

Amorphous calcium phosphates synthesized by precipitation from calcium D-gluconate solutions

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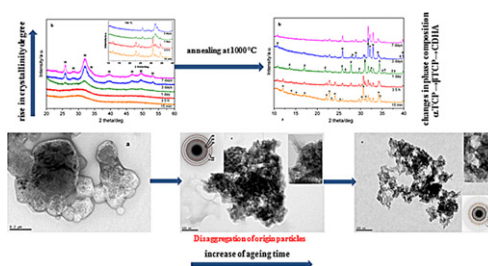
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HIGHLIGHTS

- ▶ Preparation of calcium phosphates from non-toxic calcium D-gluconate solutions.
- ▶ Rise in crystallinity causes changes in phase composition after thermal treatment.
- ▶ β -TCP phase is formed via nanocrystalline hydroxyapatite-like precursor.
- ▶ α -TCP is created from phase with high content of amorphous matrix.
- ▶ Rise of particle disaggregation to well-ordered nanoclusters with aging time.

GRAPHICAL ABSTRACT



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ABSTRACT

The amorphous calcium phosphates were synthesized by the precipitation from non-toxic calcium D-gluconate precursor solutions. The low number of nanosized well-ordered calcium deficient hydroxyapatite clusters separated with amorphous calcium phosphate matrix was found at short aging times. The content of intramolecular water in aggregates decreased with an amount of well-ordered clusters and maturation time. The majority α -tricalcium phosphate phase and calcium deficient calcium phosphate were formed after annealing of samples with a high volume fraction of amorphous matrix and nanocrystalline apatite-like phase respectively. The very fine nanocrystalline calcium deficient hydroxyapatite was intermediate phase during thermal transformation to the final β -tricalcium phosphate. The rise of disaggregation of coarse particles to smaller well-ordered hydroxyapatite clusters with aging time was verified. The different amount and size of nanocrystalline clusters were responsible for the formation of various calcium phosphate phases after thermal treatment.

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1. Introduction

The amorphous calcium orthophosphates (ACP) have a great biomedical importance due to their chemical and structural similarities to calcified mammalian tissues and they are one of the most frequent forms of calcium phosphate minerals in biological

organisms. The ACP phase is an intermediate phase in the preparation calcium phosphates by precipitation [1,2]. The formation of ACP was affected by the presence of various organic additives to starting reactants [3–5] at different pH and they can be synthesized from organic precursors [6], ethanol solutions [7], mechanochemically [8] or e.g. thermal spray synthesis [9]. It has been showed that water addition to ethanol solution of reactant enhances the creation of ACP [10]. Results of EXAFS spectroscopy verified only short range ordering in ACP, which convert to long range with rise of crystallinity of ACP during maturation [11]. Two structurally

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different types of ACP (assigned as ACP1 and ACP2) were found during aging, which differ by morphology of particles and the local environment around Ca atoms. The structure of ACP1 is close to calcium deficient hydroxyapatite whereas ACP2 atom arrangement is similar to β -tricalcium phosphate [12]. The existence of hydrogen bonding via intramolecular water in calcium deficient hydroxyapatite (CDHA) and two water molecule types at different vacancies in apatite crystal were confirmed by NMR spectroscopy [13,14]. Similarly vibrational bands correspond to intramolecular water vibrations were visible in CDHA infrared spectra. The XRD study of CDHA lattice occupancy showed the preferential loss of Ca ions in Ca2 sites and possible compensation with hydrogen phosphate ions [15]. The change in calcium phosphate particle morphologies to more polygonal form and crystallinity with aging time were observed by TEM [16]. The utilization of the pure, nontoxic and biologically friendly starting materials can be interesting in the practice because final calcium phosphate products are free from cytotoxic chemical impurities. Safronova et al. [17] synthesized nanocrystalline hydroxyapatite containing a biocompatible associated product, saccharose, from ammonium hydrogen phosphate and calcium saccharates. They obtained almost pure hydroxyapatite without any secondary calcium phosphate phases.

In this paper, we study the evolution of calcium phosphate phases synthesized by the fast precipitation from calcium D-gluconate and diammonium hydrogen phosphate solutions. The calcium D-gluconate makes possible to use highly concentrated solution (even supersaturated) without its significant crystallization. The aim was to analyze changes in the particle morphology and size, chemical and phase composition of prepared calcium phosphates in dependence on the reactant solution concentrations and aging time.

