Thermal analysis and porosimetry of natural zeolites from Mexican and Cuban deposits

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The natural zeolites from different deposits of Mexico and Cuba were studied by simultaneous Thermal Analysis. Porosity measurements by standard porosimetry were also applied. Such materials as the clinoptilolite (Tasajeras, Cuba; Tehuacán, Puebla, México; Etla, Oaxaca, México) and mordenite (Santiago de Cuba, Cuba) were investigated. For all samples XRD analysis was performed; thermo-chemical parameters and characteristics of the pore diameter distribution, including the average pore size and meso- and macro-pore surface were measured. Similarities and differences in the characteristics of the studied natural zeolites were analyzed.

Keywords:

Introduction

Natural zeolite minerals are crystalline aluminosilicate species composed of a three-dimensional arrangement of silicon-oxygen (SiO\(_4\)) and aluminum-oxygen (AlO\(_4\)) tetrahedra, bound by vertices [1]. Built in such a way framework contains open cavities in the form of channels and cages. Due to isomorphous substitution of tetravalent Si by trivalent Al, AlO\(_4\) tetrahedron becomes charged, with the "-1" charge. To get Coulomb equilibrium, charge-compensating cations enter the zeolite pores. Because they do not constitute elements of crystalline structure, these cations are commonly exchangeable. So, zeolite voids are usually occupied by extra-framework cations and by H\(_2\)O molecules [1]. The channels have cross-sections in the range from 0.3 until 1.2 nm, and are large enough to allow the passage of guest species.

Common extra-framework cations of natural zeolites are Na\(^+\), K\(^+\), Ca\(^{2+}\) as well as traces of Mg\(^{2+}\), Sr\(^{2+}\) and Ba\(^{2+}\) [2,3]. Majority of them can be exchanged with NH\(_4^+\) ions. The type and density of the exchangeable cations influence the stability of the crystal lattice and the thermal behavior of a zeolite. High Si/Al ratios and the presence of K\(^+\) ions favored to increase the stability of the crystal structure upon heating. Moreover, the ion-exchangeable cations can be located in hydrated forms in the cavities of zeolites, and their removal leads to the reformation of the pore structure and the removal of the amorphous Al-species [4]. In the hydrated phases, dehydration occurs at temperatures mostly below about 400 °C and is largely reversible [2,5]. Zeolite group of minerals currently include more than forty naturally occurring species, and is the largest group of silicate minerals [6].

Among sedimentary natural zeolite, the more important structures, as regarding their occurrence and practical applications, are clinoptilolite, mordenite, chabazite and phillipsite [2,7-9]. The first two were selected for study in this present work. According to the International Zeolite Association (IZA), 3-letter structure codes for these zeolite structures are HEU and MOR respectively [7]. Clinoptilolite is a member of the heulandite group of natural zeolites. The unit cell is monoclinic C-centered with Na\(^+\), K\(^+\), Ca\(^{2+}\) and Mg\(^{2+}\) as the most common charge-balancing cations. Unit cell parameters for the \((Na_{1.84}K_{0.16}Mg_{0.2}Ca_{1.24})(Si_{29.84}Al_{6.16}O_{72})\cdot 21.36H_2O\) form are as follow: \(a = 17.662\ \AA\), \(b = 17.911\ \AA\), \(c = 7.407\ \AA\), and \(\alpha = 90°\), \(\beta = 116.4°\), \(\gamma = 90°\). The Si/Al ratio is more than four [2,4]. Gas or vapor molecules penetrate the crystalline structure through a series of intersecting channels, each layer of channels separated by a dense, gas-impermeable layer of tetrahedra [6]. Typical chemical composition of mordenite species is Na\(_{8}Al_{8}Si_{4}O_{24}\)\(\cdot 24H_2O\); the unit cell is orthorhombic. Parameters of the simple mordenite cell vary between \(a = 1.8052–1.8168\ nm\), \(b = 2.0527\ nm\), \(c = 7.501–7.537\ nm\), \(\alpha = \beta = \gamma = 90°\). The Si/Al ratio is found between 4.5 and 5.5 [2,10,11].

