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POROSITY, CHARACTERIZATION AND STRUCTURAL PROPERTIES OF NATURAL ZEOLITE – CLINOPTILOLITE – AS A SORBENT

The characterization and porous structure of raw and modified clinoptilolite as a sorbent has been investigated by nitrogen adsorption, X-ray diffraction, X-ray fluorescence, Fourier transform infrared spectroscopy, differential thermal analysis, scanning electron microscopy and atomic force microscopy methods. The nitrogen adsorption data revealed that the total pore volume and specific surface area were increased after modification. The nitrogen adsorption was used to determine percent of mesoporosity. The TG data show that 14 wt. % of clinoptilolite is lost after heating up to 1200 °C. Two types of porosities – primary porosity (microporosity) and secondary one (meso- and macroporosity) have been observed.

1. INTRODUCTION

Clinoptilolite is one of the most common natural zeolites, easily obtained from mines, suitable as a sorbent due to its natural characteristics. Although many researchers classified it in heulandite family [1] but its Si/Al ratio and thermal stability makes it different from heulandite ($4 \leq \text{Si/Al} < 5.2$ and $\text{Si/Al} < 4$ [2, 3] at 750–800 and 450–550 °C [4], respectively). According to Coombs [3], the heulandite family minerals are classified by the dominant exchangeable cation as follows: K-, Na-, Ca- and Sr-heulandite as well as K-, Na- and Ca-clinoptilolite. But previously this family was divided into Si-poor and Si-rich heulandite, Si-poor and Si-rich clinoptilolite species [5]. The crystal structure of clinoptilolite and heulandite has 3-dimensional aluminosilicate framework, which specific structure causes the developed system of micro-

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pores and channels occupied by water molecules and exchangeable cations. Unit cell parameters of both crystals are similar to each other. According to the results of X-ray diffraction (XRD) studies, clinoptilolite unit cell parameters are as follows: $a = 17.66 \text{ \AA}$, $b = 17.963 \text{ \AA}$, $c = 7.400 \text{ \AA}$ and $\beta = 116^\circ 47'$ [6]. Those for heulandite are: $a = 17.718 \text{ \AA}$, $b = 17.897 \text{ \AA}$, $c = 7.428 \text{ \AA}$ and $\beta = 116^\circ 25'$ [7]. Two-dimensional channel system is formed in the heulandite/c clinoptilolite minerals (parallel to a and c axes) row based on the features of aluminosilicate framework structure. There are two channels running parallel to each other and to the c axis: a channel consisting of a 10-member (tetrahedron) ring of the size of $4.4\text{--}7.2 \text{ \AA}$ and a channel consisting of an 8-member ring with the size of $4.1\text{--}4.7 \text{ \AA}$ and a channel run parallel to a axis consisting of an 8-member ring with the size of $4.0\text{--}5.5 \text{ \AA}$ [1]. Some different information about channel windows of the heulandite family minerals is published by other researchers: $2.8\text{--}4.7 \text{ \AA}$ of the channel run parallel to a axis and $3.1\text{--}7.5$ and $3.6\text{--}4.6 \text{ \AA}$ of channels run parallel to c axis [8].

The cited data is ambiguous and cannot clear the problem of identifying the clinoptilolite framework structures and porous parameters. Pore sizes of the aluminosilicate framework of the clinoptilolite are also indefinite. It should be noticed that the mentioned ambiguity makes problem in the study of the zeolite porous structures using adsorption methods. A correct choice of adsorbate is the main difficulty.

Presence of secondary porosity is also interesting and may create some problems in the study of porous structure of clinoptilolite similarly as in other zeolites. The primary porosity (microporosity) occurs because of the specific crystal structure of zeolite mineral grains, whereas the secondary porosity is connected with grain sizes of zeolite and other minerals in the zeolite rocks [9]. The mesopores are active surfaces for catalysis, transport channels, and adsorption of relatively large molecules. Also some technological properties which may not be explained by adsorption in micropores, might be explained by secondary porosity.

According to some results of structural investigations, clinoptilolite is characterized as a mineral adsorbent with microporous structure [10]. On the other hand, a high value of total mesopore volume on polymodal pore size distribution was obtained by other researchers using adsorption methods on natural clinoptilolite [9, 11]. Presence of mesopores may result in inaccurate analysis of porous structure of the zeolite.

The main goal of this study was to investigate physical and structural properties, the heterogeneity and the hierarchy of the clinoptilolite pores in order to select proper sorbate for clinoptilolite by using: X-ray diffraction (XRD), X-Ray fluorescence (XRF), Fourier transform infrared spectroscopy (FTIR), nitrogen adsorption/desorption method, scanning electron microscopy (SEM), atomic force microscope (AFM), and thermogravimetric analysis (TGA).

2. EXPERIMENTAL

Materials. Clinoptilolite rock from Aftar region (the West Semnan, Central Alborz Mountains, 200 km East of Tehran, Iran) was used in this study. The powdered samples were sieved down to less than 70 μm in diameter and submitted to XRD, XRF, DTA, TGA and FTIR.

X-ray diffraction (XRD). X-ray powder diffraction analysis was performed using XRD analysis instruments (Philips X'Pert pro, Netherlands). The samples were first ground, mounted on holders then introduced for analysis. The source consisted of: CoK_α radiation ($\lambda = 1.79 \text{ \AA}$), monochromator on secondary optics, 40 kV power and 35 mA current. Each sample was scanned within the 2θ range of 4–85. XRD analysis shows that clinoptilolite is the main mineral in the sample and contents of albite and mordenite are low.

