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Thermal Stability and Acidic Strength of Preyssler-Type Phosphotungstic Acid, $H_{14}[P_5W_{30}O_{110}Na]$ and It's Catalytic Activity for Hydrolysis of Alkyl Acetates

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Abstract. Full structural analysis of Preyssler-type phosphotungstic acid, $H_{14}[P_5W_{30}O_{110}Na]$, using ^{183}W NMR, ^{31}P NMR, and IR spectroscopy, as well as complete elemental analysis revealed that $H_{14}[P_5W_{30}O_{110}Na]\cdot 44H_2O$ was obtained in pure form.

$H_{14}[P_5W_{30}O_{110}Na]$ started to decompose by heating at 373 K and was less stable than Keggin-type phosphotungstic acid, $H_3PW_{12}O_{40}\cdot 6H_2O$, which was stable even after heating at 673 K.

Acidic strength measurements using trimethyl phosphine oxide ($Me_3P{=}O$) as a probe molecule indicated that the acidic strength of $H_{14}[P_5W_{30}O_{110}Na]$ was greater than that of $H_3PW_{12}O_{40}$ on the basis of the amount of acid in an aqueous solution. $H_{14}[P_5W_{30}O_{110}Na]$ was less active than $H_3PW_{12}O_{40}$ for hydrolysis of alkyl acetates on the basis of acid amount. However, $H_{14}[P_5W_{30}O_{110}Na]$ was more active than $H_3PW_{12}O_{40}$ for hydrolysis of alkyl acetates with small alkyl groups on the basis of catalyst weight because acid amount per weight of $H_{14}[P_5W_{30}O_{110}Na]$ was about two times higher than that of $H_3PW_{12}O_{40}$.

Introduction

Heteropolyacids (HPAs) are known as metal-oxygen clusters showing strong acidity and high oxidation ability.[1, 2] Due to the attractive properties, HPAs have been utilized as catalysts even in industrial processes, such as hydration of isobutylene to *tert*-butanol, polymerization of tetrahydrofurane, and selective oxidation of methacrolein to methacrylic acid.

Among the various HPAs, a phosphotungstic acid, $H_3PW_{12}O_{40}$, is the most widely used acid catalyst and it has a so-called "Keggin" structure in which the central PO_4 tetrahedron is surrounded by 12 WO_6 octahedra with T_d symmetry (Figure 1 (a)). The Keggin-type phosphotungstic acid has been used as an acid catalyst for a variety of organic reactions in a homogeneous way as well as a heterogeneous way.[1,2] The phosphotungstic acid shows higher acidity than that of sulfuric acid and can contribute to the development of more effective and greener reactions.

On the other hand, a heteropoly acid with a structure other than a Keggin structure is rare, and further exploration of new and significant catalyses with HPAs is still desired. In 1985, the structure of Preyssler-type HPA[3] was revealed by *Pope*'s group.[4] The Preyssler-type phosphotungstate, $[P_5W_{30}O_{110}Na]^{14-}$, has approximate D_{5h} symmetry and consists of a cyclic assembly of five $[PW_6O_{22}]^{3-}$ units, each derived from the Keggin anion, $[PW_{12}O_{40}]^{3-}$, by removal of two sets of three corner-shared WO_6 octahedra. A sodium ion is located within the polyanion on the fivefold axis (Figure 1 (b)). This anion can be isolated as potassium-sodium mixed salt, and the potassium and sodium cations can be ion-exchanged by protons to give the acidic form.[4]

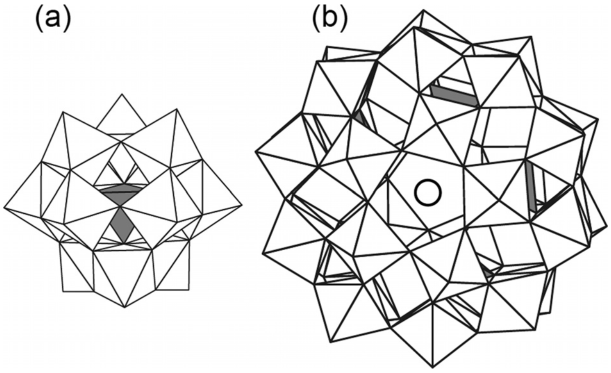

Figure 1. Structures of (a) Keggin-type and (b) Preyssler-type phosphotungstates. Dark polyhedra indicate PO_4, white ochtahedra indicate WO_6, and the circle indicates sodium cation.

