



# Discrimination of infrared fingerprints of bulk and surface POH and OH of hydroxyapatites



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## ABSTRACT

The identification of the nature of the surface acid base pairs present on hydroxyapatites surface is a key point to rationalize their catalytic properties. To investigate the possible involvement of acidic protonated phosphate (POH) and/or of basic OH emerging from the channels, the spectroscopic fingerprints of the surface sites have to be discriminated from bulk  $\text{HPO}_4^{2-}$  and  $\text{OH}^-$  groups. This was monitored by infrared spectroscopy (i) using isotopic H–D exchanges, either implemented in mild conditions (353–373 K) or at higher temperature (573 K) to selectively label the lone surface or to achieve deep deuteration, respectively (ii) following then the perturbation induced upon adsorption probe molecules. Two bulk contributions are observed in the  $\nu\text{OH}$  region, one at  $3572\text{ cm}^{-1}$  that is associated to  $\text{OH}^-$  from the channels, and one at  $3657\text{ cm}^{-1}$  that was assigned to  $\text{HPO}_4^{2-}$ . Five surface contributions perturbed upon  $\text{CO}$  adsorption at 77 K can be ascribed to protonated forms of the various terminated phosphates. The formation of hydrogenocarbonate species upon  $\text{CO}_2$  adsorption evidences the presence of basic surface  $\text{OH}^-$ . However, due to complex material restructuring occurring upon  $\text{CO}_2$  adsorption that greatly modifies the H-bonding interactions, the related  $\nu\text{OH}$  fingerprint could not be formally identified. What-ever, from the formation of low intense band at  $2633$  or  $3572\text{ cm}^{-1}$  under soft deuteration or protonation conditions respectively, it is inferred that the related bands could be ascribed to both surface and bulk OD or OH.

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## 1. Introduction

Hydroxyapatites (HAp), main mineral component of bones and teeth are biocompatible materials [1] and thus used in various biology-related applications such as: reconstructive surgery [2], drug delivery [3] and bone regeneration [4–8]. Those materials have also met an increasing number of applications in the heterogeneous acid–base catalysis field [9–27], especially thanks to a large versatility of composition controlled by synthesis that varies the acid base properties. Such adaptability can probably account for the peculiar efficiency of this system toward the Guerbet reaction for the selective transformation of bio ethanol into n-butanol and heavier alcohols (all used to form biodiesel, platform molecules or

solvents), which is a very challenging reaction for biomass valorisation [17,26,28].

The common issues for all these application fields are mainly related to the nature of the interaction of hydroxyapatites with adsorbed molecules and more precisely to the nature of the surface entities that are involved. However, very little is known about the nature of the surface sites involved in biological applications due to the size of proteins and to the complexity of investigating the solid liquid interface at the molecular level. In the catalyst field, despite the fact that smaller molecules are involved, similar difficulties are encountered for the rationalization of liquid phase reactions [12,16,29,30]. Fortunately, the most challenging reactions successfully catalyzed by hydroxyapatites are the Guerbet reactions that can be carried out in gas phase conditions [17,26,28]. In this context, molecular level characterization at solid gas interface appears attainable to investigate the nature of hydroxyapatites surface sites possibly involved in the reactant adsorption processes.

Adsorption of basic or acidic probe molecules at solid gas interface followed by infrared spectroscopy is a classical approach to investigate the surface acidity and basicity, respectively [31–33]. It is possible to identify the chemical nature and spectroscopic fingerprint of the surface sites potentially involved in the interactions

