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

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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 and 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 $^3\text{He}$ and $^2\text{H}$ 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.

Keywords: modified zeolite, natural zeolite, SEM-EDS, PIXE, RBS, NRA ,spectroscopy.

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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 ground 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 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 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 at $\theta = 165^\circ$ (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 $\mu$m 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 $^12C(d,p)\ ^13C$, $^16O(d,p)\ ^17O$ and $^16O(d,g)\ ^17C$ 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 $^12C(d,p)\ ^13C$, $^16O(d,p)\ ^17O$, $^16O(d,g)\ ^17C$ 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$_2$O$_3$) 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 $\mu$m x 500 $\mu$m 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 those elements.

Figure 5 shows a XRD pattern of one of the zeolites. The spectrum reveals the presence of montmorillonite:Al$_{1.67}$Mg$_{0.33}$Si$_{2.33}$O$_{10}$(OH)$_2$Na$_{0.33}$(H$_2$O)$_{2.33}$ that constitute more that 50% of the sample. Other crystal phase identified are: quartz (SiO$_2$), anorthite (CaAl$_2$Si$_2$O$_8$), calcite (CaCO$_3$) and albite (NaAlSi$_3$O$_8$). 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 \( \text{d}^+ \text{H}^{16}\text{O} \) 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 \( ^{12}\text{C}(\text{d}, \text{p})^{13}\text{C} \) 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.
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) $^{17}$O and $^{16}$O(d, α) $^{12}$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.

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