Since the first report by *Pope*'s group, several research groups of *Heravi*, *Bamoharram*, *Gharib*, *Alizadeh*, *Hekmatshorar*, and *Feizi* have reported acid catalytic activities of the Preyssler-type phosphotungstic acid for many organic reactions such as esterification, tetrahydropyranyl (THP) protection of hydroxygroups, syntheses of dibenzo xanthene derivatives and 2,4,6-triarylpyridines, and alkylation of phenol.[5–12] We also reported that the Preyssler-type phosphotungstic acid is effective for acylation of methyl pyruvate.[13]

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To obtain further information on the Preyssler-type phosphotungstic acid, in this study, we investigated the thermal stability, acidic strength, and hydrolysis activity of alkyl acetates of the Preyssler-type phosphotungstic acid.

Results and Discussion

Preparation and Structural Characterization of $H_{14}[P_5W_{30}O_{110}Na]$

The potassium and sodium cations of $K_{12.5}Na_{1.5}[P_5W_{30}O_{110}Na]$ were exchanged using Dowex-50W proton exchange resin to produce the Preyssler-type phosphotungstic acid. The ^{183}W NMR (Figure 2 (a)), ^{31}P NMR (Figure 3 (a)), and IR spectra (Figure 4 (a)) are very similar to those of the parent potassium-sodium mixed salts, indicating that the Preyssler-type structure can be retained after the proton exchange process. No other phosphotungstate species was detected by ^{31}P NMR, ^{183}W NMR, and IR spectroscopy. No potassium was found and one equivalent of sodium to a Preyssler-type molecule, which occupies the central cavity of a Preyssler-type molecule, was detected by elemental analysis. No sulfur or carbon was detected, which indicated that no contamination by proton exchange resin occurred. No chlorine, which was used for the preparation of the potassium salt, was detected. These results strongly indicate that Preyssler-type phosphotungstic acid can be prepared in high purity.

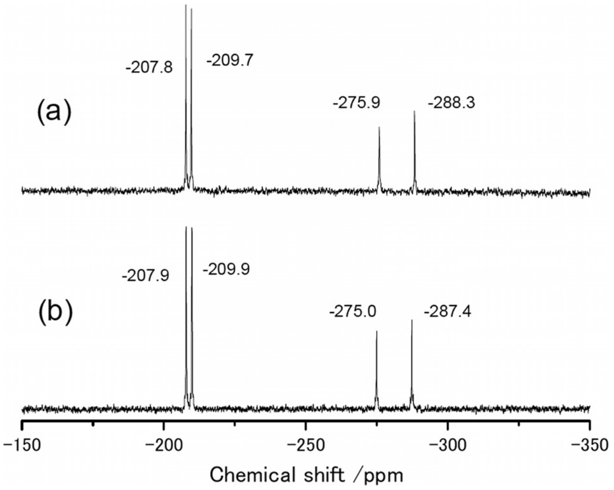

Figure 2. ^{183}W NMR spectra of Preyssler-type phosphotungstates: (a) acid form ($H_{14}[P_5W_{30}O_{110}Na]$ (ca. 1 g) dissolved in D_2O (3 mL)) and (b) lithium salt ($K_{12.5}Na_{1.5}[P_5W_{30}O_{110}Na]$ (ca. 1 g) dissolved in D_2O (3 mL) with the help of Li-resin).

Thermal Stability

The obtained Preyssler-type phosphotungstic acids were heated in a muffle oven and then analyzed by solution ^{31}P NMR and IR. In the ^{31}P NMR spectrum of Preyssler-type phosphotungstic acid heated at 373 K for 1 hour, several small peaks together with the peak of Preyssler-type phosphotungstic acid were observed (Figure 3 in a box). With increase in the heating temperature, the peak intensity of the Preyssler-type phosphotungstic acid gradually decreased and the intensities of unassigned peaks increased (Figure 3), suggesting decomposition of the Preyssler-type phosphotungstate framework. The IR spectra also indicate decomposition of Preyssler-type phosphotungstate after heating (Figure 4). These results indicate that the Preyssler-type phosphotungstic acid started to decompose at 373 K.

