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Artigo

Synthesis, Optimization and Characterization of Zeolite Beta (BEA): Production of ZSM-5 and $NaAlSiO_4$ as Secondary Phases

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Síntese, Otimização e Caracterização da Zeólita Beta (BEA): Produção de ZSM-5 e $NaAlSiO_4$ como Fases Secundárias

Resumo: A escolha dos parâmetros de síntese influencia a obtenção de um material adequado para utilização em várias aplicações. Neste trabalho, zeólita beta (BEA) foi obtida com sucesso por síntese hidrotérmica, avaliando os seguintes parâmetros: razão Si/Al, tempo e temperatura de cristalização. Os materiais sintetizados foram caracterizados por análise de difração de raios X (XRD), espectroscopia de infravermelho com transformada de Fourier (FTIR), termogravimetria (TG e DTG) e isotermas de adsorção e dessorção de N_2. A difração de raios X mostrou que a alteração de apenas um destes parâmetros atua sobre a formação da estrutura microporosa desejada. BEA foi obtido na razão Si/Al igual a 8, com um tempo de cristalização de 4 dias a 170 °C, apresentando uma área específica de 437 m^2g^{-1} e um volume de poros de 0.106 cm^3g^{-1}. Em outros ensaios, foram obtidas fases secundárias de $NaAlSiO_4$ e SiO_2, bem como zeólita ZSM-5, analcima, omega e Linde B2.

Palavras-chave: BEA; razão Si/Al; Tempo; Temperatura.

Abstract

The choice of synthesis parameters influences obtainment of a suitable material for use in several applications. In this paper, zeolite beta (BEA) was successfully obtained by hydrothermal synthesis, assessing the following parameters: Si/Al ratio, time and crystallization temperature. The synthesized materials were characterized by X-ray diffraction (XRD), Fourier-Transfer Infrared (FTIR) spectroscopy, thermogravimetry (TG and DTG) and N_2 adsorption-desorption isotherm analyses. X-ray diffraction showed that the change of only one of these parameters acts on the formation of the desired microporous structure. BEA was obtained in the Si/Al ratio equal 8, with a crystallization time of 4 days at 170 °C, presenting a specific area of 437 m^2g^{-1} and a pore volume of 0.106 cm^3g^{-1}. In other assays, secondary phases of $NaAlSiO_4$ and SiO_2 were obtained, as well as ZSM-5 zeolite, analcime, omega and linde B2.

Keywords: BEA; Si/Al ratio; Time; Temperature.

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Synthesis, Optimization and Characterization of Zeolite Beta (BEA): Production of ZSM-5 and $NaAlSiO_4$ as Secondary Phases

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1. Introduction

Molecular sieves are porous solids capable of selectively adsorbing different sized molecules. Zeolites are microporous molecular sieves with a structure consisting of crystalline aluminosilicate in a three-dimensional arrangement of tetrahedra TO_4 (SiO_4 or AlO_4^-) connected by oxygen atoms. The size and shape of porous channels provide selectivity to zeolites, enabling changes in morphology, composition and porosity, as well the combination of active species with material structure.[1-3] In addition to their properties as molecular sieves, zeolites also chemically interact with some molecules due to their surface acidity provided by structural aluminum atoms or by charge imbalance from broken bonds at the structural extremities.[4-6]

Zeolites are generally synthesized under hydrothermal conditions using hydrogels prepared from aluminate, silicate and hydroxide solution. Natural sources such as diatomite, kaolinite and other clay minerals have also been used in the synthesis of zeolites.[7-9] By varying the composition of synthesis solutions it is possible to obtain zeolites with different structures or the same zeolite showing different chemical compositions.[10-12] In summary, keeping the conditions of preparation fixed, a simple variation in the Si/Al ratio may result in different zeolites, for example, faujasite X and sodalite (Si/Al < 2), mordenite and faujasite Y (2 < Si/Al < 5), ZSM-5, ZSM -12 and Beta (Si/Al > 5).[13]

Zeolite beta (BEA) is a large pore crystalline aluminosilicate. The intergrowth of two polymorphs (A and B) related to each other, with the possibility of there being a third (C), makes up the structure of BEA. Polymorphs are constituted by a three-way system of channels delimited by rings of 12 interconnected members.[1]

