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Studies on the Uptake of Some lanthanide Metal Ions on 1, 10-Phenanthroloine, and 4, 4-Bipyridine Intercalated Products of Zirconium Phosphate by Radio Tracer Technique

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Abstract: Crystalline α -zirconium phosphate, α -Zr(HPO₄)₂.H₂O, was prepared via HF-method. Its metastable alcohol form, α -Zr(HPO₄)₂.2C₂H₅OH, was prepared and subjected to intercalate with 1,10-Phenanthroloine, and 4,4⁻-Bipyridine to give well defined composites α -Zr(HPO₄)₂ (Phen)_{0.5}.2H₂O , α -Zr(HPO₄)₂ (4,4⁻-Bipy)_{0.35}.1.2H₂O, respectively. Uptake of metal ions La³⁺, Sm³⁺, Eu³⁺, Gd³⁺ and Yb³⁺ on the resultant 1,10-phenanthroline and 4,4⁻-bipyridine intercalated products was investigated by radio tracer technique in HNO₃ solution of pH1, and pH4. The radio tracers used were ¹⁴⁰La, ¹⁵³Sm, ^{152m}Eu, ¹⁵⁹Gd and ¹⁷⁵Yb. The selectivity order (Kd values) at pH4 found to be for: (i) α -Zr(HPO₄)₂ (4,4⁻-Bipy)_{0.35}.1.2H₂O; Eu(2936) > Sm (2660) > La(2185) > Yb(2072) > Gd(1782). The Kd values at pH1 found to be quite low, less than12 for the resultant intercalated products. The cation exchange of the lanthanide metal ions occurs with the residual protons in POH groups. However, we cannot rule the possibility of some complex formation of lanthanide metal ions with intercalated materials.

Keywords: Uptake of lanthanides; Zirconium phosphate; 1,10-phenanthroloin; 4,4- - bipyridine intercalated products; Radiotracer.

1. Introduction

Two dimentional (2D) Layered tetravalent metal phosphates with general formula α -M^{IV} (HPO₄)₂.H₂O (where M = Ti, Zr, Hf, Ge, Sn) have been known for sometime. The most extensively studies were on α -zirconium phosphate [1].

The structure of alpha zirconium phosphate, α -Zr(HPO₄)₂.H₂O, was solved using single-crystal methods [2]. Its interlayer distance found to be 7.6 Å. The structures of layered α -type compounds of tetravalent metal phosphates were shown to be iso-structure with α -Zr(HPO₄)₂.H₂O.

Alpha zirconium phosphate, α -Zr(HPO₄)₂.H₂O, is insoluble inorganic ionexchanger [3], proton conductor [4], exhibit good thermal stability, [3, 5], eco-friendly [1], solid acid catalyst [6, 7], possess intercalating properties so that various kinds of polar organic molecules can be accommodate in the interlayer region giving a great variety of compounds in which the guests are bound to inorganic host with a strength depending on the nature of the organic molecule, ionic intercalation for alkyl and aryl amines weak bonds for alcohols and glycols [5, 7-10].

The intercalation of organic ligands and their coordination compound in layered inorganic materials present promising field of investigation and often offer an interesting way of preparing a great variety of composite materials [5, 11].

It was reported [11] that diimines such as 1,10-phenanthroline and 2,2⁻-bipyridine can be inserted between the layers of preswelling alpha zirconium phosphate, giving well ordered non-stoichiometric organic-inorganc composites with an expand of interlayer spacing of α -Zr(HPO₄)₂ (Phen)_{0.5}.2H₂O and α -Zr(HPO₄)₂ (2,2⁻-Bipy)_{0.25}.1.5H₂O, with interlayer space of !3.5Å,10.9Å, respectively [6, 11]. Their finding indicate that the 1,10-phenanthrolie is almost vertical, while 2,2⁻-bipyridine is somewhat sidewise slanted.

Transition metal ions such as Ni(II), Cu(II), Pd(II), Pt(II), Rh(II)..etc., inserted into such type organic-inorganic composites by ion exchange can be subsequently coordinate to the ligand throughout of the layers. The process occurring general with further expansion of the interlayer distance to allow an optimum orientation of the complex

formed in-situ [12, 13], various compounds were obtained which were characterized by chemical, and thermal analysis ,x-ray diffraction patterns, to obtain evaluation of host-guest interaction for such type of composites [5, 13].