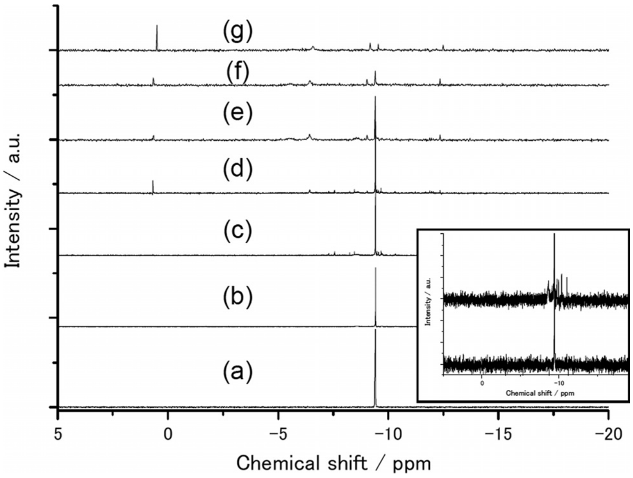

Figure 3. ^{31}P NMR spectra of Preyssler-type phosphtungstic acids (a) before and (b) after heating at 373 K, (c) 423 K, (d) 473 K, (e) 523 K, (f) 573 K, and (g) 623 K for 1 hour. Extended spectra of (a) and (b) are presented in a box.

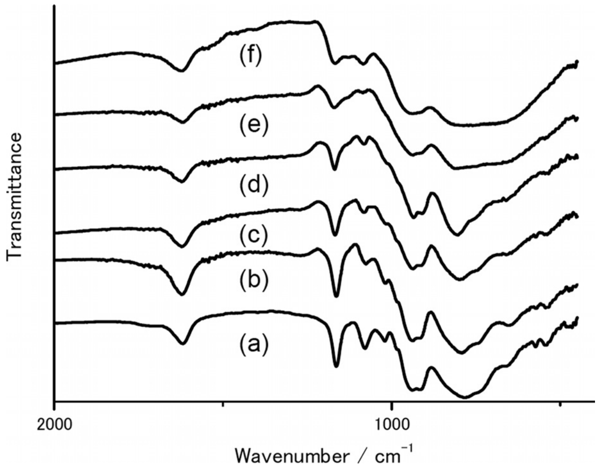

Figure 4. IR spectra of Preyssler-type phosphotungstic acid (a) before and (b) after heating at 473 K, (c) 523 K, (d) 573 K, (e) 623 K, and (f) 673 K for 1 hour.

On the other hand, Keggin-type phosphotungstic acid was stable up to 723 K. No other obvious ^{31}P NMR signal was observed even after heating at 723 K (Figure S1), and the IR spectra after heating at 723 K were unchanged (Figure S2). The thermal stability is in good agreement with the reported value (741 K).[1,2] Thermal stability of Preyssler-type phosphotungstic acid is lower than that of Keggin-type phosphotungstic acid. Therefore, we focus to use Preyssler-type phosphotungstic acid in an aqueous solution as a homogeneous catalyst.

Acidic Strength Measurement

Acidic strength of Preyssler-type phosphotungstic acid was compared with those of Keggin-type phosphotungstic acid and sulfuric acid using trimethyl phosphine oxide ($Me_3P=O$) as a probe molecule. Trialkyl phosphine oxide is known as an acidic strength indicator both in a solid state and in solution.[14–17] Trialkyl phosphine oxide is protonated to form trialkyl phosphine hydroxide cation (Equation (1)). This reversible reaction is so much faster than the ^{31}P NMR time-scale that only one ^{31}P NMR signal is detected. The peak moves to a more positive chemical shift if the acidic strength and amount of proton increase. Therefore, the acidic strength can be estimated by the peak shift:

$$Me_3P=O + H^+ \text{ [larr] } Me_3P\text{-}OH^+ \quad (1)$$

The chemical shift of trimethyl phosphine oxide was plotted against proton-trimethyl phosphine mole ratio (Figure 5 and Figure S3). When the amount of acid was increased, the chemical shift moved in a more positive direction. The shift in the presence of Keggin-type phosphotungstic acid was larger than that in the presence of sulfuric acid, indicating that the acidic strength of Keggin-type phosphotungstic acid is greater than that of sulfuric acid. It was also found that the shift in the presence of Preyssler-type phosphotungtic acid was larger than that in the presence of Keggin-type phosphotungstic acid, indicating that the acidic strength of Preyssler-type phosphotungstic acid per one proton in aqueous solution is greater than that of Keggin-type phosphotungstic acid per one proton.

