

## NEW STUDIES ABOUT THE MODIFIED MORDENITES\*

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Mordenite is one of the rarer, but still somehow more widespread, members of the zeolite group of minerals. It has an orthorhombic unit cell of topological space-group symmetry Cmc<sub>m</sub> ( $a = 18.13$ ;  $b = 20.5$ ;  $c = 7.52$  Å) with chemical formula: (Ca, Na<sub>2</sub>, K<sub>2</sub>)Al<sub>2</sub>Si<sub>10</sub>O<sub>24</sub>·7H<sub>2</sub>O (hydrated calcium sodium potassium aluminum silicate).

The structure of mordenite can be described as composed of edge-sharing five-membered rings of tetrahedra, forming chains along *c*-axis.

Natural mordenite occurs in rather large quantities in some altered vitreous tuffs. It has a characteristic fibrous habit and if finely crystalline it may be added to the group of asbestiform minerals causing lung diseases.

The aim of this work is to obtain some modified mordenites, by modifying the SiO<sub>2</sub>:Na<sub>2</sub>O molar ratio and the stirring time. We have synthesized five mordenites using SiO<sub>2</sub>:Na<sub>2</sub>O molar ratio between 2–10 and the stirring time between 2 and 4 hours. For all the samples the porous volume, the relative density, the absorptive properties and the X-ray diffraction were determined.

For the porous volume, we can observe that the smallest value was to the first mordenite (11.4 cm<sup>3</sup>/g) and the highest value for the five's mordenite (14.03 cm<sup>3</sup>/g).

The increasing of the porous volume determines an increasing of the density values and at the same time an increasing of the absorptive properties.

X-ray data were performed at room temperature with a 1400 Philips PW diffractometer, with Cu anticathode and Ni filtered.

*Key words:* zeolite, mordenite, porous volume, density, X-ray diffraction, absorptive properties.

### 1. INTRODUCTION

Mordenite is one of the most siliceous natural zeolites. It has an orthorhombic unit cell of topological space-group symmetry Cmc<sub>m</sub> ( $a = 18.13$  Å,  $b = 20.5$  Å,  $c = 7.52$  Å) with idealized chemical composition Na<sub>8</sub>Al<sub>8</sub>Si<sub>40</sub>O<sub>96</sub>·24H<sub>2</sub>O. The structure of mordenite can be describe as composed of edge-sharing five membered rings of tetrahedral (secondary building unit 5-1) forming chains along

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*c* axis [1]. However, the mordenite framework can also be more comprehensibly envisioned as composed of puckered sheets parallel to (100), made up of six membered rings of tetrahedral [2, 3]. These sheets are interlinked by four membered rings such that large, ellipsoidal twelve membered (12MRc: aperture  $7 \times 6.5 \text{ \AA}$ ) and strongly compressed eight membered rings (8MRc: aperture  $5.7 \times 2.6 \text{ \AA}$ ) define channels parallel to *c* axis. Another set of compressed eight membered rings (8MRc: aperture  $3.4 \times 4.8 \text{ \AA}$ ) connects the wide channels with strongly compressed channels parallel to *b*. At least for large extra framework ions and molecules mordenite has only a one-dimensional channel system for diffusion, [4]. The eight membered ring channels, running along *b*, which emerge from the wide tubes are staggered at the intersection with the strongly compressed channels (aperture  $5.7 \times 2.6 \text{ \AA}$ ) before they end again in the wide tubes. Extra framework cations in mordenite mainly occupy three sites. Two of these sites are close to the four membered rings and are located in the connecting channels parallel to *b* axis. Another cation position is located at the center of the main twelve ring channels, [3].

Natural mordenite occurs in rather large quantities in some altered vitreous tuffs. It has a characteristic fibrous habit and if finely crystalline it may be added to the group of asbestiform minerals causing lung diseases, [5], and [6].

Mordenite is also synthesized in large quantities, mainly for industrial application as a catalyst. From a technical point of view two different varieties of mordenite are distinguished, [7]. Large-port mordenite exhibits the properties predicted for a zeolite with accessible twelve membered ring channels: (1) molecules with a diameter  $> 4.5 \text{ \AA}$  can be introduced into the large channels; (2) the  $\text{NH}_4^+$  and H-exchanged forms are able to crack significant amounts of hexane at  $450^\circ\text{C}$ . Largeport mordenite is hydro thermally synthesized in the Na-form between  $175$  and  $260^\circ\text{C}$ . Small port mordenite accepts only molecules with a diameter  $< 4.2 \text{ \AA}$  and is thus less favorable for industrial applications. Small port mordenite are usually obtained under hydrothermal synthesis conditions between  $275$  and  $300^\circ\text{C}$ , [7]. In addition, most natural mordenites have properties characteristic of small-port mordenite.

