

Boron Incorporation by Hydrothermal Synthesis Into SAPO-5 and SAPO-11 Molecular Sieves

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Silicoaluminophosphates SAPO-5 and SAPO-11 were synthesized using the hydrothermal method, 170 °C with triethylamine and dipropylamine as the structure directing agents, respectively. This work aimed the incorporation of boron into the structures obtained by modifying the composition of the system, using as a reaction equation: $\text{Al}_2\text{O}_3:\text{P}_2\text{O}_5:x\text{SiO}_2:y\text{B}_2\text{O}_3:1,5\text{TEA (or DPA)}:50\text{H}_2\text{O}$, with $x, y=0-0.2$. The phase was identified by XRD and characterized by FTIR, TGA/DTG, TPD-NH₃ and nitrogen adsorption at -196 °C. The structure parameters confirmed the obtaining of pure structures, showing a slight contraction in the parameters of the unit cells, indicating the presence of boron in the crystal lattice. The Brønsted sites, were modified up to a maximum of boron ($y = 0.1$) and for higher content, the acidity was not significant. The modification of weak acidity related to the appearance of isolated BO₃ groups, indicating that the silicon atoms were not sufficiently distributed for the formation of sites.

Keywords: Boron, SAPO, AFI, AEL.

1. Introduction

When dealing with microporous materials, molecular sieves with a crystalline structure such as zeolites, aluminophosphates (ALPOs) and silicoaluminophosphates (SAPOs) (also known as zeotypes, as they have the same basic building blocks as zeolites) are of outstanding importance in research due to their structural ordering, different topologies and flexibility of composition, enabling applications with the combination of high performance, product selectivity and energy savings^{1,2}.

The advantages that allow the applicability of these materials derive mainly from their acidic properties: distribution of strong (Brønsted) and weak (Lewis) sites. Thus, aiming to increase acidity in a controlled way, the introduction of heteroatoms with valences equal to or close to those that normally exist in these materials allows optimizations ranging from the possibility of new applications to the discovery of new structures^{3,4}.

SAPOs are zeotypes that emerged from the introduction of silicon in the structure of aluminophosphates, showing a high tolerance to incorporation of cations that silicoaluminophosphates have, as well as their moderate acidity, highly effective in methanol to olefin (MTO) conversion reactions⁵⁻⁸ and hydroisomerization of alkanes⁹⁻¹².

SAPO-5, AFI structure, and SAPO-11, AEL structure, are some of the SAPOs that have been studied, due to their contributions in obtaining different distributions of products in the reactions mentioned above, in addition to

being versatile when it comes to increment of properties^{5,13}. Usually, improvements in the properties of SAPOs also include increases in the Brønsted acid strength of these materials, ranging from modifications to the synthesis process to the inclusion of steps after the preparation of the material, with the use, for example, of solutions of a cationic heteroatom source, normally metallic, such as copper¹⁴, platinum¹⁵, iron¹⁶ etc^{17,18}.

Among the cations that provide acidic characteristics to these structures, boron has shown greater influence on sites of lower acid strength in porous materials. In the literature, it is possible to verify in recent years that researches aimed at the addition of boron in crystalline structures are mainly focused on zeolites (such as ZSM-5) and other inorganic structures¹⁹⁻²³. Recent studies show that the addition of semi-metal boron in the structure of zeolites and zeotypes can promote an increment in their acidity, maintaining or increasing the conversion of the reactions, and at the same time, delaying the hydrogen transfer reactions, characteristic of coke formation^{4,19,24}.

On the other hand, there is still a good potential for studies on the addition of boron to SAPOs, even in those with greater industrial interest such as SAPO-5, or with a porous diameter close to the zeolites most discussed in the literature, such as SAPO-11. This work studied the incorporation of boron into the structures of SAPO-5 and SAPO-11 through changes in the composition used for hydrothermal crystallization, with the objective of modifying the acidic properties of these catalysts.

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2. Experimental

2.1. Materials

For the preparation of AFI and AEL structure samples, colloidal silica (Ludox AS-30, Sigma-Aldrich), aluminum isopropoxide ($\geq 98\%$, Alfa-Aesar), phosphoric acid (85% , Sigma-Aldrich) and boric acid ($99,5\%$, Êxodo Científica) were used as a source of silicon, aluminum, phosphorus and boron, respectively. Triethylammonium, TEA (99% , Merck) and di-n-propylamine, DPA (99% , Merck) were applied as templates for the synthesis of SAPO-5 (AFI) and SAPO-11 (AEL), respectively.

2.2. Synthesis of SAPO-5 and SAPO-11

The samples were synthesized adapting the methodology of Lok et al.²⁵ and Qiu et al.²⁶, for the hydrothermal synthesis of SAPO-5 with the chemical composition of gel being Al_2O_3 : P_2O_5 : x SiO_2 : y B_2O_3 : 1.5 TEA: 50 H_2O , where x , $y = 0$ to 0.2 . For the synthesis of SAPO-11, DPA was used as organic directing agent with similar composition²⁵. The gel preparation was carried out at room temperature and started with the dilution of aluminum isopropoxide in $2/3$ of the total amount of water required in the synthesis under mechanical stirring for 10 min. Then, phosphoric acid was added, followed by stirring for 60 min. Next, the corresponding template diluted in $1/3$ of the total amount of water required was added under stirring for 60 min. Finally, colloidal silica was added, where the gel was stirred for another 60 min. At the end of the preparation, the synthesis gel was transferred to stainless-steel autoclaves for crystallization in a static system at 170 °C for 20 h and cooled afterwards slowly to room temperature. All samples were synthesized in duplicate.

