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Characterization of Tricalcium Phosphate Powder Prepared by Rapid Reaction Between $Ca(OH)_2$ and H_3PO_4

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Abstract— The present study concerns the characterization of the apatitic tricalcium phosphate ($Ca_9(HPO_4)(PO_4)_5(OH)$: TCPa) prepared by rapid reaction between $Ca(OH)_2$ and H_3PO_4 at room temperature without pH adjustment. The formation of pure β-$Ca_3(PO_4)_2$ without impurity phase such as pyrophosphate ($Ca_2P_2O_7$) or hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) was confirmed by heat treatment of TCPa at 1000°C for 15h. The Fourier Transform Infrared Spectroscopy and X-ray Diffraction analysis show the change of OH^-, HPO_4^{2-} and PO_4^{3-} functional groups depending on the calcination temperature. The change of lattice parameters, were refined using FULL PROF program and compared to the standard values and to values found in the literature. The reactivity and β-TCP's purity were confirmed by rapid dissolution in acid solution.

Index Terms— Tricalcium phosphate, Neutralization method, Thermal treatment, Calcination time, Dissolution.

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1 INTRODUCTION

INTENSE interest has been shown recently towards using calcium phosphate ceramics as bone substitutes in dental and orthopedic application [1], [2]. The tricalcium phosphate (β-$Ca_3(PO_4)_2$: β-TCP) has been shown to be resorbed in vivo with new bone growth replacing the implanted TCP [3]. This property is a significant advantage of β-TCP to other biomedical materials which are not resorbed and replaced by natural bone. The literature on bone substitutes considers this biological performance is mainly related to the conditions and methods of preparation of β-TCP.

The synthesis of pure tricalcium phosphate powder is not so much reported in the literature review compared with that of hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$: HAP). The most common method is a "wet-Chemical" synthesis which results in the formation of a Ca-deficient apatite ($Ca_9(HPO_4)(PO_4)_5(OH)$: TCPa). Upon heating to 700-800°C, Ca-deficient apatite will transform to the tricalcium phosphate (β-TCP), with the loss water of as described by

$$Ca_9(HPO_4)(PO_4)_5(OH) \rightarrow \beta-Ca_3(PO_4)_2 + H_2O \quad (1)$$

equation (1).

A specific difficulty linked with Ca-deficient apatite synthesis is the high variability of the powder composition after calcinations even for every low variations of the calcium/phosphorus molar ratio of the initial precipitate [4]. Pure β-TCP is formed after calcinations of Ca-deficient apatite with molar ratio Ca/P= 1.50. For Ca/P molar ratio higher than 1.50, HAP is formed as a second phase. For Ca/P value low than 1.50 another second phase appears: Calcium pyrophosphate ($Ca_2P_2O_7$). The biological properties as resorbability is depend strongly on the composition and the ratio Ca/P [5], [6]. The presence of pyrophosphate or hydroxyapatite phase, can limit the resorbability of tricalcium phosphate. Consequently, their preparation needs a high level of control if one wants to obtain reproducible purity and precise techniques of characterization must be used. To prevent the formation of phasic impurities, pure TCPa is obtained generally under heating (70-85°C) and of pH range (8-11) adjusted by addition of acid or base [7], [8]. Another study using room temperature but with maturation time more than 24h, the Ca/P ratio must tend to stability [9]. Another study shows that at pH of 7 and at temperature of 30°C a ripening of 10 h must be used [8].

In the present study, the apatitic tricalcium phosphate (TCPa) with a Ca/P molar ratio of 1.50, was prepared by a rapid reaction between $Ca(OH)_2$ and H_3PO_4 at room temperature and without pH adjustment. This preparation can be regarded as a non-polluting and a low-cost method of producing.

The transformation of TCPa to the pure β-TCP without phasic impurity was examined according to the NFS 94-067.

