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Solution combustion synthesis of bioceramic calcium phosphates by single and mixed fuels—A comparative study

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Abstract

Calcium phosphate based bioceramics have been synthesized by a modified combustion synthetic route using both citric acid and succinic acid separately and in mixture as fuels and nitrate and nitric acid as oxidants. Calcium nitrate and diammonium hydrogen phosphate were used as calcium and phosphate sources. The effects of citric acid to succinic acid ratio on the phase formation have been investigated. The precursors and the calcined products have been characterized by powder X-ray diffraction, Fourier-transform infrared spectroscopy and scanning electron microscopy. Succinic acid has been used as a fuel for the first time to synthesize hydroxyapatite.

Hydroxyapatite phase is formed when either citric acid or succinic acid is used as a fuel and β-tricalcium phosphate phase is formed when a mixture of citric acid and succinic acid is used as a fuel as revealed by powder X-ray diffraction. The average crystallite size of the synthesized powder determined by Debye–Scherrer formula is found to be in the range of 55–65 nm. Surface morphology of the samples was imaged using scanning electron microscope. Chemical analysis shows that the Ca:P ratio in synthesized ceramics is 1.67. Results are discussed in terms of the phases present in the precursors formed during single and mixed fuel approaches and also its carbonate content present in hydroxyapatite products.

Keywords: A. Powders: chemical preparation; B. Spectroscopy; D. Apatite; E. Biomedical applications

1. Introduction

Out of several calcium phosphate bioceramics, hydroxyapatite (HAP) and tricalcium phosphate (TCP) are the most commonly used constituents for bone replacement due to its less solubility in physiological environment. Composites of β-TCP and HAP, not only mimic that of human bone but also posses very good osteoconductivity and excellent biocompatibility [1]. The percentage of β-TCP in the composite is decided based on the characteristics required for the specific application. The function of β-TCP in the composite is to help the rapid bonding of artificial bones to natural ones by means of its fast resorbable nature in physiological pH. It is reported that most of the TCPs are resorbed within 6 weeks after implantation. The various applications of these composites are defect filling in total hip revision, spinal fusion, hand and foot surgery, fracture repair and joint reconstruction.

Synthesis of HAP/TCP composite especially in nanosized forms has been an active area of research by various groups. Hydroxyapatite and β-TCP have been synthesized by the traditional solid-state reaction and wet chemical methods such as co-precipitation and sol–gel methods [2–4]. The problem associated with the solid-state reaction is its high temperature calcination and the large particle size of the resultant product [5]. The co-precipitation method improves reactivity of the components but the incomplete precipitation results in the alteration of stoichiometry which results in undesirable impurities [6]. The sol–gel method can reduce the segregation of metal elements and improve the chemical homogeneity during the decomposition of the polymeric precursors at high temperatures but the major disadvantages of the sol–gel process is the high cost of the starting material (metal alkoxides) and sometimes (or) often the precursor formed is extremely moisture sensitive [7]. However, sol–gel method has been employed to synthesize a variety of materials using cheap organic compounds as gelling agents cost effectively [8–10].

Recently, there has been a growing interest in synthesizing ceramic materials by self-propagating combustion synthesis

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(SPCS) and microwave assisted synthesis [11–12]. It has been reported that sub micron [13] sized hydroxyapatite could be synthesized by SPCS using urea as the fuel and nitric acid as oxidizer. The success of the process is due to an intimate blending among the constituents using a suitable fuel which also acts as a complexing agent (e.g., citric acid, urea, sucrose, etc.) in an aqueous medium and a vigorous exothermic redox reaction between the fuel and an oxidizer (i.e., nitric acid).

The advantage of SPCS to synthesize HAP is that the product formed is carbonated hydroxyapatite which is biomimetic. It is well known that carbonate ion can partially substitute both the phosphate and the hydroxyl group of the hydroxyapatite structure. When CO_3^{2-} substitutes for OH^- ions it is termed as site A substitution and when it replaces PO_4^{3-} ions then it is termed as site B substitution [14]. The carbonate content of bone mineral is about 4–8% by weight percentage [15] and it is found to vary [16–17] depending on the age of the individual with an increase of A type substitution in the old bone. Contradictorily type B substitution is common in the bone of young human beings. Carbonated hydroxyapatite can be used as a temporary lattice as it possesses more solubility and bioactivity than the stoichiometric hydroxyapatite.

