



Preparation of caesium-substituted phosphomolybdic acid via solid-state ion exchange method



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ABSTRACT

In this paper, we report the preparation of caesium-exchanged phosphomolybdic acid, Cs₃PMo₁₂O₄₀, via the solid-state reaction between caesium chloride and ammonium phosphomolybdate. The calcination of this mixture was performed at 400 °C–600 °C. The thermal genesis of Cs₃PMo₁₂O₄₀ from its precursors was explored using thermo-gravimetric (TGA), differential thermal (DTA), Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD), field emission scanning electron microscope (FE-SEM) and energy dispersive X-ray analyses. The results obtained indicated that pure ammonium phosphomolybdate hydrate first lost its crystal water and later decomposed at temperatures higher than 450 °C. In the CsCl and (NH₄)₃PMo₁₂O₄₀ mixture, it was demonstrated that Cs⁺ moves into exchange positions at such temperature without destroying the Keggin structure of the heteropoly compound.

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1. Introduction

In the last two decades, heteropoly acids and their salts have become green solid catalysts to catalyse both acid-catalysed and redox processes. The most common class of these heteropoly compounds (HPCs) is composed of those that are based on the 'Keggin-type' polyanions. It is important for understanding the catalytic behavior of HPCs to distinguish between the two classes of structures: (i) the primary structure, which is composed of a central tetrahedron (XO₄; X is normally P, Si or Ge) surrounded by 12 MO₆ octahedra (M usually being Mo, W or V) arranged in four groups of three-edge-sharing M₃O₁₃, and (ii) the secondary structure, which is composed of the three-dimensional arrangement of the polyanion and counter cation [1–3]. HPCs have been extensively studied as a catalyst for many catalysed organic reactions, both in homogeneous and heterogeneous systems, such as the dehydration of ethanol [4] and glycerol [5]; the hydrocracking of *n*-decane [6]; the alkylation of toluene [7] and *p*-cresol [8]; the esterification of acetic [9], lauric [10] and oleic [11] acids; and the oxidation of propane [12–14], cyclohexane [15,16] and isobutene [17].

The salts of HPAs can be prepared by the partial or total exchange of the protons in HPAs by different cations without affecting the primary

Keggin structure of the heteropoly anion. The exchange process is usually conducted by wet chemical synthesis followed by calcination at a suitable temperature [18,19]. As a result, a wide range of acid strengths can be obtained. Alkali-exchanged HPAs exhibit dramatic changes in surface area, pore size and hydrophobicity in comparison to the parent HPA [2]. When large cations (e.g., NH₄⁺, Cs⁺, K⁺ and Rb⁺) are introduced, the solid salts obtained are characterised by an increased surface area, a higher thermal stability and a lower solubility in water than the parent acid [2,20].

Solid-state ion exchange (SSIE) is an interesting method for the preparation of ion-exchanged zeolites in the absence of liquid water [21–27]. This method consists of heating a mixture of two powders, where one is the zeolite, in its H- or NH₄-form, and the other is the active phase salt precursor, usually metal chloride. Mixing is performed by ball milling [21–23] or in a mortar [24–27]. The heat treatment is conducted in vacuum or in a flow of gas. During the calcination process, the exchange process initially occurs at the solid–solid interface between the precursor salt and the zeolite grains with the evolution of HCl or NH₄Cl, respectively. This process is not equilibrium limited because the gases generated during the exchange escape continuously from the system. In principle, the solid-state exchange method allows one to exchange multivalent cations into zeolite sites, which is normally very difficult because of the large size of a hydrated metal complex [24]. Moreover, this method proved to be free of the restrictions of the conventional ion-exchange process, such as the formation of FeOOH-hydroxides in solution during the preparation of Fe-ZSM-5 [23], time consumption [25] and the environmental problems arising from the relatively large amounts of waste solutions [26].

