**Ion Beam Analysis of zeolites type Li-ABW synthesized by hydrothermal method**


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This work reports a method to synthesize and characterize Li-ABW zeolites by a hydrothermal method. These materials are good candidates for CO$_2$ capture because of the high reactivity between the Li$^+$ with CO$_2$ to form Li$_2$CO$_3$. We performed an elemental profile concentration using Ion Beam Analysis (IBA). The elastic backscattered (EBS) proton energy spectra from the Al, Si, O and Li nuclei, in combination with the α’s particles from the $^7$Li (p, α)$^4$He Nuclear Reaction (NR) energy spectra, were employed for this task. X-Ray diffraction was also applied to determine the crystalline structure.

Keywords: Natural zeolites; RBS; NRA; spectroscopy.

El objetivo de este trabajo fue sintetizar y caracterizar zeolitas Li-ABW. Estos materiales son buenos candidatos para capturar CO$_2$ por la alta reactividad del Li con el CO$_2$ para formar Li$_2$CO$_3$, pero su uso está todavía en desarrollo. La caracterización se hizo determinando la concentración elemental, para lo cual se empleó análisis con haces de iones (IBA, por sus siglas en inglés) y la identificación de la fase cristalina se determinó mediante Análisis por difracción de Rayos-X.

Descriptores: Zeolitas naturales; RBS; NRA; espectroscopía.

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**1. Introduction**

Zeolites are crystalline aluminosilicates hydrated containing pores and cavities of molecular dimensions, their structures are formed by regular and uniform channels and cavities (ca. 3-15 Å), creating a nanoscale framework [1]. The channels are formed by the link of the 4, 5, 6-member rings of SiO$_4^{1-}$ or AlO$_4^{1-}$ tetrahedral. These cavities can be filled with water or other guest molecules. The general chemical formula of a zeolitic crystallographic unit cell is $M_{x/n}Al_xSi_yO_{2(x+y)}w$ $H_2O$ [1,2], where M is an exchangeable cation (i.e., I or II Groups) with valence n; x and y represent the number of Al and Si atoms, respectively; w is the number of water molecules. Other main features of the zeolitic materials are their pore size and their framework’s chemical composition, according to Al/Si ratio, giving them distinctive properties and selective interaction with adsorbed molecules [3]. These exceptional properties have led to numerous technical applications as bulk powder form (catalysts, adsorbents and ion exchangers) [1,3,4]. So that, the synthesis of new microporous frameworks and the manipulation of known zeolite structural types are important first steps in expanding the catalog of selective catalysts and materials for separation processes [4]. It is well known that zeolites are good ion-exchangers, which is the reason why the metal-exchanged zeolites are so much intensively studied experimentally and theoretically due to their interesting adsorption properties and catalytic activity. The knowledge of the structure, environment, and distribution of adsorption and active sites in zeolites is critical for a proper understanding of the interaction between the zeolite and the probe molecule [5]. The structure and coordination of extra framework cations in zeolites can be determined by X-ray and neutron-diffraction analysis [2], Nuclear magnetic resonance (NMR) spectroscopy is also an integral tool and DFT/MM calculations in the structural characterization [5], Mossbauer spectroscopy [6], etc.

On the other hand, low-silica zeolites with Al/Si ratio of 1:1, such as zeolite A, zeolite P and zeolite X, exhibit the highest ion exchange capacity. These zeolites have important industrial applications, being used as adsorbents or substitute for sodium tri-polyphosphate (STPP), the traditional water-softening agent in detergents [1,3]. Also aluminosilicate ceramics can be synthesized using low-silica zeolites as a precursor [5].

In this work a low-silica zeolite with lithium was synthesized using the hydrothermal method. The obtained zeolitic phase is called Li-ABW and will be applied to sorption CO$_2$
and others gases, but mainly CO$_2$ capture due to the high reactivity between the Li$^+$ with CO$_2$ to form Li$_2$CO$_3$ as occurred with other materials [7].

