

INFLUENCE OF SOME PROCESS PARAMETERS ON STRUCTURE AND MOLECULAR PROPERTIES OF CALCIUM PHOSPHATE NANOPOWDERS

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ABSTRACT

Sol-gel route has been regarded as one of the versatile techniques to prepare calcium phosphate (CaP) nanoceramics. Extensive studies encapsulating sol-gel based synthesis procedures showing effects of various process parameters on physico-chemical, structural, thermal and biological properties of CaP based synthetic powders. Hence it is always a tedious task to choose a particular synthesis methodology in light of dearth of a single detailed literature incorporating the comparison and effects of different synthesis procedures. In the present study, authors comprehensively studied the effects of phosphorous reagents, and other processing parameters on chemical composition of synthetic CaP powder. XRD and FTIR techniques were used for systematic characterization. This manuscript has been expected to fulfill the need of opting for a particular route to synthesize CaP nanopowders.

Keywords: Calcium phosphate, hydroxyapatite; XRD, FTIR, sol-gel

1. Introduction

Over the past decades, demands of calcium phosphate (CaP) based bioceramics have been continuously increased consequently wide efforts have been devoted to develop its synthesis routes [1]. It is widely known that among the CaP salts, Hydroxyapatite (HAP) is the principal inorganic constituent of human bones and teeth [2] and have been extensively studied owing to its various biological characteristics viz. non-immunogenicity [2], non-inflammatory behavior [2], high osteoconductivity and/or osseointegration [2] and good biocompatibility [3,5]. Over the last many years, diverse CaP synthesis methods have been suggested claiming control over its varied properties. With such a great variety of synthesis routes; choosing a specific route to synthesize a well defined powder for a specific application can be so laborious [1] and often leads to dilemma.

After an extensive literature review to synthesize CaP based powder including solid state synthesis [6-7], mechano-chemical synthesis [8,9,19], conventional chemical precipitation technique [10-11], hydrolysis [12], hydrothermal [13] and many more methods; only sol-gel route is among the wet chemical technique which has recently attracted much attention due to its many advantages including high product purity, homogeneous composition, low synthesis temperature [1,4], nano-dimensional structure size, narrow particle

size spread and stoichiometric Ca/P ratio (1.67) etc. Typical sol-gel process usually comprises of various steps viz. mixing of Ca^{2+} and PO_4^{3-} reagents in aqueous and/or an organic solvents followed by aging at different temperatures and periods, gelation, centrifugation/drying and finally heating at higher temperatures, known as calcination/sintering. A little alteration in any of these process parameters causes a dominating change in varied properties of final product. Certain investigations have been reported, revealing the effects of different Ca^{2+} [14,18,33] and PO_4^{3-} precursors [14-18,20,21,22,34], water and/or ethanol as solvents [15,17], combination of stirring time [2,20-22], aging time and temperature [2,20-22], drying temperature and time [2,3,20,21] followed by different calcination temperatures and their respective timings [2,3,20,21] on physico-chemical constitution, crystallinity, crystal size and shape, thermal behavior [35] and finally biocompatibility aspects [36]. Many a times, it has been a common observation that such synthesis procedures are not elaborated in a meaningful manner which further shoots up the bewilderment of naïve researchers.

Keeping it in mind, authors synthesized nano-dimensional CaP based powders using phosphorous pentoxide (PP) and calcium nitrate tetrahydrate (CNT) as Ca^{2+} ion sources. Resultant nanopowders were analyzed for their structural constitution in a comprehensive manner.

2. Materials and method

CNT [$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$; Merck, 98%) and PP [P_2O_5 ; Merck, 97%] were used as Ca^{2+} and PO_4^{3-} ion sources. DDH₂O (lab made) and ethanol [$\text{C}_2\text{H}_5\text{OH}$; Merck, 99.9%] were used as solvents. Synthesis protocol of CaP nanopowder has been shown in Figure 1.

