

EFFECT OF CALCINATION ON THE STRUCTURE OF A NATURAL MEXICAN ZEOLITE: STUDY BY XRD AND SEM-EDS

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Abstract: In the present work it is disclosed the morphological characterization of zeolitic powders, for scanning electron microscopy (SEM by its acronym in English), the results are also attached obtained by energy X-ray spectroscopy dispersive (EDS). This material (HE) subjected to a grinding of 3 hours (ZNM025) and subsequently treated thermally by a period of 4 hours, to temperatures of 250 (ZNM250), 350 (ZNM350) and 500°C (ZNM500), respectively. HE set of samples was characterized to know the changes produced with regard to the sample original (ZNM025). By maintaining a fixed amplification of 1000x, the micrographs show it following: a non-uniform distribution in particle size, the which can be grouped into 4 types; small (< 1 μm), medium (1 – 5 μm), large (6 – 10 μm), and extra-large (> 10μm). Elemental analysis by EDS confirms the presence of nanoparticles of oxides of iron (Fe_xO_y); that HE is occluded in the channels and in the pores of the zeolites; which are transformed or undergo a change in its structure, due to the thermal process; also I know confirm the existence of others items as he aluminum, silicon, sodium, calcium, oxygen, among others.

Keywords: Zeolite, grinding, treatment thermal, X-rays, SEM-EDS.

INTRODUCTION

Zeolites are a group of materials belonging to the tectosilicates (silicates three-dimensional), the which are constituted by networks of tetrahedra of SiO₄ and AlO₄, linked together by the carbon atoms oxygen present in the vertices.

These minerals follow this formula empirical $M_{x/n} Al_x Si_y O_{2(x+y)} wH_2O$ [1, 2].

The union of small tetrahedrons generate units' secondary construction, which are rings formed by four six tetrahedra, rings double either structure polyhedral. The third branch was produced, due to the different ways in

which the secondary units are linked together t(see Figure 1), for finally build the countless amount of zeolite structures [3].

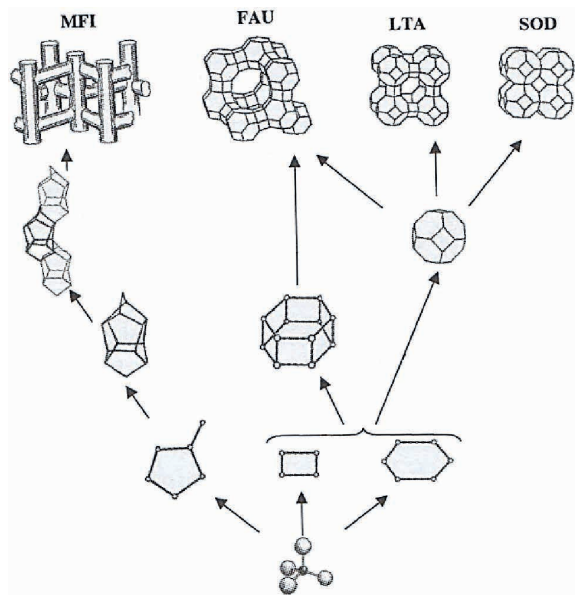


Figure 1. Construction of the different zeolite families.

The calcinations affect in a degree considerable to the structure of the zeolite, occur several phenomena as: i) the decrease in cell volume due to detachment of water either of molecules organic, ii) transformation of phases towards a further metastable, iii) structural collapse, iv) amorphous phase increase or decrease of the crystallinity and v) variation of the size of crystallite [4].

Today, it is found in the literature an amount minimum of articles, that board he issue of the calcinations in zeolites natural; and less still, there is information related to the application these materials in the degradation of compounds highly toxic of origin organic, which would be a new field for pure chemistry [5]; for that reason, it is decided write this article, that the center mainly in the catalytic properties, which are modified by the calcination of the ore, and that promote better performance when it comes to oxidizing organic compounds azo type.

