Applied Surface Science 279 (2013) 97–102

Contents lists available at SciVerse ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Surface fractal dimensions and textural properties of mesoporous alkaline-earth hydroxyapatites☆

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ARTICLE INFO

Article history:
Received 12 March 2013
Received in revised form 12 April 2013
Accepted 13 April 2013
Available online 23 April 2013

Keywords:
Alkaline-earth hydroxyapatites
Surface fractal dimension
Hydroxyl groups
Textural properties
XRD
FTIR

ABSTRACT

This work examines the surface fractal dimensions (D_f) and textural properties of three different alkaline-earth hydroxyapatites. Calcium, strontium and barium hydroxyapatite compounds were successfully synthesized via chemical precipitation method and characterized using X-ray diffraction, scanning electron microscopy, energy dispersive X-ray spectrometry, Fourier transform infrared spectroscopy, and N_2-physisorption measurements. Surface fractal dimensions were determined using single N_2-adsorption/desorption isotherms method to quantify the irregular surface of as-prepared compounds. The obtained materials were also characterized through their surface hydroxyl group content, determined by the mass titration method. It was found that the D_f values for the three materials covered the range of 0.77 ± 0.04–2.33 ± 0.11; these results indicated that the materials tend to have smooth surfaces, except the irregular surface of barium hydroxyapatite. Moreover, regarding the synthesized calcium hydroxyapatite exhibited better textural properties compared with the synthesized strontium and barium hydroxyapatites for adsorbent purposes. However, barium hydroxyapatite shows irregular surface, indicating a high population of active sites across the surface, in comparison with the others studied hydroxyapatites. Finally, the results showed a linear correlation between the surface hydroxyl group content at the external surface of materials and their surface fractal dimensions.

1. Introduction

The synthesis and characterization of a new material suitable for use as a potential adsorbent during an adsorption process as a technique for wastewater treatment are essentially the first steps to develop and understand a retention process. In this context, it is widely recognized that the textural or surface properties of materials are crucial for removing a specific contaminant from aqueous media [1]. Indeed, these textural and surface properties of materials strongly depend directly on their method of preparation and starting chemical precursors used [2]. In recent years, rapid technological development has led the use of new materials with optimum characteristics for use as adsorbents. For instance, many inorganic materials are successfully used to remove specific undesirable contaminants present in many wastewater treatment systems, including agricultural, municipal, industrial, and nuclear wastewaters [3]. Some of those potential materials used as adsorbents include activated carbon, metallic oxides and oxyhydroxides, carbonates, and calcined phosphates [4]. Calcined phosphate compounds, recently have shown considerable promise to play an important role in environmental remediation, due to their chemical, surface, and structural properties [5]. For this reason, the selection of a specific solid to explore its adsorption capacity highly depends on its textural and surface properties; therefore, detailed knowledge of these properties is needed.

The hydroxyapatites in the present study are calcined alkaline-earth phosphates with the chemical formula $M_{10}(PO_4)_6(OH)_2$, where M = Ca, Sr, or Ba. These materials are part of apatites group with hexagonal structures and are present in rocks and sediments [6]. They exhibit a very low water solubility ($\sim K_{sp} < 10^{-40}$) under alkaline conditions, are available at low cost, and exhibit high thermal and chemical stability, influenced by their composition and synthesis methods [7]. Abundant data exist on natural or synthetic calcium hydroxyapatite preparations with different characteristics for applicability in various technologies, including as bone substitutes and for treatment of liquid waste [8,9]. However, little work has been reported on strontium and barium

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http://dx.doi.org/10.1016/j.apsusc.2013.04.042

hydroxyapatites synthesis, or their surface and microstructural characterization and over-all surface fractal dimensions.

In the case of an adsorption process, the fractal dimension (D_f) is associated with surface active sites (functional groups as carbonyl, carboxyl, and hydroxyl, among others), presents on solid adsorbent surface, which are available for intimate chemical, physical, or mechanical interaction with a variety of chemical species (anions or cations) present in aqueous solutions. Their magnitude is relevant for many important physicochemical processes (i.e., adsorption, adhesion, surface diffusion, and catalysis) according to Farin and Avnir [10]. Considering such surface irregularities at the atomic or molecular level, solid surfaces may exhibit surface fractal dimensions in the complete range $2 \leq D_f < 3$; where $D_f \leq 2$ is for regular or perfectly smooth surfaces, intermediate D_f values for irregular surfaces and $D_f = 3$ for highly irregular surfaces [11].

Therefore, this study was dedicated (a) to textural characterizations of three different alkaline-earth hydroxyapatites synthesized via chemical precipitation, in order to understand as these textural properties could be determining in adsorption processes, (b) to the determination and discussion of the fractal dimensions of these ceramics, and (c) to correlation the surface fractal dimensions of as-prepared alkaline-earth hydroxyapatites with their hydroxyl group (active sites) content available at their external surface.

