Facile Sol-Gel Synthesis of Calcium Phosphates: Influence of Ca/P Ratio and Calcination Temperature

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Abstract. Calcium phosphates (CP) have been synthesized by sol-gel method in various calcium to phosphorus molar ratio and calcination temperatures. The objective of this study was to understand the influence of molar ratio Ca/P and calcination temperature on crystalline phase of CP. Sol-gel synthesis of calcium phosphates have been performed at room temperature by mixing calcium nitrate and phosphoric acid at Ca/P molar ratio 1.0, 1.3 and 1.5. Gel of synthesis products were dried at 110°C to produce powder then measured by thermal analysis of Differential Scanning Calorimetry-Thermogravimetric Analysis (DSC-TGA). Powders of CP were calcined at 110, 400 and 600°C based on thermal analysis result. Crystalline phase and chemical bonds of calcined CP powders were characterized by X-Ray Diffractometer (XRD) and Fourier Transform Infrared Spectrophotometer (FTIR).

Keywords: calcium phosphates, sol-gel, molar ratio, calcination temperature

1. Introduction
Calcium phosphates (CP) as main component of natural material in bone and teeth are widely used as main materials in dental and orthopedic applications such as bone graft, implant coating, dental and bone restorative materials and ceramic [1]. The versatile applications of CP are caused by the similar chemical composition and structure with mineral phase in bone and teeth, mostly good chemical stability and great biocompatibility [2]. According to their properties and applications, study about CP become very attractive.

Based on the chemical compositions, there are several types of CP such as amorphous calcium phosphate (ACP), monocalcium phosphate monohydrate (MCPM) and anhydrous (MCP), dicalcium phosphate dihydrate (DCPD) and anhydrous (DCP), tricalcium phosphate (α-TCP and β-TCP), tetracalcium phosphate (TTCP), hydroxyapatite (HA), fluorapatite (FA) and oxyapatite (OA) [3]. The many types of these materials make the production of CP to be more interesting to explore the influence of some synthesis parameters such as Ca/P ratio and calcination temperatures. These synthesis parameters have a key role to get the type of CP and crystalline phase of the products. In this study, CP were synthesized using sol-gel method in various Ca/P ratios and calcination temperatures. This method is excellence to apply the products for various purposes such as for coating, cement and powder with various physical structures. Crystalline phase of products has been investigated to determine the type of calcium phosphate for the further suitable biomedical applications.

2. Experimental Method
2.1. Materials
Calcium nitrate tetrahydrate (Ca(NO₃)₂·4H₂O, 99%), absolute ethanol (C₂H₆O, 99%), phosphoric acid (H₃PO₄, 85%) were obtained from Sigma-Aldrich without any further purification treatment.

2.2. Synthesis of Calcium Phosphates
Calcium phosphates were synthesized by sol-gel method at room temperature in various molar ratio of calcium to phosphorus (Ca/P) 1.0, 1.3 and 1.5 of ethanol solution. Ca(NO₃)₂·4H₂O (1.0–1.5M, 100 mL) was dissolved in ethanol by constantly stirred until homogenous solution obtained then H₃PO₄ (1M) was
added constantly drop wise until white sol formed. The white sol was stirred steadily for two hours at room temperature. After stirring, white sol was aged for a week and then dried at 110°C for 24 hours. The final step was calcination at various temperature 110, 400 and 600°C based on DSC-TGA result.

2.3. Characterization of Calcium Phosphates

The calcination temperatures of CP were determined by DSC-TGA (Metller Toledo) in air with heating rate 10°C per minute from 25 to 1000°C. Crystalline phase of all CP produced were performed by XRD (X’Pert PRO PANalytical) with CuKα radiation (λ=1.5406Å) in 2θ range start from 10° to 60°. The chemical bond on CP was characterized by FTIR spectrophotometer (IRTracer-100 Shimadzu) in wave number range from 4000 to 450 cm⁻¹.

3. Results and Discussion

Sol-gel synthesis of CP was successfully conducted in various molar ratio by simple-step of solvation and reaction process to obtain white sol. The sol was aged to produce white gel then dried to form stable white-powder. The powder then was measured by DSC-TGA to acquire thermal profile in CP thermogram. The thermal profile of CP from DSC-TGA is presented in Figure 1.