Among several types of natural and synthetic zeolites already reported in literature,[14] BEA has received special attention from the scientific community regarding its high Si/Al ratio, high surface acidity and hydrothermal stability. In addition, it shows differential catalytic properties such as activity, selectivity and resistance to deactivation over time of use, mainly in catalytic cracking reactions, alkylation and acylation of aromatic hydrocarbons, and alkane hydroisomerization, among others already reported.[15]

Research on variation in the Si/Al ratio, time and temperature of zeolite synthesis has shown that modification of these parameters is able to change the physical properties of zeolites.[16,17] Variation in temperature and crystallization time guided the formation of the most stable phase for zeolite synthesis, or contributed to the growth of different crystalline structures.[13-16] Therefore, in this work, BEA was synthesized by the hydrothermal method, varying the synthesis conditions such as time, temperature and Si/Al ratio. The obtained materials were characterized and the generated phases were identified by different material analysis techniques in order to propose the best conditions to obtain a greater fraction of zeolite beta.

2. Experimental Procedure

2.1. Synthesis of Materials

Preparation of microporous BEA type materials was performed using the hydrothermal method, following procedures described in the literature.[18-20] The reagents used in synthesis were TEOS (Sigma Aldrich) as a source of silicon, Al_2O_3 (Vetec) as a source of aluminum, NaOH (Vetec) as a source of sodium, TEAOH (Sigma Aldrich) as a structural driver and distilled water, forming a system containing $1Na_2O–xAl_2O_3–10SiO_2–27.5TEAOH–yH_2O$, where x and y varies stoichiometrically in relation to the Si/Al ratio. The proportions were 0.250; 0.357; 0.625 for x and 395; 410; 425 for y,

respectively. The Si/Al ratios used in this study were 8, 14 and 20, and the other synthesis conditions are shown in Table 1.

Table 1. Conditions employed in the synthesis of zeolites

Si/Al ratio	Crystallization time (Days)	Crystallization temperature (ºC)
8	2	135
8	2	170
8	4	135
8	4	170
14	3	152
14	3	152
14	3	152
20	2	135
20	2	170
20	4	135
20	4	170

The resulting material was filtered, dried at 100 °C for 12 hours and calcined in air at 550 °C for 6 hours.

2.2. Characterization

All the calcined and uncalcined samples were initially characterized by X-ray diffraction (XRD) using radiation CuKα (λ = 1.542 Å) at 30 kV and 30 mA with Shimadzu XRD-7000 equipment to determine the best conditions for obtaining BEA. Data were collected over a range of angular variation between 5 and 55°. Pattern acquisition and treatment were performed in X'pert HighScore software provided by PAN alytical. Position and intensity of observed peaks were compared with data supplied by JCPDS reference cards (Joint Committee on Powder Diffraction Standards) through the *International Center for Diffractional Data* (ICDD) library.

Obtained BEA was characterized by Fourier-Transfer Infrared (FTIR) spectroscopy, thermogravimetry (TG and DTG) and N_2 adsorption-desorption isotherm.

FTIR was performed in a Perkin Elmer spectrometer in the mid-infrared region between 400 to 4000 cm^{-1} and resolution of 4 cm^{-1}. TG and DTG were performed in the range of 30-800 °C at a heating rate of 10 °C min^{-1}, using a SDTQ600 thermobalance (TA Instruments) in a nitrogen atmosphere (N_2). Nitrogen adsorption-desorption at -196 °C was applied in NOVA 2000 Quantachrome equipment in the P/P0 range of 0.05 - 0.35, running BET and BJH methods to quantify specific area, volume and pore diameter. All characterizations were performed at the Catalysis and Refining Laboratory and Environmental Technologies Laboratory of the *LCR/LABTAM* Center of Primary Processing and Reuse of Produced Water of *NUPPRAR/UFRN*.

3. Results and Discussion

3.1. X-ray Diffraction of the Synthesis Products

Zeolite phase growth was followed up by XRD. Figures 1, 2 and 3 show X-ray diffractograms for samples with Si/Al ratios of 8 and 20, with crystallization time of 2 and 4 days at 135 °C and 170 °C, as well as Si/Al ratio of 14 with crystallization time of 3 days at 152 °C, respectively, as shown in Table 1.

