SOL-GEL SYNTHESIS OF ZINC CONTAINING

CALCIUM PHOSPHATE BIOMATERIALS

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Abstract $\text{Ca}_{3-x}\text{Zn}_x(\text{PO}_4)_2$ with $x=0$ to 20 mole % was prepared by a sol-gel method starting from $\text{Ca}(\text{OEt})_2$, H_3PO_4 and $\text{Zn}(\text{OAc})_2$ reagents in ethanol. Amorphous and nanosized powders with controlled compositions were obtained. Crystallization into β -TCP occurred at about 600 °C. Zinc substituted for calcium in the β -TCP structure up to $x=12$ mole % as solid solution. For upper x values, the scholzite $\text{CaZn}_2(\text{PO}_4)_2$ phase was detected. Powders were pressed and sintered into ceramics at 1100 °C. Dense ceramics were obtained. EDAX revealed homogenous distributions of zinc, calcium and phosphorus.

INTRODUCTION

Calcium phosphate ceramics are widely used as biomaterials for damaged bones and teeth due to their chemical and structural resemblance with the mineral part of hard tissues. Indeed, calcium phosphate ceramics are not only biocompatible but also bioactive or resorbable.¹ Furthermore, zinc is an essential trace element for human growth, being involved in many biological processes. Recently, zinc has been found to stimulate bone formation and bone growth *in vivo* and *in vitro*.² Zinc could be preferably retained by tricalcium phosphate [β - $\text{Ca}_3(\text{PO}_4)_2$; β -TCP] among calcium phosphate ceramics, judging from its crystallographic and thermodynamic properties.³ β -TCP ceramics are also gradually resorbed in the human body.¹ Therefore, zinc containing β -TCP ceramics could release zinc gradually to stimulate bone growth. They could be considered as candidates for the next generation of bioceramics. The present study was undertaken to synthesize, through a new sol-gel process,⁴ β -TCP including various amounts of zinc:

EXPERIMENTAL PROCEDURE

Ca-Zn-PO₄ powders were precipitated in ethanol. A solution of Ca(OEt)₂ was first obtained by reacting calcium with ethanol. Then, stoichiometric amounts of zinc acetate and *o*-phosphoric acid (85 %) solution were added to the Ca(OEt)₂ solution in a reaction flask (Table 1). The (Ca+Zn)/P molar ratio of reagents was fixed at 1.50 while the Zn/(Ca+Zn) ratio was increased from 0 to 20 mole %. The precipitate was aged for 1 week at 25 °C under N₂. Finally, gels were centrifuged at 4000 rpm for 10 min and dried at 120 °C overnight. The powders were calcined at 850 °C for 5 h in air. TCP-xZn powders were mixed with binders (PEG & PVA, 1 & 3 wt. %) dried at 60 °C and sieved (<75 µm). Powders (0.8 g) were pressed at 1000 kg/cm² into pellets (Ø=16 mm) and sintered into ceramics at 1100 °C for 5 h.

The particle size distribution of gels was measured with a super dynamic laser scattering spectrophotometer (SDLS, Photol 7000) equipped with an Ar laser (λ=488 nm, 900 mW, Spectra-Physics). Data were analyzed by the Marquadt method. X-ray diffraction (XRD) patterns of xerogels and calcined powders were recorded on a Rigaku RINT 2000 diffractometer with a Cu K_α radiation (λ=1.5405 Å, 40 kV, 40 mA). The texture of the ceramics was observed by a scanning electron microscope (SEM, Jeol JSM-6400) equipped with an EDAX analyzer.

TABLE 1. Preparation conditions of calcium zinc phosphate powders

Samples	Ca metal ^a (g ; mole)	Zn(OAc) ₂ .2H ₂ O (g; 10 ³ mole)	H ₃ PO ₄ ^b (g ; mole)
TCP	12.06 ; 0.301	-	23.04 ; 0.200
TCP-0.1Zn	11.99 ; 0.299	0.071 ; 0.324	23.05 ; 0.200
TCP-0.5Zn	11.95 ; 0.298	0.332 ; 1.51	23.07 ; 0.200
TCP-1Zn	11.89 ; 0.297	0.662 ; 3.02	23.11 ; 0.200
TCP-5Zn	11.40 ; 0.285	3.294 ; 15.01	23.05 ; 0.200
TCP-10Zn	10.81 ; 0.270	6.595 ; 30.05	23.05 ; 0.200
TCP-12.5Zn	10.61 ; 0.265	7.685 ; 35.01	23.08 ; 0.200
TCP-15Zn	10.21 ; 0.255	9.881 ; 45.02	23.07 ; 0.200
TCP-20Zn	9.61 ; 0.240	13.175 ; 60.02	23.04 ; 0.200

^a +800 ml of ethanol. ^b +200 ml of ethanol.

RESULTS AND DISCUSSION

Calcium zinc phosphates (TCP-xZn) were precipitated in ethanol starting from calcium ethylate, zinc acetate and *o*-phosphoric acid. The particle size distributions of the gels were measured by SDLS spectrophotometry. For both TCP and TCP-10Zn gels, nearly the same distribution was obtained as shown in Figure 1. The size distributions are centered at 70 nm. The precipitation of nano-sized particles is due to the lowered solvation of ethanol compared with water. The solubility of calcium phosphate strongly decreases in ethanol and hence, the crystal growth is inhibited.⁴ Moreover, XRD analysis revealed an amorphous nature for all the xerogels obtained and no other phases were detected. Therefore, the sol-gel synthesis yielded to amorphous and ultra-fine calcium zinc phosphate powders.

FIGURE 1. Particle size distributions of TCP and TCP-10Zn gels measured by SDLS.

The thermal behavior of calcium zinc phosphates was studied by XRD. For example, the XRD patterns of heated TCP-10Zn powder are shown in Figure 2. Up to 500 °C, the powders remained amorphous. At higher temperatures, crystallization into the β -TCP phase occurred. Patterns of heated TCP-xZn showed a shift of XRD lines to higher angles with the uptake of zinc. This shift is due to the incorporation of zinc in the β -TCP structure. At higher x values than 12 mole %, scholzite $[\text{CaZn}_2(\text{PO}_4)_2]$ was detected. Therefore, amorphous TCP-xZn powders crystallized at around 700 °C and could form $\text{Ca}_{3-x}\text{Zn}_x(\text{PO}_4)_2$ solid solution.

After calcination, the calcium zinc phosphate powders were easily pressed and sintered. For all the ceramics, calculated relative densities and measured shrinkage were

about 95 and 15 %, respectively. EDAX maps revealed homogeneous distributions for calcium, zinc and phosphorus elements in the ceramics. Therefore, no chemical and phase segregation occurred during the sintering process.

FIGURE 2. XRD patterns of TCP-10Zn powder heated at 500, 600 and 800 °C.

SUMMARY

The sol-gel process allows the preparation of amorphous and nano-sized zinc containing calcium phosphates. The powders crystallized at around 600 °C into the pure β -TCP phase. The incorporation of zinc in the structure gave stable $\text{Ca}_{3-x}\text{Zn}_x(\text{PO}_4)_2$ solid solution. Powders are easily sintered into dense and homogenous β -TCZP ceramics. Hence, these new bioceramics could promote bone growth locally by releasing zinc into surrounding body fluid.

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