Inclusion of L-Alanine, L-Arginine, L-Aspargine, L-Serine and Proline into \( \theta \)-Type Zirconium Phosphate

Sadek Shakshooki, Abdurrahman Rhuma, and Fadel Siala

Abstract—Layered \( \theta \)-Type zirconium phosphate \((0-\text{Zr(HPO}_4)_2\cdot 1.88\text{H}_2\text{O})\) was prepared by the reaction of zirconium oxychloride in HF solution with dilute \( \text{H}_3\text{PO}_4 \) at 15°C. The resulting compound was intercalated with amino acids L-alanine, L-arginine, L-asparagine, L-serine and proline respectively at room and 600°C temperatures. The structure properties of the obtained products were characterized by Fourier transform infrared spectroscopy (FT-IR), X-ray powder diffraction (XRD) and thermal analysis (TG/DTA). FT-IR spectrum results demonstrated that the effectiveness of the vibrational spectra in characterizing of the resultant product was supported by TG/DTA and X-ray analysis. Moreover, the vibrational spectroscopic investigation shows that water molecules were appeared very characteristic infrared bands that can be assigned to regular hydrogen bonding of each molecule to adjacent OH group of (POH). Furthermore, amino acids inclusion products were found to retain the layered structure and the loading are closely dependent on the nature of the amino acid.

Index Terms—Inclusion, amino acids, \( \theta \)-type zirconium phosphate.

I. INTRODUCTION

Tetravalent metal phosphates are very insoluble compounds which were known as amorphous for some time [1], [2]. The discovery of their crystalline layered structure by Clearfield and Stynes in 1964 [3] represents the fundamental step in the chemistry of these compounds and found to be \( \alpha \)-layer of type. Their layered crystalline materials resemble clay minerals [4]. The layered materials receiving great attention because of their size, structure, and possible biochemical applications [5] that have been proven to be good carriers for organic polar molecules. Examples of these are zirconium phosphates [4] taking advantage of the expandable interlayer space of the layered materials. Researchers have been capable of encapsulating functional biomolecules into these inorganic matrices protecting them from interacting with environment, avoiding denaturation and enhancing their shelf [4]-[6].

Porous layered \( \text{M}^{IV} \) phosphates with \( \alpha, \theta \) and \( \gamma \)-structures [7]-[9]. \( \alpha\text{-M}^{IV}(\text{HPO}_4)_2\cdot \text{H}_2\text{O}, \theta\text{-M}^{IV}(\text{HPO}_4)_2\cdot 5\text{H}_2\text{O} \) and \( \gamma\text{-M}^{IV}, \text{PO}_4\cdot 2\text{H}_2\text{PO}_4\cdot 2\text{H}_2\text{O} \) are well known compounds, (where \( \text{M} = \text{Ti}, \text{Zr}, \text{Hf}, \text{Sn}, \text{Ce} \)). These materials contain structural POH groups with labile protons and therefore potential candidates as Intercalates [10], ionic co-conductance materials [11], solid acid catalysts [12] and sensors [13].

\( \theta \)-zirconium phosphate, \( \text{Zr(HPO}_4)_2\cdot 5\text{H}_2\text{O} \), has an interlayer spacing of 10.4 Å is readily prepared from protonation of its parent monosodium form \( \text{Zr(\text{NaPO}_4)(PO}_4)_2\cdot 5\text{H}_2\text{O} \) or from hydration of the metastable alcohol form \( \text{Zr(HPO}_3)_2\cdot (\text{C}_2\text{H}_5\text{OH})_2 \) [1], [14]. \( \theta \)-zirconium phosphate \( \text{Zr(HPO}_4)_2\cdot 5\text{H}_2\text{O} \), has a tendency to exchange large size metal ions, such as \( \text{Cs}^+, \text{Mg}^{2+}, \text{Ba}^{2+} \), divalent and trivalent transition metal ions and to intercalate bulky amines [1], [8].

Amino acids are biologically important organic compounds made from amine (-NH\(_2\)) and carboxylic acid (-COOH) functional groups, along with a side-chain specific to each amino acid. The key elements of an amino acid are carbon, hydrogen, oxygen, and nitrogen, though other elements are found in the side-chains of certain amino acids.

To date only few reports on intercalation of amino acids into \( \alpha \), or \( \gamma \)-layered \( \text{M}^{IV} \) phosphates [15]-[18] are available. In this study the synthesis and characterization of novel \( \theta \)-type zirconium phosphate amino acids intercalated products were investigated.

II. MATERIALS AND METHODS

A. Chemicals

\( \text{ZrOCl}_2\cdot 8\text{H}_2\text{O}, \text{H}_3\text{PO}_4 \) (85 %) and amino acids L- Alanine \( \text{C}_3\text{H}_7\text{NO}_2 \), L-Asparagine \( \text{C}_4\text{H}_7\text{NO}_4 \), L-Proline \( \text{C}_5\text{H}_9\text{NO}_2 \), L-Serine \( \text{C}_3\text{H}_7\text{O}_3\text{N} \) and L-Lysine \( \text{C}_6\text{H}_{14}\text{N}_2\text{O}_2 \); used are of BDH, hydrofluoric acid HF (40%) of Reidel De-Haen. Other reagents used were of analytical grade.

