Catalysis Communications 30 (2013) 19–22

Contents lists available at SciVerse ScienceDirect

Catalysis Communications

journal homepage: www.elsevier.com/locate/catcom

Short Communication

# Novel gallium and indium salts of the 12-tungstophosphoric acid: Synthesis, characterization and catalytic properties

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ARTICLE INFO

*Article history:*
Received 17 September 2012
Received in revised form 3 October 2012
Accepted 16 October 2012
Available online 22 October 2012

*Keywords:*
$GaPW_{12}O_{40}$
$InPW_{12}O_{40}$
Etherification
1-phenylethanol
$C_1$–$C_4$ alkanols
Unsymmetrical ethers

ABSTRACT

The objective of this study was the preparation, characterization and testing of the catalytic properties of the $GaPW_{12}O_{40}$ and $InPW_{12}O_{40}$ salts of 12-tungstophosphoric heteropolyacid (HPW). The samples were characterized by XRD, IR, SEM, and $^{31}P$ and $^{1}H$ MAS NMR spectroscopy. The acid properties of the solids were directly accounted for by applying $^{1}H$ MAS NMR. The salts were screened in the etherification of 1-phenylethanol with $C_1$–$C_4$ alkanols in dichloromethane as a solvent to yield the corresponding $C_6H_5-CH(OR)-CH_3$ unsymmetrical ethers. In comparison with pure HPW, the new salts revealed generally a higher selectivity of ethers formation at 65 °C.

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## 1. Introduction

Heteropolyacids constitute an important class of solids, which are composed of large anions neutralized by protons and exhibit a wide range of composition and architecture. In the most important structure of the heteropolyacids (HPAs), the anions adopt the Keggin structure [1,2]. Some heteropolyacids with the Keggin structure belong to the strongest known solid acids. For example, the differential heat of ammonia sorption on HPW was 175 kJ/mol; first portions of ammonia were, however, sorbed with $Q_{diff}$ close to 200 kJ/mol, thus pointing out to the presence of superacid sites in the solid [3]. After the strong acidity of HPAs had been recognized, the solids were screened in different reactions catalyzed by acid sites [4]. The major disadvantage of using pure HPAs stems from their low specific surface area and relatively low thermal stability. These disadvantages can be overcome by supporting HPAs on solids with well-developed area. Both encapsulation of HPW in the zeolite Y supercages [5,6], or supporting it from inorganic and organic solutions, are the methods of choice [7,8]. In the quest for developing of new, high-performance solid catalysts, the aluminum salt of 12-tungstophosphoric acid was suggested for Friedel–Crafts acylation and preparation of ethers [9,10]. Recently, etherification of *n*-butanol was studied over Keggin heteropolyacids containing cobalt, boron, silicon and phosphorus as central atoms [11]. If not all the protons available in HPA's are exchanged by metal cations, as it is found in a well-known $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ salt, then the presence of the Brønsted acid sites in the solid is understandable. Neutral salts, like $AlPW_{12}O_{40}$, shouldn't possess strong acid sites. However, it was shown that $AlPW_{12}O_{40}$ dehydrated at 373–523 K still contains Brønsted acid sites and is as superacidic as dehydrated $H_3PW_{12}O_{40}$ [12].

In this contribution we have focused on the yet unknown HPW salts of the 3rd group cations. The objective of this study was to prepare, characterize, and test gallium and indium salts of 12-tungstophosphoric acid, $GaPW_{12}O_{40}$(GaPW) and $InPW_{12}O_{40}$(InPW). Pure HPW and its aluminum salt $AlPW_{12}O_{40}$ were used for comparison purposes. The etherification of 1-phenylethanol with $C_1$–$C_4$ alkanols to yield the corresponding $C_6H_5$–CH(OR)–$CH_3$ unsymmetrical aryl alkyl ethers was chosen as the liquid-phase test reaction.

## 2. Experimental

### 2.1. Samples preparation

Gallium and indium salts of the 12-tungstophosphoric acid were prepared using the corresponding nitrate, dissolved in water. The nitrate solution was then added to the HPW solution in a small amount of water. The resultant solution was acidified by $HNO_3$ until the pH = 1, in order to prevent depolymerization of the heteropolianion and formation of lacunar ions. IR spectra have shown unambiguously that the $PW_{11}O_{39}^{7-}$ lacunar forms were not formed during synthesis (cf. data in Supplementary Material, SM). The solution was kept under stirring at the ambient temperature for 1 h. Crystallization of

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http://dx.doi.org/10.1016/j.catcom.2012.10.012

the salts was carried out at 50 °C. The crystals formed were quickly rinsed with the cold water, dried in air at ambient temperature and kept in a desiccator over the magnesium nitrate solution.