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2 MATERIALS AND METHODS

2.1 powders synthesis

Apatitic tricalcium phosphate powders were synthesized by reaction between the calcium hydroxide and orthophosphoric acid according to the method described by Akao et al with some modifications. The calcium oxide powder, prepared by calcination of $CaCO_3$, is dispersed in double distilled water. The solution of orthophosphoric acid (1mol/l) was then added rapidly at 22 °C into $Ca(OH)_2$ suspension (0.5 mol/l) using a vigorous stirring (500T/min). The calcium / phosphor molar ratio of the reagents is fixed at 1.50 ± 0.02 and the used reagents were of analytical grade. The variation of pH during the preparation is reported in figure 1. The pH values were measured using a pH-meter (HANNA INSTRUMENT). The resulting precipitate was filtered, dried at 60°C/12h and calcined at different temperatures for 15 h.

2.2 Characterization of powders

Infrared Spectra of powders were recorded on a Fourier Transform Spectrometer (SHIMADZU FTIR-8400S) with a resolution of 4 cm^{-1} and 20 scans. 1% of the powder samples were mixed with 99% KBr, and then pressed in a 13 mm die, the range of FTIR-spectrum was taken of 400 to 4000 cm^{-1}

The formed phases were identified on dried and calcined powder using the X-ray diffraction (diffractometer BRUKER D8 ADVANCED). Copper Kα radiation (λ= 1.5406) produced at 50kV and 20mA scanned the diffraction angles 2θ in the range 10-65°, using a step size of 0.02° and a step time 30s. Crystallographic identification was accomplished by comparing the experimental XRD patterns to standards complied by the joint committee on powder diffraction standards (JCPDS), which was card #09-0432 for HAP, #09-0169 for β-TCP and #09-0346 for pyrophosphate. Lattice parameters were determined using the Rietveld refinement FULL PROF program version 2012. The crystallite size of the calcined samples was calculated using the Scherrer formula (2).

$$D = 0.9\lambda/\beta\cos\theta \qquad (2)$$

Where λ is the wavelength of the used Cu Kα radiation, β is the full width at the half maximum of the β-TCP line and θ is the diffraction angle.

Laser diffraction was used to analysis particle size on the Mastersizer 2000 (from Malvern Instruments Ltd.). The surface area was determined by the BET method based on nitrogen adsorption at the surface of the powder (Micromeritics ASAP 2010).

2.3 Dissolution tests

The dissolution tests were carried out under acidic medium at pH close to 4.8±0.2 involved by the in vivo degradation of the phosphocalcic implants [10]. The calcined powder was manually ground, and the particles less than 125 μm were separated by sieving. 200 mg of powder was soaked in 100 ml of buffer solution of acetic acid-sodium acetate (pH=4.8 ± 0.2) at constant temperature of 37.0 ± 0.1°C for fixed periods of time. The solution was kept under mechanical agitation and at sufficient speed to keep all the grains in suspension. At the end of each period, the liquid phase was separated and analyzed. The ion concentration of calcium was determined by atomic emission spectrophotometer, argon plasma and inductive coupling (ICPAES) (ThermoJarrel Ash. Atom Scan 16).

3 RESULTS AND DISCUSSION

3.1 Curve of pH

The influence of pH on the formation of calcium phosphates is linked to the properties of phosphate-containing solutions. Due to the triprotic equilibria in these systems, variations in pH alter the relative concentrations of the protonated forms of orthophosphoric acid and thus both the chemical composition and the amount of the calcium phosphate that forms by direct precipitation. This complex equilibrium makes the control and prediction of CaP precipitation much more difficult.

In this study, apatitic tricalcium phosphate powder was prepared by the neutral reaction of calcium hydroxide and orthophosphoric acid without pH adjustment. The curve reported in Fig.1 shows the change in pH during the preparation: a region (a) corresponds to the hydration of calcium oxide; the pH is equal to 13. The second region (b) was obtained after addition of the acid solution and the neutralization of calcium hydroxide. The result shows that the pH at the end of reaction is stabilized at 6.5.

