

CHAPTER I

INTRODUCTION

1.1 Background and Rationales of Study

Phosphorus has been called “the key to life” because it is directly involved in most life processes. Phosphorus is second only to nitrogen in frequency of use as a fertilizer element. Phosphorus occurs in the soil in both mineral and organic forms. Three different phosphorus ions H_2PO_4^- , HPO_4^{2-} , or PO_4^{3-} are found in the soil.^[1] The predominance of one or another of these forms in solution depends largely on pH, as illustrated in Figure 1.1.

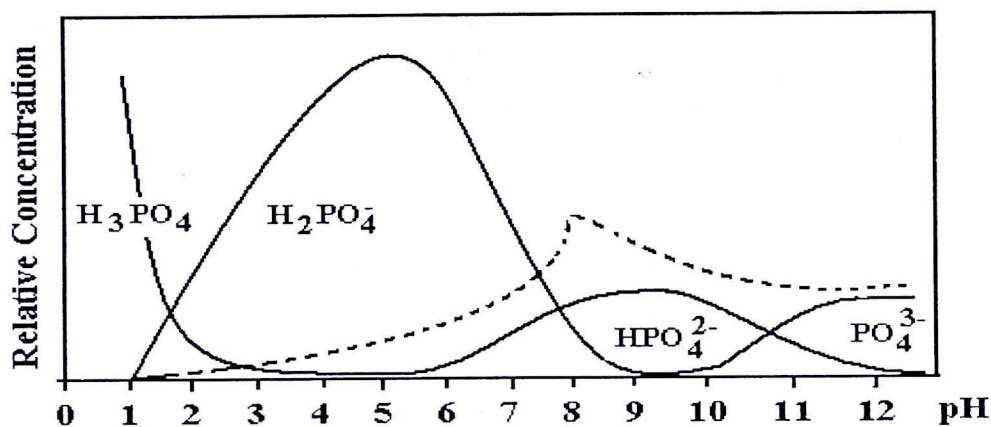


Figure 1.1 A schematic illustration of relative proportions of phosphate ions in solution at different pH levels in a $\text{Ca} - \text{H}_3\text{PO}_4$ system. The dashed line shows the upper limit on available P in solution imposed by the solubility of calcium phosphates above pH 6.5 or of iron and aluminum phosphates below pH 6.5 [1].

Most of the phosphorus absorbed by plants is in the monovalent orthophosphate form, H_2PO_4^- . Some HPO_4^{2-} may be used or even required by some plants, but the H_2PO_4^- is the one most readily absorbed by plants. Phosphorus availability varies with solubility, amount of water present, and the phosphate ion must move to reach the plant root to be absorbed. The solubility of phosphorus ions depend greatly on pH because pH influences both the kind of phosphorus ion present

and the concentrations of precipitating ions. When soil pH falls below 5.8, phosphorus reacts with iron to produce an insoluble iron compound. Above pH 6.0, the reaction tends to reverse to free phosphorus [1].

Metal phosphates are of considerable industrial interesting properties nowadays because of their wide applications in laser host, ceramic, dielectric, electric, magnetic, and catalytic processes. Additionally, metal phosphates are among the widest spread minerals in the class of phosphates. Thermal treatment of metal phosphates has a great synthetic potential as it may turn simple compound into advanced materials, such as ceramic, catalysts, dye pigments and glasses [1].

Layered acid phosphates are of continuing academic and industrial interest because of their extensive use as heterogeneous catalyst. Some of them can undergo ion exchange and reversible hydration in the same way as zeolite. The interlayer species are water [2,3], ethanol, and ethylene glycol [4]. The water of crystallization can undergo reversible dehydration-rehydration provided that it is not heated beyond 200 °C. Among several metal phosphates with open architectures that have been synthesized and characterized, the family of zinc phosphate appears to be extensive studied. This is not surprising, considering that the zinc phosphates are associated with the same total charge as the aluminosilicates zeolite. This open-framework phosphate has channels along all the crystallographic directions with the disordered cations, those are located in these channels [5]. The widespread applications of inorganic microporous materials with open-framework structures in heterogeneous catalyses, separations and ion exchange processes have stimulated considerable research interest in using organic templates to direct the synthesis of porous materials. Since the first synthesis of microporous aluminophosphate molecular sieve in 1982, a great deal of attention has been paid to synthesize openframework metal phosphate materials [6]. Among the vast family of open-framework metal phosphate materials, bivalent including the transition metal phosphates such as $\text{MHPO}_4 \cdot \text{H}_2\text{O}$ ($\text{M} = \text{Zn}, \text{Co}, \text{Ni}$) constitute an important group. Especially, cobalt can easily exhibit tetrahedral in addition to five- and six-coordination. Cobalt doping will give rise to interesting magnetic properties and enhance the catalytic performance [7]. The subunit of $\text{MHPO}_4 \cdot \text{H}_2\text{O}$ and structure of ring layer of the $\text{MHPO}_4 \cdot \text{H}_2\text{O}$ illustrated in the figure 1.2

