

STUDY OF FAUJASITE-TYPE ZEOLITE MODIFIED WITH LA AND NH₄¹⁺

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Abstract: The acidity of faujasite zeolite was modified through ion exchange, it is treated in the present study, the Na¹⁺ cation, part of the initial structure of faujasite, was removed by cations such as NH₄¹⁺ and La³⁺. The obtained molar ratio of the precursor oxides for the formulation of the seed gel was: SiO₂/Al₂O₃ = 12.26; Na₂O/Al₂O₃ = 13.27 and Na₂O/SiO₂ = 2.16. In the case of the structural gel, the following molar ratios were reported: SiO₂/Al₂O₃ = 10.90; Na₂O/Al₂O₃ = 11.92 and Na₂O/SiO₂ = 2.18. The optimum crystallization temperature was 90 °C for the seed gel and 80 °C for the structural gel. The zeolite obtained was characterized by X-ray diffraction (XRD), through comparative analysis between the diffractograms of the zeolite developed and NaY-type faujasite patterns. By means of BET surface area analysis, a specific surface area of

875 m².g⁻¹ and a pore radius of 5.88 Å were determined, and the morphological analysis was complemented by scanning electron microscopy (SEM). The ion exchange behavior for the case of ammonium ion, reported an exchange of 59.8 mg.g⁻¹ under the best experimental conditions (8 h, 20 cm³.g⁻¹), while in the case of lanthanum ion it was 38 mg.g⁻¹ (24 h, 50 cm³.g⁻¹).

Keywords: Faujasite, ammonium, lanthanum, hydrothermal

1. INTRODUCTION

Zeolites are crystalline aluminosilicates, with a three-dimensional structure, formed by TO₄ tetrahedra (T = Si, Al) that form cavities of molecular dimensions, the same that can host cations, water molecules or other species; because the pores adsorb structures that fit perfectly into the cavity, these act as sieves of molecules, therefore zeolites are a set of molecular sieves or nanoreactors (Cejka, et al., 2007).

The sodalite (β-cavity), is a basic structure found in the most important zeolites (type A, X, and Y), which is a truncated octahedron, whose vertices symbolize the atoms of silicon (Si) and aluminum (Al), with the oxygen atom between them (Roland and Kleinschmit, 2005).

The way the sodalites are joined gives the type of zeolite that can be obtained, when the β-cavities are joined between the cubic units they give rise to a type A zeolite, where a new cavity formed by 8 T atoms is formed. If the sodalite binds between the hexagonal prisms, the result is a faujasite-type zeolite (FAU), and a new cavity is created called a super-box or α-cavity (diameter 1.2 nm) and whose window is formed by 12 T atoms (Gómez, 2001; Roland and Kleinschmit, 2005).

A representation in polyhedra is shown in Figure 1, where the super-box characteristic of a faujasite-type structure is formed by smaller boxes such as the sodalite or β-cavity (Roland and Kleinschmit, 2005).

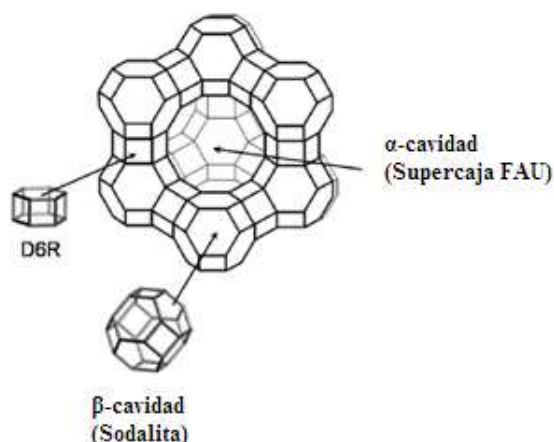
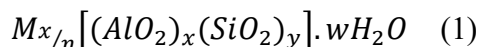


Figure 1. Structure of a faujasite-type zeolite, showing its characteristic cavities and channels. (Macias et al. 2012)

All zeolites have the general formula shown in Equation (1).



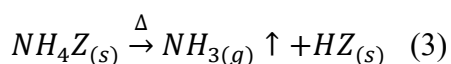
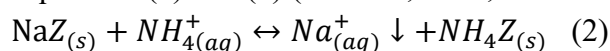
Where M is a group IA or IIA cation, n the valence of the cation, "x" and "y" represent the total number of tetrahedra per unit cell, and w the water content (H. van Bekkum et al., 2001). The (SiO₄)⁴⁻ and (AlO₄)⁵⁻ tetrahedra constitute the basic unit of zeolite. The tetrahedron formed by silicon and oxygen are electrically neutral within the structure, but when replaced by aluminum tetrahedra, the electrical balance is lost, which are compensated by interchangeable metal cations that are located within the zeolite cavities (Calleja, 2009).

In the faujasite-type structure, two types are denoted: zeolite X and zeolite Y, which differ in silica content. The X-type structure presents a Si/Al ratio between 1 to 1.5; while the Y-type zeolite has Si/Al ratios greater than 1.5 (Frising and Leflaive, 2007). The porous structure of the FAU-type zeolite, forms three-dimensional systems of cavities: those comprised by the super-cavities (α -cavities) of 13 Å of diameter which connected to four other super-cavities forms a 7 Å window and the cavities formed by sodalites (β -cavities) which due to their reduced size are not accessible to organic molecules, not so in the 13 Å super-cavity, which is the access route for organic molecules, giving this type of structure catalytic properties in fluidized catalytic cracking refining processes (Guisnet and Ramoa, 2006).

The presence of metal cations as charge compensators in the zeolite cavities makes possible post-synthesis processes with catalytic applications. The removal of metal cations leads to the creation of active sites, i.e. each aluminum tetrahedron corresponds to a proton or exchangeable cation site.