B. Instruments Used for Characterization

X-Ray powder diffractometer Siemens D-500 was applied by using Ni-filtered CuK\(_\alpha\) (\( \lambda = 1.54056 \text{Å} \)). TG/DTA SII Extra 6000 Thermogram and TG/DTA Perkin-Elmer SH were used to identify the thermal behavior of the obtained compounds. Forier Transform FT-IR spectrometer was carried out on FT/IR-600. All obtained spectra were measured within a spectral range of 4000–400 cm\(^{-1}\). pH Meter WGW 521 were also used in this study to estimate the ion exchange properties of \( \text{Zr(HPO}_4)_2\cdot 1.88\text{H}_2\text{O} \). The investigation of C, H and N contents were analyzed with GMBH Vario Elemental Analyzer.

C. Preparation of \( \text{Zr(HPO}_4)_2\cdot 1.88\text{H}_2\text{O} \)

50ml of 0.5M ZrOCl\(_2\cdot 8\text{H}_2\text{O} \) in 3M HF was added into Pyrex round bottom flask containing 200ml of (4.6M) \( \text{H}_3\text{PO}_4 \) (prior to mixing, the solutions were cooled at \( \sim 15°C \)). The
mixture prepared was kept under constant magnetic stirring at ~15ºC for 3 days. The resultant precipitate was then washed with distilled water by addition and decantation of distilled water in order to obtain the pH 3 of the solution, then filtered and dried in the air.

D. Exchange Capacity Determination

Exchange capacity was determined by addition of 25 ml of 0.10 M NaCl solution to 100 mg of the θ-Zr(HPO₄)₂.1.88H₂O, with constant continuous stirring for 24 h, then titrated with 0.10 M of NaOH solution.

E. Inclusion of Amino Acids

Inclusion procedure was performed by addition of 0.1 M aqueous solutions of amino acids L-alanine, L-arginine, L-serine, L-lysine, L-asparagine and proline, respectively, into θ-Zr(HPO₄)₂.1.88H₂O.

Typically; to 0.25 g of θ-Zr(HPO₄)₂.1.88H₂O, 20 ml of 0.1 M L-serine were added at room temperature ~25 ºC and kept for 72 h with constant continuous stirring. In order to obtain the best intercalation condition for this guest molecule was filtered, washed with distilled water and dried in the air. Similar intercalation procedure was carried out with L-alanine, L-arginine, L-asparagine and proline. The products were designed as comounds I-V.

III. RESULTS AND DISCUSSION

0-type zirconium phosphate, θ-Zr(HPO₄)₂.1.88H₂O, was prepared and characterized by chemical, X-ray, thermal analysis and by FT-IR spectroscopy. The exchange capacity was determined by Na⁺ ions titration.

A. XRD Pattern of θ-Zr(HPO₄)₂.1.88H₂O

Data presented in Fig. 1 shows the X-ray powder diffraction pattern of the θ-Zr(HPO₄)₂.1.88H₂O, exhibit the presence of diffraction maxima with basal spacing equal to 9.85 Å and also exhibit lamellar structure. Negatively charged layers are formed by macroanions \( [M_4(IV)\ (HPO_4)_{12}]^{20^-} \) and protons (H⁺) bonded to the oxygen adjacent to the anionic layer form positively charged layers. However, the water molecules occupying crystallographic sites are located almost in the center of interlayer cavities.

B. FT-IR Spectra of the θ-Zr (HPO₄)₂.1.88H₂O

FT-IR becomes a key tool to investigate structure. Fig. 2 show FT-IR spectra of θ-Zr (HPO₄)₂.1.88H₂O in the range 4000-400 cm⁻¹ wave number.

A tentative assignment of various vibrational 3 modes is proposed based on previous works preformed in other M(IV) phosphate compounds [18].

The FT-IR spectra of θ-Zr(HPO₄)₂.1.88H₂O show the same trend of modes. From Fig. 2, the narrow bands at 3604.65 cm⁻¹, 3434.11 and band at 1640.39 cm⁻¹ are assigned to vibrational modes of H₂O molecules suggest that water molecules are located at well defined crystallographic sites. These bands at 3604.65 cm⁻¹ and 3434.11 cm⁻¹ were also attributed to an O-H asymmetric modes of interlayer water molecules. The band at 1640.39 cm⁻¹ also corresponds to H-O-H bending modes and the broad band at 3147.10 cm⁻¹ assigned to (P) OH stretching mode of the hydrogen bond, it had shoulder at 3310 cm⁻¹ attributed to O-H stretching coming from symmetry lowering effect of the H₂O interlayer molecules.

At the region 1273.21-1054.46 cm⁻¹, the bands are assigned as P-O symmetry stretching of PO₄ groups, while at 976.33 cm⁻¹ is characteristic to the bonding in plane of the (P-O) bond.

In the region 609.14-515.39 cm⁻¹, the bands ascribed to the presence of δ(PO₄) and to vibrational of water molecules (609.14 cm⁻¹), while at 671.64 cm⁻¹ is connected with O-H bond (out of plane).