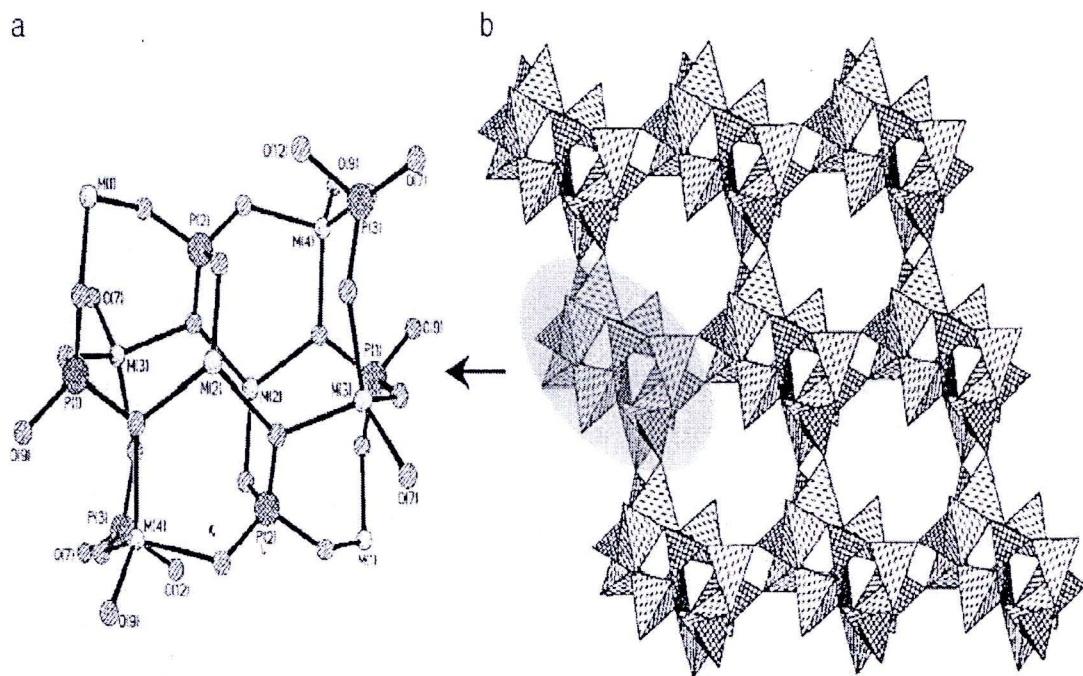


Figure 1.2 The subunit of $\text{MHPO}_4 \cdot \text{H}_2\text{O}$ (a) and structure of the ring layers of $\text{MHPO}_4 \cdot \text{H}_2\text{O}$ ($\text{M} = \text{Zn}, \text{Co}, \text{Ni}$) viewing down the c -axis direction (b).

Amorphous metal phosphate hydrates, $\text{M}^{\text{I}}\text{M}^{\text{II}}\text{PO}_4 \cdot n\text{H}_2\text{O}$ ($\text{M}^{\text{I}} = \text{alkali}$, $\text{M}^{\text{II}} = \text{transition metals}$) form a wide family of compounds showing interesting properties of high potential to use as catalysts for selective oxidation reaction, being particularly effective for oxidative dehydrogenation [8]. Transition metal phosphates of type LiMPO_4 ($\text{M} = \text{Fe}, \text{Mn}, \text{Co}, \text{Ni}$) with an olivine structure have attracted considerable attention as cathode materials for rechargeable lithium-ion batteries [9]. These materials are excellent for their cycleability, thermal stability, low-cost, and environmental friendliness [10]. LiMPO_4 has a highly stable three-dimensional framework due to strong P-O covalent bonds in $(\text{PO}_4)^{3-}$ polyanion, which prohibits the liberation of oxygen.

