

Studies on structural, textural and acid-base properties of Ca and Sr hydroxyapatites modified with alkali metal/CO₃²⁻ species

L. Silvester^{1,2}, J.-F. Lamonier^{1,2*}, C. Lamonier^{1,2}, R.-N. Vannier^{1,2,3}, C. Pirovano^{1,2,3},
M. Frère^{1,2}, F. Dumeignil^{1,2,4}

¹Univ. Lille Nord de France, Lille, 59000, France

²CNRS UMR8181, Unité de Catalyse et Chimie du Solide, Villeneuve d'Ascq, 59655, France

³ENSCL, Villeneuve d'Ascq, 59655, France

⁴Institut Universitaire de France, Maison des Universités, 10 Boulevard Saint-Michel, Paris, 75005, France

* Corresponding Author, e-mail: jean-francois.lamonier@univ-lille1.fr, telephone: +33(0)320434950

Introduction

Hydroxyapatite (HAP) is the most stable calcium phosphate salt at normal temperatures and pH between 4 and 12. It is the main inorganic constituent of biological hard tissues in animal organisms and is of great interest in catalysis. Stoichiometric HAP, Ca₁₀(PO₄)₆(OH)₂ has a Ca/P molar ratio of 1.67 but in nonstoichiometric forms Ca/P ratio ranges from 1.5 to 1.7 and is represented by the formula Ca_{10-x}(HPO₄)_x(PO₄)_{6-x}(OH)_{2-x}.nH₂O; 0 < x ≤ 1, n = 0-2.5. The apatite lattice is very tolerant of substitutions, vacancies and solid solutions. For example, Ca can be replaced by Sr, Ba, Pb, Na, K, Cu, Co, Pd or vacancies and OH/PO₄ by HPO₄, AsO₄, VO₄, SiO₄ or CO₃. These substitutions enabled HAP to use in various catalytic reactions like dehydration, oxidative dehydrogenation, alkylation, thiolation etc. Since the HAP contains both acid & basic sites in single crystal lattice it can be used in catalyzing the industrial potential Guerbet reaction, where specific tuning of acid-base sites is required [1]. In this work we have studied the structural, textural and acid-base properties of stoichiometric and deficient Ca/Sr HAP whose acid-base properties were tailored using Na/CO₃²⁻ species introduced during precipitation synthesis.

Experimental

HAP solids were prepared by the precipitation method in which 0.56M Ca(NO₃)₂.4H₂O solution and 0.1M (NH₄)H₂PO₄ were titrated at 80°C with an aqueous solution of ammonia to a pH of 9.5-10. The precipitate formed was washed with deionized water, dried and calcined at 400°C. Stoichiometric (Hap) and Ca-deficient (HapD) were prepared as described by Lamonier et al. [2]. Stoichiometric carbonated (Hap-CO₃) and sodium carbonated (Hap-Na-CO₃) hydroxyapatites were obtained by precipitation procedure fixing the (Ca+Na)/P ratio to 2. In this case, carbonates ions introduced in the structure provide from atmospheric CO₂. Two Ca-rich hydroxyapatites were also synthesized, the first one (HapE-CO₃) was obtained using a high Ca/P ratio of solution (5.5) in order to introduce carbonates ions in the Hap structure. More carbonates ions were also introduced in a Ca-rich hydroxyapatite using sodium carbonate instead of sodium nitrate precursor during the synthesis (HapE-Na-CO₃). Stoichiometric (Sr-Hap) and deficient (Sr-HapD) strontium hydroxyapatites were also synthesised similar to calcium HAP.

The crystal structures were specified by powdered X-ray diffraction (XRD). Surface morphology of the samples was studied using Scanning electronic microscopy (SEM). Surface areas were measured with conventional BET nitrogen adsorption apparatus. The different HAP's were also characterized using Infrared, Raman and X-ray photoelectron spectroscopies. Thermal stability of the solids evaluated under flowing air using thermo gravimetric analysis (TGA). Bulk Ca/P ratios of HAP were determined by inductively coupled plasma analysis (ICP). Acidic properties of different HAP's were studied by 2-phenylethylamine (PEA) thermal desorption in a thermogravimetric (TGA) apparatus. Results from N1s XPS study of the surfaces saturated with PEA probe complemented the study permitting the determination of the nature of acid sites on different samples [3].

Results and Discussion

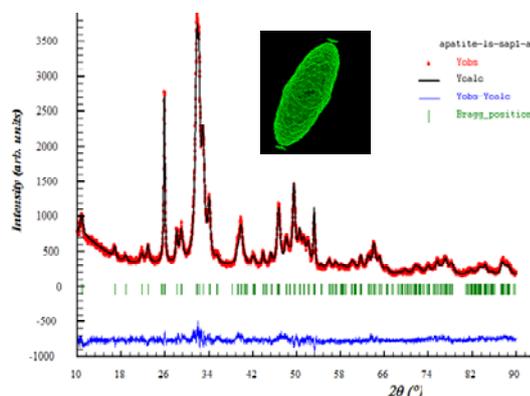


Figure 1: Rietveld refinement of Hap

XRD analyses and Rietveld refinement confirmed the formation of a well crystalline hydroxyapatite structure with anisotropic crystallite shapes. When the apatites richer in carbonate are considered, broadening of the (300) peaks are lower than that of the (002) peaks, indicating that the crystallites become more spheroidal, with a decrease in length/thickness ratio. Hydroxyapatite crystallized in the hexagonal P63/m space group and lattice parameters 'a' and 'c' were determined using Rietveld refinement. Rietveld refinement confirmed the formation of well crystalline HAP structure with anisotropic crystallite sizes. An example of stoichiometric apatite is given in figure 1, crystallite shape is anisotropic with the crystallite size of 8nm along (0 1 0) and 26nm along (0 0 1).