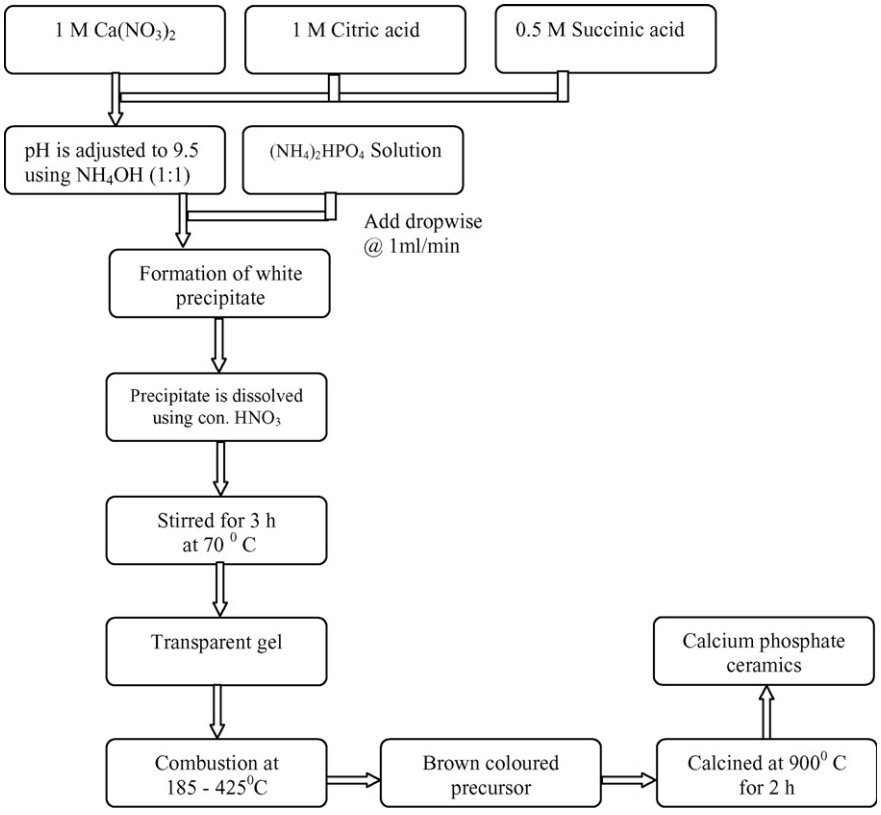
In the present work, we have employed succinic acid as a new fuel for the synthesis of hydroxyapatite by SPCS. The self-ignition temperature of succinic acid is 425 °C and by mixing citric acid with it we succeeded in bringing down the auto ignition temperature to 290 °C. As the thermochemistry of SPCS is controlled by the nature of fuels, we have analyzed the effects of fuel ratio on the phase formation of different calcium phosphates bioceramics. The ratio between hydroxyapatite and different calcium phosphates is expected to influence the properties of the bioceramic products. We also obtain carbonated hydroxyapatite by this method.

2. Experimental

Stoichiometric amounts of powders of $Ca(NO_3)_24H_2O$ (>99%, AR, Rankem), $(NH_4)_2HPO_4$ (99%, AR, Merck) and citric acid (99.7%, AR, SRL) were dissolved in demineralized water at room temperature to yield 1 M stock solutions. A 0.5 M stock solution of succinic acid is prepared by dissolving appropriate amount of it in luke warm demineralized water.

The sample for which citric acid is used as a fuel is named BCC (Bioceramic Citric) and succinic acid as fuel is named BCS (Bioceramic Succinic). For the samples BCC and BCS equal volumes of the fuel and calcium nitrate are taken in an uncovered glass beaker and stirred with a magnetic stirrer for 10 min at room temperature. The solution is acidic (around pH 1.6) which is adjusted to pH 9.5 using NH_4OH. Stoichiometric amount of $(NH_4)_2HPO_4$ solution is then added drop wise to the mixture under stirring condition which forms a gelatinous white precipitate. The formed precipitate is dissolved using concentrated nitric acid and the pH is adjusted to 1. Now the clear solution is stirred constantly using magnetic stirrer and the temperature is raised to 70 °C and maintained for 2 h in an uncovered glass beaker (refer Flow Chart 1).