2. Materials and methods

Calcium phosphates were synthesized by co-precipitation from the calcium D-gluconate (98%, Sigma–Aldrich) and diammonium hydrogen phosphate (analytical grade, Merck) water solutions. Three different concentrations of reactant solutions were used – supersaturated (Sup) (0.200 mol/dm³), saturated (Sat) (0.070 mol/dm³) and undersaturated (Under) (0.035 mol/dm³) solutions in respect to calcium D-gluconate. Calcium D-gluconates solutions were immediately added to diammonium hydrogen phosphate solutions at room temperature. The mixtures were fast stirred at 300 rpm using mechanical stirrer (HEIDOLPH RZR 2020) for 15 min in Ar atmosphere (99.999 vol%) for minimization of the contact between water suspension of precipitates with air CO₂. The mole ratio of Ca/P in the final mixtures was set to 1.67 and the pH was kept at 10.0 by an addition of NH₃ (aq). After 15 min, 3.5 h, 1, 3 and 7 days of aging, the part of precipitates were isolated from suspension, washed with de-ionized water, ethanol; filtered over the membrane filter (Millipore, 0.2 μ m pore size), dried at 105 °C for 4 h and powders were crushed, sieved (Mesh 250) and annealed at 1000 °C for 30 min in air.

The phase composition of samples was analyzed by the X-ray diffraction analysis (XRD, Philips X' PertPro, Cu K α radiation), infrared spectroscopy (FTIR Shimadzu IRAffinity1, 400 mg KBr + 1 mg sample) and the differential scanning calorimetry, thermogravimetric analysis (Mettler 2000C). The morphology and particle size of powder samples were observed by the transmission electron microscopy (JEOL JEM 2100F). The final Ca/P ratios in precipitates were determined by the chemical analysis after dissolution in HNO₃ (1 + 3), where the calcium content was determined by the complexometry (EDTA) and phosphorus as the P–Mo–V complex by the colorimetry. The specific surface areas of synthesized dried calcium phosphates were measured using BET method

(N₂ adsorption at –196 °C, GEMINI). pH values during synthesis were adjusted by the pH-meter (WTW, Inolab 720) with combined electrode SenTix 41.

3. Results

3.1. XRD analysis of synthesized and annealed calcium phosphates, changes in specific surface areas

The XRD patterns of calcium phosphates prepared from solutions with different concentration and aging time are shown in Fig. 1. In all records, it is clearly verified the formation of ACP after 15 min of mixing, which does not differ one to other and they are independent on starting reactant solution concentration. ACP without visible changes in XRD patterns are preserved after 3.5 h of aging in the Sat and Super precipitates whereas it can be still found in Under sample patterns after 1 day maturation. The recrystallization of ACP to apatite like nanocrystalline phase was confirmed after 1 day maturation of Sat and Super samples and gradual continued with prolongation of maturation. The crystallinity sizes in nanocrystalline apatite-like phases were determined from XRD records using the Scherrer equation and the line corresponds to the reflection from (0 0 2) plane was selected for calculations (Table 1). The very small crystallite sizes were measured in Sat (9 nm) and Super (11 nm) powder phases after 1 day aging, which rose up to 19 nm in Super sample after 7 days. In the case of Under sample, the crystallite sizes were 14 and 16 nm after 3 and 7 days aging respectively.

XRD patterns of calcium phosphate powders after annealing at 1000 °C are given in Fig. 2. From detailed analysis of patterns resulted that the crystalline α - and β -tricalcium phosphate (TCP) (JCPDS 29-0359, JCPDS 09-0169) and hydroxyapatite (Hap) (JCPDS 24-0033) were present in samples. The α -TCP phase with a lower fraction of the secondary Hap phase and minority β -TCP phase prevails in Under samples aged up to 1 day. On the other side, the highest volume fractions of α -TCP phase were found after annealing of the 15 min matured Sat and Super samples and the amount of this phase correspondingly decreased in 1 and 3 days matured samples with simultaneously rise in contents of the β -TCP and Hap phases. Note that the high amount of β -TCP phase was found in 3 day matured Sat and Super samples with the lower content of Hap phase and a very small fraction of the α -TCP phase. No similar composition was observed in annealed Under sample. After annealing of samples prepared for a longer aging times, the composition changed and the Hap was majority phase with low amounts of α - and β -TCP phases.

The results of specific surface area measurement of dried powder samples clearly showed interesting fact (Table 1) that the values rapidly increased in samples matured for a longer time (from 1 and 3 days in Sat, Super and Under samples) despite of the rise in the crystallinity size or recrystallization of the calcium phosphate particles with aging time. The specific surface areas were higher in Under sample in comparison with other and decreased with the degree of starting solution saturation. It is evident from the chemical analysis of dried samples, the mole Ca/P ratios were lower than in stoichiometric hydroxyapatite (1.67) and the ratio <1.60 was determined in Under sample up to 1 day aging. After 7 days aging, the Ca/P mole ratio in all samples rose to 1.65, which is value close to the stoichiometric Hap.

3.2. Analysis of FTIR spectra of synthesized and annealed calcium phosphates at 1000 °C

In FTIR spectra of dried Sat and Under samples matured for various time (Fig. 3), the broad band around 3447 and peak at

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