

## ZEOLITES AS MESOPOROUS MATERIALS

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**Abstract.** Zeolites are natural volcanic minerals with a number of unique characteristics. Zeolites were formed when volcanic ash was deposited in ancient alkaline lakes. The interaction of the volcanic ash with the salts in the lake water altered the ash into various zeolite materials. Some natural and synthetic zeolites (molecular sieves) are discussed in this paper. They have various properties, like cation exchange, adsorption and molecular sieving (passing of a gas or a liquid through the zeolite), dehydration and rehydration, siliceous composition and resistance to radiation, making them useful in industry. By the encapsulation of various substances in their mesoporous matrix, like porphyrins or metalloporphyrins, new materials are formed, which are very useful, for example, as oxidation catalysts, in domains like wastewater treatment or photodynamic therapy([1], [2]). In this paper we have studied the structure of some natural and synthetic zeolites. The zeolites were analyzed by means of various analytical methods, like X-ray diffraction and FT-IR methods.

**Keywords:** zeolites, mesoporous materials, catalysts

### 1. INTRODUCTION

The porous materials, also called molecular sieves, cover microporous, mesoporous and macroporous domains depending on their pore dimensions (table 1). Since the discovery of microporous zeolites, the development of advanced porous materials having channels of tunable dimensions at the atomic, molecular and nanometer scale has become a fast-growing interdisciplinary field. This has resulted in materials with improved or new properties, which broadened their application range beyond the traditional use as catalysts and adsorbents.

**Table 1. Pore dimension of zeolites and molecular sieves**

Pore size (Å)	Definition	Typical material	Cycle size	Pore diameter (Å)
>500	macroporous			
20-500	mezoporous	MCM-41		15-100
<20	microporous			
	Very large pores	cloverite	20	6x13,2
		JDF-20	20	6,2x14,5
		VPI-5	18	12,1
		AIPO4-8	14	7,9x8,7
	Large pores	faujasite	12	7,4
		AIPO4-5	12	7,3
		ZSM-12	12	5,5x5,9
	Medium pores	ZSM-48	10	5,3x5,6

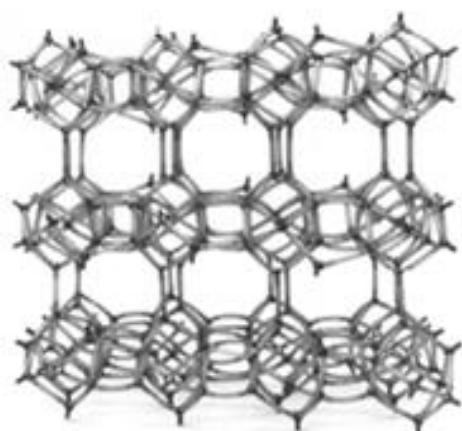
Pore size (Å)	Definition	Typical material	Cycle size	Pore diameter (Å)
		ZSM-5	10	5,3x5,6
	Small pores	CaA	8	4,2
		SAPO-34	8	4,3

Hence, zeolites and related porous materials may find applications in modern areas ranging from microelectronics and molecular device manufacturing to medical diagnosis [3].

Natural zeolites are found as crystals, slightly coloured; often, the coloration is due to very fine iron oxide powders or due to other similar impurities. From a chemical point of view, zeolites differ by their cation content and the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio.

Investigations carried out during last years have indicated potential possibilities of application of natural zeolites for concentration and separation of non-ferrous metal ions. Their non-swelling, chemical stability in various caustic media, thermostability and possibility of regeneration as well as a high rate of sorption equilibrium are advantageous. These features of natural zeolites promote their use in the environment protection chemistry and industry [4]. Natural clinoptilolites (fig. 1) and mordenites from various deposits in Japan, USA, Italy, Greece, South Africa, Bulgaria, Romania and Ukraine are used for the concentration of Cd(II), Cr(III), Cu(II), Fe(II), Mn(II), Ni(II), Pb(II), Zn(II), Sr(II), and NH<sub>4</sub><sup>+</sup>. Modified zeolites from Mexico are also used for anion sorption, in particular CrO<sub>4</sub><sup>2-</sup> and F<sup>-</sup> [5]. Additionally, they were applied for waste disinfections. Platinum metal ions are often present, though in small amounts, in wastes of jewelry and electrical engineering production; therefore, previous concentration should be maintained both for their determination and utilization

using such adsorbents as zeolites. Natural zeolites are also used as catalysts whose properties can be improved by incorporation of certain metals, metal complexes into the zeolite structure [6], [7].



