

SYNTHESIS AND CHARACTERIZATION OF FEED GRADE MONOCALCIUM PHOSPHATE, $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ IN AQUEOUS MEDIUM

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ABSTRACT

The feed grade monocalcium phosphate monohydrate, $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ was prepared by the reaction of CaCO_3 and H_3PO_4 at elevated temperature in aqueous solution. The obtained precipitates were characterized by powder X-ray diffraction, infrared spectroscopy (FTIR), and thermal analysis (TG, DTA) techniques. The chemical composition of final products was evaluated by analysing the phosphorus and calcium content in the samples.

Keywords: monocalcium phosphate monohydrate, aqueous medium, feed grade.

1. INTRODUCTION

The compounds in the $\text{CaO}-\text{P}_2\text{O}_5-\text{H}_2\text{O}$ system have been investigated extensively for rather long period of time. Some of them are mainly used as bone substitutes in the biomedical industry due to their biocompatibility, low density, chemical stability, as well as high wear resistance [1]. Calcium phosphates with their characteristics of being light in weight, chemically stable and compositionally similar to the mineral phase of the bone are preferred as bone graft materials in hard tissue engineering. In addition to dicalcium phosphate, monocalcium phosphate is also used as the food additive for animals. It supplies both phosphorus and calcium which are indispensable for the growth of various types of animals. Inorganic P, and Ca sources are used as a supplement to organic feedstuffs to obtain the required level of P and Ca for optimum production and bone mineralisation [2].

The previous preparation methods of these calcium phosphate ceramics include precipitation method [3, 4], hydrothermal and or solvothermal reactions [1, 2, 5], structural directing agent (templated) method [6], sol-gel method [7], microemulsion synthesis [8], micelle synthesis, [9], mechanochemical synthesis, [10], sol-gel combustion method, [11], microwave irradiation [12], and sonication assisted synthesis method [13]. While advantages can be found in these general preparation methods, their two main disadvantages include inhomogeneity, and lack of stoichiometry. These are avoided when the material is synthesized using solution-based method which facilitates the formation of polycrystalline homogeneous particles with improved

properties. The successful application of the required materials depends on the morphology and purity of the main components. The preparation methods need to obtain well-defined chemical microstructure mainly dependent on the conditions of synthesis.

The investigation and understanding of structure and properties of feed grade calcium phosphate will be important. This research will mainly focus on the synthesis and characterization of monocalcium phosphate monohydrate, a typical example in the aqueous calcium phosphate systems.

2. MATERIALS AND METHODS

2.1. Reagents

All chemicals used for the experiments, except for phosphoric acid, are reagent grade and commercial available. Phosphoric acid of technical grade, is supplied by Duc Giang chemicals and detergent power joint stock company. All chemicals are used as received without any further purification.

2.2. Synthesis procedure

The typical example for the synthesis of monocalcium phosphate monohydrate is as follow: 23 g of phosphoric acid 85% H_3PO_4 is diluted with 14 g of water, then the formed solution was heated to $90^\circ C$ in water bath. Calcium carbonate (10 g) was then gradually added in small portions, and the slurry was stirred continuously for c.a. 1 hour to form homogeneous mixture. The product was dried at $95^\circ C$ until the weight remains unchanged, and obtained 25 g white powder.

2.3. Analytical methods

The qualitative analysis for the presence of elements in the sample is done with energy dispersive analysis. A small amount of sample powder is mounted on carbon rod and measured on an OXFORD Link ISIS energy-dispersive X-ray spectrometer.

The chemical analysis for evaluating content of phosphorus is measured by vanadomolybdophosphoric acid colorimetric method on a Thermo Scientific SPECTRONIC 20D+ spectrophotometer at the wavelength of 470 nm. The Ca content in the sample is determined by volumetric titration against EDTA standard solution.

The powder sample X-ray diffraction is measured on a D8 Advance Bruker diffractometer Cu anode, $\lambda(CuK\alpha) = 1.54056 \text{ \AA}$, at room temperature with the two theta angle from 5° to 70° , step 0.030° , and dwelling time of 1.0 sec for each step.

