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New extraction procedure for protonated polyoxometalates prepared in aqueous-organic solution and characterisation of their catalytic ability

Tadaharu Ueda[a,*], Keisuke Yamashita[a], Ayumu Onda[b]

[a] Department of Applied Science, Faculty of Science, Kochi University, Kochi 780-8520, Japan
[b] Hydrothermal Research Institute, Faculty of Science, Kochi University, Kochi 780-8520, Japan

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ABSTRACT

Although POMs prepared in aqueous-organic solutions have been reported to exhibit interesting chemical properties and may be efficient catalysts, they could not be isolated in their protonated form using the normal extraction method. In this study, a new procedure of isolating protonated POMs, $[S_2V_xM_{18-x}O_{62}]^{(4+x)-}$ and $[AsV_xM_{12-x}O_{40}]^{(3+x)-}$ (M = Mo, W; x = 0–2), which were prepared in an aqueous-organic mixed solution, was developed by modifying and optimising the extraction conditions. Isolated protonated POMs were characterised using IR and Raman spectroscopy, and their acidity was measured using a Hammett indicator. The acidity of $H_4S_2W_{18}O_{62}$, $H_5S_2VW_{17}O_{62}$, $H_4S_2Mo_{18}O_{62}$, and $H_3As_2W_{18}O_{62}$ was stronger than that of $H_3PW_{12}O_{40}$. Their catalytic ability was investigated in multiple types of organic reactions, including pinacol rearrangement, acetal formation with benzaldehyde and ethylene glycol, and the Friedel-Crafts acylation of anisole with ethyl pyruvate. They exhibited greater catalytic ability than commercially available POMs such as $H_3PM_{12}O_{40}$ and $H_4SiM_{12}O_{40}$ (M = Mo, W).

1. Introduction

Recently, extensive attention has been directed toward the catalytic applications of POMs, as they exhibit strong acidity and high stability and are less corrosive than many existing alternatives [1]. In addition, the use of POMs as catalysts rarely leads to side reactions, unlike the use of sulfonic acid and hydrochloric acid in many organic syntheses. The stronger acidity of POMs compared to that of common mineral acids, such as sulphonic acid and hydrochloric acid, makes them highly suitable as catalysts for various organic reactions such as the Friedel-Crafts, Mannich, and Prins reactions. Protonated POMs such as Keggin-type $H_3PW_{12}O_{40}$ (Fig. 1(a)) are directly used as catalysts in homogeneous systems. Furthermore, methods to adsorb protonated POMs onto silica gel and other porous materials have been developed to avoid contamination and to allow repeated re-use [1(g)]. The number of reports on the catalytic use of POMs has been increasing. In particular, numerous reports of the catalytic use of $H_nXM_{12}O_{40}$ (X = P, Si; M = Mo, W; n = 3, 4) have appeared in the literature because these POMS are commercially available, highly stable, and strongly acidic. In general, protonated POMs are prepared in an aqueous solution and are extracted with acidic diethyl ether, which is called the “etherate method” [2]. However, the preparation and isolation of numerous novel POMs as tetra-alkylammonium salts in an aqueous-organic mixed solution has been reported; for example, $[SM_{12}O_{40}]^{2-}$ and $[S_2M_{18}O_{62}]^{4-}$ (M = Mo, W) [3] have been characterised using X-ray analysis, spectroscopy, and electrochemical methods [4,5]. The Wells-Dawson-type POM $S_2Mo_{18}O_{62}{}^{6-}$ (Fig. 1(b)) exhibits photocatalytic activity; it catalyses the photocatalytic reaction of benzyl alcohol with the help of electrochemical oxidation [5(p)]. The acid strength of POMs is generally well known to follow the order: $H_3PW_{12}O_{40} > H_3PMo_{12}O_{40} > H_4SiW_{12}O_{40} > H_4SiMo_{12}O_{40}$, which is also largely consistent with the order of their catalytic ability. In addition, Murakami et al. reported the acid strength of other Keggin-type POMs: $H_3PW_{12}O_{40} > H_4SiW_{12}O_{40} > H_4GeW_{12}O_{40} > H_5BW_{12}O_{40} > H_5FeW_{12}O_{40} > H_6CoW_{12}O_{40}$. These results imply that a smaller anion charge of Keggin-type POMs results in greater acidity. POMs with smaller charge density are expected to exhibit stronger acidity on the basis of the general reported trend of POM acidity; thus, the isolation of $[SM_{12}O_{40}]^{2-}$ and $[S_2M_{18}O_{62}]^{4-}$ (M = Mo, W) in their protonated forms is important. Moreover, they exhibit high redox potentials, indicating that they could serve as strong oxidants. Recently,

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* Corresponding author at: 2-5-1 Akebono-cho, Kochi 780-8520, Japan. Tel.: +81 88 844 8299; fax: +81 88 844 8359.
E-mail address: chuji@kochi-u.ac.jp (T. Ueda).

