

Article

Synthesis and Cation Exchange of LTA Zeolites Synthesized from Different Silicon Sources Applied in CO₂ Adsorption

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Abstract: Zeolites have a well-ordered crystalline network with pores controlled in the synthesis process. Their composition comprises silicon and aluminum, so industrial residues with this composition can be used for the synthesis of zeolites. The use of zeolites for CO₂ adsorption is feasible due to the characteristics that these materials have; in particular, zeolites with a low Si/Al ratio have greater gas adsorption capacities. In this work, the synthesis of LTA (Linde Type A) zeolites from silica fumes obtained from the industrial LIASA process and light coal ash is presented. We explore three different synthesis routes, where the synthesized materials undergo cation exchange and are applied in CO₂ adsorption processes. Studying the synthesis processes, it is observed that all materials present characteristic diffractions for the LTA zeolite, as well as presenting specific areas between 6 and 19 m²/g and average pore distributions of 0.50 nm; however, the silica fume yielded better synthesis results, due to its lower impurity content compared to the light coal ash (which contains impurities such as quartz present in the zeolite). When applied for CO₂ adsorption, the standard materials after cation exchange showed greater adsorption capacities, followed by the zeolites synthesized from silica fume and, finally, the zeolites synthesized from coal ash. By analyzing the selectivity of the materials for CO₂/N₂, it is observed that the materials in sodium form present greater selectivity when compared to the calcium-based materials.

Keywords: zeolite; CO₂ adsorption; CO₂/N₂ selectivity



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1. Introduction

Zeolites are crystalline molecular sieves formed by TO₄ bonds, where T can represent aluminum or silicon. These bonds form complex and well-defined structures with a large microporous area, excellent thermal stability, and controlled porosity [1–3].

Researchers are increasingly focusing on the study of zeolite synthesis, seeking to develop more sustainable [4–6], efficient [7], and economical [8] routes; explore different structural properties [9]; and examine their use in alternative processes [5,10–12]. These studies are significant as parameters such as the Si/Al ratio in the gel, the solid/liquid ratio, alkalinity, crystallization time, and temperature are crucial factors in achieving the desired structure during settling [13].

The main method for synthesizing zeolitic materials is through the hydrothermal route, where an alkaline solution containing the synthesis components is used and is placed at a high temperature with autogenous pressure for a certain time, simulating natural synthesis conditions [2]. However, other synthesis methodologies have also been studied to obtain different properties in the material, such as the use of mechanochemistry and microwaves, among other methodologies [14–16].

Due to the fact that zeolites primarily consist of silicon and aluminum, industrial residues with this composition can be used for synthesis [6,17]. The use of residual materials for the synthesis of zeolites has two main advantages: it is a cost-effective synthesis process, as zeolites are an industrial waste [18], and it also provides value for companies that work with silicon and aluminum [6].

Zeolite LTA, also called zeolite A, is one of the most commercially known zeolites and is the subject of continuous and constant studies involving zeolite materials [17,19]. Commonly synthesized with sodium, it has a Si/Al ratio equal to 1, which guarantees its suitability for ion exchange processes; however, it presents characteristics suitable for applications in other areas such as catalytic processes, ethanol dehydration, gas separation, sensors, green chemistry, and membranes [17,20,21].

The unit cell contains the chemical formula $\text{Na}_{96}\text{Al}_{96}\text{Si}_{96}\text{O}_{384}\cdot 27\text{H}_2\text{O}$ with a three-dimensional pore system [22]. These pores are perpendicular to each other and connected by eight-membered rings, creating a large cavity—known as the α -supercavity—which is surrounded by eight sodalite boxes and connected by four double rings of four members [23], as shown in Figure 1.

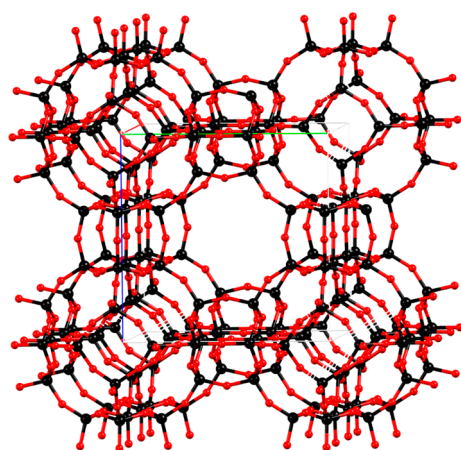


Figure 1. Unit cell of the LTA zeolite. Red indicates oxygen atoms and black indicates T atoms.

There are different ways to carry out the CO_2 capture process, such as cryogenics [24,25], separation through membranes [26,27], chemical absorption [28], and so on; however, adsorption on solid materials stands out as a highly promising industrial technology, due to its maturity compared to other technologies [29,30].

The use of zeolites for the adsorption of CO_2 has provided a solution for numerous industrial problems associated with the adsorption process, leading to a rise in research involving activities with these materials.

These materials have a wide variety of possible structures and configurations, with pore opening specificity and the polarity of the adsorbent playing crucial roles in the adsorption and separation of gases [31,32]. As CO_2 is a molecule that has a very large quadrupole moment, the use of materials with high polarity facilitates the process of capturing this gas [32].

