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In vitro hydroxiapatite formation on the Ca doped surface of ZSM-5[Ga] type zeolite

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Abstract

A high SiO_2/Al_2O_3 ratio ZSM-5[Ga] type zeolite was synthesized. Then an ionic exchange of Na by Ca ions on the surface was performed. The in vitro bioactivity was assessed by immersing samples in Simulated Body Fluid (SBF) for different periods of time. Bonelike apatite was formed on the zeolite as early as 7 days of immersion. This indicates that this ZSM-5[Ga] zeolite with a Ca-functionalized surface is a potential material for bone tissue regeneration.

Keywords: Zeolite; Biomaterials; Gallium; Bioactivity

1. Introduction

Silica-based bioactive glasses have supplied successful alternatives for repairing small to medium bone defects [1]. The shift toward biologically based methods for repair and regeneration of living tissues has led to a third generation of biomaterials [2–5]. These biomaterials include ordered mesoporous materials, which are excellent candidates since they possess fascinating textural properties (surface area and porosity) [6]. Nowadays, there is sufficient evidence that leads to the possibility of direct and relevant participation of gallium in the skeleton metabolism. Gallium ions are also clinically effective against bone desorption, for osteoporosis treatment and cancer-related hypercalcemia [7,8]. Gallium promotes the mineralization of the calcium and phosphorus bone apatite and has non-toxic effects on osteoclasts. On the other hand, gallium, apart from being an antimicrobial agent [9], also plays a vital role in normal physiological functions related to bone metabolism. It was reported that gallium protects the hydroxyapatite matrix, thereby improves the biomechanical properties of the skeletal system [10].

The aim of this work was the synthesis of a bioactive ZSM-5[Ga] type zeolite and its functionalization with Ca^{2+} ions by an ionic exchange.

2. Experimental section

2.1. Synthesis and functionalization of the selected zeolite

The ZSM-5[Ga] zeolite synthesis was performed according to the method reported by Awate et al. [11]. The obtained ZSM-5[Ga] was functionalized by immersing 5 g of zeolite in its sodic form in 1000 mL of 0.1 M $CaCl_2$ aqueous solution at 70 °C for 6 h under magnetic stirring. The solid product was washed 3 times with 500 mL of deionized water and dried at 100 °C for 24 h. A white powder (5 g) was obtained. Disk-shaped Ca-functionalized ZSM-5[Ga] zeolite samples (0.2 g in weight each) were obtained by uniaxial pressing for 30 s at 499 MPa using a manual hydraulic press.

2.2. In vitro bioactivity assessment

The SBF was prepared according with a well-known method [12]. Then, one disk of zeolite was immersed in 150 mL of SBF for 7, 14 or 21 days and kept under

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physiological conditions of pH and temperature. After completing each immersion period, the samples were washed with water and dried at room temperature for 24 h.

2.3. Characterization methods

The loss on ignition (LOI) of the synthesized zeolite was determined at 950 °C for 1 h using a furnace (Thermolyne F6200-60-80), the thermal stability of the zeolite was determined by gravimetric and differential thermal analysis in air (TGA/DTA, Pyris Diamond Tg/DTA equipment) and the chemical analysis was performed by X-ray fluorescence spectroscopy (XRF, Bruker S4 Pionner). Furthermore, ZSM-5[Ga] zeolite samples, before and after immersion in SBF, were analyzed by X-ray diffraction (XRD, Phillips X'Pert 3040), scanning electron microscopy (SEM, Phillips XL30) and energy dispersive spectroscopy (EDS, X'Pert, Phillips, Holland).

3. Results and discussion

The chemical composition (wt%) of the synthesized ZSM-5[Ga] type zeolite was: SiO_2 (93.28), Al_2O_3 (0.287), Ga_2O_3 (4.574), Fe_2O_3 (0.17), Na_2O (1.34) and volatile material (0.0651).

The XRD pattern (Fig. 1a) of the synthesized powder, before immersion in SBF, indicates that ZSM-5[Ga] is the unique crystalline phase present with their characteristic peaks at 8 and 9 2θ degrees. The SEM image of this sample shows that the morphology is not well defined: it consists mainly of rectangular shape crystals of different sizes

