



Ethanol conversion over cesium-doped mono- and bi-cationic aluminum and gallium H₃PW₁₂O₄₀ salts



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ABSTRACT

The objective of this study was synthesis, characterization, and catalytic testing of mono-cationic (GaPW₁₂O₄₀, AlPW₁₂O₄₀) and bi-cationic (CsGa_{0.5}H_{0.5}PW₁₂O₄₀, CsAl_{0.5}H_{0.5}PW₁₂O₄₀) salts of tungstophosphoric acid. These heteropoly salts are characterized by Brønsted acidity derived from protons generated by dissociation of water molecules coordinated to the metal atoms. Catalytic activity of the studied salts was evaluated based on ethanol conversion and compared with the well-known parent heteropolyacid H₃PW₁₂O₄₀. The reaction products, ethylene and diethyl ether, were monitored simultaneously by FTIR spectroscopy and chromatographic analysis. The infrared studies indicated that ethylene is formed not only from ethanol but also by diethyl ether decomposition. Cs-doped bi-cationic catalysts exhibited higher activity for ethylene and ether formation than the mono-cationic salts. The following order of catalytic activity was established: H₃PW₁₂O₄₀ > CsGa_{0.5}H_{0.5}PW₁₂O₄₀ ~ CsAl_{0.5}H_{0.5}PW₁₂O₄₀ > GaPW₁₂O₄₀ > AlPW₁₂O₄₀. It is in agreement with the order of their acid strength determined by microcalorimetry and specific surface areas of the studied catalysts.

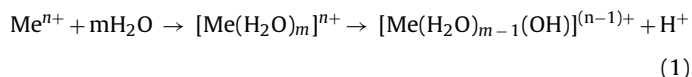
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1. Introduction

The heteropolyacids exhibit useful catalytic properties, both acidic and redox, which have been the subject of many studies. These properties can be controlled by either substituting the constituent hetero-elements or/and by full/partial exchange of the protons in a heteropolyacid by metal cations. This work concerns the second approach to the modification of heteropoly compounds.

Heteropolyacid salts can be divided into two groups. The first group are the salts in which not all protons are exchanged with cations and contain residual protons of the heteropolyacids. The second group are the completely exchanged salts without protons from the original heteropolyacids. Both groups may behave as bifunctional catalysts and be able to catalyze both acidic and redox processes. The acidic properties of heteropoly salts result from the presence of the residual unchanged protons (salts from first group) and/or from water molecules coordinating metal cation that were introduced into heteropoly salts. The water coordinated to the metal atoms [Me(H₂O)_m]ⁿ⁺ can be dissociated and generate

additional acid protons are generated [1]:



The potential benefits from replacement of heteropolyacids by their salts generated a lot of interest resulting in considerable number of papers reporting catalytic behaviour of the heteropoly salts [2,3,4]. The salts with monovalent cations such as K⁺, Cs⁺, Ag⁺, NH₄⁺ of H₃PW₁₂O₄₀ with different contents of cations are known to be effective catalysts for various acid-catalysed reaction. In this contribution we focus on the salts of 12-tungstophosphoric acid H₃PW₁₂O₄₀ with trivalent cations belonging to the 13th group of elements: gallium and aluminum. Two series of salts were synthesized. First one was a series of mono-cationic salts with the formula MePW₁₂O₄₀ where Me = Ga³⁺, Al³⁺. The second series consisted of bi-cationic salts containing additional cesium cations: CsMe_{0.5}H_{0.5}PW₁₂O₄₀ where Me = Ga³⁺, Al³⁺.