## 2. EXPERIMENTAL METHODS

For structural analysis synthetic mordenites being obtained by two different methods were used.

### Method I.

Synthetic mordenite samples were synthesized using an aluminosilicate gel obtained by mixing sulphate solution with hydroxysilica. After crystallization the obtained mordenites were filtered, and washed with bidistilate water. The sample was dried for 4 hours at  $100\text{--}110^\circ\text{C}$  and calcinated for three hours at  $400^\circ\text{C}$ .

### Method II.

The mordenite samples were synthesized using same aluminosilicate gel, but it was mixed for about 2 h and 40 min. For the crystallization 7 days were used. Mordenites were filtered, and washed with bidistillate water. The samples were dried for 2 hours at 100–110°C and calcinated for six hours at 500°C.

After that, the samples were studied with a polarizing microscope and the single crystal were examined with a scanning electron-microscope and showed well-defined, but slightly curved faces and no apparent twinning. The average size of the mordenite crystals was about  $0.06 \times 0.05 \times 0.05$  mm. The chemical composition of the synthetic mordenite determined by electron-microscope was  $\text{Na}_6\text{Al}_6\text{Si}_{42} \cdot n\text{H}_2\text{O}$ . The Si/Al ratio of 7/1 is in exact agreement with the analytical data given by Warzywoda, [8], for their synthesis mordenite obtained under corresponding conditions. According to Sand the applied synthesis conditions (175°C and excess of sodium silicate) should lead to large-pore mordenite. This property was tested by ion exchange with diluted solutions of bulky, organic dye molecules such as methylene blue ( $\text{C}_{16}\text{H}_{18}\text{N}_3\text{S}^+$ ), thionine blue ( $\text{C}_{12}\text{H}_{10}\text{N}_3\text{S}^+$ ), DAMS<sup>+</sup> ( $\text{C}_{16}\text{H}_{19}\text{N}_2\text{S}^+$ ) and benzothiazole dye ( $\text{C}_{11}\text{H}_{14}\text{NS}^+$ ). Successful incorporation of dye ions could be monitored by polarized light microscopy showing characteristic colors and pleochroism of the individual crystals, [9].

X-ray data collection of the fibrous natural mordenite ( $0.05 \times 0.05 \times 0.3$  mm, elongated parallel to *c* axis) sample was performed at room temperature with an 1400 Philips PW diffractometer using graphite monochromatic  $K_\alpha$  radiation. Data reduction, including Lorentz and polarization correction, was performed with the SDP program package.

X-ray data collection of the synthetic mordenite was performed at room temperature with synchrotron radiation ( $\lambda = 0.70192$  Å) on the single crystal diffraction line where diffracted intensities were registered with a MAR image plate. In the single crystal diffraction pattern of the synthetic mordenite sample, measured by synchrotron radiation, 75 reflections were observed which should be systematically absent, all with *hkl* values of  $h + k = 2n$  and  $l = 2n + 1$ . Observation of these forbidden reflections is an artifact related to the frame-integration procedure and coincides with the diffuse scattering described below.

In the same time the RMN spectra were plotted using an AVANCE 400 MHz spectrometer at 9.35 T.

## 3. RESULTS AND DISCUSSION

For analyzing the mordenite samples that we have obtained, we determined the porous volume, the density, the RMN spectra and X-ray spectra.

In order to establish the porous volume, the calculation relation is:

$$V_p = \frac{8V_1}{G_1}, \text{ (cm}^3\text{/g)}$$

where:  $V_p$  is porous volume,  $V_1$  is water volume and  $G_1$  is the catalyst weight.

The results are presented in the Table 1.

Table 1

Porous volume for mordenite samples

Mordenite	Molar ratio SiO <sub>2</sub> :Na <sub>2</sub> O	$V_p$ [cm <sup>3</sup> /g]
M-1	2	11.41
M-2	4	12.08
M-3	6	12.62
M-4	8	13.02
M-5	10	14.03

One can observe an increase of porous volume for the mordenite samples, the highest value being for the M-5 mordenite.