The goal of ion exchange is generally to produce Brönsted and Lewis acid sites. Brönsted acidity is defined as when the species has a proton that can be donated, in the case of zeolite, a hydrogen atom (proton) is bonded to an oxygen atom that is connected to the Si and Al tetrahedra. Lewis acidity is defined when the species is electron deficient, so it has the ability to accept electrons during interaction with other species. Lewis acid sites create a strong electrostatic field capable of polarizing the adsorbed molecules resulting in their activation (Ramesh, 1998; Sami, 2013).

Na-zeolite, is the structure that is mostly synthesized, and is the main source for obtaining NH₄-zeolites, of great use in acid catalysis reactions, where the sodium cation is exchanged by the ammonium cation forming the NH₄-Z structure, and after a calcination process at 400 °C a deammonification of the zeolitic structure occurs, remaining of the H-Z form, as shown in Equations (2) and (3) (Sherhan, 2011; Roland and Kleinschmit, 2005).

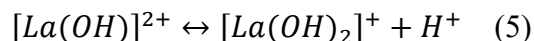
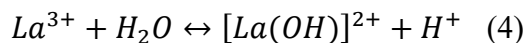


The H⁺ proton in the H-Z structure is bonded to oxygen atoms to form OH groups, and consequently the Si-O (H)-Al structure is formed, the same being called the Brönsted acid site.

The deammonification step is possible only under a thermal process, hence zeolite X cannot form an acidic H-Z structure, because its crystalline structure is destroyed when subjected to high temperatures (Guisnet and Ramoa, 2006). Figure 2 illustrates the ion exchange process between ammonium and a zeolite.

Zeolites exchanged with rare earths (ReY) are of high catalytic use, particularly in the cracking process. During ion exchange lanthanum is introduced into the super-box in hydrated form, and upon dissociation of the water molecules, the formation of Brönsted acid sites takes place. Lanthanum in hydrated form tends to form two species, the product of the dissociations of the water molecules.

water molecules, as shown in Equations (4) and (5) (Guisnet and Ramoa, 2006):



In the first species, lanthanum within the zeolite structure, is bound to one hydroxyl and two oxygen atoms, while in the second species, it is bound to two hydroxyls and one oxygen atom. The presence of these two species causes charge variations, which allows a more favorable energetic incorporation into the zeolite cavities, and the proton sites generated are responsible for the catalytic cracking process (Guisnet and Ramoa, 2006; Schüßler, 2013).

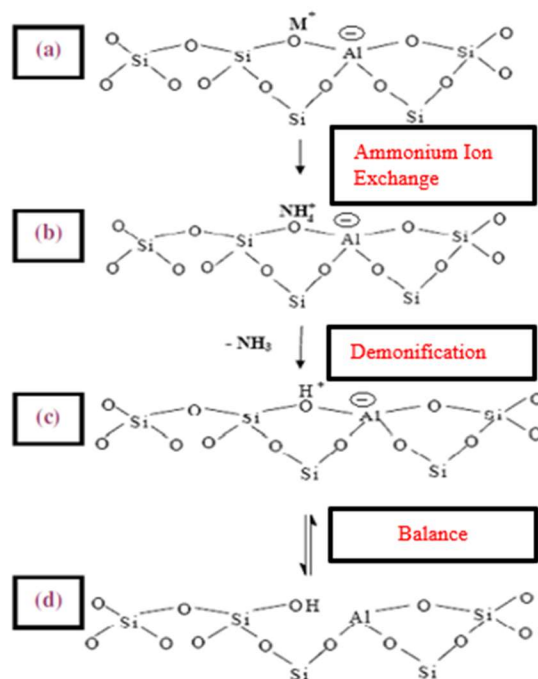


Figure 2. a) Structure of a zeolite, where M is any metal cation. b) Formation of the NH_4^+ -Z structure by ion exchange process with the ammonium ion. c) Removal of the NH_3 - ion by thermal processes. d) Equilibrium process, the formation of the Brønsted acid site (Si-OH-Al) is observed. (Sherhan, 2011).

In the present investigation, the aim is to obtain a zeolite of the faujasite Y type, by means of hydrothermal processes, to subsequently modify its exchangeable structural cation (Na^+) with NH_4^+ and La^{3+} cations, by means of ion exchange. (Na^+), with NH_4^+ and La^{3+} cations, by means of ion exchange. The processes of obtaining and post-synthesis modification of faujasite are oriented to contribute to a research not yet developed in the country. The obtaining of the fluidized catalytic cracking catalyst.

2. METHODOLOGY

2.1 Materials and Reagents

In the synthesis process of NaY zeolite, the following reagents were used in technical grade: granular sodium aluminate (50 - 56 % Al_2O_3 , 40 - 46 % Na_2O), granular sodium silicate (10.6 % Na_2O , 25.5 % SiO_2), sodium hydroxide (NaOH), distilled water (H_2O), potable alcohol (CH_3OH).

In the post-synthesis modification process, the reagents used were in reagent grade: ammonium nitrate (NH_4NO_3), lanthanum nitrate hexahydrate ($LaNO_3 \cdot 6H_2O$), distilled water (H_2O).

2.2. Obtaining a faujasite-type zeolite NaY

2.2.1. Synthesis Process

A solution was obtained using 2.09 g of sodium aluminate, 8.14 g of sodium hydroxide and 40 g of water; it was stirred at room temperature until completely dissolved with the help of a magnetic stirrer, then 18.28 g of sodium silicate was added, it was stirred for 10 minutes more until the mixture was homogenized, then the solution was left to age at 90 °C (Lutz, et al., 2011; Xu, et al., 2007) in an oven for 24 h. This solution is known as seed gel, which had the following synthesis molar ratios: $\text{SiO}_2/\text{Al}_2\text{O}_3 = 12.26$; $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3 = 13.27$ and $\text{Na}_2\text{O}/\text{SiO}_2 = 2.16$ (Robson, 2001; Xu et al, 2007).