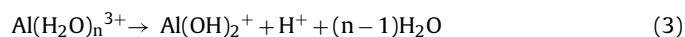
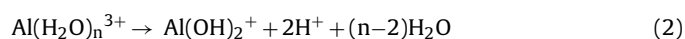
The mono-cationic heteropoly salts are usually obtained by addition of the stoichiometric amount of a metal salt, such as carbonate [5,6], nitrate [7], chloride [8] or sulphate [9], to an aqueous solution of heteropolyacids. These products are isolated by solvent evaporating or precipitate as insoluble solids and are separated

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by filtration. The 12-tungstophosphoric salts containing mono-valent cations such as cesium $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$ [10], potassium $\text{K}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$ and silver cation $\text{Ag}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$ [2], where x is equalled 1 to 3 are well described in the literature. The synthesis of heteropolyacid salts containing trivalent cations such as Al^{3+} has been also reported. In 1982 $\text{AlPW}_{12}\text{O}_{40}$ salt was synthesized by Ono [7] by mixing the aqueous solution of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ and $\text{Al}(\text{NO}_3)_3$. Besides aluminum nitrate other aluminum compounds were used: $\text{Al}(\text{i-OC}_3\text{H}_7)_3$ [11], carbonate [12], chloride [9], and $\text{AlO}(\text{CH}_3\text{COO})_4$ [13]. Silviani and Burns [14] modified the synthesis of heteropoly salt by using aluminum sulphate and removed SO_4^{2-} ions in the form of insoluble BaSO_4 by addition of BaCO_3 and final elimination of CO_3^{2-} ions by heating. The aluminum salt was also obtained by electrochemical method, in which Al^{3+} ions were generated from metallic Al anode during electrolysis of pure heteropolyacid solution. The heteropoly anion was reduced by aluminum but became reoxidized with atmospheric oxygen [15].

In our studies the preparation of $\text{AlPW}_{12}\text{O}_{40}$ was performed starting from aluminum nitrate as described in [16]. The authors assigned ^1H MAS NMR signals observed to $\text{AlPW}_{12}\text{O}_{40}$ dehydrated at 100–250 °C to: acidic protons at 9.1 ppm and OH groups; $\text{Al}(\text{OH})_2^+$ at 4.2 ppm and $\text{Al}(\text{OH})_2^+$ at 5.6 ppm. They concluded that these moieties were formed by dissociation of water molecules coordinated to aluminum cation due to dehydration according to the reactions:



The experiments with adsorption of deuterated pyridine as probe molecule over $\text{H}_3\text{PW}_{12}\text{O}_{40}$ and $\text{AlPW}_{12}\text{O}_{40}$ upon dehydration at 100 and 250 °C indicated that both of these compounds exhibit superacidic behaviour. In contrast to $\text{AlPW}_{12}\text{O}_{40}$, which is well characterized, there is limited information in the literature concerning the synthesis and catalytic characterization of mono-cationic salt of 12-tungstophosphoric acid with the gallium cation, $\text{GaPW}_{12}\text{O}_{40}$ [17]. The salts of heteropolyacid with the 13 group cations were tested in the etherification of 1-phenylethanol with C_1 – C_4 alkanols in dichloromethane as a solvent and showed higher selectivity to ethers than pure $\text{H}_3\text{PW}_{12}\text{O}_{40}$.

In this work we also included the previously unknown bi-cationic salts: $\text{CsGa}_{0.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ and $\text{CsAl}_{0.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$. The preparation of only one bi-cationic heteropoly salt containing both cesium and gallium cations $\text{Cs}_{2.5}\text{Ga}_x\text{H}_y\text{PVMo}_{11}\text{O}_{40}$ was described in the past [18]. In that study the appropriate amounts of $\text{Ga}(\text{NO}_3)_3$ and Cs_2CO_3 were added to the aqueous solution of heteropolyacid $\text{H}_4\text{PVMo}_{11-x}\text{W}_x\text{O}_{40}$. The catalytic activity of these compounds was tested in propane oxidation.

The purpose of the present study is to compare catalytic activity of mono-cationic salts without cesium with bi-cationic cesium salts in ethanol conversion as the test reaction. Additionally, the comparison with the well known and studied pure heteropolyacid $\text{H}_3\text{PW}_{12}\text{O}_{40}$ can be very valuable. Our interest in these salt is based on the literature reports that salts with the formula: $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$ ($x = 1-3$) were found to be excellent catalysts exhibiting significant activity in many acid-base catalytic reactions such as n-butane isomerization [19], methanol conversion [19], esterification of benzoic acid with n-butanol [20], dehydration of ethanol and transformation of m-xylene [21]. This activity was attributed to very high “surface acidity” and porosity [22].