The thermogravimetric analysis of the synthesis is measured on Setaram Labsys Evo S60/58988 thermal analyzer. The sample (the initial weight of 13.15 mg) is put on an alumina crucible and heated from room temperature to $800^\circ C$ at the heating rate of $10^\circ C/ \text{min}$, under flow of air, with the flow-rate of 20 mL/ min. The weight and heat flow of sample is recorded during heat treatment.

A small amount of the product is mixed with KBr, pelletized, and measured in transmission mode with the blank sample of pure KBr, on a Jasco FTIR-4200 series spectrophotometer over the range $4000\text{--}400 \text{ cm}^{-1}$ with the spectral resolution of 4 cm^{-1} .

3. RESULTS AND DISCUSSION

3.1. Composition of the synthesized product

Chemical composition of final product is first evaluated qualitatively with the energy dispersive X-ray spectroscopy (EDX). The typical EDX spectrum of the product is shown in Figure 1.

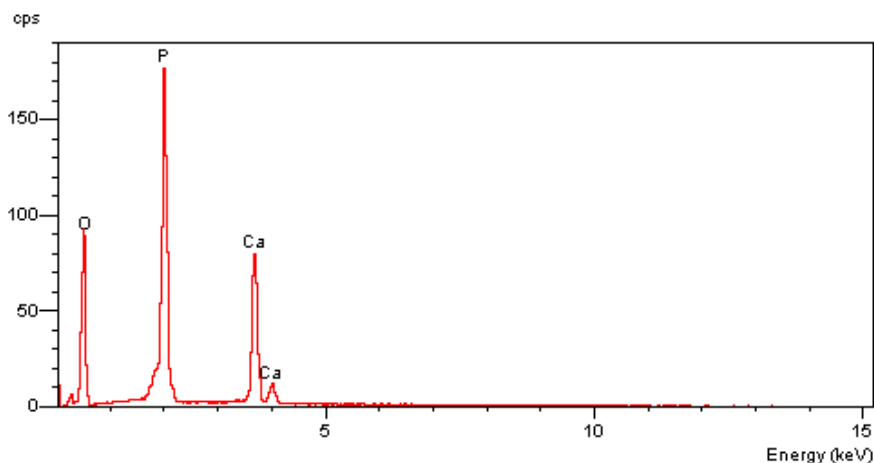


Figure 1. The energy dispersive X-ray spectroscopy pattern of the final product.

The EDX spectrum confirms that the synthesized sample contains Ca, P and O elements. The chemical analysis for the weight content of Ca and P of the sample shows the values of 15.74, and 24.75 %, respectively, which agrees with the ones of 15.89 % for Ca and 24.58 % for P as calculated from the chemical formula of $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ as expected.

3.2. Crystal structure of the synthesized product

The addition of CaCO_3 into the reaction mixture contains various phosphate species may form some types of compounds or structure. The phase investigation of the final product will be informative because it shows which phase is prominent in the synthesis conditions.

The crystal structure of the sample is investigated with powder X-ray diffraction (XRD). The X-ray diffraction patterns of the sample (a) and the simulated one from the data of MacLennan (b) [14] are shown in Figure 2.

The Figure 2 shows that the powder pattern of the sample is comparable to the one of $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$, which agrees with the results of chemical composition analysis. The figure 2 also shows that there are no additional peaks detected. It means that phase in the final product is $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$. The preliminary Rietveld analysis for the determination of crystal structure of the final product from the powder X-ray data shows that the title compound crystallizes in triclinic system with space group of $P1, \bar{1}$ and the lattice parameters of $a = 5.6125 \text{ \AA}$; $b = 11.8821 \text{ \AA}$; $c = 6.4324 \text{ \AA}$; $\alpha = 98.3516^\circ$; $\beta = 117.7303^\circ$; $\gamma = 83.5106^\circ$. The determined crystal system and lattice parameters are very close to the ones in the work of MacLennan [14].

