

Synthesis and Thermal Behavior of Novel Pillared Θ -Type Zirconium Phosphate 1,10-Phenanthroline Zn(II), Cd(II), Cr(III), Fe(III) and La(III) Materials

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Abstract Θ -Type zirconium phosphate, $\text{Zr}(\text{HPO}_4)_2 \cdot 1.88\text{H}_2\text{O}$, was prepared and characterized. Reaction of 0.1M 1,10-phenanthroline in ethanol with Θ -type $\text{Zr}(\text{HPO}_4)_2 \cdot 1.88\text{H}_2\text{O}$, lead to the formation of Θ -type $\text{Zr}(\text{HPO}_4)_2 (\text{Phen})_{0.276} \cdot 0.5\text{H}_2\text{O}$. Novel pillared materials: Θ -Zr(H)_{1.1}(PO₄)₂(Phen)_{0.276}(Zn)_{0.45}1.1H₂O, Θ -Zr(H)_{1.95}(Phen)_{0.276}(PO₄)₂(Cd)_{0.051}1.1H₂O, Θ -Zr(H)_{0.5}(PO₄)₂(Phen)_{0.25}(Cr)_{0.5}0.45H₂O, Θ -Zr(H)_{0.8}(PO₄)₂(Phen)_{0.275}(Fe)_{0.4}1.43H₂O, Θ -Zr(H)_{0.82}(PO₄)₂(Phen)_{0.275}(La)_{0.39}1.3H₂O, were prepared and characterized by chemical, X-ray diffraction, thermal analysis and FT-IR spectroscopy. Their metal ions contents were determined. The pillared materials show the increase of their thermal stability which can be related to metal ions effect. These materials can be considered as new solid acid catalysts, inorganic ion exchangers and as ionic conductance materials.

Keywords Θ -Type Zirconium Phosphate, Pillared Θ - type Zirconium Phosphate - 1,10-phenanthroline

1. Introduction

Tetravalent metal phosphates are very insoluble compounds with good thermal stabilities and high ion exchange capacities[1,2]. The discovery of their crystalline materials[3,4], represent a fundamental step in chemistry of these compounds with general formula α -M(IV) (HPO₄)₂ H₂O, and γ -M(IV)PO₄H₂PO₄2H₂O, (where M = Ti, Zr, Hf, Ge, Sn, Ce). These materials contain structural POH groups with labile protons. They can exchange their protons with counter ions such as alkali, alkaline earth, transition divalent and trivalent metal ions[1-4] and act as intercalates[1,2 5,6]. Increase attention direct toward their intercalation[5,6], catalytic[7], electrical conductance[8], and sensors[9]. Layered zirconium phosphates have potential applications as inorganic fillers, sorbents and solid acid catalysts[14-16].

This class of compounds can bond themselves to pillaring reactions by metal amine complexes exchanged in their interlayer. Successful pillaring of these type of layered materials can accomplished via amine intercalation reaction [17-21]. They can form complex pillars between the layers as its formation in-situ by ion exchange of transition metal ions and ligand intercalation. As catalysts attracted attention recently and still in their infancy[22-24]. However, to date very little work on pillared materials of layered zirconium

and titanium phosphates. In our Laboratory we are carrying out systematic studies on novel lamellar M(IV) phosphates. Here we are reporting synthesis and thermal properties of novel of Θ -type zirconium phosphate 1,10-phenanthroline -Zn(II), Cd(II), Cr(III), Fe(III) and La(III) pillared materials.

2. Materials and Methods

Chemicals:

$\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, H_3PO_4 (85%), $\text{CdCl}_2 \cdot 6\text{H}_2\text{O}$, 1,10-Phenanthroline, HF, HCl (purchased from BDH), $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Cr}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$ (purchased from LTD), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (purchased from ERBA), NaOH, NaCl (T-Baker), $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (purchased from Riedel-de Haen) were used as received. Other reagents used were of analytical grade.

Instruments used for characterization

- X-ray powder Diffractometer PW/1710 Philips, using Ni-filtered CuK_α ($\lambda = 1.5405\text{\AA}$).
- Nexus 670 FT-IR Nicolet spectrophotometer.
- Derivatograph MOM-C Budapest, Hungary and Shimadzu TGA-60H TG/DTA.
- Atomic Absorption Spectrophotometer Alpha4 (SPEX).
- Perkin-Elmer 2400 automatic elemental analyzer
- pH Meter GW 521.