(a)



(b)

**Figure 1. (a) Clinoptilolite structure, (b) mineral representation.**

Zeolite/mesoporous molecular sieve composites (ZMC) are made using zeolites as silica-alumina source [8]. Mesoporous molecular sieves have several characteristics such as high surface area, ordered pore structure and large pore volume. The advantages are suggested to be useful for separation, purification and catalytic processes.

The synthetic zeolites are obtained by crystallization of hydrated aluminosilicate gels, generally prepared from aqueous solutions of aluminate or silicate or from solid reactive phases, at different temperatures and pressures, and also by artificial zeolitification of natural raw materials. Particularly, the potential uses of Al-containing mesoporous molecular sieves as acid catalysts have been attractive due to their tunable uniform mesostructures. However, the weak or moderate acidity arising from the amorphous character of the mesoporous material reduces their extensive uses. The low acidity and hence moderate catalytic activity of aluminium-containing ordered mesoporous materials, particularly Al-MCM-41, is generally attributed to the well-known absence of structural order in the aluminosilicate matrix.

On the other hand, zeolites are typical microporous materials with many types of crystal structures, which have strong acidity due to their crystal structures. However, the pore sizes of these zeolites are limited to micropore regions [9], [10].

## 2. MATERIALS AND METHODS

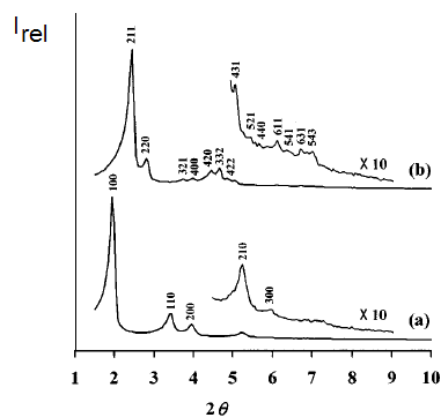
- X – Ray DRON CoK $\alpha$  X-ray diffractometer.
- IR spectrophotometer, Carl Zeiss Jena.
- Optima 2100 DV (Perkin Elmer) inductive coupled plasma spectrometer.

The clinoptilolite was thermally activated before being analyzed. The sample was introduced in an electrical oven, at room temperature. The heating was started, at a rate of 5 – 10<sup>0</sup>C/min, up to 500<sup>0</sup>C. The temperature was kept constant for 2 hours. After the time passed, the sample was cooled and weighted. To analyze the zeolites that were chosen, especially X-ray Diffraction (for clinoptilolite, MCM-41 and X-71), FT-IR and elemental analysis (for clinoptilolite) were used.

## 3. RESULTS

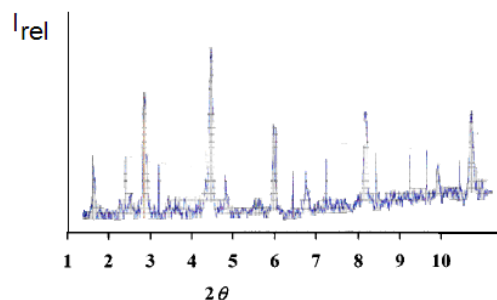
We present here the results obtained after analyzing the samples of clinoptilolite and of the molecular sieves (AIMCM-41, MCM-41 and X-71).

For MCM-41 and AIMCM-41, the following X-ray diffractograms were obtained Figure 2.