The XRD data in Figure 1 show characteristic diffraction peaks of ZSM-8 (JCPDS 048-0134), zeolite omega (JCPDS 044-0011), analcime (JCPDS 072-0445), zeolite Linde B2 (JCPDS 038-0328), SiO_2 (JCPDS 003-1092) and $Na_2CO_3.1.5H_2O_2$ (JCPDS 011-0656) for the synthesized samples. The material prepared with a Si/Al ratio of 8 and crystallization time of 4 days at 135 °C propitiated the formation of a defined crystal structure, compared to the material with a crystallization time of 2 days in the same Si/Al ratio and temperature conditions. The samples of Si/Al ratio of 20 and crystallization time of 2 and 4 days at 135 °C showed XRD patterns with similar profiles. Thus, the increase in the material crystallization time did not significantly influence the formation of obtained crystalline structures. After calcination, it was observed that the materials had maintained the growth phases, even in face of a significant increase in diffraction peak intensity.

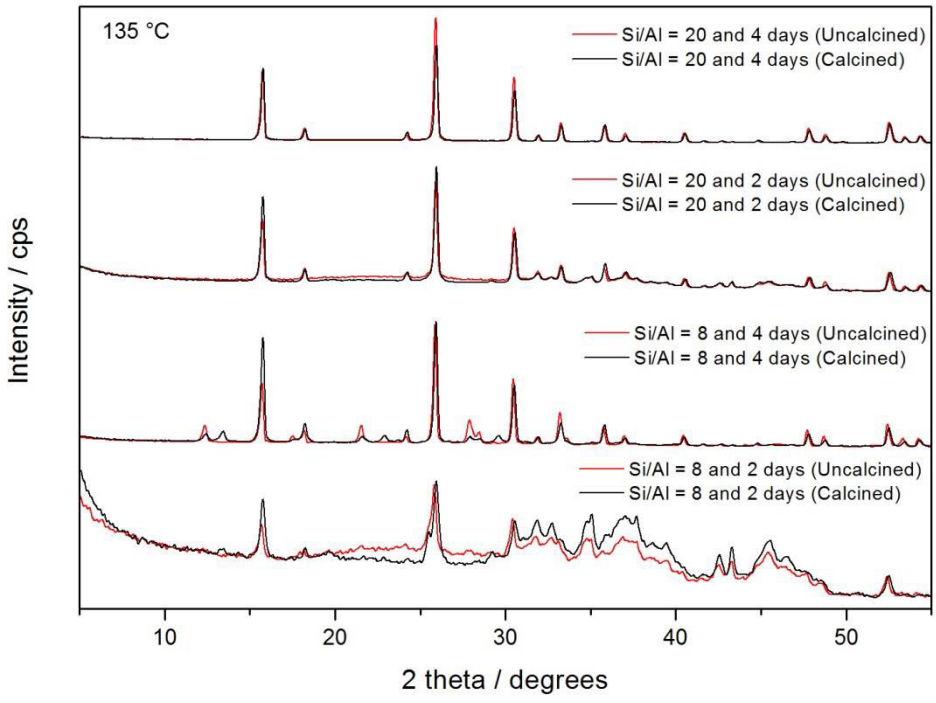

Figure 1. XRD of the calcined and uncalcined products obtained with Si/Al ratios of 8 and 20 and crystallization time of 2 and 4 days at 135 °C

