DEALUMINATION OF ZEOLITES WITH VOLATILE REAGENTS. MODIFICATION OF THE ADSORPTION PROPERTIES OF HUNGARIAN NATURAL ZEOLITES WITH PHOSGENE*

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A novel dealuminating procedure was applied to natural mordenites and clinoptilolites originating from the Tokaj Mountain deposits in Hungary, and the ensuing changes in composition, structure and adsorption properties were assessed. The highest adsorption capacity was attained at a dealumination temperature of 873 K; this was a result of the removal of impurities and bulky cations while near perfect crystallinity was maintained. Crystallinity was retained up to 1073 K in the case of mordenite, whereas clinoptilolite underwent loss of crystallinity above 873 K. The immersion wetting enthalpies decreased monotonously due to the increasing hydrophobicity. The procedure seems to be promising for the production of zeolites with varying surface energies.

Introduction

Among the mineral resources of Hungary, the natural zeolites occurring in and near the Tokaj Mountains are playing an ever increasing role. Besides the efforts to synthesize "tailor-made" zeolites for the petrochemical and organic industries, extensive research is being carried out to widen the field of application of the natural zeolites, too [1]. In this respect promising results have been achieved in their use for the adsorptive purification of gaseous exhausts (*e.g.* environmental protection [2]), air separation [3] and agricultural application (upgrading of soils [4], animal breeding, etc.).

NEMECZ and VARJÚ first reported on the clinoptilolite deposits in the Tokaj Mountains in the early 1960's [5]. Since that time a great number of papers have dealt with the structures, compositions and potential uses of mordenite- and clinoptilolite-bearing sediments [6—11]. Recently, a conference was organized on these topics [12].

It is well known that natural zeolites crystallized in a saline environment from volcanic sediments and, depending on the circumstances, contain various amounts of impurities in the form of crystalline minerals and amorphous constituents (volcanic glass, etc.). For practical applications, some sort of pretreatment (grinding, ion-exchange, etc.) is indispensable. Among the possible modifications influencing adsorption, ion-exchange, etc., the different dealuminating procedures are of paramount importance [13].

If a proportion of the framework aluminium is dissolved or removed the thermal and hydrothermal stability of zeolites is influenced beneficially. In the process the electronegativity of the framework increases, rendering the Brönsted centres more acidic. Simultaneously, the dealuminating agents remove most of the impurities blocking the interconnecting windows between the large cavities and/or pore entrances.

A dealuminating procedure developed at the Applied Chemistry Department of József Attila University [14—15] has been used to investigate natural mordenites and clinoptilolites from the aspects of their compositions, structures and adsorption properties.

Experimental

The specimens under study were sediments from the Tokaj Mountains, containing mordenite and clinoptilolite in various amounts.* The zeolite-bearing rocks were crushed and sieved. The sieve fraction of 1.0—1.6 mm was used subsequently. Its composition was determined by measuring the NH_3 content of the NH_4^+ forms obtained after multiple ion-exchange with NH_4Cl solution [10]. For the mordenite and clinoptilolite sediments, a mordenite content of 31% and a clinoptilolite content of 48% resulted. Quartz, clay minerals and volcanic glass constituted the non-zeolitic impurities.

The dealumination was carried out in a tube reactor made of quartz, with phosgene ($COCl_2$) and a 1:1 mixture of CO and Cl_2. No significant difference could be observed in the effectiveness of the agents, because phosgene decomposition reached 50% at 773 K and completeness at 1073 K [16].

Prior to dealumination, the samples were heat-treated at 773 K in a stream of N_2 for 2 h. Thereafter, the dealumination followed at the preselected temperature (between 773 K and 1073 K) in a stream of $COCl_2$ (rate of flow: 20 cm³/min) for 2 h. The gas stream was next changed again: the flow of N_2 was maintained for a further 2 h in order to desorb the products. The cool sample was washed free of Cl^- ions and dried at 390 K.

The volatile metal halides (from the impurities and metal ions in ion-exchange and framework positions, respectively) produced a fall-out after the reactor tube. This was dissolved and analysed for Al^{3+} (by complexometry) and Fe^{3+} (spectrophotometry). The same ions were determined in a caustic melt of the non-treated samples.

