Key Engineering Materials
ISSN: 1662-9795, Vols. 434-435, pp 624-626
doi:10.4028/www.scientific.net/KEM.434-435.624

Online: 2010-03-29

In-situ Templating Synthesis of Thermally Stable Hydroxyapatite with Ordered Nanostructures

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Keywords: Hydroxyapatite; ordered nanostructure; thermal stability.

Abstract. Alkyl phosphates, the products from the reaction between phosphorous pentoxide and various alcohols, were used as the in-situ templates of nanostructure as well as phosphorus source of HAP. The obtained precursor samples had ordered nanostructures:lamellar structure for dodecyl and n-octyl phospahes templated samples, cubic for n-pentyl and hexagonal for ethyl phosphates templated samples. The calcined ethyl phosphate templated sample was pure HAP with a specific surface area of $42m^2/g$, and sustained with an orderly hexagonal nanostructure at 400°C. But the calcination at 400°C caused the collapse of other alkyl phosphates templated nanostructures.

Introduction

In the past five years, various hydroxyapatites with lamellar [1, 2], or worm-like [3, 4] or irregular nanostructures [5] have been successfully synthesized using various ionic or nonionic surfactants as the template. But most of these nanostructures collapsed when HAP samples were under a weak heat-treatment (<400°C) to completely remove the organic templates. The poor heat resistance of HAP mesostructures will limit the applications of mesoporous HAP in catalysts.

Herein, alkyl phosphates from the reaction between phosphorous pentoxide and various alcohols were used as the in-situ templates of nanostructure as well as phosphorus source of HAP, and orderly hexagonal nanostructured HAP was successfully prepared, for the first time. The synthetic samples were characterized by means of WAXRD, SAXRD, electron microscopy and gas absorption.

Experimental Procedure

The product of the reaction between P_2O_5 and various alcohols as well as dodecyl phosphate ester was mixed with $Ca(NO_3)_2{\cdot}4H_2O$ ethanolic solution respectively, with a Ca/P ratio of 1.67/1, under 80°C water bathing and being stirred. The starting solution concentration was 3mol/l for $Ca(NO_3)_2{\cdot}4H_2O$. The mole ratio of P_2O_5/alcohol was 1/3. Subsequently, the mixed solution was added with aqueous ammonia to adjust the pH as 9, and continuously stirred and refluxed at 80°C in water bath for 48h. The final product was directly dried in air at 100°C for 24h. White powders were obtained after calcined at different temperatures for 3h with a rate of 2°C/min. The dodecyl phosphate templated sample was denoted as S12, n-octyl as S8, n-pentyl as S5, and ethyl as S2. Phosphorous pentoxide reacted with the alcohols respectively according to the method presented by Tracy [6], and the contents of the formed alkyl phosphate esters were determined according to McFarlane [7].

The nanostructure and crystalline phase of the samples was analyzed by SAXRD and WAXRD respectively, on a Philips X'pert diffraction instrument with Cu-Kα incident radiation (40kV, 35mA). The details of the nanostructures were investigated by transmission electron microscopy (TEM Philips, EM20) operating at 200kV. And the specific surface area was measured using Nitrogen sorption method operated at 77K with an Autosorb-1 Gas Sorption instrument (Quantachrome Corporation, US).

Results and Discussion

Fig. 1 shows the SAXRD patterns of the as-dried samples. A strong diffraction peak and one or two weak peaks below 2θ=15° can be seen in all the patterns. These peaks shift to be a higher diffraction angle on decreasing the carbon number of the alcohol templates. These suggest all the HAP precursor