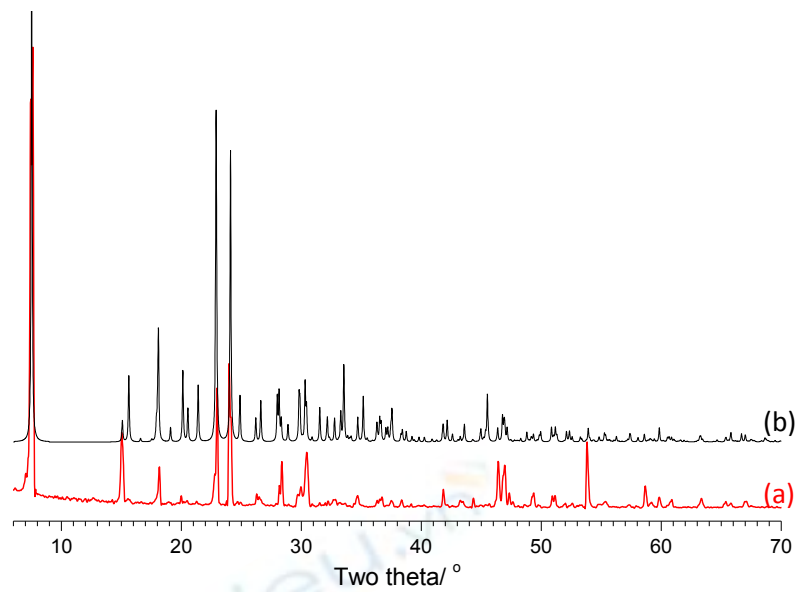


Figure 2. The powder pattern of the final product (a) and the simulated one of Ca(H₂PO₄)₂·H₂O (b) from MacLennan [14].

3.3. Thermogravimetric analysis of the synthesized product

The thermogravimetric pattern of the product is given in Figure 3. Figure 3 shows the weight loss between 30 to 800 °C and divided into different steps which related to the elimination of water molecules from the sample.

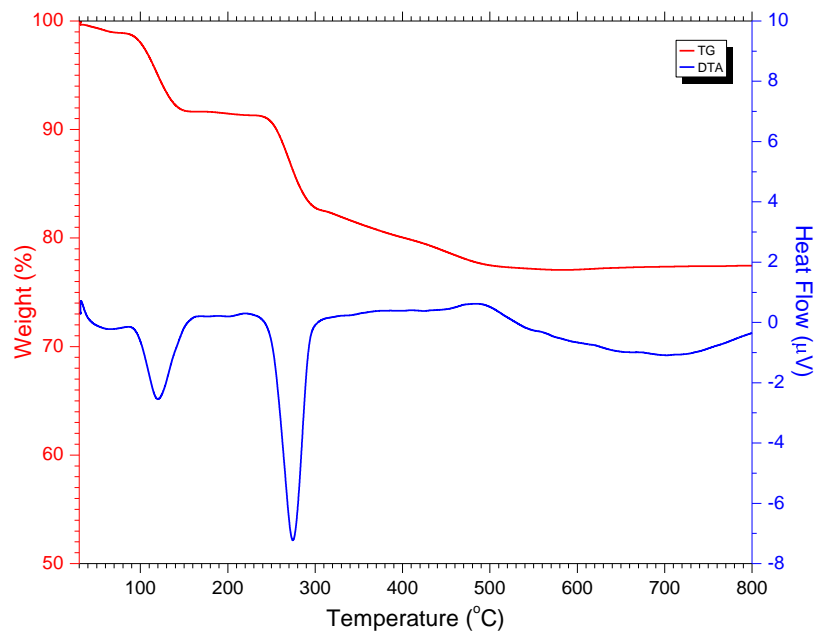
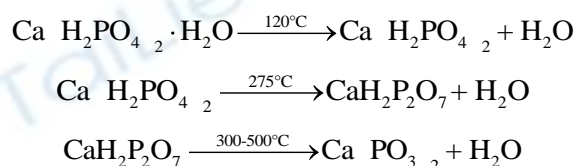


Figure 3. The thermogravimetric spectrum of the synthesized product.