Preparation of Θ -type zirconium phosphate

50ml 0.5M $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ in 3M HF were mixed with 200ml of (4.6M) H_3PO_4 in Pyrex round bottom flask (prior to mixing, the solutions were cooled at $\sim 15^\circ\text{C}$). The mixture

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Published online at <http://journal.sapub.org/chemistry>

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was left at $\sim 15^{\circ}\text{C}$ for 3 days. The resultant precipitate was washed with distilled water, by addition and decantation of distilled water up to pH 3. The resultant product was filtered and dried in air for 72 hrs at room temperature $\sim 25^{\circ}\text{C}$.

Preparation of Θ -type zirconium phosphate-1,10-phenanthroline

110 ml of 0.1M 1,10 phenanthroline in ethanol were added to 1.5g Θ -type zirconium phosphate, $\text{Zr}(\text{HPO}_4)_2 \cdot 1.88\text{H}_2\text{O}$, with stirring at room temperature. After complete addition the stirring was continued for 5 days at room temperature and 5 hrs at 50°C . The resultant product was filtered, washed with ethanol and dried in air for 48 hrs.

Preparation of Θ -type zirconium phosphate-1,10-phenanthroline Zn(II)

To 100mg of Θ -type zirconium phosphate-1,10-phenanthroline, 3.5 ml of 0.05 M $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ in HNO_3 solution of pH 4 solution were added, followed by addition of 3.5 ml of distilled water with stirring at room temperature. The stirring continued for 24 hrs at room temperature ($\sim 25^{\circ}\text{C}$). The product was filtered, washed with distilled water, and dried in air for 48 hrs. The filtrate plus water washing were collected and diluted up to 100 ml.

Preparation of pillared Θ -type zirconium phosphate-1,10-phenanthroline Cd(II)

To 100mg of Θ -type zirconium phosphate-1,10-phenanthroline, 3.5 ml of 0.05M $\text{CdCl}_2 \cdot 6\text{H}_2\text{O}$ in HNO_3 solution of pH 4 solution were added, followed by addition of 3.5 ml of distilled water, with stirring, at room temperature. The stirring was continued for 24 hrs, at room temperature, the product was filtered washed with distilled water and dried in air for 48 hrs. The filtrate plus water washing were

collected and diluted up to 100 ml.

Preparation of pillared Θ -type zirconium phosphate-1,10-phenanthroline Cr(III)

To 100mg of Θ -type zirconium phosphate 6 ml of 0.05 M $\text{Cr}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$ in HNO_3 solution of pH 4 were added with stirring at room temperature. The stirring was continued for 24 hrs. The product was filtered washed with distilled water and dried in air for 48 hrs. The filtrate and water washing were collected and diluted up to 100 ml.

Preparation of pillared Θ -type zirconium phosphate-1,10-phenanthroline Fe(III)

To 100mg of Θ -type zirconium phosphate -1,10-phenanthroline 6 ml of 0.05 M $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in HNO_3 solution of pH 4 were added with stirring at room temperature. The stirring was continued for 24 hrs. The product was filtered washed with distilled water and dried in air for 48 hrs. The filtrate and water washing were collected and diluted to 100 ml.

The above mentioned filtrates plus water washing were kept for atomic absorption analysis for the remaining Zn^{2+} , Cd^{2+} , Cr^{3+} , Fe^{3+} metal ions.

Preparation of pillared Θ -type zirconium phosphate-1,10-phenanthroline La(III)

To 100mg Θ -type zirconium phosphate -1,10-phenanthroline, 6 ml of 0.05 M $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ in HNO_3 solution of pH 4 were added with stirring at room temperature. The stirring was continued for 24 hrs at room temperature. The product was filtered washed with distilled water and dried in air for 48 hrs. The filtrate and water washing were collected diluted to 100 ml. (kept for analysis of La^{3+} ions by EDTA method).

