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MORPHOLOGY AND STRUCTURE CHANGES OF DEALUMINATED CLINOPTILOLITE

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Abstract: NH_4^+-clinoptilolite samples, dealuminated by means of ammonium hexafluorosilicate were used for morphological and structural investigations. The changes of structure were measured by XRD analysis and surface characteristics measurements. The influence of the dealumination on the morphology was monitored using scanning electron microscopy (SEM). The dissolution-degradation process (amorphous phase formation) was found during dealumination. The products of the isomorphous substitution of the aluminium by silicon exhibit an increase of the specific mesopore surface up to discret Si/Al ratio. The extraframework species are supposed in pore system of dealuminated clinoptilolite.

Key words: clinoptilolite, dealuminated, morphology.

Introduction

The modification of zeolites by dealumination in order to optimise their stability and sorption selectivity has become important in various areas of technology and industry. Breck (1985) proposed a chemical method of dealumination, consisting of the treatment of zeolite with $(NH_4)_2SiF_6$ in aqueous solution at relatively low temperatures (up to 100 °*C*). He reported that aluminium is extracted from the framework in the form of a soluble complex, while silicon is inserted in the vacancies left by the aluminium.

Various methods were used to characterize dealuminated zeolites. Meyers et al. (1988) investigated the properties of dealuminated mordenites. The aluminium content was determined by bulk chemical analysis, and the crystallinity was determined by XRD.

Garralon et al. (1988) and Wang et al. (1990) used XRD method to assess the thermal stability of dealuminated zeolites. Breck (1985) used the peak heights as the measure of the crystallinity loss during the dealumination process.

Meyers et al. (1988) identified the mordenite structural changes based on the surface area and porosity data. The increase of the specific surface area and micropore volume was observed in the case of synthetic mordenites, because of the removal of amorphous phase from the mordenite structure after acid dealumination. Chauvin et al. (1990) studied the influence of dealumination on the chemical composition and crystallinity degree of faujasite, mazzite and offretite evaluating the results of the chemical analysis, XRD, volumetry and scanning electron microscopy.

The aim of this work is to study the changes in the composition, structure and morphology of the natural clinoptilolite during the dealumination process.

Materials and methods

The rhyolite tuff from Nižný Hrabovec (East Slovakia) with 0.8 -1.6 *mm* granulometry was used as a starting material. Clinoptilolite content ((70±5) mass %) quartz, feldspar and cristobalite were determined by XRD method as described by Horváth et al. (1990). A similar method, based on the XRD reflections peak area measurements (integral intensities) was used in the crystallinity evaluation of the dealuminated samples. Four typical clinoptilolite diffraction reflections (0.901, 0.513, 0.280 and 0.274 *nm*) were used to determine clinoptilolite crystallinity. NH_4^+-clinoptilolite preparation and dealumination by means of $(NH_4)_2SiF_6$ are described elsewhere (Grejták et al. 1992). The chemical composition of the starting and dealuminated samples of clinoptilolite are given in Tab. 1. Crystallochemical formulae were determined using Barrer's method (Barrer et al. 1967).

The X-ray powder diffraction traces were taken with a Philips Difractometer Ni-filtered, CuK_α radiation and scanning speed 2 Θ/min.

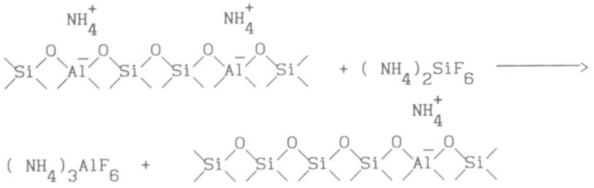
A SEM TESLA BS-300 was used for SEM studies. The samples were prepared by sputtering Au in sputter coater BALZERS SCD-050 and scanned in 10 000 enlargement.

Carlo Erba Sorptomatic 1800 was used for the specific surface area and pore distribution determination (the standard static-volume method of nitrogen adsorption). The specific surface area was calculated using B.E.T. equation and t-line method was used to evaluate the micropore volume. The samples were heated for 3 hours in the electric oven at 500 °*C* in the static air and then for 4 hours at 300 °*C* and 10 *torr* before specific surface area measurement.