We have also determined the density value, using the formula:

$$\rho = \frac{m_1}{V_1 - \frac{m_2 - m_3 - m_1}{d}},$$

where:  $V_1$  is the balloon-flask volume,  $m_2$  – final weight of the balloon-flask,  $m_3$  – the weight of the empty balloon-flask,  $m_1$  – the weight of the catalyst sample and  $d$  – water density at 25°C.

The density values are presented in Table 2.

Table 2

The density values for the mordenite samples

Mordenite	$\rho$ [g/cm <sup>3</sup> ]
M-1	2.1094
M-2	2.1139
M-3	2.1251
M-4	2.1383
M-5	2.1572

We can see the increase of the density values; the highest value is for the M-5 mordenite and the smallest for the M-1 mordenite.

From X-ray data one can observed the existence of characteristic mordenite phases' picks at  $2\theta$  angle: 14.5 for M-1, 14.7 for M-2, 15 for M-3, 17 for M-4 and for M-5 17.2. These values are in good agreement with literature data.

In figure nr. 1–5 the X-ray spectra are presented and from the curves we can presume that we had a mixture of crystalline and amorphous phases.

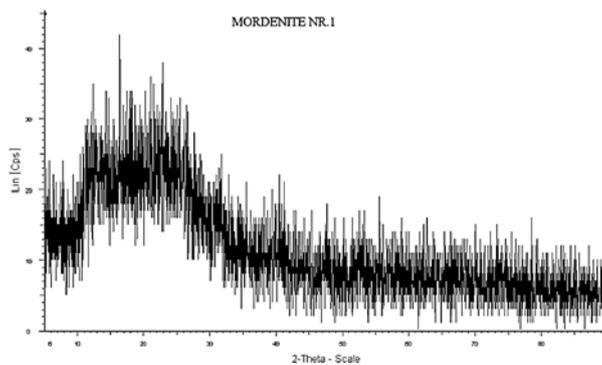


Fig. 1 – X-ray spectra for M-1 sample.

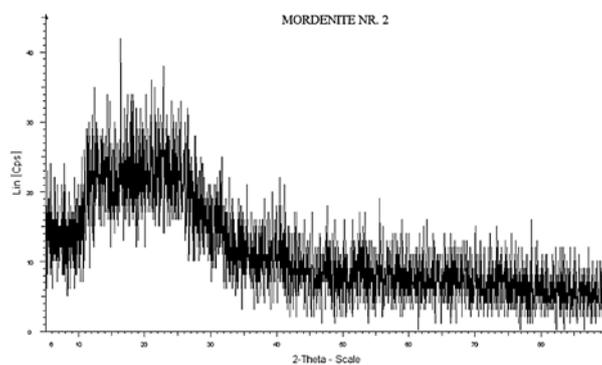


Fig. 2 – X-ray spectra for M-2 sample.

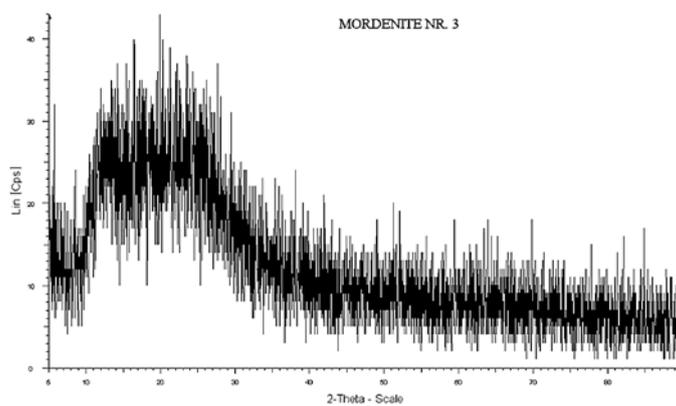


Fig. 3 – X-ray spectra for M-3 sample.

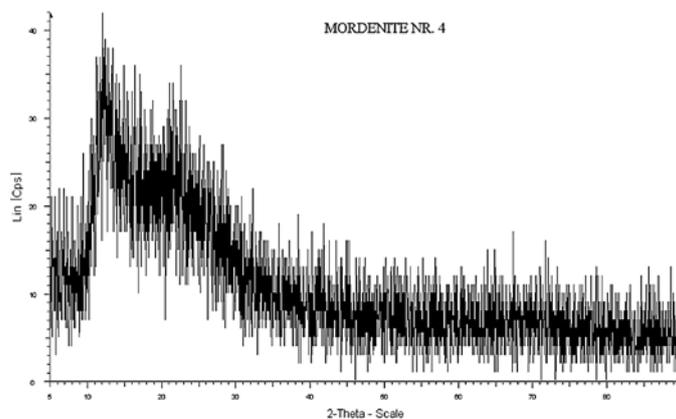


Fig. 4 – X-ray spectra for M-4 sample.