When the solution becomes highly viscous and transparent, the temperature is allowed to rise fast until the combustion



Flow Chart 1. The synthesis of hydroxyapatite by self-propagating combustion method.

Table 1
Starting compositions, auto ignition temperature and major phase formed

Sample name	Volume (ml)				Auto ignition temperature (°C)	Major phase formed
	$Ca(NO_3)_2$ (1 M)	$(NH_4)_2HPO_4$ (1 M)	Citric acid (1 M)	Succinic acid (0.5 M)		
BCC	20	12	20	0	185	HAP
BCS	20	12	0	40	425	HAP
BCCS 1	20	12	20	20	290	TCP
BCCS 2	20	12	20	40	290	TCP
BCCS 3	20	12	20	60	290	TCP
BCCS 4	20	12	20	80	290	TCP

reaction takes place. In order to facilitate proper combustion of fuel sufficient supply of oxygen should be provided so that it is carried out in the open vessel. Combustion takes place in the temperature range of 170–450 °C with continuous evolution of gases. Temperature at which the combustion takes place is measured by a thermocouple placed closer to the surface of the gel. The precursor obtained is calcined at 900 °C for 2 h to result in HAP.

We also tried to carryout the reaction with a mixture of succinic and citric acid as fuels and the ratios are given in Table 1. Samples are named as BCCS (Table 1). All the precursors were calcined at 900 °C for 2 h.

3. Characterization

Phase purity of the synthesized hydroxyapatite sample was analyzed in Philips D-500 X-Ray Diffractometer, using Cu Kα, Ni filtered radiation. Various group frequencies of the bioceramic products were determined using FT-IR (Thermo Nicolet, Avatar 330 FTIR Spectrometer, USA) studies using KBr pellet sampling technique. The morphology of the synthesized hydroxyapatite was studied and evaluated by scanning electron microscopy (Stereoscan 440, Leica, UK).

4. Chemical analysis

The calcium/phosphorous ratio of the samples was measured by wet chemical method. The phosphorus content was analyzed colorimetrically. Calcium was estimated through standard complexometric titration by EDTA method. The Ca:P ratio was found to be 1.67 for all the samples.

5. Results and discussion

The energetics of the combustion reaction is dependent upon the ligand groups of the fuel and the compositional ratio of fuel to nitrate. The addition of citric acid to aqueous calcium nitrate solution gives a transparent calcium citrate solution whereas with succinic acid it gives a transparent calcium succinate. Both citric acid and succinic acid act as a fuel for combustion as well as it forms a polymer matrix, which avoids the precipitation of ions. In sample BCC, the citrate–calcium–phosphate solution on heating forms a transparent gel which undergoes self-ignition at 185 °C and forms a black coloured precursor with the evolution of large amounts of gases whereas in the sample BCS, the succinate–calcium–phosphate gel undergoes self-ignition at 425 °C and forms a pale yellow precursor. In order to provide sufficient oxygen supply the combustion was performed in an open chamber in both the cases. The auto ignition temperature is 290 °C when mixed fuel is used irrespective of the ratio between succinic to citric acid (Table 1). The temperature measurement is done using thermometer until the gelation occurs. When the gel starts to decompose, a thermocouple mounted closer to the surface of the gel is used to measure the temperature. For all samples the transformation of solution to gel state takes around 2 h and the time taken for the gel to reach the auto ignition temperature is approximately 20 min. Combustion reaction takes place for 1–2 min based on the fuel ratio.

Swelling of gel before ignition is due to the evolution of carbon dioxide produced by the decomposition of citrate and succinate. The evolution of brown coloured fumes before ignition indicates the formation of nitrogen dioxide as one of the gaseous products due to the oxidation of gel matrix by nitric acid. The precursor formed is calcined at 900 °C for 2 h to result in hydroxyapatite. The calcination temperature of the precursor was chosen based on the phase diagram of hydroxyapatite and various calcium phosphates.