Several groups reporting adsorption results have used different zeolites, such as Miyamoto, M. et al. (2012) [33] who obtained adsorption of 5.10 mmol/g on Si-CHA zeolites, Chen, C. and Ahn, W. (2014) [34] who obtained 5.68 mmol/g in LTA zeolite with mesopores, and Wang, Y. et al. (2018) [18] who obtained 0.75 mmol/g in LTA zeolite made from waste. Another example is the work of Lozinska, M. et al. (2012), which showed the adsorption of CO_2 in RHO zeolites with different cations, obtaining 3.55 mmol/g in the standard zeolite.

The use of zeolite LTA in the adsorption of CO_2 has structural advantages, as it has a small pore opening, which makes it efficient for adsorption processes and gas separa-

tion [35], in addition to having a great capacity for cation exchange, which guarantees an increase or reduction in pore size depending on the cation [35–37].

The compensating cation in the zeolite structure has a significant influence on the adsorption of CO₂, especially in zeolites with low Si/Al ratios. As the amount of aluminum in the network increases, a greater number of cations is necessary to balance the charge [38]. The choice of the ideal cation is extremely important because it influences how gases interact with the material [13].

LTA zeolites are normally synthesized with Na⁺ cations and are mainly exchanged for K⁺ and Ca²⁺ cations. Different pore openings are obtained in each case: with K⁺, the pore opening is close to 3 Å; with Ca²⁺, the pore opening is close to 5 Å; and, with Na⁺, the pore opening is close to 4 Å [39,40].

In this study, we verify the influence of different sources of silicon in the synthesis of zeolite LTA and carry out the process of cation exchange for calcium in the synthesized materials. The materials (synthesized and exchanged) are applied in a CO₂ adsorption process and compared with a commercial LTA zeolite in order to observe whether there is any change in the adsorption capacity of the materials synthesized from the used waste products.

2. Materials and Methods

The following reagents were used in this research: Miliq water; aerosol 200 silica; light coal ash from Florianopolis supplied by the Universidad Federal de Santa Catarina (UFSC); silica fume from the company LIASA; sodium aluminate P.A. 50%–56%; Al, 0.05%; Fe, 40%–45%; Na, (Riedel-de Haen, Buchs, Switzerland), sodium hydroxide P.A.-ACS 97% (Dinamica, Miyazaki, Japan); commercial zeolite 4A; calcium chloride P.A., 97% (Vetec, Speyer, Germany); 99.9% carbon dioxide gas; 99.9999% nitrogen gas; and 99.9999% argon gas.

2.1. Synthesis of Zeolites

The synthesis of the standard zeolite was based on the methodology presented on the IZA (International Zeolite Association) website [41], with a NaOH solution containing 84.050 g of H₂O and 0.489 g of NaOH. This solution was divided into two equal parts: in the first solution (i), 8.109 g of sodium aluminate was added and stirred until dissolved; in solution (ii), 16.010 g of H₂O, 3.009 g of NaOH, and 5.250 g of silica aerosil were added and stirred until homogenized. After homogenizing, both solutions were mixed and stirring was continued for 30 min. The formed gel was then transferred to Teflon autoclaves and placed in a heating block at 100 °C for 4 h. After the crystallization time, the material was removed, vacuum filtered, and washed with distilled water until the washing water reached pH 7.

The zeolite synthesis procedure from the silica fume followed a similar procedure to that of the standard zeolite, with modifications made only to the quantities used; for this, the residue was initially analyzed using X-ray fluorescence (XRF) with a Bruker S2 Ranger (Billerica, MA, USA) using Pb anode radiation with a maximum power of 50 W, a maximum voltage of 50 kV, and a maximum current of 2 mA. XRF analysis utilized an XFlash[®] Silicon Drift Detector. Subsequently, the necessary amounts of each material for the synthesis were determined based on the analysis results, replacing aerosil silica.

To carry out the synthesis with coal fly ash, two different procedures were used, as described by Cruz et al. [19]. These procedures outline different methods for synthesizing zeolites from residue; thus, we selected two methods that presented the most satisfactory results.

For the first chosen procedure, a solution containing NaOH, sodium aluminate, untreated ash, and H₂O was placed in a reflux system and underwent magnetic stirring for 120 min in an oil bath at 80 °C. After this time, the synthesis gel was placed in Teflon autoclaves and kept in a heating block at 100 °C for 4 h.

For the second chosen procedure, the alkaline melting process was added before carrying out the synthesis, and ash was placed in a crucible at a ratio of 1.5 g/g (g of NaOH/g of ash) and taken to a muffle furnace at a temperature of 200 °C. After the melting process, the samples were macerated, water was added, and the hydrothermal process as outlined above was continued at 80 °C for 120 min. After 20 min of stirring, sodium aluminate was added. Finally, the synthesis gel was placed in Teflon autoclaves and crystallized at 100 °C for 4 h. After the crystallization time, both materials were washed and filtered as the standard sample.

2.2. Cation Exchange

After material synthesis, the cation exchange process was performed. All materials were applied to the same procedure: 0.1 mol/L of calcium chloride was added to a flask containing the desired material to be exchanged, at a ratio of 1 g of zeolite for 50 mL of solution; the flask was then placed in a reflux system in an oil bath at 80 °C for 16 h, as presented in the work of Rigo et al. [22]. After this time, the material was vacuum filtered and washed with deionized water until the washing water reached the initial pH of the material, after which it was dried in an oven overnight at 60 °C. The nomenclature used for each material is shown in Table 1.

Table 1. Nomenclature of synthesized materials.