Sartorius electronic microbalance was used for equilibrium adsorption capacity measurements. Adsorption capacities of sample were measured at 25 °*C*, at a water vapour pressure of 1.36 *kPa* and at a cyclohexane vapour pressure of 3.73 *kPa*. The samples were calcined for 3 hours at 500 °*C* before adsorption.

Results and discussion

Isomorphous substitution of aluminium by silicon can be described by the scheme:



The chemical composition of the starting and dealuminated clinoptilolite samples (Tab. 1) shows that the reaction leads to an increase of the Si/Al ratio. The values of the Si/Al ratio were measured for bulk clinoptilolite containing grains. A gradual dealumination of the clinoptilolite containing grains from the surface to the centre of the grains can be suggested. The presence of different amounts of silicates or hydrated hexafluoro-complexes on the clinoptilolite crystallites at the fresh fracture surface of the grains in comparison with the grain surface (Fig. 1) of dealuminated samples, gives evidence of the more intensive dealumination at the grain surface than at the internal surface of the grains. The surface layer at the dealuminated grains cannot be removed despite their intensive washing by boiling water.

The XRD analysis of the surface layer of the dealuminated rock grains showed lower clinoptilolite crystallinity compared to the internal parts of the grain. The surface layer of the clinoptilolite rocks grains was separated by means of dry clinoptilolite containing rock grains abrasion during 24 hours. The higher content of quartz, plagioclase and cristobalite was observed in the surface layer of dealuminated grains.

Table 1: Characterization of the dealuminated samples.

sample	reaction time[h]	composition	Si/Al ratio
D	0	$Ca_{2.0}Mg_{0.1}Na_{0.6}K_{1.9}Al_{6.7}Si_{29.3}O_{72}$	4.37
D_0	0	$(NH_4)_{6.7}Al_{6.7}Si_{29.3}O_{72}$	4.37
D_1	1	$(NH_4)_{6.03}Al_{6.03}Si_{29.97}O_{72}$	4.97
D_3	3	$(NH_4)_{5.26}Al_{5.26}Si_{30.74}O_{72}$	5.84
D_4	6	$(NH_4)_{5.04}Al_{5.04}Si_{30.96}O_{72}$	6.14
D_5	9	$(NH_4)_{4.88}Al_{4.88}Si_{31.12}O_{72}$	6.38
D_6	16	$(NH_4)_{4.21}Al_{4.21}Si_{31.79}O_{72}$	7.55
D_{11}	24	$(NH_4)_{4.15}Al_{4.15}Si_{31.85}O_{72}$	7.67

From Tab. 1 it can be concluded, that 2.55 aluminium atoms have been extracted per unit cell in the case of D_{11} sample whereas the amount of fluorosilicate in the solution had been designed in order to extract 4.8 aluminium atoms per unit cell.

Higher dealumination lowers the crystallinity degree of the clinoptilolite. A longer experimental time (24 hours) produces materials with ca 45% crystallinity determined by means of XRD (Tab. 2). For comparison, the crystallinity loss of the dealuminated samples was determined by the method of micropore volume measurement. The results of specific surface (S_{BET}), mesopore specific surface (S_{MESO}) and micropore volume (V_{MICRO}) are given in the Tab. 2.

The micropore volume values were calculated on the basis of the theory of adsorbate monolayer formation in the micropores.