### 2.2. X-ray diffraction patterns

X-ray diffraction patterns were acquired on a Siemens D5005 diffractometer with Cu $K_\alpha$ radiation, at 40 kV and 40 mA, with a stepsize of 0.02°/1 s. The unit cell parameters were fitted using the Bruker AXS: TOPAS V2.1 software.

### 2.3. Nuclear magnetic resonance spectroscopy

The solid-state NMR experiments were performed on a Bruker MSL 400 spectrometer at resonance frequencies of 400.3 and 161.9 MHz for $^1$H and $^{31}$P nuclei, respectively. Flip angles of π/2 for $^1$H and $^{31}$P and repetition times of 10 s for $^1$H and 60 s for $^{31}$P nuclei were used. The $^1$H and $^{31}$P MAS NMR spectra were recorded with a sample spinning rate of about 10 kHz. The data were processed with the Bruker software WINNMR and WINFIT.

### 2.4. Procedure for etherification reactions

The catalytic tests were carried out in a glass, batch reactor working under atmospheric pressure, and using, unless not specified otherwise, 5 mol% of a catalyst. Blank tests showed that neither 1-phenylethanol (1-PE) nor styrene (one of the etherification by-products) reacted with $C_1$–$C_4$ alkanols in the absence of a catalyst. Before the catalytic studies, the catalysts were dehydrated in vacuum at 150 °C for 6 h. The substrates, 1-PE and $C_1$–$C_4$ alkanols, were used in the 1:1 molar ratio, and 5 cm$^3$ of dichloromethane was used as a solvent. The process was carried out for 4 h at chosen temperature, sampling the products, and carrying out quantitative analysis by a Varian CP-3800 gas chromatograph equipped with a FID detector and the 30 m × 0.32 mm DB-WAX capillary column.

## 3. Results and discussion

### 3.1. Characterization of the samples

X-ray diffraction patterns of the pristine HPW and its gallium and indium salts are depicted in Fig. 1. Data on parent HPW are included in SM. The gallium GaPW salt exhibits the strongest reflections at 2θ = 5.9°, 7.8°, 8.8°, 10.3°, 17.9°, 25.4° and 34.7° (Fig. 1b). No other phases were found, in particular $Ga(NO_3)_3 \cdot 8H_2O$ [ICSD 00-012-0398] and $Ga_2O_3$ [ICSD 04-004-5292]. GaPW is monoclinic and belongs to the space group $P2_1/c$. The unit cell constants are listed in Table 1.

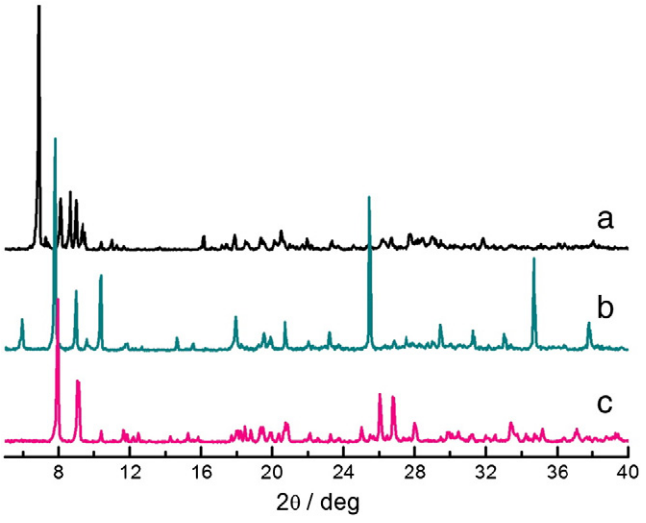



**Fig. 1.** X-ray diffraction patterns of the pristine HPW·13-14$H_2O$ (a), and the GaPW·13$H_2O$ (b) and InPW·23$H_2O$ (c) salts.

The indium InPW salt shows the strongest reflections at 2θ = 7.9°, 9.0°, 18.1°, 20.7°, 26.0°, 26.8° and 33.4° (Fig. 1c). No other phases were found in this sample as well, in particular a hydrated indium nitrate, $NO(In(NO_3)_4)$ [ICSD 00-030-0877], or the possible products of the InPW decomposition, like $InPO_4 \cdot 2H_2O$ [ICSD 04-009-3660] or $In_6WO_{12}$ [ICSD 01-0373-5973]. InPW is monoclinic and belongs to the space group $P2_1/c$ (Table 1).