Zeolites	Cation Na ⁺	Cation Ca ²⁺
Standard zeolite	NaA	CaA
Commercial zeolite	NaA-Com	CaA-Com
Zeolite from light coal ash without pre-treatment	NaA-Cz	CaA-Cz
Zeolite from coal fly ash with alkaline melt pre-treatment	NaA-Cz-FA	CaA-Cz-FA
Zeolite from silica fume	NaA-LI	CaA-LI

2.3. Characterization of Materials

The residues were characterized via X-ray diffraction (XRD) using a Bruker D2Phaser equipped with a Lynxeye detector (Stockholm, Sweden) and copper radiation (CuK α λ = 1.54 Å) with a Ni filter. The XRD analysis was performed with a 10 mA current, 30 kV voltage, and a 2-theta range between 3° and 50°. The instrument settings included a divergent slit of 0.6 mm, a central slit of 1 mm with a setup equal to 0.02°, and an acquisition time of 0.1 s. X-ray fluorescence (XRF) was performed with a Bruker S2 Ranger using Pb anode radiation with a maximum power of 50 W, a maximum voltage of 50 kV, and a maximum current of 2 mA. XRF analysis utilized an XFlash[®] Silicon Drift Detector.

To calculate the relative crystallinity of the material, reference angles 2θ were used (7.3°, 10.3°, 12.6°, 16.3°, 21.9°, 24.2°, 26.4°, 27.4°, 30.2°, 31.1°, 32.8°, 33.6°, 34.5°, 36.0°, 36.8°, 44.5°, and 47.6°) as provided by Wang et al. [18]. The relative crystallinity was calculated using Equation (1), where the reference zeolite was commercial zeolite.

$$\%Cristalinidade\ relativa = \frac{\sum \text{intensity of sample peaks}}{\sum \text{Reference peak intensity}} * 100 \quad (1)$$

The zeolites underwent characterization using XRD, argon adsorption and desorption with an ASAP 2020Plus instrument from Micromeritics, Norcross, GA, USA (where a pre-treatment of 200 °C for 10 h was performed such that the material released any gas present in its structure), and scanning electron microscopy (SEM) with a TESCAN MIRA 4 (Brno, Czech Republic). For SEM, a secondary in-beam SE detector with an energy of 10 KeV was used. With the data obtained in the adsorption and desorption isotherms, data treatments were performed. The Brunauer–Emmett–Teller (BET) equation was used to obtain the specific area, the t-plot was used to calculate the area and volume of micropores, and the

Horvath–Kawazoe method was used to obtain the distribution of micropores present in the materials.

2.4. CO₂ Adsorption Isotherms and CO₂/N₂ Selectivity Calculation

CO₂ adsorption data were obtained using the ASAP2050 instrument from Micromeritics; a pre-treatment of heating at 1 °C/min to 60 °C was performed while forming a vacuum at 1.33 kPa/s from 101.32 kPa to 1.33 kPa. After reaching the desired temperature and pressure, the pressure was reduced to 0.006 kPa, where it remained for 10 min. After 10 min, heating at 10 °C/min to 200 °C occurred, and once reached, the temperature was maintained at 200 °C for 600 min.

After this treatment, the sample passed through a high vacuum of 0.0006 kPa for 60 min before starting the analysis. The analysis process under these conditions occurred via pressure variation at a constant temperature, where 56 equilibrium pressures between 0.6 kPa and 1000 kPa were observed. The N₂ adsorption isotherms, for selectivity calculation, were also carried out following this method, calculating the selectivity using Equation (2).

$$\text{Selectivity} = Q_{\text{CO}_2}/Q_{\text{N}_2} \quad (2)$$

where Q_{CO_2} is the amount of CO₂ adsorbed and Q_{N_2} is the amount of N₂ adsorbed at the same pressure.

3. Results and Discussion

In this section, the main results obtained during the studies are presented. We first discuss the characterization of the materials obtained from the syntheses with the residues, followed by an examination of the results after the cation exchange. Finally, the CO₂ adsorption results are presented.

3.1. Characterization of the Materials Obtained

The XRD of the residues used is presented in Figure 2; it can be seen that the ashes present several crystalline phases, including mullite (m) and quartz (q), while the silica fume does not present crystalline phases.

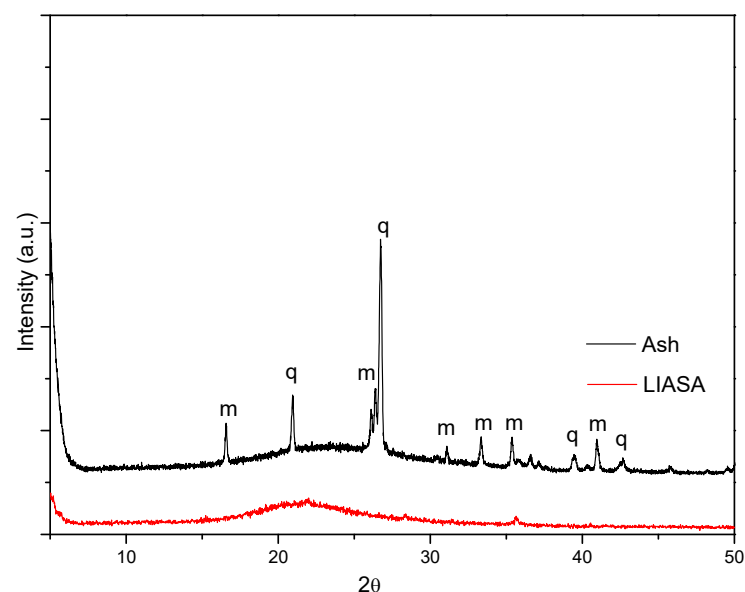


Figure 2. Diffractogram of the residues used. m—mullite (ICSD Code: 066264), q—quartz (ICSD Code: 079634).