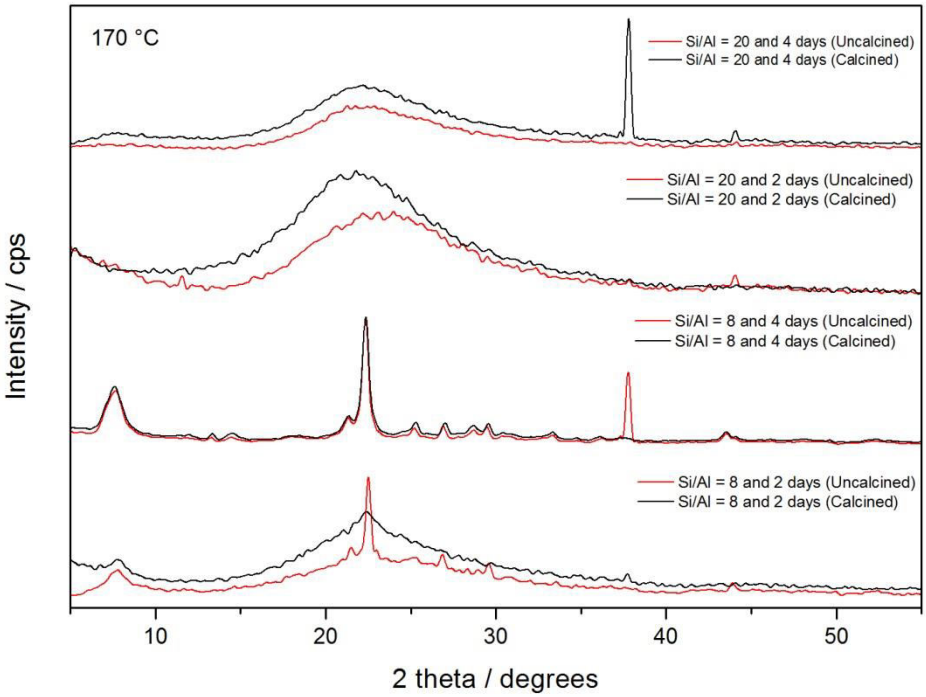

Figure 2. XRD of the calcined and uncalcined products obtained with Si/Al ratios of 8 and 20 and crystallization time of 2 and 4 days at 170 °C

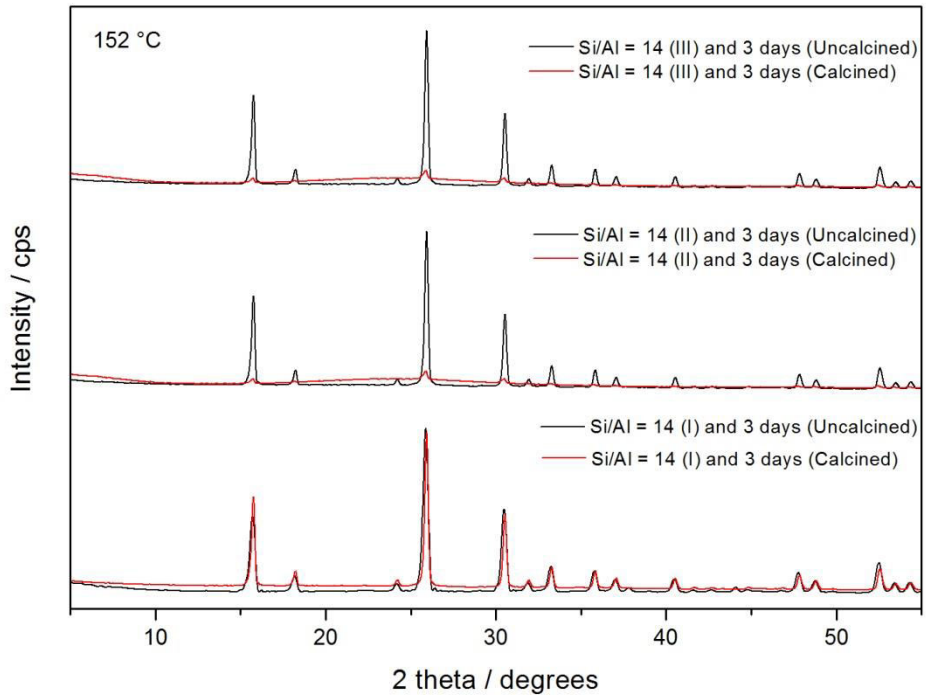

Figure 3. XRD of the calcined and uncalcined product obtained with Si/Al ratio of 14 and crystallization time of 3 days at 152 °C

The diffractograms of Figure 2 show two peaks in the 2 theta region = 7.6° (101) and 22.4° (302), in the zeolitic material with Si/Al ratio of 8 and crystallization time of 4 days at 170 C. According to the JCPDS 48-0038 cards and literature data,[21] these peaks are relative to the BEA zeolite phase. In turn, the appearance of characteristic peaks of the zeolite beta was observed in the samples with Si/Al ratio of 8 and a crystallization time of 2 days at the same temperature; however, the material lost its original structure when passing through the calcination process. It was observed that the crystallization time in this case influenced material resistance in the wall which was insufficient to maintain the same unchanged after being subjected to high temperatures. For samples with a Si/Al ratio of 20, crystallization time of 2 and 4 days at 170 °C, the XRD patterns presented an amorphous phase, indicating that the structure of zeolite beta was not formed. According to the literature[6], crystallinity relative to zeolite beta decreases with an increase in the Si/Al ratio, which might have occurred for the sample with a Si/Al ratio of 20, influencing in the formation of zeolitic structure.

