X-RAY Spectrometry

Received: 2 January 2009 Revised: 13 June 2009 Accepted: 24 July 2009

(www.interscience.com) DOI 10.1002/xrs.1213

Comparison between XRF and EPMA applied to study the ionic exchange in zeolites

V. Galván,[a] M. Torres Deluigi,[b*] L. Mentasty,[c] I. De Vito[c] and J. A. Riveros[a]

Zeolites are crystalline aluminosilicates consisting of SiO_4 and AlO_4 tetrahedral as primary units. One peculiar characteristic of zeolites is the ion exchange capacity defined as the capacity to locate specific cations in the framework of zeolites; it depends on the chemical composition and varies with the structure of the zeolite and with the cation nature.

This work studies the exchange of the Na^+ monovalent cation of 5A and 13X synthetic zeolites by the Ca^{2+} bivalent cation present in a $CaCl_2$ solution. X-ray fluorescence (XRF) and electron probe microanalysis (EPMA) techniques were used to determine the cation exchange capacity (CEC). The efficiencies of the two X-ray detectors were compared and the minimum detection limits of the zeolite elements were calculated.

Although both techniques differ in the sample excitation mode, the results obtained were compatible. The results showed that the CEC was higher for the 5A zeolite, in agreement with its lower SiO_2/Al_2O_3 ratio and its greater BET area. It was also found that the amount of Na^+ ions exchanged by Ca^{2+} ions was in complete agreement with the corresponding molar balance. The determination of the CEC using X-ray spectroscopy techniques can be considered a novelty as XRF and EPMA techniques permit to analyze the sample directly.

Introduction

The fundamental building units in natural and synthetic zeolites are tetrahedral SiO_4 and AlO_4. Zeolites are tectosilicates of the alkaline and alkaline-earth metals, i.e. they are formed by linking these tetrahedrals together to give three-dimensional anionic networks in which each oxygen of a given tetrahedron is shared between this tetrahedron and one of four others. Thus, there is no unshared oxygen in this framework of interconnecting pore and channel structures. This fact means that in zeolites $(Al + Si):O = 1:2$. For every Si^{IV} that is replaced in the framework by Al^{III}, a negative charge is created, which is neutralized by an electrochemical equivalent cation.[1]

Four or more TO_4 primary units connected to one another constitute secondary units or building blocks[2] that form rings with as many edges as TO_4 tetrahedra that are connected. The way TO_4 units connect to one another is the criterion used to classify and designate zeolites,[3] irrespective of the chemical composition or the specific symmetry of the crystalline solid.[4]

One of the most salient building blocks is probably sodalite,[5] which is the parent structure for synthetic zeolites of the A type as well as natural zeolite faujasite (the crystalline structure of synthetic zeolites of the X and Y types corresponds to faujasite). A-type zeolites are composed of sodalites (or alpha cages) joined by a double 4-ring (D4R). If sodalites were joined by a double 6-ring (D6R), faujasite or X zeolites would be formed by almost spherical supercages, with entirely different topology, cavity size, channel size and number, and different molecular sieving properties.[6]

One peculiar characteristic of zeolites is the ion exchange capacity defined as the capacity to locate specific cations in the framework of zeolites.[7] The cation exchange capacity (CEC) of a zeolite depends on the chemical composition and varies with the structure of the zeolite and with the cation nature. The CEC depends on the number of exchangeable positions, and these values depend on the SiO_2/Al_2O_3 ratio as a high CEC corresponds to zeolites with a low SiO_2/Al_2O_3 ratio.[8] The literature on the ion exchange properties of zeolites is extensive.[9–11]

X-ray fluorescence (XRF) analysis has been applied to carry out elemental analyses to study the electronic structure of materials and also to characterize different synthetic zeolites.[12–14] In this work, the CEC of 5A and 13X synthetic zeolites has been studied by determining the exchange of Ca^{2+} by Na^+ using XRF and EPMA. The main difference between these spectroscopic techniques is the sample excitation mode and size (photons in XRF and electrons in EPMA)

Experimental

The 5A zeolite with $SiO_2/Al_2O_3 = 2$ and 13X zeolite with $SiO_2/Al_2O_3 = 2.46$ were commercial zeolites in pellet purchased from Fluka AG, Switzerland. The compositions of the unitary cells of the 5A and 13X zeolites were as follows: $Ca_{4,5}Na_3[(AlO_2)_{12}(SiO_2)_{12}] \times H_2O$ and $Na_{86}[(AlO_2)_{86}(SiO_2)_{106}] \times H_2O$ respectively.

