Journal of Industrial and Engineering Chemistry 20 (2014) 1236–1242

Contents lists available at ScienceDirect

Journal of Industrial and Engineering Chemistry

journal homepage: www.elsevier.com/locate/jiec

Short communication

Production of poorly crystalline tricalcium phosphate nanopowders using different mechanochemical reactions

Bahman Nasiri-Tabrizi *, Abbas Fahami

Materials Engineering Department, Najafabad Branch, Islamic Azad University, Najafabad, Isfahan, Iran

ARTICLE INFO

Article history:
Received 28 March 2013
Accepted 1 September 2013
Available online 7 September 2013

Keywords:
Mechanochemical
Tricalcium phosphate
Morphological characteristics
Nanopowder
Reaction mechanism

ABSTRACT

Poorly crystalline nano-sized tricalcium phosphate powders were successfully synthesized by two distinct mechanochemical reactions. Results revealed that the structural features as well as morphological characteristics were influenced by the chemical composition of reagents. The obtained nanopowders exhibited average sizes about 21 and 28 nm. According to the TEM/SEM observations, the synthesized powders showed cluster-like structures composed of spheroidal particles with a mean size of about 23 nm and ellipsoidal particles with an average size of about 30 nm. The proposed method as a new vision in powder technology can be used for mass production of nanostructured tricalcium phosphates.

1. Introduction

Among the various bioceramic materials, amorphous calcium phosphates (ACPs) are one of the most frequent forms of calcium phosphate minerals in biological organisms and play a crucial role in several biomedical applications. ACP is present in many biomaterials and preparations for instance in coatings of metallic endoprostheses, either as a transitory phase or in the end product. It is utilized in self-setting injectable cements, where it is responsible for the setting reaction. Moreover, ACP is found in several composite materials used in odontology as a remineralising phase for enamel and dentine and its inclusion in toothpaste formulations as a remineralising agent for early carious lesions has been proposed [1–3].

The various amorphous calcium phosphates (ACPs) have been distinguished only by Ca/P ratio [4]. Amorphous tricalcium phosphate (ATCP), with an atomic Ca/P ratio of 1.5 and the chemical formula $Ca_3(PO_4)_2{\cdot}xH_2O$, is most widely found in amorphous precipitates obtained in alkaline media (pH range 9–11) [4]. It has been reported that in the absence of mineral ions other than Ca^{2+} and PO_4^{3-} the composition of ACP is restrained to the mentioned chemical formula for charge balance reasons [1]. In more acidic solutions, ACPs can contain HPO_4^{2-} ions instead of PO_4^{3-}, leading to a lower Ca/P ratio. However, such phases are unstable and convert very rapidly into dicalcium phosphate dihydrate (DCPD, $CaHPO_4{\cdot}2H_2O$). In addition, in non-aqueous or ethanol–water media ACPs with a much lower Ca/P ratio than composition of ATCP can be obtained that corresponding to amorphous octacalcium phosphate (AOCP, $Ca_8H_2(PO_4)_4{\cdot}xH_2O$) or amorphous dicalcium phosphate (ADCP, $CaHPO_4$) [5–7]. Also, ACPs with a Ca/P ratio higher than 1.5 can only be obtained in the presence of foreign ions, most frequently carbonate and oxide ions. It should be noted that the composition of ATCP can change on ageing due to the internal hydrolysis. The hydrolysis process led to a range of compositions represented as: $Ca_9(PO_4)_{6-x}(HPO_4)_x(OH)_x$ [8]. In general, ACPs can be synthesized by two main routes which include wet rout (in aqueous medium at low temperature) and dry process (using high energy processing or high temperatures) [9–18]. Depending on the method of the formation and experimental circumstances, the outcomes can show a Ca/P ratio ranging from 1 to 2 or even higher. In the wet processes, the by-product is almost water as a result, the probability of contamination during the process is very low [19]. According to literature [1,3,8], the wet synthesis route of ACP is based on the double decomposition of a calcium and phosphate salt in aqueous or water–alcohol solutions. In addition to the wet procedures, various types of ACPs can be synthesized by dry method [14–17]. For example, a crystalline to amorphous transition has been detected for various calcium orthophosphates at very high (up to 10 GPa) pressures [18]. Among different dry processes, mechanochemical treatment has recently been receiving particular attention as an alternative method to prepare calcium phosphate-based nanopowders with tailored properties [19–21]. The mechanochemical synthesis has benefit of simplicity, high reproducibility, and low processing cost. In this

* Corresponding author. Tel.: +98 3114456551; fax: +98 3312291008.
E-mail address: bahman_nasiri@hotmail.com (B. Nasiri-Tabrizi).

1226-086X/$ – see front matter © 2013 The Korean Society of Industrial and Engineering Chemistry. Published by Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jiec.2013.09.002

method, melting is not essential and the synthesized powders have nanostructural characteristics [22]. Thus, when the mass production of calcium phosphate-based nanopowders is required, the mechanochemical processes can be served.

Although the various types of ACPs have been produced by several researchers in different conditions [9–18], production and characterization of nano-sized amorphous tricalcium phosphates (n-ATCPs) are still a much-discussed question [23]. It has been found that the basic structural units of ATCP are roughly spherical clusters which randomly packed in spherical particles with water in the interstices [23,24]. However, several details in mechanosynthesis of n-ATCPs still remain unclear. Thus, the main purpose of this study was to produce poorly crystalline tricalcium phosphate by two distinct mechanochemical reactions. In addition, structural features and morphological characteristics of the synthesized nanopowders were characterized by powder X-ray diffraction (XRD), Fourier transform infrared (FT-IR) spectroscopy, scanning electron microscopy (SEM), and transmission electron microscopy (TEM) techniques. Based on the obtained data, the reaction mechanism of the formation of n-ATCPs was proposed to clarify the reactions occurring during the mechanochemical process.