Structural changes in the treated samples were assessed by X-ray diffraction and i.r. spectroscopy. X-ray diffractions were registered in the interval $3° < 2\theta < 34°$ using a Dron—3 diffractometer. The i.r. spectra were recorded on KBr pressed pellets containing 0.5% zeolite, on a Specord IR—75 instrument.

Water contents were determined by thermogravimetry with a MOM—Q Derivatograph. Adsorption of N_2 was measured volumetrically at 77 K on samples heat-treated at 507 K under continuous pumping. The immersion wetting enthalpies were measured in an LKB—2107 sorption microcalorimeter at 298 K after appropriate pretreatment.

Results and discussion

The amounts of Al and Fe removed by dealumination are plotted in Figs. 1 and 2 as functions of the temperature. Table I contains the same data as percentages of the original contents.

In contrast to synthetic mordenites [14], phosgene removes only less than 40% of the Al, even at 1073 K, whereas the loss reaches 90% for Fe. The differences might be accounted for by the fact that in the case of natural zeolites the zeolite crystals are embedded in a glass-like matrix which is difficult for the gaseous reactant(s) to penetrate, while ion constitutes a separate haematite phase [7, 17], only a minor amount residing in the zeolite, and even this part being found in exchange positions.

For checks on the crystallinity retained after dealumination, X-ray diffractograms were taken as well. Figure 3 shows the respective intensities relative to the most
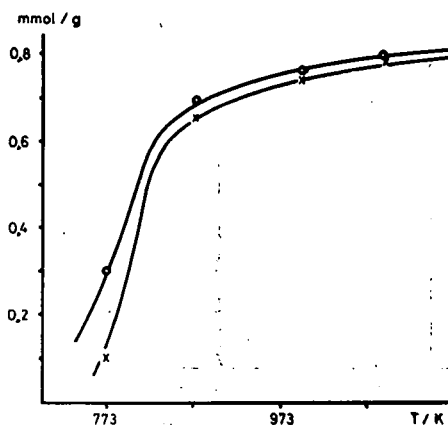

Fig. 1. Amount of Al removed from zeolites as a function of the temperature of dealumination (x mordenite, o clinoptilolite)
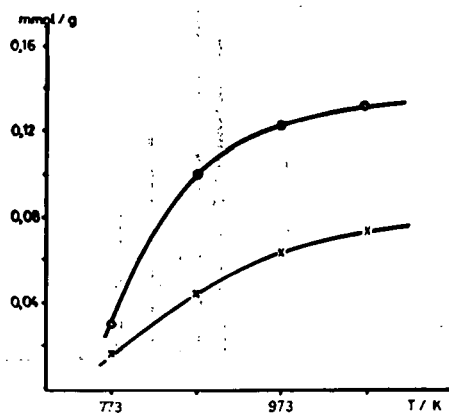
Fig. 2. Amount of Fe removed from zeolites as a function of the temperature of dealumination (x mordenite, o clinoptilolite)

Table I

Amounts of Al^{3+} and Fe^{3+} removed as percentages of Al^{3+} and Fe^{3+} originally present

		base sample mmol/g	temperature of dealumination/K			
			773	873	973	1073
			%			
mordenite	Al	2.2	4.55	30.7	34.6	36.8
	Fe	0.093	18.3	47.3	78.5	86.1
clinoptilolite	Al	2.04	14.7	34.3	37.8	39.2
	Fe	0.146	19.8	68.5	84.2	91.7

intense reflexion of the original samples. (In fact, the most intense reflexion appears at 0.33 nm, due to quartz [6]; this was omitted from the drawing). The Figure reveals that crystallinity is well retained even after treatment of the samples with phosgene at 1073 K, though a systematic change in the intensities is clearly discernible: the intensities of the low-index planes decrease, while simultaneously a few of the higher-index planes become more intense. Similar results have been obtained for the dealumination of synthetic mordenite [18, 19]. A precise explanation is not yet available.