Subsequently, a solution consisting of 4.5 g of sodium aluminate; 0.12 g of sodium hydroxide and 117.8 g of water was obtained and stirred until completely dissolved at room temperature, then 36.61 g of sodium silicate and 7.30 g of the gel-seed solution were added (Lutz, et al. 2011) and stirred for 10 min until a single phase was reached. Then the solution was subjected to a crystallization or aging process in an oven at 80 °C for 48 h (Roland and Kleinschmit, 2005; Robson, 2001; Cundy and Cox, 2003). This solution is referred to as a structural gel, and the molar ratios of the oxides according to the formulation were: $\text{SiO}_2/\text{Al}_2\text{O}_3 = 10.90$; $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3 = 11.92$ and $\text{Na}_2\text{O}/\text{SiO}_2 = 2.18$.

The gel was allowed to cool for 30 min, and the gel was washed and filtered with water and methanol to lower the pH of the precipitate formed to a value equal to 9 (Xu et al. 2007). The filtered zeolite was subjected to a drying process in an oven at 100 °C for 12 h.

In the synthesis process, the variables and their respective study values were experimented with as shown in Table 1, which were assumed to be the most important according to preliminary observations. In the experimentation process to define each parameter, the remaining variables were set at a mean value of the study range, while the analyzed parameter was varied in the values to be experimented.

2.2.2 Characterization of the synthesized sample

The crystalline structure was studied by X-ray diffraction (XRD), using a Brunker AXS, model D8 Advance with $\text{CuK}\alpha = 0.154$ nm and a scanning speed of 2° per minute. The obtained diffractogram was compared with the standard diffractogram ICDD-PDF# 00-012-0228 corresponding to a Na-FAU of formula $2\text{Na}-2\text{Al}-3.3\text{Si}-10.6\text{O}-7\text{H}_2\text{O}$.

The morphological structure was examined by microscopy.

Table 1. Variables analyzed in the production of a faujasite-type zeolite

Variables	Value range
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T_{semilla}	Seed crystallization temperature	20, 90, 110 °C
$X_{\text{SiO}_2/\text{Al}_2\text{O}_3}$	Seed molar ratio	10 - 13
$X_{\text{Na}_2\text{O}/\text{Al}_2\text{O}_3}$	Seed molar ratio	10 - 14
$X_{\text{Na}_2\text{O}/\text{SiO}_2}$	Seed molar ratio	1 - 3
T_{cristal}	Zeolite crystallization temperature	80, 90, 100, 110, 120 °C
t_{cristal}	Crystallization time	24, 48, 72 h
$Y_{\text{SiO}_2/\text{Al}_2\text{O}_3}$	Structural gel molar ratio	10 - 13
$Y_{\text{Na}_2\text{O}/\text{Al}_2\text{O}_3}$	Structural gel molar ratio	10 - 14
$Y_{\text{Na}_2\text{O}/\text{SiO}_2}$	Structural gel molar ratio	0,5 – 2,5

The scanning electron microscopy (SEM) with a Bunker equipment model Vega Tescan with X-ray detector. Surface area, volume and pore size were determined by the physisorption isotherm analysis technique using the BET method with the Nova 4200 equipment. Unit cell size was calculated according to ASTM D3942-03.

2.3. Ion exchange

2.3.1 Ion exchange process

The post-synthesis process of ion exchange occurred between the sodium cation (Na^{1+}) of the zeolite, and the ammonium (NH_4^{1+}) and lanthanum (La^{3+}) cations obtained from ammonium nitrate and lanthanum nitrate hexahydrate solutions, respectively.

In the case of NH_4^{1+} ion, 20 cm³ of a 1 M ammonium nitrate solution was prepared, the same was put in contact with 1 g of zeolite, the resulting solution/zeolite ratio was 20 cm³.g⁻¹ (Karim, et al., 2013; Punyapalayakul, et al., 2009), for a contact time of 8 h at 60 °C. However, further tests were performed by varying the solution/faujasite ratio (10 cm³.g⁻¹ and 15 cm³.g⁻¹) and contact times (4 h and 24 h) to analyze the behavior of the faujasite. Subsequently, the solution was filtered and washed with distilled water, with a total volume (filtered solution + washing solution) of 118.5 cm³ and the modified zeolite was recovered.

To determine the amount of ammonium ions adsorbed by the zeolite from the ammonium nitrate solution, the recovered solution was sent for spectrophotometric analysis in a HACH Dr 2800 model, and the presence of Na^{1+} ions from the zeolite in the contact solution was quantified by atomic absorption analysis with a Perkin Elmer AAnalyst 300 spectrophotometer. The zeolite

modified with NH_4^+ cation ($\text{NH}_4\text{-Z}$) was subjected to a deammonification process by calcination at $400\text{ }^\circ\text{C}$ for 6 h to form zeolite H-Z (Hidalgo, et al. 1984; Punyapalayakul, et al., 2009).

For La^{3+} ion exchange, 0.5 g of unmodified zeolite was contacted with 25 cm^3 of a 0.5 M lanthanum nitrate solution at $80\text{ }^\circ\text{C}$, the concentration ratio being $50\text{ cm}^3\cdot\text{g}^{-1}$ (Sugunan and Thomas, 2005; Huang, et al., 1995), and contact times of 4 h, 8 h and 24 h were evaluated. The solution was then filtered and washed with a total volume (filtered solution + wash solution) of 140 cm^3 and the modified zeolite was recovered. The recovered solution was sent for spectrophotometric analysis in a Perkin Elmer Optima 8000 optical ICP equipment. The La^{3+} modified zeolite was finally subjected to a calcination process at a temperature of $500\text{ }^\circ\text{C}$ for 6 h (Fuess, et al., 1995; Sugunan and Thomas 2005).