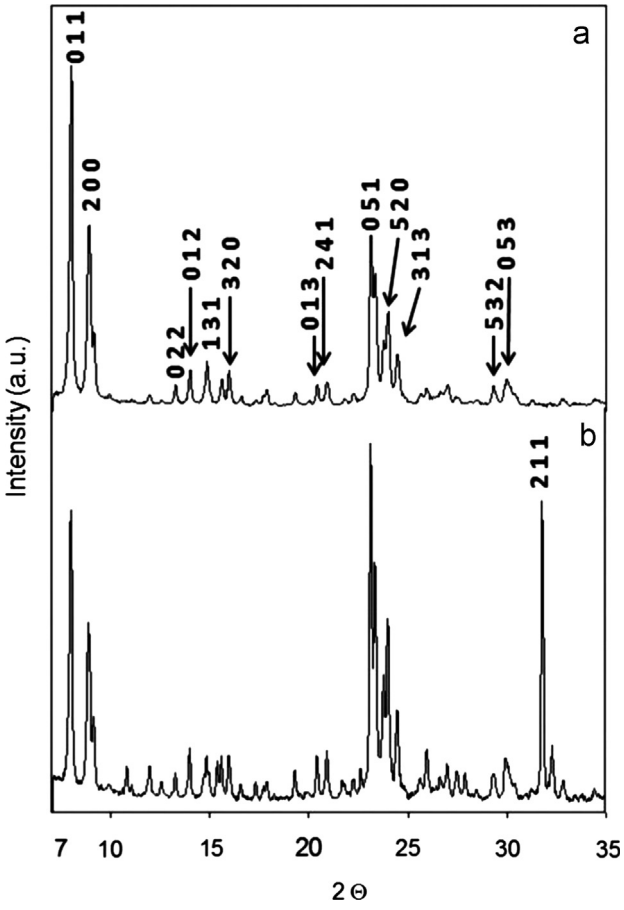

Fig. 2. XRD patterns of ZSM-5[Ga] zeolite: (a) before and (b) after 21 days of immersion in SBF.

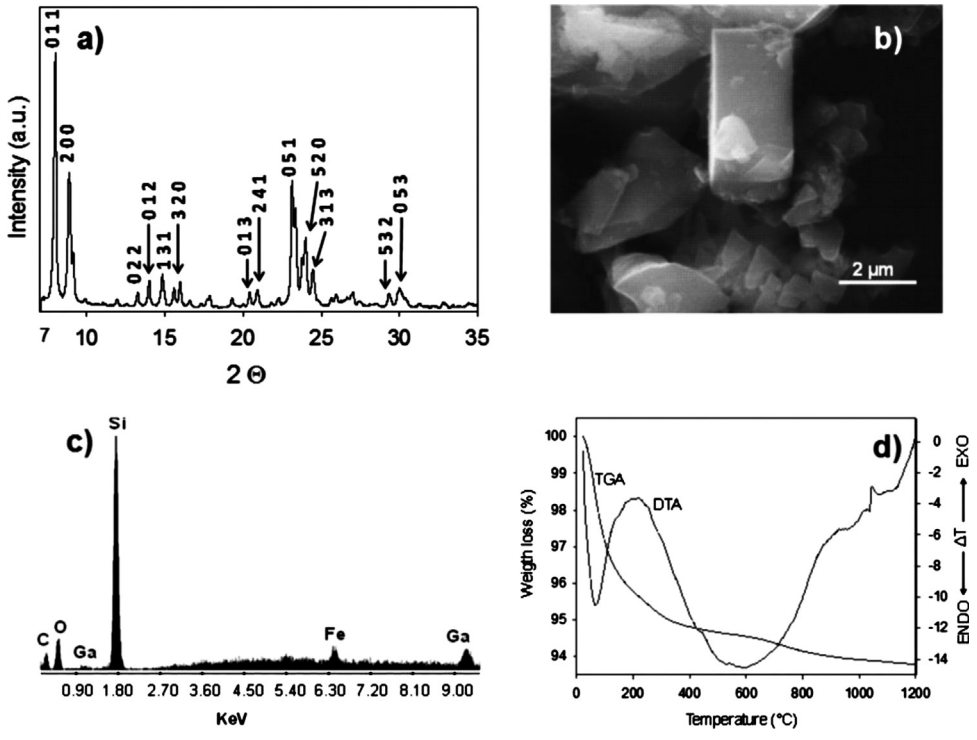

Fig. 1. ZSM-5[Ga] zeolite before immersion in SBF: (a) XRD pattern; (b) SEM image; (c) EDS spectrum; and (d) DTA/TGA analysis.