**Figure 2. X-ray diffractogram of AIMCM- 41(a) and MCM-41 (b)**

For the X – 71 molecular sieve, the following X-ray diffractogram was obtained:



**Figure 3. X - ray diffractogram of powdered X-71 zeolite.**

For clinoptilolite, the following X-ray diffractogram was obtained:

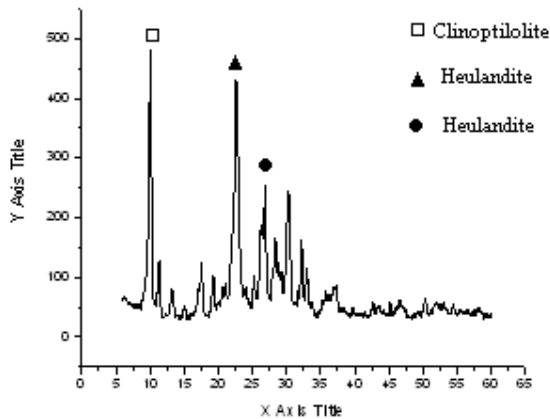


Figure 4. X-ray diffractogram of clinoptilolite.

After the FT-IR analysis of the clinoptilolite sample, the following spectrum was obtained:

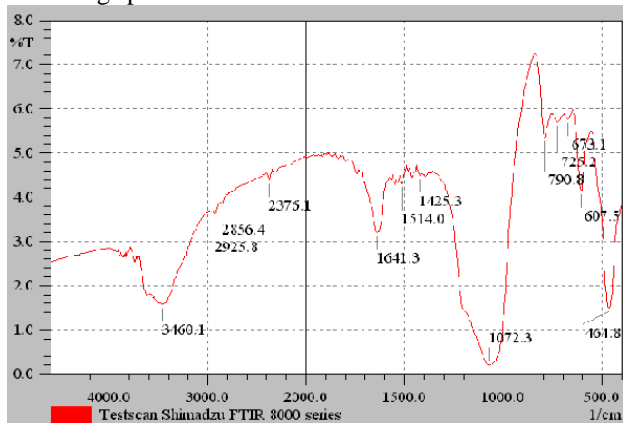


Figure 5. IR spectrum of the clinoptilolite sample.

After the elemental analysis of the clinoptilolite sample, the following results were obtained and listed below (table 2):

Table 2

Sample	Element	Emission (nm)	Element concentration, ppm (mg/kg)	Recalculated conc. (% w/w)	
				oxide	sulphate
Clinoptilolite	Al	396.153	27380	5.17	-
Clinoptilolite	Ca	422.673	6578	0.92	-
Clinoptilolite	Fe	259.939	7471	1.07 (Fe <sub>2</sub> O <sub>3</sub> )	2.03 (FeSO <sub>4</sub> )

#### 4. DISCUSSIONS

The mesoporous zeolite **MCM-41** is characterized by the high quality of the crystalites. The peak (100) is thin and intense, which is a proof for the mentioned crystallinity. The pore diameter of this zeolite is 32,5Å. The **X-71 zeolite** has a FAU topological structure. It was selected for analysis because of the large free volume of 0.5 cc/cc, determined by a system of channels and cavities with relative big dimensions, of 7.4Å, which

puts it in the big pore zeolites category. This zeolite has a great accesibility for big molecules.

The X-ray diffractogram initially shows a well crystallized X type zeolite, with a cubical symmetry. The calculated network constant for the initial sample was  $a_0 = 25,0995\text{Å}$ . From the volume of the elemental network the Si/Al molar ratio can be estimated, having a value of 1.027, which is in the typical range of the X-type zeolite.

**Clinoptilolite** is the most abundant and most used (95%) natural zeolite. This structure of clinoptilolite is formed of three tetraedric dimensional arrangements of SiO<sup>4</sup> and AlO<sub>4</sub><sup>-2</sup>, consisting in a network of tunnels and interconnected cages, as shown in figure 1(a). The tetravalent silicium ions are replaced by trivalent aluminium ions, the resulted negative charge being stabilized by the cations. The greater the replacement percentage of the the silicium ions with aluminium ions, the greater the absorption capacity of the cations. In this way, the Si/Al ratio, which varies between 2.7 and 5.2 (for clinoptilolite), and the quantity of cations determin the properties of the most zeolites. The free volume of clinoptilolite is very close withe one of the cations. This blocking effect can be reduced by acid treatmnet, in which the aluminium ion is extracted and the adsorption capacity increases.