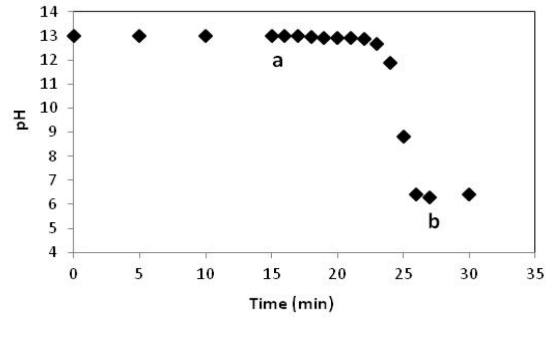


Fig.1. Variation of pH during the hydrataion of CaO and the precipitation of apatitic tricalcium phosphate.

From the experimental results, in the bulk pH high than about 12 favors the precipitation of an amorphous hydrate calcium phosphate $Ca_9(PO_4)_6,nH_2O$ according to the reaction (3). The tricalcium phosphate begins to be hydrolyzed as soon as precipitated, and leads to the formation in the solid of HPO_4^{2-} and OH- ions according to the reaction (4). This transition which causes a decrease in pH.

$$9Ca + 6PO_4 + nH_2O \rightarrow Ca_9(PO_4)_6,nH_2O \ (TCPh) \quad (3)$$

$$Ca_9(PO_4)_6,nH_2O \rightarrow Ca_9(HPO_4)(PO_4)_5(OH) \ (TCPa) \quad (4)$$

The purity of the synthesized powder was examined by the Fourier Transform Infrared Spectroscopy and X-ray Diffraction analysis according to the NF S 94-067.

3.2 FTIR spectroscopic analysis

The specter of FTIR (Fig.2.a) shown the characteristic bands of apatitic phosphate groups: v_2 PO_4 (460 cm^{-1}), v_4 PO_4 (560-600 cm^{-1}), v_1 PO_4 (960 cm^{-1}) and v_3 PO_4 (1020-1120 cm^{-1}). The band at 875 cm^{-1} is ascribed to P-O (H) stretching mode of hydrogenophosphate groups. These analyze show that for prepared powder dried at 60 °C, only an apatitic tricalcium phosphate structure is detected. The absence of the bands at 630 cm^{-1} attributed to OH shows that the prepared apatite, dried at 60 °C, is poorly crystallized.

The calcinations of apatitic tricalcium phosphate during 15 hours at different temperatures show the following results: The specter of FTIR (Fig.2b) of the powder calcined at 250°C shown the characteristic bands of phosphate groups and the bands at 630 cm^{-1} attributed to OH groups. At the temperature of 450°C, the specter of FTIR (Fig.2c) shows a band in the region of 727 cm^{-1} characteristic of pyrophosphate groups ($P_2O_7^{4-}$) due to the condensation of HPO4^{2-} groups in calcium-deficient apatite that usually occurs in the range 350-720°C according to a mechanism (eq 5) proposed by Mortier et al [11]. This band disappeared after heat treating at 750°C according to the eq(6). The formation of β-TCP was reported in literature at range 700°C-800°C [12], [13], [14], [15] and within the range of 650-750°C reported by Ishikawa and al [16].

The specter of FTIR (Fig.2e) of the powder calcined at 1000°C show the formation of β-TCB, which confirms the absence of trace of pyrophosphate.

$$Ca_9(HPO_4)(PO_4)_5(OH) \xrightarrow{450°C} Ca_9(P_2O_7)_{0.5}(PO_4)_5(OH) + H_2O \quad (5)$$

$$Ca_9(P_2O_7)_{0.5}(PO_4)_5(OH) \xrightarrow{750°C} 3Ca_3(PO_4)_2 + H_2O \quad (6)$$

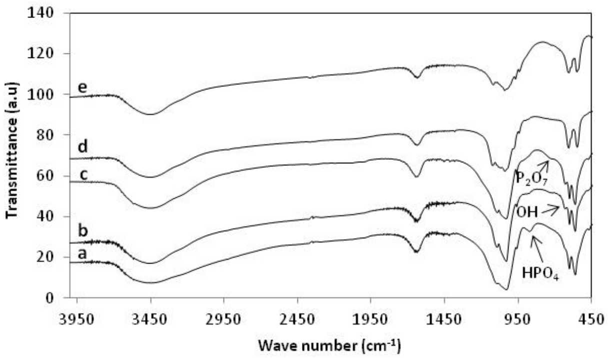


Fig.2. FTIR spectrum of as-prepared Ca-deficient apatite dried and calcined at different temperatures a) 60°C, b) 250°C, c) 450°C, d) 750°C and e) 1000°C.