The final product was obtained by washing with distilled water, centrifugation and dried in an oven at 100 °C for 24 h. The samples were calcined at 450 °C for 3 h in a synthetic air atmosphere at 200 mL min^{-1} . The samples were named according to the structure (SAPO, BSAPO or BAPO) followed by the amount of boron/silicon present in the synthesis gel, as shown in Table 1 and 2. Samples S5 and S11 have the composition of the SAPO-5 synthesis gel (AFI) and SAPO-11 (AEL), respectively, used as a basis for modifications to the compositions.

2.3. Characterization

The X-ray diffraction (XRD) analysis was performed in a Shimadzu XRD-6000 diffractometer, $CuK\alpha$ ($\lambda = 0.1542$ nm), Ni filter, using a voltage of 40 kV and a current of 30 mA. The data was collected in the 2θ range between 3 and 40° , with goniometer velocity of $2^\circ\ min^{-1}$ and step of 0.02° . The area of the diffraction peaks located in the 2θ regions between 18.4° and 23.5° for AFI and 19.4° and 24.1° for AEL structures were used to calculate the crystallinity of the materials, according to Equation 1²⁷.

$$CR\ (\%) = \left(\frac{\sum A_{amostra}}{\sum A_{padr\tilde{a}o}} \right) \times 1 \tag{1}$$

The structure refinement by Rietveld method of the synthesized samples was performed in Maud software (Materials Analysis Using Diffraction). The refinement was based on the AFI and AEL structures, using the CIFs available in the IZA database and the diffraction peak profiles were modeled using a pseudo-Voigt function. FT-IR spectra were obtained in a Fourier Transform Infrared spectrometer Shimadzu IRTracer-100, in the region of $4000 - 400\ cm^{-1}$, in transmittance mode. The thermal analyzes (TGA/DTA) were performed in a Shimadzu DTG-60H thermobalance, with a heating rate of $10\ ^\circ C\ min^{-1}$ under air atmosphere ($50\ mL\ min^{-1}$) from ambient temperature to $800\ ^\circ C$. The NH_3 -TPD profiles were determined in a SAMP3 Termolab multipurpose analytical system, where the samples were treated at $400\ ^\circ C$ under a $30\ mL\ min^{-1}$ helium flow rate for 40 min, then cooled to $100\ ^\circ C$ and subjected to ammonia adsorption for 45 min, followed by desorption in the temperature range of $100 - 800\ ^\circ C$, with a heating rate of $10\ ^\circ C\ min^{-1}$. Nitrogen adsorption-desorption measurements at $-196\ ^\circ C$ were performed on a Micromeritics ASAP 2020 equipment in the P/P_0 range between 0.01 and 0.99 . The samples were previously degassed at $350\ ^\circ C$ for 12 h, under vacuum of $2\ \mu mHg$. The specific surface area was calculated by the BET method, the micro and mesoporous volumes were determined by the t-plot method and the pore size distribution was obtained from the adsorption isotherm branch by the BJH method.

Table 1. Coding, composition and relative crystallinity of samples of the AFI structure.

Sample	Synthesis composition						Relative crystallinity (%)
	Al_2O_3	P_2O_5	DPA	SiO_2	B_2O_3	H_2O	
S5	1	1	1.5	0.2	0	50	84
BS5_0.1B0.2Si	1	1	1.5	0.2	0.1	50	75
BS5_0.2B0.2Si	1	1	1.5	0.2	0.2	50	91
S5_0.1Si	1	1	1.5	0.1	0	50	91
BS5_0.1B0.1Si	1	1	1.5	0.1	0.1	50	97
BS5_0.2B0.1Si	1	1	1.5	0.1	0.2	50	89
B5_0.1B	1	1	1.5	0	0.1	50	97
B5_0.2B	1	1	1.5	0	0.2	50	100

Table 2. Coding, composition and relative crystallinity of samples of the AEL structure.

Sample	Synthesis composition						Relative crystallinity (%)
	Al ₂ O ₃	P ₂ O ₅	DPA	SiO ₂	B ₂ O ₃	H ₂ O	
S11	1	1	1.5	0.2	0	50	90
BS11_0.1B0.2Si	1	1	1.5	0.2	0.1	50	81
BS11_0.2B0.2Si	1	1	1.5	0.2	0.2	50	87
S11_0.1Si	1	1	1.5	0.1	0	50	75
BS11_0.1B0.1Si	1	1	1.5	0.1	0.1	50	95
BS11_0.2B0.1Si	1	1	1.5	0.1	0.2	50	79
B11_0.1B	1	1	1.5	0	0.1	50	100
B11_0.2B	1	1	1.5	0	0.2	50	100

3. Results and Discussion

3.1. Obtainment of the pure phases and crystallinity of the samples

Figure 1 shows the diffractograms of samples synthesized with and without boron, using TEA as template. The XRD patterns present the formation of pure and crystalline phase, without amorphous species or mixture of phases, with peaks characteristic only of the AFI structure, SAPO-5, in the 2 θ region, indicating that, depending on the composition, boron exerted influence only on the relative crystallinity of the samples, as shown in Table 1²⁸.