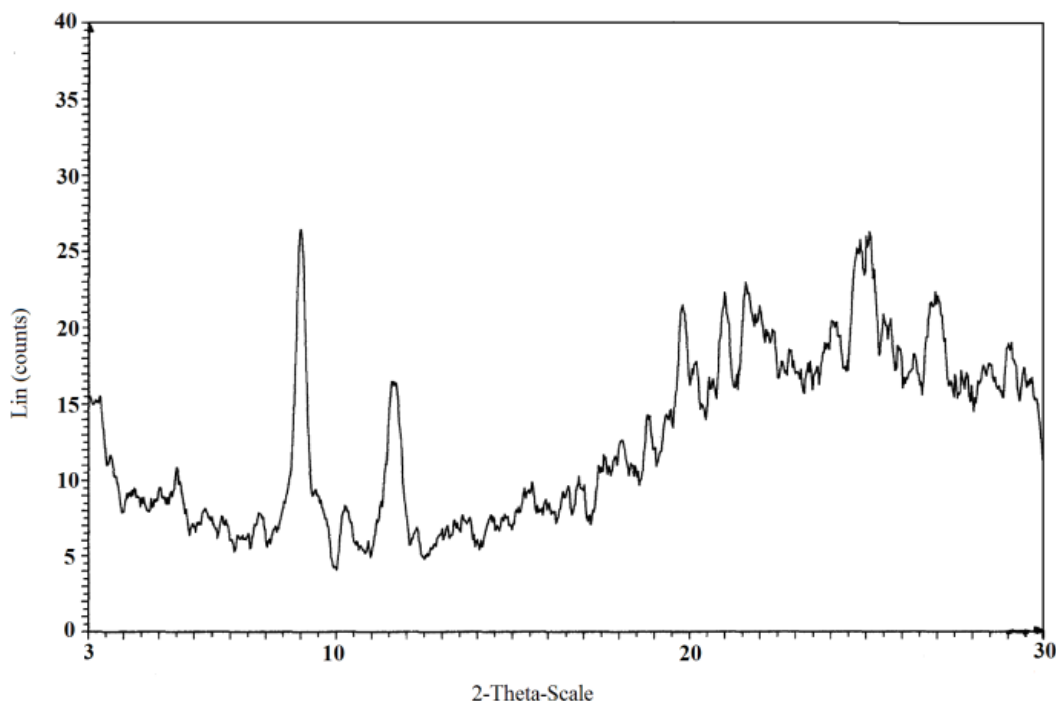


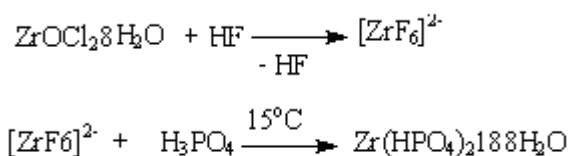
Figure 1. X-ray diffractogram of Θ -type $\text{Zr}(\text{HPO}_4)_2 \cdot 1.88\text{H}_2\text{O}$

Exchange capacity

Exchange capacity of Θ -type zirconium phosphate was determined by addition of 25 ml of 0.10 M NaCl solution to 100 mg of the material, with stirring for one hour and then titrated with 0.10 M NaOH solution.

3. Results and Discussions

Θ -Type zirconium phosphate, $\Theta\text{-Zr}(\text{HPO}_4)_2 \cdot 1.88\text{H}_2\text{O}$, was prepared from reaction of tetravalent zirconium salt and H_3PO_4 in HF solution. The reaction can be described as:



The resultant product was characterized by chemical, X-ray and thermal analysis and by FT-IR spectroscopy. Its exchange capacity was determined by Na^+ ions titration.

XRD

Figure 1 shows the X-ray powder diffraction pattern of the Θ -type zirconium phosphate, shows the presence of diffraction maxima with basal spacing equal 9.85 Å. The Θ -type materials exhibit lamellar structure. Negatively charged layers are formed by macroanions $[\text{M}_n(\text{IV})(\text{HPO}_4)_2]^{2-}$ and protons (H^+) bonded to the oxygen adjacent to the anionic layer form positively charged layers. The water molecules occupying crystallographic sites are located almost in the center of interlayer cavities.

FT-IR

FT-IR becomes a key tool to investigate structure of tetravalent metal phosphates [1,2,22].

Figure 2 Shows FT-IR spectrum of Θ -type zirconium phosphate in the range 4000-400 cm^{-1} wave number. The narrow bands at 3604.65, 3434.11 cm^{-1} and band at 1640.39 cm^{-1} are assigned to vibrational modes of H_2O molecules, suggest that water molecules are located at well defined crystallographic sites. These bands at 3434.11, 3434.11 cm^{-1} were also attributed to O-H asymmetric modes of interlayer water molecules. The band at 1640.39 cm^{-1} also corresponds to H-O-H bending modes. 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 H_2O interlayer molecules. The bands at the region 1273.21-1054.46 cm^{-1} are assigned as P-O asymmetry stretching of PO_4 groups, while a band at 976.33 cm^{-1} is characteristic to the bonding in plane of the (P-O) bond. The bands in the region 609.14 to 515.39 cm^{-1} ascribed to the presence of $\delta(\text{PO}_4)$ and to vibration of water molecules (609.14 cm^{-1}), while the band at 671.64 cm^{-1} is connected with O-H bond (out of plane). A tentative assignment of

various vibration modes is proposed based on previous works performed in other M(IV) phosphate compounds [1,2,22].