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with adsorbed molecules by coupling the data related to the perturbations of the vibrators associated to the probe molecules to those related to the surface entities ( $\nu\text{OH}$ , for instance) [33–36]. Whereas the involvement of surface  $\text{PO}_4^{3-}$  and  $\text{Ca}^{2+}$  ions in adsorption processes will be discussed in a forthcoming paper, the present paper aims at characterizing both surface hydroxyl OH (corresponding to structural column like hydroxyl emerging at the surface that are in close vicinity with calcium cations) and POH groups (corresponding to the surface termination of some phosphates groups) and identifying their infrared spectroscopic fingerprints by investigating their interaction with acidic and basic probe molecules. However, considering that the hydroxyapatite system is a bulk catalyst and that its specific surface area is quite low (usually around  $40\text{ m}^2\text{ g}^{-1}$ ), the spectroscopic contributions from the bulk entities prevail on the spectroscopic contributions of the surface entities. Using surface infrared modes, ATR for instance (attenuated total reflection mode), enhances the signal of surface species relatively to bulk ones, provides useful information, the adsorbed species [37]. However, this mode is not suitable for the investigation of the terminal OH groups because of the low sensitivity in this wavenumber regions and the dominating presence of water bands [38]. The use of transmission mode associated to probe molecule adsorption is therefore more appropriate to investigate the surface properties despite the lack of sensitivity associated to the characterization of bulk catalyst (OH groups mainly present in the bulk). Thus, to overcome this difficulty, first, isotopic H–D exchanges are used to discriminate the infrared signatures of the minority of the surface contributions from the majority of the bulk contributions. To confirm the surface or bulk location of the  $\nu\text{OH}$  and corresponding  $\nu\text{OD}$  vibrators of the various vibrators, back D–H exchanges are performed *via* an intermediate deuteration of the whole material. Then, the assignments of these OH and OD vibrators belonging to hydroxyl that will be hereafter referred to as basic hydroxyl groups and as protonated phosphate groups (hereafter referred to as POH or POD that are expected to be acidic) are discussed thanks to adsorption of acid and basic probe molecules, respectively. Since stoichiometric hydroxyapatites were found more selective than calcium deficient hydroxyapatites in the Guerbet reaction [17], a stoichiometric hydroxyapatite is considered.

## 2. Experimental

### 2.1. Sample preparation and characterization

Stoichiometric calcium hydroxyapatite sample of formula  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$  was prepared following the precipitation method already described in literature [39–42]. An aqueous solution of  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  ( $[\text{Ca}] = 0.216\text{ mol L}^{-1}$ ) which pH was adjusted to 10 [43] by addition of  $1\text{ mol L}^{-1}$   $\text{NH}_4\text{OH}$  was brought to 353 K under nitrogen atmosphere [44]. An aqueous solution of  $(\text{NH}_4)_2\text{H}_2\text{PO}_4$  ( $[\text{P}] = 0.130\text{ mol L}^{-1}$ ) which pH was also previously adjusted to 10 by addition of concentrated  $\text{NH}_4\text{OH}$ , was then added dropwise ( $\sim 2.2\text{ mL min}^{-1}$ ) to the calcium solution. A white precipitate was formed. The heating under stirring is then maintained for 4 h under reflux with periodic addition of  $\text{NH}_4\text{OH}$  in order to keep the pH above 9.0. The precipitate was then washed several times with distilled water centrifugated and dried at 373 K overnight. Finally, the dried sample was heated under argon flow ( $150\text{ mL min}^{-1}$ ) up to 623 K ( $5^\circ\text{C min}^{-1}$ ) and maintained at this temperature for 90 min.

The Ca and P contents were determined from elemental analysis performed by ICP-AES by the “Service Central d’Analyse” of the CNRS (Vernaison, France). The results confirmed that a stoichiometric sample (Ca/P ratio of  $\sim 1.67$ ) was obtained. XRD diffractogram recorded with a Siemens diffractometer equipped with a copper

anode generator ( $\lambda = 1.5418\text{ \AA}$ ) confirmed that the sample exhibits the hydroxyapatites structure (ICDD pattern 01-074-9780(A)). It can thus be assumed that stoichiometric HAp sample was obtained. Specific surface area was measured by adsorption of  $\text{N}_2$  on a Micromeritics (ASAP 2010) apparatus. Sample was outgassed at 573 K overnight before adsorption, and the specific surface area, calculated from the BET method was  $39\text{ m}^2\text{ g}^{-1}$ .