In the $^{31}$P MAS NMR spectrum of HPW, two signals can be discerned at −15.2 and −15.0 ppm, indicating that different counter cations, like $H_3O^+$ and $H_5O_2^+$, are present in the hydrated material (Fig. 2a). All the terminal oxygen atoms in the Keggin heteropolyanion are linked via the *equivalent* hydrogen bonds with these counter cations [13]. In the $^{31}$P MAS NMR spectra of GaPW and InPW, the cations are present probably as hexaaqua complexes $[M(H_2O)_6]^{3+}$, where M = $Ga^{3+}$, $In^{3+}$. For GaPW, two strong signals are seen at −15.0 and −15.6 ppm (Fig. 2b). The signals in this region are very sensitive toward hydration state of the sample [14]. Finally, interaction of Keggin units with cations may bring about formation of lacunar forms or dimers, all these species giving rise to the signal at −13.5 ppm [13,15]. The signals at −13.4 ppm of the salts in the present study (Fig. 2b,c) are, however, significantly weaker than found in AlPW [12].

Acidic and non-acidic protons can be directly observed via $^1$H MAS NMR due to their different chemical shifts, $\delta_{1H}$ [16,17]. Thus, a detailed insight into the nature, accessibility, and reactivity of Brønsted acid sites in various classes of catalysts, including heteropolyacids, may be accounted for [12,18]. The $^1$H MAS NMR spectra of the hydrated and dehydrated GaPW and InPW materials are shown in Figs. 3 and S3 (SM), respectively. At ambient temperature, two signals at 7.6 and 9.2 ppm can be observed for GaPW. The strong signal at 7.6 ppm is superimposed onto a much broader signal, and a signal at 9.2 ppm occurs as a medium intensity hump. The signal at 7.6 ppm corresponds to $H_5O_2^+$ groupings ($H_2O$ adsorbed on the Brønsted acid sites) [12,19], while the hump at 6.6 ppm is due to physisorbed water (Fig. 3a). After dehydration at 120 °C, a single, symmetrical line and high intensity line appears at 9.2 ppm (Fig. 3b) assigned to the "free" protons (i.e., strong Brønsted acid sites). These acid sites are formed during dehydration by dissociative decomposition of water molecules located on the $Ga^{3+}$ or (cf. below) $In^{3+}$ cations:

$$[M(H_2O)_n]^{3+} \rightarrow M(OH)_2^{+} + 2H^{+} - (n-2)H_2O$$
$$[M(H_2O)_n]^{3+} \rightarrow M(OH)^{2+} + H^{+} - (n-1)H_2O\,,\ \text{where M} = Ga^{3+},\ In^{3+}.$$

Such a mechanism resembles closely formation of protons on cation-exchanged zeolites [20]. Upon further dehydration, the intensity of this line remains approximately constant, thus demonstrating the thermal stability of Brønsted acid sites up to at least 250 °C (Fig. 3c). This finding is very important and encouraging from a catalytic standpoint.

Finally, the $^1$H MAS NMR spectra of InPW reveal generally a similar behavior (Fig. S3, SM). Upon dehydration at 120 °C, the line at 9.2 ppm, corresponding to the acidic protons, dominates and then ca. 70% of its intensity is lost upon dehydration at 250 °C. Other lines of protons in the range 3.9–7.6 ppm are also present (Fig. S3 b). We conclude that the bare Brønsted acid sites in InPW at 9.2 ppm are much less stable thermally than in GaPW.

### 3.2. Etherification of 1-phenylethanol with $C_1$–$C_4$ alkanols

Etherification constitutes an important class of reactions catalyzed by inorganic and organic acids. The products formed are symmetrical or unsymmetrical ethers. If, for example, etherification between the normal alkanols and alkylaromatic alcohols is carried out, then

**Table 1**
Unit cell parameters (Å) of the monoclinic gallium and indium salts of HPW.

| Sample | a | b | c | β |
|---|---|---|---|---|
| $GaPW_{12}O_{40}\cdot\sim13H_2O$ | 9.907 (±0.004) | 22.790 (±0.008) | 19.42 (±0.01) | 91.02° (±0.1) |
| $InPW_{12}O_{40}\cdot\sim23H_2O$ | 9.861 (±0.004) | 22.50 (±0.01) | 19.48 (±0.01) | 91.0° (±0.1) |

precious unsymmetrical ethers are formed. Ethers are widely used in pharmaceutical, cosmetic and specialty chemicals industries [21]. Heteropolyacids containing Brønsted acid sites catalyze a number of organic reactions [4]. However, not only heteropolyacids, but also their salts can be active acid catalysts.