The diffractograms of Figure 3 present similar profiles to the materials with a Si/Al ratio of 20, crystallization time of 2 and 4 days at 135 °C, and do not show the formation of the zeolite beta structure. The synthesis was carried out in triplicate to show the reproducibility of employed method. It can be seen that the performed calcination method did not destroy the structure of the formed materials, but instead maintained them.

3.2. Characterization of Zeolite Beta

According to the X-ray diffraction results, the material with a Si/Al ratio of 8 and 4 days at 170 °C obtained a zeolite beta structure. The material phases were identified, with zeolite beta (BEA) (JCPDS 48-0038) being the main phase, and zeolite ZSM-5 (JCPDS 43-0321) and $NaAlSiO_4$ (JCPDS 33-1203) the secondary phases, as shown in Figure 4.

According to the literature,[18-20] the synthesis of zeolite beta with Si/Al >10 ratio also results in the formation of zeolite analcime phase, which is in agreement with the results obtained in this study. In the crystallization temperature of 180 °C, the formed ZSM-5 phases and impurities were not identified. However, these secondary phases were lowered by using the same gel composition, and lowering the temperature to 170 °C.

Among the parameters studied, X-ray diffraction showed that zeolite beta was obtained with a Si/Al ratio of 8, and crystallization time of 4 days at 170 °C. Thus, according to these results, the main characterizations were focused on the obtained material, being the objective of this study.

Figure 5 shows the TG and DTG curves of zeolite beta with a Si/Al ratio of 8, crystallization time of 4 days at 170 °C.

In Figure 5, mass loss events in the temperature range of 100 °C related to moisture present in the material were observed, and in the range between 200 °C and 500 °C due to the organic driver which is degraded during the process. It was also observed that all the organic matter was removed from the material in the temperature around 500 °C. Therefore, the temperature used in zeolite beta calcination was effective in removing organic material from the pores of the zeolitic material, thus preserving the ordered structure, as shown in the XRD analysis of Figure 2 for zeolite beta obtained with a Si/Al ratio of 8, and crystallization time of 4 days at 170 °C.

Figure 6 shows the Infrared spectra for calcined and uncalcined zeolite beta samples with a Si/Al ratio of 8.

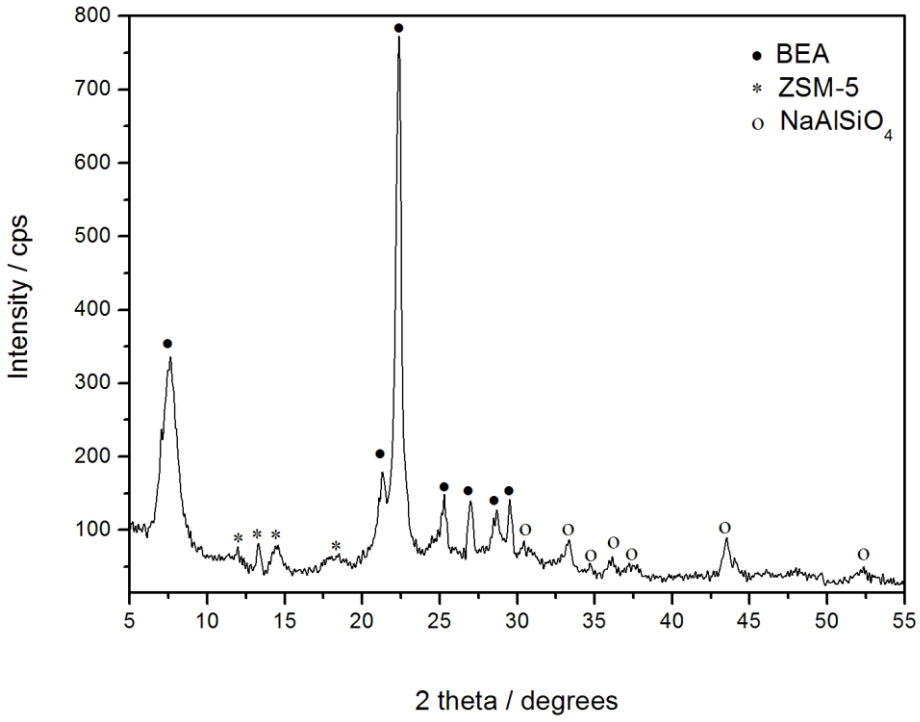

Figure 4. Identification of the zeolite beta sample's formed phases with a Si/Al ratio of 8 and crystallization time of 4 days at 170 °C