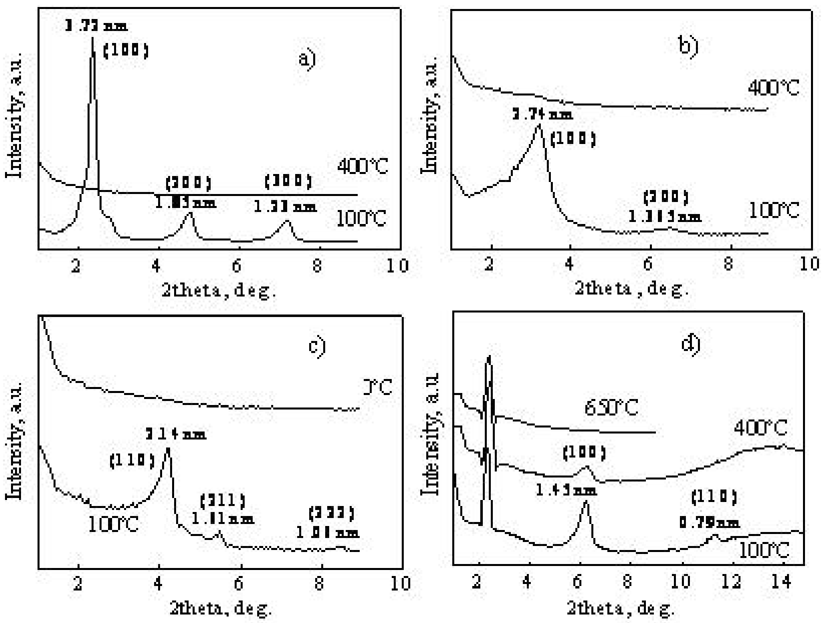

Fig.1. SAXRD patterns of the samples prepared by in-situ template with different carbon number: a) S12, b) S8, c) S5 and d) S2

samples have ordered nanostructures, and the relative positions of the peaks determine the kind of nanostructures. The as-dried S12 and S8 samples have a lamellar structure with a layer length of about 3.7 and 2.74nm respectively (both d/dmax ratios were closed to be 1:1/2:1/3, dmax was d value of the highest peak). The as-dried S5 sample possibly possesses cubic nanostructures [8, 9]. And the as-dried S2 sample has a hexagonal structure with a d (100) value of 1.4 nm (d/dmax ratio was closed to be 1:1/31/2). The inter-space (d value of the highest peak) of these samples is in proportion to the carbon number of alcohols. But when the precursors were calcined at 400°C for 3h, the nanostructure of as-dried S12, S8 and S5 disappeared. The hexagonal structure inside as-dried S2 still sustained after being calcined at 400°C for 3h, as shown in Fig. 1d. It's worthy to note that there exist irregular nanostructures inside S2 samples (2θ=3.7°), and this nanostructure can sustained at 650°C.

Fig. 2 demonstrates the TEM micrographs for the lamellar structure of the as-dried S12 and the hexagonal structure of the calcined S2. The as-dried S12 sample was in fiber-like, but the calcined sample had polyhedron morphology which was from $Ca_2P_2O_7$ (XRD not shown). The lamellar structure of the as-dried S12 were oriented parallel to the longitudinal direction of fiber with a layer periodic spacing of about

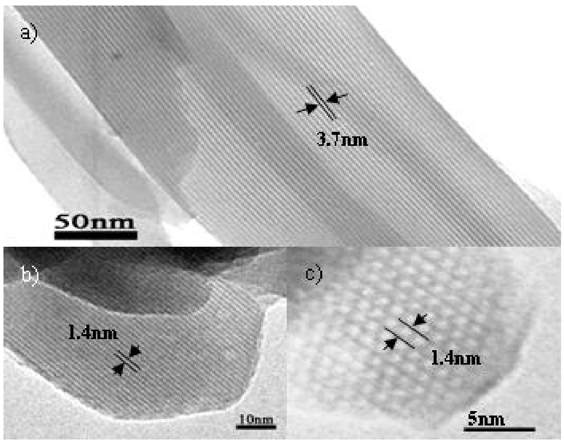

Fig. 2. TEM micrographs of different nanostructures: a) lamellar for S12, b) and c) hexagonal for S2