Clinoptilolite behaves differently, due to its lower thermal stability. A diffractogram is presented for this sample in Fig. 4. In agreement with literature data, an appreciable loss of crystallinity accompanies dealumination at 973 K, followed by complete structural collapse at 1073.
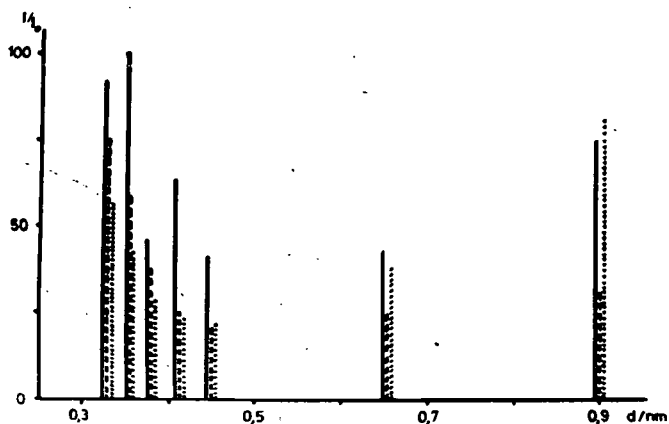

Fig. 3. Simplified X-ray patterns of mordenites: — base sample, - -- sample dealuminated at 873 K, ... sample dealuminated at 1073 K
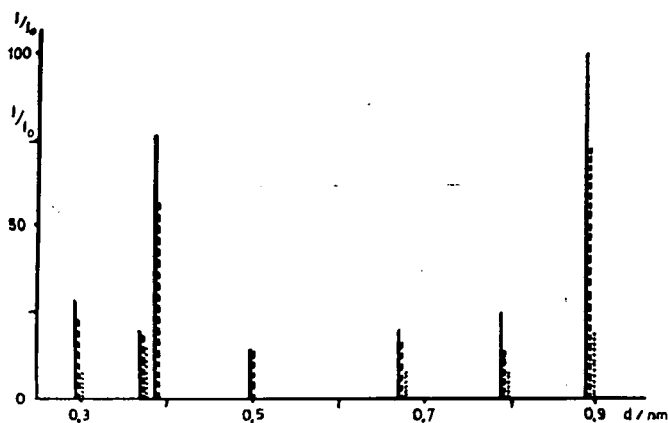

Fig. 4. Simplified X-ray patterns of clinoptilolites: — base sample, - - - sample dealuminated at 773 K, ... sample dealuminated at 973 K

Similar conclusions can be drawn from the i.r. spectra: it follows from Fig. 5 that elevation of the temperature of treatment leads to removal of the impurities, the specimens becoming increasingly "clean", and the spectrum taken after dealumination at 973 K is nearly indistinguishable from that of synthetic mordenite. These effects are observable in the clinoptilolite spectra too, but from 873 K on the i.r. bands reflect the first signs of lattice destruction (Fig. 6).

These results are in excellent agreement with Beyer's observations on acid- and heat-treated mordenites and clinoptilolites [20].

The adsorption isotherms of the original and the treated samples are shown in Figs. 7 and 8. The specific surface areas (listed in Table II) attain a maximum at 873 K, due to two opposite effects: increase of the temperature of dealumination "cleans up" the structure; and impurities and bulky cations blocking the channels are

Table II

BET surface areas of samples dealuminated at different temperatures (m²/g)

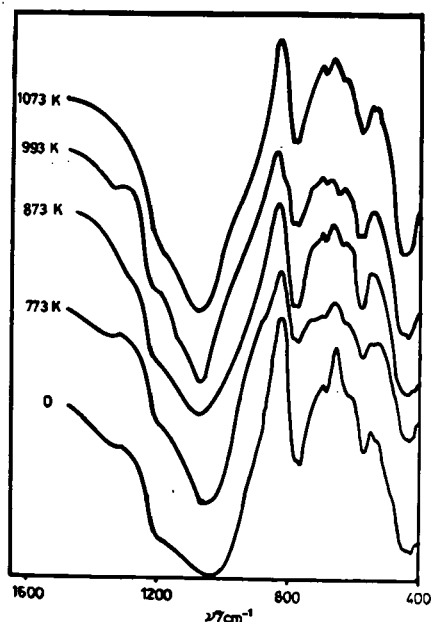|	base sample	773 K	873 K	973 K	1073 K
natural mordenite	47.0	53.0	127.8	117.2	91.6
natural clinoptilolite	32.8	52.25	82.9	48.6	—