The purity and crystallinity of the materials selected for this work was proved by X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR), revealing good crystallinity. BET surface areas were determined by N_2 adsorption in a Micromeritics - Accusorb 2100-E equipment, obtaining values of 394 and 331 m^2/g for the 5A and 13X zeolite respectively.

---

[*] Correspondence to: M. Torres Deluigi, Departamento de Física, Facultad de Ciencias Físico, Matemáticas y Naturales, Universidad Nacional de San Lui, Ejército de los Andes 950, 5700 San Luis, Argentina.
E-mail: charo@unsl.edu.ar

[a] Facultad de Matemática, Astronomía y Física, Universidad Nacional de Córdoba, Medina Allende y Haya de la Torre, 5000 Córdoba, Argentina

[b] Departamento de Física, Facultad de Ciencias Físico, Matemáticas y Naturales, Universidad Nacional de San Luis, Ejército de los Andes 950, 5700 San Luis, Argentina

[c] Facultad de Química, Bioquímica y Farmacia, Universidad Nacional de San Luis, Chacabuco 917, 5700 San Luis, Argentina

Ionic exchange

The zeolites selected were previously dried in an oven at 90 °C for 12 h to eliminate the adsorbed water. The ionic exchange was carried out in a discontinuous reactor at an operational temperature of 40 °C with a $CaCl_2$ solution (0.1 N). Samples were extracted at different time intervals (between 1 and 240 min), washed many times with bidistilled water to take away the solution residue and dried in an oven. They were then ground at a grain uniform size and compacted in a pill-like shape in a boric acid substrate.

Standard samples of zeolites without exchange were also prepared to perform the quantitative analysis with EPMA and XRF. These standards exhibit a known chemical composition, which, in addition, is very similar to the exchanged zeolites' composition.

X-ray fluorescence-energy dispersive spectrometry

The spectra of the selected zeolites were obtained using a noncommercial energy dispersive spectrometer (EDS), which has a Canberra solid-state detector of Si(Li) with a 10 mm^2 area and a 12-μm beryllium window. The detector resolution, determined by the full-width half-maximum (FWHM) of the Mn$K\alpha$ line, is of 180 eV. A tube with a Cr cathode was used as the X-ray source, and irradiation was carried out with a conventional geometry of $\pi/4$. In order to guarantee the adequate excitation of all the sample elements and a low dead time, the following working conditions were selected: 20 kV and 5 mA. The acquisition time was of 1800 s with a dead time below 3%.

The quantification of the amount of Ca^{2+} exchanged in both types of zeolites was carried out with the AXIL program,[15] which uses the method of 'fundamental parameters' developed by He and Van Espen.[16] It was assumed that the hydrogen and oxygen atomic concentrations remained constant in all the exchanged samples, and they remained equal to the standard sample concentrations. Prior to the quantification, all the element intensities were normalized in relation to the intensity of the SiK_α line, as the concentration of silicon did not change in the exchange process, because this element is part of TO_4 primary units of the zeolites and, therefore, Si^{IV} is not an extraframework cation that can be replaced during the ion exchange. Differences due to changes in the sample thickness and lack of homogeneity were thus corrected.

Electron probe microanalysis – energy dispersive spectrometer

The EDS (EDAX-Genesis 2000) is attached to LEO 1450 VP microscope from the Laboratorio de Microscopía Electrónica y Microanálisis (LABMEM) of the Universidad Nacional de San Luis (UNSL) and has a resolution of 129 eV (Mn $K\alpha$). The spectra were obtained during 200 s, with 15 kV, 1 nA of specimen current and a take-off angle of 30°.

