

THERMOGRAVIMETRIC STUDY OF TEMPLATE REMOTION OF NIOBIUM ALUMINOPHOSPHATE

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Abstract

Niobium-aluminophosphate materials with AEL structure (NbALPO-11) were synthesized by the hydrothermal method at 170°C for a period of 72 h. The chemical composition of the gel was: DIPA:Al₂O₃:(1-x)P₂O₅:xNb₂O₅:80H₂O, where x=0.025, 0.050 and 0.100 (DIPA=di-isopropylamine template). The obtained materials were characterized by X-ray fluorescence, X-ray diffraction, infrared spectroscopy, scanning electron microscopy and thermogravimetry. From TG, was observed that the remotion of the template occluded in the porous of the NbALPO-11 materials, occurred in two steps, the first in the temperature range from 180 to 260°C, due to physically adsorbed DIPA molecules, and the second step, from 300 to 410°C, attributed to the DIPA decomposition to propene and ammonia.

Keywords: aluminophosphate, molecular sieves, niobium, template

Introduction

In the beginning of the 80's, a new class of molecular sieves was reported by researchers from Union Carbide [1]. These new materials represent a series of crystalline, microporous aluminophosphates (ALPO's), prepared by hydrothermal treatment of a reactive aluminophosphate gel in the presence of an organic template (such as amine or a quaternary ammonium salt), which acts as a structure-directing agent [1–3].

The structures of the aluminophosphate molecular sieves are three-dimensional networks in which AlO₄ and PO₄ tetrahedral are interconnected via oxygen atoms. The aluminophosphate with AEL structure (ALPO-11), exhibits one-dimensional channel system with 10-membered ring pores. The pore opening is elliptical in shape with diameters of 3.9×6.3 Å [4]. This channel system presents interesting properties of shape selective for application in several reactions of industrial interest. The acidity in ALPO-11 due to terminal hydroxyl groups and structural defects, which generate weak Lewis acid sites [5]. The introduction of metals in ALPO's structure during the hydrothermal synthesis improves the acid properties of these materials [6].

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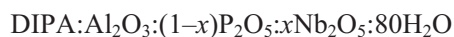
After synthesis, the aluminophosphates materials are submitted to a thermal treatment (calcination) for remotion of the template occluded inside the porous of the material, for application as adsorbent or catalyst [6–7].

In this work we studied the hydrothermal synthesis, characterization and template remotion by TG, of niobium containing aluminophosphate with AEL structure.

Experimental

The aluminum and phosphorus inorganic sources were pseudoboehmite (Catapal B, Vista Chemical) and phosphoric acid (85%, Merck). Niobium was supplied from niobium oxalate hydrated (CBMM, AD-463) and di-isopropylamine, DIPA (98%, Riedel) as the template agent.

For the synthesis of niobium containing aluminophosphate (Nb-ALPO-11) the following molar compositions was used:



where $x=0.025, 0.050$ and 0.100 .

The synthesis mixture was prepared according to a procedure reported by Araujo *et al.* [8]. The reactive gels were transferred to stainless steel autoclaves lined with PTFE, heated at 170°C for a period of 72 h. The obtained products were recovered by filtration, washed with deionized water and dried at 100°C for 6 h.

The unit cell volume and the degree of crystallinity of the materials were determined in a Philips powder diffractometer with monochromatic CuK_α irradiation in the range $2\theta=5\text{--}40^\circ$. The morphology and size of the crystals were determined by scanning electron microscopy, using a Carl Zeiss microscope. Infrared measurements were performed in a Fourier transform infrared spectrometer, FT-IR Prospec (Midac Co.) using the KBr technique, in the region of $1400\text{--}400\text{ cm}^{-1}$. The chemical compositions of the materials were determined by X-ray fluorescence using a Philips BW 2400 equipment.

The studies of the template remotion were performed by thermogravimetric analysis in a DuPont TA-2950 thermobalance, at a heating rate of 5°C min^{-1} , in the temperature range from ambient to 1000°C using nitrogen flow of $60\text{ cm}^3\text{ min}^{-1}$. In the experiments ca 10 mg of the as-synthesized materials was used.

