

PHYSICO-CHEMICAL STUDIES ON CATION-EXCHANGED MORDENITES. I. THERMOGRAVIMETRIC ANALYSIS AND MICROSTRUCTURE

S. A. ABO-EL-ENEIN, R. SH. MIKHAIL AND H. A. EL-WAKIL*

Department of Chemistry, Faculty of Science, Ain Shams University, Cairo (Egypt)

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ABSTRACT

In the present study, various transition metal cationic forms of mordenites were prepared. The results of chemical and thermogravimetric analysis could be used to derive the chemical formulae of these mordenites. The indication gained from thermogravimetric studies both in vacuo and in air is that the high vacuum procedure causes a partial collapse in the mordenite structure and this effect is connected with the degree of reversibility of water loss and water re-uptake by the various mordenite samples.

The scanning electron micrographs showed that the exchangeable cations do not affect the microcrystals of these mordenites but their effect is mainly restricted to the intracrystalline regions and the amorphous character of the microcrystallites.

INTRODUCTION

Mordenite is one of the zeolite family which has a high silica to alumina mole ratio and shows a great thermal stability after dehydration as well as acid resistance¹. Crystal structure studies²⁻³, as obtained from X-ray and electron diffraction examinations, showed that the mordenite is orthorhombic with prevailing space group *Cmcm*. The unit cell of sodium mordenite has the dimensions $a = 18.13$; $b = 20.49$; $c = 7.52$ Å and the chemical formula is $\text{Na}_{28}\text{Al}_{18}\text{Si}_{140}\text{O}_{96} \cdot 24\text{H}_2\text{O}$. Its molecular sieve property is attributed to a system of large elliptical channels parallel to [001] having a free diameter of 6.95 Å, and being interconnected by smaller channels parallel to [010] of 2.8 Å free diameter. Some of the cations in mordenite are thought to be located in these channels.

Despite the sufficient intensity of research work devoted to zeolites, surprisingly very little is directed to the mordenite type zeolite regarding the essential structure and physico-chemical characteristics that determine the basic events in their applicability as adsorbents as well as effective and selective catalysts in many reactions.

* Present address: Basic Science Department, Faculty of Petroleum and Mining Engineering, Suez Canal University, Suez, Egypt.

In recent years, scanning electron microscopy (SEM) has been extensively used. The simple sample preparation techniques together with the large depth of focus makes it a very useful tool for the study of the morphological characteristics of various solids.

The object of the present investigation is to study the dehydration and rehydration of synthetic sodium mordenite and their transition metal cationic forms. Correlating the differences in thermal behaviour to the differences in chemical composition and the conditions under which the dehydration-rehydration processes take place is of prime importance. Also it is aimed to throw some light on the morphological and microstructural characteristics of the synthetic sodium mordenite together with its transition metal cationic forms.

EXPERIMENTAL

The starting material used in this investigation was the synthetic sodium mordenite $\text{Na}_2(\text{AlO}_2)_2(\text{SiO}_2)_{10} \cdot 7\text{H}_2\text{O}$. Five transition metal cationic forms (Cr^{2+} , Mn^{2+} , Co^{2+} , Ni^{2+} , and Cu^{2+}) were prepared from the original sodium mordenite by cation exchange processes. The exchangeable cation content was determined by analyzing for the cations in their aqueous solutions before and after the exchange process⁴. The results of chemical analysis as well as the proposed chemical formulae for all of the dehydrated samples are given in Table I.

Thermogravimetric analysis (TGA) was carried out using silica spring balances of McBain-Bakr type⁵; the balances having sensitivities ranging between 300–400 mm g^{-1} and carrying very light buckets containing the samples. The silica spring

TABLE I

THE WEIGHT PERCENT OF THE EXCHANGED CATIONS AND THE PROPOSED CHEMICAL FORMULA FOR THE VARIOUS ANHYDROUS MORDENITE SAMPLES