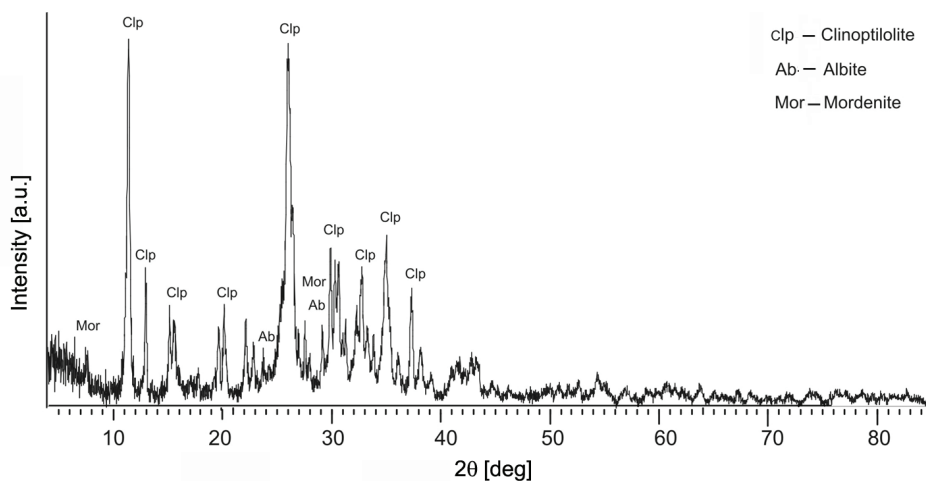


Fig. 1. XRD pattern of clinoptilolite powder sample

Figure 1 shows the XRD pattern of clinoptilolite sample. XRD pattern of the sample shows sharp diffractions that can be attributed to clinoptilolite [12]. The d spacing of clinoptilolite at the asymmetric position of (400) is 3.97 \AA .

X-ray fluorescence (XRF) and specific gravity. X-ray fluorescence of the sample has been studied using XRF Analysis Instruments (Philips Magix Pro, Netherlands). The result shows that SiO_2 , Al_2O_3 and CaO are main components. The main exchange cations are Ca, K, Na and Mg, and loss on ignition (LOI) is 13.44 wt. %. Table 1 demonstrates chemical composition of the sample. The determined density of the clinoptilolite sample (weight – 3.007 g, volume – 1.421 cm^3 at 23.9 $^\circ\text{C}$) was 2.103 g/cm^3 .

Table 1

Table 1. Chemical composition [wt. %] of the clinoptilolite of Aftar region (the west Semnan, central Alborz Mountains, 200 km East of Tehran, Iran)

SiO ₂	Al ₂ O ₃	CaO	K ₂ O	Na ₂ O	MgO	Fe ₂ O ₃	SrO	TiO ₂	ZrO ₂	L.O.I
68.17	11.05	3.93	1.11	0.64	0.62	0.53	0.25	0.19	0.06	13.44

Fourier transform infrared spectroscopy (FTIR). Fourier transform infrared spectroscopy of the clinoptilolite has been studied using FTIR Analysis Instruments (Bruker vertex70, Germany). The samples were traced in the range of 4000–400 cm⁻¹ and the band intensities were expressed in transmittance (%).

Adsorption–desorption methods. The clinoptilolite samples were crushed to obtain grains 0.5–1 mm in diameter, washed with distilled water and dried at room temperature (25 °C, relative humidity 45%) (air-dried). The treatment of crushed samples of clinoptilolite (10 g) was performed by addition of 250 cm³ of the 2 M solutions of HCl. After 24 h solid phases were separated from the solutions and dried at room temperature. The structural parameters of samples were determined by low-temperature nitrogen adsorption/desorption method. The samples were outgassed at 300 °C under vacuum for 5.0 h to attain a constant weight. The specific surface area (S), the total pore and micropore volumes (V_{tot} and V_{mic}) and the average pore diameter (D) were calculated using the adsorption data, obtained via NOVA 2200e instrument (Quantachrome Nova 2200e, USA). Using the Brunauer–Emmett–Teller (BET) method, the specific surface area (S_{BET}) was calculated. V_{tot} was then evaluated by converting the volume of nitrogen adsorbed at $p/p_s \approx 0.98$ to the volume of liquid adsorbate. Using the Barrett–Joyner–Halenda (BJH) method, the mesopore surface area S_{BJH} and the mesopore volume V_{BJH} were calculated. The micropore volume was calculated by the t -plot method. The Saito–Foley [13] models were applied for micropore size calculations.

Differential thermal analysis. In DTA, the differences in temperature between the sample and a reference material such as α -Al₂O₃ is recorded while both are subject the same heating program. In investigation, TGA is commonly used with DTA to follow the hydration reactions. The thermal behaviour of clinoptilolite was investigated in the temperature range 38–1200 °C using a DTA/TGA thermal analysis instruments (Netzsch STA409 PC Luxx, Germany). The experimental conditions were: increasing the temperature from ambient to 1200 °C at the heating rate of 10 °C/min, N₂ gas dynamic atmosphere and alumina as a reference material.