2.3.2 Characterization of the modified zeolite

The modified zeolites were analyzed by X-ray diffraction, the obtained diffractograms were compared with the ICDD-PDF# 00-012-0228 pattern, used to validate the NaY crystalline structure, and the study was complemented by Fourier Transform Infrared Spectrometry (FTIR) analyzing the main bands of the spectrum between $4\ 000 - 400\text{ cm}^{-1}$, with a Perkin Elmer spectrophotometer, Spectrum One model.

In the case of the NH_4^+ cation, based on the ions adsorbed by the zeolite for concentrations of 10, 15, 20 $\text{cm}^3\cdot\text{g}^{-1}$, the affinity between the synthesized zeolite and the cation under study was analyzed using the Freundlich isotherm model. The linearized form is shown in Equation (6).

$$\ln q_e = \ln k_f + \frac{1}{n} (\ln C_e) \quad (6)$$

Where: q_e is the amount of ammonium adsorbed on one gram of zeolite ($\text{mg}\cdot\text{g}^{-1}$), k_f the Freundlich constant, associated to the adsorption capacity, n an indicator of the adsorption intensity and C_e the concentration of ammonium in the solution ($\text{mg}\cdot\text{L}^{-1}$). A value of $n > 1$ indicates that adsorption occurred under favorable conditions, it should be added that this analysis was performed on the contact solution, not the zeolite (Kabwadza and Wazingna, 2014; Kučić, et al, 2012).

3. RESULTS AND DISCUSSION

3.1 Synthesis of a faujasite-type zeolite NaY

3.1.1 Influence of seed gel crystallization temperature.

The best crystallization temperature was obtained at $T = 90\text{ }^\circ\text{C}$, the diffractogram obtained showed the existence of the characteristic peaks of a FAU type zeolite ($2\theta = 6.19^\circ$, 10.11° and 11.86°), in addition to the fact that most of the peaks did fit the ICDD-PDF# 00-012-0228 pattern. However, the peak $2\theta = 12.3^\circ$ did not correspond to the compared pattern, being this peak typical of X-type faujasites, and it was present in the diffractograms of all the temperatures tested ($20\text{ }^\circ\text{C}$, $90\text{ }^\circ\text{C}$ and

110 °C). The diffractogram that presented the lowest intensity of the aforementioned peak was the one at $T = 90$ °C. The results corresponding to 20 °C and 110 °C, had the presence of extra peaks that did not belong to the comparative pattern.

High temperatures produce rapid crystallization processes, resulting in large crystals, and less crystalline structures, even amorphous (Yu, 2007), so the peaks of the diffractogram at 110 °C were less defined than those experienced at lower temperature.

3.1.2 Influence of the molar ratios of the seed gel.

The molar ratios according to the precursor oxides, which best fitted the NaY pattern were: $\text{SiO}_2/\text{Al}_2\text{O}_3 = 12.26$; $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3 = 13.27$ and $\text{Na}_2\text{O}/\text{SiO}_2 = 2.16$. The presence of decimals in the numerical values of the ratios is due to the fact that sodium silicate (10.6 % Na_2O , 25.5 % SiO_2) and sodium aluminate (50 - 56 % Al_2O_3 , 40 - 46 % Na_2O) contain non-bipartite concentrations of their constituent oxides. For such reason, in the experimentation we tried to approach the levels recommended bibliographically and indicated in Table 1 (Cundy and Cox, 2003; Lutz, et al., 2011; Robson, 2001; Roland and Kleinschmit, 2005; Xu, et al., 2007).

The theoretical $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio was defined in terms of the highest value at which the diffractogram still matched the reference pattern, this because Y-type faujasites exhibit Si/Al ratios > 1.5 . An important observation obtained in the diffractograms, was that the lower the Si/Al ratio the more intense was the peak $2\theta = 12.3^\circ$, this is explained because its location is typical of an X-type faujasite, so the molar ratio in which diffractogram presented lower intensity of the peak $2\theta = 12.3^\circ$ was chosen.

The amount of sodium aluminate used determines the concentration of aluminum in the structure, so to obtain a NaY type zeolite ($\text{Si}/\text{Al} > 1.5$) the amount of sodium aluminate present should be as low as possible, however when experimenting with the ratio $\text{SiO}_2/\text{Al}_2\text{O}_3 = 13$ (upper limit of the study range), the diffractogram showed a range of peaks that did not match that of a NaY-type zeolite, this implies that to synthesize a fujasite with low aluminum content or high Si/Al ratios (greater than 5) it is necessary to incorporate organic temperers, which help to maintain the zeolitic structure (Cundy and Cox, 2003; Garcia and Li, 2015).

3.1.3 Influence of the crystallization temperature of the structural gel.

Thus, obtaining the structural solution, the gel crystallization temperature was a sensitive parameter. Working at high temperatures ($T \geq 110$ °C) was not suitable, the solution formed reached the boiling point, altering the resting conditions of crystallization, so it was not possible to achieve the FAU type crystalline structure at 110 °C, even some of the tests at 120 °C were reported as amorphous structure.

For samples synthesized at temperatures between 90 and 100 °C, the peaks were adjusted to the comparison pattern, however, the peak $2\theta = 12.3^\circ$, which corresponds to the NaX type zeolite, was still evident. The crystallization temperature at which the aforementioned peak was not obtained was at 80 °C.