Sample results have been submitted of

zeolite, where the techniques of XRD and UV-Vis [6, 7], concluding in the following: the treatment thermal it affects significantly so much in the size of crystallite, as in the displacement of some peaks of diffraction, besides, it was noticed an increase of the efficiency catalytic, to degrade the textile compound reactivate Black 5. In this work, he analyzed different XRD peaks, with the aim of determine the change of intensity and of FWHM (width to half height), of the zeolite natural calcined to 250 and 500 °C, besides HE calculation the diameter average of crystallite for the phases identified; that's how it was done a characterization structural of the material [7, 8].

In addition, for this study he aim main is to find the variation of the size of particle in function of the treatment thermal applied, for it is necessary analyze several spikes of diffraction wearing XRD and Debye-Scherrer, and finally HE identify the chemical elements that are present in the structure chemistry of the zeolites, said information is obtained by the EDS technique.

METHODOLOGY

The zeolite was extracted of a deposit sedimentary in Catano-Etla, Oaxaca, Mexico; his shape corresponds to a tuff, which consists in a rock with an irregular geometry and, greenish color with small dark spots on its surface. The mineral rock was reduced to dust fine applying a grinding mechanics during 3 hours, for it which one used a mechanical ball mill.

The resulting powders were subjected to a calcination process for 4 hours, keeping that temperature stable at that lapse; for keep constant the temperatures (250, 350 and 500 °C) was indispensable carry out the curves of calibration; the equipment used for the treatment thermal was a muffle thermolyne sybron model programmable Asching

Furnace Type 2000.

The microscopy electronics of swept (SEM), it was essential to know the morphology of the powder, for this, these conditions were controlled in the laboratory: microscope of electrons 3D FEG (FOCUSED ION BEAM), using a bombardment of electrons with 15 kV, 16 nA, a vacuum of 100 mbar and various scale factors.

Regarding the spectroscopy EDS (Energy-dispersive X ray Spectroscopic by their acronym in English), it was used a potential 15 kV (same equipment used for SEM), with a magnification of 5 kX for all the samples studied, the analysis was punctual about an agglomerate, changing continually the center of the beam of light incident. Are measurements (SEM-EDS) were made in the Center of Nanosciences and Micro and Nanotechnologies of the Instituto Politécnico Nacional - Mexico (CNMN-IPN).

RESULTS AND DISCUSSION

In the continuation, it was presented the characterization morphological through SEM, for the 4 zeolites studied, it is also given to know the chemical composition through of EDS. Finally, the graphs are discussed with a criterion from the spot of view academic and scientific.

A. SCANNING ELECTRON MICROSCOPY

By half of SEM, it was got different micrographs of the materials in study; Various magnifications were used. From 1000x until 50000x, with values intermediate, in this study only photographs at 1000x (see Figure 2), because of this manner, HE they can differentiate big changes, in comparison with the higher magnifications.

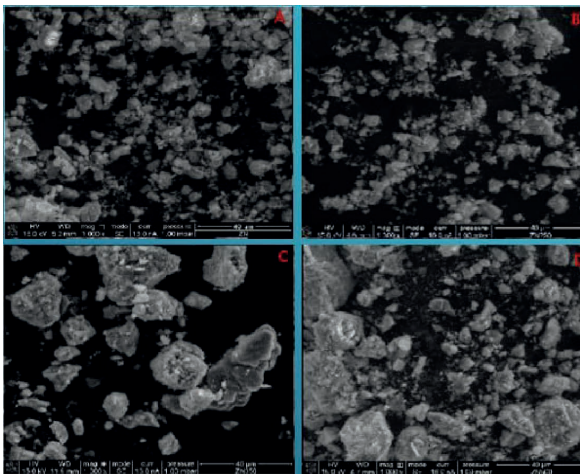


Figure. 2. SEM micrographs of the natural zeolite, using a magnification of 1000x: A) ZNM025, B) ZNM250, C) ZNM350 and D) ZNM500, with a scale of 40 µm.