Electron microscopy study. SEM is a powerful technique applied in microimaging of a variety surfaces. This technique can be used in exploring the surface structure to determine particle size and texture on that surface. Porous structure of the clinoptilo-

lite has been studied using scanning electron microscopy (LEO 1450VP, England) and atomic force microscopy (ARA-AFM 0101/A, Iran) which was mounted using Mount Instruments (STRUERS, Labopress3, Denmark).

3. RESULTS AND DISCUSSION

The nitrogen adsorption/desorption isotherms for natural and acid treatment clinoptilolite are shown in Fig. 2a.

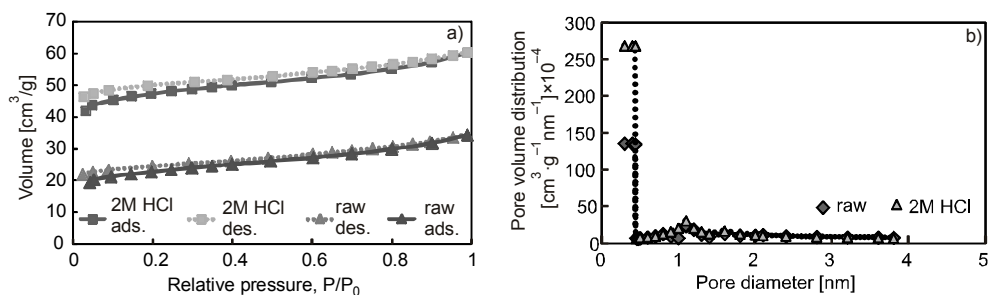


Fig. 2. Nitrogen adsorption/desorption isotherms (a) and pore size distribution by the Saito–Foley model (b)

Table 2

Parameters of the clinoptilolite porous structures by the nitrogen adsorption/desorption method

Clinoptilolite sample	Specific surface area [m ² ·g ⁻¹]		Pore volume [cm ³ ·g ⁻¹]			Pore diameter [nm]	
	S_{BET}	S_{BJH}	$V_{\text{tot}}(\text{BET})$	$V(\text{BJH})$	$V_{\text{mic}}(t\text{-plot})$	D_{av}	$D(\text{BJH})$
Air-dried	84.45	47.20	0.053	0.035	0.0254	2.51	1.26
Treated 2 M HCl	177.6	77.32	0.093	0.047	0.0626	2.09	1.20

Table 2 shows values of some important parameters obtained from the analysis of the isotherms. Figure 2a shows that low temperature nitrogen adsorption on raw clinoptilolite is expressed by isotherm of I type by BDDT classification with the hysteresis loop of the type H4 (Fig. 2a) according to IUPAC classification [14]. The isotherm curve rises too sharply at the beginning at a slight relative pressure ($P/P_0 < 0.05$). The steep rise of the isotherm curve under the lowest relative pressure is caused by the presence of free micropores in the adsorbent samples in which nitrogen adsorption occurred. But the micropore volume values for raw zeolite determined by Saito–Foley (SF) model (Fig. 2b) and calculated by t -plot (Table 2) were 0.0399 and 0.0254 cm³·g⁻¹, respectively. The nitrogen adsorption on the modified clinoptilolite can be expressed by isotherm of the I type with a wide hysteresis loop which does not close at low relative

pressure (Fig. 2a). This phenomenon is due to presence of cations or minerals blocking the pore channels and the limited extent of zeolite crystalline structure reduces its sorption activity but Acid treatment produces an improved adsorbent [15].

The increase of the micropore volumes of the acid-treated clinoptilolite is obviously caused by unblocking of the channels of alumino-silicate framework structure of the zeolite through dealumination and decationation during acid leaching. The nitrogen molecules cannot penetrate in clinoptilolite micropore channels which are occupied by exchangeable cation [10, 11].

Acid treatment of natural clinoptilolite has rendered improved sorbent, via the mechanism of decationation and dealumination, and also by dissolution of any amorphous silica blocking the channels of the clinoptilolite structure. The cation blocking effects in treated zeolite is thus minimized by acid treatment, lowering its cation-exchange capacity by leaching Al^{3+} from framework positions and introducing H^+ into the few remaining cation sites [15]. Beside these factors, other parameters including the method of preparation of adsorbent and adsorbate selection can increase the pore volumes and specific surface area, thus other parameters should be considered. The low nitrogen adsorption can be caused by the stronger interaction of highly polar water molecules with electric field created by the cations of the microporous structure [10]. Contributions of the micropore volume for the treated clinoptilolite increase more than 2.4 times and are evaluated as $0.0626 \text{ cm}^3 \cdot \text{g}^{-1}$ by t -plot. In Figure 2b, the Saito–Foley model shows that the main part of micropores is near 0.4 nm in size.