Present paper describes the results of intercalation of 1,10-phenanthroline and 4,4⁻-bipyridine into the metastable alcohol form α -Zr(HPO₄)₂.2C₂H₅OH to give well defined composites α -Zr(HPO₄)₂ (Phen)_{0.5}.2H₂O and α -Zr(HPO₄)₂ (4,4⁻-Bipy)_{0.35}.1.2H₂O, respectively. We extend this study on the uptake of some lanthanide metal ions, La³⁺, Sm³⁺, Eu³⁺, Gd³⁺ and Yb³⁺, on the above intercalated composites which was investigated by radio tracer technique.

2. Materials and Methods

2.1. Chemicals

 $ZrOCl_2.8H_2O$, of Merck, HF 40%, H₃PO₄,(85%) of Reidel Dehaein, 1,10-phenanthroline and 4,4⁻- bipyridine of BDH, Nitrates of La(III) , Sm(III) , Eu(III) , Yb(III) and Gd(III) were of (Sigma Co). Other chemical used were of analytical grade.

2.2. Preparation of α-Zr(HPO₄)₂.H₂O

Crystalline layered alpha zirconium phosphate was synthesized by the HF-method according to method reported [14], in which zirconium fluoro complex ($0.5M ZrOCl_2.8H_2O$ in 3MHF) was reacted with $6M H_3PO_4$ in plastic container that was heated at $60-70^{\circ}C$ for a period of one week, keeping the volume constant by addition of distilled water when necessary. The resultant precipitate was filtered washed with distilled water up to pH3, and left to dry in air.

2.3. Preparation of Metastable Alcohol Form A-Zr(HPO₄)₂.2C₂H₅OH

Meta stable alcohol form α -Zr(HPO₄)₂.2C₂H₅OH, was prepared by treating monosodium form α -Zr(NaPO₄)(HPO₄).5 H₂O with ethanol-1% HCLO₄ solution , according to method reported [8, 11].

2.4. Intercalation of 1, 10-Phenanthroline And 4,4⁻ Bipyridine

The diimines 1,10-phenanthroline and 4,4⁻-bipyridine, were used as guest molecules. In Elmeyer flask 0.1M of each of the diimine in ethanol-water solution (1:1) were contacted, separately, with α -Zr(HPO₄)₂.2C₂H₅OH of molar ratio 3 to 1, respectively, with stirring at room temperature for 5 days. The resultant compounds were filtered, washed with absolute ethanol.

2.5. The Equilibration Experiments

0.1g of each of diimines intercalated product was placed in polyethylene bottle (vol.25cm³), soaked in 7.5ml HNO₃ solution of the desired pH. Aliquots of 500 μ L (4x10⁻⁵ mmole) from each tracer were mixed in separate vail, then added to each Diimines intercalated product. The polyethylene bottles were shaken for 24hrs, followed by centrifugation at 2000 rpm for 15min. The supernatant were collected in another bottles and counted on a high pure Ge-deterctor coupled into a computer software package system(Sileina) through analog to digital(A/D) data acquisition and spectral analysis. The radiotracers used were ¹⁴⁰La(ti_{1/2}=40.1 hrs), ¹⁵³Sm(ti_{1/2}=47.1 hrs), ^{152m}Eu(ti_{1/2}=9.35 hrs) , ¹⁵⁹Gd(ti_{1/2}=18.48 hrs) and ¹⁷⁵Yb(ti_{1/2}=10.1 hrs), which were prepared daily at facilities of Tajura research center for irradiating required concentrations of the high purity nitrates of these elements(Sigma Co) with neutrons.

The Kd value of each lanthanide metal ions results from equilibration of diimines intercalated products at pH1 and pH4 were calculated according to equation :

$$Kd = A_{st} - A_{sol}/A_{sol} \times 100$$

Where A_{st} represent the radio activity of the standard solution containing the radiotracers and A_{sol} is the radioactivity of the solution which equilibrated with α -Zr(HPO₄)₂ (Phen)_{0.5} .2H₂O, α -Zr(HPO₄)₂ (4,4⁻-Bipy)_{0.35} .1.2H₂O, respectively.

2.6. Instruments Used for Characterization

X-Ray powder diffractometer Siemens D-500, using Ni-filtered CuK α (λ = 1.54056Å), Drivatograph MOM-C type thermobalance , Budapest, Hungary, Fourier Transform IR spectrometer, model IFS 25 FT-IR, Bruker, pH Meter WGW 52.

