

EVALUATION OF THE ALPO-11 CRYSTALLINITY BY THERMOGRAVIMETRY

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Abstract

The evaluation of the crystallinity of several samples of ALPO-11 was performed by X-ray diffraction and thermogravimetry. Through XRD, the degrees of crystallinity of the samples were determined by the measurement of the area of the peaks at 2θ ranging from 20.7 to 24.1 degrees. The sample that presented the largest area was considered as 100% crystalline and the areas of the other samples were normalized in relation to this. From TG, the degree of crystallinity was determined considering the mass loss in the temperature range from 453 to 653 K that is related to removal of di-isopropylamine molecules used during the synthesis procedure. The quantity of di-isopropylamine on the material is proportional to the degree of crystallinity.

Keywords: aluminophosphate, crystallinity, thermogravimetry

Introduction

The aluminophosphate molecular sieve represents a class of porous inorganic materials [1], which are synthesized through the hydrothermal method, using amine or ammonium quaternary salt as template, and Al:P molar ratio of 1.0. These solids are denoted as ALPO-11, where '11' is an indicative number of the structure type and show excellent physical properties [2-6]. The crystalline ALPO-11 has an AEL topology, and is a member of the aluminophosphate molecular sieve family, which exhibits a unidimensional channel system with 10-membered ring pores. The pore opening is elliptical in shape with diameters of $3.9 \times 6.3 \text{ \AA}$. The symmetry of ALPO-11 is orthorhombic with unit cell dimensions $a=13.5336$, $b=8.4821$ and $c=8.3703 \text{ \AA}$ [7]. Figure 1 illustrates the framework of AlPO_4 -11 viewed along [100] direction [7, 8].

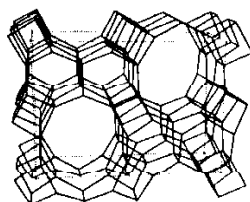


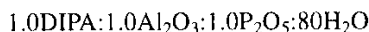
Fig. 1 The framework of the ALPO-11 viewed along [100] direction [7]

Aluminophosphate materials exhibit properties similar to that of zeolites, indicating that they can be used as adsorbents, catalysts and catalyst supports in several chemical processes. The main advantages of the ALPO's compared with other supports, are related with the possibility of varying the following physicochemical properties: pore size, pore shape, dimensionality of the pore system, presence or absence of cages, acid sites properties, surface properties, void volume and framework compositions. Thus, the study of the crystallization parameters and its relation with the characteristics of the final materials is very important. Since the first synthesis of ALPO-11, several works have been made concerning this molecular sieves [9–11], however few is known about its crystallization.

Thermogravimetry is being increasingly used for characterization of porous materials. In general, the experiments are simple, but sometimes the result seems complexes. This work shows that from a simple TG curve, it is possible to estimate the crystallinity of aluminophosphate samples. To this, it must be assumed that the effective participation of the template in the ALPO 11 structure gives information concerning the framework of a sample, and crystallinity as well. The results can be compared by other techniques, such as infrared spectroscopy and X-ray diffraction.

Experimental

The synthesis procedure consists of first combining amounts of a reactive hydrated alumina, such as pseudoboehmite (Catapal B), 85% phosphoric acid (Merck), di-isopropylamine, hereafter DIPA (Riedel) and distilled water. These reactants were combined to obtain a gel with the following stoichiometric proportion:



The preparation of the reactive gel was made according with data of the literature [12, 13], which is the following: i) pseudoboehmite was slurred in half of total volume of water required by 60 min; ii) the phosphoric acid was diluted with the volume of water remainder; iii) the phosphoric acid solution was added to the suspension attained in (i), and aged by 200 min and iv) addition slowly of DIPA to the mixture, and aging for an additional time of 30 min.

The gel was divided in seven parts and transferred into Teflon lined stainless-steel autoclaves and heated in an oven at temperature of 200°C. To the study of the crystallization process, the autoclaves were removed from the oven in specified times and quenched in cold water. According to each time of crystallization, the samples were denoted as S2h, S4h, S6h, S10h, S15h, S48h and S74h. The solid products were separated of the supernatant liquid by filtration, washed with water distilled, and dried at 100°C for 6 h. The calcination of the samples was performed by heating at 500°C in nitrogen flow ($60\text{ cm}^3\text{ min}^{-1}$) for a period of 4 h, and after in dry air atmosphere for 12 h, under the same flow.

