



Phosphonate-hydroxyapatite hybrid compounds prepared by hydrothermal method

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ABSTRACT

Calcium hydroxyapatite (CaHAp) was prepared in the presence of two alkylphosphonates, the tert-butyl phosphonic acid TBPOH and the 2-carboxylethylphosphonic acid 2-CEPA, by hydrothermal method at 120 °C for 15 h. The modification of hydroxyapatite by grafting organic moieties is confirmed by IR and NMR MAS (¹H and ³¹P) spectroscopy and chemical analysis. X-ray powder diffraction patterns show that the incorporation of organic moieties induces a significant loss of the material crystallinity and a clear increase of the unit cell lattice parameter *a* as function of 2-CEPA grafting rate. The specific surface area (SSA) increases with increasing phosphonate amount especially for 2-CEPA. All techniques show the lower reactivity of TBPOH due to the steric effects of tert-butyl, whereas the 2-CEPA with a linear chain and double acidic functions is more reactive and can replace the OH⁻ groups of the apatitic structure.

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1. Introduction

Calcium hydroxyapatite Ca₁₀(PO₄)₆(OH)₂, (CaHAp) is an important inorganic compound widely used in biology and chemistry [1]. The compound is specifically known for its particular properties of ionic exchange, affinity of adsorption, and its capacity to establish links with organic molecules of different sizes. This material is used in the abduction of rare earths and heavy metals [2], but a limited number of studies concerns the removal of organic compounds from solutions [3,4]. The inorganic–organic hybrids obtained have interesting applications due to the combination of some characteristic properties of the inorganic substrate (mechanical and chemical properties, exchange capacity, bioreactivity, optical properties) with those of the organic graft (polymerization, surface tension). Such modified materials are used in catalysis [5], chromatography [6] and biomedical domain [7].

The interaction between calcium hydroxyapatite and organic molecules has been the subject of many studies [7,8] that show the excellent adsorption properties of apatite. Different processes of fixation have been proposed, based on the interactions between calcium or phosphate ions on the apatitic surface and the anionic or cationic groups of the organic molecule: carboxylate, phosphate, phosphonate and amino groups. Moreover, several studies showed the possibility of ionic exchange between phosphate ions of the apatite and organic ions such as R-PO₄²⁻, R-SO₄²⁻ and R-COO⁻

[9,10]. The substitution of OH⁻ ions of the tunnel by large molecules such as hydroxyethyl methacrylate phosphate has been mentioned in Ref. [7].

The aim of this work is to study the synthesis of CaHAp by hydrothermal method, in the presence of alkylphosphonates. Two phosphonic acids, tert-butyl phosphonic acid (C₄H₉PO(OH)₂) and 2-carboxylethyl phosphonic acid (HOCC₂H₄PO(OH)₂), were used in order to compare the influence of the phosphonate nature on the reactivity with hydroxyapatite, the texture of synthesized materials, their surface area and porosity. In the text, the two alkylphosphonates tert-butyl phosphonic acid and 2-carboxylethyl phosphonic acid will be respectively designed by TBPOH and 2-CEPA.

2. Experimental

Hydroxyapatite (CaHAp) was synthesized by adding a 0.75 M calcium nitrate solution (15 ml) and 0.25 M diammonium hydrogen phosphate solution (25 ml) into a flask containing a dilute solution of ammonium hydroxide in order to keep the pH above nine during precipitation.

The reactions were carried out at room temperature under stirring and nitrogen stream. The obtained solution was treated in autoclave (*V* = 60 ml) under hydrothermal conditions at 120 °C, for 15 h. The products were filtered, washed with double distilled water, and dried overnight at 100 °C [11].

Grafted CaHAp-(TBPOH)/(2-CEPA) was obtained following a similar procedure except for the phosphorus containing solutions that were prepared by mixing (1 - *x*) moles of (NH₄)₂HPO₄ with *x*

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mol ($x=0.05, 0.1$ and 0.2) of tert-butyl phosphonic acid TBPOH or 2-carboxylethylphosphonic acid 2-CEPA.

3. Characterization techniques

The resulting solids were characterized using a Rigaku X-ray powder diffractometer with an INEL CPS120 linear gas detector). The IR spectra were recorded on a Bio-Rad FTS FT-IR spectrophotometer as KBr pellets in the $4000\text{--}400\text{ cm}^{-1}$ region. Solid-state MAS NMR spectra were recorded at 121.5 MHz on a Bruker spectrometer, Advance 300 (rotor 4 mm, spinning rate 2–12 kHz). The calcium and phosphorus contents were obtained by ICP. The chemical analysis of the carbon has been determined according to the ANNE method [12]. Specific surface area (SSA) measurements were performed by BET method (adsorptive gas N_2 , carrier gas He, heating temperature 150°C) using an EMS-53 sorptometer and KELVIN 1040/1042 software (Costech International).

4. Results and discussions

4.1. Elemental analysis

The results of the chemical analysis of the synthesized materials are summarized in Table 1.

The values of Ca/P ratio remain almost constant for all materials. The chemical analysis of carbon element reveals that the weight percentage of the latter increases progressively, with the increase of the grafting rate of 2-CEPA and TBPOH. For the prepared compounds with $x=5$ and $x=10\%$ of organic phosphorus, the rate of carbon is higher for 2-CEPA although it contains less carbon atoms than TBPOH. This may be explained partly by the nature of the aliphatic chain, since the steric effects due to the largest tert-butyl group limits the reactivity of TBPOH. On the other hand, the 2-CEPA can be more reactive since it has two acidic functions (carboxylic and phosphonic). However, for the CaHAp-(TBPOH) ($x=20\%$) compound, the percentage of carbon measured is clearly higher than that treated by (2-CEPA). This could be explained by the formation of a new complex between the $\text{C}_4\text{H}_9\text{PO}_3^{2-}$ groups of TBPOH and the Ca^{2+} ions, as confirmed by DRX and NMR spectroscopy.