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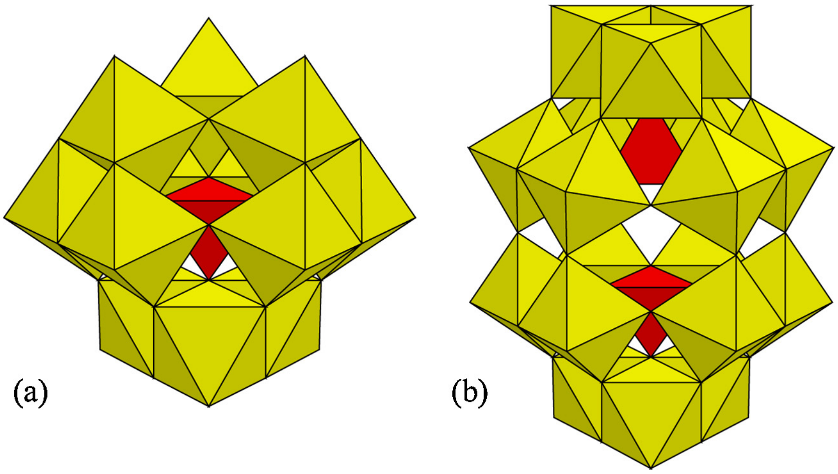


Fig. 1. Structure of (a) Keggin- and (b) Wells-Dawson-type POMs.

we reported that water-miscible organic solvents lead to the stable formation of $[AsV_xM_{12-x}O_{40}]^{(3+x)-}$ (M = Mo, W; x = 0–2), which are less stable than $[PV_xM_{12-x}O_{40}]^{(3+x)-}$ in aqueous solution [6,7]. The literature contains fewer reports of catalysis by $[AsV_xM_{12-x}O_{40}]^{(3+x)-}$, most likely because of the toxicity of arsenic. However, for academic reasons, a comparison between the catalytic ability of $[AsV_xM_{12-x}O_{40}]^{(3+x)-}$ and that of the corresponding $[PV_xM_{12-x}O_{40}]^{(3+x)-}$ (x = 0–2) would be important and interesting.

Because an organic solvent such as acetone or acetonitrile mixes with diethyl ether to form a single phase, POMs synthesised in aqueous-organic solutions cannot be isolated in the protonated form through the normal etherate method. In this study, we developed a new procedure for the isolation of protonated $[S_2V_xM_{18-xx}O_{62}]^{(4+x)-}$ and $[AsV_xM_{12-x}O_{40}]^{(3+x)-}$ (M = Mo, W; x = 0–2) by modifying the common etherate method. The resulting protonated POMs were characterised by elemental analysis and IR spectroscopy; their acidity was measured by UV–Vis spectrophotometry using a Hammett indicator; and their homogeneously catalytic ability was compared with that of various POMs.

2. Experimental

The ^{1}H NMR measurements were performed on a JEOL Model JNM-LA400 spectrometer. All yields were determined by ^{1}H NMR. Raman spectra were recorded on a Horiba Jobin Yvon model HR-800 spectrophotometer. The argon line at 514.5 nm was used for excitation. The Raman measurements were obtained at 20 °C. The IR spectra were obtained on a Jasco FT/IR-460 plus spectrophotometer using the KBr pellet method. UV–Vis spectra were recorded on a Jasco Model V-670 spectrophotometer using a quartz cell with a path length of 1 mm. All reagents were of analytical grade and were used as received.

3. Acidity measurement

The acidity measurements were performed according to the literature method, as follows [8]. Isolated protonated POMs were added to CH_3CN, which had been dried over 3A molecular sieves containing 3.5×10^{-5} M 1,9-diohenyl-1,3,6,8-nonatetraen-5-one (dicinnamylacetone: $pK_a = -3.0$). The concentration of the protonated POMs was set to 4.86×10^{-3} M on the basis of the number of protons per POM. The UV–Vis spectra were measured using a quartz cell (L = 1 cm) in the 190–850 nm region.

