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Article

Insight in the crystallization kinetics of $AlPO_4$-11 molecular sieve using di-isopropylamine as template

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Abstract: The hydrothermal synthesis of aluminophosphate molecular sieve type $AlPO_4$-11 was processed from chemicals containing psueudobohemite, 85% phosphoric acid, water, and di-isopropylamine as templating agent. The crystallization of the samples was studied by taking samples in times from 2 to 74 hours. The obtained white powder products have been characterized by XRD patterns, FT-IR spectra, thermogravimetric data, scanning electron microscopy and pH measurement of the mother liquor. The pore volume, as determined from TG and DTG curves, was ca. 0.17 cm^3g^{-1}. The crystallization process of the aluminophosphate exhibited in its initial phase a behavior of first order reaction with a specific velocity constant of ca. 0.25 h^{-1}, as determined from XRD and FT-IR data.

Keywords: Hydrothermal synthesis; Microporous materials; Aluminophosphate; Crystallization kinetics

1. Introduction

One of the most important materials in the chemical and petrochemical industry are molecular sieves, as they have open structures containing pores and cavities. These materials generally known as zeolites, aluminophosphates and silicoaluminophosphates are widely used as adsorbents, catalysts and ion exchangers in addition to applications in nanotechnology, in the area of optical sensors, due to their electronic properties [1].

The aluminophosphate molecular sieves represent a class of microporous materials free of silica, first reported in 1982 by Wilson et al. [2], which are synthesized by the hydrothermal method. These solids are denoted as $AlPO_4$-n, where “n” is an indicative number of the structure type. After the discovery of aluminophosphates, various related materials have been synthesized [3-6].

Microporous $AlPO_4$-11 has an AEL topology, and is a member of the aluminophosphates molecular sieves family, which exhibits one-dimensional channel system with 10-membered ring pores. The pore opening is elliptical in shape with diameters of 3.9 x 6,3 Å. The symmetry of $AlPO_4$-11 is orthorhombic with unit cell dimensions a = 13.5336, b = 8.4821 and c = 8.3703 Å [7]. Figure 1 illustrates the framework of $AlPO_4$-11 viewed along [100] direction [7,8].

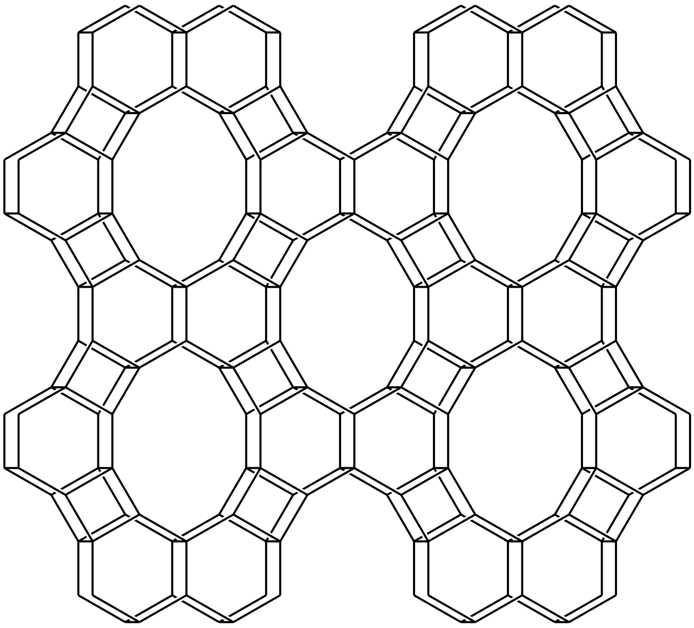

Figure 1. Structural framework of the aluminophosphate $AlPO_4$-11 viewed along [100] direction [7]

It is well known that the catalytic properties exhibited by a microporous material are strongly dependent on the synthesis procedure. Many of the aluminophosphate materials exhibit properties similar to that of zeolites, for instance, molecular sieve effect, specific channel and cage system, indicating that they can be used as adsorbents, catalysts and supports in several chemical processes such as paraffin/isoparaffin separation, isomerization and alkylation. The main advantages of the AlPO's compared with other supports, are related with the possibility of vary 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 $AlPO_4$-11, several works have been made concerning this molecular sieves [9-11], however few is known about its crystallization kinetics. Several studies have been reported on the mechanism of crystallization of molecular sieves using dry gel and solid transformation method [12,13], synthesis of nanocrystal [14], ionothermal procedure [15] and membranes with distinctive porosities [16]. Recently, the synthesis of aluminophosphate using eutectic solvent [17] and non-hydrolytic sol-gel reactions [18] have been reported for preparation of high surface materials. However, many processes in hydrothermal crystallization are still not well understood.

