



Effect of phosphorus precursors on the structure of bioactive calcium phosphate silicate systems



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ABSTRACT

The main aim of this work was to synthesize calcium phosphate silicate bioceramics by a low energy-consuming sol-gel method applying various phosphorous precursors (triethyl phosphate, phosphoric acid, and ammonium hydrogen phosphate). The investigations concentrated on the influence of phosphorous initial compounds on the bond and crystalline structures and the material quality. The application of the alkoxide and inorganic P-precursors results in considerably different textures. The inorganic PO₄-containing precursors lead to sol formations. The sol systems can be characterized by a randomly bonded aggregate structure. Monolith gel systems can only be prepared by using TEP. The alkoxide P-precursor more effectively furthers the connection between the phosphorous and silicon tetrahedra than the inorganic phosphate compounds. Over the P-precursors, the catalyst also affects the structure and properties. In the present work, a special attention was paid to identify the P—O—Si bonds in the FTIR and ³¹P NMR spectra. The bond systems were investigated by FTIR, ³¹P and ²⁹Si MAS NMR spectroscopies, the morphology by SEM, WAXS, and XRD measurements, and the water solubility of the ceramic systems also was tested.

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1. Introduction

Several kinds of bioceramics have been studied for the repair, reconstruction, and replacement of diseased or damaged parts of the body, especially the bone. Calcium phosphates (Ca₃(PO₄)₂, Ca₂P₂O₇), and calcium hydroxyapatite (Ca₅(PO₄)₃OH, HAP), have been studied for implants and bone augmentations, because the composition of major inorganic constituent of bone is close to poorly crystalline, calcium deficient, carbonated apatite [1–6]. The bioactivity of the ceramics can be attributed to the formation of an apatite-like layer on their surfaces. This layer considerably enhances the capability of bone bonding. Silicon content favours the formation of apatite-like layers [7]. The calcium phosphate silicate systems (CaPSi) can be effectively used as injectable bone cement, which shows excellent in vitro bioactivity and moderate degradability [8]. In calcium phosphate silicate systems, the phosphorous atoms indicate the crystallinity of the calcium phosphate phase, stabilize the wollastonite at high temperature, and the phase of SiO₂ even at low temperature [9–13]. The speed of the apatite layer's formation depends on the ratio of Ca/Si, specific surface area, and the roughness of the surfaces. The lower SiO₂ and higher CaO content increase, while the higher surface area decreases the speed of layer formation [14–19].

The importance of silicon as a trace element in bone was first identified by Carlisle [20,21], who studied the influence of silicon on the bone formation and calcification. Since Carlisle works many scientists have made Si substituted HAP [2–4,6,22] or P-containing calcium silicate [12].

There are three different ways to obtain ternary compositions in the CaO–SiO₂–P₂O₅ system:

1. *Conventional melt-quenching processes* are starting from inorganic powders (e.g. CaCO₃ [2–3,23–28,29]; SiO₂ [1–4,23–30] and Ca(H₂PO₄)₂ [23,24]; CaHPO₄ [1,4]; H₃PO₄ [26–28,53–56]; NaH₂PO₄ [29]; (NH₄)₂HPO₄ [29,32]; Ca₂P₂O₇ [2,3]; Ca₃(PO₄)₂ [33]; or P₂O₅ [30]). The grind, homogenized and pressed disk are generally heated at different temperatures (800–1200 °C).
2. *Sol-gel technique* uses metal alkoxides (e.g. Si(OC₂H₅)₄, TEOS; (C₂H₅O)₃PO, TEP) [57,58] or inorganic salts (e.g. Ca(NO₃)₂·4 H₂O) as precursor and nitric acid [12,16,34–42] or hydrochloric acid [36–41] as catalyst. A typical process for calcium phosphate silicate gels is the cogelation of TEOS, TEP and hydrated calcium salt in an inorganic acidic aqueous or ethanol solutions.
3. *Precipitation method's* starting materials may be NH₃; H₃PO₄; Ca(OH)₂ and silicon acetate [42–46] or TEOS [10,47]. Ammonia is taken as a precipitating agent. The precipitation methods are generally combined with thermal decomposition, in which the precipitated basic salts transform into oxide products.