4. Isolation of protonated POMs

Reaction mixtures for various POMs were prepared according to the method reported in the literature [3,6,7,9,10]. Each reaction mixture was poured into a separatory funnel, followed by the addition of diethyl ether and n-hexane. The ratio of diethyl ether and n-hexane to the reaction mixture was as follows: reaction mixture:diethyl ether:n-hexane = 1:2:1 for $[S_2V_xW_{18-x}O_{62}]^{(4+x)-}$, 1:2:1.25 for $[S_2Mo_{18}O_{62}]^{4-}$, 1:2:2 for $[S_2VMo_{17}O_{62}]^{5-}$, 1:1:0.5 for $[AsW_{12}O_{40}]^{3-}$, 1:2:0.5 for $[AsVW_{11}O_{40}]^{4-}$, 1:1:0.5 for $[AsV_2W_{10}O_{40}]^{5-}$, 1:1:1 for $[AsMo_{12}O_{40}]^{3-}$, 1:1:0.2 for $[AsVMo_{11}O_{40}]^{4-}$, and 1:1:0.15 for $[AsV_2Mo_{10}O_{40}]^{5-}$. In the case of $H_3AsM_{12}O_{40}$ (M = Mo, W), a heavy oil phase containing the protonated POMs appeared after the separatory funnel was shaken and was then separated before continuing to the next procedure, as below. In the case of other POMs, no oil phase appeared after being shaken only with the addition of diethyl ether and n-hexane, and acid and water were therefore added as follows: hydrochloric acid (conc.) was added at a volume ratio of 0.1 for $[S_2VMo_{17}O_{62}]^{5-}$, 0.6 for $[AsVMo_{11}O_{40}]^{4-}$, and 1 for $[AsV_2Mo_{10}O_{40}]^{5-}$, $[AsVW_{11}O_{40}]^{4-}$, and $[S_2Mo_{18}O_{62}]^{4-}$, whereas sulphonic acid at volume ratios of 0.2 and 0.3 were added for $[AsV_2W_{10}O_{40}]^{5-}$ and $[S_2V_xW_{18-x}O_{62}]^{(4+x)-}$, respectively. In the case of $H_3AsMo_{12}O_{40}$ and $H_3AsW_{12}O_{40}$, the heavy oil was heated at ca. 80 °C to dryness. For $H_{3+x}AsV_xM_{12-x}O_{40}$ (M = Mo, W; x = 1,2) and $H_4S_2W_{18}O_{62}$, the extracted heavy oil was allowed to stand at r.t.; a crystal formed and was separated by filtration. In the case of $H_4S_2Mo_{18}O_{62}$, $H_5S_2VMo_{17}O_{62}$, $H_5S_2VW_{17}O_{62}$, and $H_6S_2V_2W_{16}O_{62}$, after the addition of a few drops of conc. H_2SO_4 to the extracted heavy oil with stirring or in an ultrasonic bath, the solution was allowed to stand at r.t. or dried in vacuo at ca. 80 °C. When a crystal appeared, it was separated by filtration, washed with n-hexane, and dried in vacuo. Elemental analysis was performed after the compounds were dried. The detailed results of the elemental analysis are shown in Tables S1 and S2.

5. Results and discussion

5.1. IR and Raman spectroscopy

Table 1 shows the peak IR and Raman bands for protonated POMs isolated in this study and for the previously prepared tetraalkylammonium POM salts. The IR spectra (Figs. S1-S11) of the protonated form and the tetraalkylammonium salt of each POM were compared. The IR spectra and peak bands for the protonated form were identical to those for the tetraalkylammonium salts

Table 1
Peak frequencies (cm^{-1}) of the protonated form and tetra-alkylammonium salt of POMs.

Compounds	Cation	IR				Raman
		X—Oa	M═Od	M—Ob	M—Oc	M═Od
$S_2W_{18}O_{62}{}^{4-}$	H^+	1178; 1074	990; 968	(sh)	795	1003
	TPA	1180; 1076	986; 966	906	804	1007
$S_2VW_{17}O_{62}{}^{5-}$	H^+	1195; 1174; 1070	982; 960	(sh)	793	994
	1-TBA	1175; 1075	978	901	803	990
	4-TBA	1200; 1174; 1072	978; 958	901	802	989
$S_2V_2W_{16}O_{62}{}^{6-}$	H^+	1198; 1174; 1071	981; 959	(sh)	788	1002
	TBA(H)	1202; 1160; 1070	977; 955	901	798	995
$S_2Mo_{18}O_{62}{}^{4-}$	H^+	1169; 1068	969	862	773	989
	TPA	1170; 1070	966	880	792	–[a]
$S_2VMo_{17}O_{62}{}^{5-}$	H^+	1168; 1069	966	866	773	989
	TBA	1183; 1166; 1069	956	876	792	975
$AsW_{12}O_{40}{}^{3-}$	H^+	912	986	865	794	1001
	TBA	914	984	875	796	1001
$AsVW_{11}O_{40}{}^{4-}$	H^+	909	983	862	778	1009
	TBA	906	971	870	792	991
$AsV_2W_{10}O_{40}{}^{5-}$	H^+	905	983	865	780	1018
	TBA(H^+)	905	969	870	790	992
$AsMo_{12}O_{40}{}^{3-}$	H^+	894	963	846	769	992
	TBA	896	962	856	792	984
$AsVMo_{11}O_{40}{}^{4-}$	H^+	894	963	841	768	989
	TBA	891	951	852	789	989
$AsV_2Mo_{10}O_{40}{}^{5-}$	H^+	893	963	845	769	1001
	TBA(H^+)	890	948	851	785	980