3.1.3 Influence of structural gel molar ratios.

The molar ratios that most closely matched the faujasite-type zeolitic structure were: $\text{SiO}_2/\text{Al}_2\text{O}_3 = 10.90$; $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3 = 11.92$ and $\text{Na}_2\text{O}/\text{SiO}_2 = 2.18$. Results with $\text{SiO}_2/\text{Al}_2\text{O}_3 > 12$ ratio were not satisfactory, i.e. it was not possible to achieve the desired structure (FAU), diffractograms were obtained without the characteristic peaks of FAU type zeolite ($2\theta = 6.19^\circ$, 10.11° and 11.86°). This is due to the fact that synthesizing zeolites with high silica content implies the use of structure-directing agents, known as SDA ("specific structure-directing agent") or organic tempering agents, for example, the best known is tetra-propyl ammonium TPA^+ (Cundy and Cox, 2003; Robson, 2001; Yu, 2007).

The diffractogram obtained at the recommended molar ratios was defined by looking for the highest Si/Al ratio that matched the ICDD-PDF# 00-012-0228 pattern. It is important to emphasize that the theoretical formulation molar ratio is not the final structural molar ratio of the zeolite (Yu, 2007).

3.1.4 Crystallization time of zeolite type FAU

The aging time chosen was 48 h, because it showed more defined peaks than the ones crystallized at 24 h. In crystallization processes for zeolites with high silica content, long crystallization times are recommended; however, the zeolite synthesized in the present study is of medium content, so a time of 48 h is sufficient for a good formation of small crystals.

Very short aging times do not allow the nucleation process to be completed in solution; at least 2 h is necessary just to activate and initiate the crystallization of the aluminosilicate (Arifuzzaman, et al., 2010). Prolonged crystallization times ($t > 24$ h) increase the supersaturation of the solution increasing the formation of crystals with zeolite Y-type structure.

Figure 3 shows the diffractogram of a zeolite with crystallization time 48 h, and at the best synthesis conditions analyzed above: seed gel ($T = 90$ °C, $\text{SiO}_2/\text{Al}_2\text{O}_3 = 12.26$; $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3 = 13.27$; $\text{Na}_2\text{O}/\text{SiO}_2 = 2.16$); structural gel ($T=80$ °C, $t = 48$ h, $\text{SiO}_2/\text{Al}_2\text{O}_3 = 10.90$; $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3 = 11.92$; $\text{Na}_2\text{O}/\text{SiO}_2 = 2.18$). The peaks obtained correspond to the locations of the standard diffractogram ICDD-PDF# 00-012-0228, it was possible to eliminate the presence of the peak $2\theta = 12.3^\circ$; and after a qualitative analysis it is concluded that the alumino-silicate synthesized in this study corresponds to a zeolite type Faujasite NaY.

3.2 Morphology of synthesized Zeolite

3.2.1 BET Analysis

By means of adsorption isotherm analysis (BET) using nitrogen gas, performed on the zeolite that most closely matched the standard diffractogram, a surface area of 874.51 m².g⁻¹, an average micropore and mesopore radius of 5.88 Å and 17.25 Å respectively and an average micropore volume of 0.32 cc.g⁻¹ were determined.

In catalysis, surface area is considered extremely important for active metal impregnations. The value obtained implies that the process performed is good, the area obtained is comparable to commercial faujasites, as an example, some related studies report the following areas for NaY type faujasites: 731.5 m².g⁻¹, 686 m².g⁻¹, 625 m².g⁻¹ (Karami and Rohani, 2009; Wittayakun, et al. 2007; Maesen, et al. 2000).

Concerning the micropores of the zeolitic structure, the value

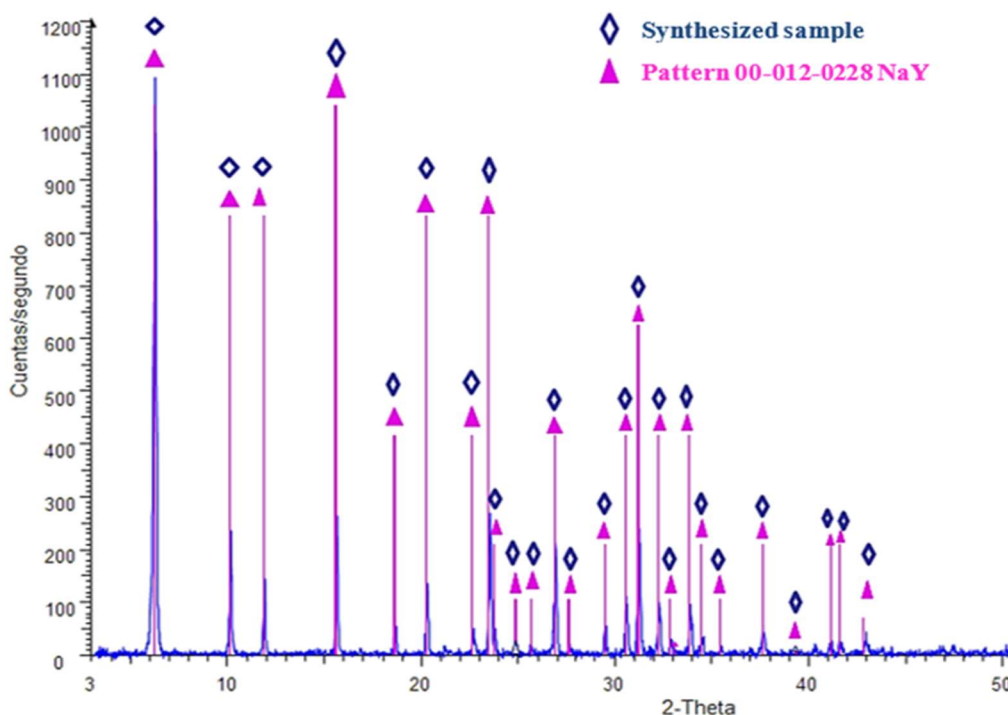


Figure 3. Diffractogram obtained at conditions: seed gel (T = 90 °C, SiO₂/Al₂O₃ = 12,26; Na₂O/Al₂O₃ = 13,27; Na₂O/SiO₂ = 2,16); structural gel (T = 80 °C, t = 48 h, SiO₂/Al₂O₃ = 10,90; Na₂O/Al₂O₃ = 11,92; Na₂O/SiO₂ = 2,18

found for the pore diameter was 11.76 Å, it must be taken into account that it corresponds to an average value.