3.3 X-ray Diffraction analysis

The XRD pattern for the precipitated powder calcined at different temperatures during 15h is illustrated in Fig.3. The calcined powder at 250 and 450°C (fig. 3a and 3b) shows only the apatitic tricalcium phosphate phase poorly crystallized. At 750°C (fig. 3c), a significant transformation was observed of apatitic tricalcium phosphate to pure β-TCP, no presence of another phase (as pyrophosphate (JCPDS N° 009-0346) or hydoxyapatite (JCDPS N° 009-0432), all the diffraction peak positions match well with the standard XRD pattern of β-TCP (JCDPS N° 009-0169). The formation of the pure and well crystallized β-TCP phase is confirmed by the diffraction of X-ray powder calcined at 1000 °C during 15 hours and no traces of impurities were observed (fig. 3d).

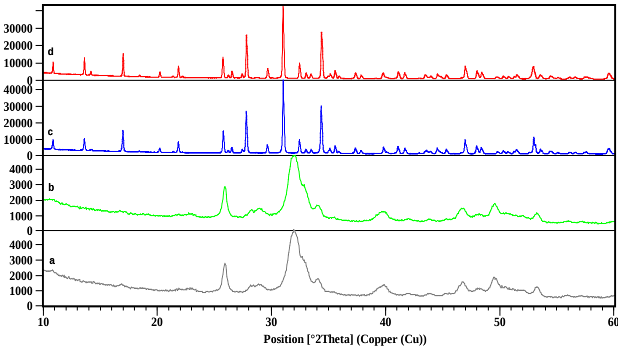


Fig.3. XRD patterns of as-prepared sample calcined at different temperature a) 250°C, b) 450°C, c) 750°C and d) 1000°C

3.4 Rietveld refinement result

The lattice parameters (a, b and c) of calcined β-TCP powder were determined by Rietveld refinement using FullProf (2012) (fig. 4). The refined values are in agreement with the values found by Gibson and al [17], kannan and al [18] and J.Zhao and al [19]. These values are consistent with the standard values (JCDPS N° 009-0169) a=b= 10.4290 Å, c= 37.3800 Å).

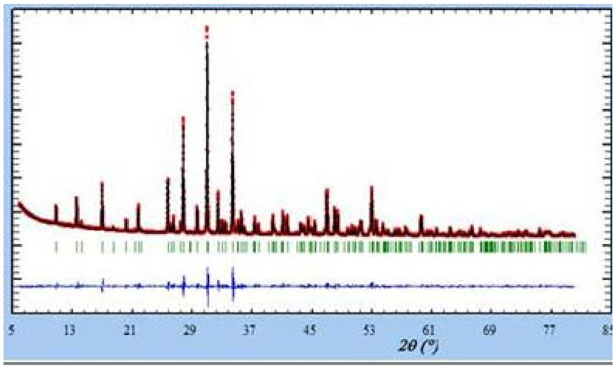


Fig.4. Rietveld refinement analysis of pure β-TCP calcined at 1000°C.

The effect of temperature on the lattice parameters was study. The result shows (Fig.5) that the lattice parameter (a) was decreased with heating of temperature up to 980°C and remains stable up to 1050°C. The lattice parameter (c) was increased with increasing of temperature.

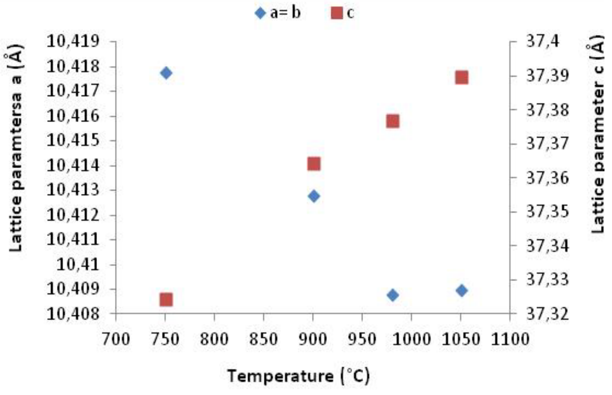


Fig.5. Effect of temperature on the lattice parameters.