<i>Sample</i>	<i>Weight percent of the exchanged cations</i>	<i>Proposed chemical formula (dehydrated)</i>
Original synthetic sodium mordenite (Na-M)	—	$\text{Na}_2(\text{AlO}_2)_2(\text{SiO}_2)_{10}$
Chromium sodium mordenite (Cr-Na-M)	4.5	$\text{Cr}_{0.25}\text{Na}_{1.75}(\text{AlO}_2)_2(\text{SiO}_2)_{10}$
Manganese sodium mordenite (MnNa-M)	4.2	$\text{Mn}_{0.21}\text{Na}_{1.79}(\text{AlO}_2)_2(\text{SiO}_2)_{10}$
Cobalt sodium mordenite (CoNa-M)	2.7	$\text{Co}_{0.135}\text{Na}_{1.865}(\text{AlO}_2)_2(\text{SiO}_2)_{10}$
Nickel sodium mordenite (NiNa-M)	2.2	$\text{Ni}_{0.11}\text{Na}_{1.89}(\text{AlO}_2)_2(\text{SiO}_2)_{10}$
Copper sodium mordenite (CuNa-M)	0.7	$\text{Cu}_{0.035}\text{Na}_{1.965}(\text{AlO}_2)_2(\text{SiO}_2)_{10}$

balances were enclosed in pyrex glass tubes attached to a vacuum line. Heating was carried out by means of a small electrical tubular furnace, the temperature of which was regulated so as to increase linearly with time at a rate of $3.0\text{--}3.5\text{ }^{\circ}\text{C min}^{-1}$. The readings were taken with the aid of a cathetometer, reading to 0.01 mm .

A Leitz - AMR 1000 (West Germany) scanning electron microscope was used in this investigation. In the present study, the hydrated mordenite samples were dried in a nitrogen atmosphere (free from CO_2) at $60\text{ }^{\circ}\text{C}$ for 24 h in order to remove the moisture. Freshly fractured specimens were placed in a vacuum evaporator with cathode rays and coated with a thin layer of gold of about $300\text{--}400\text{ \AA}$ thickness. The specimens were then stored in a desiccator prior to SEM examination.

X-ray diffraction patterns were obtained by means of a philips X-ray diffraction unit using a silicon crystal as an internal standard for the d -spacings produced.

RESULTS AND DISCUSSION

Dehydration in air

The results of TG in air on all investigated samples are graphically represented in Fig. 1 in terms of the percentage loss at different temperatures based on the dry weight.

From these results, it was found that as the temperature rises the water loss increases. The rate of dehydration seems to be accelerated in the low temperature

