Characterization of Natural and Modified Zeolites Using Ion Beam Analysis Techniques.

E. Andrade[a], C. Solis[a] , J. M. Aceves[b], R. Miranda[b], J. Cruz[a], M.F. Rocha[c] and E.P. Zavala[a]

[a]*Instituto de Física, Departamento de Física Experimental, Universidad Nacional Autónoma de México., Apdo. Postal 20-364, 01000, México.*
[b]*Facultad de Estudios Superiores Cuautitlan , Departamento de Química, Universidad Nacional Autónoma de México, C.P. 74540.*
[c] *Escuela Superior de Ingeniería Mecánica y Eléctrica, Instituto Politécnico Nacional, U.P. "Adolfo López Mateos", Zacatenco, Del. Gustavo A. Madero, Mexico D.F. 07738, Mexico.*

Abstract. Zeolites are very important materials in catalytic and industrial processes. Natural, modified and synthetic zeolites have a wide range of uses because of their good adsorption their ion exchange capacity and catalytic properties. Mexico is an import source of natural zeolites, however their utilization in the natural form is limited due to the presence of impurity trace metals. For example, metals such as vanadium and chromium inhibit the elimination of sulfur in hydrocarbons. Therefore it is important to know the whole composition of the zeolites. In this work, we report the elemental characterization of zeolites using different IBA techniques. A ^{3}He and ^{2}H beam were used to measure the major element concentrations (Si/Al, ,O, C) by RBS and NRA. PIXE and SEM-EDS were used to measure the total trace element content (V, Cr, Fe, Ni, Cu, Zn, Rb, Sr, Zr, Pb etc). XRD technique was also applied to study the zeolite structure.

Corresponding author:Tel. +52-55-5622-5055, fax: 52 555622-5046
E-mail address: andrade@fisica.unam.mx

1. Introduction

Zeolites are materials with a wide range of industrial applications [1]. The production of gasoline uses thousand of tons per year. Zeolites have also application in agriculture [2], aquaculture [3], solar energy storage, etc. The production of ecological detergent is another use of these materials. New uses of these solids are reported continuously.

Zeolites are a group of hydrated crystalline alumino-silicate minerals that may be obtained either from natural sources (certain volcanic rocks) or manufactured synthetically. There are, however, many natural zeolite materials with no synthetic counterpart and vice versa. Natural zeolites could be modified in order to improve the physical and chemical properties. A complete material

characterization is required, in order to explore the potential use of zeolites. In particular, detection of trace elements calls for analytical procedures able to provide high sensitivity, accuracy and reproducibility, and at the same time be practical and simple, so to allow processing high number of samples.

The main objective of this work is to determine most of the elemental concentration of natural and modified zeolites, applying a combination of Ion Beam Analysis (IBA) and Scanning Electron Microscopic coupled with Energy Dispersive X-ray (SEM-EDS) techniques. Trace and major element composition of these materials are reported. We also analyzed clay samples from the same place where the natural zeolites were collected.

2. Experimental

Natural zeolites and clays from the same place were collected from Tlaxcala and Oaxaca states in Mexico. All these materials were grounded and reduced to a fine powder in order to make pellets 1 cm in diameter and 3 mm thick. These pellets were irradiated with different particle beams.

We applied different IBA methods for the determination of the atomic composition of the samples, since a complete analysis is not possible with a single method. The sensitivity of the Rutherford backscattering (RBS) is good for the detection of heavy elements and is low for light elements. Nuclear Reaction Analysis (NRA) using a $^2H^+$ beam is often used to measure concentrations of medium light elements such as oxygen and carbon. Particle induced X-ray emission (PIXE) and SEM-EDS have a good sensitivity to measure trace elements. An X-ray Diffractometer (Phillips Model Krystalloflex 5000) was also used for structure measurements.

Pellets were bombarded with 3 different ion beams produced by the National Autonomous University of Mexico CN 5.5 MV Van de Graaff and the 9SDH-3 MV NEC pelletron accelerators [4]: I) A 2 MeV ^3He beam for RBS method, II) a 1.30 MeV deuterium beam for a combination of RBS/RNA method, III) an external 3 MeV proton beam for PIXE analysis, IV)) a SME-EDS operated with a 20 keV electron beam (JEOL model-5600LV).

For the RBS and NRA experiments a 500 μm thick surface barrier detector equipped with standard electronics set at $\theta = 165°$ was used to measure the particle energies produced by the sample bombarded. A not absorbing foil in front of the detector was used in order to measure, in the same spectrum, the low energy region corresponding to the elastically backscattered beam particles ($^2H+$ and $^3He^+$) and the high energy region corresponding to the particles produced by NR on O and C.