According to the literature, almost all of compositions show higher a-axis and c-axis parameter values of β-TCP calcined at 850°C/3h, and then decrease with the temperature increased from 850°C to 1050°C/3h [19]. The study of Gibson and al [17] described the effect of calcinations temperature on the lattice parameters of β-TCP, showing a decrease in the a-axis and c-axis up to 800°C/2h, followed by a steady increase from 800 to 1100°C/2h. The differences of the lattice parameters present between our study and the values of lattice parameters reported in the literature [17], [18], [19] show the transformation of pure phases is not completed at 750°C and further changes tend to occur between 750° and 980°C. The effect of calcinations time can also leads to the variation of the values of the lattice parameters. In the present study, samples were calcined during 15 hours, while other researches were using as calcinations time two and three hours, this difference of time's calcinations has an effect on lattice parameters that occur during the transformation from apatitic tricalcium phosphate to β-TCP. These structural changes probably involve some minor rearrangement in the PO4 tetrahedral. It has been reported that there are three different types' crystallographically non-equivalent PO4 groups in the β-TCP structure [20].

3.5 Crystallites size, size distribution and Specific surface area

The curve of crystallites size of samples calcined between 900 and 1050°C (fig. 6) has shown the increasing of crystallite size when temperature increases and the value remains stable (106 nm) between 980 and 1050°C. Gibson and al found that a crystallites size increase with temperature between 500 and 730°C/2h [19]. Kannan and al [7] found a crystallites size increase with increasing of temperature between 700 and 1100°C. In our study, the increase in crystallite size of powders calcined between 980 and 1050°C when compared to the crystallite size of powders calcined at 900°C and the stability of crystallite size between 980 and 1050°C can caused by effect of calcinations time.

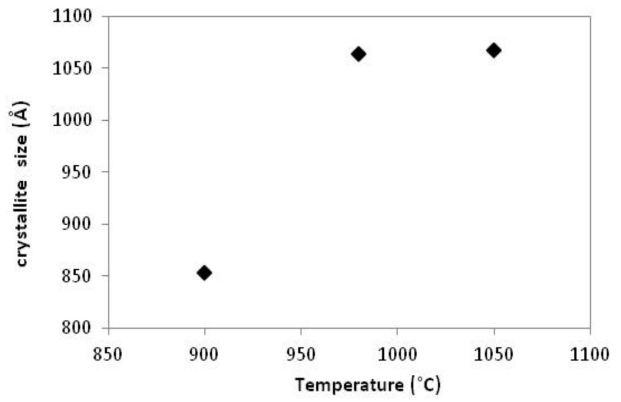
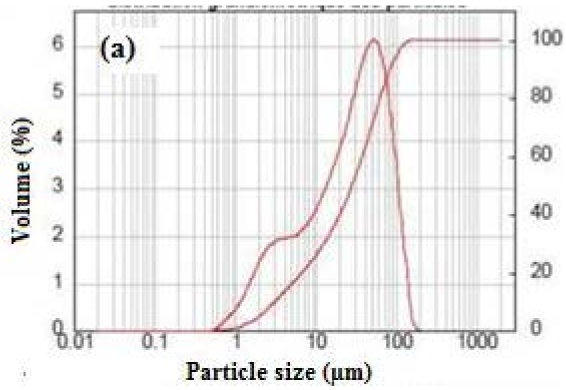