These spectra were also normalized in relation to the SiK_α line to correct the roughness sample and lack of homogeneity and geometric differences in the irradiation. Quantification was performed with the MULTI program,[17] which considers excitation with electrons and carries out the ZAF correction of the matrix effects.

Comparison of the efficiencies of X-ray detectors

As the detectors were Si(Li) crystals in EPMA and in XRF, the efficiency of both techniques, calculated using a linear combination of the exponential attenuation law, was compared (Fig. 1). Table 1 shows the parameters used. The detector used in EPMA permits to analyze light elements such as O and Na, whereas the efficiency of the detector used in XRF is extremely low for these elements.

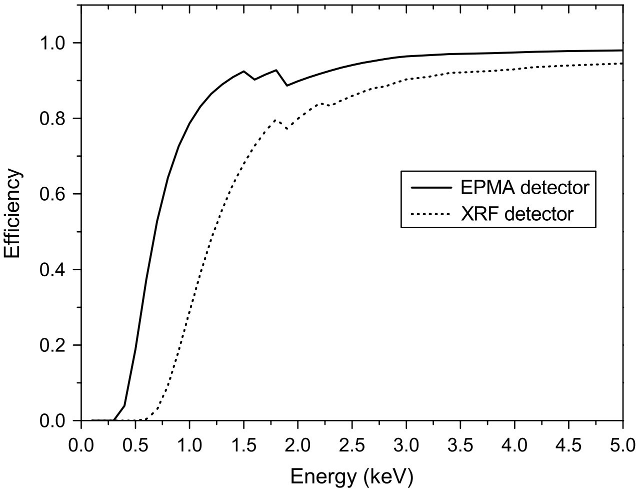

Figure 1. Efficiencies of the Si(Li) detectors used in EPMA (solid line) and XRF (dash dot line) as a function of the energy.

Table 1. Characteristics of the Si(Li) detectors used in XRF and EPMA

	Window		Metallic contact		Dead layer
Detector	Material	Thickness (cm)	Material	Thickness (cm)	Thickness (cm)
XRF	Beryllium	1.2×10^{-3}	Au	1×10^{-6}	10×10^{-6}
EPMA	Polymer	3×10^{-5}	Al	4×10^{-6}	8.5×10^{-6}

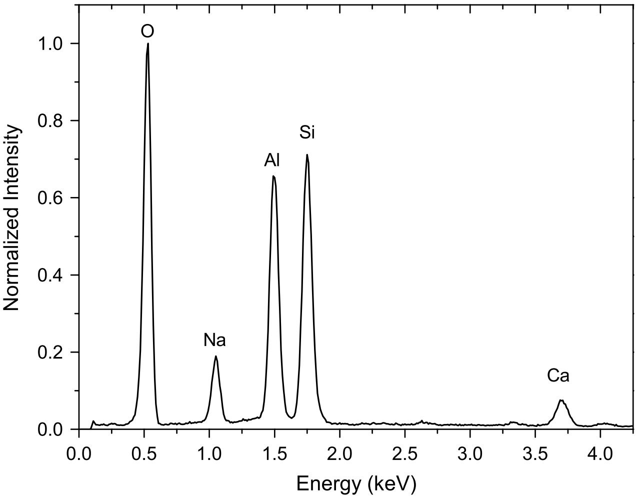

Figure 2. Spectra acquired with EPMA-EDS for the 13X zeolite after two exchange hours.

The different detectors' efficiencies were evident in all spectra measured. In particular, Fig. 2 and Fig. 3 show the spectra obtained with EPMA and XRF for the 13X zeolite after two exchange hours, respectively.