The presence of crystalline phases of quartz and mullite in the ashes makes it difficult to dissolve silica in the solution, requiring modification of the zeolite synthesis process. In the case of silica fume, this process would not be necessary.

Analyzing the XRF results presented in Table 2, there is a noticeable difference between the two residues. While the ashes have a good amount of silicon (54.25%) and aluminum (24.09%), almost equivalent to the amount used in the standard synthesis, the silica fume only has a high amount of silicon, making it necessary to increase the amount of aluminum during the synthesis.

Table 2. XRF of waste used.

Component	Coal Ash Light (%)	Silica Fume (%)
SiO ₂	54.25	93.36
Al ₂ O ₃	24.09	1.90
Na ₂ O	1.50	-
CaO	2.60	0.36
K ₂ O	4.03	1.65
MgO	2.00	1.6
Cl	-	0.5
Fe ₂ O ₃	8.12	0.26
TiO ₂	1.75	-
Others	4.26	0.37

However, the silica fume has a smaller quantity of impurities than the ashes. Silica fumes contain impurities such as iron, magnesium, and potassium, with the total impurity level reaching 4.24%, while the ashes have a total impurity level of 22.76%.

In Figure 3, the diffractograms of the zeolites synthesized from the analyzed residues are presented. All XRDs presented reflections in the respective diffraction planes characteristic of the LTA zeolite, observed in the diffractogram in the IZA database (Database of Zeolite Structures).

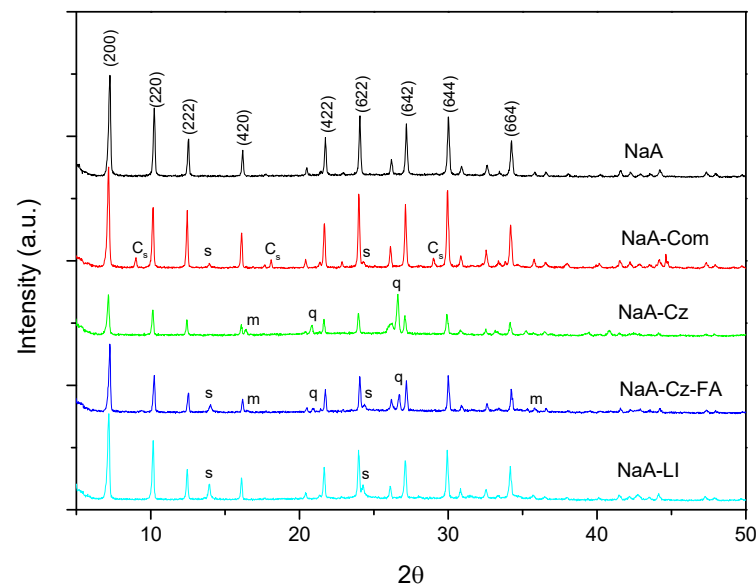


Figure 3. Diffractogram of LTA zeolites synthesized from different silicon sources. Cs—sodium carbonate (ICSD Code: 35191), s—sodalite (ICSD Code: 98814), m—mullite (ICSD Code: 066264), q—quartz (ICSD Code: 079634).

It is observed that the commercial zeolite contains impurities of sodium carbonate in the structure, while the zeolites synthesized from ashes exhibit crystalline phases corre-

sponding to the residues; namely, quartz and mullite. In the zeolite synthesized from the silica fume, there is a slight presence of reflections of the sodalite zeolite.

When examining Figure 4, note that cation exchange did not cause structural changes in the materials, maintaining all the diffractions already observed in Figure 3.

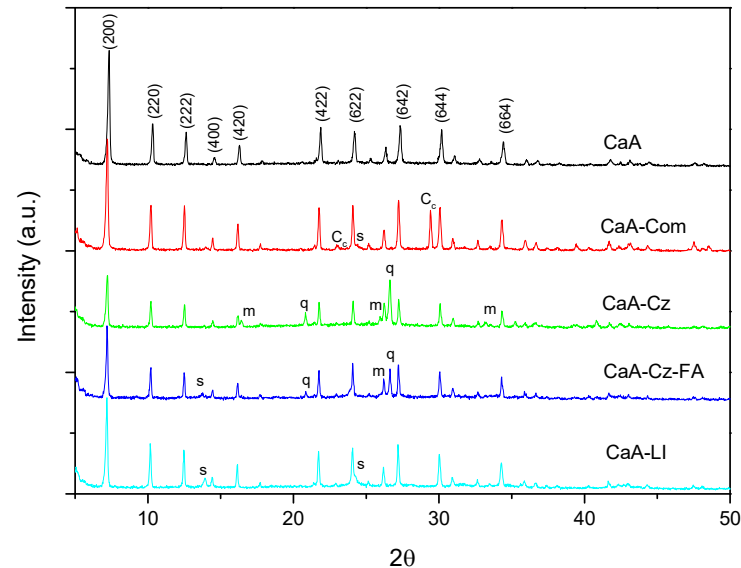


Figure 4. Diffractogram of LTA zeolites after cation exchange. C_c—calcium carbonate (ICSD Code: 16710), s—sodalite (ICSD Code: 98814), m—mullite (ICSD Code: 066264), q—quartz (ICSD Code: 079634).