The 'c' value showed a slight increase with addition of sodium to Hap. This increase in c-axis values leading to the expansion in cell volume has been already reported for all sodium-substituted apatites when compared to pure Hap. High amounts of carbonate ions in HapE-CO₃ and HapE-Na-CO₃ resulted in a decrease in the a-axis values and this behavior can be explained by considering that the carbonate ion reduced the a-axis when replacing the phosphate ion, confirming that carbonate ion enters the apatite structure in site B.

Table 1: Chemical composition and surface area of the hydroxyapatites.

Reference	Hap	HapD	Hap-CO ₃	Hap-Na-CO ₃	HapE-CO ₃	HapE-Na-CO ₃	SrHap	SrHapD
Ca/P ratio	1.69	1.62	1.63	1.72	1.90	2.39	1.69	1.61
Surface area/m ² .g ⁻¹	113	124	107	109	76	77	49	67

Electron micrographs of the apatites were well in agreement with Rietveld refinement in which the particles turn out to be spherical for high carbonate containing apatite. The SEM images of all the apatites have shown different morphology in the shape of particles. The particles of stoichiometric and deficient Ca/Sr HAP were irregular shaped agglomerates and that of carbonated apatites were flat needle shaped clusters. The calcium rich apatite particles were found to be capsule (HapE-CO₃) and spheroidal (HapE-Na-CO₃) shaped which is in agreement with the reports that formation of equiaxed crystal for HAP's rich in carbonate [4]. The specific surface area of all the Ca HAP's except Ca-rich hydroxyapatites were higher than 100 m²/g. The surface areas of Sr HAP's were found to be smaller due to the increase in crystallite size as obtained from Rietveld refinement.

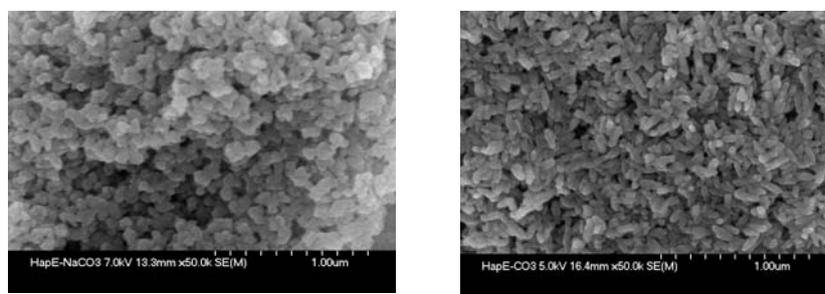


Figure 2: Morphology of Ca-rich apatites; HapE-Na-CO₃ (left) and HapE-CO₃ (right)

FTIR spectra were recorded in 400 cm⁻¹ to 4000 cm⁻¹ range using KBr pellet method (1mg solids in 100mg KBr). The spectra of deficient and stoichiometric apatites were similar with small amount of atmospheric CO₂. But substantial differences were observed for the carbonated apatites. There are two modes of substitution of the CO₃²⁻ ion in the apatite lattice, either replacing OH⁻ or PO₄³⁻ ions, known respectively as A and B-type substitutions. In precipitated carbonate apatites the predominant substitution appears to be CO₃²⁻ ions for PO₄³⁻ ions. Peaks in the Raman spectra confirmed the formation of apatite solids but no substantial differences were observed in Raman spectra of the Ca/Sr apatites.

The XPS results indicate that the surface Ca/P ratio is lower than compared to bulk determined using ICP which proved that phosphate groups are more exposed to the surface than Ca. Also the amount of surface CO₃²⁻ species is higher for the Ca-rich species than for the stoichiometric and deficient ones. Acidic and basic properties of the hydroxyapatites can be correlated to the Ca/P atomic ratio, basic properties arising from an excess of Ca²⁺ and acidic properties from a deficiency of Ca²⁺. The amount of the acid sites were determined by quantifying the total mass loss of PEA during PEA-TPD run, assuming a 1:1 stoichiometry for the PEA adsorption on the acid site. In complementary way to the TPD approach, XPS investigation of the saturated PEA surfaces allows to determine the Bronsted (B) or Lewis (L) nature of the acid sites. The XPS of all PEA saturated solids showed a broad N1s band which can be decomposed into two components indicating the presence of Bronsted and Lewis sites. The results of PEA-TPD and XPS indicated a significant variation of amount and nature of acid sites depending on (i) the Ca/P ratio and (ii) the carbonate species present in the samples.

Acknowledgement

The research leading to these results has received funding from the European Union Seventh Framework Programme (FP7/2007-2013) under grant agreement n° 241718 EuroBioRef.

References

1. T. Tsuchida, J. Kubo, T. Yoshioka, S. Sakuma, T. Takeguchi, W. Ueda, Reaction of ethanol over hydroxyapatite affected by Ca/P ratio of catalyst, *J. Catal* 259, 2008, 183–189.
2. C. Lamonier, J.-F. Lamonier, B. Aellach, A. Ezzamarty, J. Leglise, Specific tuning of acid/base sites in apatite materials to enhance their methanol thiolation catalytic performances, *Catal. Today*, 2010, *In press*.
3. A. Gervasini, C. Messi, D. Flahaut, C. Guimon, Acid properties of iron oxide catalysts dispersed on silica–zirconia supports with different Zr content, *Applied Catalysis A: General* 367, 2009, 113–121.
4. Legeros, Racquel Z.; Trautz, Otto R.; Legeros, John P.; Klein, Edward; Shirra, W. Paul, Apatite Crystallites: Effects of Carbonate on Morphology, *Science*, 155, 1967, 1409-1411.

