



Short Communication

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

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ABSTRACT

The objective of this study was the preparation, characterization and testing of the catalytic properties of the GaPW₁₂O₄₀ and InPW₁₂O₄₀ salts of 12-tungstophosphoric heteropolyacid (HPW). The samples were characterized by XRD, IR, SEM, and ³¹P and ¹H MAS NMR spectroscopy. The acid properties of the solids were directly accounted for by applying ¹H MAS NMR. The salts were screened in the etherification of 1-phenylethanol with C₁–C₄ alkanols in dichloromethane as a solvent to yield the corresponding C₆H₅–CH(OR)–CH₃ 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}PW₁₂O₄₀ salt, then the presence of the Brønsted acid sites in the solid is understandable. Neutral salts, like AlPW₁₂O₄₀, shouldn't possess strong acid sites. However, it was shown that AlPW₁₂O₄₀ dehydrated at 373–523 K still contains Brønsted acid sites and is as superacidic as dehydrated H₃PW₁₂O₄₀ [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, GaPW₁₂O₄₀(GaPW) and InPW₁₂O₄₀(InPW). Pure HPW and its aluminum salt AlPW₁₂O₄₀ were used for comparison purposes. The etherification of 1-phenylethanol with C₁–C₄ alkanols to yield the corresponding C₆H₅–CH(OR)–CH₃ 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 HNO₃ until the pH = 1, in order to prevent depolymerization of the heteropolianion and formation of lacunar ions. IR spectra have shown unambiguously that the PW₁₁O₃₉⁷⁻ 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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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 α 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 ^1H and ^{31}P nuclei, respectively. Flip angles of $\pi/2$ for ^1H and ^{31}P and repetition times of 10 s for ^1H and 60 s for ^{31}P nuclei were used. The ^1H 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 \times 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 $2\theta = 5.9^\circ, 7.8^\circ, 8.8^\circ, 10.3^\circ, 17.9^\circ, 25.4^\circ$ and 34.7° (Fig. 1b). No other phases

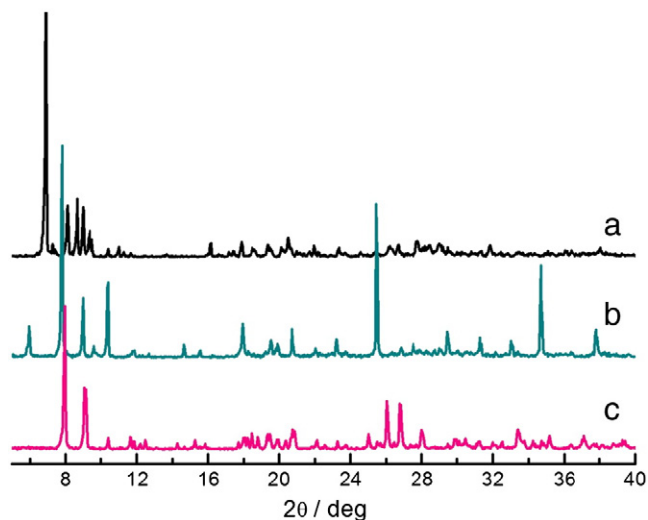


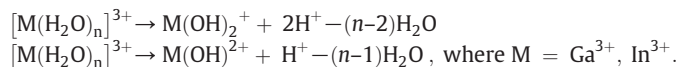
Fig. 1. X-ray diffraction patterns of the pristine HPW·13-14H $_2$ O (a), and the GaPW·13H $_2$ O (b) and InPW·23H $_2$ O (c) salts.

were found, in particular Ga(NO $_3$) $_3$ ·8H $_2$ O [ICSD 00-012-0398] and Ga $_2$ O $_3$ [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.

The indium InPW salt shows the strongest reflections at $2\theta = 7.9^\circ, 9.0^\circ, 18.1^\circ, 20.7^\circ, 26.0^\circ, 26.8^\circ$ 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 $_4$ ·2H $_2$ O [ICSD 04-009-3660] or In $_6$ WO $_2$ [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 $_3\text{O}^+$ and H $_5\text{O}_2^+$, 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 $_2\text{O}$) $_6$] $^{3+}$, 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 ^1H MAS NMR due to their different chemical shifts, δ_{H} [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 ^1H 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 $_5\text{O}_2^+$ groupings (H $_2\text{O}$ 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:



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 ^1H 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

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