To screen the catalytic properties of acid sites containing GaPW and InPW salts, the etherification between 1-phenylethanol (1-PE) and low molecular weight alkanols R–OH (methanol, ethanol, *n*-propanol, *n*-butanol), was chosen. The desired reaction products were unsymmetrical ethers of the type $C_6H_5-CH(OR)-CH_3$. Etherification was studied at the 45-118 °C temperature range. First, the amount of a catalyst used for the process was optimized. These preliminary tests applying 2.5–10 mol% of a catalyst revealed that the best performance was obtained when using 5 mol% of a catalyst. This amount of a catalyst was therefore kept constant in all the subsequent experiments. Second, the effect of temperature was studied, ranging from 45 to 118 °C. In general, the lower selectivity toward ethers was observed both at low and high temperatures within the range studied. Thus, 65 °C was chosen as a reference temperature for the tests. At 65 °C, all the samples studied were found to be active etherification catalysts, with the nearly total conversion of 1-PE (98–100 mol%) after 30 min of the reaction time. However, different selectivities to the ethers were observed on the catalysts studied. Apart from desired unsymmetrical ethers, different by-products were found in reaction products. Of these, styrene, formed by dehydration of 1-phenylethanol, was present in larger amounts and was therefore specified separately (Fig. S4, SM). Interestingly, no etherification between the two R–OH molecules to symmetrical R–O–R ethers was evidenced. In Fig. 4 the results of the catalytic tests are summarized, showing the corresponding ether $C_6H_5$–CH(OR)–$CH_3$ yield as a function of the catalyst and R–OH alcohol. Several features can be seen in Fig. 4. In all the cases, despite of the length of the alcohol alkyl group, the lowest ether yields were found over pristine heteropolyacid HPW.

Similarly, in the etherification experiments carried out with methanol, the highest yields of the corresponding ether (1-methoxyethylbenzene, 1-MeEB) were obtained over all four solids. The highest yields of ethers were observed over the GaPW salt, reaching 82% of 1-MeEB when using methanol (ca. 10% higher in comparison with HPW). Slightly lower yields were observed for AlPW. Nevertheless, in all the cases the ether yields obtained over the gallium, aluminum and indium salts were superior in comparison with pure HPW. The trends in reaction selectivity was: GaPW > AlPW > InPW > HPW. The relatively lower performance of InPW might be tentatively ascribed to the lower thermal stability of acid sites and the presence of other protons at 3.9–7.6 ppm (Fig. S3b, SM).

As it is seen in Fig. 4, the yield of the ethers decreases with the increase of the alkyl chain length in R–OH. Similar observation was made in the etherification of *p*-methoxybenzyl alcohol with $C_1$–$C_4$ alkanols [22]. Polarities of the alcohols are decreasing in the order of dielectric constants (ε), these being equal to 32.6, 24.6, 20.4 and 17.5 for methanol, ethanol, propanol and butanol, respectively. Dichloromethane is less polar (ε = 8.9), thus bringing about increased interactions with an alcohol upon increasing the size of the alkyl group. This fact, coupled with the low initial concentration (0.46 mol/dm$^3$) of the alkanols in substrates, might be suppressing the main reaction of an alcohol with the preadsorbed 1-phenylethanol to form ether.

## 4. Conclusions

The new, phase-pure gallium and indium salts of 12-tungstophosphoric acid were successfully prepared and characterized. Unit cell parameters of the monoclinic crystals were determined. Upon dehydration at moderate temperatures, the Brønsted acid sites became visible in the $^1$H MAS NMR spectra, which were formed by a mechanism resembling proton formation in zeolites. These acid sites were more stable thermally in GaPW. Catalytic activity of the salts was demonstrated in preparation of the $C_6H_5-CH(OR)-CH_3$ unsymmetrical ethers under mild conditions. The etherification selectivity was in a following order: GaPW > AlPW > InPW > HPW. The yield of the ether depended on the alkanol used, and the maximum selectivity to the ether, 1-methoxyethylbenzene, was observed for the reaction of methanol with 1-phenylethanol over $GaPW_{12}O_{40}$ (82 mol%). To conclude, this work opens up further applications of these salts in numerous reactions known to proceed on the acid sites.