It should be taken into account that it corresponds to an average value, so that in FAU type zeolites, the micropores generally present openings in ranges from 4 to 8 Å corresponding to the so-called

boxes or channels and ranges greater than 8 Å corresponding to the super boxes (14 Å) (Guisnet and Ramoa, 2006).

The reason for the selectivity of zeolitic catalysts is that the reaction takes place inside the zeolite pores. For catalytic processes of hydrocarbon isomerization, halogenation of aromatics, among others, it is necessary the presence of micropores in their structures, this because the dimensions of the pore sizes are well defined, not so in other microporous structures, that have a wider distribution of sizes, and because their dimensions give them the property of being selective for both reactant and product (Ryan, 2006).

The results obtained also show the presence of mesopores with an average diameter of 34.5 Å, which is a small dimension within the range of mesopores, this result is of interest, because for catalysis processes, it is not very favorable to have mesopores of large dimensions, however the presence of these pores play an important role as facilitators of the diffusion of molecules (Guisnet and Ramoa, 2006).

For zeolites, a pore volume of 0.1 to 0.35 cc.g⁻¹ is reported in the literature (Auerbach, et al., 2003), so the value obtained is within the expected range. The pore volume is an indicator of the capacity of molecules that can be stored or retained in each channel of the structure; consequently, having a value of 0.32 cc.g⁻¹, it is in the upper range for zeolitic structures, indicating a high retention capacity in their pores.

3.2.2 SEM analysis

The best zeolite sample synthesized was morphologically characterized. Figure 4 shows that the zeolite is approximately 80 µm in size and has a solid structure with a porous surface.

3.2.3 Unit cell size

The unit cell size (a_0) of the faujasite crystal structure was 24.85 Å, as shown in Table 2, which is within the typical range of the zeolite studied (24.2 - 25.0 Å). Equations (7) and (8) are the ones used to calculate this parameter and are recommended by Guisnet and Ramoa, and are also suggested in ASTM D3942 considering the peaks corresponding to the miller indices (5 3 3), (6 4 2) and (5 5 5).

(5 5 5).

$$d_{hkl} = \frac{\lambda}{2 \sin \theta} \quad (7)$$

$$a_0 = [d_{hkl}^2 (h^2 + k^2 + l^2)]^{1/2} \quad (8)$$

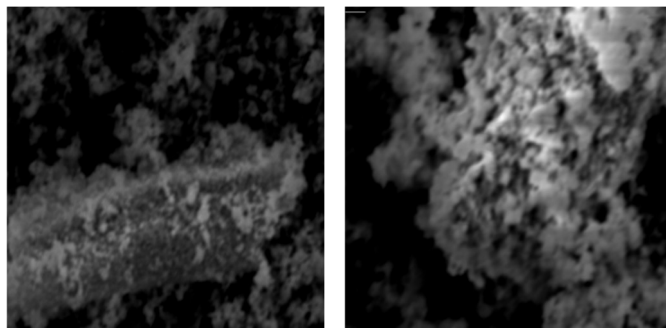




Figure 4. Scanning electron microscopy of a sample of synthesized faujasite. Synthesized faujasite. Image (a) corresponds to 800x while image (b) to 1000x.

Where λ is the wavelength of the X-ray radiation and has a value of 1.54 Å and $dhkl$ is the reflection distance between planes. Equation (9) proposed by Breck and Flanigen was applied to calculate the number of aluminum atoms present in the unit cell, which resulted in $N_{Al} = 76$.

$$N_{Al} = 115.2(a_0 - 24.191) \quad (9)$$

Guisnet and Ramoa suggest Equation (10) for the calculation of the Si/Al ratio, knowing that the total number of silicon and aluminum atoms that can form the unit cell is 192 (Guisnet and Ramoa, 2006).

$$\left(\frac{Si}{Al}\right) = \frac{192 - N_{Al}}{N_{Al}} \quad (10)$$

Depending on the size of the unit cell, the ratio was: Si/Al = 1.52. This result is good because if we compare the chemical formula of the standard used (2Na-2Al-3.3Si-10.6O-7H₂O) it has a Si/Al ratio = 1.65, a value that is similar to the one obtained with Equation (9) (Si/Al = 1.52), besides that it remains above the value 1.5; necessary condition to say that the zeolite synthesized is of Y type.

3.3 Ion exchange modification of synthesized faujasite-type zeolite.

3.2.3 Modification of zeolite with ammonium cation (NH₄⁺)

Los resultados de la cuantificación del ion NH₄⁺ antes y después del proceso de intercambio iónico, analizado mediante un análisis de espectrofotometría en un equipo HACH se presentan en la Tabla 3.

The best result was for a contact time of 8 h, in the study a migration value of the cation to the zeolite of 59.8 mg per gram of zeolite was obtained. It was also observed that for a time of 24 h,

the presence of the ion in the solution increased, this would be due to the fact that according to Equation (2), the ion exchange process is reversible and there would exist a

Table 2. Parameters used in the unit cell calculation.

2θ	h	k	l	λ (Å)	d_{hkl}	a₀ (Å)	a₀ promedio (Å)
23,70	5	3	3	1,54	3,74	24,58	
26,90	6	4	2	1,54	3,31	24,77	24,85
30,70	5	5	5	1,54	2,90	25,19	

desorption of the ions previously adsorbed by the zeolitic structure.

The influence of the solution-zeolite ratio on the ion exchange modification process was analyzed, the results are shown in Table 4, which were obtained by quantifying the ammonium ion present in the contact solution.