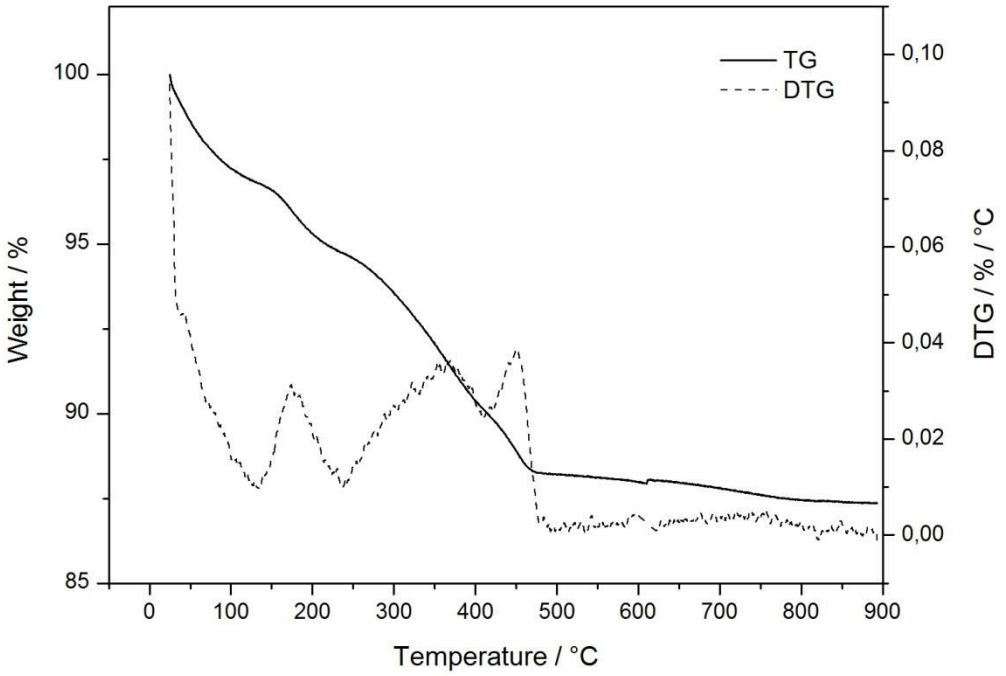

Figure 5. TG and DTG curves at a heating rate of 10 °C min^{-1} for the uncalcined zeolite beta with a Si/Al ratio of 8 and crystallization time of 4 days at 170 °C