O_a: Oxygen bonded with sulfur atom; O_b: Corner-shared Oxygen; O_c: Edge-shared Oxygen; O_d: Terminal Oxygen.

[a] No peak was obtained because of combustion by laser.

within a small shift. C. Rocchiccioli et al. reported the features of the IR spectra of various salts of Keggin-type POMs and indicated that stronger electrostatic anion–anion interactions and smaller counter-cation size lead to an increase in the stretching frequencies, particularly to higher M-Od (terminal) stretching frequencies [11]. The M-Od stretching frequencies in the spectra of all of the protonated POMs in this study were higher than those of the corresponding tetraalkylammonium salts. In addition, in the case of spectra of all of the protonated POMs, no peaks appeared at ca. 1480 and 1380 cm^{-1}, which are associated with the bending vibrations of the C–H bond of the tetraalkylammonium cation. These results indicate that the protonated forms of all of the investigated POMs could be isolated with our newly developed procedure without inducing a structural change. With respect to the spectrum of $H_5[S_2VW_{17}O_{61}]$, three peaks appeared at 1200–1140 cm^{-1} because two isomers, resulting from substitution of vanadium at different positions, are always included [10] and because isolation of the pure isomers is not currently possible.

5.2. Acidity of POMs

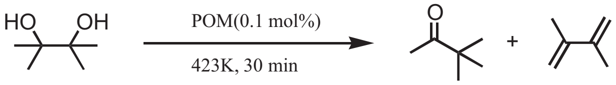
The acidity of the POMs was measured using the Hammett indicator, and the obtained data are presented in Table 2. Many protonated POMs, including $H_3PW_{12}O_{40}$ and $H_3PMo_{12}O_{40}$, are well known to exhibit stronger acidity than mineral acids such as H_2SO_4 and HCl [8,12]. Furthermore, $H_4S_2W_{18}O_{62}$, $H_5S_2VW_{17}O_{62}$, and $H_4S_2Mo_{18}O_{62}$ are more strongly acidic than commercially available $H_3PW_{12}O_{40}$. The acidity of Keggin-type POMs decreases as the number of protons increases, as follows: $H_3PW_{12}O_{40} > H_4SiW_{12}O_{40} > H_4GeW_{12}O_{40} > H_5BW_{12}O_{40} > H_5FeW_{12}O_{40} > H_6CoW_{12}O_{40}$. The total size of the Keggin-type POMs is nearly identical, even when the central atom, referred to as the heteroatom, is changed. The difference in acidity should be dependent on the total charge of the Keggin-type POMs. However, compared with the acidity of a series of protonated POMs with the same structure that were isolated in this study, the acidity decreased in the order $H_4S_2W_{18}O_{62} > H_5S_2VW_{17}O_{62} > H_6S_2V_2W_{16}O_{62}$; $H_4S_2Mo_{18}O_{62} > H_5S_2VMo_{17}O_{62}$; $H_3AsW_{12}O_{40} > H_4AsVW_{11}O_{40} > H_5AsV_2W_{10}O_{40}$; $H_3AsMo_{12}O_{40} > H_4AsVMo_{11}O_{40} > H_5AsV_2Mo_{10}O_{40}$. Similar to the Keggin-type series $H_nXM_{12}O_{40}$, the acidity of the protonated POMs decreases with increasing total charge or with increasing number of vanadium atoms in the POM.

5.3. Catalytic ability of protonated polyoxometalates

Numerous reports on the acidic and oxidative catalytic ability of POMs have appeared in the literature [1]. They exhibit excellent catalytic properties, as they are stronger but less corrosive

Table 2
Acidity of protonated POMs obtained from UV–Vis spectra with Hammett indicator.