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Although many studies report the preparation of metal exchanged heteropoly acids, to the best of our knowledge, all of them are based on the wet chemistry route. There are no reports about the preparation of these compounds using the solid-state ion exchange method. Thus, this investigation is devoted to study the preparation of caesium-substituted phosphomolybdic acid via the solid-state interaction between caesium chloride and the ammonium salt of phosphomolybdic acid. For this purpose, different physicochemical techniques were employed to investigate the solid-state interaction accompanying the thermal treatment of the CsCl and $(\text{NH}_4)_3\text{PMo}_{12}\text{O}_{40}$ mixture. Such techniques include thermogravimetric analysis (TGA), differential thermal analysis (DTA), Fourier transform infrared (FT-IR) spectroscopy, X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM) and energy dispersive x-ray (EDX) spectroscopy.

2. Experimental

The reagents used in this investigation were analytical grade chemicals. The stoichiometric amounts of CsCl, required for the complete substitution of the ammonium ions, and $(\text{NH}_4)_3\text{PMo}_{12}\text{O}_{40}\cdot 6\text{H}_2\text{O}$ salt were mixed in an agate mortar for 1 h. Portions of the parent mixture obtained were heated at 400 °C, 500 °C and 600 °C for 1 h in a static air atmosphere and then quenched to room temperature. For comparison, portions of $(\text{NH}_4)_3\text{PMo}_{12}\text{O}_{40}\cdot 6\text{H}_2\text{O}$ salt without CsCl addition were calcined under the same conditions. For simplicity, the samples obtained will be referenced by the abbreviations $\text{NH}_4\text{PMo-X}$ for ammonium phosphomolybdate-containing samples and CsPMo-X for the caesium-containing samples, where X indicates the calcination temperature.

Powder X-ray diffraction (XRD) patterns were recorded using a Philips diffractometer (type PW 103/00) with $\text{CuK}\alpha$ radiation ($\lambda = 1.5405 \text{ \AA}$) at 35 kV and 20 mA with a scanning rate in 2θ of $0.06^\circ \text{ min}^{-1}$. The simultaneous TGA and DTA curves were recorded with a Shimadzu DT-60 instrument apparatus at a heating rate of $10^\circ \text{ C min}^{-1}$. The FT-IR spectra of the different calcination products were found by the KBr disc technique in the wavelength range of $4000\text{--}400 \text{ cm}^{-1}$ using a Thermo-Nicolet-6700 FT-IR spectrophotometer. The morphology of the samples was analysed by field-emission scanning electron microscopy (FE-SEM) on a JEOL model JSM-7600F microscope. The compositions were examined by energy-dispersive X-ray spectroscopy (EDX) in the SEM.

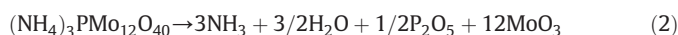
3. Results and discussion

3.1. Thermal analyses

Fig. 1a shows the TGA thermogram obtained by heating the parent $(\text{NH}_4)_3\text{PMo}_{12}\text{O}_{40}\cdot 6\text{H}_2\text{O}$ at $10^\circ \text{ C min}^{-1}$ to 600 °C. Two weight loss (WL) steps can be observed here; the first one extends from ambient to approximately 300 °C and leads to a WL% of 5.4. This value is very close to 5.44%, which is expected for the dehydration of the parent salt according to



The second WL step, which is maximised at 450 °C (DTG curve), is accompanied by a WL of 4.15%. This value is close to that (4.1%) expected for the decomposition of the Keggin anion and the evolution of constitutional water together with ammonia gas according to



In this context, Ilhan et al. [28] reported two WL steps during the thermal decomposition of ammonium phosphomolybdate. During the second step, they observed weight losses of 3.69%–3.77% depending on the sample weight, which is also close to the theoretical loss.