The FT-IR spectrum of the samples BCC (Fig. 1) and BCS (Fig. 2) show the characteristic peaks corresponding to OH^- (631 and 3571 cm^{-1}) and PO_4^{3-} (570, 602, 1045, 1089 cm^{-1}) vibrations, together with the weak bands of the CO_3^{2-} group (875 and 1450 cm^{-1}). Carbonate can substitute in $Ca_{10}(OH)_2(PO_4)_6$ on two possible sites [14] which are distinguished by FT-IR spectroscopy. Our results indicate that the samples are carbonate substituted hydroxyapatite. Intense

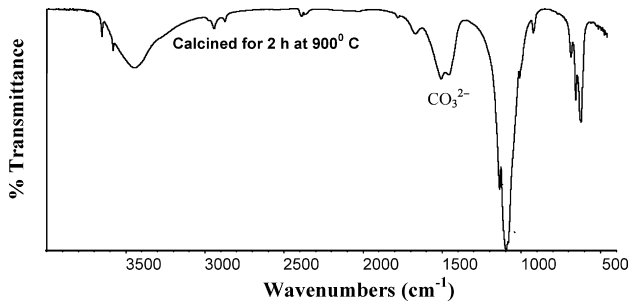


Fig. 1. FT-IR spectrum of HAP synthesized using citric acid as fuel.

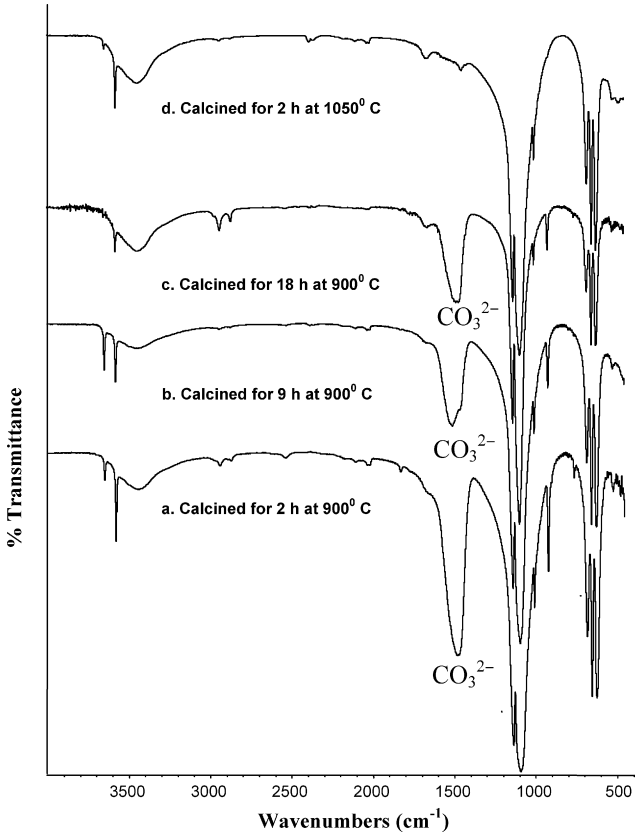


Fig. 2. FT-IR spectra of HAP synthesized using succinic acid as fuel.

peaks at 875 and 1450 cm^{-1} indicate the substitution of carbonate ions in phosphate site (site B). Intense peaks at 3571 cm^{-1} and absence of peak at 1550 cm^{-1} indicates that there is no carbonate substitution in OH site (site A). FT-IR spectra of BCS sample (Fig. 2) shows more intense peaks for carbonate ions compared to BCC sample (Fig. 1) which is due to the formation of calcium carbonate as an impurity phase which is evident from the XRD pattern (Fig. 4).

