

Structure properties of dealuminated Y zeolites*

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The structure of a modified zeolite of the type Y was investigated, which has been prepared by hydrothermal modification of the sodium-ammonium form NaNH_4Y followed by the extraction of those aluminium atoms which have been removed from their positions in the lattice in the course of the modification.

The results of the measurement of both adsorption isotherms of benzene and mercury porosimetry performed on the structure modified in this way were correlated with the values obtained by measurements carried out with the original NaY form. The following conclusions were drawn:

1. In the course of the hydrothermal treatment of the zeolite a decrease in the volume of the micropores takes place which is due to the decay of a part of the elementary structure units — the cubooctahedra — and the resulting formation of secondary mesopores.

2. The silicium atoms liberated in this way cause an annealing of the lattice defects originating from the hydrolytical removal of a part of aluminium atoms, *i.e.* they fill the vacancies in the unperturbed part of the structure.

Изучалась структура модифицированного цеолита типа Y, полученного из натриево-аммониевой формы NaNH_4Y путем гидротермальной обработки и последующей экстракции тех атомов алюминия, которые при обработке были удалены со своих мест в решетке.

Сопоставление результатов измерений изотерм адсорбции бензола и данных ртутной порометрии, полученных для модифицированной таким образом структуры, с соответствующими данными, полученными для исходной формы цеолита NaY, привело к следующим выводам:

1. В процессе гидротермальной обработки цеолита происходит уменьшение объема микропор в результате разрушения части элементарных структурных единиц — кубооктаэдров, приводящего к возникновению вторичных мезопор.

2. Освободившиеся при этом атомы кремния устраняют дефекты решетки, возникшие при вымывании части атомов алюминия, т.е. заполняют вакансии в оставшейся ненарушенной части структуры.

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Synthetic zeolites of the types A and X appeared on the market for the first time in 1954. Since that time their application has spread into all branches of industry, mainly in the field of chemistry.

These zeolites are used as markedly hydrophilic adsorbents with a high adsorption capacity. The total volume of pores amounts to $0.5 \text{ cm}^3/\text{cm}^3$, their radii to 0.2–0.4 nm, according to the type of cations present. In some separation processes the molecular sieve effect of the zeolitic structure is exploited, e.g. in the separation of *n*- and iso-paraffins.

The imperfect structure stability of these adsorbents in acid medium and under the influence of elevated temperature in the presence of water vapour represents a certain disadvantage. It has been proved [1] that the instability of the zeolitic lattice is centered on the tetrahedrally coordinated aluminium atoms.

The reduction of the content of aluminium in the lattice under preservation of the faujasite structure was the aim of the successful synthesis of a new type of Y zeolite with the ratio $n(\text{Si}):n(\text{Al})=1.5$ to 3. As it appeared later, this zeolite found its main application in the domain of catalysis. However, neither Y zeolites exhibit a perfect lattice stability under the above conditions. Such a stability was attained only by a modification of the structure causing an additional increase in the ratio $n(\text{Si}):n(\text{Al})$ by the extraction of a part of the aluminium atoms from the lattice.

The process may be carried out either thermally or chemically. The thermal dealumination is performed by the influence of higher temperature (above 400°C) under an elevated pressure of water vapour. In the chemical dealumination a part of the aluminium atoms is removed from the lattice by extraction with ethylenediaminetetraacetic acid followed by a thermal treatment of the product at 500°C . For the thermal dealumination, *i.e.* stabilization of the structure a partially decationized zeolite is used as precursor, since it has been found [2] that only those aluminium atoms may be removed from the structure without decreasing the crystallinity of the product the charges of which are not compensated by cations. Recently a further technique of dealumination of Y zeolites has been described [3] consisting in the direct substitution of a part of aluminium atoms in the lattice by silicon atoms by the action of SiCl_4 on the zeolite.

In our work we have used the thermal method for the preparation of stabilized, *i.e.* partially dealuminated zeolites.

Under the conditions outlined in the Preparation scheme the stabilization process takes place in two steps:

a) In the first step a part of aluminium lattice atoms is hydrolyzed and the aluminium oxy compounds formed are localized in the cavities of the zeolite. As it has been shown by the results of XPS measurements [4] these compounds behave as neutral particles, analogically to *e.g.* metal atoms formed by the reduction of cations. By the influence of elevated temperature they migrate to the surface of the

monocrystal, where they form more voluminous clusters. This migration is a diffusion process and its rate depends on both temperature and time.

b) In the second step the annealing of the lattice vacancies by silicium atoms takes place. The vacancies are filled by those atoms which have been liberated by the decay of some of the cubooctahedra. The hypothesis suggesting that these "subsidiary" silicium atoms originate from the amorphous occluded SiO_2 on the zeolite surface has been disproved by the following facts: From XPS measurements it follows [4] that with samples stabilized at temperatures below 550°C , *i.e.* under conditions where the migration of the aluminium oxy compounds from the cavities does not take place as yet, the ratio $n(\text{Si}):n(\text{Al})$ in the surface layer in the stabilized form is the same as in the original unstabilized form and corresponds to the value obtained by chemical analysis of the bulk. The decay of some cubooctahedra of the lattice and the subsequent migration of the liberated silicium atoms into the aluminium vacancies in the lattice results in the formation of secondary porosity without destruction of the monocrystals.