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In our previous study, an acid- [47,48] and base-catalyzed [49] sol-gel route was developed for calcium silicate systems. Our long-range goal is to produce bioceramics in calcium phosphate silicate systems by means of a sol-gel chemistry developed for calcium silicate systems using various organic and inorganic phosphorous precursors: triethyl phosphate (TEP, $(C_2H_5O)_3PO_3$), phosphoric acid (H_3PO_4), ammonium hydrogen phosphate ($(NH_4)_2HPO_4$). The use of TEP precursor was carried out with ammonia (NH_3) or acetic acid, HAc (CH_3COOH), or without catalyst. Present work focuses on the effect of the phosphorous precursors on the bond systems and the supramolecular structures of phosphorous-containing calcium silicate bioceramics. Over the P-precursors, calcium nitrate and TEOS were provided as starting materials in the sol-gel procedures. The dried and sintered calcium phosphate silicate (CaPSi) materials were characterized by infrared (FTIR), magic angle spinning nuclear magnetic resonance (MAS NMR) spectroscopy, wide-angle x-ray scattering (WAXS), scanning electron microscopy (SEM), and by X-ray diffraction (XRD).

2. Experimental

2.1. Materials and gel synthesis

The calcium phosphate silicate (CaPSi) gel samples were produced by a low energy-consuming sol-gel technique starting from tetraethoxysilane (TEOS, $Si(OC_2H_5)_4$, 98%, Aldrich); triethyl phosphate (TEP, $C_6H_{15}O_4P$, $\geq 99.8\%$, Aldrich) and calcium nitrate tetrahydrate, ($Ca(NO_3)_2 \cdot 4H_2O$, 99%, Reanal) as precursors; 1-propanol (at. Aldrich) as solvent; and acetic acid (99–100%, Reanal), ammonia (25% aqueous solution, Reanal) as catalysts. The synthesis series were repeated starting from inorganic phosphorous-containing precursors, such as phosphoric acid (H_3PO_4 , 85% aqueous solution, Reanal) or diammonium hydrogen phosphate ($(NH_4)_2HPO_4$, at., Reanal). The ratio of precursors (Si: 0.0–2.0 mol; P: 0.1–2.0 mol; Ca: 0–2.0 mol) was varied during the synthesis series. The gelation, the aging as well as the drying processes were carried out at 80 °C. The experiments of the heat treatment were conducted in the range of 100–1000 °C (3–3h). Fig. 1 depicts the outline of the sol-gel preparation routes.

2.2. Characterization methods

Attenuated Total Reflectance (ATR) Fourier Transform Infrared (FTIR) measurements were monitored on Bruker IFS 55 instrument with

diamond ATR head (PIKE technology). All infrared spectra were collected over the range of wavenumber $4000\text{--}550\text{ cm}^{-1}$.

^{31}P Magic Angle Spinning (MAS) Nuclear Magnetic Resonance (NMR) spectra were acquired at 10 kHz sample rotation speed on a BRUKER AVANCE-III 500 MHz (magnetic field 11.744 T) spectrometer with a 4 mm ZrO_2 MAS probe, operating at room temperature. ^{31}P and ^{29}Si Larmor frequencies were 202.46 MHz and 99.36 MHz respectively. A single pulse sequence with approximately 30° flip angle (3 μs) was applied in both cases. Relaxation delay of 20 s was used in ^{31}P measurements, and 60 s delay was used during the acquisition of ^{29}Si data according to the longer relaxation time of silicon. 16–100 scans of 32 K data points were acquired for ^{31}P spectra and 1000–2000 scans of 32 K data points were detected in ^{29}Si measurements. The spectrum width of ^{31}P and ^{29}Si spectra were 300 ppm and 176 ppm respectively. The ^{29}Si chemical shift was referenced to external TMS, while the ^{31}P chemical shift was referenced to an external 80% H_3PO_4 sample. In silica-based systems, the silicon atoms occupy the centre of an oxygen tetrahedron. The silicate units are usually represented by Q^n , referring to a silicon with n bridging oxygens to other silicon atoms. Like the silicon tetrahedra, the phosphorous atoms also form tetrahedral units with bridging (n) and non-bridging oxygens. The PQ^n denotes $O = P(O - P)_n(O - X)_{3-n}$ units, where $X = H, Ca^{2+}$ in our samples. The PQ^0 unit (0 – -2 ppm) can be generally attributed to the orthophosphate (PO_4^{3-}) [50–53], PQ^1 (-6 – -12 ppm) to the pyrophosphate [50–53], and PQ^2 tetrahedron (-20 – -25 ppm) to metaphosphate [51–53,60, 65]. The PQ^3 signal appearances in the range of -30 – -40.