C. Exchange Capacity

Exchange capacity of θ-Zr(HPO₄)₂.1.88H₂O was determined by Na⁺ ions titration. The titration curve is shown in Fig. 3. The exchange capacity found to be equal to 6.2 Meq/g. The calculated value is 6.01 Meq/g. This difference is due to partial hydrolysis of HPO₄²⁻ groups due to pH effect.
D. TG/DTA of θ-Zr(HPO₄)₂·1.88H₂O

Thermal analysis of θ-type Zr(HPO₄)₂·1.88H₂O is shown in Fig. 4 and was carried out at temperature range ~25-800°C, in air atmosphere, the heating rate was 10°C/min. The thermal decomposition exhibits two weight loss stages, the loss of water of hydration followed by POH groups condensation.

The first stage is accompanied by weight losses equal to 16.52% up to 210°C which have been attributed to the loss of water of hydration. The second stage in the region 320-650°C ascribed to the loss of the structure water due to POH groups condensation. The weight losses were 5.65% and final product was the pyrophosphates ZrP₂O₇.

Amino acids L-alanine, L-asparagine, L-serine, L-arginine, and proline based θ-Zr(HPO₄)₂·1.88H₂O have been synthesized at room and at 60°C temperatures. The Loading of the amino acids at 60°C found to be less than 30% for L-arginine, θ-Zr(HPO₄)₂ (arg)₀.₃₂·H₂O almost the same for L-proline θ-Zr(HPO₄)₂ (prol)₀.₀₂·1.₁H₂O and low for L-asparagine θ-Zr(HPO₄)₂ (aspg)₀.₃₂·H₂O and L-serine θ-Zr(HPO₄)₂ (ser)₀.₃₀·0.₅H₂O. However, it was no uptake in the case of L-alanine.

Their elemental contents of C, H, N at room temperature have been characterized by elemental (C, H, N) and TGA analysis and the results are shown in Table I. The loading of the amino acid found to be dependent on its nature. The resultant amino acids inclusion products were formulated from combination of elemental and thermal analysis and were designated as compounds (I-V) and their water of hydration were calculated from the TG curve, Fig. 5-Fig. 8.

<table>
<thead>
<tr>
<th>Compound</th>
<th>C</th>
<th>H</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>(I) θ-Zr(HPO₄)₂ (anal) O.₀</td>
<td>nil</td>
<td>nil</td>
<td>nil</td>
</tr>
<tr>
<td>(II) θ-Zr(HPO₄)₂ (aspg)₀.₃₂</td>
<td>1.₆₃ H₂O</td>
<td>10.₆</td>
<td>2.₀</td>
</tr>
<tr>
<td>(III) θ-Zr(HPO₄)₂ (ser)₀.₃₉</td>
<td>0.₅H₂O</td>
<td>8.₂₇</td>
<td>1.₆</td>
</tr>
<tr>
<td>(IV) θ-Zr(HPO₄)₂ (arg)₀.₃₂</td>
<td>2.₂₂·H₂O</td>
<td>2₂.₂₂</td>
<td>4.₇₈</td>
</tr>
</tbody>
</table>

E. TGA of Amino Acids Inclusion Products

The thermal analysis used in this and other studies found to be a good tool for characterization of organic inclusion products of M(IV) phosphates with good accuracy in the range of ~2% [5], [6], [19].

TG/DTA of asparagine inclusion product θ-Zr(HPO₄)₂ (aspg)₀.₃₄·1.₆₃ H₂O compound (II) is shown in (Fig. 5).

It can be seen that thermal decomposition found to occur in two stages. The loss of water of hydration initiated at ~65°C up to 160°C, followed by de-intercalation, decomposition of the organic compound and POH groups condensation. The thermal decomposition of the organic compound found to superimpose to that of the POH groups condensation. The weight loss was accompanied by endothermic broad peak centered at ~270°C. Total weight loss found to be 31.15%.

Fig. 6 shows TG /DTA of inclusion product, θ-Zr(HPO₄)₂ (ser)₀.₃₉·0.₅H₂O compound (III). The thermal decomposition found to be occurred in two stages. Compared with Fig. 5, the loss of water of hydration initiated at ~60°C up to 150°C and followed by de-intercalation, decomposition of the organic compound and POH groups condensation, this is mainly due to the POH groups condensation started at about 300°C. The thermal decomposition of the organic compound found to superimpose to that of the POH groups condensation. The weight loss was accompanied by two endothermic broad peak centered at 200, 300°C. Total weight loss found to be 16.45%.
which very similar to that of 0-\(\text{Zr(HPO}_4\text{)}_2\) (aspg)\textsubscript{0.54}. 1.63 H\textsubscript{2}O. Total weight loss found to be 50.07% which higher than that of 0-\(\text{Zr(HPO}_4\text{)}_2\) (aspg)\textsubscript{0.54}. 1.63 H\textsubscript{2}O and 0-\(\text{Zr(HPO}_4\text{)}_2\) (ser)\textsubscript{0.39-0.5}H\textsubscript{2}O.

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REFERENCES


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