Compounds	$-H^0$
$H_4S_2W_{18}O_{62}$	2.70
$H_5S_2VW_{17}O_{62}$	2.26
$H_3AsW_{12}O_{40}$	2.19
$H_4S_2Mo_{18}O_{62}$	2.17
$H_3PW_{12}O_{40}$	2.14
$H_3AsMo_{12}O_{40}$	2.07
$H_4AsVMo_{11}O_{40}$	2.03
$H_4AsVW_{11}O_{40}$	2.00
$H_4SiW_{12}O_{40}$	1.98
$H_5AsV_2W_{10}O_{40}$	1.94
$H_5AsV_2Mo_{10}O_{40}$	1.85
$H_6S_2V_2W_{16}O_{62}$	1.82
$H_4GeW_{12}O_{40}$	1.69
$H_5S_2VMo_{17}O_{62}$	1.65
$H_5BW_{12}O_{40}$	1.55
$H_5FeW_{12}O_{40}$	1.48
$H_6CoW_{12}O_{40}$	0.88



Scheme 1. Transformation reaction of pinacol into 3,3-dimethyl-2-butanone and 2,3-dimethyl-1,3-butadiene [15].

than mineral acids, and they exhibit high stability and can be used repeatedly. Many POM-catalysed organic synthesis reactions are high yielding (>90%), so a comparison of the catalytic ability of POMs isolated in this study against reported reactions with high yields is not appropriate. Therefore, we surveyed adequate catalytic reactions that proceed with moderate yield (approximately 50%) under mild conditions and finally selected four reactions in order to compare the catalytic activity of the POMs.

Elimination of a hydroxy group is a very important reaction in various electrophilic transformations, as a variety of products, including alkenes, dienes, ethers, and carbonyl compounds, can be formed depending on the reaction conditions and the structure of the starting reagents. Although diols are well known to undergo electrophilic dehydration reactions under both homogeneous conditions with strong mineral acids and heterogeneous conditions with Al_2O_3 and zeolites, the literature contains few reports of the transformation of diols catalysed by POMs. Baba and Ono first reported a kinetic study on the dehydration of 1,4-butanediol into tetrahydrofuran [13]. The heterogeneous pinacol rearrangement of 1,1,2-triphenyl-1,2-ethanediol to triphenylacetaldehyde and diphenylacetophenone catalysed by $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ has also been investigated [14].

5.4. Pinacol rearrangement

Torok et al. conducted systematic studies on the transformation of various diols catalysed by $H_3PM_{12}O_{40}$ and $H_4SiM_{12}O_{40}$ (M = Mo, W) [15]. Among these transformations, the conversion of 2,3-dimethyl-2,3-butanediol (pinacol) into 3,3-dimethyl-2-butanone and 2,3-dimethyl-1,3-butadiene was chosen to compare the catalytic ability of our isolated POMs (Scheme 1). All reactions were performed with 0.02 mol of 2,3-dimethyl-2,3-butanediol and 0.1 mol% POM at 423 K for 30 min, and the results are presented in Table 3. In the cases of $H_4SiW_{12}O_{40}$ and $H_3PW_{12}O_{40}$ (entries 1 and 2), nearly identical yields for 3,3-dimethyl-2-butanone and 2,3-dimethyl-1,3-butadiene were observed, although selectivity was only reported for $H_3PW_{12}O_{40}$ [15]. However, 3,3-dimethyl-2-butanone was formed in higher yield when $H_{4+x}S_2V_xW_{18-x}O_{62}$ (x = 0–2) was used (entries 5–7). As the number of vanadium atoms in the POMs increased, the yield of 3,3-dimethyl-2-butanone increased. In particular, the highest yield and highest selectivity were obtained with $H_6S_2V_2W_{16}O_{62}$. When POMs containing molybdenum, such as $H_{3+x}AsV_xMo_{12-x}O_{40}$, were used for this reaction, 3,3-dimethyl-2-butanone was formed only in trace proportions. We surmised that the POMs were reduced during the pinacol rearrangement, as the colour of the reaction mixtures changed to blue, and that the acidity of the protonated POMs was lowered by the increasing anion charge that resulted from the reduction of POMs. The effect of reaction time on the yield was not investigated because of the low boiling point of 3,3-dimethyl-2-butanone (106 °C).

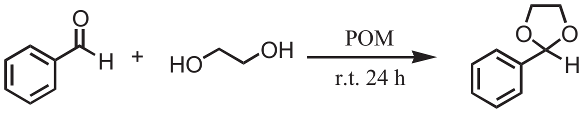
Table 3
Pinacol rearrangement catalyzed by various protonated POMs.