In this work, the syntheses procedure and crystallization kinetics of $AlPO_4$-11 were studied as a function of hydrothermal synthesis time, and subsequent analysis by X-ray powder diffraction (XRD), Fourier Transform Infrared spectroscopy (FT-IR) and thermogravimetric (TG/DTG), as well as the pH measurements of the supernatant liquid.

2. Materials and Methods

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The samples were synthesized using the following chemicals as starting materials: phosphoric acid (85%, Merck), pseudoboehmite (Catapal B, Vista Chemical), di-isopropylamine (here named as DIPA, 98%, Riedel) and distilled water. These reactants were combined to obtain a gel with the following stoichiometric proportion:

$$1.0\ \mathrm{DIPA} : 1.0\ \mathrm{Al_2O_3} : 1.0\ \mathrm{P_2O_5} : 80\ \mathrm{H_2O}$$

The synthesis procedure consists of a modified process described elsewhere [19,20], in relation to the order or mixing the reactants, which summarized as: i) pseudoboehmite was slurried in half of total volume of water required at synthesis; ii) the phosphoric acid was diluted with the volume of remainder water; iii) the phosphoric acid solution was added to the suspension obtained in the step (i) and (iv) addition of DIPA to the mixture.

The obtained gel was divided in seven parts and the portions were transferred to Teflon lined stainless-steel autoclaves and heated in an oven at temperature of 200 ^{o}C. For the crystallization process, the autoclaves were removed from the oven in times of 2; 4; 6; 10; 15; 48 and 74 hours and then quenched in cold water. The obtained samples were designed as S2h; S4h; S6h; S10h; S15h; S48h and S74h, respectively. The pH of the obtained slurry was carefully measured. The solid products were recovered from the mother liquid by filtration, washed with distilled water and dried at 100 ^{o}C for 6 hours. The calcinations of the samples were performed by heating at 500 ^{o}C in dry air dynamic atmosphere with flow of 60 cm^{3}min^{-1} for period of 12 hours.

A Philips powder diffractometer with CuKα radiation, with the diffraction angle (2θ) at range of 5-40^{o} was used to identify the $AlPO_4$-11 crystalline phase and to determination of the degree of crystallinity. Infrared measurements were performed in a Fourier Transform Infrared spectrometer, FT-IR Prospec (Midac Corp.) using the KBr wafer technique. The wafers were prepare by the mixture of ca. 0.5 mg of sample with 150 mg of KBr powder and pressed at approximately 800 MPa. The spectra were attained in the region of 1400-400 cm^{-1}. Thermogravimetric analysis (TG) was performed on a DuPont TA thermobalance, at a heating rate of 10 ^{o}C min^{-1}, in the temperature range from ambient to 1000 ^{o}C using nitrogen flow of 60 cm^{3}min^{-1}. For these analyses, a mass of 10 mg was used.

3. Results and Discussion

During each step of the gel preparation and after the specific times of the hydrothermal synthesis, the pH of the mixture was carefully measured. The obtained values and behavior of the pH are viewed in Figure 2.

During the first step of the gel preparation, the pH for the mixture of pseudoboehmite with water increased slowly from 6.90 to 7.15 in approximately 60 minutes due to the low reactivity of pseudoboehmite. After addition of phosphoric acid solution for the mixture, the pH decreased to 1.00, and was observed a formation of a viscous gel. The pH of the system increased slowly as the reaction mixture was aged with vigorous agitation until pH 1.90 after 200 minutes. This evolution of pH is due to the difficulty of phosphoric in reacting with the bulk after the surface has reacted (equation 1). When the DIPA was added to the mixture, the gel became very viscous, and the pH value skipped to 5.70 and immediately stabilized in 3.20 (equation 2).