3. Results and Discussion

Crystalline α -zirconium phosphate, α -Zr(HPO₄)₂.H₂O(α -ZrP), was prepared and characterized by chemical, x-ray, thermal analysis and by FT-IR spectroscopy.

3.1. XRD of a-ZrP

Figure 1 shows the x-ray powder diffraction pattern of the of α -Zr(HPO₄)₂.H₂O, shows presence of diffraction maxima with basal spacing equal 7.6 Å. It exhibit lamellar structure. Negatively charged layers are formed by macroanions [Zr(HPO₄)_{2n}]⁻²ⁿ 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.



Figure-1. XRD of α -Zr(HPO₄)₂.H₂O.

3.2. FT-IR of a-ZrP

FT-IR become a key tool to investigate structure of tetravalent metal phosphates [15]. Figure 2 shows FT-IR spectrum of α -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 H₂O 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 an 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 H₂O interlayer molecules. The bands at the region 1273.21-1054.46 cm⁻¹ are assigned as P-O asymmetry stretching of PO₄ 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 - 515.39 cm⁻¹ ascribed to the presence of δ (PO₄) 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 preformed in other M(IV) phosphate compounds [5, 14-16].



3.3. TGA of a-ZrP

Thermal analysis of α -zirconium phosphate, Zr(HPO₄)₂.H₂O, is shown in Figure 3, was carried out at temperature range ~20-800C°, 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 final product was ZrP₂O₇.



Metastable alcohol form, α -Zr(HPO₄)₂.2C₂H₅OH was prepared, then subjected to intercalation with 1,10phenanthroloine, and 4.4⁻-bipyridine to give well defined composites α -Zr(HPO₄)₂ (Phen)_{0.5}.2H₂O, α -Zr(HPO₄)₂ (4,4⁻) -Bipy)_{0.35}.1.2 H₂O, respectively.

Thermogravimetric analysis found to be a good tool for characterization of TVMP and their intercalated products. It was utilized as a tool for characterization of zirconium phosphate, mixed zirconium-titanium phosphates -1.10-phenanthroline-, 2,2-bipyridyne intercalated materials [11]. Accordingly well defined composites α - $Zr(HPO_4)_2$ (Phen)_{0.5}.2H₂O, α -Zr(HPO₄)₂ (4,4⁻-Bipy)_{0.35}.1.2H₂O, respectively, were obtained.

3.4. Uptake of Metal ions La³⁺, Sm³⁺, Eu³⁺, Gd³⁺ and Yb³⁺ Uptake of metal ions La³⁺, Sm³⁺, Eu³⁺, Gd³⁺ and Yb³⁺ on the resultant 1,10-phenanthroline and 4,4⁻ -bipyridine intercalated products was investigated by radio tracer technique in HNO₃ solution of pH1, and pH4. Selectivity order (Kd values) at pH4 were found to be for:

(i) α -Zr(HPO₄)₂ (Phen)_{0.5}.2H₂O, were La(16135) > Yb (13600) > Eu(12300) > Sm(9987) > Gd(5510).

(ii) α -Zr(HPO₄)₂(4,4⁻-Bipy)_{0.35}.1.56H₂O, were Eu(2936) > Sm (2660) > La(2185) > Yb(2072) > Gd(1782).

The Kd values for metal ions at pH1 found to be quite low, less than12 for the resultant intercalated products. The cation exchange of the lanthanide metal ions occurs with the residual protons in POH groups. However, we cannot ruleout the possibility of some complex formation between the metal ions with intercalated products [13].

4. Conclusion

Crystalline α-zirconium phosphate, α-Zr(HPO₄)₂.H₂O and its intercalated products α-Zr(HPO₄)₂ (Phen)_{0.5}.2H₂O , α -Zr(HPO₄)₂ (4,4⁻-Bipy)_{0.35}.1.2H₂O, were prepared and characterized. Uptake of metal ions La³⁺, Sm³⁺, Eu³⁺, Gd³⁺ and Yb³⁺ on the resultant 1,10-phenanthroline and 4,4⁻ -bipyridine intercalated products were investigated by radio tracer technique. Based on the selectivity order(Kdvalues) for each metal ions, it is clear that highest uptakes were achieved for α -Zr(HPO₄)₂ (Phen)_{0.5}, 2H₂O. The lower Kd values at pH 1 (about 12) can be attributed to reprotonation effect, which ends with the release of the lanthanide metal ions that have been exchanged with the residual protons in POH groups. However, we cannot ruleout the possibility of some complex formation of lanthanide metal ions with intercalated materials.

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