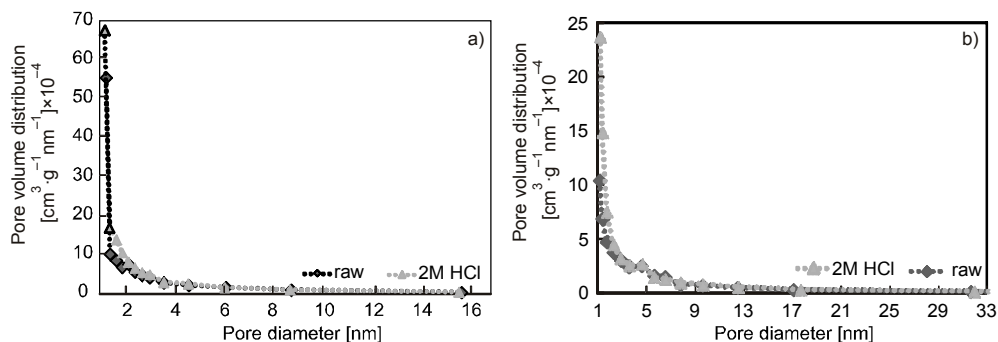


Fig. 3. Pore size distribution from the adsorption (A) and desorption branch (B) by the BJH model

In Figure 3b, the BJH curves of nitrogen desorption show descent distribution of pore volume in the mesoporous section (2–50 nm). One can see that upon increasing pore diameter, the pore volume decreased. In mesopore range, dominate pores of ca. 2.3 nm although a slight maxima occur corresponding to pores of 4.58 nm for raw zeolite. Figure 3b shows that the curve of treated zeolite is similar to that of the raw one but with higher pore volume distribution at the beginning of the process. Figure 3a

shows that dominating pore size in mesopore range occurs at ca. 2.16 nm for zeolite treated with 2 M HCl and a clear maximum of pore volume at near 2.16 nm for the raw one. Figure 3b shows that pores of 2.3 nm in diameter dominate in mesopore range evaluated by the BJH method from the desorption branch for raw zeolite. According to the analysis of the data listed in Table 2, The BJH specific surface area of the clinoptilolite increased after acid treatment from 47.20 to 77.32 $\text{m}^2 \cdot \text{g}^{-1}$ for the pore size lower than 180 nm. The BET specific surface area increased from 84.45 to 177.6 $\text{m}^2 \cdot \text{g}^{-1}$. In this case, the total pore volume increased by 75.5% and the BJH pore volume increased by 34.3% after acid treatment of zeolite.

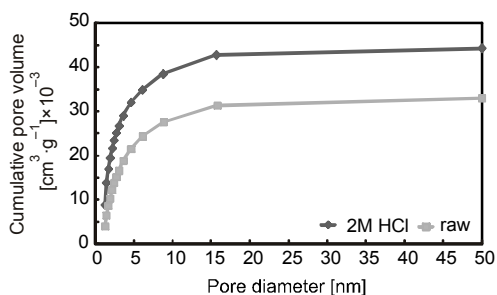


Fig. 4. Cumulative pore volume from the adsorption by the BJH model

In Figure 4, for the BJH adsorption of nitrogen the dependence of cumulative pore volume in function of the pore diameter is shown. V_{BJH} determined for modified clinoptilolite is 0.0442 $\text{cm}^3 \cdot \text{g}^{-1}$ in the pore size range of 1.2–50 nm but the cumulative pore volume in the range of 2–50 nm (mesopore range) is just 0.0248 $\text{cm}^3 \cdot \text{g}^{-1}$ (V_{meso} equal to cumulative pore volume V_{BJH} in the range of 2–50 nm is 0.0248 $\text{cm}^3 \cdot \text{g}^{-1}$).

The value of $V_{\text{meso}}/V_{\text{tot}} = 0.0248/0.093 = 0.267$ of modified clinoptilolite may point that mesopores containing 26.7% are considerable fraction of the total pore volume for the pore size lower than 50 nm, although micropores dominate. The average pore diameter of the modified samples is also smaller in comparison with the starting material.

These results for nitrogen adsorption are close to those for the clinoptilolite samples from other deposits [9] except for the specific surface area. It is higher similarly as that reported by Oliveira et al. [16] most probably because of fine grained samples in the range of 0.5–1 mm in diameter. These results will allow us referring this zeolite as micro-mesoporous material. It can be assumed that fine graining of clinoptilolite will lead to increase of specific area and consequently increase of adsorption capacity. The nitrogen adsorption isotherm reflects all parts of the zeolite porous volume except the volume occupied by water molecules and exchangeable cations. It is likely that the nitrogen molecule with molecular diameter of 0.37 nm is too large for the micropore channels of the zeolite occupied by exchangeable cations and water molecules. Barrer [17] reported adsorption values of the natural clinoptilolite evaluated as 0.02, 0.055, 0.0065, 0.101 and 0.135 $\text{cm}^3 \cdot \text{g}^{-1}$ for benzol, ethanol, isopentane, methanol and water,

respectively. According to these data, a smaller water molecule of the diameter of 0.26 nm is a better choice for characterization of the clinoptilolite microporous structure. Cakicioglu-Ozkan [18] investigated water vapour adsorption on the treated clinoptilolite by 1.6 M HCl (water vapour temperature – 100 °C) showed that the surface area and total micropore volume were about 319 m²·g⁻¹ and 0.116 cm³·g⁻¹, respectively.