$$\mathrm{H_3PO_4} + \mathrm{AlOOH} = \mathrm{AlPO_4} + 2\mathrm{H_2O} \tag{1}$$
$$\mathrm{AlPO_4} + \mathrm{(C_3H_7)_2NH} = \mathrm{AlPO_4 \cdot (C_3H_7)_2NH} \tag{2}$$

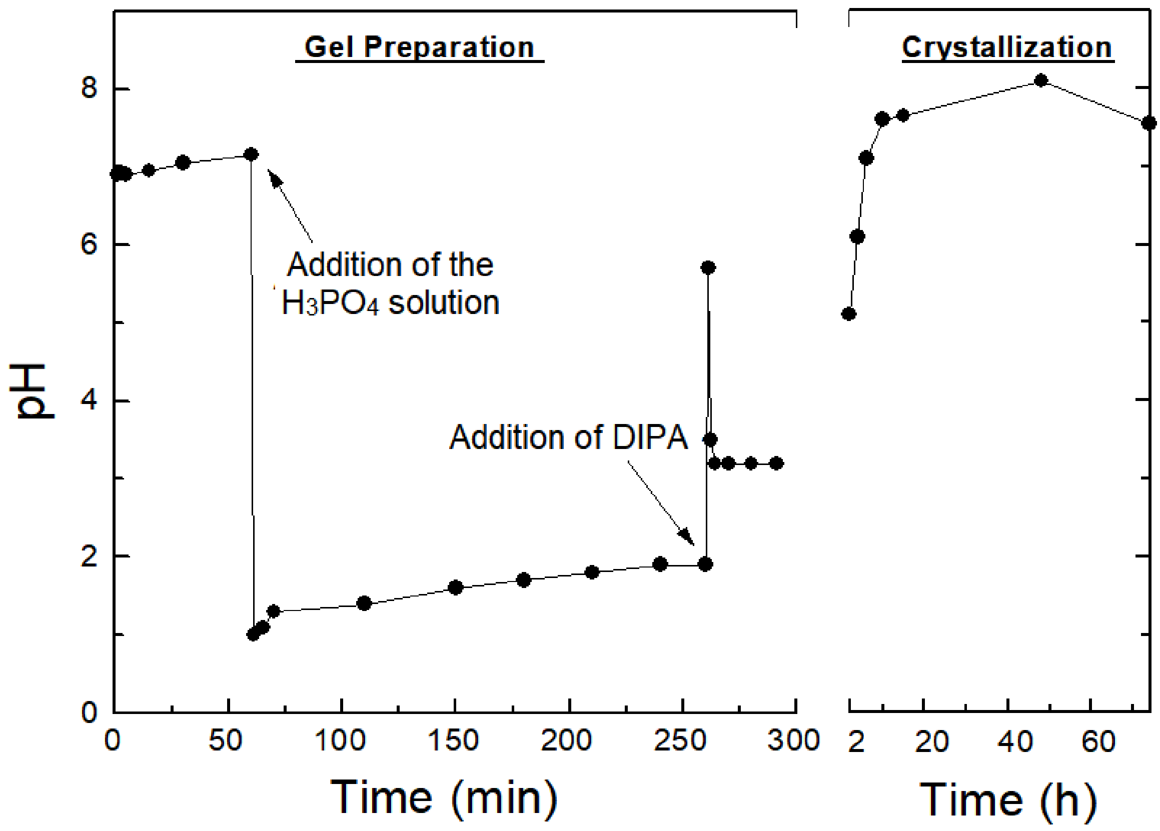

Figure 2. Curves of pH during the gel preparation and after remotion of each sample during the crystallization process.

The sample obtained in 2 hour of heating presented a pH of 5.10. The XRD analysis of this sample did not indicate a crystalline phase of the material, as shown in Figure 3. It was assumed that this pH increasing was due to the reaction of phosphoric acid with pseudoboehmite to form amorphous aluminum phosphate. The samples S4h, S6h, S10h and S15h exhibited crescent values of pH evidencing that the reaction of formation of amorphous aluminum phosphate is still occurring, however the XRD profiles shows characteristics peaks of ALPO4-11. The pH in the sample S48h presented the greater value among all the samples, ca. 8.10, evidencing that all phosphoric acid was consumed at the reaction with the pseudoboehmite and a basic pH is due to the excess of amine in solution. The pH decreasing for S74h sample 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 also observed for synthesis of VPI-5 with di-n-propylamine [21].