2. Materials and methods

2.1. Preparation of alkaline-earth hydroxyapatites

All alkaline-earth hydroxyapatite compounds were chemically prepared via the chemical precipitation method, followed by calcination according to the procedure reported by Kanna et al. [12]. Appropriate high purity metal nitrates; calcium nitrate tetrahydrate $Ca(NO_3)_2{\cdot}4H_2O$ (Aldrich), strontium nitrate tetrahydrate, $Sr(NO_3)_2{\cdot}4H_2O$ (Aldrich), barium nitrate tetrahydrate, $Ba(NO_3)_2{\cdot}4H_2O$ (Aldrich), and diammonium hydrogen phosphate $(NH_4)_2HPO_4$ (Aldrich) were used for the synthesis as starting chemical precursors of analytical grade without further purification. When separated, diammonium hydrogen phosphate solutions were added to stoichiometric proportions of respective alkaline-earth metal nitrates dissolved in deionized water; the pH of each solution was adjusted to pH 9.0 with 0.1 M NH_4OH solution. The mixtures were maintained under constant stirring for 20 h at room temperature. The liquid and solid phases were separated by centrifugation. Then, the resultant solids were filtered, washed with abundant deionized water, dried in oven at 120 °C for 3 h, and finally calcined at 1000 °C for 3 h. The resulting alkaline-earth hydroxyapatite powders were used for further characterization and surface fractal dimensions studies. For these purposes, several homogeneous as-prepared samples have been investigated in order to outline the general physicochemical makeup of various coating, and data were considered representative of a bigger sample. Then, all experimental data were considered as the average of triplicate determinations; a good reproducibility was obtained; standard deviations were usually less than 5% of mean values.

2.2. Characterization

The crystallinity and the purity of the calcium, strontium, and barium hydroxyapatites as-prepared powders were evaluated by X-ray diffraction (XRD) analysis using a Siemens D-5000 diffractometer connected to an X-ray tube of copper anode. The K_α was selected by means of a monochromatic of diffracted beam. The diffraction patterns were scanned with a sweep of 5–70° in 2θ angles with a ramp of 0.035°/7 s. The obtained spectrums were compared with the Joint Committee on Powder Diffraction Standards (JCPDS) files.

The surface physical morphology of these alkaline-earth hydroxyapatite synthesized powders were analyzed by using the scanning electron microscopy (SEM) technique (JEOL-JMS 5900 LV). Energy dispersive X-ray spectrometry (EDS) analysis for chemical composition was recorded for the as-prepared hydroxyapatites in 5900 JEOL JMS-LV.

Fourier transform infrared spectroscopy (FTIR) studies were performed to study the surface functional groups of the alkaline-earth hydroxyapatites, with a scanning range of 4000–500 cm^{-1} by using a spectrophotometer (Nicolet Magna 550); the samples were mixed to KBr in the conventional way.

The specific surface areas were computed by the Brunuauer–Emmet–Teller (BET) method. Mean pore diameters, total pore volumes, and N_2 adsorption/desorption isotherms of the as-prepared materials were determined by N_2-physisorption measurements using an integrated catalyst analyzer (BEL Japan INC model Belsorp Max); the samples were heated with N_2 gas at 200 °C for 2 h before measurements.

Solids in aqueous suspension are generally electrically charged; this charge is attributed to the presence of diverse superficial functional group types that are responsible for electrostatic attractions between the adsorbent surface and chemical species (anions or cations) present in aqueous solutions at different pH values [13]. For instance, functional groups on surface materials are considered surface active sites which could be determining in adsorption processes; therefore, a determination of their surface concentration is necessary to deduce the amount of sites in an active state in a sample [14]. Hence, in this case, milliequivalents of hydroxyl groups (OH^-) by gram of solid were determined by the mass titration method using NaOH and HCl solutions, respectively [15].

Using the fractal analysis approach, the surface irregularities of mesoporous hydroxyapatites were estimated in a single step analyzing the N_2-adsorption/desorption isotherms at 298 K by plotting values of the surface fractional multilayer coverage $\ln(V/V_m)$ against relative pressure $In[\ln(p_o/p)]$, where V_m is the molar volume, V is the N_2 gas volume at standard temperature and pressure adsorbed at equilibrium pressure p and p_o is the adsorbate saturation pressure [16]. In this case, the respective linear equations were obtained with a correlation coefficient (R^2) close to unity, using the resulting slopes that take the values $(D_f - 3)/3$, based on Pfeifer's theory [17] and according to Eq. (1) in linearized form:

$$ln\left(\frac{V}{V_m}\right) = \frac{D_f - 3}{3\{[\ln[\ln(p_o/p)]]\}} + \text{constant} \quad (1)$$

According to Ismail and Pfeifer [18], it is possible establish a linear correlation between the amount population of surface active sites (surface functional groups) available at the external surface of the materials and their fractal dimension (D_f), determined from physical adsorption of nitrogen. Then, experimental fractal analysis has shown that the degree of surface irregularities can be expressed by the parameter D_f.

3. Results and discussion

3.1. XRD analysis

Fig. 1 shows X-ray diffraction patterns of as-prepared calcium, strontium, and barium hydroxyapatites via the chemical precipitation method. The X-ray diffraction pattern results for calcium hydroxyapatite (Fig. 1a) revealed the presence of large quantities of amorphous phase, a non-crystalline structure, which showed diffraction lines characteristic of calcium hydroxyapatite. This was confirmed by comparing the obtained data with the JCPDS No. 76-0694 file in the conventional way. The X-ray diffraction result