The ability of the clinoptilolite to selectively adsorb cations is named “molecular sorting”. The preferenece order for various cations, in a decreasing way, is Cs<sup>+</sup> > Rb<sup>+</sup> > K<sup>+</sup> > NH<sub>4</sub><sup>+</sup> > Ba<sup>+2</sup> > Sr<sup>+2</sup> > Na<sup>+</sup> > Ca<sup>+2</sup> > Fe<sup>+3</sup> > Al<sup>+3</sup> > Mg<sup>+2</sup> > Li<sup>+</sup>, Pb > NH<sub>4</sub><sup>+</sup> > Cu, Cd > Zn, Co > Ni > Hg and K<sup>+</sup> > NH<sub>4</sub><sup>+</sup> > H<sup>+</sup> > Na<sup>+</sup> > Sr<sup>+2</sup> > Ca<sup>+2</sup> > Mg<sup>+2</sup> > Li<sup>+</sup>. Clinoptilolite has a cation exchange capacity of at least 1.25 meq/g and was used in many ways as ion exchanger for wastewater treatment. An ion exchange capacity of 1.55 meq/g of a zeolite was registered in a study made in Mexico. In Chile, a zeolite made of clinoptilolite and mordenite showed an ion exchange capacity of 1.02 meq NH<sub>4</sub><sup>+</sup> g<sup>-1</sup>. Values of 8.149 up to 15.169 mg N/g were reported. Clinoptilolite has a great affinity for NH<sub>4</sub><sup>+</sup> in comparison with other cations abd is used, among other, as ion exchange resin to remove ammonia. The ion selectivity depends on the capacity of the hydrated cation to enter in the pores and canals, thing that depends on the cage nature, function of the Si/Al ratio value in clinoptilolite.

#### 5. CONCLUSIONS

The zeolites that were analyzed show structures that are characterized by large pores and large cavities that are suited to encapsulate big molecules, like porphyrines or metallo-porphyrins. The materials tha will be obtained after encapsulation will be tested as photocatalysts.

## 6. AKNOWLEDGEMENTS

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## REFERENCES

- [1] Ruren Xu, Wenqin Pang, Jihong Yu, Qisheng Huo, Jiesheng, Chemistry of Zeolites: Synthesis and Structure, Environmental Engineering and Management Journal, January/February 2008, Vol.7, No.1, 73-75.
- [2] Avelino Corma and Hermenegildo García, "A unified approach to zeolites as acid catalysts and as supramolecular hosts exemplified", J. Chem. Soc., Dalton Trans., 2000, 1381–1394.
- [3] Shizhong Wang, Ruomei Gao, Feimeng Zhou and Matthias Selke, Nanomaterials and singlet oxygen photosensitizers: potential applications in photodynamic therapy, J. M a t e r . C h e m . , 2 0 0 4 , 1 4 , 4 8 7 – 4 9 3 .
- [4] E. Chmielewska-Chorvatova, J. Lesny, J. Radioanal. Nucl. Chem. Lett., 1995, 201, 293.
- [5] O. Korkuna et al., Microporous and Mesoporous Materials, 2006, 87, 243–254.
- [6] T. Enhold, M. Sychrev, I.M. Astrelin, M. Rozwadowski, R. Gołębiewski, in: M. Rozwadowski (Ed.), Third Polish-Germany Zeolite Colloquium, Proceedings, Torun , Poland, April 3–5, 1997, Nicola Copernicus University Press, Torun, 1998, pp. 137–149.
- [7] M. Sychev, R.A. van Santen, in: M. Rozwadowski (Ed.), Third Polish-Germany Zeolite Colloquium, Proceedings, Torun, Poland, April 3–5, 1997, Nicola Copernicus University press, Torun , 1998, pp. 225–238.
- [8] Goto et al, Journal of Porous Materials, 2002, 9, 43–48.
- [9] S. Inagaki, Y. Yamada, and Y. Fukushima, Studies in Surface Science and Catalysis, 1996, 105, 109.
- [10] Javier Agúndez, Isabel Díaz, Carlos Márquez-Álvarez, Joaquín Pérez-Pariente and Enrique Sastre, High acid catalytic activity of aluminosilicate molecular sieves with MCM-41 structure synthesized from precursors of colloidal faujasite, CHEM. COMMUN., 2003, 150–151.