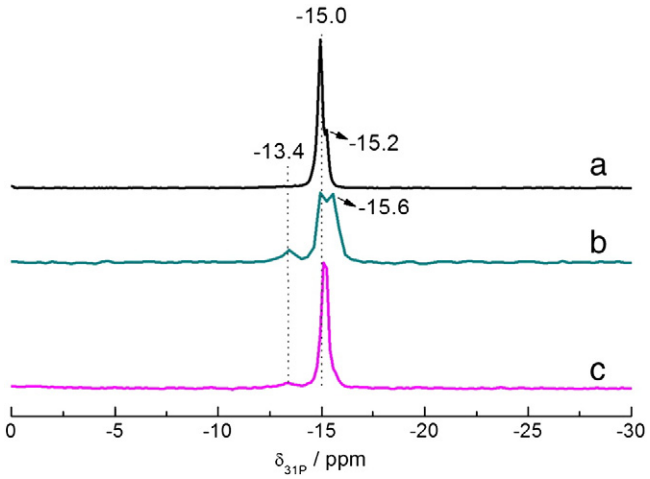



**Fig. 2.** $^{31}$P MAS NMR spectra of pristine HPW·13-14$H_2O$ (a), and the GaPW·13$H_2O$ (b) and InPW·23$H_2O$ (c) salts.

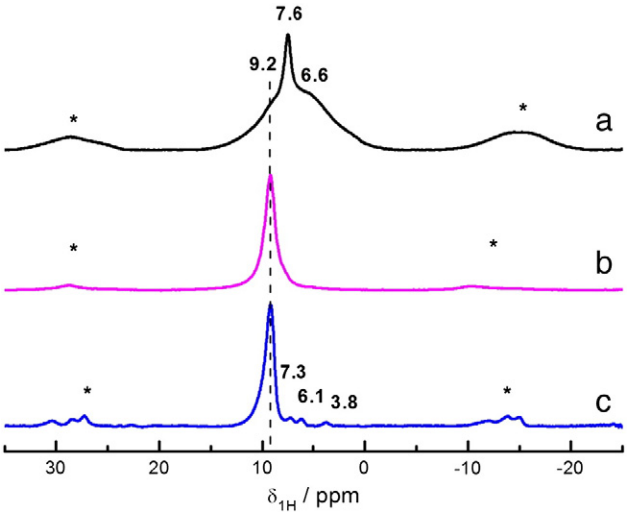



**Fig. 3.** $^1$H MAS NMR spectra of GaPW: (a) hydrated (~13$H_2O$), (b) dehydrated at 120 °C, and (c) dehydrated at 250 °C.

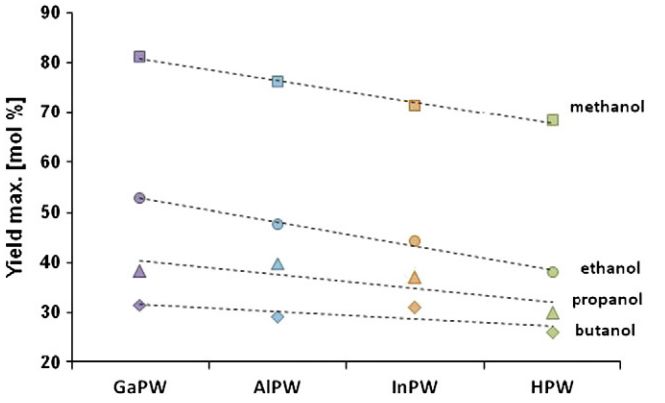



**Fig. 4.** Etherification of 1-phenylethanol with $C_1$–$C_4$ alkanols. The maximum yield of the $C_6H_5-CH(OR)-CH_3$ ether as a function of the catalyst and R–OH (where R= $CH_3$, $C_2H_5$, $n$-$C_3H_7$, $n$-$C_4H_9$), is shown. Reaction conditions: 5 mol% of a catalyst, temperature 65 °C.

## Acknowledgment

We thank Dr. E. Bielańska (J. Haber Institute of Catalysis and Surface Chemistry, Kraków), for SEM and EDX measurements.

## Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.catcom.2012.10.012.

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Supplementary Material

# Novel gallium and indium salts of the 12-tungstophosphoric heteropolyacid: synthesis, characterization and catalytic properties

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## 1. Experimental

### *1.1. Scanning Electron Microscopy*

SEM microphotographs were obtained using a Jeol JSM-7500 F microscope. The microphotographs were acquired in a Secondary Electrons Imaging mode, at 15-20 kV. Qualitative and quantitative analysis of chemical composition of the materials were carried out using the same microscope.