From Figure 2 the following can be given explanation; a distribution is observed uniform in particle size; which it can be arranged in 4 types; small (<1 µm), medium (1 – 5 µm), large (6 – 10 µm) and extra-large (>10 µm). For the sample not calcined (see Figure 2A) have sizes of the order little and medium, most falls off in the first range; for ZNM250 and ZNM350 (see Figure 2B and 2C) the particles have size medium in his most, and some big; for the case of ZNM500 (see Figure 2D), the size trend is leans towards large and extra-large.

The growth that is apparent is due, to the agglomeration of particles that are smaller (cumulus), that form sizes of the order of 2 either 3 times elderly. Is say, that t he particle growth is proportional to the heat supplied, the higher it is, the size will increase of considerable manner due to the grouping of cumulus small or medium.

B. ENERGY-DISPERSIVE X-RAY SPECTROSCOPY

HE presents he spectrum of the analysis chemical carried out by the EDS technique (see Figure 3), the presence of iron oxides

(Fe_xO_y), because through X-rays could not be visualized, due to that his composition relative is very low, these oxides, the which are very important for carry to cape processes photocatalytic; already that act as sites active, located on the inner surface or in zeolite cavities; said Fe_xO_y are responsible of speed up reactions chemicals, for example: the oxidation-reduction of a molecule organic, as he Colorant Black 5 (RB5) reagent [8].

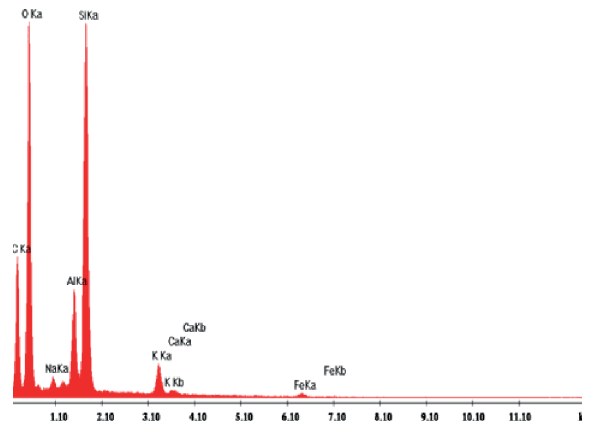


Figure 3. Analysis chemical elementary about a spot spherical, for the sample zeolitic to 25 °C (ZNM025).

Table I shows the elements chemicals present in natural zeolite not calcined and in its calcined forms.

| Sample | ok (%Wt) | Na _k (%Wt) | to the _k (%Wt) | yes _k (%Wt) | Faith _k (%Wt) |
|--------|----------|-----------------------|---------------------------|------------------------|--------------------------|
| ZNM025 | 71.35 | 1.42 | 6.00 | 20.23 | 0.10 |
| ZNM250 | 76.42 | 1.26 | 6.76 | 15.20 | 0.07 |
| ZNM350 | 70.41 | 1.38 | 6.83 | 20.76 | 0.12 |
| ZNM500 | 69.66 | 1.87 | 6.84 | 21.01 | 0.14 |

Table I: COMPOSITION CHEMISTRY DETERMINED BY EDS FOR THE DIFFERENT SAMPLES ZEOLITICS.

It was identified several elements, some of they are singular as: silicon and aluminum that form part whole of the samples, the predominance of oxygen is due to the presence of oxides, that was manifested in the

form of alumina (Al_2O_3) and silica (SiO_2) and nanoparticles of oxides of iron (Fe_2O_3).

It has a value between 2.2 and 3.2, which indicates that there is a phase transformation, from a non-state very stable towards a metastable state.

C. X-RAY DIFFRACTION

The diffractograms of powders, obtained with radiation and it is showed in the Figure 4. Where, different phases crystalline, that make up to the zeolitic samples and, in addition, are shown the interplanar distances of some peaks, as well as the structural changes that are happening.