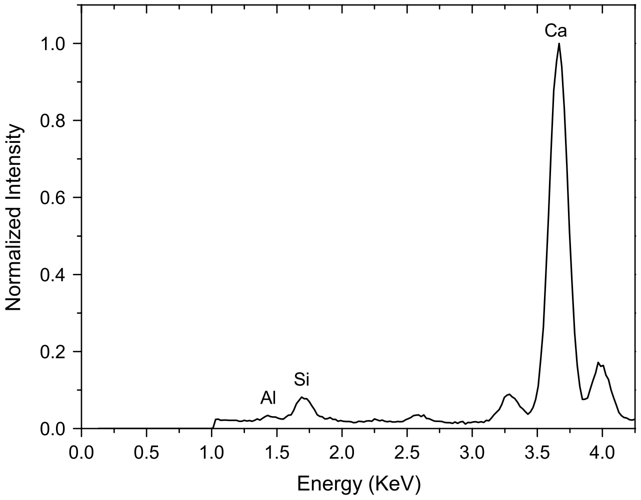

Figure 3. Spectra acquired with XRF-EDS for the 13X zeolite after two exchange hours.

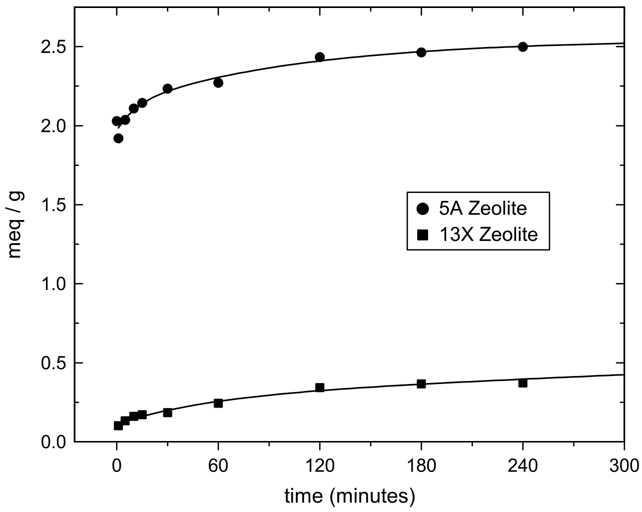

Figure 4. Ion exchange capacities (meq/g) of Ca^{2+} as a function of the exchange time determined by XRF in 5A and 13X zeolites.

Table 2. Minimum limit of detection (MLD) for the pattern of the 5A zeolite in EPMA and XRF

	MLD	
Elements	EPMA (ppm)	XRF (ppm)
O	260	Undetectable
Na	60	Undetectable
Al	80	18 000
Si	90	560
Ca	90	20

Comparison of the minimum limits of detection

The minimum limits of detection (MLD) for the zeolites elements are shown in Table 2.

Considering the detectors' efficiencies and the MLD, Ca and Na were quantified using measurements carried out with XRF and EPMA, respectively. This procedure also helped corroborate that both methods produce totally compatible results.

Analysis of the Results

The percent concentrations by weight of Ca were calculated for both zeolites using the spectra measured with XRF. The CEC was then obtained as the quotient between the concentration of Ca (C_{Ca}) and the unitary cell weight. Figure 4 shows the curves obtained, and it can be observed that the meq/g of Ca^{2+} values exchanged in the 5A zeolite are higher than those in the 13X zeolite for all the exchange time.

Comparison of XRF and electron probe microanalysis

The molar balance of Ca^{2+} concentration in the unitary cell of 5A zeolite as a function of the time can be expressed as the initial concentration plus the exchanged concentration:

$$Ca^{2+}(t) = 4,5 + Ca^{2+}{}_{exch}(t) \tag{1}$$

Ca^{2+} and Na^{+} are related according to the expression:

$$Ca^{2+}{}_{exch}(t) = 1/2(3 - Na^{+}{}_{exch}(t)) \tag{2}$$

where 1/2 indicates the exchange ratio of Na^{+} by Ca^{2+} and $(3 - Na^{+}{}_{exch}(t))$ is the concentration of Na^{+} in time t.