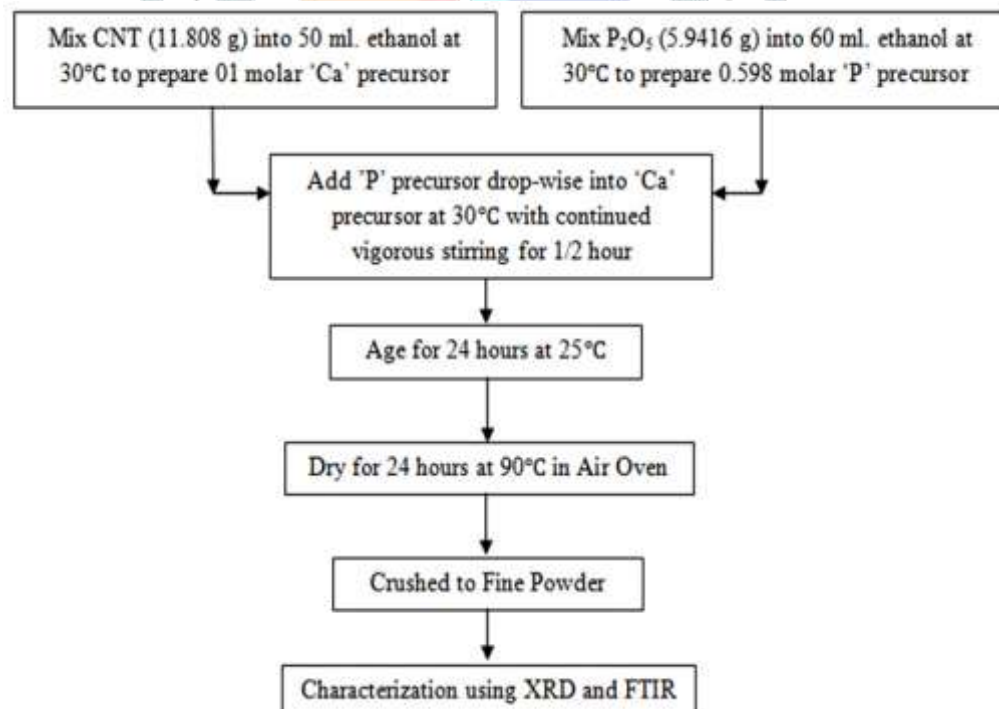


Figure 1. Synthesis methodology

2.1. Powder Characterization

XRD (Philips X'Pert 1710) was performed using CuK_α radiations. Different structural parameters were determined using fundamental crystallographic formulae. Calcium to phosphorous (Ca/P) molar ratio was calculated using Eq. (1):

$$\frac{Ca}{P} = \frac{10-x}{6} \tag{Eq. (1)}$$

Chemical stability of HAP powder was represented in terms of chemical equation on the basis of calcium deficiency, (x) by using Eq. (2):



FTIR (Perkin Elmer) spectra were recorded from 500-4000 cm⁻¹ for each sample.

3. Results and discussion

3.1. Qualitative and quantitative phase analysis

XRD patterns of CaP-I nanopowders sintered at different temperatures and corresponding results have been shown in Figure 2 and Table 1, respectively.