The morphology have been studied by a FEI Quanta 3D FEG scanning electron microscope (SEM). The SEM images were prepared by the Everhart-Thornley secondary electron detector (ETD), its ultimate resolution is 1–2 nm. Since the conductance of the particles investigated is high enough to remove the electric charge accumulated on the surface, the SEM images were performed in high vacuum without any coverage on the specimen surface. For the best SEM visibility, the particles were deposited on a HOPG (graphite) substrate surface.

Wide-angle X-ray scattering (WAXS) measurements were conducted at JUSIFA beamline of HASYLAB at DESY in Hamburg. A 1D MYTHEN detector was used as a WAXS detector. The WAXS data were collected over the 2θ -range of 7–30° with a step size 0.0212°. Identification of phases was achieved by comparing the diffraction patterns with standard PDF cards.

X-ray Diffraction (XRD) measurements were carried out by using a Philips (PW1130) X-ray generator set up with a Guinier-chamber. The chamber has a diameter of 100 mm and the patterns were recorded

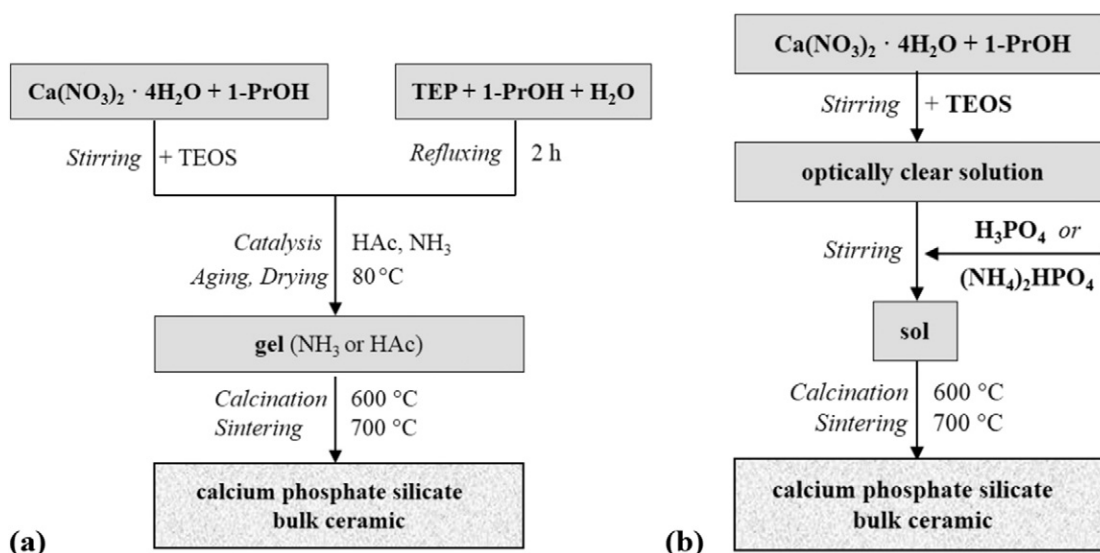


Fig. 1. Outline of the sol-gel preparation with TEP (a) and H_3PO_4 or $(NH_4)_2HPO_4$ precursors (b).

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