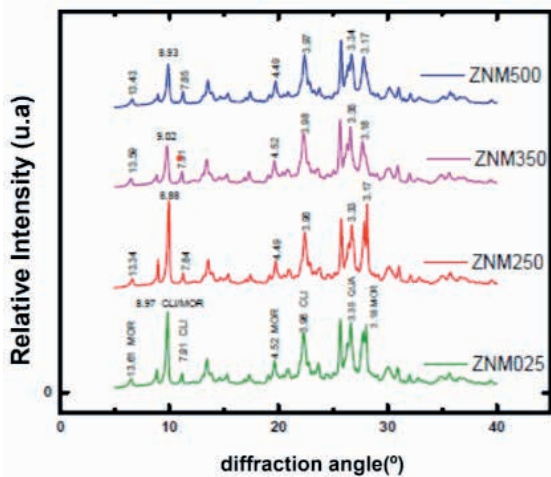


Figure 4. Patterns of diffraction of the samples zeolitic to 25, 250, 350 and 500 °C, respectively. With the phases identified as: MOR = Mordenite, CLI = clinoptilolite and WHAT = α -quartz.

Of the Figure 4, it was appreciated various elements, including the crystal structure (correspondent to the spikes sharp and widths) that has the zeolite, besides the presence of a phase amorphous (background either pattern background, from 18° to 30° from 2θ , approximately), because the sample is made of SiO_2 (glass), which is a constituent important, that not has a periodic arrangement of its atoms that reason, does not satisfy the Bragg

condition to diffract and then a background is formed not uniform (belly either package) [9 - 11].

The predominant crystalline phases correspond to clinoptilolite, mordenite and, to a lesser extent, α - quartz. From X-ray analysis, the peaks that do not have a label or identification are known to be signals due to erionite, heulandite, feldspar phases [12].

Although there is not peaks related to iron oxides, it was found an experimental evidence that, confirm their presence in the composition (in concentrations very low, that not is possible detect by DRX) in the zeolites; One of them consists in bringing a field closer magnetic (magnet) about a dissolution of water with zeolitic powder (prepared in a flask), after a considerable time, it was observed that a small amount of nanoparticles are attracted toward the magnet surface [12-14].

The processes thermal applied to the original sample (ZNM025) cause several effects, such as: a) transformation of a phase to another, b) structural collapse, and c) increase decrease of the amorphous phase [4, 15]. Table II shows the variation of as increase the phase amorphous in function of the calcination temperature.

| Sample | % Amorphicity |
|--------|---------------|
| ZNM025 | 34.78 |
| ZNM250 | 36.27 |
| ZNM500 | 39.41 |
| ZNM500 | 41.76 |

TABLE II: COMPOSITION OF THE PHASE AMORPHOUS OF THE SET OF SAMPLES.

In the study [7, 8] HE presented results of the analysis of the spikes in $2\theta=13.45^\circ$ and 19.61° , which correspond to the mordenite and clinoptilolite phases were measured two peaks located at 11.19° and 32.02° ; for both phases were necessary determine he width, area, and center of the beak, as well as the

average crystallite size.

Now, for this job, it was added information complementary analyze the crystallite size in the 2 peaks new located in 8.87° (mordenite) and 26.32° (clinoptilolite) [16]; he calculation of the crystallite size parameter (L) was made with the Debye-Scherrer method, equation (1). According to Table III, it is observed that the crystallite size of the mordenite is nearly three times larger than the clinoptilolite, although these phases are not being comparing because they are in different positions, one can distinguish that some factors affect the size of the crystallite.

$$L = K \cdot \lambda / \beta \cos \theta \quad (1)$$

The variables correspond to: $K= 0.89$ is a constant

$\lambda= 0.154$ nm

$\beta=$ Width of the peak in radians

$\theta=$ Half of the angle of diffraction

| Phase | Position angular ($^\circ$) | L (nm) |
|----------------|-------------------------------|--------|
| clinoptilolite | 26.25 | 24.52 |
| mordenite | 8.85 | 73.12 |

TABLE III: DETERMINATION OF THE SIZE OF CRYSTALITE FOR 2 PHASES ZEOLITICS.