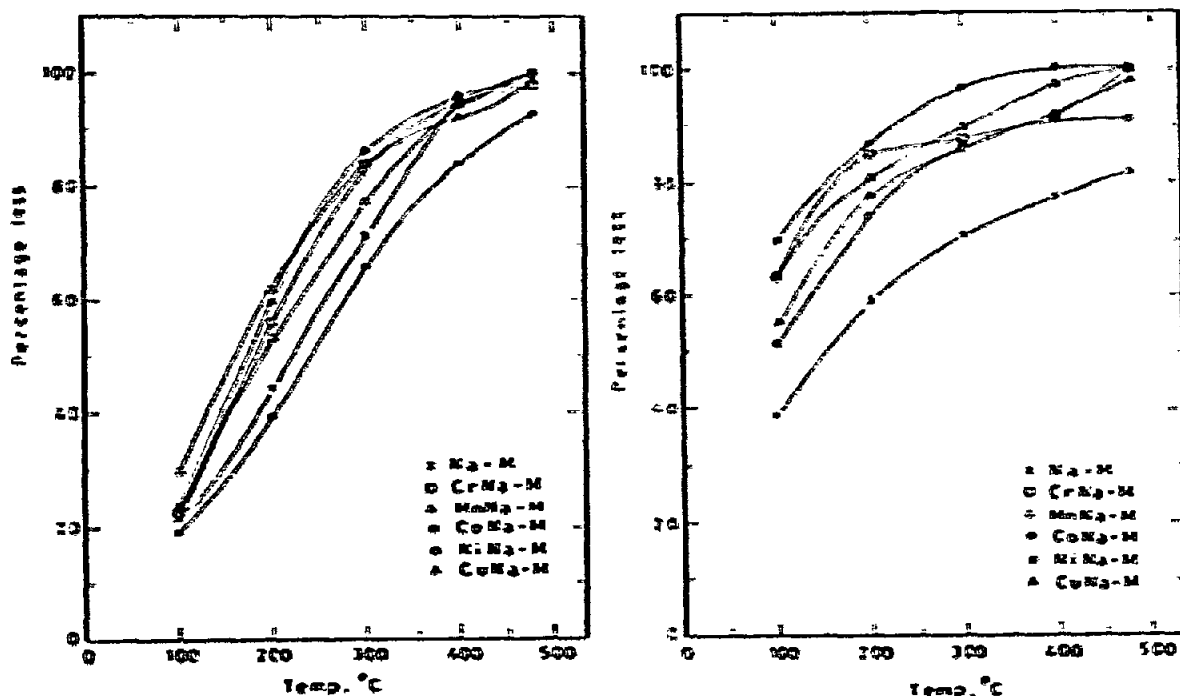


Fig. 1. Percentage loss for the various mordenite samples heated in air.

Fig. 2. Percentage loss for the various mordenite samples heated in vacuo.

range and then proceeds at a smaller rate in the high temperature range. All the samples were found to lose about 19-30% of their zeolitic water upon heating at 100°C. With increase in temperature, the original (Na-M) together with (MnNa-M) and (NiNa-M) samples were found to lose 100% of their zeolitic water upon heating at 480°C, whilst the (CrNa-M), (CuNa-M), and (CoNa-M) samples lose only 98, 99 and 93% respectively.

Dehydration in vacuo

The results of TG in vacuo are shown in Fig. 2. These results indicate that, similar to dehydration in air, the water loss increases as the temperature rises. All the samples were found to lose 51-70% of their zeolitic water upon heating at 100°C except the original (Na-M) sample which loses only 39% of its water. By increasing the temperature to 480°C, it was noticed that (CrNa-M), (CoNa-M), and (MnNa-M) samples lose 100% of their zeolitic water, whilst the original (Na-M), (CuNa-M), and (NiNa-M) samples lose 82, 98 and 91% respectively. Figure 2 shows also that unlike all other samples, the (CrNa-M) sample loses a very small fraction of its zeolitic water in the temperature range 200-300°C.

From the results of thermogravimetric analysis both in air and in vacuo, some interesting observations were drawn which could be summarized as follows.

(i) The water loss in vacuo is larger than that in air especially in the low temperature range (i.e. vacuum procedures accelerate the dehydration, especially at low temperature). Therefore, the difference between vacuum and air dehydration is appreciable only in the low temperature range and decreases with rise of temperature until they both become almost the same at 480°C for most samples.

(ii) In some particular cases, however, the water loss in air exceeds that in vacuo, and this is seen to take place in the high temperature range (400-480°C). The results shown in Fig. 1 and 2 indicate clearly this effect for the original (Na-M) sample together with its Mn^{2+} and Ni^{2+} exchanged forms. This effect might be attributed to a partial collapse in the mordenite structure due to the high vacuum procedure at high temperatures — a phenomenon which may be tentatively explained as follows: in the lower temperature ranges, the cations of the mordenite structure still retain some of their water of hydration, and thus they are free to migrate in the mordenite channels, while at higher temperatures, a higher degree of the dehydration is attained, and the dehydrated cations rest still in the channel walls, and in so doing they block some of the pockets which are located at right angles to the main channels. This might hinder the removal of some of the zeolitic water molecules which are located within these pockets.