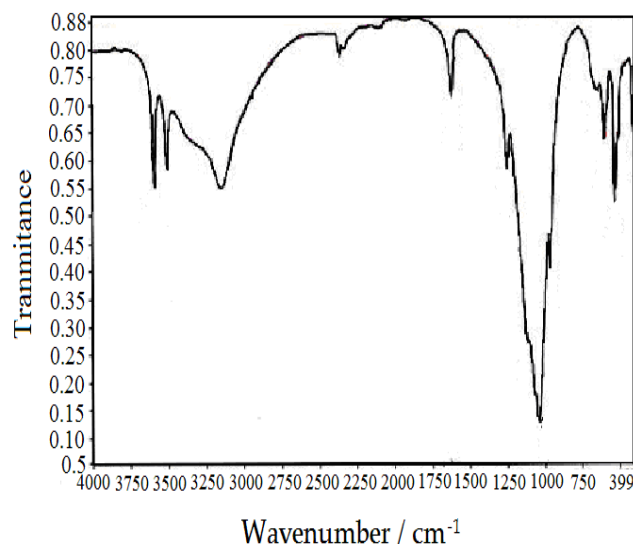


Figure 2. FT- IR-spectra of Θ -type $\text{Zr}(\text{HPO}_4)_2 \cdot 1.88\text{H}_2\text{O}$

Exchange capacity

Exchange capacity of Θ -type zirconium phosphate was determined by Na^+ ions titration. The titration curve is shown in Figure 3. The exchange capacity found to be equal to 6.2 Meq/g. The calculated value 6.01 Meq/g. The difference is due to partial hydrolysis of HPO_4^{2-} groups due to pH effect.

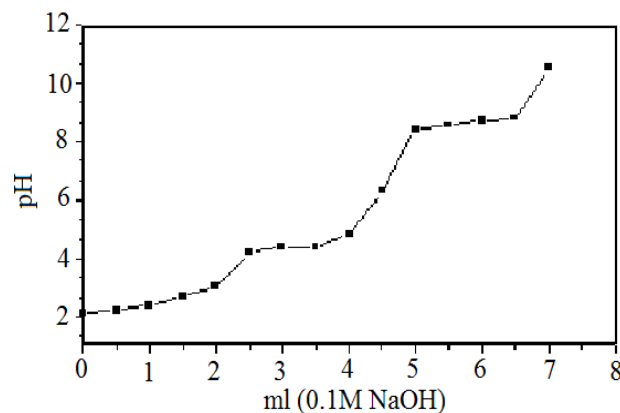


Figure 3. Na^+ ions titration curve of Θ - type of $\text{Zr}(\text{HPO}_4)_2 \cdot 1.88\text{H}_2\text{O}$.

TG/DTA Θ -Type zirconium phosphate

Thermal analysis of Θ -type $\text{Zr}(\text{HPO}_4)_2 \cdot 1.88\text{H}_2\text{O}$ is shown in Figure 4, was carried out at temperature range ~ 25 -800 $^\circ\text{C}$ in air atmosphere. The heating rate was 10 $^\circ\text{C}/\text{min}$. The thermal decomposition exhibits two weight loss stages, the loss of water of hydration followed by POH groups condensation. The final product was ZrP_2O_7 . The thermal decomposition found to follow the same trends of thermal decomposition of tetravalent metal phosphates [1-3,22]. The thermal decomposition was accompanied by endothermic peaks.