Results and discussion

The X-ray diffractogram of the niobium-aluminophosphate samples are characteristic of the AEL phase [9], except for the sample with $x=0.100$ that present a contaminant phase not completely identified, as can be visualized in Fig. 1. This contaminant phase is probably extra-framework niobium oxide (indicated by arrows in Fig. 1). The degrees of crystallinity of the samples are given in Table 1. The obtained results indicate that the materials present an excellent degree of crystallinity. The values of unit cell volume, given in Table 1, were higher than that of ALPO-11 [4], evidencing

an expansion in the unit cell, occasioned by the niobium incorporation in the framework.

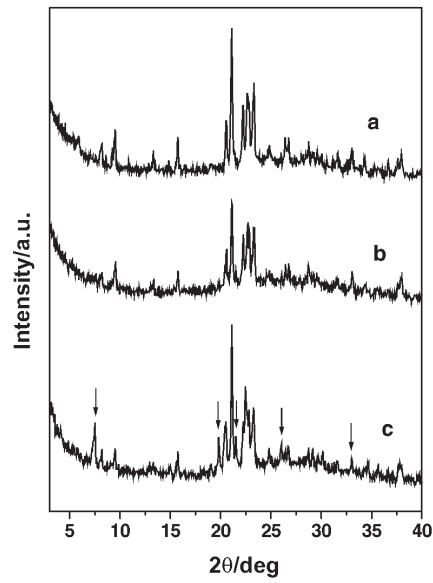


Fig. 1 XRD patterns of NbALPO-11, a - $x=0.025$; b - $x=0.050$; c - $x=0.100$

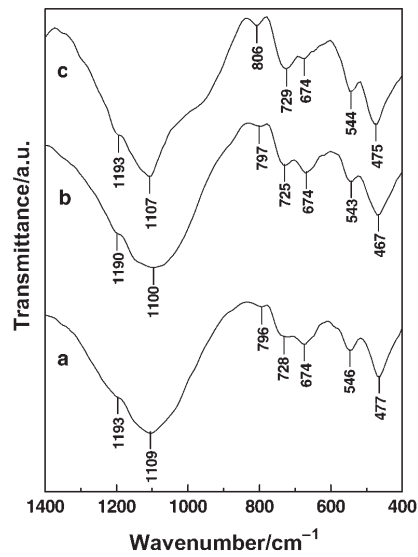


Fig. 2 FTIR spectra of NbALPO-11, a - $x=0.025$; b - $x=0.050$; c - $x=0.100$

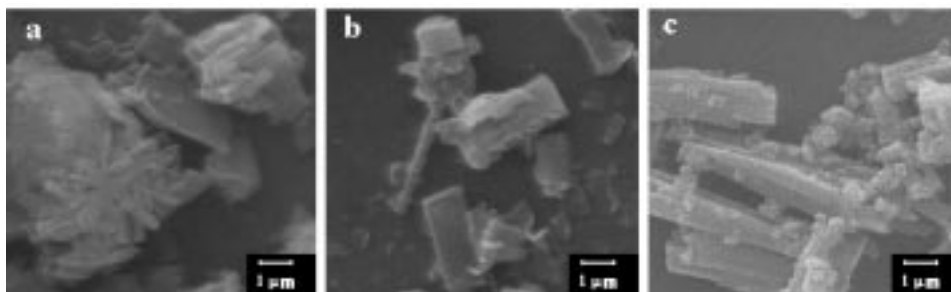


Fig. 3 Scanning electron micrographs of the NbALPO-11 samples, where: a – $x=0.025$, b – $x=0.050$, and c – $x=0.100$