The samples were characterized by several techniques, such as XRD, FT-IR and TG. To identify the ALPO-11 phase and to determination of the degree of crystallinity, a Philips powder diffractometer with CuK_α radiation, with the diffraction an-

gle (2θ) at range of $5\text{--}40^\circ$ was used. Infrared measurements were performed in a Fourier Transform Infrared spectrometer, FT-IR Prospec (Midac Corp.) using the KBr wafer technique. The spectra were attained in the region of $1400\text{--}400\text{ cm}^{-1}$. TG analysis was performed on a DuPont TA-951 thermobalance, at a heating rate of 10 K min^{-1} , in the temperature range from ambient to 1000°C using nitrogen flow of $60\text{ cm}^3\text{ min}^{-1}$. To these analyses, it was used a mass of approximately 10 mg of sample.

Results and discussions

During each step of the gel preparation, mixture of pseudoboehmite with water, the pH increased slowly from 6.90 to 7.15 in approximately 60 min due to low reactivity of pseudoboehmite that practically did not suffer hydrolysis. Also, the pH decreased to 1.0 afterward the addition of phosphoric acid solution and subsequent formation of a viscous gel. The pH of the system increased slowly as the reaction mixture was aged with vigorous agitation until steady in 1.9 after 200 min. This evolution of pH at the precursor mixture is due to the difficulty of H_3PO_4 in reaction with the surface of the pseudoboehmite particles. In step 3, it was added DIPA to the mixture and the gel became very viscous. The pH value skipped to 5.70 and immediately stabilized in 3.20.

The X-ray profiles of the samples are shown in Fig. 2. The retirement next 2 h of heating (S2h) presented a pH of 5.10. The XRD analysis did not indicate crystalline phase to this sample. It was assumed that the increase of pH was occasioned by re-

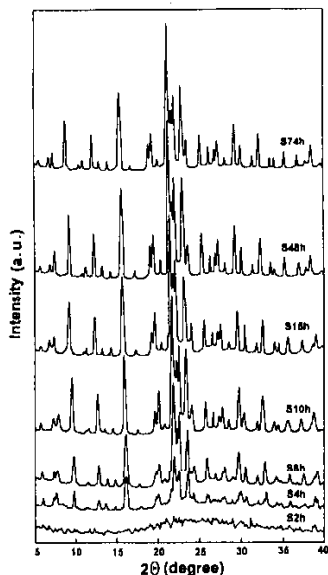


Fig. 2 XRD pattern of the samples obtained during the crystallization of ALPO-11

action of phosphoric acid with the pseudoboehmite to form amorphous aluminum phosphate that already was accelerated by the increment in the temperature of the system until 200°C.

The samples retirement between 2 and 15 h (S4h–S15h) exhibited crescent values of pH evidencing that the reaction of formation of amorphous aluminum phosphate still is happening, however the XRD profiles shows the appearance of peaks characteristics of ALPO-11. This indicates that the crystalline aluminophosphate was formed from the amorphous phase. The pH in the sample S48h presented the greater value among all the samples, ca 8.10. It can be explained in terms of that all phosphoric acid was consumed at the reaction with the source of aluminum and basic pH is due to the excess of amine in solution. The pH decreasing of the sample S74h probably was occasioned by the dissolution of the material already crystallized in the mother liquor which released species in solution that lowered the pH. This phenomenon was observed too at the synthesis of VPI-5 with *n*-dipropylamine [14]. Another factor that reinforces this hypothesis, is the diminution of the crystallinity of sample S74h, as measured by XRD and FT-IR techniques. XRD analysis were performed with the calcined samples to verify the stability of the ALPO-11.

The FT-IR spectra of the solid phase obtained during the crystallization are shown in Fig. 3. These spectra were obtained for the as-synthesized samples.

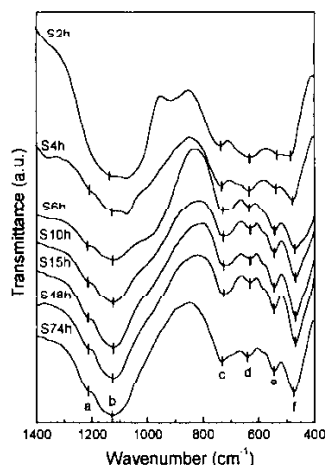


Fig. 3 FT-IR spectra of the samples obtained during the crystallization of ALPO-11

The attribution for the main absorption bands in the 1400–400 cm^{-1} structural region of the spectra were reported by Araujo *et al.* [9]. These are absorption bands, due to internal vibrations of the TO_4 tetrahedral, with $T=\text{Al}$ or P , which are structure insensitive, and others owing the external vibrations of the tetrahedral that are structure sensitive. This last type of vibration can be used as an indicative property of the degree of crystallinity of the material [15].