Observing the scanning electron microscopy images of the materials, it can be noted that all of them present the typical morphology of the LTA zeolite, both in sodium and calcium form, as can be seen in Figure 5.

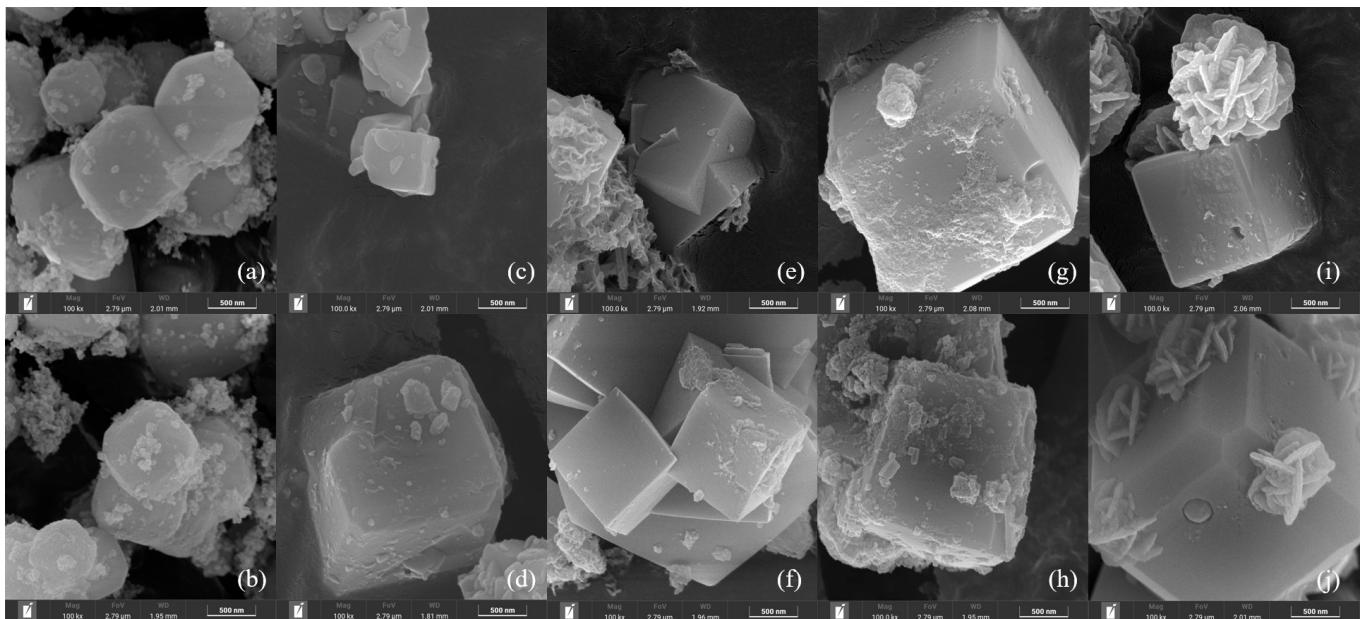


Figure 5. Scanning electron microscopy of zeolites: (a) NaA, (b) CaA, (c) NaA-Com, (d) CaA-Com, (e) NaA-Cz, (f) CaA-Cz, (g) NaA-Cz-FA, (h) CaA-Cz-FA, (i) NaA-LI, and (j) CaA-LI.

It is possible to observe that the zeolites synthesized from residues present some impurities, originating from the residues used, in the case of the zeolites NaA-LI and

CaA-LI. The presence of other zeolitic phases can be seen, with typical characteristics of sodalite. The commercial zeolite showed zeolite crystals with traces of silica.

When analyzing the argon adsorption and desorption isotherms, the difference between the zeolites before and after the cation exchange is noticeable, as shown in Figure 6.

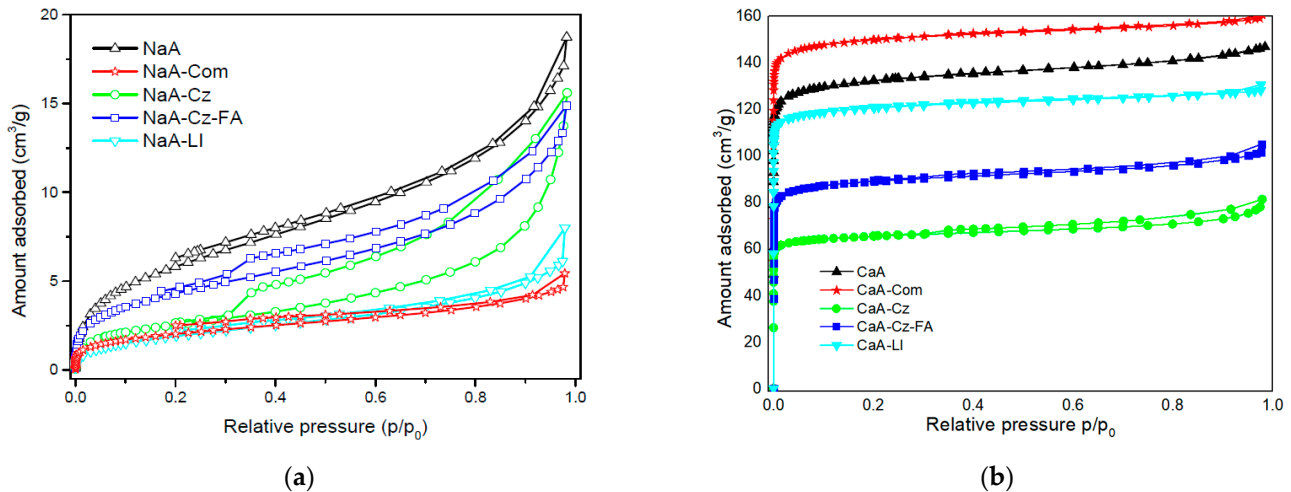


Figure 6. Argon adsorption and desorption isotherm at 77 K of (a) sodium and (b) calcium zeolites.