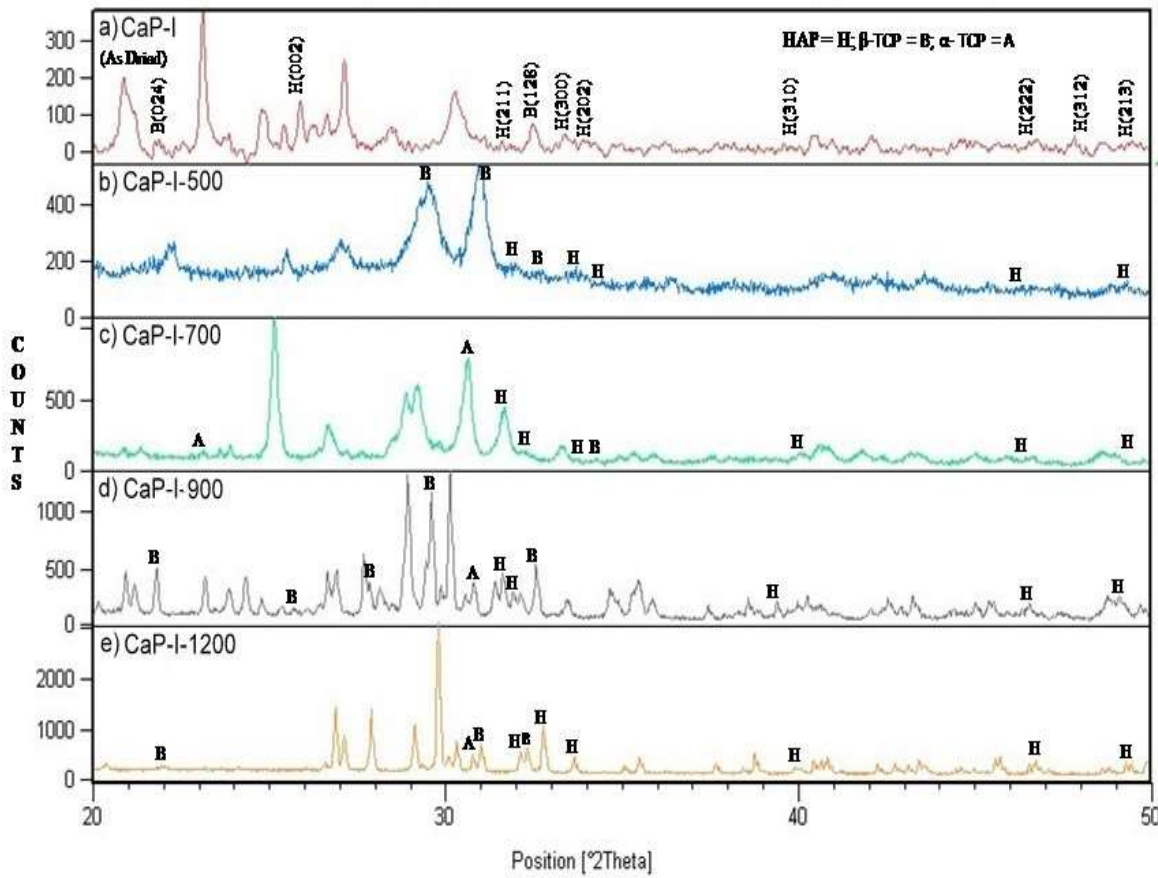


Figure 2. XRD patterns of CaP-I nanopowders sintered at a) as dried, b) 500°C, c) 700°C, d) 900°C and e) 1200°C

Chemical reactions to form apatite ionic structure as per the synthesis methodology of CaP-I have been proposed in Eq. 3-5.

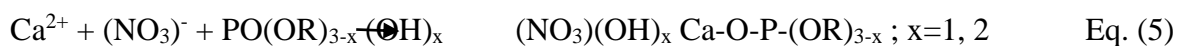
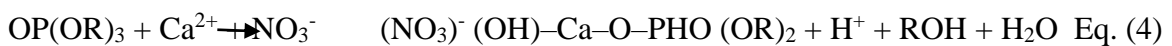


Table 1. Structural Properties of CaP-I nanopowders

Parameters	CaP-I-As Dried	CaP-I-500	CaP-I-700	CaP-I-900	CaP-I-1200
Major Phases	HAP; β -TCP	HAP; β -TCP	HAP; β -TCP; α -TCP	HAP; β -TCP; α -TCP	HAP; β -TCP; α -TCP
HAP Lattice Parameters (nm)	a=9.380; c=6.887; c/a=0.734	a=9.498; c=6.921; c/a=0.728	a=9.376; c=7.267; c/a=0.774	a=9.443; c=8.103; c/a=0.857	a=9.396; c=6.849; c/a=0.728
Mean Crystallite Size (nm)	48.757	70.71	93.753	98.782	135.798
Weight Fractions	HAP=0.3451 β -TCP=0.3451	HAP=0.0653 β -TCP=1	HAP=0.3224 β -TCP=0.6672	HAP=0.2752 β -TCP=0.3373	HAP=0.307 β -TCP=0.1754
Estimated Ca Deficiency, x	0.519	0.942	0.690	0.583	0.381
Ca/P Ratio	1.58	1.50	1.55	1.56	1.60

By adopting the synthesis methodology of CaP-I, multiphase calcium phosphate (MCP) nanopowder was derived consisting of β -TCP and HAP in major proportions along with certain peaks belonging to α -TCP were also noticed. As dried gel Figure 2(a) indicates amorphous nature of powder [25] consisting of almost equal proportions of β -TCP and HAP characterized by weak intensity and broader peaks. Upon increasing the temperature to 500°C; biphasic structure converted into monophasic i.e. β -TCP only accompanied by a little amount of HAP. Crystallite size and crystallinity of all phases were observed to increase with the sintering temperature as indicated by reducing peak widths ascribed by various patterns shown and calculated in Figure 2 and Table 1, respectively [2,24,25]. HAP and β -TCP were observed to be the major phases present throughout along with traces of α -TCP started appearing after 500°C showing its decomposition behavior [25]. In contrast to Costescu [2] which revealed the complete absence of β -TCP above sintering temperature of 1000°C, synthetic CaP-I powders still contained resorbable TCPs even up to 1200°C [35-36]. Lattice parameters of HAP crystals were also found to increase primarily 'c' axis dimension with the increase in sintering temperature in accordance with various researches [2,24,33-34]. Effect on Ca²⁺ deficiency and Ca/P molar ratio with respect to sintering temperature has been enumerated in Table 1 confirmed the nature of synthesized nanopowder to be BCP having Ca/P ratio in between 1.5-1.67.