From the data in Table 1, it is observed that the relative crystallinity is greater for the samples BS5_0.1B0.1Si and B5_0.2B, which may indicate that the presence of boron, respecting certain synthesis parameters, such as those used in these samples, results in a greater ordering of the crystal lattice²².

The diffractograms of the AEL structure samples showed the formation of pure and crystalline phase, as well as the exclusive presence of the characteristic peaks of the structure in the 2 θ region, shown in Figure 2, demonstrating that the presence of boron did not affect the nucleation and crystallization process for the synthesis conditions used²⁹.

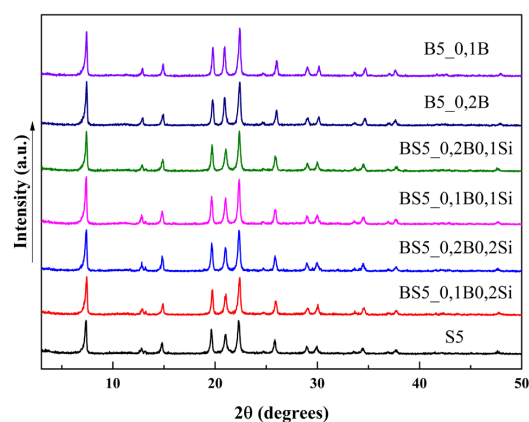
Since the pure phase was formed, the relative crystallinities of each sample were calculated according to Table 2, where the crystallinity showed a greater dependence on the composition.

In the case of AEL structure, this behavior is confirmed in the literature, where López et al.³⁰ found a direct relationship between the restriction of synthesis conditions (crystallization time, temperature, sources of reagents) and the restriction of preparation (molar composition). Thus, for the proposed conditions, the sample in which there was a total replacement of silicon by boron was the most crystalline, confirming that the presence of boron leads the system to a greater ordering of the crystal lattice²².

Table 3 exhibits the lattice parameters calculated by Rietveld structure refinement for the AFI and AEL samples, respectively. The results indicates that the replacement with boron leads to a decrease in the crystallographic parameters of the zeolites. For the AFI samples, it is observed that the lattice constant *a* decreases with the greater amount of boron in the structure. AEL samples shows similar results, with the reduction of parameters *a* and *b* as the boron

Table 3. Lattice parameters of AFI and AEL samples obtained by Rietveld refinement.

Sample	Lattice parameters		
	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)
S5	13.7994	-	8.4443
BS5_0.1B0.1Si	13.7297	-	8.4252
B5_0.2B	13.6722	-	8.4583
AFI reference	13.8271	-	8.5803
S11	8.4188	18.6533	13.3696
BS11_0.1B0.1Si	8.4139	18.6499	13.3943
B11_0.2B	8.3877	18.6228	13.3538
AEL reference	8.3120	18.7290	13.3920

**Figure 1.** XRD profiles of samples synthesized with different compositions of the AFI structure.

concentration increases. These results are an indication of the incorporation of boron in the structures, since, due to its smaller size compared to the other elements, there is a contraction of the unit cell^{26,31}.

3.2. Fourier transform infrared spectroscopy (FT-IR)

The FT-IR spectra for the samples in Figures 3 and 4 show differences in the bands corresponding to SAPO-5 compared to the samples of the AFI structure with the presence of boron, mainly in the bands related to acidic sites.

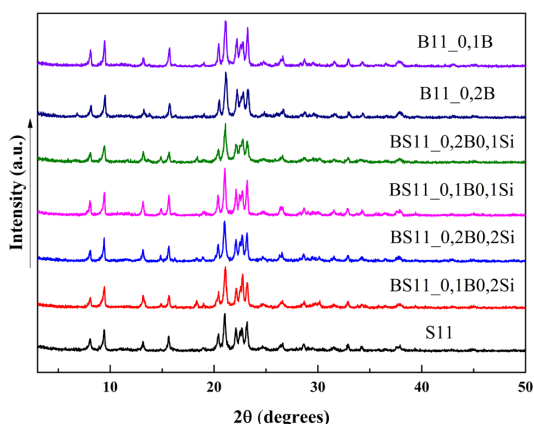


Figure 2. XRD profiles of samples synthesized with different compositions of the AEL structure.

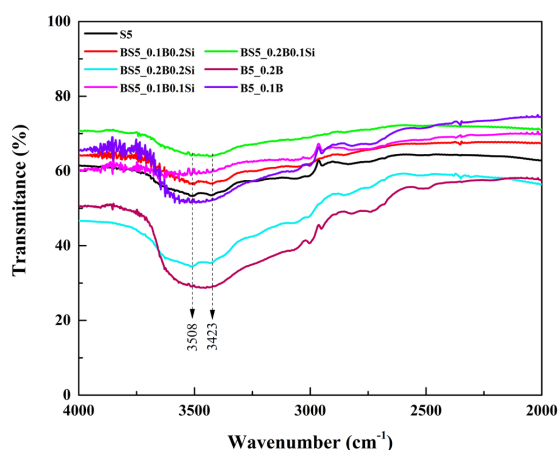


Figure 3. IR spectra in the range of 4000-2000 cm^{-1} of AFI samples with and without boron added to different compositions.

The absorption bands at 3423 and 3508 cm^{-1} , corresponding to Brønsted acid sites, initially appeared in sample S5 and lost definition as boron was added, until disappearing in samples B5_0,1B and B5_0,2B. These bands can form from Si-OH-Al bonds, so the addition/replacement of silicon by boron is responsible for this change in the behavior of the sample, which can be confirmed by NH_3 -TPD^{6,32}.