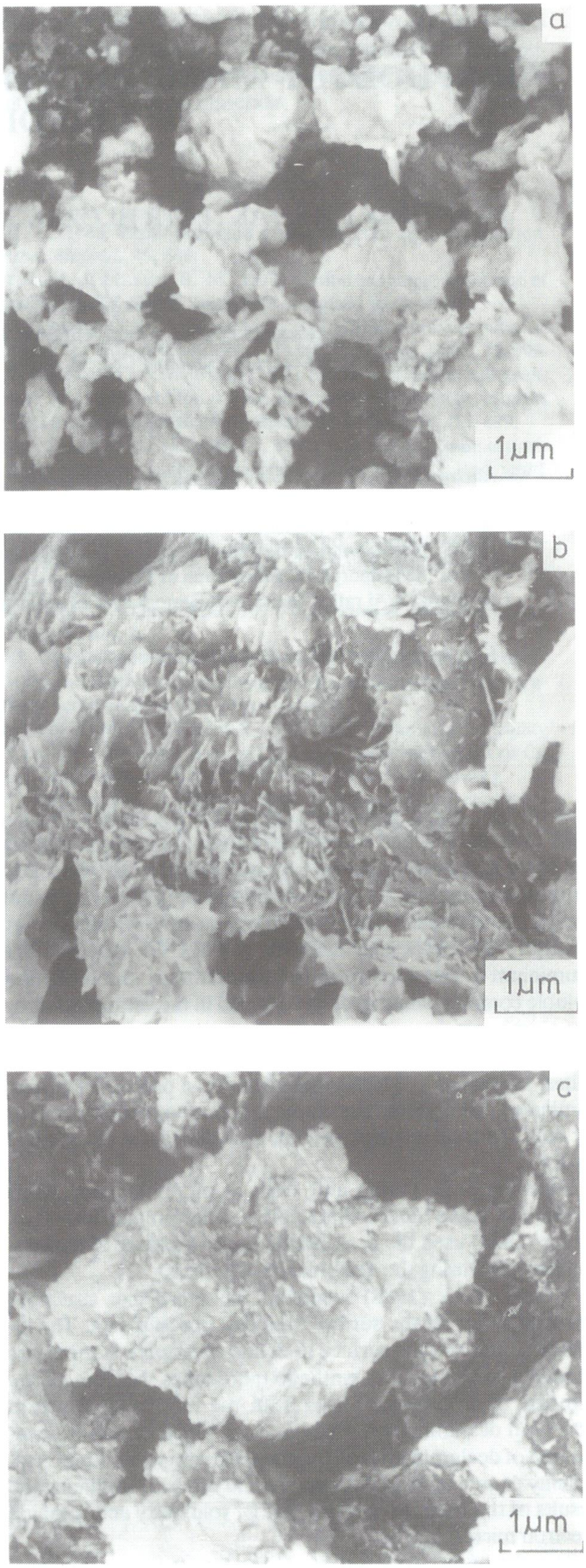


Fig. 1. a - SEM of the grain surface of clinoptilolite rock. **b** - SEM of the fresh fracture surface of clinoptilolite rock. **c** - SEM of the fresh fracture surface of sample D_{11}.

Table 2: Surface characteristics measurements of the dealuminated samples.

Sample	S_{BET}	S^a_{MESO}	V^b_{MICRO}	crystallinity XRD	crystall V_{MICRO}
	[$m^2.g^{-1}$]	[$m^2.g^{-1}$]	[$cm^3.g^{-1}$]	[%]	[%]
D	27	25	0.0009	70.0±5.0	
D_0	192	51	0.0709	100	100
D_1	187	49	0.0667	94.5±4.5	94.0
D_3	159	61	0.0556	79.0±5.0	78.5
D_4	145	54	0.0440	65.0±5.0	62.0
D_5	130	48	0.0392	58.0±5.0	54.3
D_6	102	45	0.0287	48.5±5.0	40.5
D_{11}	75	38	0.0181	45.5±5.0	25.6

[a] $d \approx (2 \mu m, 50 \mu m)$, [b] $d < 2 \mu m$

Supposing that in rhyolite tuff only clinoptilolite contains micropores, V_{MICRO} values can be taken as relative numerical values of the clinoptilolite content in the case of monoionic forms. For example, micropore volume increases approximately 80-times during the decationization process (Tab. 2).

Crystallinity of dealuminated samples was calculated from V_{MICRO} values (Tab. 2). There is a good agreement in the crystallinity determination using the X-ray and micropore volume methods. The signifficant differences between crystallinity determination exhibit only sample D_{11}. This could be attributed to the formation of insoluble silicates or aluminium complexes coating the crystals and inserting preferentially in the micropore (not in mesopores), and preventing the access of the reagents to the structural pore system (Fig. 3).