In Fig. 3, XRD pattern of BCC sample is shown which reveals the formation of single phase HAP. The smaller planar CO_3^{2-} group substitution for larger PO_4^{3-} tetrahedral group leads to decrease of the *a*-axis of the apatite lattice which is evident from the above values. The powder X-ray patterns of BCS samples obtained by calcining the precursors for different time periods are shown in Fig. 4. It shows the formation of HAP along with small amounts of $CaCO_3$ as impurity. With increase in time duration, calcium carbonate content is decreased and at

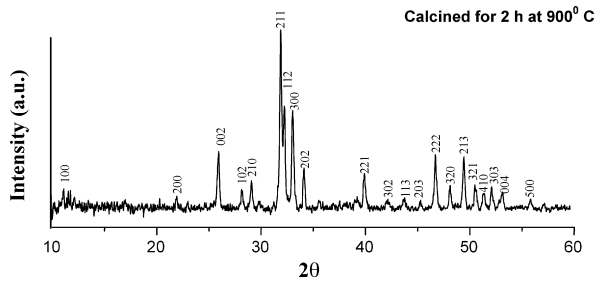


Fig. 3. XRD pattern of HAP synthesized using citric acid as fuel.

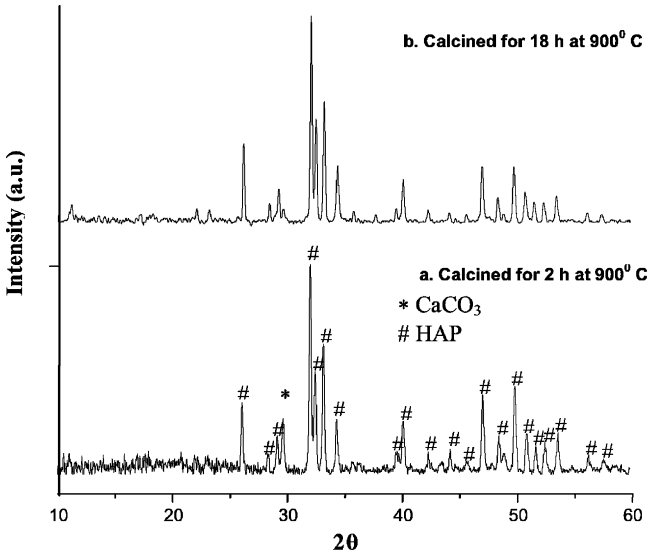


Fig. 4. XRD patterns of HAP synthesized using succinic acid as fuel.

18 h it is completely removed. FT-IR (Fig. 2) also shows that carbonate decreases with more calcination time at 900 °C. The substituted carbonate ions present in trace amounts even in 900 °C (18 h) sample detected by FT-IR is completely removed from the product by calcining at 1050 °C for 2 h (Fig. 2d). The refined lattice parameter values calculated using powder XRD are $a = 9.376$ Å and $c = 6.846$ Å for BCC sample and $a = 9.385$ Å and $c = 6.857$ Å for BCS sample in agreement with JCPDS data. The XRD patterns of BCCS1 and BCCS4 (Fig. 5) show the formation of pure β-TCP as the product when mixed fuel is used. BCCS2 and BCCS3 also form β-TCP revealed by XRD. Refined lattice parameters of TCP are $a = 10.419$ Å and $c = 37.372$ Å in agreement with JCPDS data. FT-IR spectra (Fig. 6) also confirm it. The absence of peaks due to OH is clearly seen. The SEM micrographs of hydroxyapatite

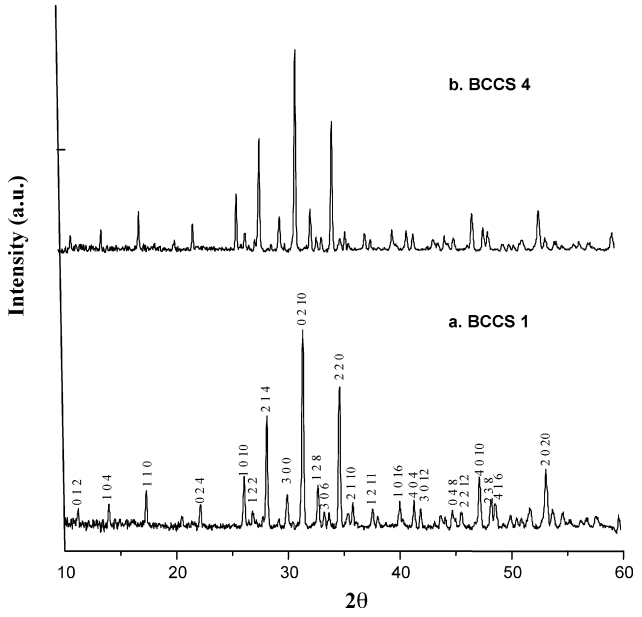


Fig. 5. XRD patterns of tricalcium phosphate synthesized by mixed fuel.

