

Wet or dry mechanochemical synthesis of calcium phosphates? Influence of the water content on DCPD–CaO reaction kinetics

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Abstract

Mechanosynthesis of calcium phosphates can be performed under wet or dry conditions. In most papers and patents, grinding under wet conditions was selected. So far, only a few papers were devoted to dry mechanosynthesis of calcium phosphates. To understand why wet mechanosynthesis was preferred, the influence of water addition on the kinetics of the mechanochemical reaction of dicalcium phosphate dihydrate with calcium oxide was investigated. The DCPD disappearance rate constant k and the final reaction time t_f were determined in each case and correlated with the water content present in the slurry. Results showed that the addition water (i) slowed down the reaction rate and (ii) increased the powder contamination by mill material (hard porcelain) due to ball and vial erosion; and that (iii) wet milling did not generate the expected products, in contrast to dry grinding, because porcelain induced hydroxyapatite decomposition with the formation of β -tricalcium phosphate and silicon-stabilized tricalcium phosphate. Consequently, dry mechanosynthesis appears preferable to wet milling in the preparation of calcium phosphates of biological interest.

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1. Introduction

A number of bone substitutes have been developed as alternatives to autogenous and allogeneous bone grafts. Among these synthetic biomaterials, calcium phosphate ceramics have been used successfully in orthopedics, dentistry and maxillofacial surgery [1–4]. Such ceramics are composed either of pure β -tricalcium phosphate (β -TCP) with a 1.5 calcium-to-phosphate (Ca/P) ratio or of stoichiometric hydroxyapatite (HA) with $\text{Ca/P} = 1.67$, or of a mixture of β -TCP and HA (biphasic calcium phosphate ceramic BCP) with $1.5 < \text{Ca/P} < 1.67$. These ceramics are generally prepared either by a solid-state reaction at high

temperature between a calcium salt and a phosphate salt or by heating a poorly crystallized hydroxyapatite or calcium-deficient hydroxyapatite (CDHA) obtained by solution precipitation [5–7].

Mechanosynthesis [8,9] is an alternative route to produce HA or CDHA during which the reaction is activated by mechanical milling. In a mill, the reactants are crushed between balls or ball and wall (horizontal or planetary ball mill, attritor, vibratory ball mill), or between rings or ring and wall (multi-ring media mill). Reagents absorb part of the energy provided by the collisions or frictions that provide the energy necessary for the reaction. Mechanosynthesis can be performed under wet or dry conditions. Wet mechanosynthesis consists in grinding an aqueous suspension of the starting materials (wet attrition or the mechanochemical–hydrothermal method) with a liquid-to-powder ratio ranging generally from 60 to 95 wt.%. In dry

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mechanosynthesis, reagent powders are directly ground without any solvent. In most papers and patents concerning mechanosynthesis of calcium phosphates, grinding was performed under wet conditions [10–24]. Beside our own works [25–30], only a few papers have been devoted to dry mechanosynthesis of calcium phosphates [31–34]. It has been shown that (i) the dry grinding of any acid calcium phosphate with any basic calcium phosphate or CaO, Ca(OH)₂ and CaCO₃ leads to calcium phosphates with intermediate basicity (HA, CDHA, DCPD, etc.) depending on the selected starting materials and their relative amounts [25] with an expected Ca/P $\pm$ 0.01 ratio [26]; (ii) the kinetics of the mechanochemical reaction can be followed [27]; (iii) the reaction rate is dependent on experimental and instrumental parameters [27,28]; and (iv) the substitution of Ca²⁺ or PO₄³⁻ by Sr²⁺ or SiO₄⁴⁻ is possible [29,30]. Thus, to understand why wet mechanosynthesis has been used in preference to prepare calcium phosphates, we investigated the influence of the addition of water on the kinetic constants of the mechanochemical reaction of dicalcium phosphate dihydrate (DCPD) with calcium oxide.