### *1.2. Infrared spectroscopy*

FT IR spectra were obtained using a Nicolet 800 spectrometer working in a transmission mode. The pellets were obtained using pure, precalcined potassium bromide.

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## 2. Results and Discussion

### *2.1. Characterization*

The pure HPW acid gives typical diffractogram with several reflections (Fig. 1). The detailed analysis allowed calculation of the unit cell constants, yielding: a = 14.03, b = 14.09, c = 13.57 (±0.01) Å, $\alpha = 112.01^{o}$, $\beta = 109.66^{o}$ and $\gamma = 61.06^{o}$ (±0.03 $^{o}$). The sample is triclinic and belongs to the space group P-1. These parameters correspond to a hydrate $HPW{\cdot}14H_2O$. Some orthorhombic crystals (space group Pcca) were also found, with the unit cell constants a = 20.7 (±0.01), b = 13.00 (±0.005), and c = 18.81 (±0.01) Å, corresponding to a hydrate $HPW{\cdot}21H_2O$. The pristine HPW is therefore a mixture of hydrates containing 13-14 or 21 $H_2O$. However, taking into account the intensity of reflections, the $HPW{\cdot}13\text{-}14H_2O$ hydrate predominates in the sample studied.

The morphology and composition of HPW and its gallium and indium salts were determined by Scanning Electron Microscopy (SEM). The microphotographs of hydrated HPW, GaPW, and InPW are depicted in Fig. S1. The pristine sample of HPW is composed of elongated, prismatic crystals with the length ca. 5-6 μm (Fig. S1a). Both salts exhibit very similar morphology and consist of plate-like crystals, with cracks developed during dehydration of samples under vacuum (Fig. S2b,c). Upon close inspection, no other phases, crystalline or amorphous, were found in the microphotographs. The composition of the samples was estimated by EDX.

In Table S1, the compositions of the samples, estimated by EDX, are listed. In particular, Ga, In, P, and W were accounted for. The measurements were carried out in chosen points and also in larger areas. In the parent HPW sample the ratio W/P is in excellent agreement with the stoichiometry of the Keggin unit, where W/P = 12. Similar ratios were found for the gallium and indium salts thus demonstrating that the procedure of salts preparation led to the untouched stoichiometry of the Keggin units. Neither decomposition nor lacunar forms of the heteropolyacid and its Ga and In salts were observed. SEM combined with EDX revealed therefore that the samples studied were pure.

**Table S1**

Composition of the pure acid and its salts determined by EDX (at%).

| Sample | P [at%] | W [at%] | $M^{3+}$ * [at%] | W/P | W/M |
|---|---|---|---|---|---|
| HPW | 7.61-7.78 | 92.22-92.39 | - | 11.9-12.1 | - |
| GaPW | 6.87-7.07 | 84.80-86.27 | 5.67-8.43 | 11.9-12.3 | 11.9-12.4 |
| InPW | 6.42-7.71 | 84.20-87.83 | 6.72-7.42 | 11.7-12.8 | 11.8-12.3 |