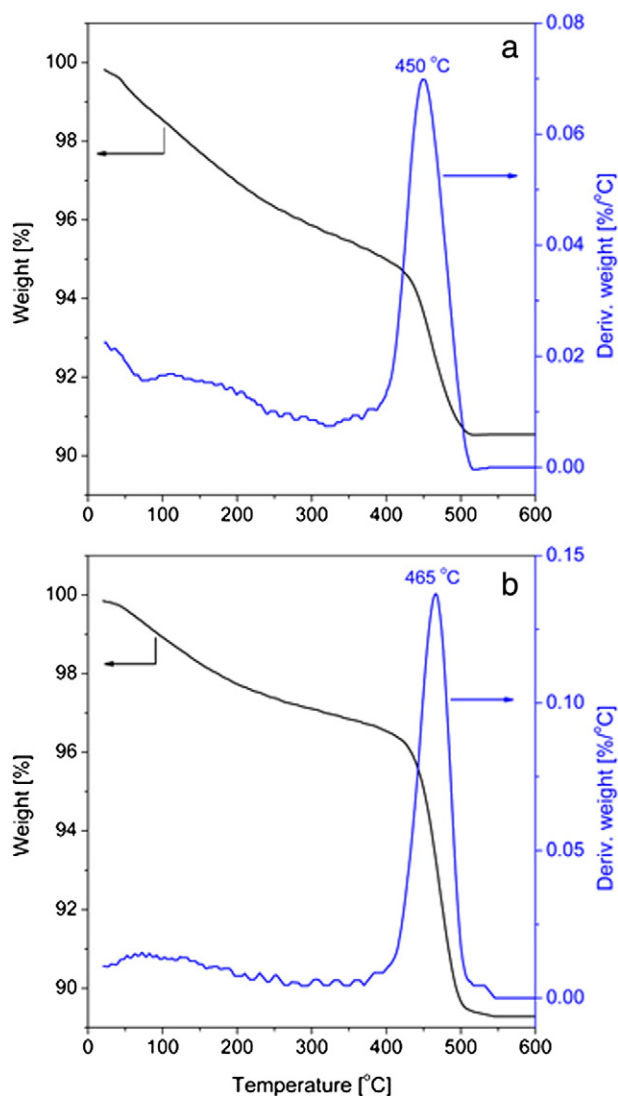
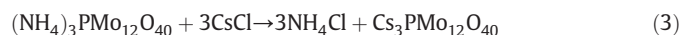


Fig. 1. TGA and DTG curves obtained by heating the pure $(\text{NH}_4)_3\text{PMo}_{12}\text{O}_{40}$ (a) and the CsCl + $(\text{NH}_4)_3\text{PMo}_{12}\text{O}_{40}$ mixture (b) in air to 600 °C.

Concurrently, Dermeche et al. [29] reported a value of 5.5 wt.%, which was found in two steps, during the removal of the ammonium ions of $(\text{NH}_4)_3\text{PMo}_{12}\text{O}_{40}$.

Fig. 1b depicts the TGA thermogram obtained for the caesium chloride mixed with the ammonium phosphomolybdate. Here, two WL steps can also be distinguished. The first one, 3.72%, is maximised at approximately 100 °C, which is attributed to the dehydration of the parent mixture. The second WL step is located at 465 °C and accompanied by a WL% of 6.9. This value is close to that (6.44%) accompanying the evolution of 3 moles of NH_4Cl during the solid-state reaction:



In this context, it was reported that NH_4Cl decomposes to HCl and NH_3 at temperatures higher than 200 °C [30]. Thus, it is plausible to suggest that the solid-state ion exchange occurs at approximately 465 °C and leads to the formation of $\text{Cs}_3\text{PMo}_{12}\text{O}_{40}$ and evolution of HCl and NH_3 gases.

DTA thermograms obtained for the pure ammonium phosphomolybdate and the caesium-containing mixture in the presence of air as a carrier gas are shown in Fig. 2. There is an exothermic effect at 500 °C and 482 °C for pure salt and the caesium- $(\text{NH}_4)_3\text{PMo}_{12}\text{O}_{40}$ mixture, respectively. Usually, the decomposition of the Keggin structure is

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