At approximately 1477 cm^{-1} , there is the occurrence of a band that is more evident for the samples in which there was total replacement of Si by B. This band has the contribution of two factors: to the Lewis sites (which are in the region between 1500 – 1460 cm^{-1}) and to the presence of boron in trigonal/tetragonal conformation, which would be in agreement with the results, since the greater the amount of boron at the expense of the amount of silicon, there will be a greater conformation of boron according to the crystal lattice^{33,34}.

Only samples S5 and BS5_0,1B0,1Si show occurrence at 1270 cm^{-1} . It could initially be attributed to asymmetric SO_4 groups; and for the sample BS5_0,1B0,1Si, the existence, also, of isolated BO_3 groups^{33,35}. However, as there are other samples that could exhibit this behavior since they have boron

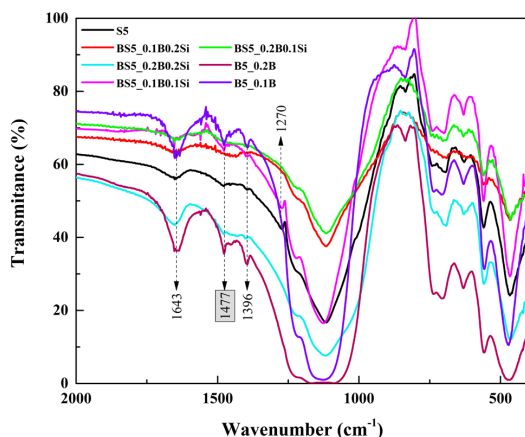


Figure 4. IR spectra in the range of 2000-400 cm^{-1} of AFI samples with and without boron added to different compositions.

and/or silicon in their composition, it can be assumed that the factor that contributed to the occurrence of this band is the composition used in the synthesis.

It is also observed that for samples with boron, there is a band at 1396 cm^{-1} , which is more evident for samples B5_0,1B e B5_0,2B, corresponding to the presence of $\text{B}(\text{OSi})_3$ bonds or to trigonal asymmetric B-O bonds, indicating a higher occurrence of dehydration of the groups containing boron or structural defects similar to those that occur with aluminum^{33,36}. From the range of 1250 cm^{-1} to approximately 400 cm^{-1} , samples show absorption bands corresponding to symmetrical and asymmetrical T-O-T bonds ($\text{T} = \text{Si}, \text{Al}, \text{P}$ or B), with the band at approximately 1100 cm^{-1} related to the most common asymmetrical tetrahedral T-O bonds in the crystal lattice^{37,38}.

In Figure 5 and 6, the spectra in the infrared region of the AEL structure samples show the appearance of characteristic bands of the AEL structure, as well as bands specific to the presence of boron.

At 3570-3300 cm^{-1} , the presence of some more evident bands is observed in the sample BS11_0,1B0,1Si, which correspond to Brønsted species, with band at 3423 cm^{-1} being related to Si-OH-Al or Si-OH bonds, and at 3515 cm^{-1} related to hydrogen bonding in B-OH and Si-OH bonds^{32,33,39}. The better resolution of these bands for the sample mentioned can be attributed to a better incorporation of boron/silicon atoms to the structure confirmed by the high crystallinity of the sample and the results obtained in the analysis of NH_3 -TPD. The sample BS11_0,2B0,2Si presented a band at 2347 cm^{-1} , which could correspond to Brønsted species, but its confirmation would be given by acidity analysis³³.

For the sample BS11_0,1B0,1Si, bands are evident in the region of 1595, 1477 and 1435 cm^{-1} . These bands are attributed to the presence of Lewis sites (which would show an increase in weak sites). In this region, there may have been an overlap of bands due to the appearance of the trigonal/tetragonal conformation of boron present in the samples, since they are more evident in the samples where the incorporation of boron occurs^{33,34}. This hypothesis is observed mainly for samples BS11_0,1B0,1Si; B11_0,1B and B11_0,2B, the only ones with the band at 1595 cm^{-1} , where

the confirmation that its occurrence would not be attributed only to Lewis sites would be given by acidity analysis.

The band at 1278 cm^{-1} is restricted to two samples: S11, which could correspond to asymmetric SiO_4 groups; and

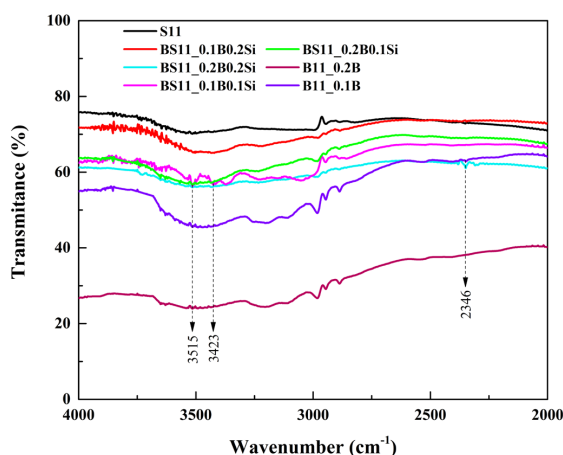


Figure 5. IR spectra in the range of $4000\text{--}2000\text{ cm}^{-1}$ of AEL samples with and without boron added to different compositions.