* - $M^{3+}$ refers to $Ga^{3+}$ or $In^{3+}$

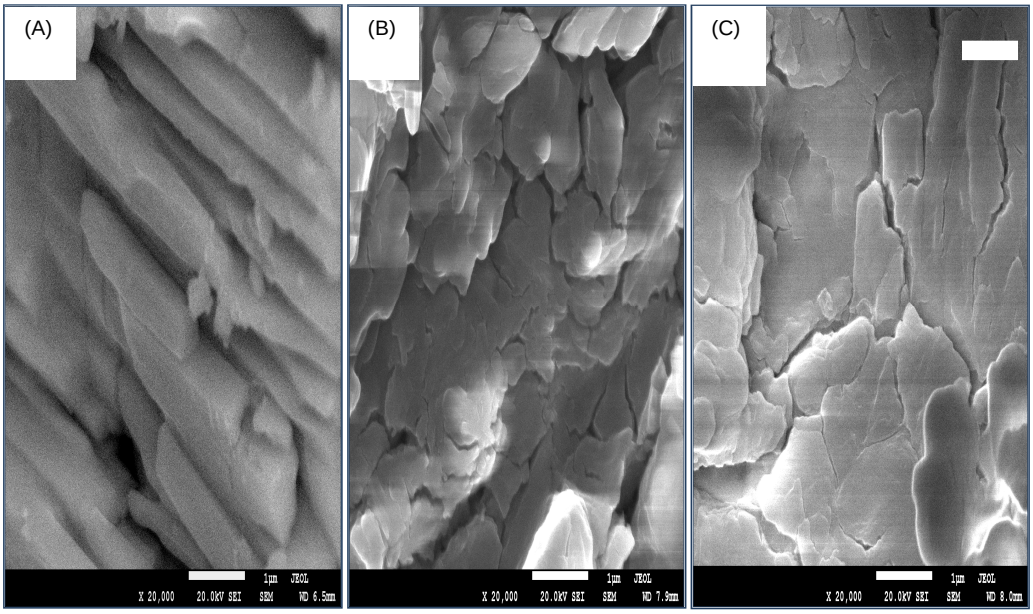



**Fig. S1.** SEM microphotographs of pure HPW (A), and the GaPW (B) and InPW (C) salts. The length of a white bar is 1 μm.

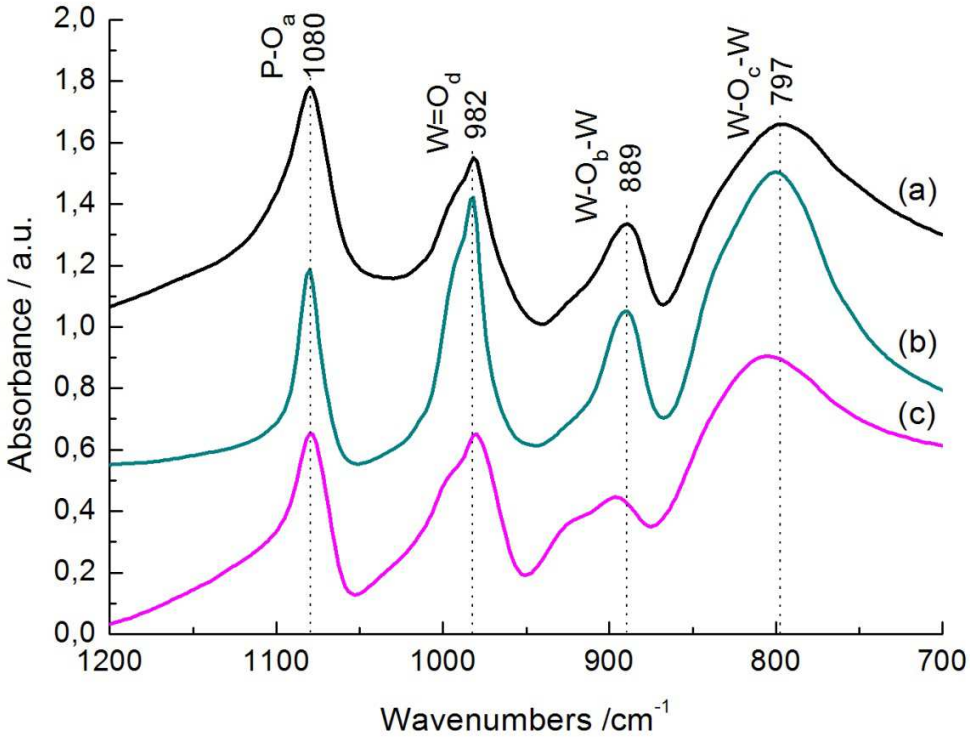



Fig. S2. FT IR spectra of the pure $HPW_{12}O_{40}\cdot 13\text{-}14H_2O$ (a), $GaPW_{12}O_{40}\cdot 13H_2O$ (b), and $InPW_{12}O_{40}\cdot 23H_2O$ (c).