The acid inorganic salts, such as hydrogen phosphates, arsenates, sulphates, selenates, etc. are known to possess optical, electrical and magnetic properties of practical importance, which are determined by the presence of very strong hydrogen bonds in their crystal lattices. Among the acid phosphates the well-known compounds of the $\text{MH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ series ($\text{M} = \text{Co}, \text{Mn},$) have been subject of numerous

investigations because of interesting ferro- and antiferroelectric phase transitions, which occur at different temperatures [11-14].

In laboratory, metal phosphate hydrates have been synthesized by various methods such as hydrothermal, soft chemical, sol-gel, solid-state reaction, aqueous solution precipitation, co-precipitation, and mechanical alloying methods.

The scope of this work will focus on the intermolecular interactions, especially hydrogen bonding in hydrates of $\text{ZnHPO}_4 \cdot \text{H}_2\text{O}$, $\text{Co}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$, $\text{Li}_2\text{Zn}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ and $\text{M}^{\text{I}}\text{M}^{\text{II}}\text{PO}_4 \cdot n\text{H}_2\text{O}$ ($\text{M}^{\text{I}} = \text{Li}$, $\text{M}^{\text{II}} = \text{Fe, Mn, Co, Ni}$) by vibrational spectroscopy (FTIR, FT Raman). The study on thermal decomposition kinetics in terms of the calculation of activation energy of some selected hydrates will be included.

1.2 Objective of the Research

1.2.1 To prepare some single and binary metal phosphate hydrates ($\text{M}^{\text{I}}\text{M}^{\text{II}}\text{PO}_4 \cdot n\text{H}_2\text{O}$, $\text{M}^{\text{I}} = \text{Li}$, $\text{M}^{\text{II}} = \text{Fe, Mn, Co, Ni, Zn}$). Their vibrational spectra (FT-IR and FT-Raman) will be recorded and assigned.

1.2.2 To study the intermolecular interactions of synthesized samples by using vibrational spectroscopy (FT-IR and FT-Raman).

1.2.3 To confirm the hydrate formula by using atomic absorption spectrophotometry (AAS) and atomic emission spectrophotometry (AES) for metal content and by thermal analysis (TG/DTG/DTA), and Karl Fischer method for water content.

1.2.4 To study the thermal decomposition kinetics of some selected hydrates.

1.2.5 Deuterated analogues of hydrates in 1.2.1 will be synthesized and their vibrational spectra will also be recorded and assigned in the same manner as in 1.2.2.

1.2.6 To study the kinetics of dehydration and rehydration processes of some selected hydrates.

1.3 Scope of Study

1.3.1 Preparation of selected hydrates according to the previously reported methods or the modified methods for a better condition.

1.3.2 Confirmation of the water content in the hydrate formula of synthesized hydrates by thermo gravimetric (TG/DTA) and Karl Fischer method, whereas the metal content is confirmed by AAS and AES methods.

1.3.3 The crystal structure of the resulting powder and calcined products will be determined by XRD.

1.3.4 The thermal decomposition of some selected hydrates will be studied by DSC and TG/DTG/DTA methods.

1.3.5 Interpretation and bands assignment of vibrational spectra based on changes in H_2O and anion vibrational modes will be carried out using factor group analysis in relation to the intermolecular interactions (water-water, ion-water).

1.3.6 The study of thermal decomposition kinetics of synthesized hydrates will lead to the calculated kinetic parameter (E_a ; activation energy).

1.3.7 The study of dehydration and rehydration processes of synthesized samples.

1.4 Research Expectation

The following information is expected to be enriched:

1.4.1 To understand the ion-water interactions in hydrates of single and binary metal phosphates by vibrational spectroscopy.

1.4.2 To understand the kinetics of thermal decompositions of selected phosphate hydrates, those determine their thermal stability and the chemical changes during the thermal treatment. This information is useful for further industrial applications.

1.4.3 To understand more about the characteristic of the selected hydrates upon dehydration without destruction of the crystal frame-work. This group of hydrate will be the potential materials for application similar to the zeolites.