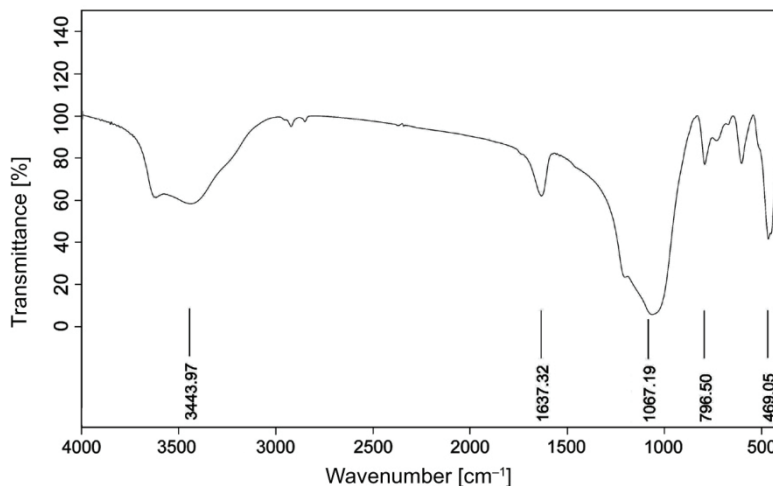


Fig. 5. The clinoptilolite Fourier transform infrared spectroscopy

FTIR results demonstrate (Fig. 5) that zeolites are significantly hydrated which is illustrated by a discrete water absorption bands in the 3500 and 1640 cm⁻¹ region. These bands, which were centered at 3444 (OH group) and 1637 cm⁻¹ refer to water molecules associated with Na and Ca in the channels and cages in the of the zeolite structure [19]. Other bands appear near 1067, 796 and 469. The 1067 cm⁻¹ band corresponds to asymmetric stretching vibration modes of internal T–O bonds in TO₄ tetrahedra (T = Si and Al). The 796 and 469 cm⁻¹ bands are assigned to the stretching vibration modes of O–T–O groups and the bending vibrations of T–O bonds, respectively [20]. These results are similar as those obtained by other authors [21, 22].

Results of TG/DTG and DTA examination of the clinoptilolite samples after heating up to 1200 °C, at the rate of 10 °C/min are shown in Fig. 6. As seen at TG curves, weight loss was continuous during heating up to 1100 °C. About 14 wt. % of the zeolite was lost as a result of thermal treatment in the range of 38–1200 °C due to dehydroxylation and dehydration. Rapid weight loss was observed in the temperature range from 38 to 400 °C, a moderate one was recorded from 400 to 1000 °C. The DTA curve shows an endothermic peak at 50–150 °C [9]. According to Perraki and Orfanoudaki [22] for weight losses at 25–100 °C and 100–200 °C are responsible hygroscopic water and loosely bonded water, respectively.

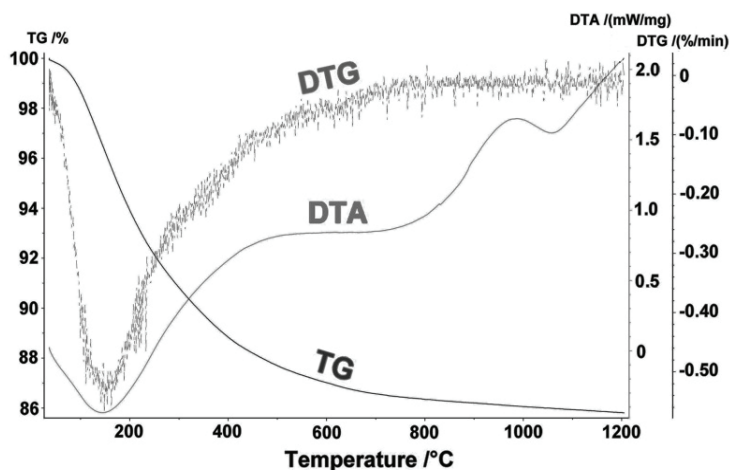


Fig. 6. DTA-TGA curve of the clinoptilolite sample

Kurkuna et al. [11] reported two forms of water – intact molecules and OH groups existing in the structure of silicate minerals (as clinoptilolite). Intact water is eliminated at below 100 °C, whereas hydroxyl groups are removed at $T > 400$ °C. According to study [1], the structural water (OH groups) is eliminated from clinoptilolite after exceeding 360 °C.

In this study, water losses of about 14% and 3% at 150–1000 °C and 400–1000 °C were observed, respectively. It should be noticed that the value of total water loss of the raw material was 14%. Similar values of 0.109 and ca. 0.12 $\text{cm}^3 \cdot \text{g}^{-1}$ were obtained by other authors [11, 22]. According to study [23] the maximum adsorption values of water vapour are ca. 0.081 $\text{cm}^3 \cdot \text{g}^{-1}$ and ca. 0.101 $\text{cm}^3 \cdot \text{g}^{-1}$ for Ba- and Na-clinoptilolite at $P/P_0 < 0.1$. Consequently, the thermogravimetric data are appropriate to characterize porous structure of the zeolite, and porous volume in particular.

SEM images demonstrate that the clinoptilolite is a lamellar texture material (Fig. 7). Increasing the dividing ability shows separate plates or bars (some microns in size) are not individual crystal grains of the clinoptilolite, but only aggregates presented by finer grains of the mineral. Such splitting of zeolite grains is typical for clinoptilolite cleavage and is a consequence of hydrothermal solution filtration [24]. Heterogeneity of clinoptilolite grains is clearly presented in Fig. 7.

In our opinion, the phenomenon of clinoptilolite cleavage is the main reason of mesoporosity. Clinoptilolite grains are flat long bars parallel to surface and 25–100 nm thick, 200–400 nm wide and 350–1000 nm long. Hence the clinoptilolite grains have latent fine-crystalline structure with the crystal sizes of $50 \times 300 \times 700$ nm on average [9]. Other investigators have established submicron sizes of individual mineral grains of clinoptilolite in clinoptilolite tuff [9]. Considering the height of cleavage degrees ranging from one to hundreds atom diameters in zeolite mineral

grains an intra-grain space may obviously take an essential part in the total volume of zeolite rocks even without micro inclusions and other factors of secondary porosity.