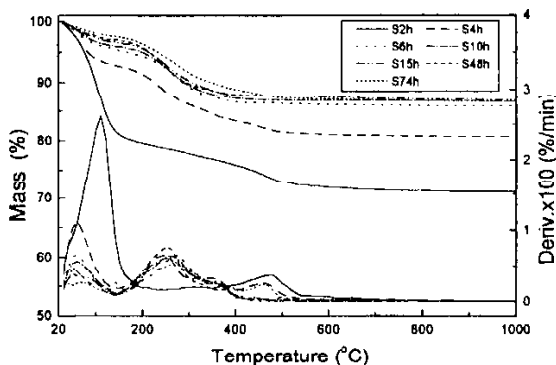


Fig. 4 TG and DTG curves of the solids obtained during the crystallization of ALPO-11

TG analysis was utilized to determine the temperature range to remove the organic template and pore volume of the samples. Figure 4 illustrates the TG curves and its respective derivatives (DTG). The TG curves of the samples S2h and S4h showed behavior different from the others. This is explained by the fact that both presented large quantity of amorphous material, as determined by XRD analyses.

From TG/DTG curves, it is important to observe that the samples retired after 6 h of heating, presented a similar behavior, with two steps of mass losses, except for the S74h sample, that presented a third step of mass loss in the temperature range from 400 to 550°C which was attributed to the presence of amorphous material, since the samples S2h and S4h also showed the same mass loss, in the same temperature range.

Table 1 Volume occupied by water and DIPA molecules into pores per gram of solid, determined from TG/DTG curves

Sample	Pore volume occupied by molecules/(cm ³ g ⁻¹) ^a		
	water	DIPA	total
S6h	0.048	0.129	0.177
S10h	0.047	0.121	0.168
S15h	0.038	0.126	0.164
S48h	0.034	0.134	0.168
S74h	0.027	0.126	0.153

Table 1 shows the pore volume values occupied by water and DIPA molecules per gram of solid. These values were obtained by DTG curve through the identification of two steps of mass losses, one relative to the water in the temperature range from ambient to 150°C and the other relative to the di-isopropylamine in the temperature range from 180 to 380°C, in which the mass of each event was measured. For transforming the mass values in volume, it was assumed that the water and di-isopropylamine

molecules occupy the pores of the ALPO-11 in the liquid state. A detailed description of this method is found in the reference [16]. It is interesting to note that the value of adsorption capacity reported by Wilson *et al.* [17] for the ALPO_A-11 measured over saturation of water was approximately $0.16 \text{ cm}^3 \text{ g}^{-1}$. Therefore the values reported here for pore volume total are in excellent agreement with the data of literature [17]. However both the values are larger than the theoretical value calculated from XRD crystallographic data, by Davis *et al.* [18] which was $0.134 \text{ cm}^3 \text{ g}^{-1}$. This difference is because, in the condition of saturation, occurs the adsorption on the intergranule pores (meso and macropores) and the theoretical value is only related to the microporous volume.

Analyzing the data of Table I, we concluded that all the molecules of water are into of the meso and macropores whereas the molecules of DIPA are into of the micropores. These results were also found for SAPO-5 [19]. It was observed that the values of microporous volume determined over of the molecules of DIPA are very near to the theoretical value calculated.

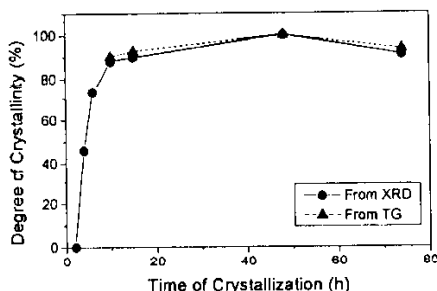


Fig. 5 Curves of percentage of crystallinity vs. the crystallization time obtained through XRD and FT-IR analyses

The degree of crystallinity of the samples was determined through XRD by the measurement of the area of the peaks at 2θ ranging from ca 20.7 to 24.1 degrees. The sample that presented larger area was considered as 100% crystalline and the areas of the other samples were normalized in relation to this. Another method used in this work to measure the degree of crystallinity was through the TG/DTG curves, using the temperature region of remotion of di-isopropylamine from the microporous of the ALPO's samples. Thus, the crystallinity of the samples was determined by the mass loss in the temperature range from 180 to 380°C. The Fig. 5 shows the curves of percentage of crystallinity vs. the crystallization time obtained through XRD and TG analysis.

It was observed that, initially the crystallinity increased rapidly attaining approximately 90% in less than 10 h, but in the intervals from 10 to 40 h, the velocity of crystallization decreased, and only after 48 h is that the sample with 100% of crystallinity was obtained. From TG, the values obtained from 10 to 74 hours were consistent with those obtained from XRD analysis, showing that the crystallization of ALPO's and probably others related materials can be studied by this proposed method.

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