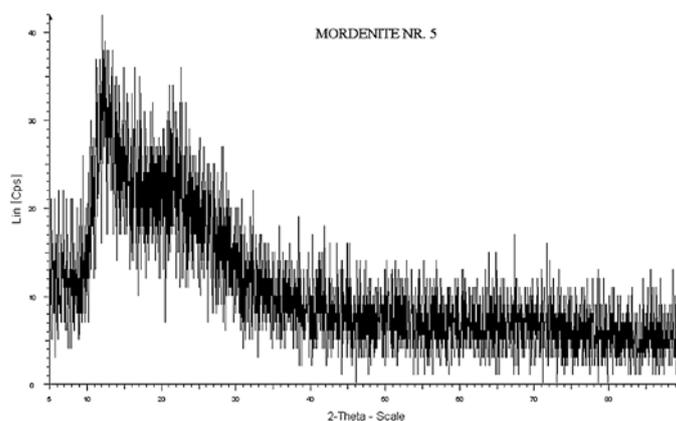
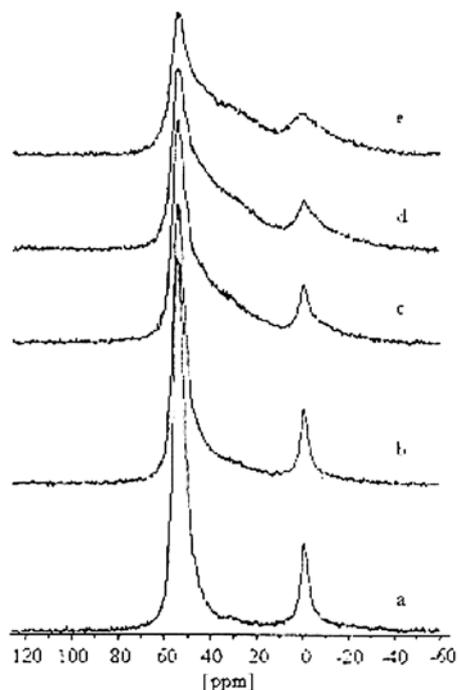


Fig. 5 – X-ray spectra for M-5 sample.

The RMN spectra were plotted using an AVANCE 400 MHz spectrometer at 9.35 T and the results confirmed the crystalline mordenite structure. The spectra are presented in Fig. 6.

The X-ray single-crystal diffraction pattern from the synchrotron data show sharp Bragg reflections, but there are also diffusing intensities modulating the background of selected sharp peaks. To visualize the diffuse scattering, reciprocal space reconstructions of  $hk0$ ,  $hk1$ ,  $hk3$ ,  $h0l$ ,  $h1l$ ,  $h2l$ ,  $0kl$ , and  $2kl$  layers were calculated using a software package. Generally speaking, diffuse scattering is absent in all reciprocal layers with  $\ell = 2n$ , *e.g.*, in  $hk0$  and  $hk2$ . Diffuse scattering is also absent in the  $h2l$  layer. Layers of the type  $hkl$  with  $\ell = 2n + 1$  are diffuse where the diffuseness is not homogeneous but particularly concentrated around selected  $hkl$  reflections with  $h + k = 2n$ , (in the layers  $hk1$  and  $hk3$  of synthetic mordenite). Scattering is most accentuated around the reflections 511

Fig. 6 – The RMN spectra for mordenite samples.



in  $hk1$ , and 713, 443, 593 in  $hk3$ . If the diffuse sheets with  $\ell = 2n + 1$  are viewed in  $0kl$ ,  $1kl$  and  $2kl$  reciprocal layers the diffuse sheets appear as diffuse streaks parallel to  $b$  decorated by sharp Bragg reflections. If the diffuse sheets with  $\ell = 2n + 1$  are viewed, *e.g.*, in  $h0l$  reciprocal layers the diffuse sheets appear as diffuse maxima smeared along  $a$  at  $h = 2n + 1$  and  $\ell = 2n + 1$ . Notice the streaked intensities at 501, 703, 505, etc. Corresponding intensities have been observed before in electron diffraction studies and were as evidence for domains of centered symmetry, [10, 16]. These fake reflections are artifacts caused by the diffuse smearing of reflections in  $b$  adjacent layers. No reflections should occur in  $h0l$  layers at  $\ell = 2n + 1$  because of the  $c$ -glide in (010) for space group  $Cmcm$  or  $Cmc2$ . The observed smeared maxima are diffuse residuals of the halos around the reflections in adjacent  $h1l$  layers (*e.g.*, reflections 511 and 713). Diffuse streaks or maxima in  $0kl$  or  $h0l$  layers are just traces of the diffuse  $hkl$  layers with  $\ell = 2n + 1$ .