2. Materials and methods

2.1. Chemicals

Chemicals of analytical reagent grade were purchased from Aldrich (HA, CaO, ascorbic acid), Fluka (DCPD), Riedel-de-Haën (Acetone), Prolabo (La₂O₃), Merck (CaCO₃, H₂SO₄ 96%, ammonium heptamolybdate tetrahydrate), Labosi (H₃PO₄ 85%) and Carlo-Erba (HCl 37%). Commercial CaO was heated at 900 °C for 2 h to remove H₂O and CO₂ and stored in vacuum desiccators. The CaO median particle size d_{50} was around 7 μ m (d_{10} – d_{90} = 2–40 μ m; calculated specific surface area = 4.3 m² g⁻¹, Mastersizer, Malvern Instruments). DCPD was used as received. Its median particle size was 8 μ m (1.6–27 μ m; calculated specific surface area, 3.5 m² g⁻¹). Water was first deionized on an ion exchange resin before bi-distillation in a quartz apparatus.

2.2. Materials

The planetary ball mill was a Retsch Instrument with a porcelain vial (500 ml, radius: 5 cm) and porcelain balls (mean diameter: 2.5 cm; mean weight: 24 g; and mean surface area: 20 cm²). The vial eccentricity on the rotating disc was 3.65 cm. Vial and disc rotation speeds were opposite and equal.

X-ray diffraction (XRD) patterns were recorded on an Automatic diffractometer composed of a Philips PW3830 HT generator, a horizontal goniometer (CGR) and X-ray tube Philips 2273/20 using a Cu anti-cathode ($K_{\alpha 1}$ 1.5405 Å) with a nickel filter followed by a quartz monochromator. Differential scanning calorimetry (DSC) analyses were carried out with a Perkin–Elmer DSC 6 differential

scanning calorimeter using indium and zinc as calorimetric and thermometric references. Infrared absorption spectra were recorded on a FTIR Perkin–Elmer Spectrum One (ATR system) in the 4000–400 cm⁻¹ range. Calcium concentrations were determined by atomic absorption spectrometry (Perkin–Elmer AA300) using an air–acetylene flame, with 0.1% w/v lanthanum chloride (La₂O₃ + HCl) as spectral buffer and standards prepared from CaCO₃ + HCl in the range 0–25 ppm. Phosphate concentrations were determined by molecular absorption spectrophotometry (Beckman Model 24, double beam) in the state of phosphomolybdate complex reduced by ascorbic acid (λ = 660 nm) [35] with standards prepared from standardized H₃PO₄ solution in the range 0–30 ppm.

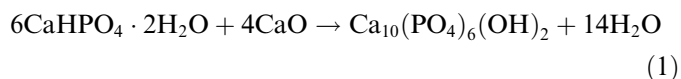
2.3. General grinding procedure

Dicalcium phosphate dihydrate and calcium oxide, each carefully measured to obtain 15 g mixtures with the desired theoretical (1.50, 1.60, 1.67) Ca/P ratio, were placed in the 500 ml vial with five balls. Then, no water (dry mechanosynthesis) or 5, 10, 15, 30, 50 or 100 ml of water was added to the powder (wet mechanosynthesis). The dry powder or the slurries were ground using a rotation speed of 350 rpm and with no change in the rotation direction until the reaction was achieved.

Because kinetics parameters depend linearly on the product of the total mass by the total surface area of the balls [28], the ball mass and diameter were regularly measured accurately after drying at 110 °C for 1 h. All results were then normalized for a 119 g total mass and a 98.5 cm² total surface area.

2.4. Powder evolution

At different intervals, depending of the transformation rate, 50–100 mg of powder or 0.2–1 ml of slurry was taken for XRD or DSC analysis in order to determine the reaction kinetics and to evaluate the changes in the powder composition. Slurry samples were first filtered under vacuum (porosity 4 sintered glass filter) then washed with acetone to remove water and stop any continuation of the reaction occurring similar to calcium phosphate cement setting. Samples obtained by dry mechanosynthesis were also washed with acetone, because of the presence of the small amount of water (5–15 wt.%) generated from the DCPD–CaO reaction [27] (Eq. (1)):



The relative amount of DCPD in the powder at each interval was determined either by XRD (area of a DCPD diffraction peak) or by DSC (enthalpy of the endotherm corresponding to the dehydration of DCPD) [27,36]. By XRD, the area of the DCPD X-ray diffraction peak at $2\theta = 11.60^\circ$ (plane 0.2.0) was calculated on patterns

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