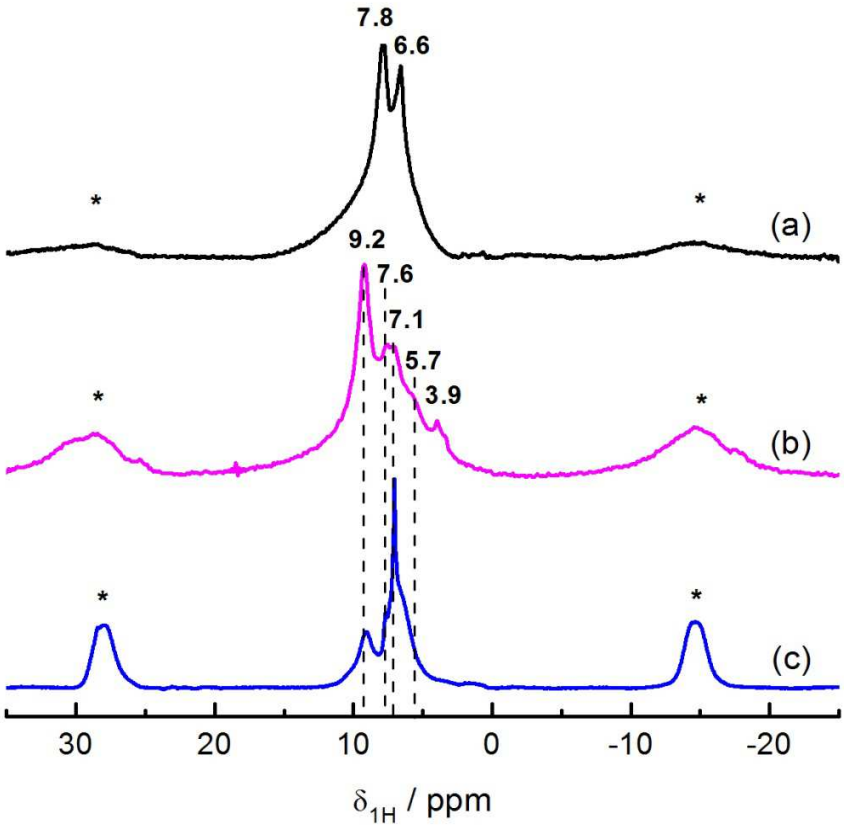



**Fig. S3.** $^{1}$H MAS NMR spectra of the InPW sample: (a) hydrated (·$23H_2O$), (b) dehydrated at 120 $^{o}$C, and (c) dehydrated at 250 $^{o}$C.

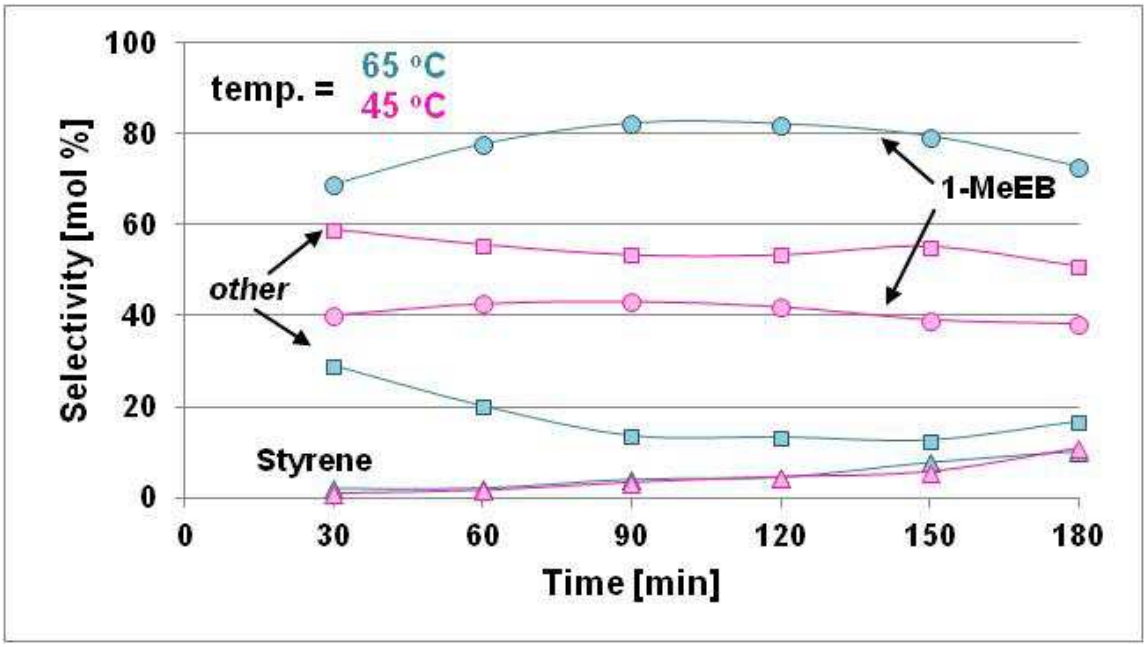



**Fig. S4.** Selectivity to 1-methoxyethylbenzene (1-MeEB), styrene and other by-products *vs.* reaction time in the etherification of 1-phenylethanol and methanol on GaPW at 45 and 65 $^{o}$C.

The by-products labelled as “other” in Fig. S4 are: two isomers of 2,3-diphenylbutane-2-ol; 1,3-diphenylbut-1-ene; 1,1-diphenylbut-1-ene; and 1,1-diphenyl-2-methylopropene, respectively.