In addition, was observed a decreasing in the crystallinity of the S74h sample, as measured by XRD and FT-IR techniques. XRD analyses were performed with the calcined samples to verify the stability of the $AlPO_4$-11. The results showed the presence of well defined crystalline phase identified as AEL structure (AEL = Aluminophosphate Eleven) $AlPO_4$-11, as shown in Figure 3.

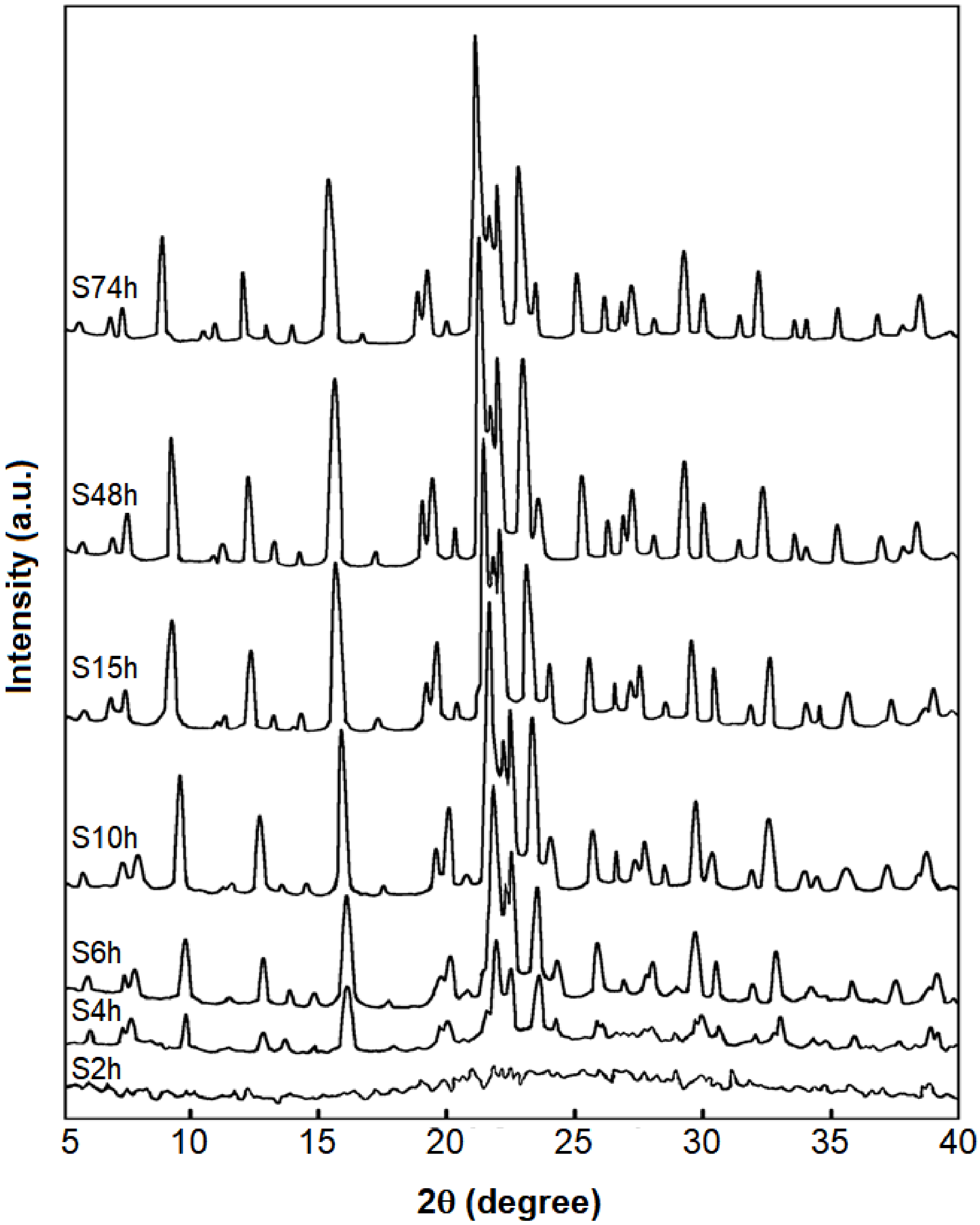

Figure 3. XRD pattern of the samples obtained during the crystallization process of ALPO4-11, monitored at different times.