From expressions (1) and (2) we obtain:

$$Ca^{2+}(t) = 4,5 + 1/2(3 - Na^{+}{}_{exch}(t)) \tag{3}$$

then

$$Ca^{2+}(t) - 1/2(3 - Na^{+}{}_{exch}(t)) = 4,5 \tag{4}$$

The concentration of $Ca^{2+}(t)$ was determined by XRF, and the concentration of $Na^{+}(t)$ by EPMA.

Figure 5 proves experimentally that the calcium exchanged in the 5A zeolite replaces the sodium existing in the unitary cell. When comparing the concentrations of the exchanged ions, it can be observed that Ca^{2+} increases in a proportional relation to the decrease of Na^{+} (see Eqn (3)). The uncertainties were calculated and are included in the figure.

Figure 6 shows the difference between the concentrations of Ca^{2+} and Na^{+} exchanged in the 5A zeolite. This difference is a constant corresponding to the initial concentration of Ca^{2+}. The fitting of the experimental points yields a line whose ordinate on the origin coincides with this constant and has a slope of zero, which proves the molar balance experimentally (Eqn (4)).

Conclusions

In this work, the higher CEC of the 5A zeolite in relation to the 13X zeolite has been demonstrated. Besides, a greater exchange capacity of the 5A zeolite, which, as expected, was in agreement with its lower SiO_2/Al_2O_3 ratio and its larger BET area, has been corroborated using the XRF and EPMA techniques.

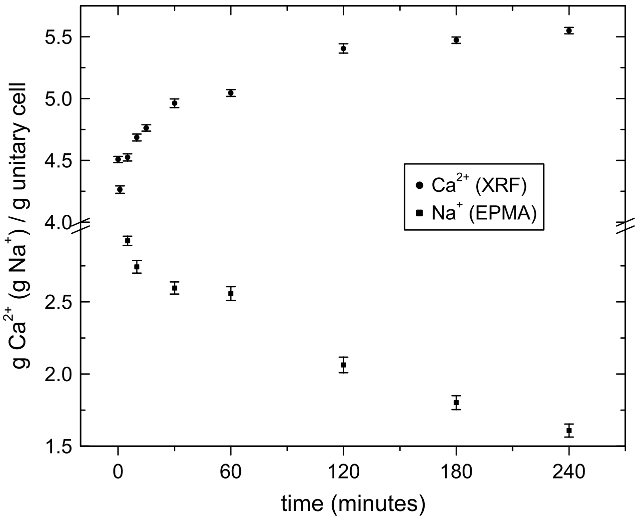

Figure 5. Na$^+$ grams (Ca^{2+} grams) per gram of unitary cell of 5A zeolite as a function of the exchange time. The errors bars correspond to the standard deviation in the concentration values of Ca and Na.

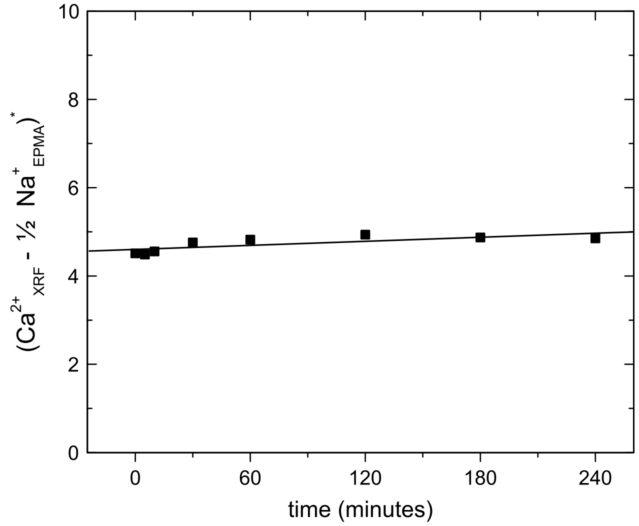

Figure 6. Difference in the concentrations of Ca2+ (XRF) and of Na+ (EPMA) as a function of the exchange time (*: Eqn (5)). The equation of the line fit to the experimental points is (4.54 ± 0.06) + (0.0015 ± 0.0005) *t*.