In the Table IV. HE show the displacements of 5 corresponding peaks to the clinoptilolite phase (peak 1, 2, 3, 4 and 5), where the first column corresponds to the sample zeolitic analyzed, the second, fourth, sixth, eighth and tenth columns are refer to the apparent center of the beak, in this place, it was located the peak point (intensity maximum), and finally, in the third, fifth, seventh, ninth and eleventh columns, it showed the variation of the position of the beak ($\Delta 2\theta_1, \Delta 2\theta_2, \Delta 2\theta_3, \Delta 2\theta_4$ and $\Delta 2\theta_5$) with regard to the sample not calcined (ZNM025); all this procedure It was performed with the WinPLOT[®] Software.

The changes constants in the position angular of the peaks, is mainly due to the removal of water molecules [14], which are adsorbed on the surface of the mineral and inside of the cell unitary, located in the channels and cavities of the zeolite, that is, the material undergoes a process of dehydration, it that causes a decrease in the volume either a contraction of the cell; as zeolite is a material highly hydrophobic [13], tends to rehydrate with water molecules, which found in the environment, these processes pass when the sample cools to the temperature atmosphere, after if there is calcined at a certain temperature, for that reason, it arose an expansion of the cell [4, 12]. All these variations are reflected in the shifts of the peaks of the pattern of X-ray diffraction.

| Sample | Beak 1 ($^\circ$) | $\Delta 2\theta_1$ ($^\circ$) | Beak 2 ($^\circ$) | $\Delta 2\theta_2$ ($^\circ$) | Beak 3 ($^\circ$) | $\Delta 2\theta_3$ ($^\circ$) | Beak 4 ($^\circ$) | $\Delta 2\theta_4$ ($^\circ$) | Beak 5 ($^\circ$) | $\Delta 2\theta_5$ ($^\circ$) |
|--------|---------------------|---------------------------------|---------------------|---------------------------------|---------------------|---------------------------------|---------------------|---------------------------------|---------------------|---------------------------------|
| ZNM025 | 9.14 | - | 10.61 | - | 22.30 | - | 28.03 | - | 31.68 | - |
| ZNM250 | 9.35 | 0.11 | 10.66 | 0.05 | 22.41 | 0.11 | 28.13 | 0.10 | 31.78 | 0.10 |
| ZNM350 | 9.12 | -0.02 | 10.53 | -0.08 | 22.31 | -0.09 | 28.07 | -0.06 | 31.66 | -0.02 |
| ZNM500 | 9.22 | 0.08 | 10.73 | 0.12 | 22.37 | 0.06 | 28.10 | 0.03 | 31.74 | 0.06 |

TABLE IV: DISPLACEMENTS OF PEAKS SELECTED OF THE CLINOPTYLOLITE, IN FUNCTION OF THE TEMPERATURE OF CALCINATION.

CONCLUSIONS

Through SEM it was confirmed that the size average of the particles is affected in great manner, by the treatment thermal applied, the changes in a growth not uniform, due to the agglomeration of particles of minor size, which come together or associate to form new particles of size elderly; the geometry is very varied, from flakes, spheres, even very irregular shapes.

The elemental analysis by EDS yielded a Si/Al molar ratio = 3, it was also identified the presence of oxygen, which was the element further predominant, he which can be exhibited in his shape of oxide, also were found in smaller proportion the atoms of sodium and potassium. The iron atom was not detected by XRD, but if it was located by this technique, finally, the calcinations not affected the percentage composition (%wt) of the treated samples.

With the analysis of XRD, he got the pattern of diffraction of the samples calcined and crystalline phases, in addition, did an approach ideal with the method of Debye-Scherrer of the size of the crystallites, corresponding to the phases clinoptilolite and mordenite, confirming he decrease in the crystalline phase depending on of the heat treatment applied. Finally, significant changes were observed in the position angular of several peaks, that he attributed to processes of hydration – dehydration of the mineral, which in a way joint cause an expansion and shrinkage of the zeolitic cell.

ACKNOWLEDGMENTS

The authors José Manuel Sanchez nurseries, Fernando Chavez Rivas thanks the support unconditional by part of BEIFI, COFFA-IPN and CONACYT, by half of the Projects BEIFI-01-2016119 and SIP-20160889, to carry out the present work. Academic support is appreciated to Dr. Francisco Cruz Gandarilla

and the technical support provided by the Dr. José Alberto Andraca Adame.

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