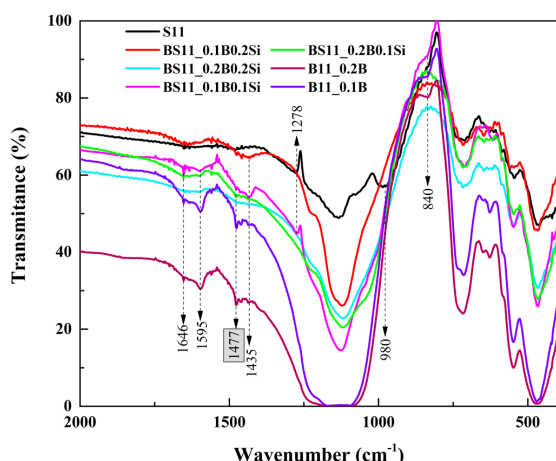


Figure 6. IR spectra in the range of $2000\text{--}400\text{ cm}^{-1}$ of AEL samples with and without boron added to different compositions.

BS11_0,1B0,1Si, which could be evidence of the existence of isolated BO_3 groups^{33,35}. It can be assumed, similarly to AFI results, that the influencing factor for the appearance of this band when boron is added is due to the composition used.

It was observed the existence of several bands common to all samples in the range of $1250\text{--}400\text{ cm}^{-1}$, corresponding to the bands of the symmetrical and asymmetrical T-O-T bonds ($\text{T} = \text{Si}, \text{Al}, \text{P}$ or B), highlighting sample B11_0,2B where the band at 840 cm^{-1} is more evident, which may correspond to boron binding, being more defined in the sample where its content is higher³⁷. Still in the range of T-O-T bands, sample S11 exhibited a band at 980 cm^{-1} , which would correspond to the presence of asymmetric Si-O-Si, indicating that in fact there was a replacement of silicon by boron in the other samples and explaining the disappearance of this band³⁸.

3.3. Thermogravimetric and thermodifferential analysis (TGA/DTA)

TGA/DTA curves for AFI structure samples are exhibited in Figure 7. The samples containing silicon in the composition (S5 and BS5_0,1B0,1Si) showed four mass loss events, while the sample with total replacement of the maximum amount of silicon by boron (B5_0,2B) shows only three events.

The mass loss percentages were calculated by derivation, Figure 7b, and their values are presented in Table 4, along with the temperature ranges for each event.

The total percentages of mass loss were close and in agreement with the literature for SAPO-5, verifying that the presence of boron in the structure does not significantly alter the thermal stability; however, it causes a certain decrease in mass loss of just over 1% as the replacement of silicon by boron occurs⁴⁰. This decrease is more pronounced when comparing the mass losses from event II, where there is gradually greater decomposition of TEA template and greater combustion of its residues in event III, resulting in less loss in event IV for the sample BS5_0,1B0,1Si. The presence of only three events in sample B5_0,2B indicates that the removal of water and structure directing agent would occur in an easier way for this sample because there is less interaction with the structure⁴¹.

The thermal behavior of the AEL structure samples is shown in Figure 8. The sample S11 presented two mass loss events in the temperature range that typically characterizes water desorption, with the second corresponding to chemically

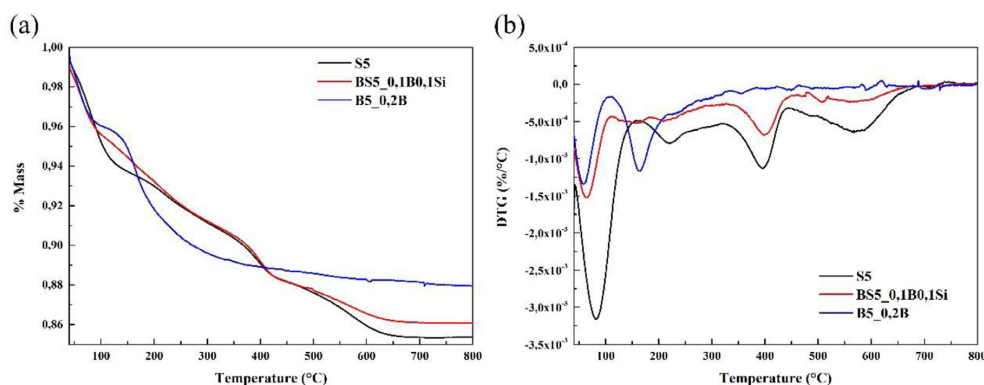
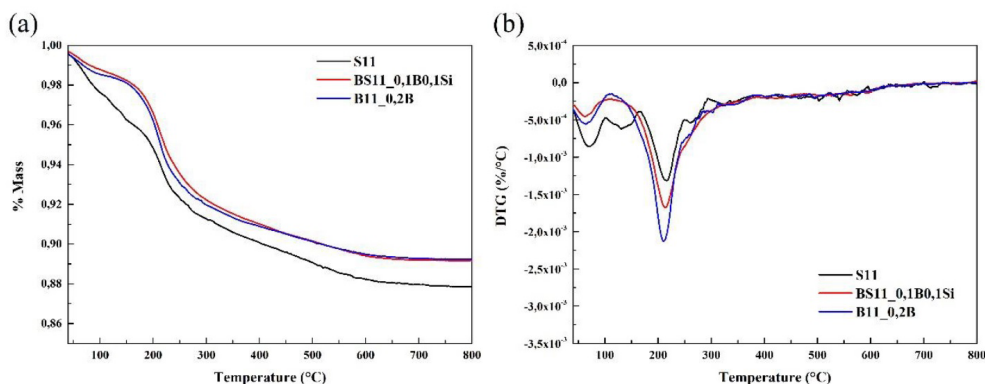


Figure 7. Profiles of (a) TG and (b) DTG of samples S5, BS5_0,1B0,1Si and B5_0,2B.