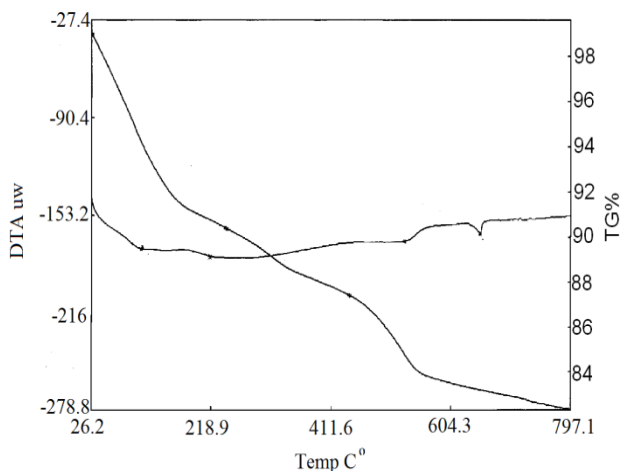


Figure 4. TG/DTA of Θ-type of $\text{Zr}(\text{HPO}_4)_2 \cdot 1.88\text{H}_2\text{O}$

TG/DTA of Θ-Type zirconium phosphate- 1,10-phenanthroline

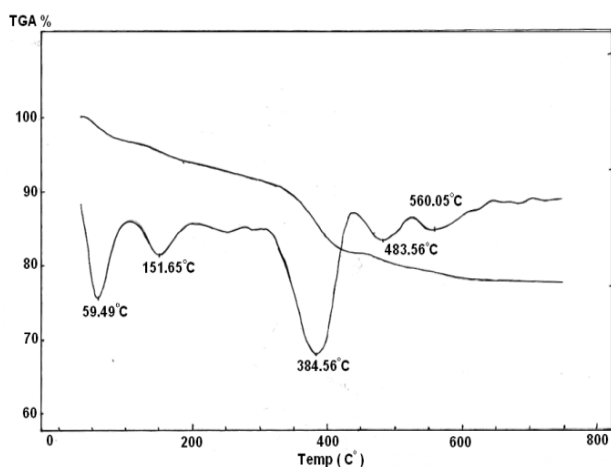
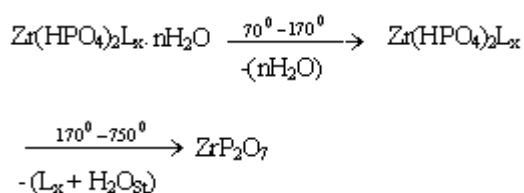


Figure 5. TGA/DTA of Θ-Type $\text{Zr}(\text{HPO}_4)_2(\text{Phen})_{0.276} \cdot 0.5\text{H}_2\text{O}$

Figure 5 shows the thermogram of the intercalated material $\text{Zr}(\text{HPO}_4)_2(\text{Phen})_{0.276} \cdot 0.5\text{H}_2\text{O}$. Its thermal decomposition occurs mainly in five stages. The first and second stages are concerned with the loss of water of hydration that occurred between ~ 40 - 170°C , followed by melting of the organic ligand, its decomposition and P-OH groups condensation up to 700°C . The total % weight loss found to be equal to 22.47%. The % of the intercalated 1,10-phenanthroline found to be 14.57%, which was found to be in agreement of the summation of its C,H,N elemental contents. The final product was ZrP_2O_7 . The decomposition accompanied by endothermic peaks, The thermal decomposition represented by the following scheme:

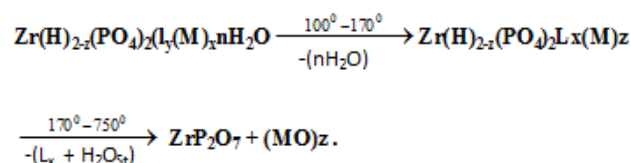


where $n\text{H}_2\text{O}$ = water of hydration, L = ,1,10-phenanthroline
x = loading of the organic base, $\text{H}_2\text{O}_{\text{St}}$ = the structural water

results from POH groups condensation. The thermal behavior of the materials found to follow the same trend of that observed for inclusion products of layered tetravalent metal phosphates[6,7,23,24]. The thermal decomposition of the organic ligand found to super imposed with POH groups condensation .

Thermal decomposition of pillared materials

The thermal decomposition of the inclusion product can be described as follows :



where $n\text{H}_2\text{O}$ = water of hydration, L = ,1,10-phenanthroline
x = loading of the organic base, $\text{H}_2\text{O}_{\text{St}}$ = the structural water results from POH groups condensation, M the mtalion equivalen. The thermal behavior of the materials found to follow the same trend of that observed for pillared materials of layered tetravalent metal phosphates[6,7,23,24]. The thermal decomposition of the organic ligand found to superimpose with POH groups condensation and the oxidation of the metal ions.