(iii) The molecular formulae for the various hydrated mordenite samples investigated could be derived from the results of TGA together with that obtained from chemical analysis. These formulae were found to be



TABLE 2

WATER LOSS AS COMPARED WITH WATER RE-UPTAKE FOLLOWING THE DEHYDRATION IN VACUO AND IN AIR

Sample	Loss at 480°C in vacuo (No. of molecules/g) ($\times 10^{21}$)	Uptake in vacuo (No. of molecules/g) ($\times 10^{21}$)	Loss at 480°C in air (No. of molecules/g) ($\times 10^{21}$)	Uptake in air (No. of molecules/g) ($\times 10^{21}$)
Na-M	4.63	0.78	5.65	5.39
CrNa-M	5.54	1.42	5.44	5.18
MnNa-M	5.77	0.86	5.89	5.61
CoNa-M	5.33	2.07	4.96	3.89
NiNa-M	6.77	1.08	6.71	5.98
CuNa-M	5.95	2.43	5.88	3.92

(c) (MnNa-M): $\text{Mn}_{0.34}\text{Na}_{1.33}(\text{AlO}_2)_2(\text{SiO}_2)_{10} 7.50 \text{ H}_2\text{O}$

(d) (CoNa-M): $\text{Co}_{0.21}\text{Na}_{1.59}(\text{AlO}_2)_2(\text{SiO}_2)_{10} 6.79 \text{ H}_2\text{O}$

(e) (NiNa-M): $\text{Ni}_{0.17}\text{Na}_{1.77}(\text{AlO}_2)_2(\text{SiO}_2)_{10} 7.22 \text{ H}_2\text{O}$

(f) (CuNa-M): $\text{Cu}_{0.05}\text{Na}_{1.90}(\text{AlO}_2)_2(\text{SiO}_2)_{10} 7.53 \text{ H}_2\text{O}$

Water loss vs. water uptake, reversibility considerations

As a general remark, it was noticed that the water loss both in vacuo and in the presence of air was not regained reversibly when the same sample was re-exposed to air saturated with water vapour. Experiments have shown that the loss of water during heat treatment is always greater than the water re-uptake, and the differences vary whether dehydration was carried out in vacuo or in the presence of air.

A typical set of data are shown in Table 2. The data were obtained by heating the various mordenite samples at 480°C for 2 h, both in vacuo and in the presence of air, determining the water loss, then exposing the samples to air saturated with water vapour, leaving them until equilibrium, and the reuptake of water was then determined.

The data clearly show that the dehydration in vacuo causes some irreversible change in the mordenite structure which impedes rehydration by water vapour. The impedance effect was much reduced when heating was carried out in the presence of air. Heating in vacuo produced some collapse of the mordenite structure as already indicated.

Morphology and microstructure

The micrographs obtained from scanning electron microscope (SEM) for the various mordenite samples indicate some interesting features which may be presented as follows.

