as the advantage of this HPA.

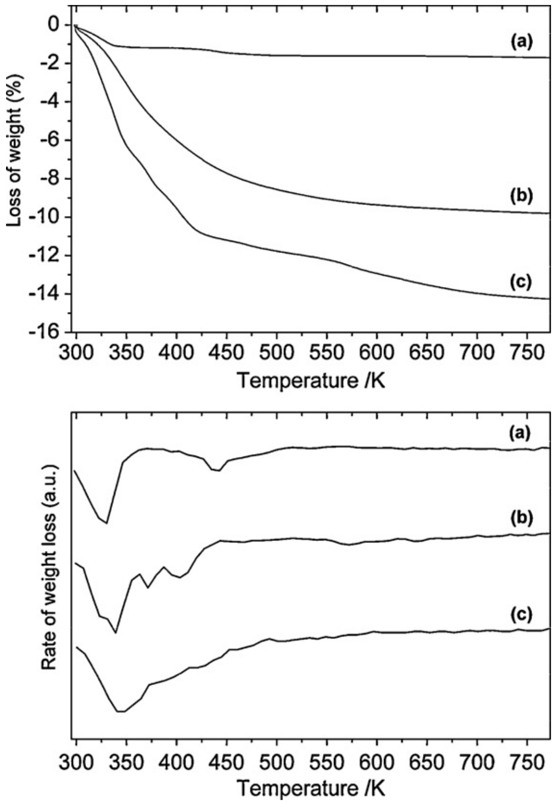

Fig. 5. Thermo gravimetric analysis (TGA) of (a) $H_3PW_{12}O_{40}$ (b) $H_6P_2W_{18}O_{62}$ and (c) $H_{14}[NaP_5W_{30}O_{110}]$: TG curve (top) and DTG curve (bottom).

3.3. Catalytic performances of Cs-substituted Preyssler-type HPAs

We found that the thermal stability of $H_{14}[NaP_5W_{30}O_{110}]$ was lower than those of other HPAs, $H_3PW_{12}O_{40}$ and $H_6P_2W_{18}O_{62}$. In terms of practical use, since the number of proton in $H_{14}[NaP_5W_{30}O_{110}]$ is almost five-times larger than that of $H_3PW_{12}O_{40}$, Preyssler-type HPA is still an attractive acid catalyst. $H_{14}[NaP_5W_{30}O_{110}]$ has low solubility to organic solvents such as acetic acid and, actually, it can work for acylation under heterogeneous conditions. This should be an advantage for utilization as a heterogeneous catalyst. From the viewpoint of practical use such as easy separation, heterogeneous catalysts would be preferable. Therefore, $Cs_xH_{14-x}[NaP_5W_{30}O_{110}]$ (x = 0, 2, 4, 8, 10, 12, and 14) were prepared and examined as catalysts. To the best of our knowledge, there are no reports for catalysis using $Cs_xH_{14-x}[NaP_5W_{30}O_{110}]$. In addition, generally, thermal stability of HPAs increases after substitution of protons with Cs^{+} [2]. Fig. 6 shows the catalytic performance of $Cs_xH_{14\text{-}x}[NaP_5W_{30}O_{110}]$. With increase in the amount of Cs^{+} substitution, catalytic performance gradually decreased. Values of their BET surface are in the range of 4–11 m^2 g^{-1}. The crystallinity of HPA salt at x = 2 was higher than that of others, meaning it has a small surface area. Notably, when more than 10 protons are substituted with Cs^{+}, no activity is

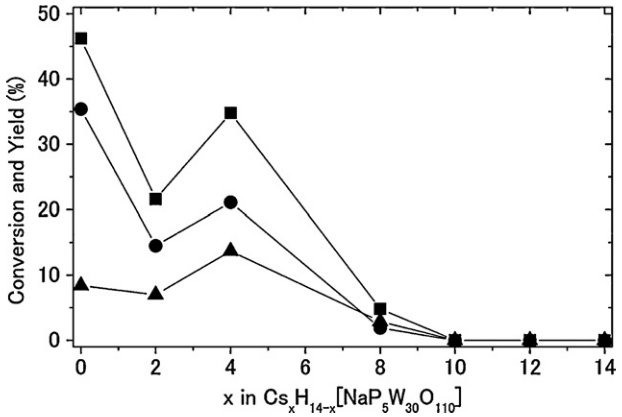

Fig. 6. Catalytic performances of $Cs_xH_{14-x}[NaP_5W_{30}O_{110}]$ at 343 K for 1 h: conversion of **1** (■), yields of **3** (▲) and **4** (●).

observed, despite the existence of protons. These results showed that $Cs_xH_{14-x}[NaP_5W_{30}O_{110}]$ can catalyze reaction at $x < 10$ under heterogeneous condition, working as solid acid catalysts. Those conversely imply that, in the range of $x \geq 10$, very weak acid-sites (protons) which cannot work for acylation remain on the surface or that these protons cannot dissociate in acetic acid any more. This result is quite different from that with $Cs_xH_{3-x}PW_{12}O_{40}$, which showed catalytic activity even in the case of thoroughly neutralized $Cs_3PW_{12}O_{40}$ [3]. This difference between $Cs_xH_{14-x}[NaP_5W_{30}O_{110}]$ and $Cs_xH_{3-x}PW_{12}O_{40}$ is supposed to reflect the acid strength. Generally, it is suggested that HPAs work as relatively weak 1–1 electrolytes in less-polar solvents such as acetic acid, in contrast to their behavior in water [1,2]. Therefore, catalytic activity of $Cs_xH_{14-x}[NaP_5W_{30}O_{110}]$ is expected to enhance in the presence of water because of promotion of dissociation. Although $H_3PW_{12}O_{40}$ can stably exist only in the low pH range, $H_{14}[NaP_5W_{30}O_{110}]$ is stable in the wider pH range than that of $H_3PW_{12}O_{40}$ such as pH 0–10 [1,2,5]. It should be the great advantage from the viewpoint of reactions under water rich conditions such as acid-catalyzed biomass conversion. Catalytic reactions using various types of phosphotungstic acids and their salts are now underway in our group.

4. Conclusions

Catalytic performances correlated the acid strength, the proton number and the stability of the phosphotungstic acids. The order of the rate constants per unit mole of catalyst was quite opposite to that per unit mole of proton: $H_{14}[NaP_5W_{30}O_{110}] > H_3PW_{12}O_{40} > H_6P_2W_{18}O_{62}$. This result showed that large numbers of protons in $H_{14}[NaP_5W_{30}O_{110}]$ is the great advantage for progressing the reaction effectively with small amount of catalyst. In addition, the stability of $H_{14}[NaP_5W_{30}O_{110}]$ in the solution was higher than that of $H_6P_2W_{18}O_{62}$ and $H_3PW_{12}O_{40}$. Moreover, catalytic performances of $H_6P_2W_{18}O_{62}$ and $H_{14}[NaP_5W_{30}O_{110}]$ for the acylation were firstly demonstrated in this research. This means that the acidity of $H_{14}[NaP_5W_{30}O_{110}]$ was still much higher than that of typical acids such as *p*-TsOH acid and H_2SO_4. Furthermore, $Cs_xH_{14-x}[NaP_5W_{30}O_{110}]$ ($x < 10$) can also catalyze the acylation, meaning they can be utilized as solid acid catalysts under heterogeneous conditions.

New applications and possibilities of Preyssler-type phosphotungstic acid for an acid catalyst, beside those of Keggin- and Dawson-type, have been clearly indicated through the results of this study.

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