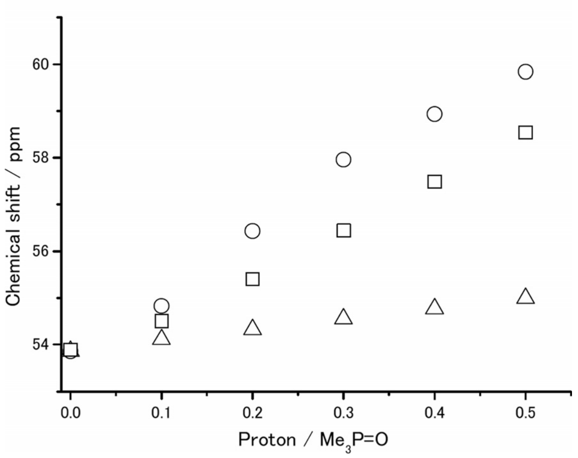

Figure 5. Change in ^{31}P NMR chemical shift of $Me_3P=O$ (1 mM) in D_2O in the presence of Preyssler-type phosphotungstic acid (open circles), Keggin-type phosphotungstic acid (open squares) and sulfuric acid (open triangles).

Hydrolysis of Alkyl Acetate

The fact that Preyssler-type phosphotungstic acid had greater acidic strength than that of Keggin-type phoshotungstic acid in aqueous solution motivated us to use Preyssler-type phosphotungstic acid as an acid catalyst for hydrolysis of alkyl acetate in water. *Okuhara*'s group already found that Keggin-type phosphotungstic acid exhibits higher catalytic activity than that of sulfuric acid or *p*-toluenesulfonic acid on the basis of acid amount.[18]

Catalytic activities of Preyssler-type phosphotungstic acid and Keggin-type phosphotungstic acid for the hydrolysis of various alkyl acetates are summarized in Table 1. In all cases, only acetic acid and corresponding alkyl alcohols were formed as reaction products. The activity was estimated from the amount of alkyl alcohols produced after reaction for 2 h and was expressed in two ways: on the basis of acid amount and on the basis of catalyst weight. Catalytic activity obtained using $H_3PW_{12}O_{40}{\cdot}6H_2O$ (Entry 2) was similar to the reported value (Entry 1), which indicated that the accuracy of our method of analysis using ^1H NMR is similar to that of the method reported in the literature.[18]

Conversions of ethyl acetate with Preyssler-type phosphotungstic acid were higher than those with Keggin-type phosphotungstic acid (Entries 2–5). Namely, the reaction rate per catalyst weight of Preyssler-type phosphotungstic acid was higher than that of Keggin-type phosphotungstic acid. However, the reaction rate per acid amount of Preyssler-type phosphotungstic acid was lower than that of Keggin-type phosphotungstic acid, because the acid amounts per catalyst weight of Preyssler-type and Keggin-type phosphotungstic acids are ca. 1.7 and 1.0 $mmol{\cdot}g^{-1}$, respectively.

Alkyl acetates with different alkyl groups such as methyl, *n*-propyl, *isopropyl*, *n*-butyl, *iso*-butyl, *tert*-butyl, and cyclohexyl were also tested for hydrolysis reaction (Entries 6–19). Conversions of alkyl acetates decreased by increasing the size of the alkyl group in the presence of both catalysts. However, the degree of conversion drop for Preyssler-type phosphotungstic acid was larger than that for Keggin-type phosphotungstic acid. Conversions of methyl acetate, ethyl acetate, and *n*-propyl acetate with Preyssler-type phosphotungstic acid were larger than those with Keggin-type phosphotungstic acid. There was no difference in conversions of *isopropyl* acetate and cyclohexyl acetate between the two catalysts. However, conversions of *n*-butyl acetate and *iso*-butyl acetate with Preyssler-type phosphotungstic acid were lower than those with Keggin-type phosphotungstic acid. Although the reason for the difference in catalytic activity is not clear at the present time, it seems that the difference is due to the difference in size and softness of Preyssler-type and Keggin-type phosphotungstates.[1, 2] Further investigation is now underway in our group.

Conclusions

Preyssler-type phosphotungstic acid starts to decompose at 373 K and is much less stable than Keggin-type phosphotungtic acid, which is stable up to 773 K. Therefore, Preyssler-type phosphotungstic acid is not suitable as a heterogeneous catalyst but should be used as a homogeneous catalyst.

Acidic strength of Preyssler-type phosphotungstic acid estimated by using $Me_3P=O$ is greater than that of Keggin-type phsphotungstic acid on the basis of acid amount. Acid catalyst

Table 1. Catalytic activities of phosphotungstic acids for hydrolysis of alkyl acetates.