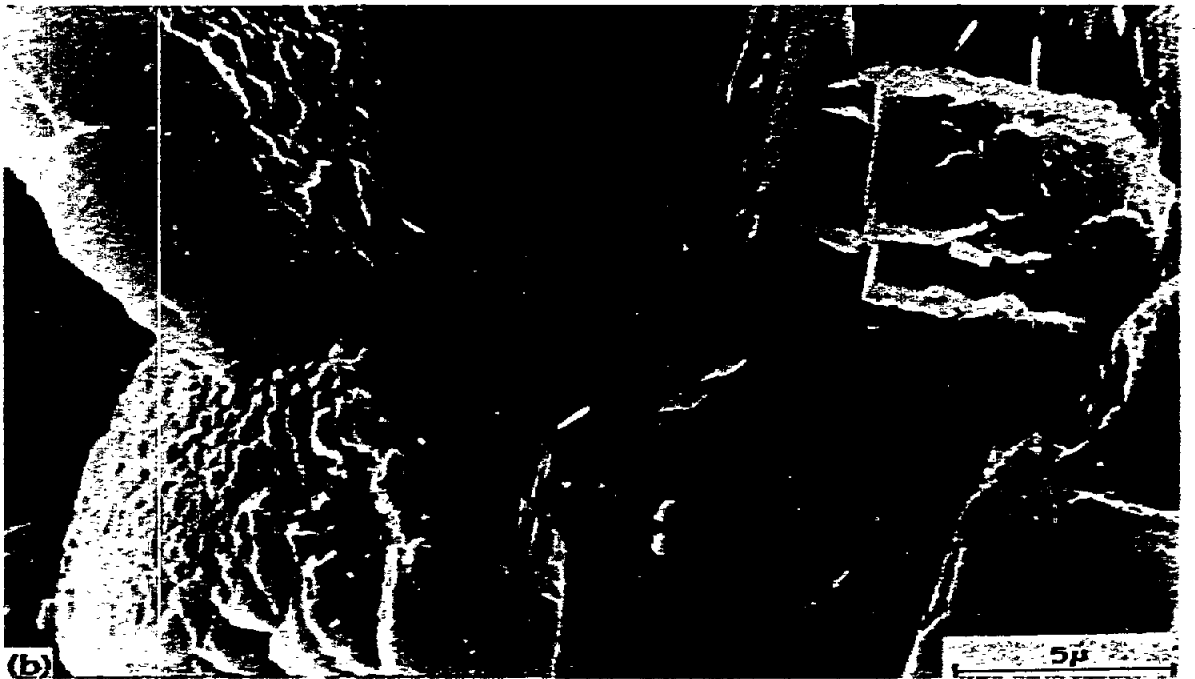


Fig. 3. SEM micrographs for Na-M.

Original synthetic sodium moräenite (Na-M). The microstructure of the (Na-M) sample showed the trapezohedral crystals (icositetrahedra) with indices hll and 24 faces, as indicated from Fig. 3(a); these crystals belong to the cubic system of the whole symmetrical class. There also appeared orthorhombic prisms with basal

pinacoids together with stacked orthorhombic bipyramid crystals and microcrystals with semi-amorphous character [cf. Fig. 3(a) and (b)].

Chromium sodium mordenite (CrNa-M). The microstructure of this sample displayed the trapezohedral crystals with orthorhombic bipyramid crystals showing