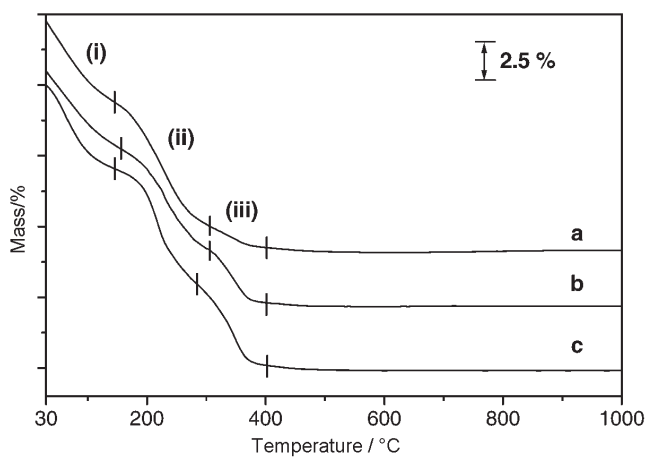


Fig. 4 TG curves of the as-synthesized NbALPO-11, where a – $x=0.025$, b – $x=0.050$, c – $x=0.100$

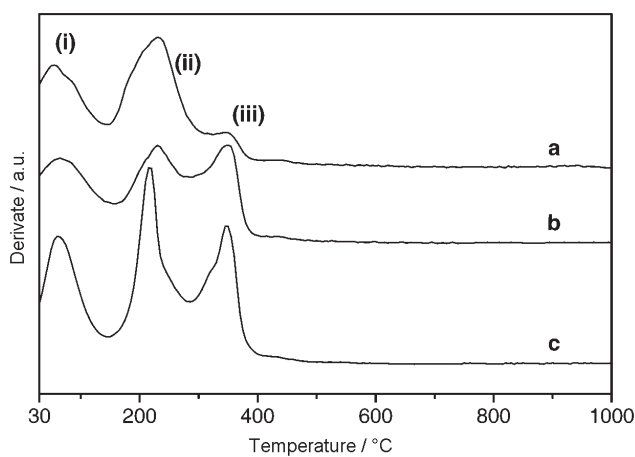


Fig. 5 DTG curves of the as-synthesized NbALPO-11 materials, where a – $x=0.025$, b – $x=0.050$, c – $x=0.100$

The infrared spectra of the synthesized materials are shown in Fig. 2. The absorption bands are similar to those found in ALPO-11 material [10], however, this spectra exhibited an additional band at ca 800 cm^{-1} which was assigned to the Nb–O bond. From scanning electron microscopy for the samples, the formation of crystals of ca 2–5 μm (Fig. 3) was observed, with orthorhombic morphology typical for AEL structure [8].

Table 1 Crystallinity, unit cell volume and chemical composition of the NbALPO-11 samples

Sample	Crystallinity/%	Unit cell volume/ \AA^3	Chemical composition
$x=0.025$	100	2139	$(\text{Al}_{0.520} \text{P}_{0.470} \text{Nb}_{0.011})\text{O}_2$
$x=0.050$	95	2136	$(\text{Al}_{0.496} \text{P}_{0.480} \text{Nb}_{0.023})\text{O}_2$
$x=0.100$	94	2140	$(\text{Al}_{0.495} \text{P}_{0.461} \text{Nb}_{0.045})\text{O}_2$

The TG and DTG curves of the materials are shown in Figs 4 and 5, respectively, where three steps at temperatures below 400°C are observed. The event (i) was attributed to desorption of intracrystalline water; the event (ii) was assigned to the removal of the physically adsorbed template, and the event (iii) was associated with the decomposition of the di-isopropylamine molecules to propene and ammonia (Hoffman elimination), as reported by Biaglow *et al.* [11] and Parrillo *et al.* [12].

The samples with $x=0.100$ presented a mass loss in the temperature range from 300 to 400°C higher than those of the samples with $x=0.025$ and 0.050. These mass loss steps can be associated not only with the desorption of the di-isopropylamine molecules, but also with other substance associated with the amorphous region or other crystalline phase, as it is demonstrated by the shoulder of the DTG peak between 300–400°C (Fig. 5, curve c).

The amount of amine desorbed in the third mass loss step increases with the niobium concentration in the material, indicating that DIPA molecules might interact with niobium atoms present in the material surface.

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