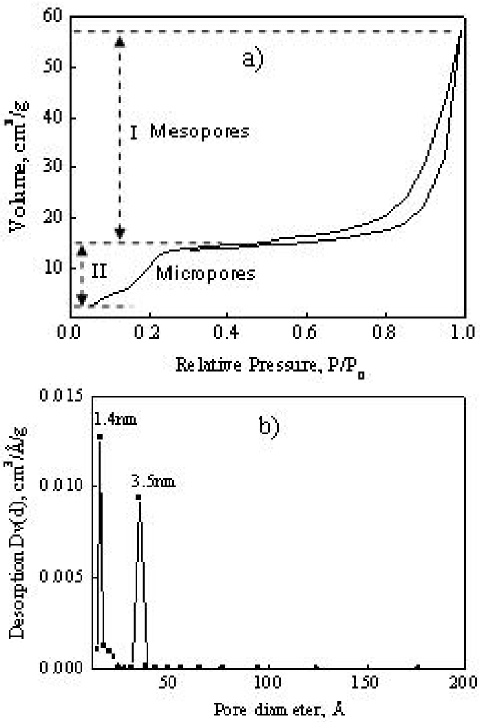

Fig. 3. a) Nitrogen adsorption-desorption curve and b) pore size distribution of HAP sample in-situ templared by ethyl phosphate (S2) and calcined at 400°C for 3h

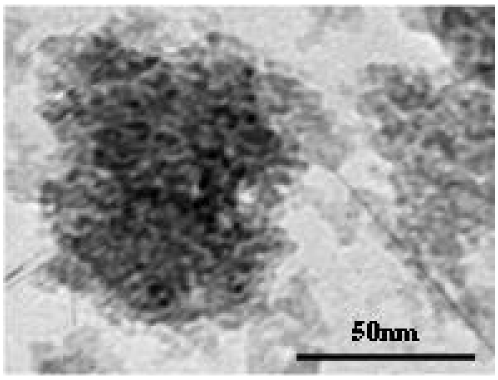

Fig. 4. TEM micrograph for the worm-like mesopores of HAP sample in-situ templared by ethyl phosphate (S2) and being calcined at 400°C for 3h

3.7nm. Fig. 2b is the hexagonal structure along the direction perpendicular to the channels, and Fig. 2c is along the direction parallel to the channels. These further confirmed the results of SAXRD. Fig.3 is the Nitrogen adsorption-desorption curve and pore size distribution of the calcined S2 at 400°C. The specific surface area was measured as $42m^2/g$. And the HAP sample possesses two pore size distribution, 1.4 and 3.5nm respectively, supporing the results of SAXD. The former (1.4nm) is from the hexaganol nanostructure of S2, and 3.5nm corresponds to the irregular nanostructures (worm-like mesopores, as shown in Fig. 4).

Alkyl phosphates with different length of alkyl chains have different packing parameters [10], resulted in various regular assemblies in solution. The added Ca^{2+} further deposited upon these regular structures and then nanostructured precursor formed. The ethanol molecules could possibly increase the inter-spacing and the stability of the nanostructures due to its association with alkyl groups. With further calcinations, the organic parts of the nanostructured precursors were oxidized, and Ca and P turned into phosphates or hydroxyapatite. The alkyl parts which were the templates of the nanostructures of S_{12}, S_8 and S_5 collapsed after calcinations due to heavy reorganization of atoms. But the nanostructure of S_2 survived, which was possibly due to the relatively short alkyl groups (resulted in low $d_{(100)}$ spacing) caused more slight reorganization of atoms. And the slight reconstruction of atoms still caused partial collapse of the nanostructure, resulted in a moderate specific area of $42m^2/g$. The products of S_{12} had no H_3PO_4 and the calcined S_{12} was $Ca_2O_2P_7$, indicating the free H_3PO_4 might be a pivotal figure in forming HAP during calcinations.

Summary

In summary, through the in-situ templating method, lamellar structure for dodecyl and n-octyl phosphates templated samples and hexagonal structure for n-pentyl templated samples were achieved, and the inter-space (d values) of these nanostructures increased in proportion to the carbon number of alcohols. The calcined ethyl phosphate templated sample was pure HAP and sustained with hexagonal structure. And the specific surface area of the obtained hexagonally nanostructured HAP sample was about $42m^2/g$. But the calcinations caused the nanostructures of dodecyl, n-octyl and n-pentyl phosphates templated samples collapsed.

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