Entry	POMs	Yield (%)	
		A	B
1	$H_4SiW_{12}O_{40}$	59 (71[a])	17 (29[a])
2	$H_3PW_{12}O_{40}$	63 (78[a])	15 (22[a])
3	$H_3AsW_{12}O_{40}$	67	12
4	$H_4AsVW_{11}O_{40}$	<50	<15
5	$H_4S_2W_{18}O_{62}$	68	13
6	$H_5S_2VW_{17}O_{62}$	77	15
7	$H_6S_2V_2W_{16}O_{62}$	82	16

A: 3,3-Dimethyl-2-butanone; B: 2,3-Dimethyl-1,3-butadiene.

[a] The yield in parenthesis of entry 1 and 2 means reported result [15].

Reaction conditions: 2,3-dimethyl-2,3-butanediol (0.02 mol), POMs (0.1 mol%), 423 K, 30 min.



Scheme 2. Acetal formation reaction of benzaldehyde and ethylene glycol [16].

5.5. Acetal formation

Sato et al. systematically investigated various acetal reactions between four types of carbonyl compounds and six types of alcohols using $H_4SiW_{12}O_{40}$ as a catalyst [16]. The advantage of this reaction is that the reaction mixture is ultimately divided into two phases: the upper phase contains the products, whereas the lower phase contains the POMs; consequently, the product selectivity should be improved and the POMs could be easily separated and re-used several times. In this study, the acetal reaction between benzaldehyde and 1,2-ethanediol was chosen to compare the catalytic activity of the POMs (Scheme 2). The results are listed in Table 4. In most cases of the use of protonated POMs and in the case of the report on $H_4SiW_{12}O_{40}$, the yield of 2-phenyl-1,3-dioxolane was approximately 30%. However, the yield was 50% when $H_5AsV_2W_{10}O_{40}$ was used. In contrast to the aforementioned systems, the number of vanadium atoms in the POMs slightly affected the product yield, with the exception that the yield tended to increase according to the number of vanadium atoms in $H_{3+x}AsV_xW_{12-x}O_{40}$. Moreover, the effect of reaction time on the product yield was examined for $H_5AsV_2W_{10}O_{40}$. The product yield increased with increasing reaction time up to 45 min and then remained constant for 48 h. This result indicates that the reaction was completed within an hour, even at room temperature.

5.6. Friedel-Crafts acylation

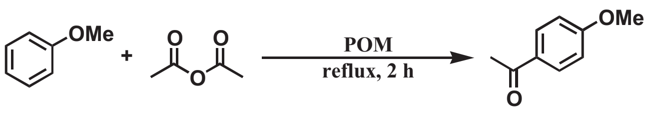
Various types of Friedel-Crafts reactions, such as alkylation and acylation, require strong Lewis acids such as $AlCl_3$ or zeolites [17]. Both protonated forms and salts of POMs have also been used in catalytic Friedel-Crafts reactions [1(l)]. Izumi et al. investigated acidic alkali salts of Keggin-type POMs as solid

Table 4
Acetal formation catalyzed by various protonated POMs.

Entry	POMs	Yield (%)
1	$H_4SiW_{12}O_{40}$	27 (32[a])
2	$H_3AsW_{12}O_{40}$	30
3	$H_4AsVW_{11}O_{40}$	35
4	$H_5AsV_2W_{10}O_{40}$	51
5	$H_3AsMo_{12}O_{40}$	Trace
6	$H_4AsVMo_{11}O_{40}$	29
7	$H_5AsV_2Mo_{10}O_{40}$	30
8	$H_4S_2W_{18}O_{62}$	23
9	$H_5S_2VW_{17}O_{62}$	28
10	$H_6S_2V_2W_{16}O_{62}$	28
11	$H_4S_2Mo_{18}O_{62}$	Trace
12	$H_5S_2VMo_{17}O_{62}$	24

[a] The yield in parenthesis of entry 1 means reported result [16].

Reaction conditions: benzylaldehyde (2.5 mmol), ethylene glycol (2.5 mmol), POMs (0.003 eq), room temperature, 24 h.