The weight loss from of the sample to 85 °C is 1.19 %, which can be ascribed for the loss of physical water in the samples. The loss from 85 °C to 160 °C is 7.18 %, that can be compared to the elimination of one crystallization water molecule for each formula of $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$, as indicated by the endothermic peak at 120 °C on the differential thermal analysis (DTA) curve. On further heating, the weight loss continues, and the weight loss from 160 to 600 °C is 14.53 % which is very close to the value of 14.29 % corresponding to the removal of two water molecules from calcium hydrogen phosphate due to the condensation of intermolecular phosphate species to form calcium metaphosphate, $\text{Ca}(\text{PO}_3)_2$, which is stable on further heating to 800 °C. It is noted that, from thermogravimetric curve, there are two steps of weight loss in this temperature range. The step from 240 to 310 °C probably corresponds to the decomposition of $\text{Ca}(\text{H}_2\text{PO}_4)_2$ and the formation $\text{CaH}_2\text{P}_2\text{O}_7$ as reported in other work [4, 15]. The decomposition of $\text{Ca}(\text{H}_2\text{PO}_4)_2$ is also endothermic as indicated in the corresponding DTA curve. The weight loss at temperature from 310 °C to 600 °C is ascribed for the decomposition of $\text{CaH}_2\text{P}_2\text{O}_7$ and the formation of $\text{Ca}(\text{PO}_3)_2$ as mentioned above. The thermogravimetric data analysis confirms that the synthesized product is calcium hydrogen phosphate monohydrate.

The phase transformation of the product during heat treatment at different temperature can be summarized as follows:



In this study, the formation of intermediated hydrated calcium dihydrogen phosphate, $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot x\text{H}_2\text{O}$, $x = 0.5$; and 0.2, during heat treatment as shown in some work on the synthesis of the title compound in organic solvents or mixture of water and organic solvents, has not been observed. The reason could be from the influence of the synthesis media for the formation of product [1, 2].

3.4. The infra-red analysis of the synthesized product

The presence of certain functional groups as well as water molecules in the product can be further studied with infrared spectroscopy (IR). The IR spectrum of the product is shown in Figure 4, which confirms the presence of crystallization water in the lattice, as well as the presence of phosphate functional groups in the samples.

Figure 4 shows that the IR results are very similar to those observed previously, and the assignment of the bands can be summarized as in [13].

The band centered at 3500 cm^{-1} is assigned for the O–H stretching of the water, and the band at approximately 1640 cm^{-1} corresponds to the H–O–H bending of water, the small bands from 2200 cm^{-1} to 2500 cm^{-1} is the H–O–H rotation and bending of water, and the weak band at 675 cm^{-1} is assigned to rocking mode of water molecules in the monocalcium phosphate monohydrate.

The band at 1238 cm^{-1} is assigned for the P–O–H in-plane bending, and some bands from 980 cm^{-1} to 1158 cm^{-1} are for the P–O stretching. The band at 886 cm^{-1} for P–O (H) stretching, and the bands from 500 cm^{-1} to 568 cm^{-1} are ascribed for the O–P–O(H) bending.