A cryogenic low energy germanium (LEG) detector was used in the PIXE experiments. A surface barrier detector set a $\theta = 176°$ (Cornell geometry), was used to simultaneously measure the backscattered (BS) proton energy spectrum with the PIXE spectra [5]. The BS spectrum was used to monitor the total beam charge for each measurement. An aluminum foil 38 μm thick was used in front of the LEG detector in order to absorb soft X-ray (with energies below Ca X-rays) to reduce pile-up pulses.

3. Results and discussion

Figure 1 shows a typical experimental energy spectrum (dots) of one of the zeolites sample (Z1) bombarded with a 2 MeV $^3He^+$ beam. The solid line represents the SIMNRA [6] simulation code used to obtain the elemental atomic concentrations. This method provides the major sample element concentrations (Si, Al and O). This analysis provide also the Fe, Ca/K and Mg concentrations, but the accuracy is poor due to the fact that these elements are in very low concentrations (a few % wt). Therefore, it is not the most appropriate technique to measure those elements.

Figure 2 shows a typical energy spectrum (dots) of the sample Z1 bombarded with a 1.30 MeV deuterium beam. Two regions can be observed in the spectrum: a) the high energy part, where the nuclear reaction (NR) yields from $^{12}C(d,p)^{13}C$, $^{16}O(d,p_1)^{17}O$ and $^{16}O(d,\alpha)^{12}C$ are indicated and b) the low energy (RBS region), due to $^2H^+$ backscattered on Si and O. A combination of RBS/NRA was applied to determine the O and C concentrations. The NR cross section for the $^{12}C(d,p)^{13}C$, $^{16}O(d,p_1)^{17}O$,$^{16}O(d,\alpha)^{12}C$ were obtained from the Ion Beam Analysis Nuclear Data Library web site (www-nds.iaea.org/iband) and they were used to obtain the O and C concentrations.

Figure 3 shows the experimental PIXE spectrum of the sample Z1 bombarded with an external 3 MeV proton beam. The trace element concentrations of the samples were deduced applying the GUPIX [7] software. The matrix elements concentration (SiO_2 and Al_2O_3) deduced from the RBS and the RBS/NRA method was used to determine the trace elements concentrations. This technique allow to measure the following elements: Ca, K, Ti, V, Cr, Mn, Fe, Zn, Sr, Rb, Zr and Pb.

Figure 4 shows the SEM-EDS X-ray energy spectrum of the sample Z1 irradiated with a 20 keV electron beam scanned in a 500 μm x 500 μm area. This method complements the PIXE measurements and allows measuring the concentration of low Z elements such as Si, Al, Mg, O and C. It may be observed in this spectrum the lack of sensitivity to measure trace elements heavier that Fe. PIXE and SEM-EDS measurements of K, Ca and Fe are in good agreement.

Figure 5 shows a XRD pattern of one of the zeolites. The spectrum reveals the presence of montmorillonite:$Al_{1.67}Mg_{.33}Si_4O_{10}(OH)_2Na_{0.33}(H2O)_3$ that constitute more that 50% of the sample. Other crystal phases identified are: quartz (SiO_2,), anorthite ($CaAl_2Si_2O_8$) calcite ($CaCO_3$) and albite ($NaAlSi3O$). Most of the elements measured with the IBA and SEM-EDS (except hydrogen that was not measured) are in the molecule compounds reported by the XRD.

Table 1 shows the comparison of the elemental concentrations of 7 samples measured with the combination of IBA and SEM-EDS. The samples M1, M2, M3 are natural zeolites. M4 (K10) and M5 (Taff) are natural modified zeolites, M6 and M7 are clay samples. The major element concentrations Si, Al and O reported were obtained with RBS. Carbon concentrations were obtained with RBS/NRA

measurements. The trace elements were measured with PIXE and SEM-EDS.

It may be observed in figures 1, 2, 3 and 4 that some elements can be detected with different techniques. For instance O can be measured by RBS, RBS/NRA and SEM-EDS techniques. The comparison of the O concentrations obtained with the RBS and the RBS/NRA methods were similar. The precision of the RBS/NRA method depends mainly on the knowledge of the d+ ^{16}O NR cross sections and they are considered well established. RBS is not a good technique to measure low O concentration. However, the good precision of the RBS method is because O is a major component of the samples (concentrations are $\geq$ 57% wt).

It is important to point out that O contents determined by SEM-EDS were about half of the concentration determined by the IBA method. This discrepancy may be due to the fact that the SEM-EDS software uses a wrong electron in O X-ray production cross sections to evaluate the O concentration.