Preparation scheme

NaY

↓ ion exchange $\text{Na}^+ \rightarrow \text{NH}_4^+$

NaNH_4Y

↓ hydrothermal treatment, $\theta = 770^\circ\text{C}$, $p(\text{H}_2\text{O}) \approx 130 \text{ kPa}$

Stabilized NaHY form (sample designated as USE-22)

↓ extraction with 0.05 M-hydrochloric acid

Decationized form USE-22 without extralattice aluminium

In our paper the results of the investigation of the sorption properties of the stabilized structure of the Y zeolite are presented. Our attention was concentrated on the characterization of the resulting secondary porosity.

Experimental

As starting material NaY zeolite produced by the Research Institute for Oil and Hydrocarbon Gases, Bratislava, was used. The sodium-ammonium form prepared by ion exchange with NH_4NO_3 from solution was stabilized at 770°C . A detailed description of the stabilization procedure was given previously [5]. The aluminium lattice atoms liberated by the stabilization were extracted by the action of 0.05 M-hydrochloric acid. The sample modified in this way was designated USE-22. Its chemical composition is given in Table 1.

Benzene used as adsorbate was purified in the way described in [6].

Table 1

Chemical composition of the starting zeolite NaY and of the stabilized form USE-22

Sample	Chemical composition of the elementary cell	Ratio $n(\text{Si}) : n(\text{Al})$ in the lattice
NaY	$\text{Na}_{53.2}(\text{AlO}_2)_{56}\text{Si}_{136}\text{O}_{384}$	2.43
USE-22*	$\text{Na}_{11.7}(\text{AlO}_2)_{23.7}(\text{SiO}_2)_{136} \cdot 16.2\text{Al}_2\text{O}_3$	5.74

* Composition of the sample before the extraction of the extralattice aluminium.

Apparatus

The adsorption equilibria of benzene vapours were determined with the instrument Accusorb 2100 E (Micromeritics, USA). This apparatus is completely made of metal, the dosage of two different volumes 30.16 cm^3 and 131.90 cm^3 of the adsorbate is possible. The pressure of the adsorbate is measured with a membrane manometer Barocell, the accuracy of the measurement amounting to 0.01 Pa in the range $0\text{--}0.5 \text{ kPa}$, 0.1 Pa in the range $0.5\text{--}5 \text{ kPa}$ and 1 Pa at higher pressures. For the determination of pressures below 0.01 Pa , a vacuum-meter VPG-1 (Laboratorní přístroje, Prague) was joined with the apparatus.

The samples were activated before the measurement by heating first at $100 \text{ }^\circ\text{C}$ for 8 h, then at $350 \text{ }^\circ\text{C}$ for 16 h, the pressure of 10^{-4} Pa was attained. The dead volume was determined with spectroscopically pure helium.

The porosimetric measurements were performed with a high-pressure mercury porosimeter Pore Sizer 9300 (Micromeritics, USA) at pressures up to 200 MPa .

Results and discussion

The molecules adsorbed on the zeolites interact on one hand with the aluminosilicate lattice and on the other hand with the cations compensating the lattice charge. The contribution of both kinds of interaction to the total adsorption energy is therefore besides other factors determined by the number and character of the cations in each structure unit. From Fig. 1, where the adsorption isotherms of benzene on the investigated samples are shown, we may see that on the NaY zeolite a strong specific interaction of the adsorbed molecules with the sodium cations takes place. This specific interaction is in agreement with the values of the adsorption heat of up to 87 kJ mol^{-1} given in [7].

The isotherm of benzene on the zeolite USE-22 is of a completely different character. In the course of the extraction with hydrochloric acid not only the aluminium oxy compounds formed but also all remaining sodium cations were removed. The adsorption of benzene on a sample which was modified in this way is

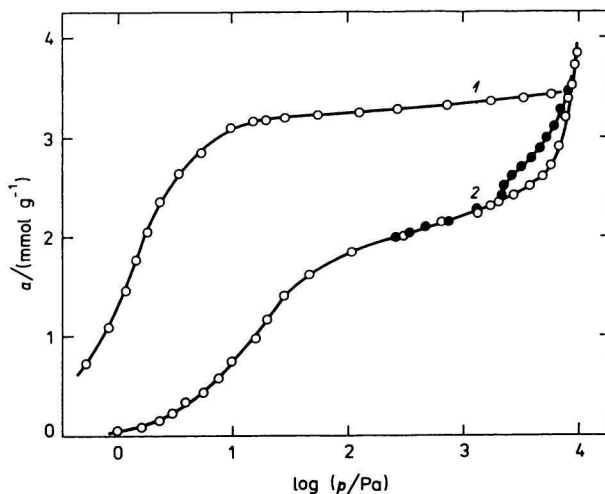


Fig. 1. Adsorption isotherms of benzene at 20 °C on zeolites NaY (1) and USE-22 (2).

therefore determined by the interaction with the zeolite lattice and takes place in the micropores as well as in the newly formed secondary pores, where at higher equilibrium pressures capillary condensation takes place. The occurrence of this phenomenon itself characterizes the size of the secondary pores. The experimental data presented in Table 2 and in Fig. 2 have been obtained by measurements with the mercury porosimeter and by calculation from the desorption branch of the adsorption isotherm of benzene. (The sudden increase of the pore volume on the porosimetric curve in the vicinity of the pore radius $r = 120$ nm is caused by the penetration of mercury into the intercrystalline volumes of the zeolite.)