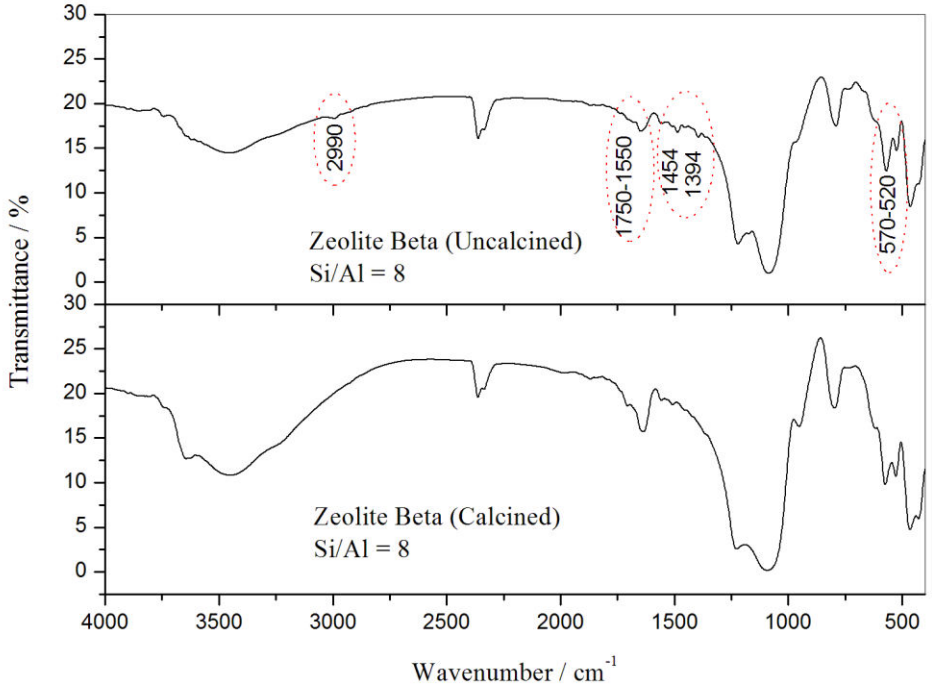

Figure 6. Infrared spectra of calcined and uncalcined zeolite beta with a Si/Al ratio of 8

An intense vibration in the range of 3730 - 2430 cm^{-1} and 1750 - 1550 cm^{-1} was verified by means of sample spectra, respectively, assigned to the stretching and bending of OH present on the inorganic material's surface, in addition to water molecules adsorbed by hydrogen bonding. Bands around 2990 and 2920 cm^{-1} related to the symmetric and asymmetric stretching of C-H bonding and CH_2/CH_3 groups are observed, as well as deformation in bonding of C-H bands at 1454 cm^{-1} and 1394 cm^{-1}, and angular deformation in C-N bands bonding around 1180 cm^{-1}. The bands in the region of 520 and 570 cm^{-1} indicate the presence of a ring-shaped structure with five members connected T-O-T (T = Si, Al), being characteristic of zeolite beta.[22-24] According to,[25,26] these bands also reflect the degree of crystallinity and structure ordering.

N_2 adsorption–desorption isotherms are shown in Figure 7.

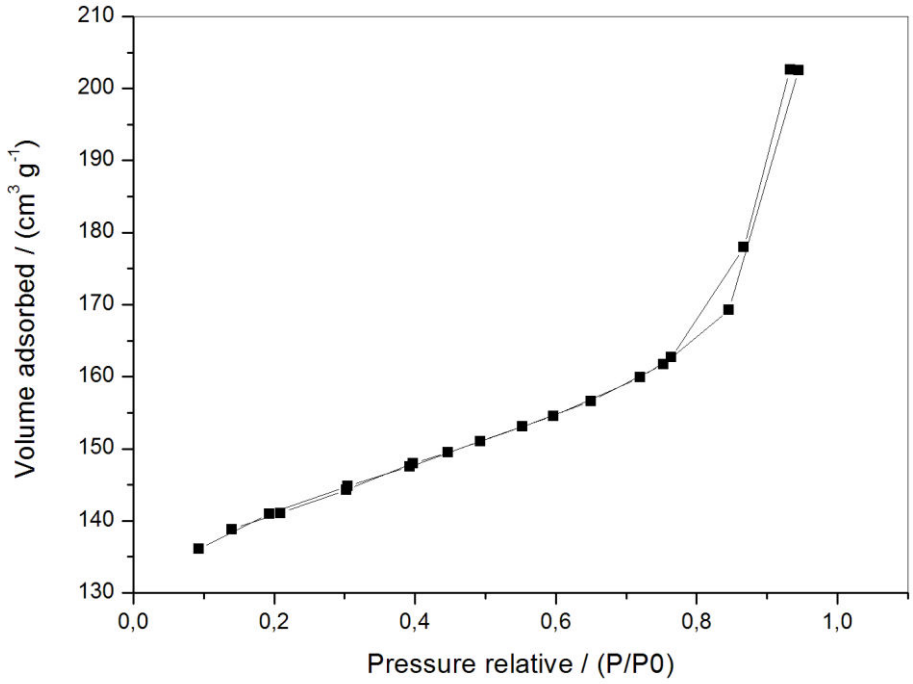

Figure 7. N_2 adsorption–desorption isotherms of zeolite beta with a Si/Al ratio of 8 and crystallization time of 4 days at 170 °C