The FT-IR spectra of the solid phase obtained during the crystallization are shown in Figure 4. These spectra were obtained for the as-synthesized samples. The attribution for the main absorption bands were done in the 1400 - 400 cm-1, structural region of the spectra [22].

From FT-IR data, two kinds of absorption bands are observed: one due to internal vibrations of the TO_4 tetrahedral, with T = Al or P, which are structure insensitive, and other due to 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.

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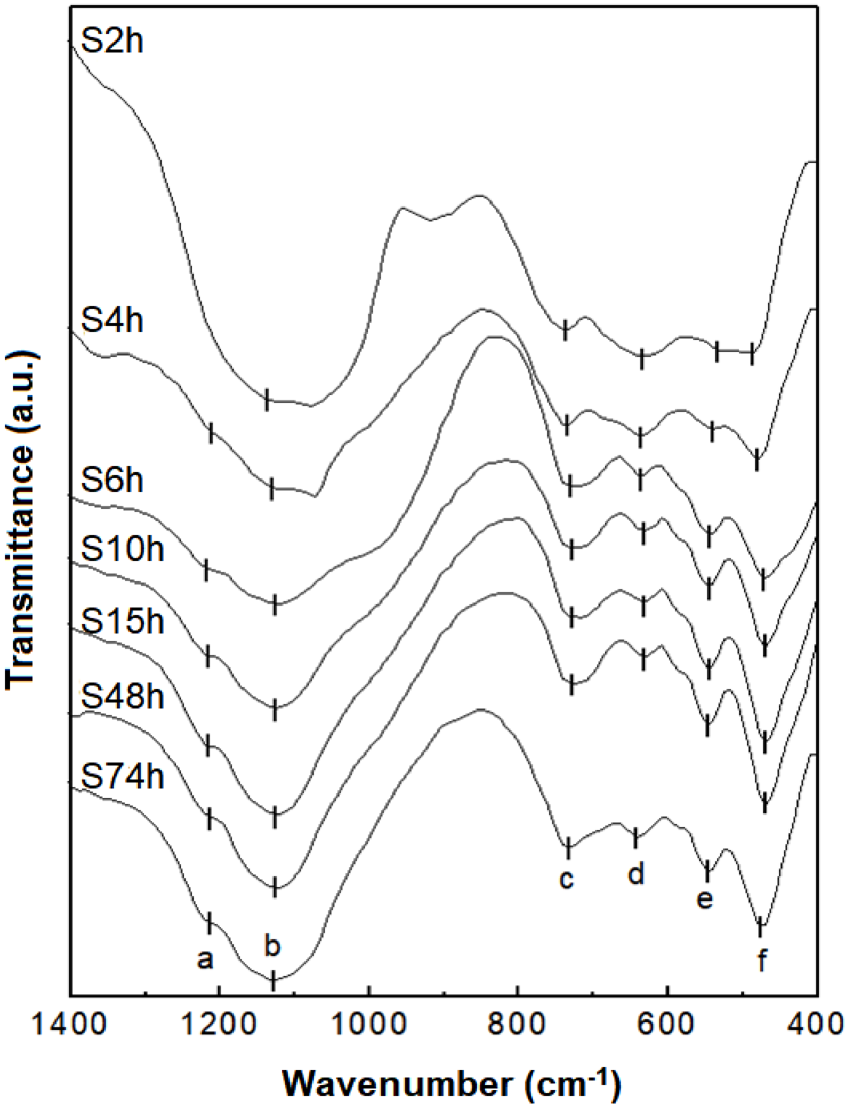

Figure 4. Infra red spectra of the samples obtained during the crystallization of ALPO4-11, at diffent synthesis time.

The thermogravimetry (TG) was used to determine the thermal stability, range of temperature to remove the organic template, and pore volume of the samples. The Figure 5 illustrates the TG curves and its respective derivatives (DTG). The TG curves of the samples S2h and S4h showed different behavior from the others, because they presented large amount of amorphous material, as determined by XRD analyses.