The course of the adsorption of benzene on the sample USE-22 in the region of micropores shows that a significant decrease of the specific interaction takes place, which is caused by the absence of cationic sorption centres. The lower sorption

Table 2

Specific volume of the micropores and of the mesopores in the starting NaY zeolite and in the stabilized form

Sample	$v/(\text{cm}^3 \text{g}^{-1})$	
	Micropores	Mesopores
NaY	0.30	0
USE-22	0.21	0.15

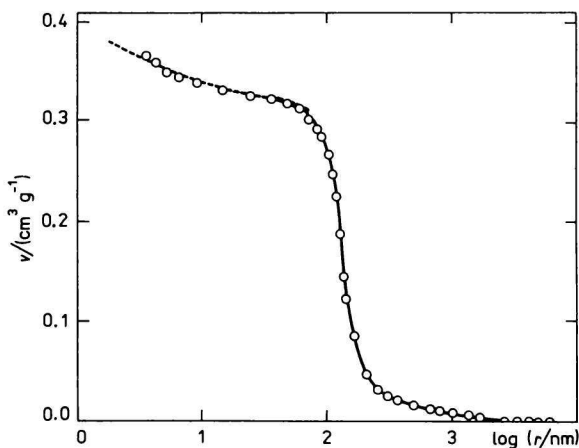


Fig. 2. Pore volume distribution in the zeolite USE-22.

—○—○— Measurements with a mercury porosimeter;
 - - - - calculated from the desorption branch of the benzene isotherm.

values in the region of micropores obtained with this sample when compared with the sample NaY have two reasons. It has been proved experimentally [8] that in the course of the stabilization a contraction of the lattice with the resulting decrease in the volume of micropores takes place. The degree of contraction is proportional to the decrease in lattice aluminium. The second, quantitatively the most important reason for the elimination of the volume of micropores is the disappearance of a part of the microporous system under the formation of larger mesopores which form a secondary pore structure. As it follows from the benzene adsorption isotherm on the sample USE-22, the decrease in the sorption capacity of the micropores is compensated by the capillary condensation in the secondary pores at relative pressures p/p_s^* above 0.2. Both the fact that the total sorption capacity is maintained and the photographs obtained with the electron microscope [9] prove that our notion how secondary porosity is formed, although the original size of the zeolite monocystals does not change, is correct.

The total value of sorption capacity of the zeolite USE-22 is 1.2 times higher than that of the sorption capacity of the zeolite NaY. This fact is consistent with our notion about the disappearance of a certain number of cubooctahedra from the lattice where the volumes formed are higher than the total volume of the corresponding micropores in the parent lattice.

* p_s — pressure of the saturated vapour of the adsorbate at the temperature of the measurement.

Conclusion

The stabilized form of the Y zeolite prepared under hydrothermal conditions exhibits a decrease in the sorption capacity in the micropores. This decrease is caused by the disappearance of a part of cubooctahedra under simultaneous formation of a secondary porous structure formed by mesopores.

References

1. Flanigen, E. M., *Proceedings of the 5th Int. Conference on Zeolites*, p. 760. (Rees, L. V. C., Editor.) Heyden, London, 1980.
2. Engelhardt, G., Lohse, U., Patzelová, V., and Zukal, A., *Proc. Int. Conf. Catalysis on Zeolites*, p. 50. Liblice, 1982.
3. Beyer, H. K. and Belenkaya, I., *Catalysis on Zeolites*. (Imelik, B., Naccache, C., Ben Taarit, Y., Vedrine, J. C., Coudurier, G., and Praliaud, H., Editors.) Elsevier, Amsterdam, 1980.
4. Gross, Th., Lohse, U., Engelhardt, G., Richter, K.-H., and Patzelová, V., *Zeolites* 4, 25 (1984).
5. Tvarůžková, Z., Patzelová, V., and Bosáček, V., *React. Kinet. Catal. Lett.* 6, 433 (1977).
6. Mach, K., Antropiusová, H., and Poláček, J., *J. Organometal. Chem.* 172, 325 (1979).
7. Regent, N. I., Stach, H., and Thamm, H., *Preprints of the Workshop Adsorption of Hydrocarbons in Microporous Adsorbents*, p. 122. Eberwalde, 1982.
8. Patzelová, V., Bosáček, V., and Tvarůžková, Z., *Acta Phys. Chem., Szeged XXIV*, 1—2, 257 (1978).
9. Patzelová, V., unpublished results.

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