### 2.2. Infrared characterizations

FTIR spectra were obtained from self-supported pellets ( $10\text{--}12.5\text{ mg cm}^{-2}$ ) placed in a quartz cell equipped with ZnSe windows ( $\text{CaF}_2$  in the case of low temperature experiments) and connected to a vacuum line allowing thermal treatments and adsorption–desorption experiments to be carried out *in situ*. Wafers were first pre-treated: after a first ramp to 623 K ( $5\text{ K min}^{-1}$ ) under argon flow ( $20\text{ mL min}^{-1}$ ), they were kept at this temperature and atmosphere for 90 min and then outgassed at 623 K for 60 min. The spectra were recorded using a Bruker FTIR Vertex 70 spectrometer, equipped with an MCT detector (resolution  $2\text{ cm}^{-1}$ , 64 scans per spectrum).

#### 2.2.1. Isotopic labeling procedures

The purpose of the present work was first to define the experimental conditions allowing, starting from the pre-treated HAp sample (623 K), to selectively label with deuterium either the sole surface or the whole material (bulk), or, starting from a fully deuterated sample, to selectively protonate its surface. Infrared spectroscopy was used to monitor the various procedures, recording spectra at each step. This was achieved by lowering the temperature of the pellet to the convenient temperature,  $T_{\text{ads}}$  then adsorbing at this temperature a given partial pressure,  $P_{\text{ads}}$ , of  $\text{D}_2\text{O}$  or  $\text{H}_2\text{O}$  for a given duration,  $t_{\text{ads}}$ . To avoid back isotopic exchanges, the atmosphere has then to be renewed: an evacuation step was thus performed for 10 min. This whole cycle was repeated twice to enhance the exchange yield. Finally an evacuation step was implemented for a given time,  $t_{\text{evac}}$ , at the  $T_{\text{evac}}$  temperature, to get rid of adsorbed molecular water (either  $\text{D}_2\text{O}$  or  $\text{H}_2\text{O}$ ), which spectroscopic contributions would hinder the detection of the  $\nu\text{OD}/\nu\text{POD}$  or  $\nu\text{OH}/\nu\text{POH}$  contributions of OH and POH groups. Soft conditions were applied to achieve the isotopic exchange  $\text{H} \rightarrow \text{D}$  or  $\text{D} \rightarrow \text{H}$  from the lone surface, adsorbing  $\text{D}_2\text{O}$  or  $\text{H}_2\text{O}$ , respectively.  $T_{\text{ads}}$  was determined paying attention on the one hand to limit the diffusion of the deuterium or hydrogen to the bulk [45] and, on the other hand, to maximize the intensity of the bands expected to belong to surface groups. Even though the deuteration already occurred at temperature as low as 353 K, (see Figure 1S in supplementary data S1),  $T_{\text{ads}}$  was finally set to 373 K to increase the relative intensities of the deuterated bands. Similarly, the final  $T_{\text{evac}} = 473\text{ K}$  also resulted from a compromise in order to allow both minimizing the diffusion to the bulk and removing the physisorbed  $\text{D}_2\text{O}$  or  $\text{H}_2\text{O}$  water. Table 1 gathers the optimized conditions for the surface deuteration, bulk deuteration and surface protonation procedures.

#### 2.2.2. Probe molecule adsorption

A 25 mg pellet that went through a surface deuteration procedure was brought to room temperature and further transferred to the beam zone that was maintained at room temperature or at 100 K with liquid nitrogen in the case of  $\text{CO}_2$  and CO adsorption, respectively. Spectra were recorded at this temperature before and after introduction of increasing doses of  $\text{CO}_2$  or CO gas up to a final equilibrium pressure of 133 Pa. The difference spectra are reported in absorbance, after subtraction of the spectrum of the sample before the probe adsorption.

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