Based on the parameters established for this study, an ion exchange capacity of 59.8 mg NH₄⁺ per gram of zeolite was obtained. It was also observed that the adsorption capacity does not increase considerably as the presence of ammonium ions in the solution increases. Experimental results from related research, have reported adsorption values between 4 and 80 mg.g⁻¹ for FAU-type zeolites, so what was obtained in this study is within experimental ranges (Kučić, et al., 2012; Abdullaha and Hussin, 2016; Montégut, et al., 2015).

The adsorption of ammonium ion was fitted to the Freundlich isotherm (R² = 0.97), the value of n was 4.54 and the Freundlich constant was K_f = 7.09 mg.g⁻¹. The result of n being greater than 1, implies that the experimental adsorption conditions were favorable, similar values of n in ion exchange processes with moderate temperature, was obtained in related research (Kučić, et al., 2012).

The Freundlich constant presented a high value in the results, indicating strong attraction between adsorbent and adsorbate, this due to the affinity of ammonium towards zeolites. The presence of the sodium ion in the ammonium nitrate solution post modification, as a consequence of being

Table 3. Results of ammonium ion analysis for different contact times.

Time (h)	Volume (cm³)	[NH₄⁺] mg.L⁻¹	NH₄⁺ (mg)	Removal NH₄⁺ /zeolita (mg.g⁻¹)
0	20	18043,0	360,8	0,00
4	20	17741,5	345,9	14,9

8	20	15595,3	300,9	59,8
24	20	17200,0	325,0	35,7

*(T=60°C, [1M], 1g zeolite)

Table 4. Results of ammonium ion analysis for different solution/zeolite ratios.

cm ³ .g ⁻¹	Ammonium concentration in solution (mg.L ⁻¹)	NH ₄ ⁺ removed per gram of zeolite (mg.g ⁻¹)
10	13315,2	57,9
15	15061,6	59,7
20	15595,3	59,8

*(T=60°C, t=8h, [1M], 1g zeolite)

displaced from the zeolitic structure was also quantified by atomic absorption analysis. In order to make a comparative study, the test was performed using 1 g of zeolite at a ratio of 20 cm³.g⁻¹.

The experimental data showed 0.0017 moles of Na⁺ removed from the zeolite while the aluminosilicate adsorbed 0.0033 moles of NH₄⁺. So the zeolite adsorbed more moles NH₄⁺ than moles of Na⁺ ion this because the adsorbed ions, one part was to compensate the outgoing sodium ions and another part must have been adsorbed in the zeolite pores.

The diffractogram of the modified zeolite, subsequently calcined at 400 °C, showed that its crystalline structure was not altered. Likewise, the FTIR analysis shows the characteristic bands for faujasite-type zeolites, according to the structural tetrahedra.

3.2.2 Modification of zeolite with lanthanum cation (La³⁺)

The introduction of rare earths to Y-type zeolites has allowed this material to be used in catalytic processes, constituting the active component in the catalyst of the fluidized catalytic cracking process (Gaare and Akporiaye, 1997).

In the results of the analysis of the contact solution by mass spectrometry in an ICP equipment, adsorption of 15.6 mg.g⁻¹, 32.6 mg.g⁻¹ and 38.0 mg.g⁻¹ were obtained for times of 4, 8 and 24 h respectively. Thus, at a time of 24 h, a higher ion exchange was obtained. This is explained since at the beginning the adsorbed lanthanum cation is present in hydrated form La(H₂O)₃⁺ being located in the super-box, however as the process performed is 80 °C, the lanthanum cation undergoes a dehydration/dehydroxylation process, decreasing the atomic radius of the molecule and migrating towards smaller cavities within the zeolitic structure (Gaare, et al, 1997). (Gaare, et al, 1997).

The modified faujasite and subsequently calcined at 500 °C for 6 h, was sent to XRD analysis, the same that by comparison of diffractograms, it was observed the displacement of the peak $2\theta = 11.86^\circ$ towards the position $2\theta = 12.3^\circ$, corresponding to X-type structures.

The introduction of the lanthanum cation in the zeolite structure, can cause levels of loss of the initial zeolitic structure, this due to the strong electronegativity of lanthanum with respect to other cations (Schüßler, 2013), as observed in Figure 5.

3.2.3 FTIR analysis

Figure 6 shows the FTIR spectra obtained for the unmodified synthesized NaY zeolite (blue) and the zeolites modified with the ammonium (red) and lanthanum (black) cations, respectively. The spectral region of study was defined in the range of 4 000 and 400 cm^{-1} , the 464 cm^{-1} band corresponded to internal vibrations of the TO (T = Si, Al) bonds, the same that is present in all three spectra. The 466 cm^{-1} peak indicated the presence of the supercage in the structure, which is formed by rings of 12 atoms. This band indicated that both the unmodified zeolite and the modified zeolites maintain the structure of a Y-type zeolite (Gonghu, 2005).

The bands corresponding to peaks 760 and 1 000 cm^{-1} are associated with TO4 tetrahedra, the same that in the modified zeolites were observed changes in the width of the bands, this due to the introduction of cations by ion exchange (NH_4 and La^{3+}) (Peter and Indrea, 2012).

It is notorious that only in the modified zeolites the bands 1 384 and 1 400 cm^{-1} were observed, the same that correspond to vibrations of OH bonds, created by removal of the Na^+ cation, also the spectrum referred to the zeolite modified with ammonium, presents a double peak in the band 1 403 cm^{-1} , this is characteristic in zeolites that have been modified with ammonium, due to the fact that there is still presence of H-N bonds (Perra, et al. 2014; Gonghu, 2005). All spectra presented the peak 1 639 cm^{-1} , the same peak that corresponds to water molecules retained in the zeolite cavities (Petit and Rondon, 2013).