From T-O-T angles we observed that distortions within the tetrahedral framework structure are very similar for synthetic and natural mordenite. Major differences occur only for angles within the four membered rings. These angles are ca.  $3^\circ$  larger in the synthetic mordenite than in natural mordenite. Removing O8 from the inversion center and splitting it into four 23% occupied sites reduced the T2-O8-T2' angle from  $180^\circ$  to  $150\text{--}165^\circ$ .

We observed a significant difference in Si,Al order between synthetic and the natural mordenite, judging from the average T-O bond length. The T1-O and T2-O bond lengths of the synthetic crystal are slightly larger than for the natural one. The T3-O and T4-O bond lengths of the natural crystal are slightly larger than for the synthetic one. T1 and T2 tetrahedral assemble the puckered (100) sheets whereas T3 and T4 tetrahedral belong to the four membered rings connecting the sheets to a framework. It has been shown, [11, 12], that Jones relationship ( $Al = 6.4116 T-O - 10.282$ ) fails to predict reliable Al concentrations for mordenite, [13]. Actually, the Jones relationship yields 4.36 Al p.f.u. (measured 7.89 Al p.f.u.) for the natural crystal and 4.82 Al p.f.u. (measured 6.02 Al p.f.u.) for the synthetic one, [13]. We have also applied a riding correction (Johnson 1970) for T-O bond length, due to rigid vibration disorder of  $TO_4$  moieties, [14]. However, the T-O riding correction is very similar for both structures. That can not explain the drastic Al underestimation for the natural crystal. The analytically determined extra framework-cation content of the natural mordenite sample was  $K_3Ca_{1.8}Na_{1.07}$  whereas the composition  $K_{2.8}Ca_{1.8}Na_2$  was obtained from the structure refinement. The excess of refined Na may be explained by some Na/ $H_2O$  disorder. Ca is situated in the center of strongly compressed eight membered channel and has short distances to the framework O atoms and bonds twice to  $H_2O$  molecule W1 with an angle of  $180^\circ$ . If we further assume that the site assignment of Ca is correct than ca. 4.8 positive charges p.f.u. remain in 12MRc and are easily accessible for cation exchange, [11, 15]. K1 (1.35 p.f.u.) is split into K1a (population 0.24) and K1b (population 0.10), separated by 0.7 Å along *c* axis. These sites are not bonded to the tetrahedral framework but are surrounded by strongly disordered  $H_2O$  in 12MRc whereas K3 occupies pockets, which are defined as the transit from 12MRc to 8MRb. Na2a and K2b are separated by 1.3 Å along the *c* axis. K2b appears to be a satellite position indicating translational disorder along the *c* axis. Na2a has no bonds to the tetrahedral framework whereas K2b bonds twice to O2 (2.70 Å) and once to O10 (2.63 Å). The K3 site was identified by the long distances to the framework with two bonds to O5 (3.05 Å) and one bond to O2' (3.1 Å).

The synthetic mordenite sample has 6 Na in the channel system, whereas 5.5 Na p.f.u. were located by the structure refinement. With 2.2 Na1 p.f.u. located in the strongly compressed 8MRc, ca. 3.8 positive charges are in 12MRc. In contrast to the Ca site in the natural sample the corresponding Na1 site in the synthetic sample is shifted from the special position and has four short bonds to the tetrahedral framework. Na<sub>2</sub> and Na<sub>3</sub> are not bonded to the tetrahedral framework but are surrounded by strongly disordered  $H_2O$  in 12MRc and only Na4a,b occupy the pocket at the transition to 8MRb but without short bonds to the framework.

#### 4. CONCLUSIONS

Five synthetic mordenites were synthesized using two different methods.

For these mordenites the porous volume, the density values, the X-ray diffraction and the RMN spectra were determined. The highest values for porous volume and density were recorded for the M-5 mordenite.

X-ray spectra show that we have a mixture of crystalline and amorphous phases.

The RMN spectra were confirmed only the crystalline mordenite structure.

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