According to the IUPAC classification (International Union of Pure and Applied Chemistry), the obtained isotherms are of type I, being characteristic of microporous materials having a high volume adsorbed at low relative pressures. The isotherm showed an accented increase in volume adsorbed at high relative pressures, indicating the presence of mesoporous interparticles. These pores are disorganized and correspond to the spacing between the particles, being related with the size and shape of particles.[27] The specific sample area was 437 m^2g^{-1}, with a pore volume of ca. 0.106 cm^3g^{-1}. In some studies in the literature, surface areas of 339 m^2g^{-1} were obtained for zeolite beta synthesized with a Si/Al ratio of 5.2 in its sodium (Na-Beta) and acid forms (H-Beta)[20], and a specific area of 310 m^2g^{-1} for zeolite H-Beta synthesized with a Si/Al ratio of 10,[28] showing that the variables used in synthesizing the material under study were important for forming the zeolitic structure, because it has a higher specific area in comparison with other studies in the literature.

The distribution of pore size for the zeolite beta with a Si/Al ratio of 8 and crystallization time of 4 days at 170 °C may be seen in Figure 8.

In Figure 8, it is observed that most pore volume (about 60%) corresponds to micropores (dp < 2 nm), and 40% corresponds to mesopores (2 < dp < 50 nm). This result confirms the observation made for adsorption isotherm in relation to the presence of microporosity and mesoporosity in the material.

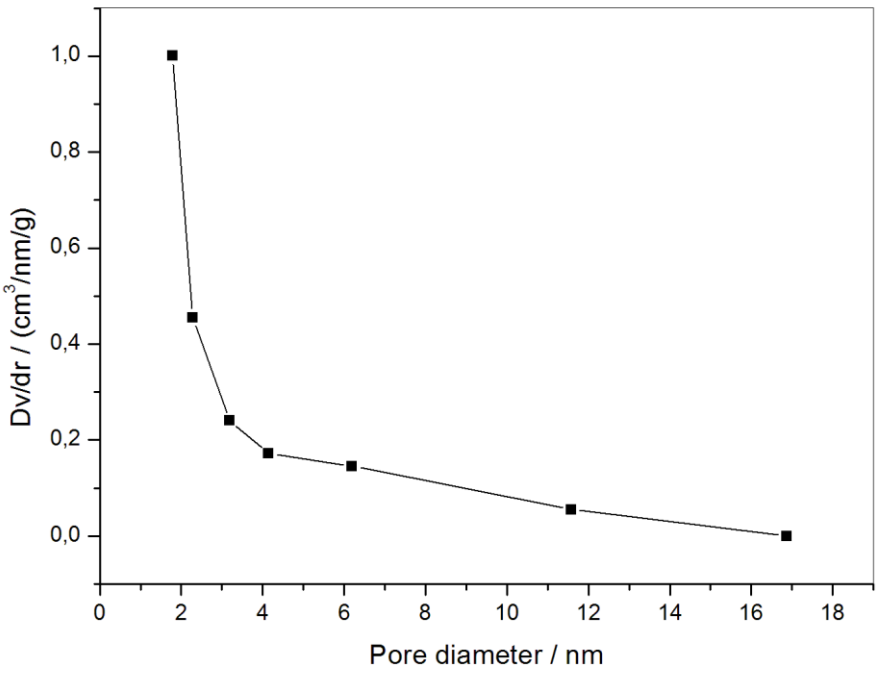

Figure 8. Pore size distribution for zeolite beta with a Si/Al ratio of 8 and a crystallization time of 4 days at 170 °C

4. Conclusion

The variables used in the material synthesis were important to the zeolitic structure growth, occurring in the Si/Al ratio of 8, with a crystallization time of 4 days at 170 °C, and showed a larger specific area of 437 m^2g^{-1}, which was higher in comparison to other studies in the literature, as well as a pore volume of 0.106 cm^3g^{-1}. N_2 adsorption-desorption isotherm showed an accentuated increase in volume adsorbed at high relative pressures, indicating the presence of mesoporous interparticles. Under these process conditions, formation of zeolite beta was associated to ZSM-5 and impure phases. The presence of impure phases were more evident for Si/Al ratios > 8, time < 4 days and temperature < 170 °C.

Pore size distribution results showed the presence of microporosity and mesoporosity of the material, which was also observed through the adsorption isotherm.

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