The C concentrations in Table 1 were measured with the RBS/NRA method and they varied from 1.7 to 3.2 % wt. The precision for these measurements depends mainly in the ^{12}C(d,p)^{13}C NR cross sections, but they are considered well established.

Some differences in composition among studied samples can be observed in table 1. For instance, elements such as Rb and Zr are lower in clays relative to natural and modified zeolites. Vanadium is detected only in the modified zeolites. High levels of S were found in the modified zeolite M7(taff). This is not surprising if we consider that this zeolite is obtained by treating natural zeolites with mineral acids such as Sulfuric acid.
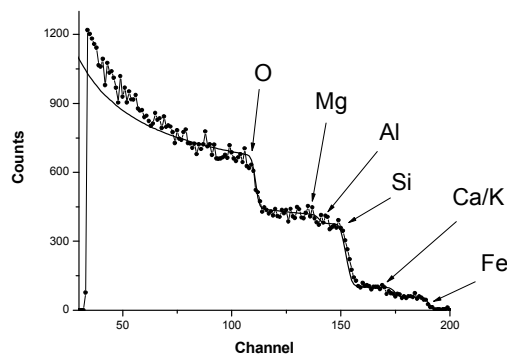

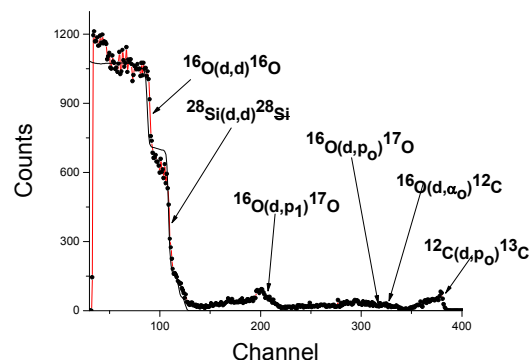
Figure 2. Experimental spectrum of 1.30 MeV deuterium beam on zeolite 1. The surface barrier detector was set a θ = 165º. The particle yields from the ^{12}C(d, p)^{13}C, ^{16}O(d,p1)^{17}O and ^{16}O(d, α)^{12}C nuclear reaction are indicated. The RBS energy region of the spectrum is also shown.
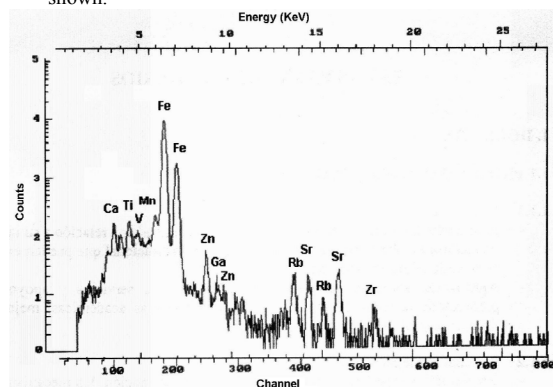

Figure 3 PIXE spectrum of the zeolite 1 obtained with an external 3 MeV proton beam. A cryogenic Ge(Li) X-ray detector was set a θ = 135º.

Figure 1. A typical RBS spectrum of a 2 MeV ^{3}He beam on zeolite 1 sample. The surface barrier detector was set a θ = 165º. The solid line represents the SIMNRA simulation code of the spectrum used to obtain the elemental atomic concentrations.
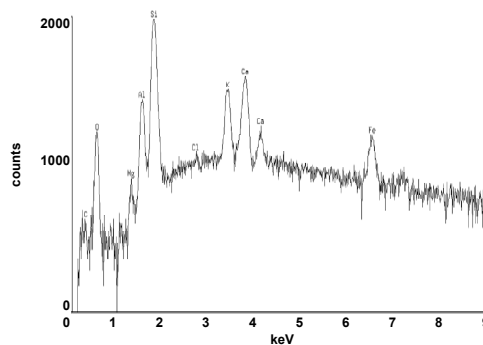

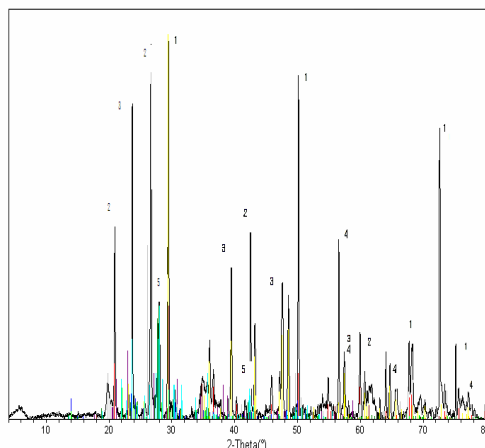Figure 4, SEM-EDS spectrum obtained with a 20 keV electron beam on the zeolite 1.