Table 4. Temperature range, partial and total mass loss of AFI/AEL samples.

Sample	Temperature range (°C)				Mass loss (%)				Total loss (%)
	I	II	III	IV	I	II	III	IV	
S5	<160	160-322	322-442	442-800	6.37	2.77	2.57	2.88	14.59
BS5_0.1B0.1Si	<112	112-326	326-519	519-800	4.17	4.50	3.335	1.44	13.45
B5_0.2B	<107	107-220	220-800	-	4.04	4.78	3.22	-	12.04
S11	<100	100-165	165-250	250-800	2.17	1.68	3.65	4.46	11.96
BS11_0.1B0.1Si	<112	112-339	339-800	-	1.13	6.99	2.50	-	10.62
B11_0.2B	<110	110-313	313-800	-	1.49	6.68	2.56	-	10.73

**Figure 8.** Profiles of (a) TG and (b) DTG of samples S11, BS11_0,1B0,1Si and B11_0,2B.

adsorbed water⁴². On the other hand, samples BS11_0,1B0,1Si and B11 exhibited a single water desorption event, which ends at approximately 110 °C.

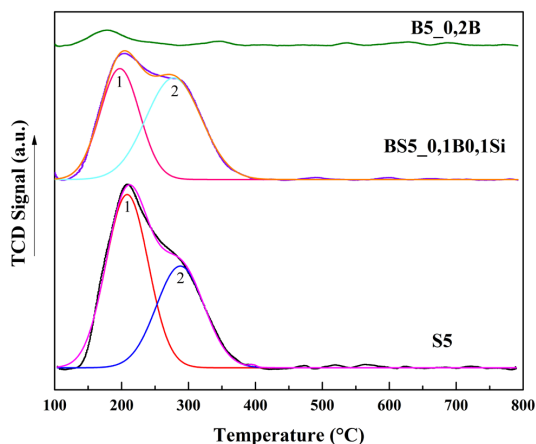
The percentages of total mass loss and in each event with its respective temperature range are shown in Table 4. It is possible to observe that the presence of boron resulted in a lower mass loss (above 1%).

The presence of boron in the AEL samples desorbs the water in a lower temperature range and desorbs the template in a single event with a greater mass loss and temperature range. In addition, there is only one more event, related to the decomposition of the DPA, indicating that the desorption, mainly of the organic species (DPA), occurs in a facilitated way due to less interaction with the AEL structure⁴¹.

3.4. Temperature-programmed desorption of ammonia (NH₃-TPD)

Figure 9 shows the TPD curves of the AFI structure samples. Initially there is the appearance of acidity in the samples S5 and BS5_0,1B0,1Si. After performing the deconvolution of the thermodesorption peaks, a change in the contribution of the acidity of the material is observed. The sample BS5_0,1B0,1Si shows a decrease in peak 1 (T < 300 °C) (weak acidity) while peak 2 (T > 300 °C) (medium acidity) is preserved⁴³. On the other hand, sample B5_0,2B exhibits a drastic decrease in any acidic characteristic, suggesting that boron has a maximum limit of incorporation into the structure to optimize the acidity increase process.

It is noted that there was a decrease in the peak identified by number 1, corresponding to weak acid sites (around 200 °C) and a small increase (less than 10%) of the medium acidity

**Figure 9.** TPD-NH₃ profiles of AFI samples obtained at different compositions.

identified by the second peak (around 300 °C). The sample B5_0,2B showed that the absence of silicon decreases the acidic characteristic of the material by more than 90% when compared to sample S5, according to Table 5.

The modification of the weak acidity in the sample BS5_0,1B0,1Si may be related to the appearance of isolated BO₃ groups instead of the trigonal conformation linked to other elements (Si, Al or P), as pointed out in the FT-IR spectra. It indicates that the atoms of silicon were not sufficiently distributed in the vicinity for the formation of sites, which could also be due to the presence of larger silicate islands.

Table 5. Acidity of samples of AFI/AEL structures with different compositions.

Sample	Acidity $\left(\frac{\mu\text{NH}_3}{g}\right)$			
	Weak acidity	Medium acidity	Strong acidity	Total acidity
S5	375	251	-	626
BS5_0.1B0.1Si	205	269	-	475
B5_0.2B	25	13	-	38
S11	332	57	-	389
BS11_0.1B0.1Si	127	-	27	154
B11_0.2B	107	23	-	130

However, the small increase in medium acidity may have occurred due to the formation of Si-OH-B bonds, where boron assumes a tetragonal conformation, indicated in the FT-IR analysis, or due to the formation of silicate islands, where at its limits the Brønsted sites are stronger⁴⁴.

The lower acidity in the sample B5_0,2B was expected due to the conformation similar to aluminum in the crystal lattice, requiring the occurrence of structural defects at the limits of the lattice for the formation of Lewis sites, which occurs between 1500 – 1460 cm⁻¹ in the FT-IR spectra of the sample, or the presence of an atom with a 4+ vicinal conformation for the formation of species with higher acid expression⁴⁵.