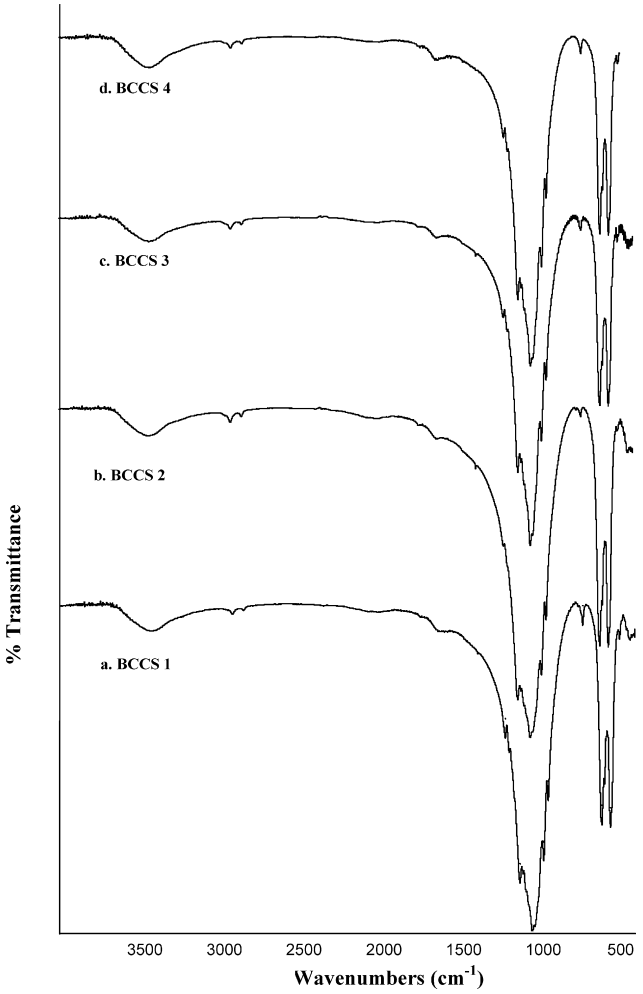


Fig. 6. FT-IR spectra of tricalcium phosphate synthesized by mixed fuel.

powders synthesized using the different fuels are shown in Figs. 7 and 8. It shows a distribution of large number of small particles with agglomeration along with pores. The dimensions of majority of the particles may be in the nanoregime.

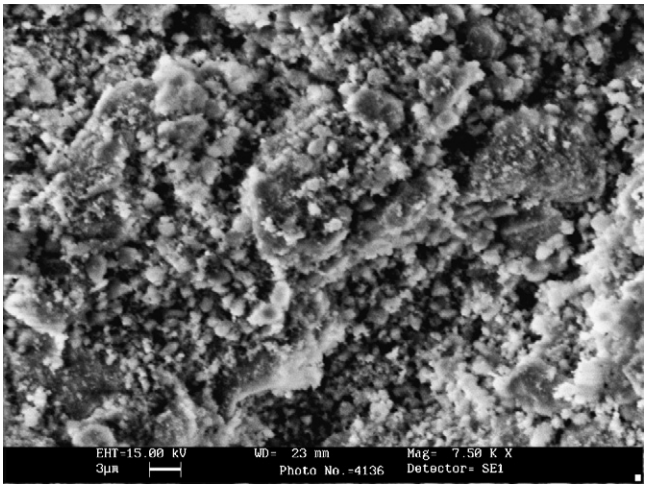


Fig. 7. SEM micrograph of hydroxyapatite synthesized using succinic acid as a fuel.