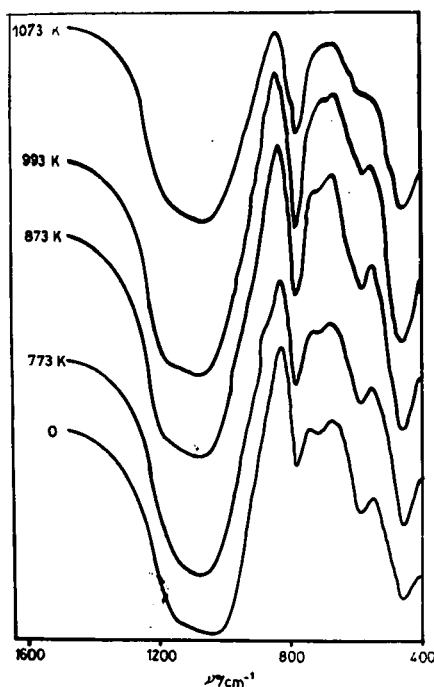*Fig. 5.* I.r. spectra of dealuminated mordenites at different temperatures

Fig. 6. I.r. spectra of dealuminated clinoptilolites at different temperatures
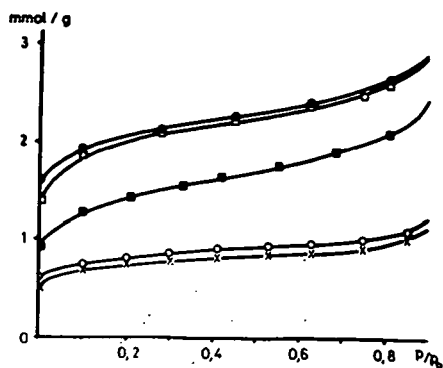
Fig. 7. Adsorption isotherms of nitrogen on dealuminated mordenites: x base sample, o sample dealuminated at 773 K, ● sample dealuminated at 873 K, □ sample dealuminated at 973 K, ▣ sample dealuminated at 1073 K
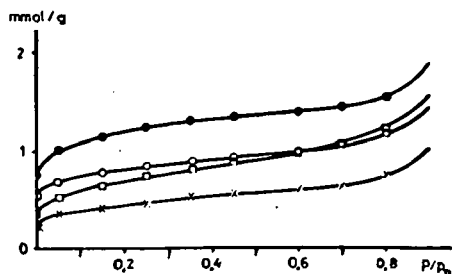
Fig. 8. Adsorption isotherms of nitrogen on dealuminated clinoptilolites: x base sample, o sample dealuminated at 773 K, ● sample dealuminated at 873 K, □ sample dealuminated at 973 K

removed or replaced by H^+ ions in the subsequent washing. Above 873 K, a partial lattice collapse results in enlargement of the channels, causing a reduction in the microporosity (mordenite) or a loss of crystallinity (clinoptilolite).

The immersion wetting enthalpies ($\Delta_w h$, in J g^{-1}) for the different samples are given in Table III. With regard to the 31% pure mordenite phase in the natural sample,

Table III

Immersion wetting enthalpies of dealuminated zeolites

	Temperature of dealumination/K	$\Delta_w h$ J/g zeol.	a mmol H_2O / g zeol.	$\Delta_w H$ J/mmol H_2O
Na-mordenite	—	190.4	7.22	26.4
natural mordenite	base sample	47.4	3.33	14.2
	773	33.6	3.61	9.31
	873	12.7	2.78	4.57
	973	11.5	1.94	5.93
	1073	6.3	1.94	3.25
natural clinoptilolite	base sample	68.3	4.72	14.47
	773	58.5	5.56	10.52
	873	33.8	4.72	7.16
	973	16.7	3.33	5.02
	1073	2.1	1.39	1.5

the value agrees well with that for synthetic mordenite. For clinoptilolite a larger value was obtained.

Dealumination results in a monotonous decrease of the immersion wetting enthalpies. This can be accounted for by two effects: a reduction in the amount of water penetrating the pore structure (as a consequence of the greater hydrophobicity), and/or a decreasing interaction of the water with the framework and exchange cations. If the amount of *adsorbed* water is measured at 2.66 kPa partial pressure (corresponding to a saturated solution of NH_4Cl in water) by thermogravimetry (column 4), and if complete pore filling is assumed in this process, the immersion wetting enthalpy values may be recalculated and expressed in J/mmol water (column 5). Up to 873 K the amount of water adsorbed at 2.66 kPa equilibrium pressure does not change considerably, and therefore it can be conjectured that the decrease of the immersion wetting enthalpy is due to the increasing hydrophobicity caused by the removal of cations, the heat of hydration of this comprising the main contribution to the wetting enthalpies. A great number of similar observations have accumulated in the past decade [21]. This dealumination procedure might allow the production of zeolites with varying surface energies, but without maintenance of the number of cations per u.c.