From TG curves is important to observe that the samples removed after 6 hours of heating (S6h sample), presented a similar behavior, with two steps of weight losses, except for the S74h sample, that presented a third step of weight loss in the temperature range from 400 to 550 oC which was attributed to the presence of amorphous material, since the samples S2h and S4h also showed the same weight loss, in the same temperature range.

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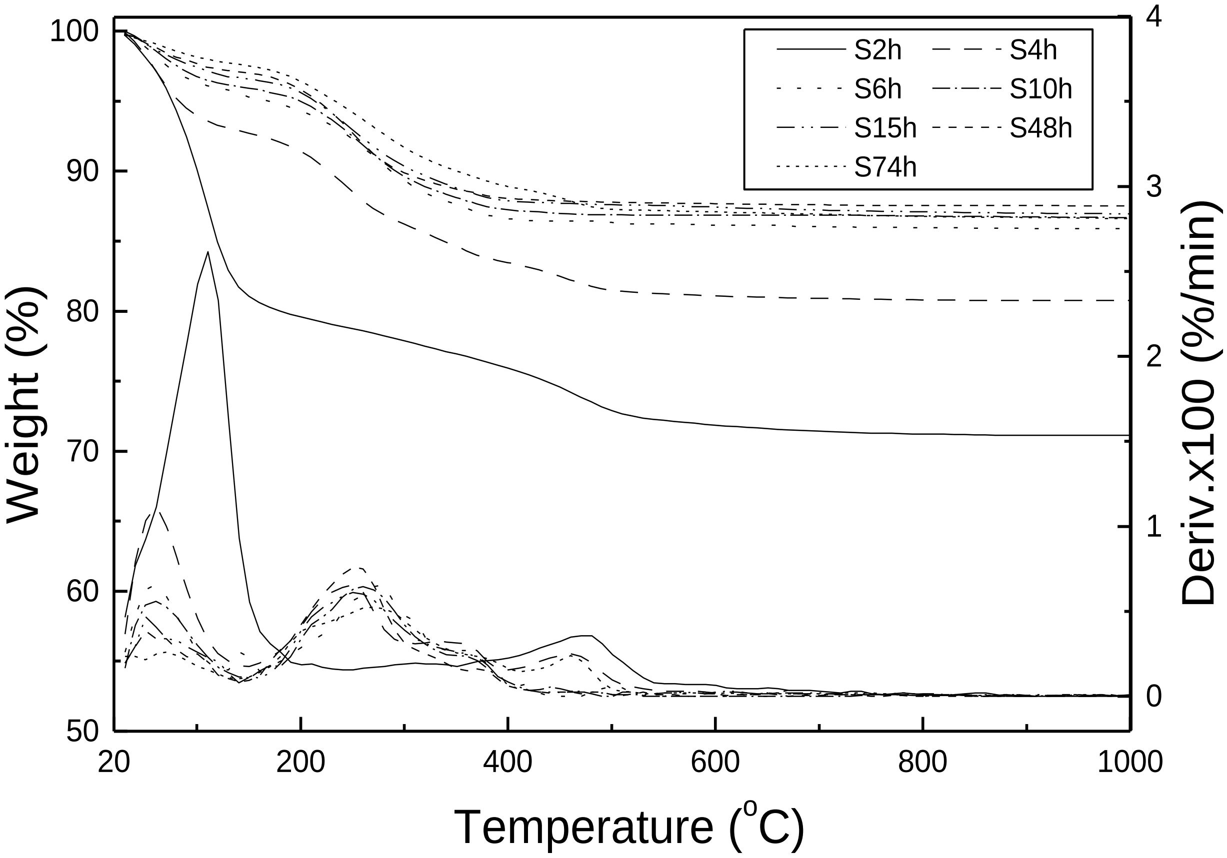

Figure 5: TG and DTG curves of the solids obtained during the crystallization of ALPO4-11, at different synthesis time.