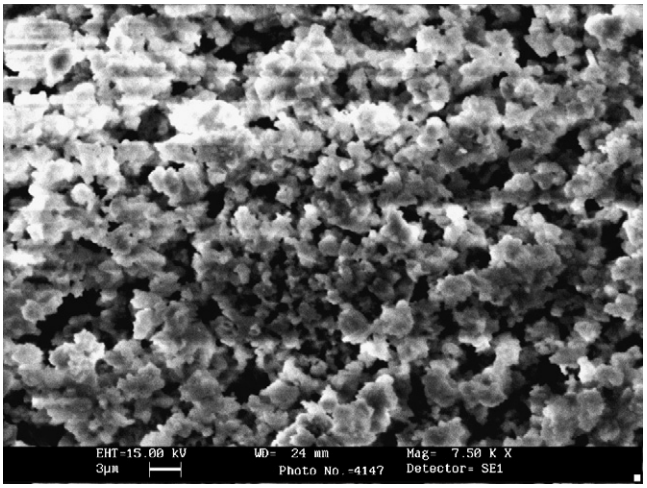


Fig. 8. SEM micrograph of hydroxyapatite synthesized using citric acid as a fuel.

As synthesized precursor of mixed fuel (Fig. 9a) is mostly amorphous and the as synthesized precursor of single fuel (Fig. 9c) shows the formation of HAP. Precursor of single fuel (succinic acid) calcined at 500 °C shows only hydroxyapatite (Fig. 9d). XRD patterns of precursor obtained using mixed fuel calcined at 500° C (Fig. 9b) shows the presence of both hydroxyapatite and tricalcium phosphate whereas the XRD patterns (Fig. 5) of precursor calcined at 900 °C show the presence of β-tricalcium phosphate only when mixed fuels are employed.

Molar heats of combustion of citric acid and succinic acid are 1983 and 1492 kJ/mol, respectively. When any one of the substance is used as a single fuel the energy released seems to be less which is evident from the experimental finding that there is only 80 °C rise of temperature at the time of combustion whereas in the case of mixed fuels the temperature rise is

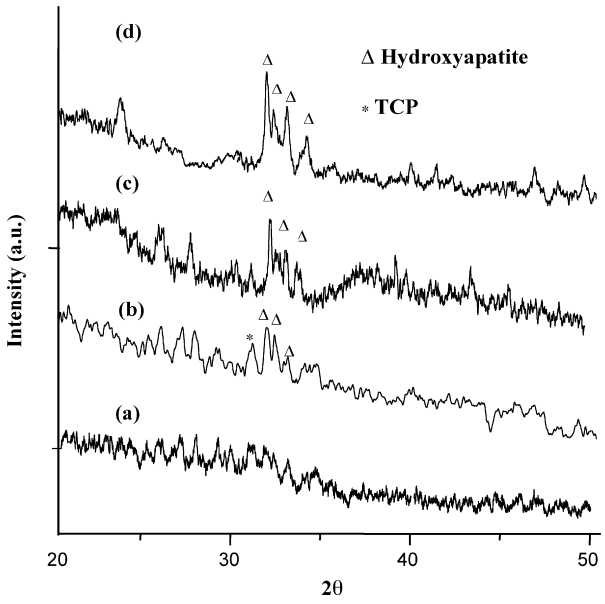


Fig. 9. XRD patterns of precursor as synthesized by (a) mixed fuel method; (b) mixed fuel calcined at 500 °C; (c) single fuel method; (d) single fuel calcined at 500 °C.

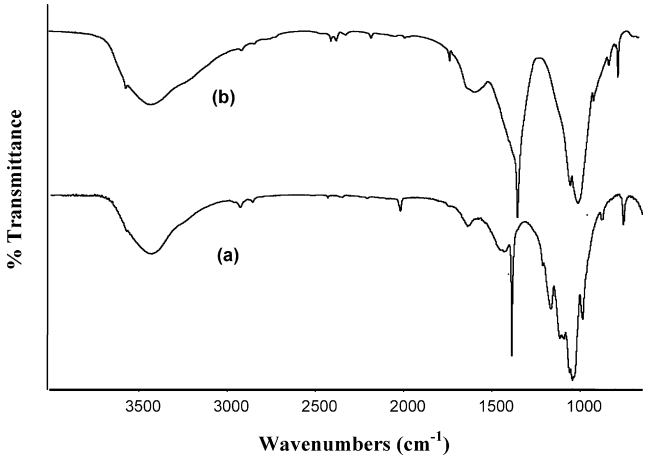


Fig. 10. FT-IR spectra of the precursors by (a) mixed fuel and (b) single fuel (succinic acid).

around 140 °C. This shows that heat of combustion is more for the mixed fuels than for the single fuel which results in the formation of β-TCP.