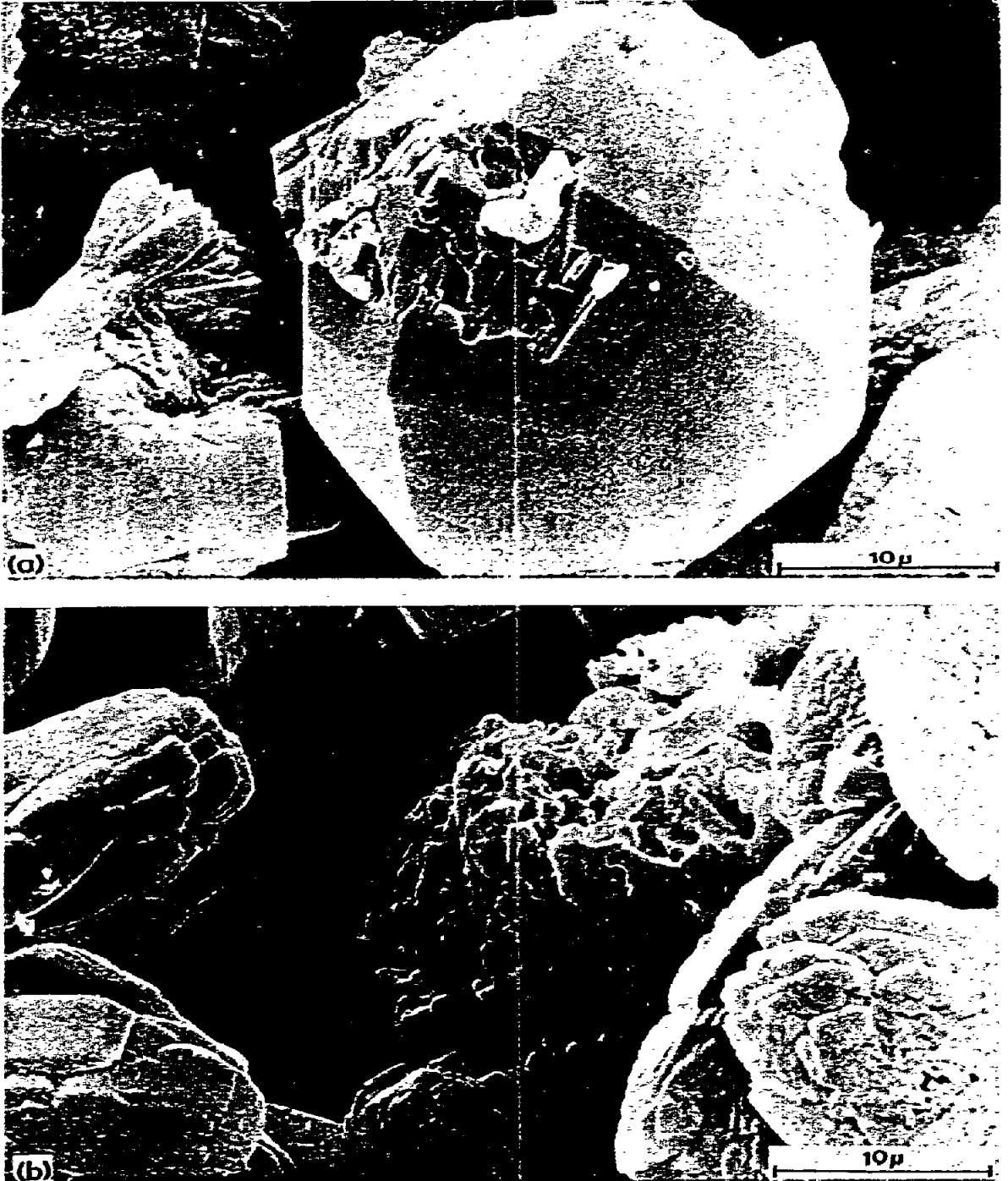


Fig. 4. SEM micrographs for CrNa-M.



Fig. 5. SEM micrographs for MnNa-M.

an oriented morphology as indicated from Fig. 4(a). The stacked crystals of sheet-like forms and orthorhombic prisms become more dominant with an intersecting morphology of microcrystallites [cf. Fig. 4(a) and (b)].

Manganese sodium mordenite (MnNa-M). The morphology and microstructure

of this sample show the existence of trapezohedral crystals together with orthorhombic bipyramid crystals in Fig. 5(a). Radiating and stacking bundles of sheet-like crystals appear also in the structure. There appeared also cubic and orthorhombic prisms stacked and agglomerated together leading to a stacking and intersecting morphology (cf. Fig. 5).



Fig. 6. SEM micrographs for CoNa-M.

Cobalt sodium mordenite (CoNa-M). The microstructure of this sample exhibited trapezohedral crystals, stacked prisms and microcrystallites. Long and stacked orthorhombic prisms, rods and sheets together with microcrystallites also appeared in the structure (cf. Fig. 6).



Fig. 7. SEM micrographs for NiNa-M.

Nickel sodium mordenite (NiNa-M). The microstructure of the (NiNa-M) sample displayed the trapezohedral crystals and the orthorhombic prisms with basal pinacoids as well as oriented orthorhombic bipyramids. There also appeared in the structure, a mixture of stacked orthorhombic bipyramids, orthorhombic prisms and microcrystallites as well as parallel sheets (cf. Fig. 7).



Fig. 8. SEM micrographs for CuNa-M.

Copper sodium mordenite (CuNa-M). In this sample the stacked sheets and the intertwined orthorhombic bipyramids make their appearance together with the trapezohedral crystals. The semi-amorphous crystallites are also present in the structure (cf. Fig. 8).

Evidently the SEM micrographs obtained for the hydrated original synthetic sodium mordenite and its cation-exchanged forms, display almost the same morphology with respect to the large main crystals but differ in the microcrystals within and beside the large crystals. The amorphous character of these mordenite samples varies with the nature of the cation used in the exchanged samples. Therefore, these cations cannot affect the macrocrystals of mordenite but their effect is only restricted to the microcrystallites and the near-amorphous part of the structure.

From X-ray analysis of the various mordenite samples, it has been found that the diffraction patterns of the cation-exchanged forms contain all the lines appearing in the diffraction pattern of the original sodium mordenite sample with only one basic difference, namely, the degree of amorphous character which increases in the presence of the various transition metal cations present in the structure. The results of X-ray show also that the presence of different exchangeable cations does not affect the main crystal structure of mordenite since all the X-ray patterns obtained show the same values of *d*-spacings.

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