For materials containing sodium (Figure 6a), type II isotherms typical of non-porous materials are observed; however, in the case of LTA, this is related to the accessibility of the pores of the material, which cannot diffuse the gases used. It is observed that, at higher p/p_0 , there is greater adsorption of Ar, and they exhibit hysteresis of the H3 type, which is related to the external area and between particles, according to the IUPAC classification [42].

The calcium-containing materials (Figure 6b) present type I(a) isotherms characteristic of microporous materials. The zeolites CaA, CaA-Com, and CaA-LI did not show hysteresis, whereas slight hysteresis was observed for the zeolites CaA-Cz and CaA-Cz-FA, classified as the H4 type, which is found in materials that exhibit aggregates of zeolitic crystals according to the IUPAC classification [42].

When carrying out the necessary calculations with the isotherm data, the results presented in Table 3 are obtained. It is noted that the materials containing calcium experience a considerable increase in their characteristic, mainly in the specific area (S_{BET}), which is directly related to the micropore area (S_m).

Table 3. Results of the analyses of argon adsorption and desorption isotherms at 77 K.

Samples	BET		t-Plot		Total Volume	Horvath–Kawazoe
	S_{BET}	S_e	S_m	V_m	V_{total}	D_{pm}
NaA	19	18	1	0.001	0.028	0.50
NaA-Com	6	4	2	0.001	0.008	0.50
NaA-Cz	8	7	1	0.001	0.024	0.50
NaA-Cz-FA	14	13	1	0.001	0.023	0.50
NaA-LI	6	5	1	0.001	0.012	0.51
CaA	468	54	414	0.181	0.227	0.55
CaA-Com	537	45	492	0.212	0.248	0.54
CaA-Cz	234	25	209	0.090	0.125	0.54
CaA-Cz-FA	316	38	278	0.121	0.163	0.55
CaA-LI	434	37	397	0.170	0.202	0.56

S_{BET} (m^2/g): specific area obtained using the BET method (total area); S_e (m^2/g): external area obtained using the t-plot method; S_m (m^2/g): micropore area obtained using the t-plot method; V_m (cm^3/g): volume of micropores obtained using the t-plot method; V_{total} (cm^3/g): total pore volume obtained using $p/p_0 = 0.99$; D_{pm} (nm): average pore diameter obtained using the Horvath–Kawazoe method.

The zeolite containing Na^+ has the characteristic of having a small specific area and, therefore, argon cannot diffuse through the interior of the material, mainly due to the quantity and position of the cations present in the structure.

The increase in area is expected as, when exchanging the monovalent cation Na^+ for the divalent Ca^{2+} , we observe a reduction in half of the number of cations and an increase in the accessibility of Ar. With greater accessibility of the probe gas inside the material, we see an improvement in the characteristics of the material.

This modification of the structure certainly increased the CO_2 adsorption capacity, as, according to Bae et al. [43], after the cation exchange process in the LTA zeolite from sodium to calcium, the calcium cations will preferentially position themselves in the six-membered ring, releasing the eight-membered rings. This change gives the zeolite much greater accessibility, allowing for the entry of gases into the zeolite structure.

3.2. CO_2 Adsorption

In the isotherm shown in Figure 7, CO_2 adsorption data for sodium and calcium zeolites are shown. It is possible to notice that there was a considerable increase in the adsorption capacities of the materials after the cation exchange.

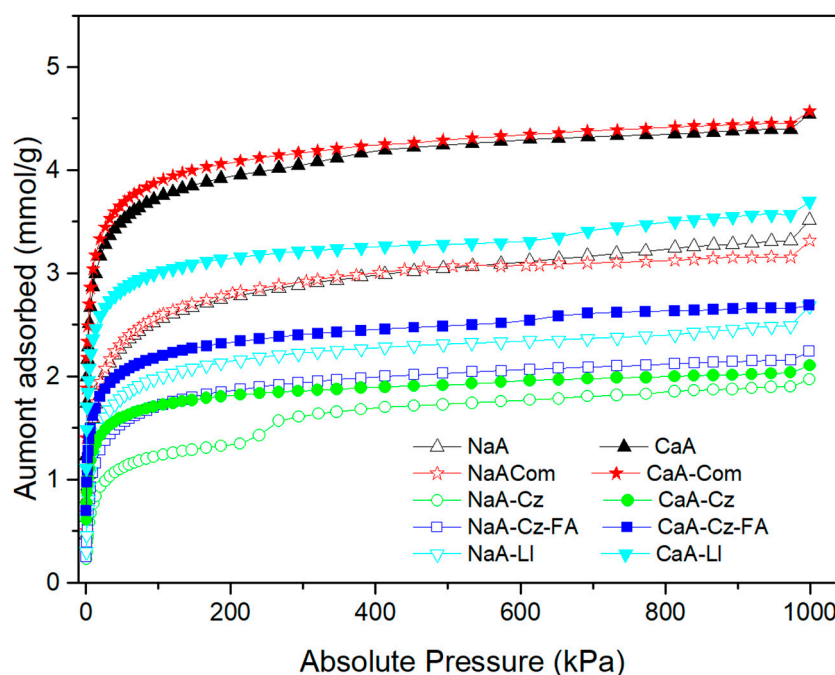


Figure 7. CO_2 adsorption isotherms on sodium and calcium zeolites at 295 K.