In general, owing to the different geometric conditions and the atomic parameters precisions, it is difficult to compare results obtained by different excitation techniques. However, the comparison between XRF and EPMA techniques carried out in this work demonstrates that compatible results can be obtained even when using spectrometers with different efficiencies.

The used techniques were found to be efficient in determining the percent concentrations by weight of the exchanged cations. It was experimentally proved that, in the 5A zeolite, during all the exchange time, calcium replaced sodium as the increase in Ca^{2+} (measured by XRF) was proportional to the decrease in Na$^+$ (measured by EPMA). This empirical result is in complete agreement with the corresponding molar balance.

Generally, the ionic exchange capacity is determined by quantifying the concentration of ions exchanged in the solution and applying conventional analytical techniques such as atomic absorption. In this work, the determination of the ionic exchange using X-ray spectroscopy techniques can be considered a novelty as XRF and EPMA techniques permit to analyze the sample directly. Besides, they exhibit other advantageous properties as they are not destructive, and require small sample amounts and a reduced total analysis time.

Acknowledgements

The authors wish to acknowledge Secretaria de Ciencia y Técnica from Universidad Nacional de Córdoba (UNC) and UNSL, Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET) and Agencia Nacional de Promoción Científica y Tecnológica (FONCYT) (PICT-BID) from Argentina for financial support.

References

[1] R. M. Barrer, *Zeolites and Clay Minerals as Sorbents and Molecular Sieves*, Academic Press: London, **1978**.
[2] W. M. Meier, D. H. Olson, *Adv. Chem. Ser.* **1970**, *101*, 155.
[3] R. M. Barrer, *Pure Appl. Chem.* **1979**, *51*, 1091.
[4] R. Navarrete-Casas, A. Navarrete-Guijosa, C. Valenzuela-Calahorro, J. D. López-González, A. García-Rodríguez, *J. Colloid Interface Sci.* **2007**, *306*, 345.
[5] D. F. Shriver, P. W. Atkins, *Inorganic Chemistry* (3rd edn), Oxford University Press: **1999**.
[6] R. A. Clifton, *Natural and Synthetic Zeolites*, Bureau of Mines Information Circular 9140, United States Department of the Interior, **1987**, pp. 1.
[7] O. Ursini, E. Lilla, R. Montanari, *J. Hazard. Mater.* **2006**, *137*, 1079.
[8] R. Szostak, *Molecular Sieves: Principles of Synthesis and Identification*, van Nostrand Reinhold: New York, **1989**.
[9] H. S. Sherry, in *The Ion Exchange Properties of Zeolites*, vol. 2, *Ion Exchange: A Series of Advances* (Ed: J. A. Marinsky), Marcel Dekker: New York, **1969**, pp. 89.
[10] D. W. Breck, *Zeolite Molecular Sieves*, John Wiley & Sons: New York, **1974**.
[11] R. P. Townsend, E. N. Coker, in *Ion Exchange in Zeolites*, vol. 137, *Introduction to Zeolite Science and Practice, Studies in Surface Science and Catalysis*, (Eds: H. Van Bekkum, P. A. Jacobs, E. M. Flanigen, J. C. Jansen), Elsevier: Amsterdam, **2001**, pp. 467.
[12] V. S. Somerset, L. F. Petrik, R. A. White, M. J. Klink, D. Key, E. Iwuoha, *Talanta* **2004**, *64*, 109.
[13] M. Adebajo, M. Long, R. Frost, *Spectrochim. Acta Part A* **2004**, *60*, 791.
[14] P. Wang, B. Shen, J. Gao, *Catal. Today* **2007**, *125*, 155.
[15] P. Van Espen, K. Janssens, J. Nobels, *Chemometr. Intell. Lab. Syst.* **1986**, *1*, 109.
[16] F. He, P. J. Van Espen, *Anal. Chem.* **1991**, *63*, 2237.
[17] J. Trincavelli, G. Castellano, *X-Ray Spectrom.* **1999**, *28*, 194.