Scheme 3. Friedel-Crafts acylation reaction of anisole and acetic anhydride [18].

catalysts for liquid-phase Friedel-Crafts reactions [18]. According to their report, anisole reacted with anhydrous acetic acid, catalysed by $H_3PW_{12}O_{40}$, to form 4′-methoxyacetophenone in 50% yield (Scheme 3), although the main topic of their study was the catalytic activity of $Cs_xH_{x-3}PW_{12}O_{40}$ and the catalytic performance of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$. Using the same procedure, we examined the catalytic activity of all POMs isolated in this study when anisole (100 mmol), acetic anhydride (5 mmol), and a POM (0.05 mol) were refluxed for 2 h. Table 5 shows the yields of 1-(4-methoxyphenyl)ethanone using various POMs. In general, the protonated polyoxotungstates exhibited better catalysis than the protonated polyoxomolybdates. The use of $H_5S_2VW_{17}O_{62}$ led to a higher yield than that achieved with $H_3PW_{12}O_{40}$ and other POMs in this study, although 1-(4-methoxyphenyl)ethanone was obtained in higher yields as the number of vanadium atoms in the $[AsV_xW_{12-x}O_{40}]^{(3+x)-}$ series increased. When molybdenum-containing POMs were used, the colour of the solution changed to dark blue shortly after the start of the reaction. This colour change indicates that the POMs were reduced and that their acidity was decreased, resulting in a lower yield of 1-(4-methoxyphenyl)ethanone. To examine the effect of reaction time on the yield, the yield was checked every 30–60 min until 360 min after the reaction catalysed by $H_5AsV_2W_{10}O_{40}$ had started. The yield increased up to ca. 150 min, then remained constant (ca. 74%). For other POMs, a longer reaction time might also have improved the product yield.

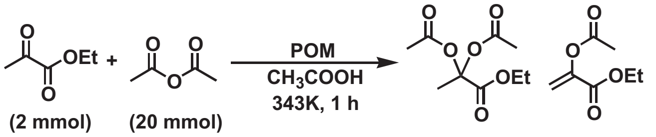
5.7. Acylation of ethylpyruvate

The production of useful chemicals and energies from biomass is an important goal [19]. The synthesis of polyacyloxyacrylate ester from lactic acid through lactate ester, pyruvate ester, and acyloxyacrylate ester has been developed, although polylactic acid can result from the polymerisation of lactic acid, which is obtained from the fermentation of glucose as a polymer from biomass. Ninomiya et al. studied the catalytic acylation of pyruvate ester with carboxylic anhydrides using a few types of POMs in addition to strong mineral acids such as H_2SO_4, HCl, and *p*-TsOH in the synthesis of polyacyloxyacrylate from lactic acid (Scheme 4) [20]. Among the various acids tested, $H_3PW_{12}O_{40}$ gave the highest product yield (61%). In this study, according to the reported reaction conditions, 2 mmol of ethyl pyruvate was reacted with 20 mmol of anhydrous acetic acid at 343 K for 1 h to form ethyl α-acetoxyacrylate in acetic acid containing various protonated POMs. Table 6 shows the results of these reactions. Although all protonated POMs were tested, no reaction proceeded or ethyl 2,2-diacetoxypropinate was formed in low yield in most cases; these results are not listed in Table 6. Better results were obtained for three types of protonated POMs: $H_4S_2W_{18}O_{62}$, $H_4S_2Mo_{18}O_{62}$, and $H_3AsW_{12}O_{40}$. Indeed, only $H_3PW_{12}O_{40}$ and $H_4SiW_{12}O_{40}$ gave good yields of ethyl α-acetoxyacrylate, although a variety of acids, including POM, were also tested in the literature. Mineral acids such as H_2SO_4, HCl, and HNO_3 are strong acids, but they are not strong enough to promote the reaction of ethyl pyruvate to ethyl α-acetoxyacrylate [20]. Notably, strong acidity is required to facilitate this reaction. In particular, $H_4S_2W_{18}O_{62}$, which is more acidic than $H_3PW_{12}O_{40}$, gave higher conversion (86% for $H_4S_2W_{18}O_{62}$ and 65% for $H_3PW_{12}O_{40}$), although the yield of ethyl α-acetoxyacrylate with $H_4S_2W_{18}O_{62}$ was less than that with $H_3PW_{12}O_{40}$ in a 1 h reaction (49% for $H_4S_2W_{18}O_{62}$ and 56% for $H_3PW_{12}O_{40}$). In general, the protonated polyoxotungstates exhibited better catalytic properties than the protonated polyoxomolybdates, similar to the results obtained for the Friedel-Crafts acylation. Furthermore, the yields of ethyl α-acetoxyacrylate and ethyl 2,2-diacetoxypropinate were investigated with $H_4S_2W_{18}O_{62}$ for longer reaction times. When the conversion ratio and yield were checked at regular time intervals up to 24 h, the conversion ratio increased to 90% over 7 h, and the yield of ethyl α-acetoxyacrylate ultimately reached 69%. In the case of $H_3PW_{12}O_{40}$, the conversion ratio (68%) and yield of ethyl α-acetoxyacrylate (61%) obtained in a 1 h reaction would be nearly the same as in a 24 h reaction on the basis of the data reported in the literature, even if the reaction proceeded at a higher temperature. The catalytic reaction rate with $H_4S_2W_{18}O_{62}$ appears to be slower than that with $H_3PW_{12}O_{40}$. However, the catalytic activity of $H_4S_2W_{18}O_{62}$ is much higher than that of $H_3PW_{12}O_{40}$, which can be attributed to the high acidity of $H_4S_2W_{18}O_{62}$.