Slosarczyk et al. [18] reported the influence of carbonate substitution on phase stability of carbonated hydroxyapatite. As the consequence of CO_3^{2-} groups replacing the PO_4^{3-} ones, accompanied by the increase in Ca/P ratio, the obtained non-stoichiometric carbonated apatites are thermally less stable than that containing no substitutions. Presence of carbonate ions in the structure lowers thermal stability of hydroxyapatite resulting in its decomposition in the temperature range of 800–900 °C leading to β-tricalcium phosphate as the secondary phase.

The mechanism proposed for the decomposition of hydroxyapatite is

$$Ca_{10}(PO_4)_6(OH)_2 \rightarrow 2\beta\text{-}Ca_3(PO_4)_2 + Ca_4O(PO_4)_2 + H_2O$$

$$Ca_{10}(PO_4)_6(OH)_2 \rightarrow 3\beta\text{-}Ca_3(PO_4)_2 + CaO + H_2O$$

Ellies et al. [19] reported both tricalcium phosphate and calcium oxide as decomposition phases but failure to locate tetra calcium phosphate could have been due to overlapping of TCP peaks over tetra calcium phosphate peaks.

XRD patterns (Fig. 9) of precursors by single fuel (succinic acid) and FT-IR (Fig. 10) of precursors by single fuel (succinic acid) show the presence of less carbonated hydroxyapatite which is stable, whereas the XRD (Fig. 9) and FT-IR (Fig. 10) of the precursor of mixed fuels shows both β-tricalcium phosphate and carbonated hydroxyapatite phase. Even though the relative intensity of carbonate peak to phosphate peak in both the samples is equal in the FT-IR spectra of precursors (Fig. 10) the intensity of carbonate peak for mixed fuels sample is only due to the substituted carbonate in hydroxyapatite whereas in the case of single fuel precursor the intensity of the carbonate peak is due to both substituted carbonate and calcium carbonate phase present in the precursor. Also in the case of mixed fuels intensity of the phosphate peak is due to both TCP and HAP but the carbonate peak is only due to substituted carbonate of HAP. Hence we conclude that the mixed fuel precursor consists of more substituted carbonate than the single fuel precursor. The formation of tricalcium phosphate is due to the decomposition of more carbonate substituted apatite by higher heat of combustion released by the mixed fuels as revealed by higher rise in temperature as discussed earlier.

Increasing carbonate content in hydroxyapatite lattice is found to bring down the decomposition temperature [20,21] at which hydroxyapatite decomposes to tricalcium phosphate and calcium oxide. At 900 °C the carbonated apatite produced by mixed fuel is totally converted into β-tricalcium phosphate which may indicate that the amount of carbonate content is more. The carbonated apatite produced by single fuel method is stable due to the lower amount of carbonate ion substitution. The reason attributed for the poor stability of more carbonated apatite is as the carbonate ions substitutes the phosphate sites the Ca:P ratio moves towards higher value [22,23] where TCP is the more stable phase.

The average crystallite size of HAP powder obtained by single fuel method was determined by Debye–Scherrer formula [24]

$$D = \frac{0.9\lambda}{B\cos\theta}$$

where D represents mean crystalite size, B stands for full width at half maximum of the peak, λ the wavelength and θ is the diffraction angle. The crystallite size of all products is in the range of 50–65 nm.

6. Conclusion

The present work demonstrates the role played by fuels on phase formation of calcium phosphate bioceramics by combustion method. Also it is shown that by adding citric acid to succinic acid the auto ignition temperature of succinic acid can be brought down to a lower temperature. A mixture of fuels always leads to TCP as a major product where single fuel results in carbonated hydroxyapatite.

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