It can be observed that the materials containing sodium and calcium present the same adsorption sequence, where all materials after the cation exchange process had an increase in CO_2 adsorption, consistent with results presented in the literature.

Thus, it is clear that the cation exchange does favor the capture of CO_2 , which can be explained by the increase in the specific area observed in the argon adsorption and desorption analyses at 77 K mainly by releasing the internal space of the structure, also observed in the analysis of the specific area. Data similar to those presented by Bae et al. [43] indicate that CO_2 interacts mainly in the eight-membered ring and between the cations present in the six-membered ring.

Table 4 shows the adsorbed quantities of materials at low pressure (15 kPa), atmospheric pressure (101.33 kPa), and high pressure (1000 kPa). It is possible to see that the increase in the adsorbed amount is observed more strongly at low pressure, with an average increase of 67% among the materials, followed by adsorption at atmospheric pressure,

which had an average increase of 47%; meanwhile, at higher pressures, the increase was only approximately 26%.

Table 4. Amount of CO₂ adsorbed by zeolites at 15 kPa, 101.33 kPa, and 1000 kPa.

Samples	Amount Adsorbed in 15 kPa (mmol/g)	Amount Adsorbed in 101.33 kPa (mmol/g)	Amount Adsorbed in 1000 kPa (mmol/g)
NaA	1.79	2.54	3.51
NaA-Com	1.76	2.58	3.31
NaA-Cz	0.85	1.22	1.97
NaA-Cz-FA	1.18	1.70	2.24
NaA-LI	1.40	1.98	2.68
CaA	3.02	3.73	4.54
CaA-Com	3.19	3.88	4.57
CaA-Cz	1.36	1.71	2.10
CaA-Cz-FA	1.72	2.19	2.69
CaA-LI	2.49	3.01	3.69

The results of standard and commercial zeolites are in accordance with what is found in the literature, as presented by Rey, F. et al. (2010) and Boer, D. et al. [44,45]; however, the result of the sample using fume silica was higher than some previously observed works, such as Wang, Y. et al. (2018) and Zgureva, D. (2016) [18,46].

This increase at low pressures is mainly caused by the considerable increase in the microporous area and volume as, at low pressures, the gas is directed primarily to the micropores.

When comparing the adsorbed quantity with the relative crystallinity, it can be observed that there is a correlation between the two, mainly when dealing with materials containing calcium, as shown in Figure 8. Materials with relative crystallinities close to that observed in the standard sample (commercial zeolite) showed greater CO₂ adsorption capacities, which may be related to the better ability of the gas to diffuse between the pores of these materials.

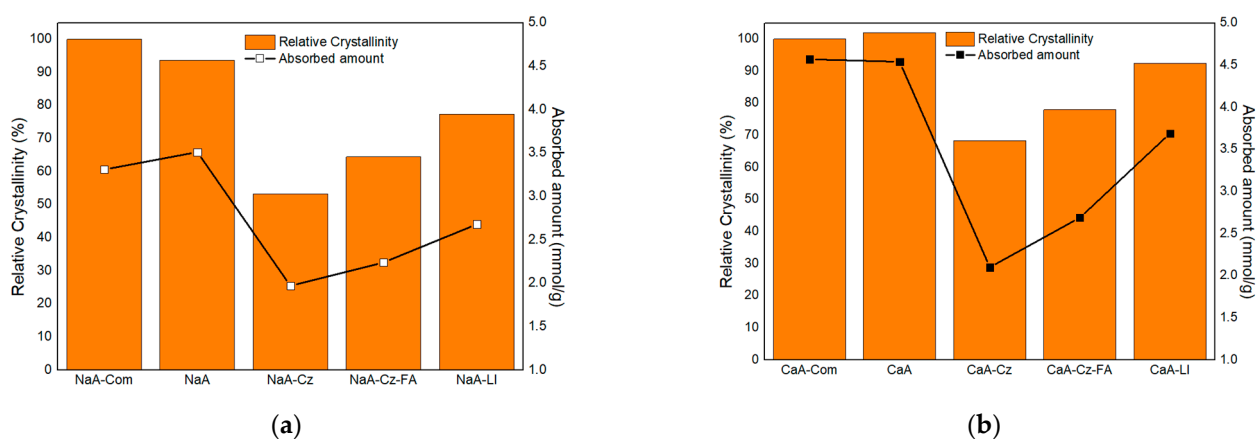


Figure 8. Relationship between relative crystallinity and amount adsorbed for zeolites: (a) sodium and (b) calcium.

3.3. CO₂/N₂ Selectivity

In Figure 9, the N₂ adsorption curves are compared to the CO₂ adsorption curves, where it is possible to see the difference between zeolites with sodium and calcium in terms of the adsorption of N₂.