Figure 1. DSC-TGA data of CP

The thermogram revealed solvent removal about 3.4% weight loss at 96.98°C in first endothermic region. The powder weight of CP is relatively stable from 110 to 310°C so that the first variation of calcination temperature is selected at 110°C. The total weight loss in second and third endothermic region is 9.72% from 350 to 550°C that indicated the excess of nitrate and organic species elimination [4]. The second variation of calcination temperature is selected at 450°C which is the end point of second endothermic region. The CP weight is relatively stable started at 600°C which is selected as the last variation of calcination temperature. There are three variations of calcination temperature under 700°C that possible to result different structure and crystallite phase.

The variation of Ca/P molar ratio at 110°C were resulted CP101, CP131 and CP151 sequentially for 1.0; 1.3 and 1.5 Ca/P ratio. The other CP products were CP104, CP134 and CP154 for all various Ca/P ratio at 400°C and CP106, CP136 and CP156 for all various Ca/P ratio at 600°C. All CP products were characterized by powder XRD that were resulted diffractogram in Figure 2.

The XRD patterns of CP are quite crystalline and present high intensity of same peaks at 2θ: 26°, 30° and 33°. All of the XRD patterns dominantly matched with JCPDS No. 70-265 correlated to Monetite or CaHPO₄ (DCP). Due to crystallite phase of DCP appear in all products of CP, DCP crystallite were calculated by Scherer equation to study the influence of Ca/P ratio and calcination temperature besides crystalline phase [5]. However, the other crystalline phase appears for some CP products based on Xpert High Score software. The crystallite phase and DCP crystallite size of all CP are in Table 1.
Table 1. Crystallite Phase and Crystallite Size of DCP with different Ca/P molar ratio and Calcination Temperature

| CP  | Ca/P | Calcination temperature (°C) | Crystallite phase            | Crystallite Size of DCP (nm) |
|-----|------|------------------------------|-----------------------------|------------------------------|
| CP101 | 1.0  | 110                          | Monophasic: DCP             | 57.1                         |
| CP131 | 1.3  |                              | Monophasic: DCP             | 85.8                         |
| CP151 | 1.5  |                              | Monophasic: DCP             | 85.71                        |
| CP104 | 1.0  | 400                          | Biphasic: DCP and HAP       | 81.52                        |
| CP134 | 1.3  |                              | Biphasic: DCP and OCP       | 70.72                        |
| CP154 | 1.5  |                              | Biphasic: DCP and TCP       | 43.67                        |
| CP106 | 1.0  |                              | Monophasic: DCP             | 107.22                       |
| CP136 | 1.3  | 600                          | Triphasic: DCP, OCP and HAP | 34.04                        |
| CP156 | 1.5  |                              | Biphasic: DCP and TCP       | 72.89                        |

The influence of Ca/P molar ratio is observed at 400 and 600°C that resulted different type crystallite phase in biphasic and triphasic CaP besides DCP. It is hard to observed the influence of molar ratio to crystallite phase and DCP size at 110°C because the similar crystallite phase and the quite similarity of DCP phase size CP131 and CP151. However, the influence of Ca/P ratio at 110°C to peak intensity at 20: 26°, 30° and 33° enlarges with increasing concentration of calcium.

The influence of calcination temperature is perceived especially at 1.3 Ca/P ratio that rises the number...
of crystallite phase and reduces DCP size. The crystallite size of DCP changes according to the number of crystallite phase which DCP size decreases with increasing number of crystallite phase. Furthermore, DCP size grows at 1.0 Ca/P ratio with enhancement of calcination temperature.

**Figure 3. FTIR Spectrum of CP**

The FTIR spectrum of CP provides information about chemical bonds and functional groups in DCP. The bands observed from 1200 to 450 cm\(^{-1}\) could be assigned to P-O and Ca-O bonds. The band of antisymmetric stretch of P-O observed at region 1140-1030 cm\(^{-1}\) [6]. In addition, the absorption bands observed at 924, 717 and 553 cm\(^{-1}\) was corresponded to the stretching vibration of P-O-H in DCP [4], the stretching vibration of Ca-O [7] and the bending vibration of P-O in PO\(_4^{3-}\) [8].

4. Conclusion
In conclusion, The Influence of Ca/P molar ratio and calcination temperature are observed at 400 and 600˚C for all Ca/P ratio that resulted mono-, bi- and triphasic of crystallite phase of Calcium Phosphates. However, dicalcium phosphate (DCP) are dominantly observed in all variation of Ca/P ratio and calcination temperature. The calcium phosphate products are potential as a biomedical material especially for calcium phosphate cement.

5. References
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