	Alkyl acetate	Conc.	Rate	
	Cat.[a]	/%	per weight /mmol·g^{-1}·min^{-1}	per acid amount /mmol (mmol acid)$^{-1}$·min^{-1}
	Ethyl acetate		Solvent: D_2O	
1	$H_3PW_{12}O_{40}$		70.4[b,c]	70.4 [b,c]
2	$H_3PW_{12}O_{40}$	36.6	68.7[b]	68.7[b]
3	$H_{14}[NaP_5W_{30}O_{110}]$	52.3	98.2[b]	57.8[b]
4	$H_3PW_{12}O_{40}$	71.2	134.7	134.7
5	$H_{14}[NaP_5W_{30}O_{110}]$	80.6	152.5	95.3
	Methyl acetate		Solvent: D_2O	
6	$H_3PW_{12}O_{40}$	77.8	175.0	175.0
7	$H_{14}[NaP_5W_{30}O_{110}]$	86.4	194.4	121.5
	n-propyl acetate	Solvent: D_2O, [D_6]acetone (2:3)		
8	$H_3PW_{12}O_{40}$	58.7	95.8	95.8
9	$H_{14}[NaP_5W_{30}O_{110}]$	60.1	98.1	61.3
	isopropyl acetate	Solvent: D_2O, [D_6]acetone (2:3)		
10	$H_3PW_{12}O_{40}$	40.7	66.4	66.4
11	$H_{14}[NaP_5W_{30}O_{110}]$	40.6	66.2	41.4
	n-butyl acetate	Solvent: D_2O, [D_6]acetone (2:3)		
12	$H_3PW_{12}O_{40}$	55.4	79.5	79.5
13	$H_{14}[NaP_5W_{30}O_{110}]$	51.2	73.5	45.9
	iso-butyl acetate	Solvent: D_2O, [D_6]acetone (2:3)		
14	$H_3PW_{12}O_{40}$	33.3	47.8	47.8
15	$H_{14}[NaP_5W_{30}O_{110}]$	31.1	44.6	27.9
	cyclohexyl acetate	Solvent: D_2O, [D_6]acetone (2:3)		
16	$H_3PW_{12}O_{40}$	35.6	41.9	41.9
17	$H_{14}[NaP_5W_{30}O_{110}]$	35.4	41.6	26.0
	tert-butyl acetate	Solvent: D_2O, [D_6]acetone (2:3)		
18	$H_3PW_{12}O_{40}$	Trace		
19	$H_{14}[NaP_5W_{30}O_{110}]$	Trace		

a) Amount of catalyst: 0.075 g, 5 wt-% ethyl acetate in D_2O (total volume: 3.0 mL, ethyl acetate: 0.15 g), Reaction temperature: 353 K, Reaction time: 2 hours. b) Reaction temperature: 337K. c) Data in reference [18].

activity of Preyssler-type phosphotungstic acid for hydrolysis of alkyl acetate is lower on the basis of acid amount but higher on the basis of catalyst weight than that of Keggin-type phosphotungstic acid.

Keggin-type phosphotungstic acid is used as an acid catalyst for a wide range of reactions. Development of an acid catalyst other than Keggin-type phosphotungstic acid is highly desired, and Preyssler-type phosphotungstic acid is one of the promising candidates. Our findings are important for the development of an acid catalyst using Preyssler-type phophotungstic acid.

Experimental Section

Materials

All of the chemicals used were of reagent grade, and they were used as supplied. Keggin-type phosphotungstic acid, $H_3PW_{12}O_{40}\cdot 6H_2O$, was purified by using a published method.[18] $K_{12.5}Na_{1.5}[P_5W_{30}O_{110}Na]$ was prepared according to a published method[19] and the purity was confirmed by IR, ^{31}P NMR, and ^{183}W NMR spectroscopy.

Characterizations

FT-IR spectra were recorded with a Nicolet 6700 FT-IR spectrometer with 2 cm^{-1} resolution. ^{183}W NMR spectra were recorded with a Varian System 500 (500 MHz) spectrometer (W resonance frequency of 20.825 MHz) using an external saturated $NaWO_4$ reference. ^{31}P NMR spectra were recorded with a Varian System 500 (500 MHz) spectrometer (P resonance frequency of 202.327 MHz) using an external H_3PO_4 reference. ^{1}H NMR spectra were recorded with a Varian System 500 (500 MHz) spectrometer (H resonance frequency of 499.827 MHz). Complete elemental analyses were performed by Microanalytisches Labor Pascher (Remagen, Germany).