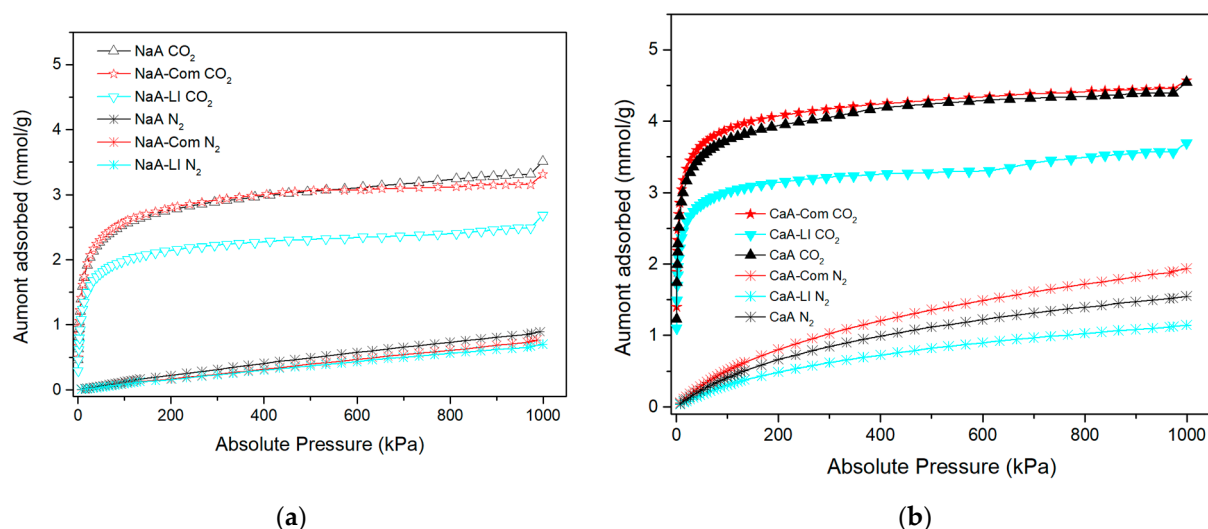


Figure 9. CO₂ and N₂ adsorption isotherms of zeolites containing (a) sodium and (b) calcium.

When analyzing the isotherms, it can be noted that the materials with the largest area—in this case, the zeolites CaA and CaA-Com—adsorbed more CO₂ and N₂, which resulted in low selectivity, whereas the zeolite CaA-LI, which presented a smaller area among the three materials, also presented lower N₂ adsorption.

For materials with sodium, this difference is clearer, where all materials had very low adsorbed amounts, which may be a reflection of the smaller surface area and pore volume, especially the micropores existing in these materials.

One of the main adsorption mechanisms in zeolites demonstrates that the presence of the Na⁺ cation in the eight-membered ring partially blocks the zeolite pore. As the kinetic size of CO₂ is much smaller than N₂, it can pass through, in addition to the interactions existing between the oxygen of the gas and the cations in the eight- and six-membered rings. When the exchange for Ca²⁺ occurs, it remains only in the six-membered ring, completely releasing the eight-membered ring, which allows a greater amount of gas to enter, thus increasing the adsorption capacity but removing the selective property of the material [37,45].

Regarding the selectivity among calcium zeolites, CaA-LI zeolite stands out, exhibiting a selectivity of 10.03 mmol_{CO2}/mmol_{N2} at atmospheric pressures, with the highest selectivity observed for calcium zeolites. As the pressure is increased, this pattern continues, with a selectivity of 3.24 mmol_{CO2}/mmol_{N2}.

The fact that commercial zeolite has the lowest selectivity among the three materials may be related to the greater area and greater crystallinity of the material, as the N₂ molecule has a lower influence related to the quadrupolar moment [18] and, therefore, the adsorption of N₂ is influenced more by the area of the material.

Therefore, having a higher specific surface area and crystallinity results in a greater N₂ adsorption capacity. The CaA-LI zeolite has the lowest crystallinity among the three materials and the smallest area, which implies lower adsorption of N₂; the standard zeolite NaA presents results of crystallinity and selectivity between the two materials.

4. Conclusions

It can be concluded that the residues considered here can be used for the synthesis of zeolite materials. In this case, the LTA zeolite presented characteristics and crystallinity close to that of the standard zeolite and a low degree of impurity. The materials have good CO₂ adsorption capacities, with the standard materials having better adsorption capacities, with maximum adsorbed amounts of 2.58 mmol/g at 101.33 kPa and 3.51 mmol/g at 1000 kPa, followed by the zeolite synthesized from silica fume, reaching 1.98 mmol/g at 101.33 kPa and 2.68 mmol/g at 1000 kPa.

The ion exchange procedure for calcium considerably favored the adsorption capacity in all zeolites, following the same order of adsorption capacity for all samples. The highest absorption capacity was observed in standard zeolites, reaching 4.54 mmol/g at 1000 kPa, followed closely by commercial zeolites with 4.57 mmol/g at 1000 kPa. The zeolite synthesized with the silica fume exhibited a lower absorption capacity of 3.69 mmol/g at 1000 kPa, and the zeolites synthesized from coal ashes demonstrated the lowest absorption capacities.

Regarding the selectivity for N₂, it was observed that the materials with sodium presented higher selectivity—between 21.16 and 25.80 mmol_{CO₂}/mmol_{N₂} at 101.33 kPa and between 7.76 and 10.03 mmol_{CO₂}/mmol_{N₂} at 1000 kPa—related to the area of the material and the distribution of cations in the structure, preventing the diffusion of gas in the material, with the best result obtained with the silica fume zeolite, followed by the commercial sample and, finally, the standard sample.

In view of this, it is possible to conclude that LTA zeolites can be applied in CO₂ capture and adsorption processes, such as the CO₂/N₂ separation process, as they present selectivity to CO₂ with mostly physical and adsorbent–adsorbate interactions and allow for the possibility of reuse.

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