TG/DTA of pillared Θ-Type zirconium phosphate -1,10-phenanthroline Zn(II)

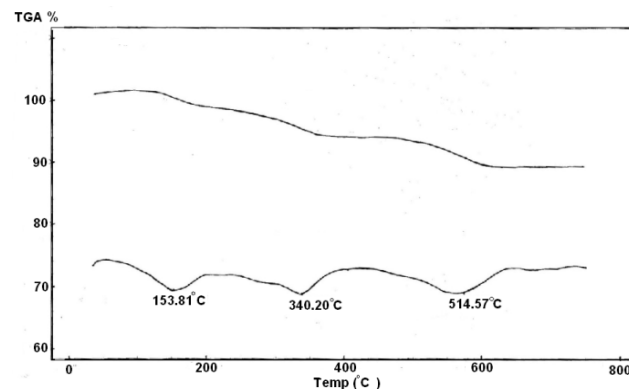


Figure 6. TGA/DTA of Θ-type $\text{Zr}(\text{H})_{1.1}(\text{PO}_4)_2(\text{Phen})_{0.276}(\text{Zn})_{0.45} \cdot 1.1\text{H}_2\text{O}$

Thermogram of pillared compound $\text{Zr}(\text{H})_{1.1}(\text{PO}_4)_2(\text{Phen})_{0.276}(\text{Zn})_{0.45} \cdot 1.1\text{H}_2\text{O}$ is shown in Figure 6. The thermal decomposition occurs in four stages The first two stages are concerned with the loss of water of hydration up to 200°C . The third and fourth stage are concerned with melting decomposition of the organic ligand and POH groups condensation. The final products were $\text{ZrP}_2\text{O}_7 + (\text{ZnO})_{0.45}$. The total % weight loss found to be equal to 21.534%.

Elemental (C,H,N) analysis related to 1,10-phenanthroline found, C=11.79, H =0.65, N=2.28 of total 14.72%. Its calculated value from TGA analysis was 13.72%. So the TGA can be easily correlate for 1,10-phenanthroline % contents , due to TGA is a good tool for formulation of such type of pillared materials[6,7,24]. The thermal decomposition of the pillared material was

accompanied by endothermic peaks at 59.89, 153.81, 340.20 and 514.5°C .

TG/DTA of pillared Θ -type zirconium phosphate 1,10-phenanthroline Cd(II)

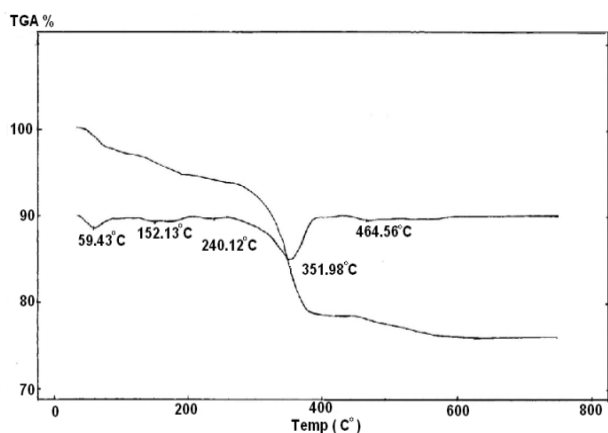


Figure 7. TGA/DTA of Θ -type $\text{Zr(H)}_{1.95}(\text{PO}_4)_2(\text{Phen})_{0.276}(\text{Cd})_{0.051} \cdot 1.1\text{H}_2\text{O}$

Figure 7 shows the thermogram of Θ - $\text{Zr(H)}_{1.95}(\text{PO}_4)_2(\text{Phen})_{0.276}(\text{Cd})_{0.051} \cdot 1.1\text{H}_2\text{O}$. The thermal decomposition found to occur in four stages. The first two stages concern with the loss of water of hydration up to 200°C, with two endothermic peak at 59.43 and 152.23°C, followed by melting decomposition of the organic ligand and P-OH groups condensation. The final products were $\text{ZrP}_2\text{O}_7 + (\text{CdO})_{0.051}$. the total weight loss found to be equal to 24.42%. The calculated value from TGA analysis for 1,10- phenanthroline found to be equal to 13.86% which was found to be in agreement with the summation of its C,H,N elemental contents.