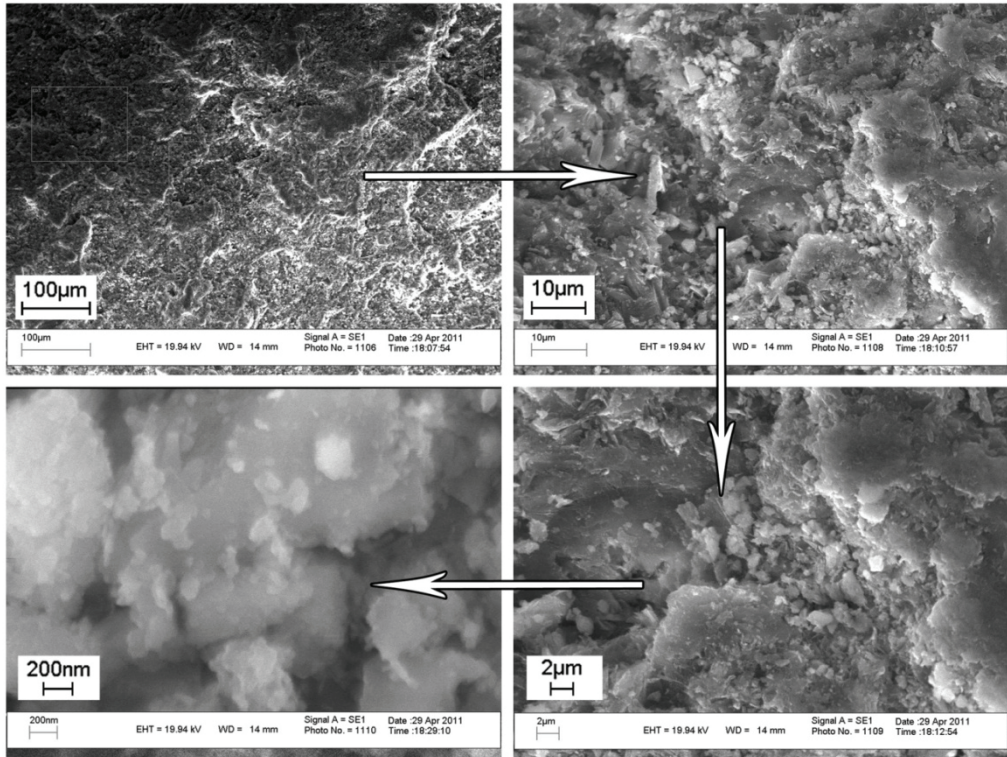


Fig. 7. The clinoptilolite crystal SEM; images of the clinoptilolite sample

The AFM results allowed observation of morphology of the clinoptilolite grain surface at various magnifications at the micro level (Fig. 8). Submicrometer sizes of the clinoptilolite grains in the clinoptilolite rock are shown in Fig. 8A-1, -2, 8B-1, -2, 8C-1, -2). The individual microcrystals of zeolite are smaller than one micrometer in the longest direction. The AFM image (Fig. 8C-1) presents the clinoptilolite microcrystal with tabular habit and well developed cleavage in the surface. The good lamellar morphology of the zeolite surface is presented in Fig. 8C-1, -2). Grain blocks of the zeolite are observed at various crystalline planes. The cleavage phenomenon is clearly visible in topographical view of Fig. 8C-2. As is seen in Fig. 8C-1, one crystal was chosen, its length and width with cross-sectional profile is shown in Fig. 8C-4, -5. In the cross-sectional profile along the length and width of the crystal, interchange of heterogeneous wrinkles is visible.