The main applications of natural zeolites are in the environmental field, particularly for catalytic processes [12-15], soil amendment [16], cement...
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manufacture [17,18], energy recovery technologies [19], pharmaceutical [20], oilsands bitumen cracking [21], wastewater purification [22,23], decontamination of radioactive elements [24], as support media for the immobilization of microorganisms [25], and environmental remediation [26].

Significant zeolite deposits are widespread in the Mexico and Cuba area and are of great interest because of their abundance and potential economic value [11,27-32]. The aim of the present study is to investigate the thermal behavior and the porosity of natural zeolites from deposits in Mexico and Cuba, in order to characterize them.

**Experimental**

**Materials.**

The samples of four kinds of natural zeolites proceeding from different locations were used in this study. Two of them are from deposits in Mexico: clinoptilolite from Tehuacan, Puebla (M2) and clinoptilolite from Etla, Oaxaca (M3). The other two samples are from deposits in Cuba: clinoptilolite from Tasajeras (M1) and mordenite derived from Santiago de Cuba (M4) (Table 1).

| Sample | Main phase | District          | Country |
|--------|------------|-------------------|---------|
| M1     | Clinoptilolite | Tasajeras        | Cuba    |
| M2     | Clinoptilolite | Tehuacan, Puebla | Mexico  |
| M3     | Clinoptilolite | Etla, Oaxaca     | Mexico  |
| M4     | Mordenite   | Santiago de Cuba | Cuba    |

**XRD analysis.**

X-ray diffraction (XRD) was used to determine what phases were present in each sample. Zeolites samples were investigated with Wide-angle X-ray diffraction (WAXD) using a D2 PHASER diffractometer (Bruker, Germany) equipped with a CoK$_\alpha$ radiation source ($\lambda=1.79$ Å) at scattering angles 20 = 5°–80°, step of 0.0202° and 1 s time per step. The Bruker TOPAS 4.2 software was used for quantitative phase analysis.

**Simultaneous thermal analysis.**

In the present study simultaneous thermal analysis (TG + DSC) of zeolite samples was carried out using a Netzsch STA 449 F1 Jupiter coupled with a quadrupole mass spectrometer QMS 403 Aélos which was used to determine the composition of evolved gases. Analysis of samples was carried out in the temperature range 40-750°C in platinum crucible at the heating rate of 10°C/min in argon stream at the rate of 90 ml/min. Temperature and sensitivity calibrations were conducted using DSC data of the melting points of standard metal materials.

**Standard porosimetry.**

Porous structure of zeolite samples was examined with standard porosimetry by means of an Automated Porosimeter 3.1 Porotech Ltd. The method of standard porosimetry (SP) deals with measurement of equilibrium distribution of working liquid between the sample and the standard (with known porometric curve) [33]. Equilibrium specific liquid content $v$ in the sample (volume of liquid in pores per weight/volume of porous sample) is plotted as a function of specific liquid content in the standard at different amount of liquid in the system. Both standard and the sample under study are weighted after drying and soaked with measuring liquid under vacuum. After removing a free liquid, both porous samples are physically contacted one to another. Then, some amount of working liquid is evaporated from this coupled sample set. Both standard and the sample are separately weighted after capillary equilibrium was established. Volume and weight of liquid inside both standard and the sample are estimated from the data by subtraction of previously recorded values for dry samples. The same operation of measurements continues systematically until all liquid from the samples is evaporated. Thus, required relation between $v$ for the sample under study and specific liquid content in the standard at different amount of liquid in the system can be plotted. This relation, together with known porometric curve of the standard (pore volume-radius distribution), gives a porometric curve for the sample under study. Data on the pore structure of the sample have been received using POROVOZ software.

**Results and discussion**

**Results of XRD analysis.**

The XRD analysis was performed to determine the phase crystal structure and chemical compositions of the natural zeolite samples proceeding from different locations of Mexico and Cuba. The XRD patterns have been indexed using the reference data-files from ICDD-PDF database (ICDD PDF-2 Release 2011 RDB). The XRD diffraction peaks of different samples matched with the different types of zeolites (Table 2). The XRD patterns (Fig. 1, Table 2) do confirm that all samples belong to zeolite group of aluminosilicate minerals.