References

[1] Natural Zeolites, Occurrence, Properties,Use, L. B. Sand, F. A. Mumpton, Eds, Pergamon Press Oxford, etc. 1978.
[2] *Klopp, G., I. Markovics, Á. Kovács:* Magyar Kémikusok Lapja, **37**, 255 (1982).
[3] *Kotsis, L., J. Árgyelán, P. Szolcsányi, K. Pataki:* React. Kinet. Catal. Lett., **18**, 149 (1981).
[4] *Valente, S., N. Burriesci, S. Cavallaro, S. Galvagno, C. Zipelli:* Zeolites, **2**, 271 (1982).
[5] *Nemecz, E., Gy., Varjú:* Földtani Közlemények, **93**, 77 (1963).
[6] *Papp, J., J. Valyon, Lné Czárán:* Magyar Kémiai Folyóirat, **81**, 442 (1975).
[7] *Jánossy, A., Lné Czárán, J. Papp:* Magyar Kémiai Folyóirat, **83**, 289 (1977).
[8] *Kalló, D., J., Papp, J. Valyon:* Zeolites, **2**, 13 (1982).
[9] *Valyon, J., J. Papp, D. Kalló:* Magyar Kémiai Folyóirat, **85**, 55 (1979).
[10] *Valyon, J., J. Papp:* Magyar Kémiai Folyóirat, **85**, 195 (1979).
[11] *Klopp, G., J. Sütő, I. Szebényi:* Proc. 5th Int. Conf. Zeolites, Napoli, 1980. p. 841.
[12] "Proc. of Invest. and Use of Hungarian Natural Zeolites Conf." MTA VEAB, Veszprém, 1982.
[13] *Fejes, P., I. Kiricsi, I. Hannus, Gy. Schöbel:* Magyar Kémiai Folyóirat **89**, 264 (1983).
[14] *Fejes, P., I. Kiricsi, I. Hannus, Á. Kiss, Gy. Schöbel:* React. Kinet. Catal. Lett. **4**, 481 (1980).
[15] *Fejes, P., I. Kiricsi, I. Hannus, Á. Kiss, Gy. Schöbel:* Hungarian patent application no. JO—276.
[16] *Náray—Szabó, I.:* Szervetlen Kémia, Akadémiai Kiadó, Budapest, 1956. Vol. I., p. 533.
[17] *Olaszi, V., Csné Csikós, A. Jánossy:* Proc. of Invest. and Use of Hungarian Natural Zeolites Conf., MTA VEAB, Veszprém, 1982, p. 155.
[18] *Fejes, P., I. Kiricsi, I. Hannus:* Acta Phys. et Chem. Szeged **28**, 173 (1982).
[19] *Kranich, W. L., Y. H. Ma, L. B. Sand. A. H. Weiss, I. Zwiebel:* Adv. Chem. Ser., **101**, 502 (1971).
[20] *Beyer, H., I. Belenkaja:* Proc. of Invest. and Use of Hungarian Natural Zeolites Conf., MTA VEAB, Veszprém, 1982, p. 43.
[21] *Chen, N. Y.:* J. Phys. Chem. **80**, 60 (1976).

ДЕАЛЮМИНАЦИЯ. ЦЕОЛИТОВ ЛЕТУЧИМИ РЕАГЕНТАМИ. МОДИФИКАЦИЯ ВЕНГЕРСКИХ ЕСТЕСТВЕННЫХ ЦЕОЛИТОВ ФОСГЕНОМ

И. Ганнуш, И. Киричи, И. Декань, П. Фееш

Применен новый метод деалюминирования естественных морденитов и клиноптилолитов Токайского месторождения (Венгрия), были оценины изменения, происходящие в результате этого в их составе, структуре и адсорбционных свойствах. Наибольшая адсорбционная емкость получена при удалении загрязнений и катионов больших размеров, когда сохраняется почти полная кристалличность. Метод может быть рекомендован для изготовления цеолитов с различной поверхностной энергией.