Table 5
Friedel-Crafts Acylation catalyzed by various protonated POMs.

Entry	POMs	Yield (%)
1	$H_3PW_{12}O_{40}$	50
2	$H_3AsW_{12}O_{40}$	46
3	$H_4AsVW_{11}O_{40}$	55
4	$H_5AsV_2W_{10}O_{40}$	63
5	$H_3AsMo_{12}O_{40}$	19
6	$H_4AsVMo_{11}O_{40}$	0
7	$H_5AsV_2Mo_{10}O_{40}$	0
8	$H_4S_2W_{18}O_{62}$	39
9	$H_5S_2VW_{17}O_{62}$	72
10	$H_6S_2V_2W_{16}O_{62}$	51
11	$H_4S_2Mo_{18}O_{62}$	14
12	$H_5S_2VMo_{17}O_{62}$	8

Reaction conditions: anisole (100 mmol), acetic anhydride (5 mmol), POM (0.05 mmol), reflux, 2 h.



Scheme 4. Acylation reaction of ethyl pyruvate with acetic anhydride [20].

Table 6
Alylation of ethyl pyruvate catalyzed by various protonated POMs.

Entry	POMs	Yield (%)	
		A	B
1	$H_3PW_{12}O_{40}$	9 (7[a])	56 (61[a])
2	$H_3PMo_{12}O_{40}$	0.3 (2[a])	3 (6[a])
3	$H_4S_2W_{18}O_{62}$	37	49
4	$H_4S_2Mo_{18}O_{62}$	21	12
5	$H_3AsW_{12}O_{40}$	25	12

A: Ethyl 2,2-diacetoxypropionate; B: Ethyl α-acetoxyacrylate.

[a] The yield in parenthesis of entry 1 and 2 means reported result [20].

Reaction conditions: ethyl pyruvate (2 mmol), aceticanhydrate (20 mmol), POM (7.5 mol% as H^+ vs. ethyl pyruvate), acetic acid (20 mmol), 343 K, 1 h.

6. Conclusion

In this study, several POMs prepared in aqueous-organic solutions were isolated in their protonated form via a modified etherate method. The detailed extraction conditions were tuned for each individual POM. Isolated protonated POMs were characterised by IR and Raman spectroscopy, and the resulting spectra were compared with the corresponding tetraalkylammonium salts. Many of the POMs were observed to be more strongly acidic than $H_3PW_{12}O_{40}$

and $H_4SiW_{12}O_{40}$ on the basis of results obtained using a Hammett indicator. Four types of catalytic reactions—pinacol rearrangement, acetal formation using benzaldehyde and ethylene glycol, and the Friedel-Crafts acylation of anisole and ethyl pyruvate—that were previously reported were selected to compare the catalytic behaviours of the protonated POMs isolated in this study. Based on the results of a series of catalytic ability tests, the catalytic ability of the newly isolated POMs should be higher than that of previously reported POMs for all cases, although different POMs exhibited better performance for different reaction systems. We concluded that the use of the modified etherate method and optimisation of the extraction conditions allow the isolation of POMs formed in an aqueous-organic mixed solvent in their protonated forms. In addition, these POMs could improve the conversion ratios and product yields in other organic syntheses. The yields of the products tested in this study are closely related to the acidity of the protonated POMs. However, this relationship is not simple. The framework components of the POMs should be essential for their yield and acidity, which implies that the POMs could directly interact with materials during catalytic reactions. However, detailed justification for this mechanism is currently unavailable. In the future, reaction conditions should be optimised according to the POMs that will be compared with the results. This process would allow researchers to elucidate the effects of acidity and the POM components on the respective catalytic reactions. In addition, further study of the extraction conditions, characterisation, and catalytic ability of other POMs is in progress, and the results will be reported in due course.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcata.2014.07.032.

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