However, the variation in the main peak positions and intensities indicate that the overall structures, chemical compositions, and the amount of
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Fig. 1. XRD analysis data for the M1 (a), M2 (b), M3 (c) and M4 (d) zeolites (* – clinoptilolite, 0 – mordenite, ■ – quartz, ● – calcite).

Table 2

Results of XRD analysis of natural zeolites samples

| Sample | Phase      | ICDD PDF-2 database number |
|--------|------------|-----------------------------|
| M-1    | Clinoptilolite | 00-047-1870                  |
|        | Mordenite  | 00-029-1257                  |
|        | Quartz     | 00-003-0444                  |
| M-2    | Clinoptilolite | 00-047-1870                  |
|        | Mordenite  | 00-029-1257                  |
|        | Quartz     | 00-003-0444                  |
|        | Calcite    | 01-083-0578                  |
| M-3    | Clinoptilolite | 00-047-1870                  |
|        | Mordenite  | 00-029-1257                  |
|        | Calcite    | 01-083-0578                  |
| M-4    | Clinoptilolite | 00-047-1870                  |
|        | Mordenite  | 00-029-1257                  |
|        | Quartz     | 00-003-0444                  |
impurities for all the samples are slightly different. Taking into account the peak characteristics and insignificant background of XRD patterns it can be concluded that these natural zeolites are of high crystallinity with minor amorphous contents (Fig. 1). This feature could play an important role in the zeolite applications as a catalyst or in energy saving technologies.

**Results of simultaneous thermal analysis.**

Fig. 2 shows the results obtained in the DSC-TGA runs at heating rate of 10 °C/min from 40 °C to 750 °C under argon atmosphere. As it can be seen, the DSC signal for the M1 sample (Fig. 1a) shows one endothermic peak at 134.2 °C with weight loss 11.03% and outgoing gas is H2O.

For the M2 sample are already observed two endothermic peaks on DSC curve. First one at 99.6°C with weight loss 9.28% and outgoing gas H2O. The second peak was detected at 760.2°C and had weight loss 3.44% with CO2 as outgoing gas. DSC data for the M3 sample are demonstrating two endothermic peaks just like results for the M2. First peak is around 132°C; the weight loss is 8.48%; and second peak is at 691.2°C with the weight loss 1.34%. The outgoing gases for first and second peaks are H2O and CO2, respectively, the same as for the M2 sample. The DSC signal for the M4 sample, like for the M1, shows only one endothermic peak at 133.4°C with weight loss 12% and outgoing gas H2O.

**Results of standard porosimetry analysis.**

The results obtained in the investigation of natural zeolites by the standard porosimetry (SP) are shown in Fig. 3. Comparison of differential and integral distribution curves of the pore volume in terms of the radius for all four samples clearly demonstrates the difference between the M1, M2, M3 and M4 samples.

Results of porosity investigations performed on the M1 sample shows that most peaks located in the area corresponding to three values of pore diameters: 0.44µm, 1µm and 2.4µm. Mostly similar results are observed for the sample M2, there are three most intensive peaks corresponding to areas 0.1µm, 0.3µm and 1.4 µm, but the difference between the M1 and M2 is in the presence of peak that corresponds to pores with diameter nearly 0.005µm. The M3 sample has two peaks on porogram at 0.003µm and 1.1µm. Another peak is weakly expressed, and corresponds to values nearly 0.005µm, 0.02µm and 0.2µm. Results of the M4 sample shows only two ar-
### Results of investigation of the natural zeolites samples M1—M4 by thermogravimetry, DSC and standard porosimetry methods

| PARAMETER                      | M1         | M2         | M3         | M4         |
|--------------------------------|------------|------------|------------|------------|
| **Porometry**                  |            |            |            |            |
| Average pore diameter, μm      | 0.70       | 1.24       | 0.15       | 0.55       |
| Porosity over weight, cm³/g    | 0.58       | 0.62       | 0.32       | 0.65       |
| Porosity over volume, cm³/cm³  | 0.51       | 0.57       | 0.46       | 0.56       |
| Meso- and macro-pore surface over weight m²/g | 56 | 153 | 110 | 127 |
| **Thermogravimetry**           |            |            |            |            |
| Δm, % (T, °C)                  | -11.03 (40-750) | -9.28 (40-556) | -8.48 (40-507) | -12.6 (40-750) |
| Outcoming gas                  | H₂O        | H₂O, CO₂   | H₂O, CO₂   | H₂O        |
| **Differential scanning calorimetry** |            |            |            |            |
| Tpeak, °C                      | 134        | 100        | 132        | 133        |
| Speak, J/g                     | -232.1     | -102.1     | -160.1     | -187.3     |