Fig.6. Effect of temperature on the crystallite size of β-TCP

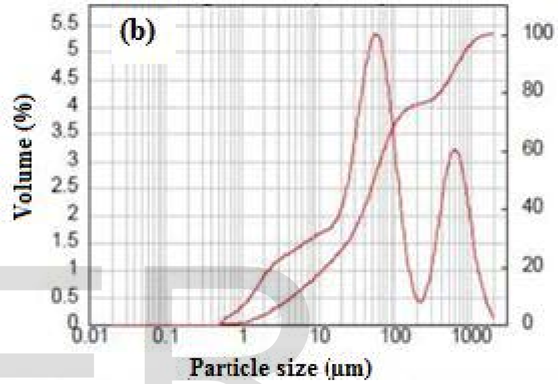
The prepared tricalcium phosphate powders were to be used as precursors for the preparation of the bioceramics. They are therefore called to be shaped and then sintered, so it's very important to know precisely the size and distribution of these particles. We conducted this characterization on the dried (105 °C) and on calcined powder (900 °C). The results are shown in histograms and cumulative values (Fig.7). The particle size distribution of the dried powder is bimodal (Fig. 7). The first population centered about 5 µm and the second majority population located to 80 µm. After calcination, the distribution is more spread out and multimodal (fig.7), with a majority population centered around 84 µm and an average population with a size distribution of about 690 µm. Calcination has an influence on the distribution of the grain size, after calcining the particles grow by agglomeration and lead the new population. This particle size distribution gives the powder a good ability to compaction and shaped.

The measurement of the surface area of apatitic tricalcium phosphate dried at 105 °C present a value 70 m²/g. This value is small than value of hydroxyapatite with molar ratio Ca/P = 1.67 (100 m²/g) prepared under the same conditions. This result can be explained by a strong cohesion between agglomerates due to interactions between groups located on the surface HPO_4^{2-} seeds. This structure gives the powder a good ability to compaction [21].



D(0.10)=3.14µm D(0.20)=6.83µm D(0.80)=63.68µm

D(0.90)=84.65µm D(0.97)=113.56µm



D(0.10)=4.81µm D(0.20)=12.87µm D(0.80)=406.85µm

D(0.90)=690.22µm D(0.97)=1056.86µm

Fig.7. Distribution of the grain size of powder dried at 105°C (a) and calcined at 900°C (b).

3.6 DISSOLUTION TESTS

Fig. 8 shows the results of ion concentrations of Ca^{2+} with the immersion time of prepared β-TCP in acidic solution. The interaction of TCP phase with the solution takes place in a very short time after soaking. The concentrations of Ca^{2+} ion released in the solution increase until 0.5 h, and then remain unchanged after 1 h. The TCP powder is completely and rapidly dissolved.

This result confirms the purity of prepared powder. Indeed, the presence of secondary phases, like pyrophosphate or hydroxyapatite, can limit the dissolution of tricalcium phosphate.

We can conclude that the result of the dissolution test shows evidence of purity and also reactivity of prepared β-TCP.

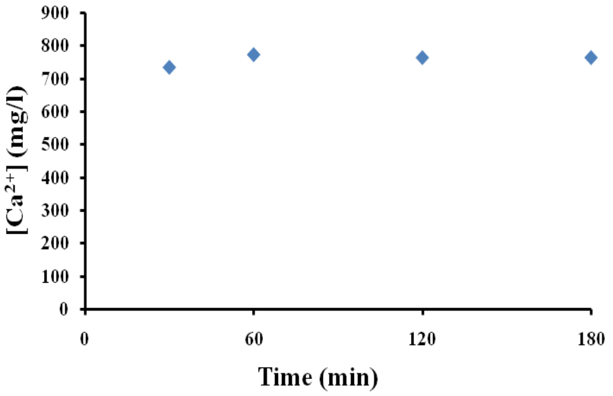


Fig.8. Dissolution of the β-TCP in acidic solution.

4 CONCLUSION

In this study, the apatitic tricalcium phosphate ($Ca_9(HPO_4)(PO_4)_5(OH$: TCPa) was prepared, at room temperature, by rapid reaction between $Ca(OH)_2$ and H_3PO_4. The result of the characterization of the precipitate powder shows that the cohesion between granules and the particle size distribution centred at 80 µm leads to Specific surface area of 70 m^2/g. The change of OH^-, HPO_4^{2-}, PO_4^{3-} functional groups, crystallites size and size distribution depend on the temperature and calcination time. The formation of pure β-$Ca_3(PO_4)_2$ was completed between 750° and 980°C. The purity of prepared β-$Ca_3(PO_4)_2$ was confirmed by rapid and total dissolution in acidic solution.

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