The TPD curves of the AEL structure samples are exhibited in Figure 10, where it is possible to observe that, after deconvolution by Gaussian function, the sample S11 shows peaks in the low/medium acidity region. In contrast, samples BS11_0,1B0,1Si and B11_0,1B show a decrease in the peak of weak acidity. In addition, despite the decrease in Lewis's acidity, the sample BS11_0,1B0,1Si exhibits a small peak at approximately 450 °C, which is characteristic of the desorption of NH₃ from strong acid sites⁴⁶.

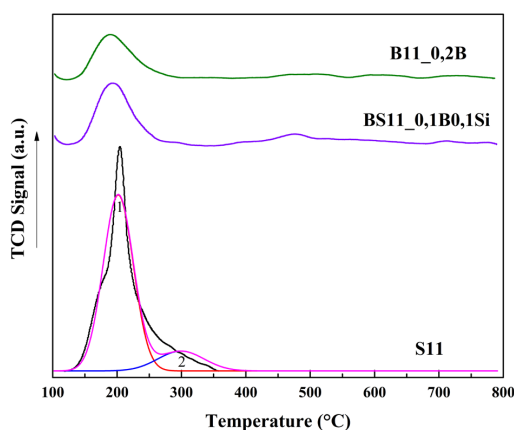
The distribution of acid sites calculated for the samples indicates that the presence of boron in the compositions used caused a decrease of more than 50% in weak sites and total acidity, when compared to the sample S11. Furthermore, the sample BS11_0,1B0,1Si did not present medium acidity to the detriment of the strong acid sites, as shown in Table 5.

From the calculation of acidity in the samples with boron in the composition and the results of FT-IR spectra, it more evident that boron is present in the samples, but without an increase in weak acidity. This increment deficiency may be related to boron having assumed a conformation preferentially similar to that of aluminum, not favoring the formation of acid sites in the sample B11_0,2B (T-O-T bonds at 840 cm⁻¹)⁴⁷.

For the sample BS11_0,1B0,1Si, the decrease in weak acid sites may have a different explanation: there is a peak due to NH₃ desorption at a temperature corresponding to strong acid sites, which when analyzed along with FT-IR spectra bands at 3570 – 3300 cm⁻¹, indicate that the composition used in the synthesis may have favored the formation of strongly acid hydroxyl groups in small amounts, since the intensity of the acidity peaks is linked to the number of sites⁴⁸.

3.5. Nitrogen Adsorption-Desorption at -196°C by BET method

In Figure 11a it is possible to observe that the samples exhibit type I isotherms, characteristic of microporous materials,

**Figure 10.** TPD-NH₃ profiles of AEL samples obtained at different compositions.

with the presence of type H4 hysteresis⁴⁹. The presence of boron in SAPO-5 and ALPO-5 causes a shift of hysteresis to regions of higher relative pressure, when compared with the SAPO-5 sample.

The sample S5 presents a hysteresis loop at approximately P/P₀ = 0.5, indicating that there is a predominance of smaller pores, which is in agreement with the pore distribution shown in Figure 11b.

The sample BS5_0,1B0,1Si shows a less pronounced hysteresis loop in a similar region to the sample S5, with the hysteresis predominantly occurring at a slightly higher relative pressure, at P/P₀ = 0.7. This small difference would be related to the pore distribution, indicating that both samples have most pores with similar sizes, but with a greater diameter distribution for the sample BS5_0,1B0,1Si, resulting in adsorption and desorption processes occurring in branches closer to each other, as shown by the pore distribution⁵⁰.

For the sample B5_0,2B, the hysteresis loop occurs at higher relative pressures than in the previous samples mentioned, indicating that the total replacement of silicon by boron caused the formation of larger pores in relation to the other AFI structure samples, which would facilitate the desorption process, also shown in the TGA/DTA curves⁵⁰. This result is in agreement with the pore distribution of the sample.

The surface area of samples S5 and B5 showed similar values, however, S5 has a smaller micropores area to the detriment of a larger external area, while B5_0,2B shows that the presence

of boron favors a larger microporous area to the detriment of the external area. In the sample BS5_0,1B0,1Si, the presence of boron and silicon in the specified amount resulted in a slight increase in the surface area (around 5%), with external and micropore areas similar to B5 (difference of approximately 0.4% between the micropore areas), according to Table 6.

These differences in the values of the micropore areas of the samples can be explained by the presence of boron. The greater its amount, until the total replacement of the silicon, the greater the areas available in the samples. The greater relative crystallinity, the mass loss events and the expressive textural properties of the samples would

indicate greater accessibility of the pores due to the lower amount of substances occluded, as in samples BS5_0,1B0,1Si and B5_0,2B compared to the sample S5, consequently influencing the surface area and volume of micropores³⁹⁻⁴¹.

Figure 12 shows the desorption isotherms and pore distribution of the samples of the AEL structure. Both samples exhibit type I isotherms, characteristic of microporous materials, and a type H4 hysteresis at different relative pressures, with the hysteresis loop in sample B11_0,2B occurring at higher relative pressure than in sample S11.

The sample S11 shows a hysteresis loop at approximately $P/P_0 = 0.5$, which may indicate that in most part there was

Table 6. Textured properties of samples of the AEL structure.