From DTG curves, was identified of two steps of weight losses, one relative to the water in the temperature range from ambient to 150 oC and the other relative to the di-isopropylamine in the temperature range from 180 to 380 oC, in which the mass of each event was measured. For transform the mass values in volume, it was assumed that the water and di-isopropylamine molecules occupy the pores of the $AlPO_4$-11 in the liquid state. A detailed description of this method is found in the reference [23]. It is interesting to note that the value of adsorption capacity reported by Wilson et al. [24] for the $AlPO_4$-11 measured over saturation of water was approximately 0.16 cm3g-1. The values reported here for pore volume total are in excellent agreement with the literature [24]. However both the values are larger than the theoretical value calculated from XRD crystallographic data, by Davis et al. [25] which was 0.134 cm3g-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. The obtained values suggest that molecules of water are into of the meso and macropores whereas the molecules of DIPA are into of the micropores of the aluminophosphate. These results were also found for SAPO-5 [26]. It was observed that the values of microporous volume determined over of the molecules of DIPA are very close to the theoretical calculated value.

The degree of crystallinity of the samples was determined from XRD by the measurement of the area bellow the peaks in the range of 2θ from 20.7 to 24.1 degrees. The sample that presented larger area was considered as 100% crystalline and the areas of the others samples were normalized in relation to this. Another method used in this work to measure the degree of crystallinity was through FT-IR spectra using the absorption band associated to vibration in the double-rings, which is a vibration of the external linkages of the tetrahedral and consequently is structure sensitive. Thus, the crystallinity of the samples was determined by the area of absorption band in the 650- 500 cm-1 region, in the same way attained over XRD. The Figure 6 shows the curves of percentage of crystallinity versus the crystallization time obtained from XRD and FT-IR analyses.

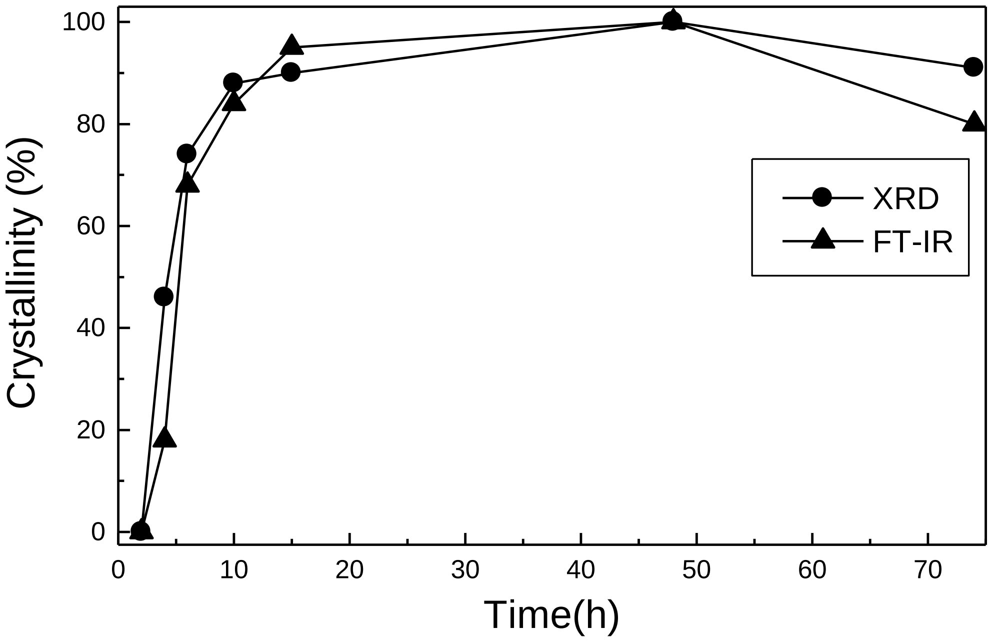

Figure 6: Curves of percentage of crystallinity versus the crystallization time obtained from XRD and FT-IR analyses.

The ALPO4-11 crystallinity increased rapidly attaining approximately 90% in ca. 10 hours, but after this time the velocity of crystallization decreased and at 48 hours was obtained the best sample (S48h) with 100% of crystallinity. In 74 hours of heating the crystallinity decreased to ca. 90%, due to dissolution of the material already crystallized. It is important to observe that the crystallinity curves obtained from XRD and FT-IR are very similar to the curve of pH after synthesis versus time of crystallization (showed in Figure 2), evidencing that the pH gives an indication of degree of crystallization of the materials.