TG/DTA of pillared Θ -type zirconium phosphate -1,10-phenanthroline Cr(III)

Figure 8 shows its thermogram of $\text{Zr(H)}_{0.5}(\text{PO}_4)_2(\text{Phen})_{0.25}(\text{Cr})_{0.5} \cdot 0.45\text{H}_2\text{O}$. The thermal decomposition found to occur in four stages, water of hydration loss occurs between 65-180°C, followed by melting decomposition of the organic ligand and POH groups condensation. The thermal decomposition was accompanied by endothermic peaks at 59.89, 152.13, 240.12, 351.98 and 464.56°C, with weight loss. The total weight % loss found to be equal 15.144%. The final products were $\text{ZrP}_2\text{O}_7 + \text{Cr}_{0.5}\text{O}_{0.75}$. Elemental (C,H,N) analysis related to 1,10-phenanthroline found, C=10.0, H = 0.55 and N = 2.1 with total % = 12.6%. The calculated value from TGA analysis for 1,10-phenanthroline found to be equal to 12.37 %. The thermal decomposition of the resulted pillared material was accompanied by endothermic peaks at 60.50, 181.83, 300, 340, 419.82 and 579.81°C, were accompanied by weight loss.

TG/DTA of pillared Θ -Type zirconium phosphate-1,10-phenanthroline Fe(III)

Thermogram of pillared $\text{Zr(H)}_{0.8}(\text{PO}_4)_2(\text{Phen})_{0.275}(\text{Fe})_{0.4} \cdot 1.43\text{H}_2\text{O}$ is show in Figure 9. The thermal decomposition occurs mainly in four stages. The first two stages are concerned with water hydration loss up to 200°C, followed by organic ligand melting , decomposition and POH groups condensation up to 700°C. The final products were $\text{ZrP}_2\text{O}_7 + \text{Fe}_{0.4}\text{O}_{0.6}$. The total weight loss found to be equal to 23.393%. The thermal decomposition found to be accompanied with endothermic peaks at 56, 177.22, 343.06, 411.49, 482 and 603.61°C.

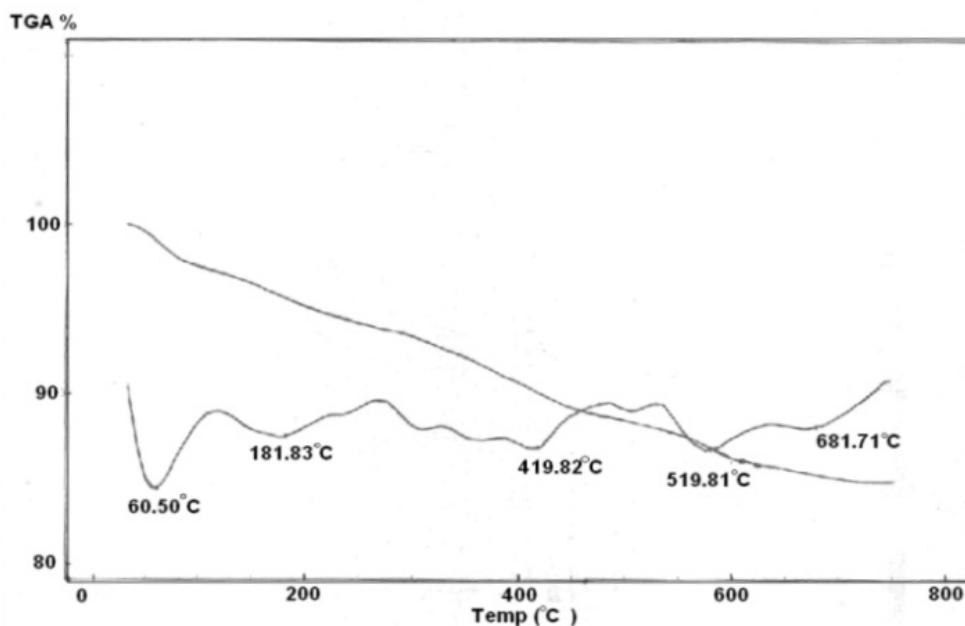


Figure 8. Figure 8 :TGA/DTA of Θ -type $\text{Zr(H)}_{0.5}(\text{PO}_4)_2(\text{Phen})_{0.25}(\text{Cr})_{0.5} \cdot 0.45\text{H}_2\text{O}$

TG/DTA of pillared Θ -type zirconium phosphate -1,10-phenanthroline La(III)

Figure 10 shows the thermogram of Θ -Zr(H)_{0.82}(PO₄)₂(Phen)_{0.275}(La)_{0.39}.1.3H₂O. The thermal decomposition found occur in four stages. The first two stages are concerned with the loss of water of hydration up to 200°C, followed by melting, decomposition of the organic ligand. The final products were ZrP₂O₇ + La_{0.39}O_{0.585}. The total weight loss found to be equal to 27.02%. The calculated value from TGA analysis for 1,10-phenanthroline found to be equal to 14.91% which was found to be in agreement with the summation of its C,H,N elemental contents. As expected, the thermal decomposition of the organic ligand found to superimpose with POH groups condensation and the oxidation of the metal ions.