Figure 5. Diffraction pattern of zeolite 1.The most important minerals detected were: (1) Montmorillonite, (2) Quartz, (3) Anorthite, (4) Calcite, (5) Albite

TABLE 1. A summary of the sample element concentrations measured with a combination of the IBA and SEM-EDS methods. The trace elements are in µg/g and the C, O, Al and Si concentrations are in % wt. The samples M1, M2, M3 are natural zeolites. M4 (K10) and M5 (Taff) are natural modified zeolites. M6 and M7 are clay samples. The error in the determination of the elements concentrations was estimated 10 %.(nd means not detectable)

Z	M1	M2	M3	M4	M5	M6	M7
C (%)	2.2	3.2	3.2	3.0	1.7	3.2	3.1
O (%)	58.2	58.7	58.9	60.0	58.9	58.2	57.6
Mg(%)	0.34	0.38	0.16	0.26	0.42	nd	0.54
Al (%)	3.2	2.8	3.0	3.0	2.9	3.0	2.8
Si (%)	24.5	24.8	25.6	27.6	25.8	24.2	27.9
S (%)	0.059	0.36	0.13	nd	4.2	0.74	0.51
Cl (%)	nd	0.11	nd	nd	nd	nd	0.42
K	9904	12019	15609	3292	16642	1246	2288
Ca	7917	4011	5767	1463	8917	1806	6219
Ti	641	954	1189	2756	2772	172	477
V	52	83	19	89	289	83	88
Cr	nd	nd	nd	46	61	nd	nd
Mn	nd	68	308	36	270	17	0
Fe	7316	9065	15558	16891	34498	9858	10452
Co	41	47	21	0	36	35	0
Ni	nd	nd	nd	nd	20	21	nd
Cu	14	13	5	nd	14	27	12
Zn	51	51	88	33	85	88	91
Rb	38	19	197	67	162	nd	7
Sr	5100	405	238	46	450	167	318
Zr	162	101	413	440	158	62	68
Pb	nd	nd	nd	nd	30	nd	nd

4.-Conclusions

This work illustrates the advantage of using IBA over standard techniques to measure a wide range of elements in zeolite materials. IBA techniques are well established techniques that provide fast, precise and reproducible analytical procedures in order to get information on a whole range of elements that can not be easily obtained by conventional techniques. In particular the detection of trace elements is relevant on the selection of zeolites for potential use in industry. For instance, vanadium and chromium inhibit the elimination of hydrogen and sulfur in hydrocarbons. Some of the samples have trace elements such as Cr and Pb. It is well known that these elements can be toxic at some concentration level. Although these atoms are in the trace level, the potential presence of toxic metals may represent a risk when these zeolites are used as animal and human food complement.

The NRA method provides an excellent determination of O and C. The precision of these determination mainly depends on the, $^{16}O(d, p_1)^{17}O$ and $^{16}O(d, \alpha)^{12}C$ and $^{12}C(d,p)^{13}C$ nuclear reaction cross sections values. These NR cross sections from the IBANDL web site are considered well established. SEM-EDS is a frequently used technique in material analysis. Our experience this technique, showed a poor accuracy in O and C determination. Therefore it is prudent to verify the C and O estimates with proper standards.

ACKNOWLEDGMENTS

REFERENCES

[1].P. Bosch, The Economic of Zeolites, Roskill, 1998, London SW9 , OJA, U.K.
[2] F. A. Mumpton, Proceedings of the National Academy of Sciences of U:S:A., Vol. 96, No.7, (1999)3643-3470
[3] H. G. Villa, Journal of the World Aquaculture Cociety., Vol 33, No. 2 (2002) 214
[4] E. Andrade, M. Feregrino, E.P. Zavala, J.C. Pineda, R. Jiménez and A. Jaidar, Nucl. Instr. and Meth. in Phys. Res. A287 (1990) 135.
[5]. J.L Ruvalcaba, JL, Monroy, J.G.Morales and K.Lopez,. Abstracts of the Ninth International Conference on PIXE and its Analytical Applications. Guelph, Canada. 2001: 62
[6].-J. A. Maxwell, W. J. Teesdale and J. L. Campbell, Nucl. Instr. Meth. B95 (1995) 407.
[7]. M. Mayer, SIMNRA User Guide Technical Report IPP 9/113 Max Plank Institut Fur Plamsmaphysik, Garching Germany.