2. Materials and methods

Calcium hydroxide ($Ca(OH)_2$, Fluka), anhydrous dicalcium phosphate ($CaHPO_4$, Merck), calcium oxide (CaO, Merck) and phosphorous pentoxide (P_2O_5, Merck) were used as precursor materials. In all the reactions, the ratio of calcium to phosphorous was 3:1 (mole ratio), i.e. the stoichiometric Ca/P content in the composition of ATCP (Ca/P = 1.5). The weight ratio of ball-to-powder, total powder mass and rotational speed used in each preparation were 20:1, 6 g, and 600 rpm, respectively. Two distinct chemical reactions were mechanically activated for 10 h using sealed tempered chrome steel vials and balls. These mechanochemical procedures are as follows:

$$CaO + 2CaHPO_4 \rightarrow Ca_3(PO_4)_2{\cdot}xH_2O \quad (\text{Activated under air atmosphere}, Ca/P = 1.5) \quad (1)$$

$$3Ca(OH)_2 + P_2O_5 \rightarrow Ca_3(PO_4)_2{\cdot}xH_2O \quad (\text{Activated under air atmosphere}, Ca/P = 1.5) \quad (2)$$

Details of milling conditions and composition of powder mixtures are shown in Fig. 1. Phase evolution and structural features of the outcomes were investigated by X-ray diffraction (Philips X-ray diffractometer (XRD), Cu-K_α radiation, 40 kV, 30 mA and 0.02° S^{-1} step scan). All measurements were conducted at room temperature of 25 °C and with the diffraction range of $20^\circ \le 2\theta \le 70^\circ$ at scan speed of 1°/min. "*PANalytical X'Pert HighScore*" software was also employed for the analysis of different peaks. The XRD patterns were compared to standards compiled by the Joint Committee on Powder Diffraction and Standards (JCPDS), which involved card #018-0303 for $Ca_3(PO_4)_2{\cdot}xH_2O$, #037-1497 for CaO, and #033-0297 for $Ca_2P_2O_7$.

The functional groups of products were measured using Fourier transformed infrared (FT-IR) transmission spectroscopy (Perkin Elmer Spectrum 65 FT-IR Spectrometer, USA) in the range 4000–400 cm^{-1} with the resolution of 2 cm^{-1}. For FT-IR analysis, the crushed samples were diluted 100-fold with KBr powder and the background noise was corrected with pure KBr data. Morphological characteristics of the synthesized powders were determined on a scanning electron microscope (LEO 435VP, LEO Electron Microscopy Ltd, Cambridge, UK). Also, the size and morphology of fine powders were observed on a transmission electron microscope (Philips CM10, Eindhoven, The Netherlands) that operated at the acceleration voltage of 100 kV.

3. Results and discussion

3.1. Phase evolution and structural features (XRD analysis)

Fig. 2 shows the XRD patterns and a schematic view of the phase composition of the 10 h milled samples. According to the XRD profiles, for both reactions a poorly crystallized structure was formed after 10 h of milling. The poorly crystallized phase is believed to be a ATCP, which is supported by the Ca/P ratio of 1.5. From Fig. 2d, the phase composition was single-phase $Ca_3(PO_4)_2{\cdot}xH_2O$ with complete agreement with the standard (JCPDS#018-0303). This shows that the synthesized powders had high phase purity. The crystallite size and lattice strain of the specimens were determined using the XRD data according to the following equations [21,25]:

$$D = \frac{K\lambda}{(b_{obs} - b_{std})(\cos\theta)} \quad (I)$$

$$E^2 = \frac{(b_{obs}^2 - b_{std}^2)}{(4\tan\theta)^2} \quad (II)$$

where b (in radians), K, λ, D, E and θ are the structural broadening, shape coefficient (value between 0.9 and 1.0), the wavelength of the X-ray used (0.154056 nm), crystallite size, lattice strain and the Bragg angle (°), respectively.

Fig. 3 displays the effect of chemical composition of raw materials on the structural evolution, average crystallite size and lattice strain of n-ATCP after 10 h of mechanical activation. The line broadening of XRD patterns in 3D view in the range 22–30° are

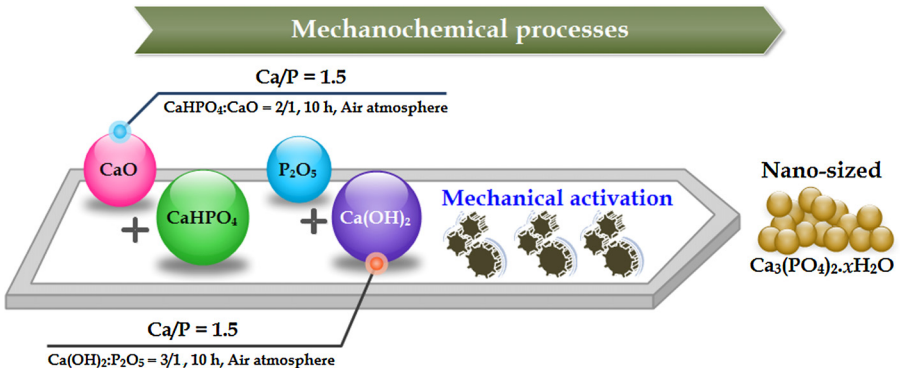

Fig. 1. Details of milling conditions and composition of powder mixtures.