Sample	Surface area (m ² /g)			V _{micro} (cm ³ /g)
	S _{BET}	S _{Micro}	S _{Ext}	
S5	313	264	49	0.106
BS5_0.1B0.1Si	330	284	46	0.114
B5_0.2B	314	283	31	0.114
S11	182	138	44	0.055
BS11_0.1B0.1Si*	-	-	-	-
B11_0.2B	263	214	49	0.086

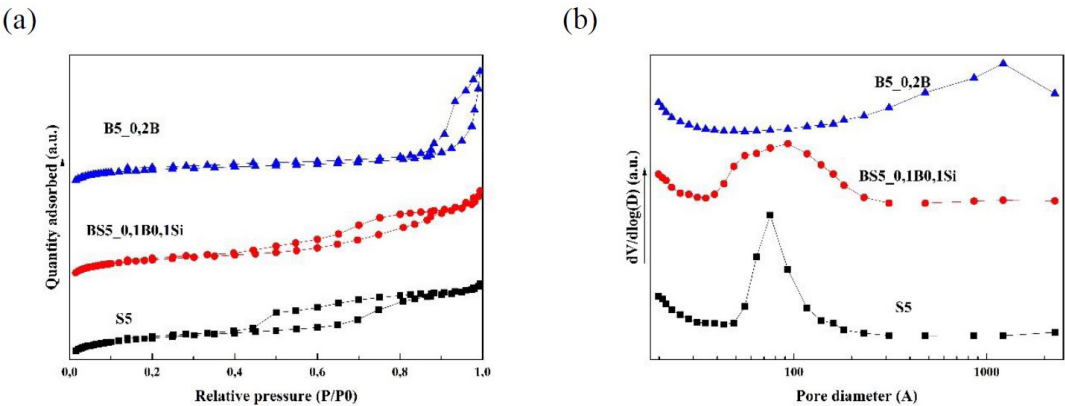


Figure 11. (a) Isotherms of N₂ adsorption/desorption and (b) pore distribution of AFI structure samples.

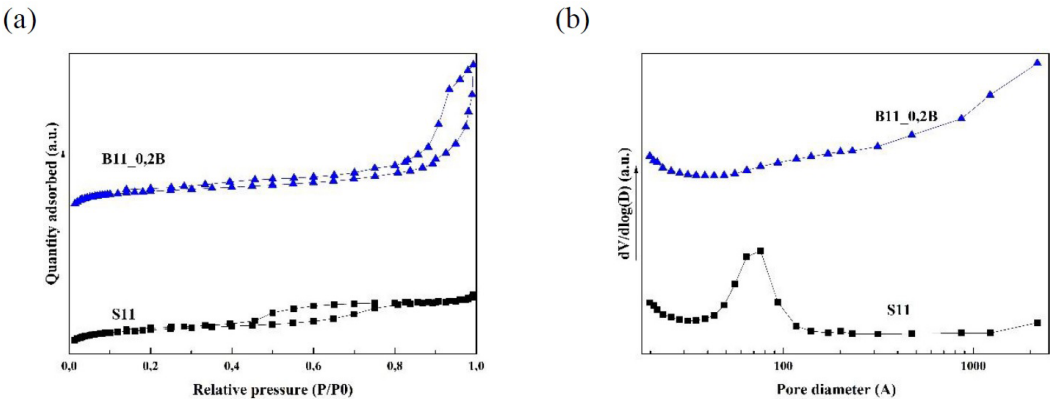


Figure 12. (a) Isotherms of N₂ adsorption/desorption and (b) pore distribution of AEL structure samples.

formation of smaller pores, according to the pore distribution shown in Figure 10b. Differently, the sample B11_0,2B exhibits a hysteresis loop at higher relative pressure, approximately $P/P_0 = 1.0$, indicating that most of the pores have a larger dimension, thus facilitating the process of condensation/evaporation in the pores, which is also in agreement with pore distribution³⁸.

It is observed that the exclusive presence of boron instead of silicon (sample B11_0,2B), caused a significant increase mainly in the superficial (approximately 44%) and microporous (approximately 55%) areas, and to a lesser extent, in the external area (around of 11%), according to the data in Table 6.

In the case of the AEL structure samples, even though the external area has increased with the presence of boron (unlike what happened with AFI samples), it is still close enough to the area of the sample S11 so that, along with the higher value of micropore area, may indicate that boron instead of silicon favored the formation of more defined crystals, justifying the greater microporous volume and the greater relative crystallinity of the sample B11_0,2B, as it would reduce the occlusion of substances such as H_2O and SDA, corroborating with the thermogravimetry events²³.

4. Conclusion

The presence of boron in the hydrothermal synthesis of the AFI and AEL structures, in any of the compositions studied, resulted in pure and homogeneous samples. In optimal amounts, it also helped to increase the crystallinity of the samples. FT-IR spectroscopy indicated the presence of boron in the structures in which it was added, as well as changes in the acidic behavior of the samples compared to the SAPOs studied. The thermal events and mass losses calculated via TGA/DTA showed that boron results in more crystalline samples than the original structures (S5 and S11), their thermal stability is not affected, however, there is less interaction with water and template molecules, which facilitates the process of removal by calcination. The acidity analysis showed that when boron was present in the hydrothermal synthesis of SAPO-5 and SAPO-11, there was a decrease in the weak acidity of the samples at the expense of sites of greater acid strength, indicating that the amount incorporated affects the acid behavior. The samples synthesized with boron presented higher surface areas and micropore volumes, as well as larger pore distributions, corroborating the thermogravimetric analyzes due to the greater accessibility of the pores.

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