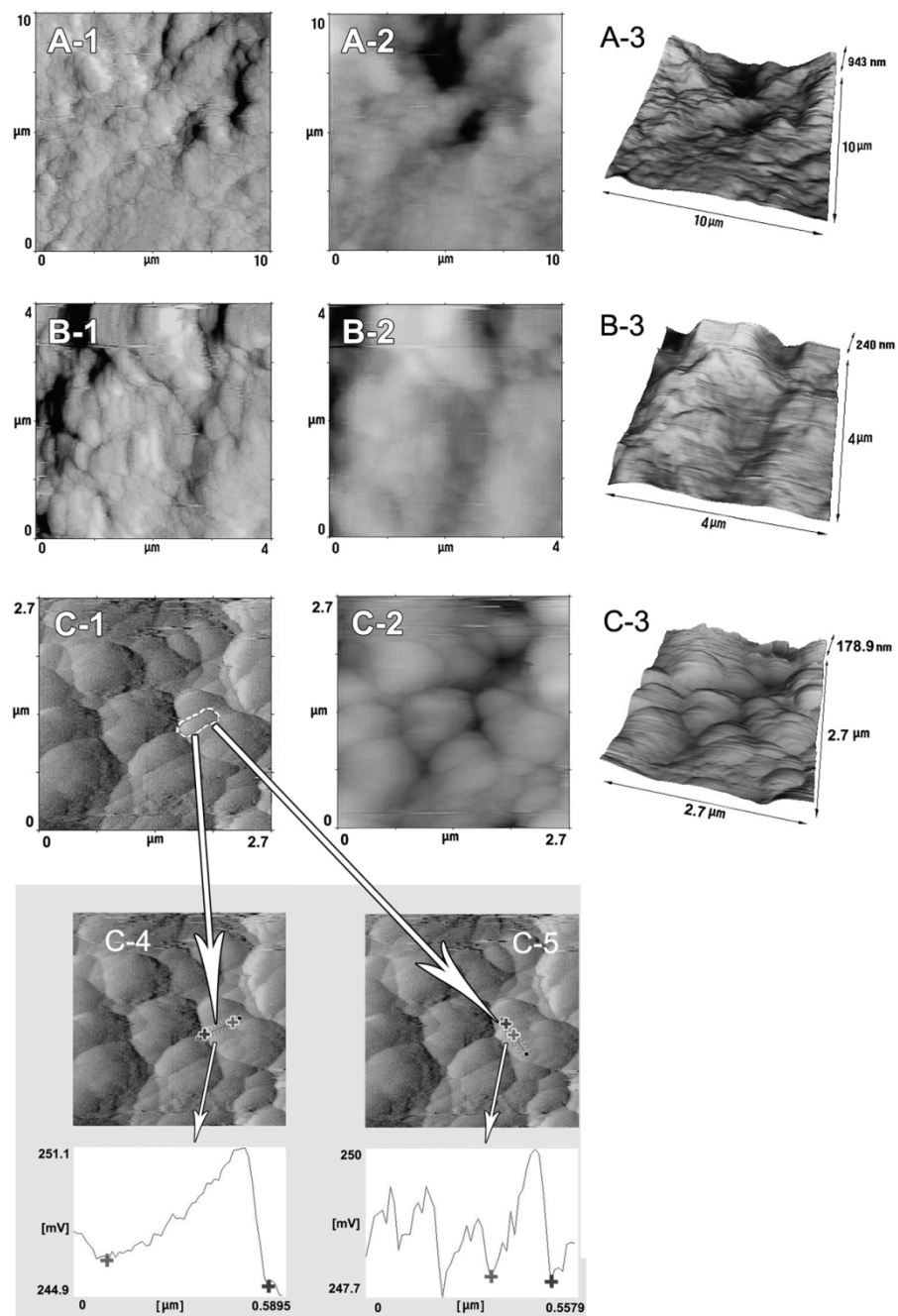


Fig. 8. AFM images of the clinoptilolite grain surface morphology (top and bottom, topographical view); AFM image with the prior preparation of mounting samples

The deposition of exchangeable cations in intraplane medium can cause strong connection between the aluminosilicate layers. Our interpretation of AFM images is based on the hypothesis of Yamamoto [25]. Sprynskyy and co-workers [9] used the geometric method to calculate total pore volume of clinoptilolite channel. They note that the calculated values (total pore volume = $0.332 \text{ cm}^3 \cdot \text{g}^{-1}$) are significantly higher than the microporosity characteristics obtained by nitrogen adsorption/desorption method. Considering a large size of N_2 molecule, nitrogen adsorption/desorption method can not provide true information about microporosity of the clinoptilolite micropores at 77 K. N_2 molecule has the kinetic diameter of 3.7 \AA , thus it is not accessible for the clinoptilolite framework with window dimensions of channels $3.1\text{--}7.5 \text{ \AA}$ and $3.6\text{--}4.6 \text{ \AA}$ or $2.8\text{--}4.7 \text{ \AA}$ [8].

It can be concluded that clinoptilolite is a natural micro- and mesoporous material with polymodal pore size distribution. The primary porosity (microporosity) is connected with the clinoptilolite framework structure, while the secondary porosity (mesoporosity) is caused by cleavage phenomenon of the clinoptilolite crystallites. Of course, the heterogeneity of the clinoptilolite rock porosity is caused by the presence of associated minerals (albite, mordenite, etc.) and heterogeneity of crystalline structure of those minerals.

4. CONCLUSION

Porous structure of the clinoptilolite has a heterogeneous nature. Two types of porosities such as primary porosity and secondary one are observed. The primary porosity can be defined as microporosity presented by nanotube system of the clinoptilolite 3-dimensional aluminosilicate framework. Mesoporosity and macroporosity form the secondary porosity. The mesoporosity is formed by slot pores determined mainly by cleavability of the zeolite crystallite. The macropores consist of pores of various forms which are located between blocks of the zeolite crystallite and other minerals in the clinoptilolite rock. The nitrogen adsorption/desorption method can be used for only mesopores and not for evaluation of micropores of raw clinoptilolite. The evaluation of the clinoptilolite microporosity by nitrogen adsorption/desorption method can be made after acid treatment when micropores of the aluminosilicate framework are unblocked during acid leaching.

Clinoptilolite is more appropriate to adsorb molecules whose kinetic diameter is lower than 3 nm because the most pores are located in the microporous range; molecules with bigger diameters are not penetrable for the clinoptilolite microporous channels. The acid treatment increases micropore volumes and the specific surface area of clinoptilolite; therefore it would improve adsorption efficiency. Heating at $400 \text{ }^\circ\text{C}$ eliminates water molecules existing in clinoptilolite channels which may unblock the channels and increase sorbate penetrating through channels, improving adsorption

efficiency. Nitrogen adsorption method showed that grains of clinoptilolite have higher specific surface area and pore volume than rock one, thus it may improve adsorption efficiency. For choosing appropriate physical and chemical modification methods for each sorbate, all of this characterization, porosity and structural properties of clinoptilolite should be considered.