Zeolite Li-ABW (LiAlSiO$_4$:H$_2$O) is a synthetic low silica zeolite, which possesses the ABW framework topology, due to, it was first synthesized by Barrer and White in 1951 [1]. The framework structure has been studied by different techniques, such as, X-ray powder diffraction by different authors [2,8,9]. Neutron powder diffraction was used by Norby [3] to identify the lithium and hydrogen positions into framework. According to framework studies [8,9], the ABW zeolite framework is formed by 4-, 6-, and 8-rings of TO$_4$-tetrahedra, and as a comment the zeolite Li-ABW shares a set of features with the natural zeolite called bikitaite Li[AlSi$_2$O$_6$] H$_2$O [10]. By the other hand, there are several methods for lithium analysis in solids: laser induced breakdown spectroscopy, atomic absorption, etc. Ion beam analysis (IBA) is an attractive technique for light elements such as Li, Be, B, etc.; however quantitative analysis is not an easy task. High energy heavy ion analysis is the best suited IBA method [11]. Particle induced gamma-ray emission (PIGE) technique with low energies accelerators has been frequently used for the quantification of Li with the help of the $^7$Li(p, $\gamma$)$^8$Be$^*$ resonance [12]. In this work, the elastic backscattered (EBS) proton energy spectra from the Al, Si, O and Li nuclei with a combination of the $\alpha$’s particles from the $^7$Li(p, $\alpha$)$^4$He Nuclear Reaction (NR) energy spectra were used to analyze the samples.

2. Experimental Details

2.1. Zeolites synthesis

The precursor gels were prepared using sodium hydroxide (LiOH, Aldrich), distilled water and Tetramethylammonium Hydroxide (TMAOH, Aldrich) as Structure Directing Agent (SDA). The silica source was either colloidal silica (Ludox AS-40, Aldrich) or aluminum isopropoxide (Al[(CH$_3$)$_2$CHO]$_3$, Aldrich). The gel composition (molar ratio) of each of the prepared gels is shown in Table I. The preparation conditions for all zeolites are also described in the table.

The precursor gel was made on a polypropylene (PP) bottle on two stages: a) first, the source of LiOH and TMAOH (ZY samples only, the ZA samples do not contain SDA) were dissolved in distilled water (solution one) under stirring; and b) the second solution system contain silica source, aluminum source and distilled water under vigorous stirring to avoid the formation of the viscous suspension. Then, the solution one was slowly added to solution two, under vigorous stirring. The final suspension was stirred during 7 days.

The last stage is called aging time and is necessary to complete the synthesis reaction. The next step is the zeolite crystallization, where an aliquot of suspension was transferred to a Teflon-lined stainless steel autoclave with a volume of 50 cm$^3$. The zeolites were crystallized hydrothermally in the temperature range from 100 to 150°C. The synthesis time was variable between 24 h and 96 h under static conditions in a convection oven. The obtained zeolite powder was rinsed with distilled water 3 times to remove the excess of template occluded in the zeolites. Finally the samples were dried into an oven preheated at 100°C during 6 hours. The zeolites obtained were characterized by X-ray diffraction, using Cu Kα radiation, with a step size of 0.02° per second from 5° to 50° on the 2 theta scale.

2.2. IBA of zeolites

Ion beam analysis was carried out at the Instituto Nacional de Investigaciones Nucleares (ININ) tandem accelerator laboratory. A 1800 keV proton beam was used to bombard pellets (5 mm diameter and 1 mm thick) prepared by compression of the fine zeolite powder. Two surface barrier detectors (100 μm and 1500 μm thickness) equipped with standard electronics, were placed at $\theta_1 = 150^\circ$, $\theta_2 = 165^\circ$, respectively were used to measure the EBS low energy protons and the higher energies $\alpha$’s particles from the $^7$Li(p, $\alpha$)$^4$He NR. In order to register in the same spectrum EBS protons and high energy $\alpha$ particles, we did not use any absorbing foil in front of the detectors.
3. Results and discussion

Figures 1a and 1b show the XRD patterns of two zeolites samples: ZA02 y ZY01, respectively. According to literature [8,9], the XRD analyses indicate that the crystalline phase corresponds to Li-ABW. The difference between both samples is the presence of SDA. On the one hand, the samples synthesized at 100°C (not shown) did not form the phase corresponding to Li-ABW. There are differences in these samples observed in the Table I, the sample ZA02 did not contain SDA but the synthesis temperature (120°C) is higher than the samples that did not form the Li-ABW phase. The sample ZY01 has the highest synthesis temperature but has lower time of synthesis than the sample ZA02. Then according to these results we can say that the most important parameters in zeolite synthesis are the synthesis time and the temperature time for the sample ZA02, and in the case of sample ZY01 the presence of SDA is very important to reduce the synthesis time. However, one important result in this work is that it is possible to prepare Li-ABW in presence or in absence of the SDA.