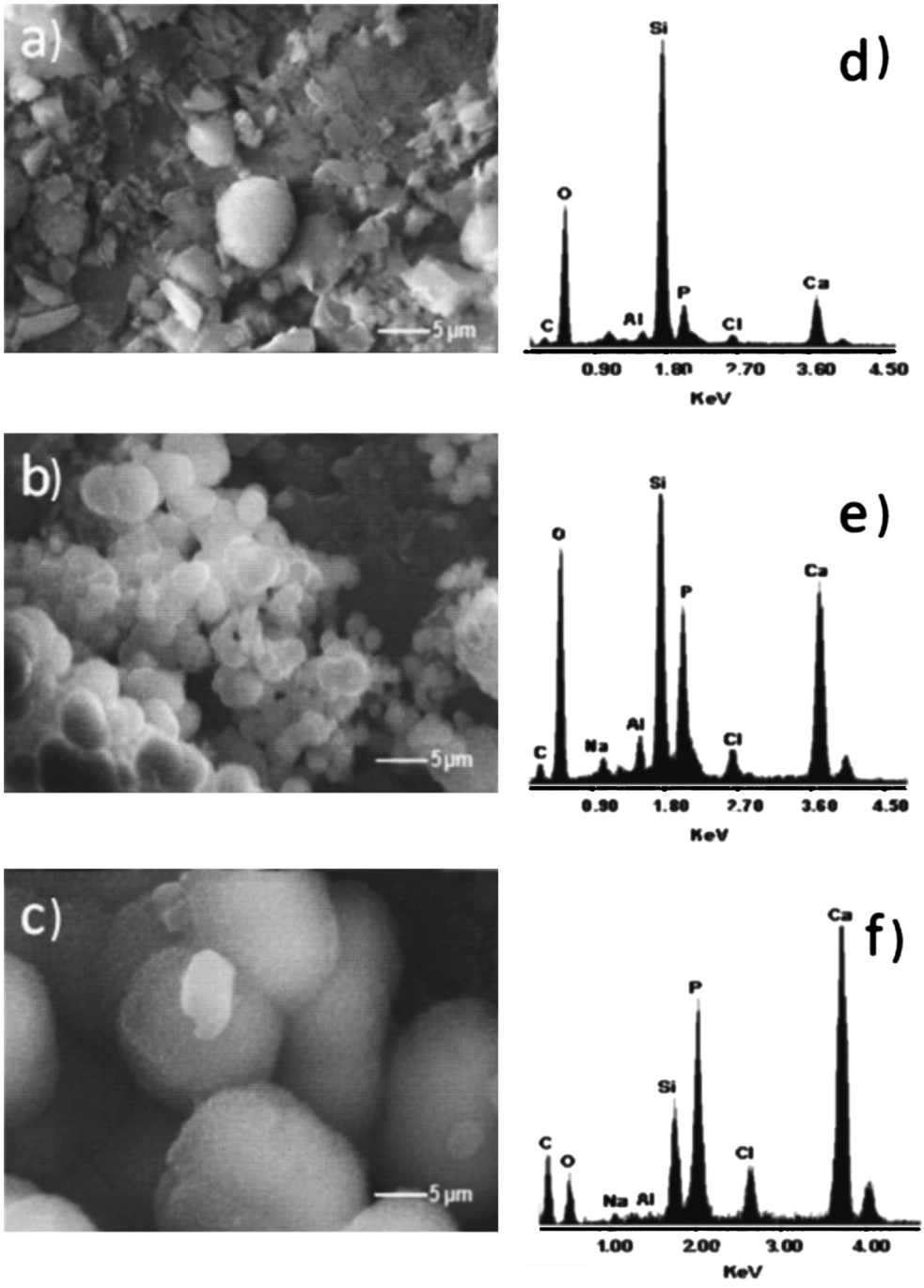

Fig. 3. SEM micrographs and EDS spectra of ZSM-5[Ga] zeolite (a) before and (b) after 21 days of immersion in SBF.

(Fig. 1b) with the same chemical composition as demonstrated by the corresponding EDS analysis (Fig. 1c).

The TGA and DTA analyses of the synthesized powders are shown in Fig. 1d, where a gradual weight loss is observed (TGA). From room temperature up to around 400 °C there is an important change in weight attributed to the loss of both organic material and physical and chemically bound water from the zeolite. The whole DTA curve is in the endothermic regime: the event up to 400 °C can be related to both the decomposition of organic material and to the loss of physical and chemically bound water. The endothermic events within the range of 400–800 °C can be due to the zeolite decomposition.

As stated in the Experimental Section 2.2, a dried disk-shaped calcium functionalized ZSM-5[Ga] zeolite was immersed in SBF during 7, 14 or 21 days. Fig. 2 shows the XRD patterns of the samples before (Fig. 2a) and after 21 days of immersion in SBF (Fig. 2b) for comparison

purposes. As observed in the XRD pattern corresponding to the disk after 21 days of immersion (Fig. 2b), a typical hydroxyapatite reflection appeared indicating that the Ca-ZSM-5[Ga] zeolite is a bioactive material that potentially will bond chemically to bone.

The SEM and EDS analysis (Fig. 3) indicates the formation of a Ca and P-rich compound in the form of spherical agglomerates on the disk-shaped Ca-ZSM-5[Ga] zeolite even after only 7 days of immersion (Fig. 3a,d). After 14 days (Fig. 3b,e) the quantity of agglomerates formed increases as well as the height of the Ca and P peaks. After 21 days of immersion, a homogeneous and continuous Ca, P-rich layer with bigger agglomerates can be observed (Fig. 3c,f). The corresponding EDS spectrum (Fig. 3f) shows clearly that the peaks corresponding to Ca and P increased drastically, while the Si peak decreased due to the thick bioactive layer formed on the ZSM-5[Ga] zeolite.

4. Conclusions

The Ca functionalized ZSM-5[Ga] zeolite is highly bioactive since apatite was formed on its surface as earlier as 7 days of immersion in SBF. These results indicate that this material may be a highly potential bioceramic for bone tissue regeneration.

Acknowledgments

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