REFERENCES

- [1] BRECK D.W., *Zeolite molecular sieves*, Wiley, New York, 1974.
- [2] ACKLEY M.W., REGE S.U., SAXENA H., *Application of natural zeolites in the purification and separation of gases*, Microporous Mesoporous Mater., 2003, 61, 25.
- [3] COOMBS D.S., ALBERTI A., ARMBRUSTER TH., ARTIOLI G., COLELLA C., GALLI E., GRICE J.D., LIEBAU F., MINATO H., NICKEL E.H., ESSAGLIA E., PEACOR D.R., QUARTIERI S., RINALDI M., ROSS R., SHEPPARD R.A., TILLMANN E., VERZZALINI G., *Recommended nomenclature for zeolite minerals: reports of the subcommittee on zeolites of the international mineralogical association, commission on new minerals and mineral names*, Can. Mineral., 1997, 35, 1571.
- [4] ALIETTI A., *Polymorphism and crystal-chemistry of heulandites and clinoptilolites*, Am. Mineral., 1972, 57, 1448.
- [5] BOLES J.R., *Composition, optical properties, cell dimensions and thermal Stability of some heulandite group zeolites*, Am. Mineral., 1972, 57, 1463.
- [6] KOYAMA K., TAKEUCHI Y., *Clinoptilolite: the distribution of potassium atoms and its role in thermal stability*, Z. Kristallogr., 1977, 145, 216.
- [7] ALBERTI A., *On the crystal structure of the zeolite heulandite*, Min. Petr. Mitt., 1972, 18, 129.
- [8] BAERLOCHER CH., MEIER W.M., OLSON D.N., *Atlas of zeolite structure types*, 6th Ed., Elsevier, Amsterdam, 2007.
- [9] SPRYNSKY M., GOLEMBIEWSKI R., TRYKOWSKI G., BUSZEWSKI B., *Heterogeneity and hierarchy of clinoptilolite porosity*, J. Phys. Chem. Solids., 2010, 71, 1269.
- [10] HERNANDEZ-HUESCA R., DIAZ L., AGUILAR-ARMENTA G., *Adsorption equilibrium and kinetics of CO₂, CH₄ and N₂ in natural zeolite*, Sep. Purif. Technol., 1999, 15, 163.
- [11] KORKUNA O., LEBODA R., SKUBISZEWSKA-ZIEMBA J., VRUBLEVSKA T., GUNKO V.M., RYCZKOWSKI J., *Structural and physicochemical properties of natural zeolites: clinoptilolite and mordenite*, Microporous Mesoporous Mater., 2006, 87, 243.
- [12] JCPDS files card Nos. 025-1349 (2000).
- [13] SAITO A., FOLEY H.C., *Curvature and parametric sensitivity in models for adsorption in micropores*, AIChE J., 1991, 37, 429.
- [14] *IUPAC reporting physisorption data for gas/solid systems*, Pure Appl. Chem., 1985, 57, 611.
- [15] HERNANDEZ M.A., ROJAS F., LARA V.H., *Nitrogen-sorption characterization of the microporous structure of clinoptilolite-type zeolites*, J. Porous Mater., 2000, 7, 443.
- [16] OLIVEIRA C.R., RUBIO J., *Isopropylxanthate ions uptake by modified natural zeolite and removal by dissolved air flotation*, Int. J. Miner. Process., 2000, 90, 21.
- [17] BARRER R.M., MAICICI M.B., *Molecular sieve sorbents from clinoptilolite*, Can. J. Chem., 1964, 42, 1461.
- [18] CAKICIOGLU-OZKAN F., ULKU S., *The effect of HCl treatment on water vapor adsorption characteristics of clinoptilolite rich natural zeolite*, Microporous Mesoporous Mater., 2005, 77, 47.
- [19] WILSON M.J., *Clay Mineralogy: Spectroscopic and Chemical Determinative Methods*, Chapman and Hall, New York, 1994.

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- [20] TANAKA H., YAMASAKI N., MURATANI M., HINO R., *Structure and formation process of (K, Na)-clinoptilolite*, Mater. Res. Bull., 2003, 38, 713.
- [21] OLAD A., NASERI B., *Preparation, characterization and anticorrosive properties of a novel polyani-line/clinoptilolite nanocomposite*, Prog. Org. Coatings, 2010, 67, 233.
- [22] PERRAKI T., ORFANOUDAKI A., *Mineralogical study of zeolites from Pentalofofos area*, Appl. Clay Sci., 2004, 25, 9.
- [23] TARASEVICH YU.I., POLYAKOVA I.G, POLYAKOV V.E., *Microcalorimetric study of the interaction between water and cation-substituted clinoptilolite*, Colloid J., 2003, 65, 493.
- [24] KOWALCZYK P., SPRYNSKY M., TERZYK A.P., LEBEDYNETS M., NAMIESNIK J., BUSZEWSKI B., *Porous structure of natural and modified clinoptilolites*, J. Colloid Interface Sci., 2006, 297, 77.
- [25] YAMAMOTO S., SUGIYAMA S., MATSUOKA O., KOHMURA K., HONDA T., BANNO Y., NOZOYE H., *Dissolution of zeolite in acidic and alkaline aqueous solutions as revealed by AFM imaging*, J. Phys. Chem., 1996, 100, 18474.