Preparation of $H_{14}[P_5W_{30}O_{110}Na]\cdot 44H_2O$

$K_{12.5}Na_{1.5}[P_5W_{30}O_{110}Na]\cdot 15H_2O$ (20 g) was dissolved in H_2O (300 mL) and passed through 50 g of Dowex 50W × 8 in the proton form packed in a glass tube (inner diameter: 15 mm), and the obtained eluent was evaporated in vacuo at 318 K (Caution: Evaporation at a higher temperature caused slight decomposition. See also Results and Discussion.).

Elemental analysis for $H_{14}[P_5W_{30}O_{110}Na]\cdot 44H_2O$, found: P, 1.72; W, 67.02; Na, 0.26; O, 30.1; H, 1.1; Cl, 0.008; K, <0.002, S, <0.005 % total 100.20 %; calcd: P, 1.88; W, 66.77; Na, 0.28; O, 29.83; H, 1.24; Cl, 0 %. **IR:** $\tilde{\nu}_{max}$ = 1164 (m), 1079 (m), 1020 (w), 980 (sh), 939 (vs), 916 (vs), 785 (vs) cm^{-1}.

^{183}W NMR (D_2O): δ = –207.8 (2 W), –209.7 (2 W), –275.9 (W), –288.3 (W). **^{31}P NMR** (D_2O): δ = –9.41.

Hydrolysis of Alkyl Acetate

Hydrolysis of ethyl acetate was carried out at 333 K with 5 wt-% ethyl acetate in D_2O (total volume: 3.0 mL, ethyl acetate: 0.15 g) for 2 h.[20] The weight of the catalyst used was 0.075 g.

Conversion and yield were estimated using ^{1}H NMR spectroscopy. Signals corresponding to ethyl acetate, ethyl alcohol, and acetic acid were observed. No other signals were observed. Therefore, we assumed that the selectivity of this hydrolysis was 100 %. Since signals of methylene (CH_2O) for ethyl acetate (4.03) and ethyl alcohol (3.52) were well separated, the conversion of ethyl acetate was calculated using the integration ratio of these two signals as follows:

Conversion = (integration of CH_2O of ethyl alcohol) / (integration of CH_2O of ethyl acetate + integration of CH_2O of ethyl alcohol).

^{1}H NMR of ethyl acetate in D_2O (HOD peak at 4.75 ppm): 1.13 ppm (CH_3CH_2, triplet, 3 H), 1.97 ppm (CH_3CO, singlet, 3 H), 4.03 ppm (CH_2O, quartet, 2 H)

^{1}H NMR of ethyl alcohol in D_2O (HOD peak at 4.75 ppm): 1.06 ppm (CH_3CH_2, triplet, 3 H), 3.52 ppm (CH_2O, quartet, 2 H)

^{1}H NMR of acetic acid in D_2O (HOD peak at 4.75 ppm): 1.97 ppm (CH_3CO, singlet, 3 H)

The calculated conversion and yield of hydrolysis of ethyl acetate in the presence of Keggin-type phosphotungstic acid were in agreement with the data previously reported by *Okuhara*'s group,[18] which indicated that our analytic method using NMR spectroscopy is suitable (Table 1, Entries 1 and 2).

Hydrolysis of other alkyl acetates was carried out by a procedure similar to that described above. In the cases of *n*-propyl acetate, *isopropyl* acetate, *n*-butyl acetate, *iso*-butyl acetate, cyclohexyl acetate, and *tert*-butyl acetate, a mixed solvent (D_2O : [D_6]acetone = 3:2) was used to obtain a homogeneous solution.

Supporting Information (see footnote on the first page of this article): (Figure S1) ^{31}P NMR spectra of Keggin-type phosphtungstic acid (a) before and after heating at (b) 723 K and (c) 773 K (Figure S2) IR spectra of Keggin-type phosphotungstic acid (a) before and after heating at (b) 673 K, (c) 723 K and (d) 773 K. (Figure S3) ^{31}P NMR spectra of $Me_3P{=}O$ (1 mM) in D_2O. (bottom) $Me_3P{=}O$ in the absence of acid. From bottom to top, amount of Preyssler-type phosphotungtic acid was increased.

Acknowledgments

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