*Fig. 3. Integral and differential distribution of pore volume vs. pore radius for the M1 (a), M2 (b), M3 (c) and M4 (d)*
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eas in pore distribution that corresponds to values of diameters about 0.003 μm and 0.7 μm. Meso- and macro-pore surface over weight was determined for all zeolites samples by standard porosimetry technique. It includes only surface of meso- and macro-pores of sample, total surface values are not used because of the specificity and accuracy of the standard porosimetry method in micro-range, as well as the application fields of natural zeolites. Average pore diameter was calculated in the range from 2 nm to the maximum recorded pore diameters, in this case pore does not exceed 6-6.5 μm.

In the Fig. 4 are shown the comparisons of such parameters as average pore diameter, porosity over volume, porosity over weight and meso- and macro-pore surface over weight of all investigated zeolites. In this study presented data about “porosity over weight” and “porosity over volume”, the difference in these parameters can be very significant if in the sample are present large amount of closed pores. Working liquid cannot fill these pores in the process of measurement, but nevertheless they occupy a certain amount of sample volume.

All results of thermal behavior and the porosity properties of natural zeolites obtained in this study presented in Table 3.

Analysis of the data shows that the samples M1 (clinoptilolite from the Tasajeras deposit, Cuba, and M4 (mordenite from the Santiago de Cuba deposit) demonstrate similar endothermic effects of dehydration accompanied by loss of weight and have the 5°C difference in the temperature of the beginning of thermal effect. The other two samples of the clinoptilolite from Tehuacan, and Etla deposits have on two thermal effects. The first endothermic effects of water loss have almost the same onset temperature, but there is the 32°C difference in the temperature of peak. In addition to thermal effects of dehydration, the samples M2 and M3 have endothermic thermal effects of degradation with the weight loss and release of CO₂. Peak temperature difference in this case is more than 80 degrees and the weight loss of the sample M2 more than twice higher than the weight loss of the sample M3. Minimum value of pore diameter was fixed for the sample M4 (about 0.003 microns), while the lowest average pore diameter corresponds to the sample M3 (0.15 microns). The most widespread distribution of the pore diameter has been obtained for a the sample of M1 (in the area nearby 0.44 - 2.4 micron), while the most narrow distribution of pore diameter refers to the sample M4 (in the area nearby 0.003 - 0.7 microns). It is observed that the surface area of the M2 sample is considerably higher than that of other samples. The difference in the characteristics of the porosity of the samples can be caused by the features of the geological formation of the island and mainland zeolites.

Conclusions

Samples of natural zeolites (three clinoptilolite structures and one mordenite) from different locations of Mexico and Cuba were investigated by the complex of methods: by XRD analysis, simultaneous TG/DSC analysis and standard porosimetry. The thermo-chemical parameters, such as the thermal effects of degradation processes of zeolites, mass loss of samples in the temperature range of 40 - 750 degrees, and distribution of pore diameters including the average pore size were identified. The difference in investigated zeolites was shown, including minimal quantities of impurities for the

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**Fig. 4.** Comparison of average pore diameter (a), porosity over weight (b), porosity over volume (c), meso- and macro-pore surface over weight (d) of different zeolites

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M3 and M4 samples, the lowest values of porosity characteristics for the sample of M3 (clinoptilolite from Etla deposit, Mexico), as well as some similarities in the thermochemical properties of the samples by geographic location of deposits (one endothermic effect for samples from Cuba and two endothermic thermal effect for samples from Mexico). The highest values of surface area and largest average pore diameter corresponding to clinoptilolite samples from Tehuacan deposit allow us to suggest that these natural zeolites can be successfully used for catalytic performances. The data that was obtained in this study can represent great interest for geological researches of the regularities of formation of island and mainland deposits of natural zeolites in Latin America.

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