4.2. IR spectroscopy

The infrared spectra of pure and modified hydroxyapatite by variable rates of 2-CEPA and TBPOH (Figs. 1 and 2) show the presence of vibration bands characteristic of phosphate group: ν_1 (963 cm^{-1}), ν_2 (459 cm^{-1}), ν_3 ($1036\text{--}1100\text{ cm}^{-1}$), ν_4 ($563\text{--}602\text{ cm}^{-1}$).

For the spectra of samples synthesized in the presence of TBPOH or 2-CEPA, new peaks characteristics of organic moieties are observed such as $\delta_{(\text{CH}_2)}$ (743 cm^{-1}), $\nu_{(\text{COO}^-)}$ ($872, 1568\text{ cm}^{-1}$) and $\nu_{(\text{CH})}$ (2929 cm^{-1}). These bands are more intense for CaHAp-(2-CEPA) ($x=20\%$), in agreement with its higher reactivity than that of TBPOH. For all apatites synthesized in the presence of 2-CEPA or TBPOH, the intensity of hydroxyl band ν_s at 3577 cm^{-1} decreases progressively

Table 1
Chemical composition (± 0.02) of the ungrafted and grafted hydroxyapatite.

Sample	$x\%$	wt.%C	Ca/P
CaHAp	0	0.12	1.61
CaHAp-(TBPOH)	5	0.36	1.60
	10	0.73	1.58
	20	1.70	1.54
CaHAp-(2-CEPA)	5	0.54	1.61
	10	1.02	1.60
	20	1.40	1.59

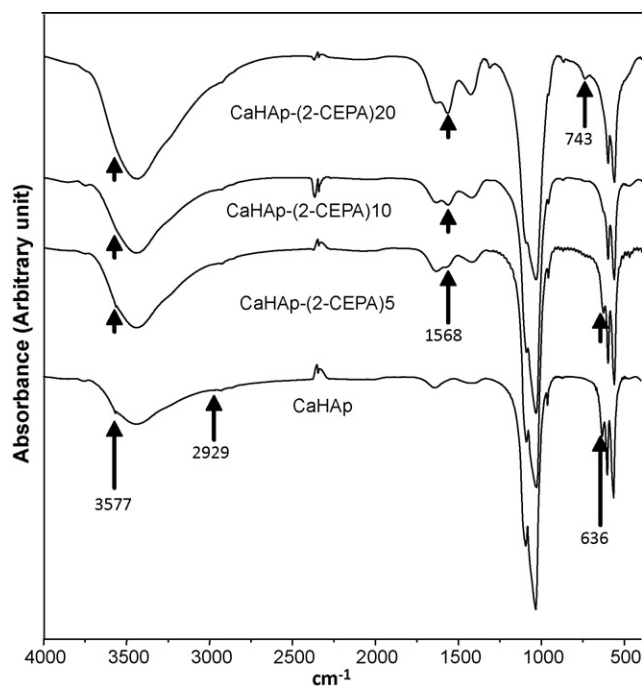


Fig. 1. Infrared spectra of CaHAp-(2-CEPA) with different 2-CEPA rates.

with grafting increasing, in good agreement with the decrease in the degree of crystallinity. For the libration hydroxyl band ν_L at 636 cm^{-1} , the intensity decreases with the increasing of 2-CEPA concentration in the solid phase, up to complete disappearance at $x=20\%$. However, this ν_L band persists for the apatites synthesized in the presence of TBPOH. These results confirm the conclusions of chemical analysis about the major reactivity of 2-CEPA.

4.3. X-ray diffraction

The X-ray diffraction patterns of all products prepared are represented in Figs. 3 and 4.

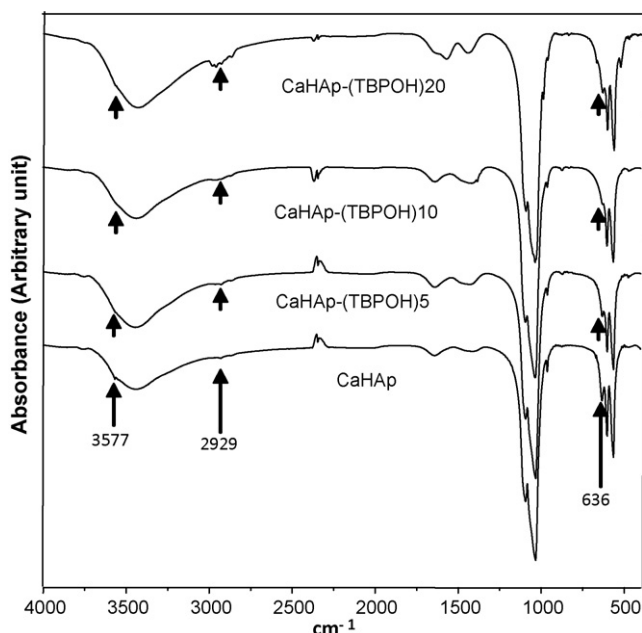


Fig. 2. Infrared spectra of CaHAp-TBPOH with different TBPOH rates.

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