The bands located in the region 3 444 - 3 465 cm^{-1} corresponded to vibrations of OH bonds, attributed to water molecules or ion exchange processes, comparing this peak between the three spectra, a change in the areas is observed, which shows a variation of the OH vibrations corresponding to the modified zeolites (Akdenis, 2000). Some experimental investigations relate the location of this band to Lewis acid sites (Fioravanti, 2012).

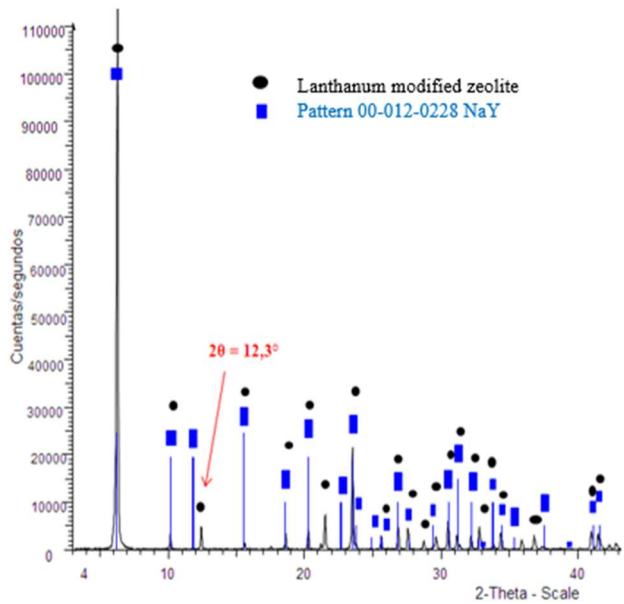


Figure 5. Diffractogram of lanthanum-modified zeolite compared to the standard ICDD-PDF# 00-012-0228

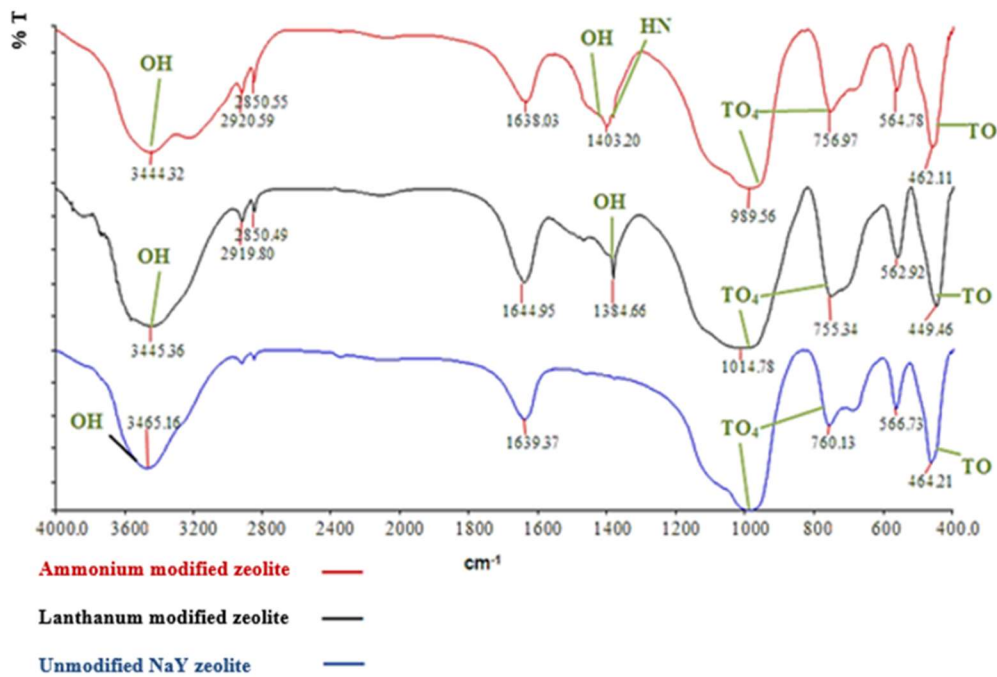


Figure 6. FTIR spectra of unmodified zeolite and zeolites modified with ammonium and lanthanum, respectively.

4. CONCLUSIONS

A zeolite was obtained with the presence of micropores with diameters of 11.76 Å and a surface area for the zeolite of 874.5 m².g⁻¹, these values are within the range for faujasites oriented to catalytic activities.

According to the pattern to which the synthesized zeolite was adjusted, the chemical formula is 2Na-2Al-3.3Si-10.6O-7H₂O, being the Si/Al ratio = 1.6; which implies that it is a Y-type faujasite.

For the conditions posed in this process the seed gel had a SiO₂/Al₂O₃ = 12.26 ratio while the structural gel SiO₂/Al₂O₃ = 10.90, however it was not possible to obtain a Na-FAU type structure for theoretical SiO₂/Al₂O₃ ratios > 13.

The crystallization temperature of the seed gel and structural gel were sensitive parameters to obtain a Y-type zeolite, the expected results were not obtained at crystallization temperatures above 110 °C. For this process, crystallizing the solutions at temperatures between 80 and 90 °C allowed obtaining the Y-type zeolite.

The zeolite obtained in this study had an ammonium ion absorption capacity of 59.8 mg.g⁻¹ for the best conditions (8 h and 20 cm³.g⁻¹) and for the lanthanum cation it absorbed 38 mg.g⁻¹ at optimum conditions (24 h, 50 cm³.g⁻¹).

The FTIR spectra showed bands related to TO₄ (T = Si, Al) clusters that form the super box typical of a faujasite, this peak was located at 466 cm⁻¹. Similarly, in the spectra of the modified zeolites, an increase in the area of the bands corresponding to 760 and 1 000 cm⁻¹ was evidenced, due to the introduction of cations by ion exchange. The presence of peaks in the 3 444 - 3 465 cm⁻¹ zone indicates the possibility of having a zeolite with Lewis acid sites.

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