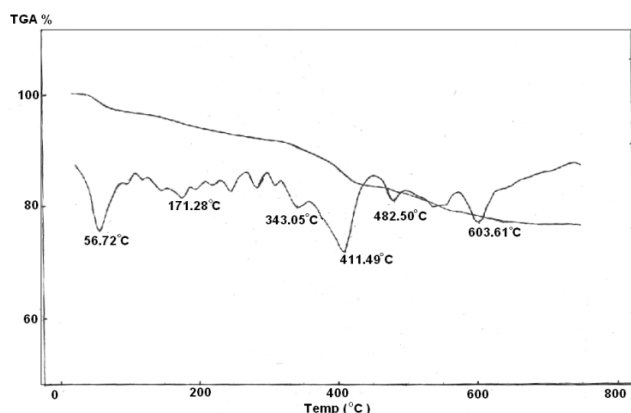


Figure 9. TGA/TDA of Θ -Zr(H)_{0.8}(PO₄)₂(Phen)_{0.275}(Fe)_{0.4}.1.43H₂O

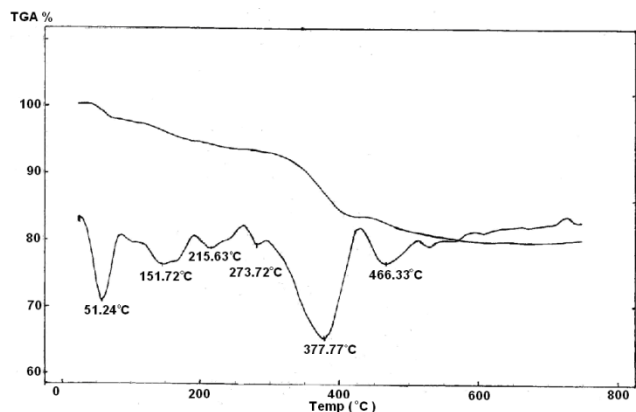


Figure 10. TGA/TDA of Θ -Zr(H)_{0.82}(PO₄)₂(Phen)_{0.275}(La)_{0.39}.1.3H₂O

The thermal decomposition of Θ -type zirconium phosphate -1,10-phenanthroline and its pillared materials were accompanied with endothermic peaks (figures 5-10).

Pillared Θ -Type zirconium phosphate-1,10-phenanthroline and their Zn(II), Cd(II), Cr(III), Fe(III) and La(III) compounds are complexes formed "in-situ", have been chosen because of their possible applications as solid acid catalysts.

C,H,N data, which are related to 1,10-phenanthroline of Θ -type zirconium phosphate-1,10-phenanthroline intercalated product and its pillared materials, found to

correlate with their thermal analysis. It was found, that the intercalation of the organic ligand does not alter the symmetry of the phosphate groups and does not change all the acidic sites of the host layers, that is due to "cover effect".

The resultant materials were formulated according to elemental (C,H,N) analysis, thermal analysis and their metal ions uptake.

4. Conclusions

This study shows that Θ -zirconium phosphates can be obtained by direct precipitation method, the HF method. The formulation of the investigated pillared Θ -zirconium phosphate is based on a fact that M(IV) phosphates are stable materials and extremely insoluble. The final products from thermal treatment are the pyrophosphates and metal oxides. The pillars formed or when the Θ -zirconium phosphates were used as ion exchangers and intercalate material, i.e. in its counter ions adsorbed forms. The loading of the organic ligand found to be quite low from the direct intercalation of 1,10-phenanthroline, this is due to covering effect. The pillared materials show the increase of their thermal stability which can be related to metal ions effect. These materials can be considered as new solid acid catalysts, inorganic ion exchangers and as ionic conductance materials.

ACKNOWLEDGEMENTS

To Departments of Chemistry, Faculty of Sciences, Tripoli University and Sebha University for providing research facilities, to microanalysis centre of Cairo University for elemental and TGA analysis.

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