Figures 2 and 3 show the experimental (dots) and simulated (solid lines) spectra for the ZA02 and ZY01 samples, respectively, bombarded with 1800 keV proton beam. Each spectrum has been divided in two parts: a) a low energy region, that corresponds to the energies of the elastically backscattered (EBS) protons form the zeolite nuclei, and b) a high energy region (NR), that corresponds to the energies of the α particles from \( ^7\text{Li}(p,\alpha)^4\text{He} \). The EBS and NR regions in the spectrum are totally separated, since the \( ^7\text{Li}(p,\alpha)^4\text{He} \) NR has a large positive “Q-value” (14.470 MeV). Kinematic calculations show that α particles from the sample’s surface has an energy of 7740 keV, compared to 1580 keV for EBS protons from the Si nuclei. The solid line in the spectrum represents the SIMNRA [13] simulation of the EBS spectrum from the Si, Al, O and Li nuclei. Non-Rutherford cross sections for the EBS protons on Li, O, Al and Si nuclei obtained from the Ion Beam Analysis Nuclear Data (IBANDL) was used for the spectra analysis. It may be observed in the spectrum that Li EBS counting yield contribution to the spectrum is small and masked by the larger number of events from proton scattering of heavier elements in a larger sample depth. This is due to the small proton Li cross sections, compared to the other nuclei in the sample. If the SIMNRA simulation is only performed to the EBS region of the spectrum it will give ambiguous Li concentrations. Lithium contribution to the EBS proton spectrum is so small that one acceptable simulation of the EBS spectrum is without Li. The simultaneous SIMNRA simulation of the EBS and the \( ^7\text{Li}(p,\alpha)^4\text{He} \) NR regions was used to eliminate the Li ambiguities in the analysis.
Figure 3. Experimental spectrum (dots) of a zeolite (ZY1) bombarded with 1800 keV proton beam. The particle detector was set at 150°. The solid lines represent the spectrum SIMNRA simulation. The partial contributions of Si, Al, O, C and Li to the simulation are also shown. Left side corresponds to the EBS region of the spectrum, while right side shows the ⁷Li(p,α)⁴He Nuclear Reaction.

The low α counting yield is due because ⁷Li(p,α)⁴He NR has a small cross section compared to the EBS for Si, Al, O and C nuclei. However, the α spectrum is background free because there are not other particles interfering in that energy region.

SRIM version 2008.03 stopping powers were used to estimate the sample depth probed as 12.4 µm by our proton beam. We used a uniform concentration with depth of all the constituent elements for the SIMNRA simulation for the ZA01, ZA02 and ZA03 samples. However, for the ZY01 and ZY02 samples a higher Li concentration near the surface was used for the SIMNRA simulation. For example, the Li concentration for sample ZY01 was 28 at.% for the first 3000×10¹⁵ atoms/cm² layers and this concentration falls down to 22 at.% after this sample depth.

Table II summarizes the elemental concentrations of 5 zeolites with the IBA method. It may be observed that the Li concentration was fairly constant in the 17.2 – 22.0 at.% range, in spite of the different parameters in the zeolites preparation. For carbon, the concentrations are relatively high in the 5.0-20.0 at.% range.

4. Conclusions

The IBA method was based in the simultaneous simulation of the EBS and NR regions of the spectra using SIMNRA. The proton EBS cross sections of Si, Al, O and Li and the ⁷Li(p,α)α NR cross sections, available in the IBANDL web site, have been used for the simulation. The accuracy of the atomic concentrations measured depends of how well the EBS and NR cross sections are known. The good simulation of standard materials with known composition (LiOH, Li₄SiO₄) illustrates the usefulness of the method when using known IBANDL cross sections. The Li concentration determination of the samples analyzed can provided a useful feedback to evaluate sample production parameters, especially if this zeolite can be used for CO₂ retention.

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