Ethanol conversion has been widely employed as a test reaction for probing acid properties of different catalysts [23,24], including heteropolyacids. We monitored this reaction using in-situ infra-red analysis (FTIR) and gas chromatography. The interaction between reagent in gas phase and heteropoly salts at various reaction temperature was analysed.

2. Experimental

2.1. Materials and synthesis of heteropoly salts

Ethanol absolute (99.8 % pure, supplied by POCh Gliwice) was used as a reagent in the ethanol conversion. The reaction products, ethylene $\geq 99.5\%$ (Aldrich), diethyl ether (p.p.a. supplied by POCh Gliwice) and acetaldehyde $\geq 99.0\%$ (Aldrich) were used for the recording of IR spectra for gaseous compounds and for calibration in chromatographic analysis. All substrates for preparation of the used salts, such as $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (HPW), gallium, aluminum nitrates and cesium carbonate were commercial samples from Sigma–Aldrich.

Mono-cationic salts: gallium $\text{GaPW}_{12}\text{O}_{40}$ (GaPW) and aluminum $\text{AlPW}_{12}\text{O}_{40}$ (AlPW) salts of 12-tungstophosphoric acid were prepared according to the published method [17], using aqueous solution of Ga^{3+} and Al^{3+} nitrate, respectively. These solutions were added in stoichiometric amounts to an aqueous solution of HPW and acidified with a few drops of nitrate acid to avoid the formation of lacunary structures. The mixtures were stirred for 1 h at ambient temperature.

Bi-cationic salts: $\text{CsGa}_{0.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ (CsGaHPW) and aluminum $\text{CsAl}_{0.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ (CsAlHPW) salts of 12-tungstophosphoric acid were obtained in a similar way as mono-cationic salts. In the case of bi-cationic salts, Cs_2CO_3 solution was added dropwise into cationic salts solution, synthesized as mentioned above. As the result the suspensions of CsGaHPW and CsAlHPW were produced and then were stirred for 2 h at ambient temperature in a covered container. The both mono- and bi-cationic salts were dried by evaporation at 50 °C.

The morphology of the salts was studied by means of a Field Emission Scanning Electron Microscope JEOL JSM – 7500 F (Japan) equipped with the energy dispersive EDS system. Specific surface area was determined in accordance with the standard Brunauer–Emmet–Teller (BET) method from the nitrogen adsorption–desorption isotherm using a Quantasorb Jr. The total content of water in the catalysts was roughly measured by Moisture Analyzer MAC50 Radwag. The water loss from samples upon heating was evaluated using more precise method, derivatographic analyses (TG/DTA analyses) done by a Netzsch STA 409 PC/PG derivatograph. The heating rate of 5 °C min^{-1} was applied in all experiments. The acidity of samples was determined by microcalorimetric measurements. The heat of sorption of gaseous ammonia diluted with nitrogen was measured at 100 °C by Microscal gas flow–trough microcalorimeter FMC–4112, with the ammonia uptake measured concurrently by thermal conductivity detection. The use of this instrument was described in detail in [25]. Nitrogen (Linde Gas Polska; 99.999%) was used as a carrier gas. A mixture of 3% ammonia and 97% of nitrogen (Linde Gas Polska) was used.

2.2. Confirmation of the Keggin anion preservation during the preparation of salts

The retention of Keggin anions throughout the salts synthesis was confirmed by FTIR spectroscopy, following the changes in the range of skeletal vibrations, i.e., 1200–400 cm^{-1} . Several drops of an aqueous solution of the heteropolyacid $\text{H}_3\text{PW}_{12}\text{O}_{40}$ and its salts (ca. 0.01 g) were deposited onto silicon wafers and the excess of solvent was evaporated under ambient conditions. The wafers were then placed in a special holder and inserted into IR cell (240 mL), closed with thallium bromide (KRS-5) windows. Spectra were recorded using *Excalibur 300 Series Digilab* spectrometer, equipped with DTGS detector, working with spectral resolution of 4 cm^{-1} in the MID-IR range (4000–400 cm^{-1}). All spectra concerning skeleton

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