The reaction of amorphous aluminum phosphates to crystalline aluminophosphates was considered as a first order reaction, since it depends only of the concentration of the amorphous aluminum phosphates, once the organic template is in excess. Thus, the degree of crystallinity was used as the conversion degree of this reaction. Kinetics data for the $AlPO_4$-11 crystallization were determined by the plot of [-ln(1- x)] versus the time of crystallization, as shown in Figure 7, where "x" is the crystalline degree, as determined from XRD and FT-IR data.

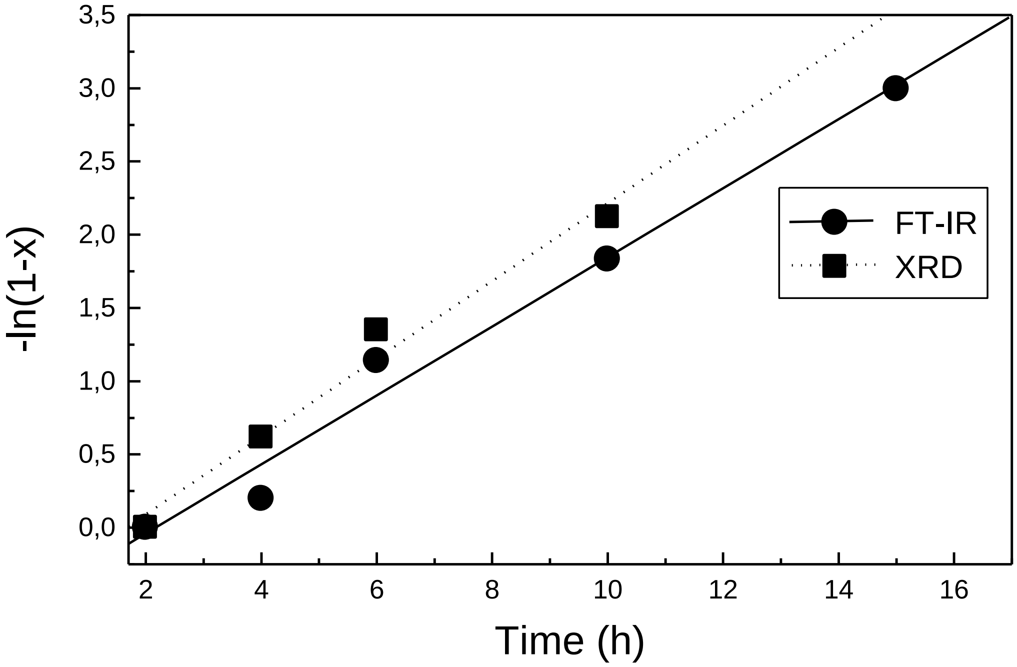

Figure 7: Plots of [-*ln*(*1* - *x*)] versus the time of crystallization for ALPO4-11, obtained from XRD and FT-IR data.

Applying the $y = kx + l$ equation, where k is the velocity constant of crystallization of $AlPO_4$-11, were determined values of 0.26 and 0.24 h^{-1} from XRD and FT-IR data, respectively. The coefficient of correlation obtained was of *ca.* 0.99, showing that this proposed model is well adjusted to the experimental data, and can be used satisfactorily on the study of crystallization of aluminophosphate molecular sieves, and probably other related materials [27].

5. Conclusions

From a systematic study of the hydrothermal synthesis and crystallization process of aluminophosphate type $AlPO_4$-11, by remotion of samples in specific time, it was concluded that there is an ideal time for crystallize $AlPO_4$-11 material, which at temperature of 200 ^oC was found to be approximately 48 hours. After this time, occurs dissolution of the material already crystallized. The crystallinity of the $AlPO_4$-11 samples can be determined by FT-IR considering the area of the absorption band associated to the external tetrahedral vibration in the double-rings in the 650-500 cm^{-1} region, that is structure sensitive, with results analog to those obtained by XRD analysis. Thermogravimetric analysis can be used as an alternative method for the determination of pore volume, which showed an excellent precision. The crystallization reaction of $AlPO_4$-11 exhibited in its initial phase a behavior of a first order reaction, with a specific velocity constant of ca. 0.25 h^{-1}, determined from XRD and FT-IR data.

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Conflicts of Interest: The authors declare no conflict of interest.

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