Crystallinity of CaP-I powders was observed to increase with the rise of sintering as indicated by decreasing peak width reflections of (002) and (310) planes as shown in Table 2 and complements with the various research findings [2,3,25]. Chemical stability of CaP-I powders can be proposed in terms of Eq. (6) based on Ca deficiency, x as

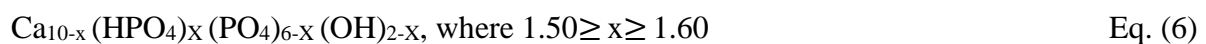


Table 2. Peak width measurement of (002) and (310) reflections to represent crystalline behavior of CaP-I powders

	Planes	CaP-I-As Dried	CaP-I-500	CaP-I-700	CaP-I-900	CaP-I-1200
Peak Width (2θ)	(002)	0.1673	0.1171	0.1673	0.1004	0.1224
	(310)	0.0836	0.0612	0.1673	0.0816	0.1428

3.2. FTIR analysis

Ionic structure of synthesized CaP-I nanopowders have been shown in Figure 3.

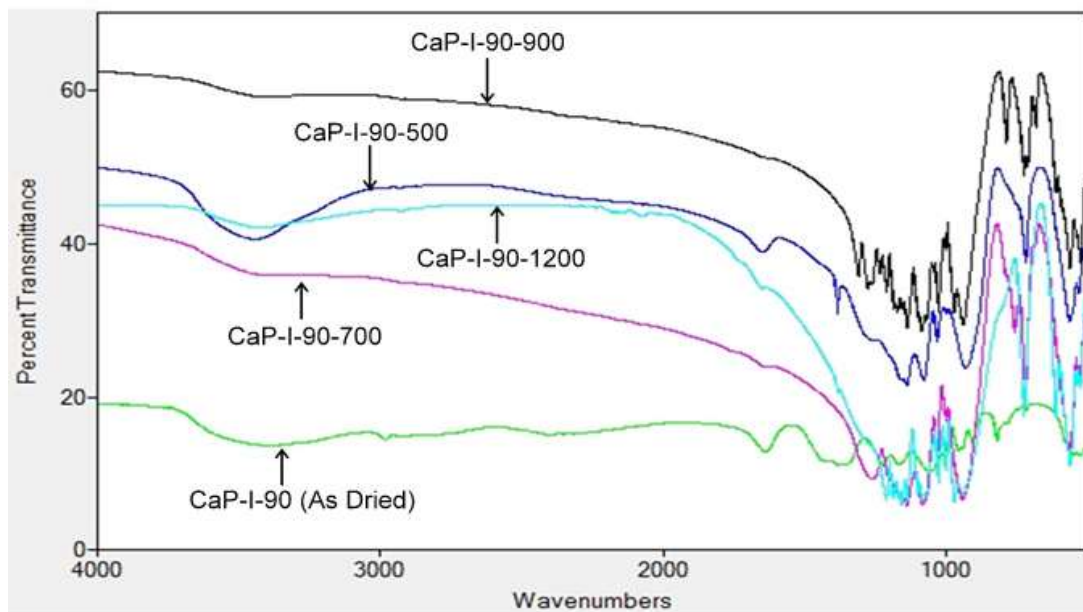


Figure 3. FTIR spectra of CaP-I powders

Various constituent functional groups viz. water-adsorbed deformation ($3441, 3431, 3423 \text{ cm}^{-1}$); OH- water adsorbed deformation ($1647, 1639 \text{ cm}^{-1}$) [33]; carbonate stretching band ($1384, 1383, 1382 \text{ cm}^{-1}$) [35-36]; $\delta\text{OH HPO}_4^{2-}$ ($1211, 1210 \text{ cm}^{-1}$); $\nu_3 \text{ HPO}_4^{2-}$ ($1139, 1138 \text{ cm}^{-1}$) along with $\nu_3 \text{ PO}_4$ ($1086, 1080, 1045, 1033 \text{ cm}^{-1}$); $\nu_1 \text{ PO}_4$ ($1073, 973, 959 \text{ cm}^{-1}$) [33-34]; $\nu_4 \text{ PO}_4$ ($613, 566, 565 \text{ cm}^{-1}$) [37], $\nu_2 \text{ PO}_4$ (471 cm^{-1}) were detected in CaP-I nanodimensional powders as shown in Figure 3.

4. Conclusion

CaP nanopowders with biphasic structure were synthesized using different synthesis conditions. Ca/P ratio was found to lie between 1.5-1.67 which is an indication of their resorbable nature. Based on the results of present investigation; structural constitution of all synthesized powders was noticed to resemble having little variation in one or two parameters. Presence of HAP phase at the lower temperature in all the powders turned out to be a main achievement. Reduced decomposition temperature of apatite to β -TCP was also observed. Admittedly, other desirable properties viz. high thermal stability and powder crystals of nano-dimensional size recommend the synthesized powders suitable for biomaterial applications.

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