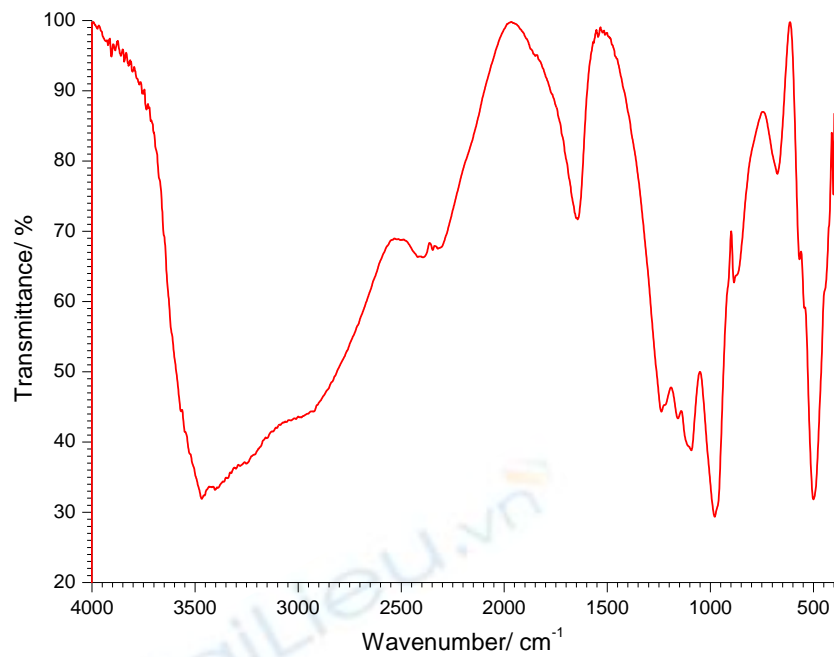


Figure 4. The Fourier transformation infrared spectrum of the final product.

3.5. The crystal morphology the product

In order to study the crystal morphology, the scanning electron microscopy (SEM) image of the obtained product is measured with the magnification of 200 times, and given in Figure 5.

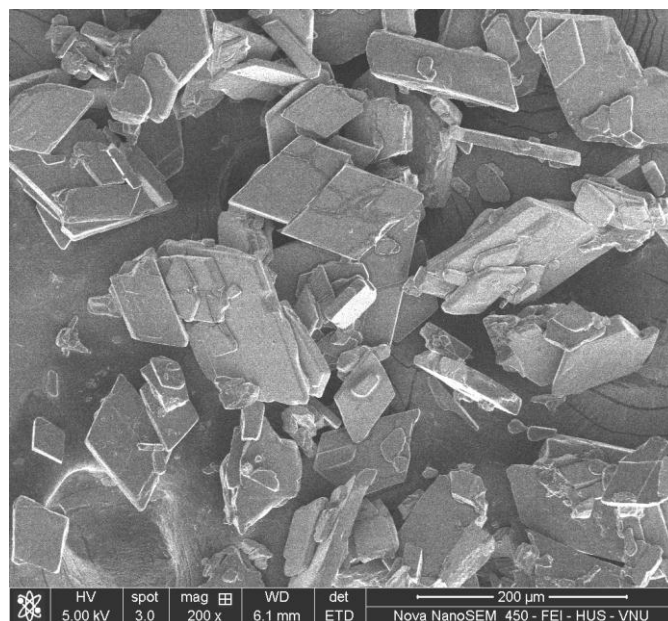


Figure 5. The SEM image of the synthesized product.

Figure 5 shows that the shape of product particles are parallelogram-like crystals, most of crystals are somewhat larger whereas the others are smaller. The size of large crystals is about 80 – 100 μm in length, 70 – 80 μm in width, and the thickness of 15 – 20 μm . The formation of rather large crystals could be the result of lengthening the reaction and crystallization time which favours the crystal growth, and pure phase of the desired product. The obtained crystal morphology in the experiment also agrees with the results of synthesis the title compound in organic solvents, except that the crystal size is larger.

4. CONCLUSIONS

The synthesis and structural characterization of monocalcium phosphate monohydrate by the reaction of phosphoric and calcium carbonate at elevated temperature in aqueous medium achieve apparent success. The use of water in the synthesis will make the production on the large scale easy to perform and the use of concentrated phosphoric acid is not required for the manufacture. The chemical composition analysis results, XRD data, IR spectrum confirm that the synthesized product is monocalcium phosphate monohydrate, $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$, one form of animal food additives.

The study for the optimization of synthesis conditions and their impact on presence of dicalcium phosphate dihydrate, free phosphoric acid or other forms of phosphates, if any, and their contents in the sample, as well as physical and chemical properties is still in progress.

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