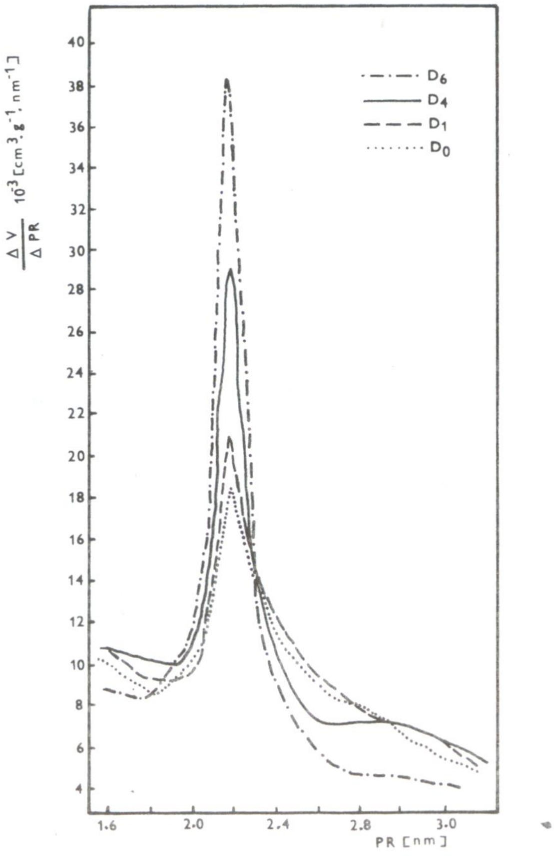


Fig. 2. Dependence of the $\frac{\Delta V}{\Delta PR}$ parameter on the pore radius (PR).

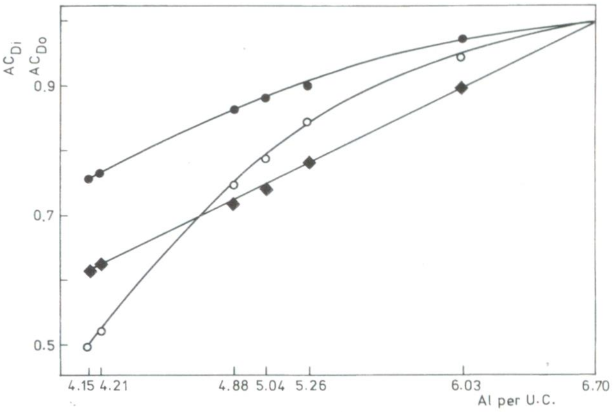


Fig. 3. Dependence of the adsorption capacity of dealuminated sample (AC_{D1}) to adsorption capacity of the sample D_0 (AC_{D0}) ratio on the number of the aluminium atoms per unit cell.
● - equilibrium adsorption capacities of cyclohexane vapour,
o - equilibrium adsorption capacities of water vapour,
◆ - theoretical adsorption capacities in dependence of the aluminium content.

The process of dealumination by ammonium fluorosilicate method implies that the degree of the aluminium extraction is higher than the rate of silicon insertion (Chauvin et al. 1990). When more aluminium atoms are extracted from the framework before silicon atoms are inserted, the structure is destroyed, as in the case of the mineral acids or chelating agents dealumination. Defects were thus created, resulting in loss of crystallinity.

Silicates at the surface and in micropores would transform upon calcination into products, blocking the porosity of the zeolite and decreasing the micropore volume of the extremely dealuminated samples. This can be the reason of the significant difference between the experimental adsorption capacities of the water vapour and theoretical ones, calculated on the basis of aluminium content, proportional to framework aluminium content (Fig. 3).

Taking into account S_{MESO} values (Tab. 2, Fig. 2) we can conclude:

- the formation of the mesopores in the clinoptilolite structure during the initial stages of reaction;
- the increase of the relative mesopore volume with dealumination extent increasing, although S_{MESO} decreases.

Formation of mesopores is related to the opening and connection of the 8- and 10- member rings in the clinoptilolite structure. This would be the reason for the shape of the curves (Fig. 3). The decrease of cyclohexane adsorption capacity is not so intensive as in the case of water adsorption capacity. So we can conclude that the mesopore formation is connected with micropore destruction. In the case of longer dealumination time the mesopore destruction was achieved (Tab. 2), although the relative volume of the mesopores with an average radius 2.2 *nm* increases.

Conclusions

Except isomorphous substitution the dissolution degradation of the zeolite by detaching Al without substitution by Si may be considered. The dissolution-degradation mechanism could be attributed to formation of channel opens. The extraframework species, blocking the pore system access could be connected with hydrolysis of the hexafluoro-complexes.

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