

## STABILIZED Y-TYPE ZEOLITES WITH HIGH CONTENT OF Na CATIONS

By

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(Received 30<sup>th</sup> January, 1978)

A series of stabilized forms of NaHY zeolites has been prepared containing 87, 67, 53 and 31% of the total amount of Na cations in the NaY zeolite, respectively. The composition, structural character and sorption properties are described and discussed.

The stability of these zeolites does not depend on the degree of stabilization, the intensities of phenomena connected with the process of stabilization depend on the Na<sup>+</sup> content and the temperature of stabilization.

Ultrastable Y zeolites, their synthesis and properties have been first described by MCDANIEL and MAHER [1]. Since that time, several methods have been reported for preparing, from Y-type zeolites, materials with ultrastable properties [2—4]. A number of articles has been published concerning their crystal structure [5, 6], infrared spectra [7—10], formation mechanism [2—4] and acidic properties [11, 12]. These materials are of considerable interest for their catalytic properties.

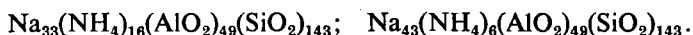
As follows from the patent literature [13], the ion exchange capacity of the ultrastable (US) zeolite is substantially lower than that of the parent zeolite.

A concentration of residual Na cations higher than 1% by weight of Na<sub>2</sub>O is undesirable as it lowers the catalytic activity neutralizing the acidic centres on the catalyst [14].

On the other hand, a stabilized form containing an appreciable amount of sodium cations exhibits a higher ion exchange capacity. Such a form has the faculty of combining the properties of a metal exchanged Y zeolite with those of a stabilized Y zeolite. We have therefore investigated the products resulting from the stabilizing process on zeolites with a high concentration of metal cations.

In the present paper we describe and discuss the composition, structural character and sorption properties of a series of stabilized Y zeolites containing 87, 67, 53, and 31% of sodium cations, respectively, present in the original NaY form.

As starting material for preparing stabilized NaHY zeolites four types of NaNH<sub>4</sub>Y were used, their unit cell compositions being:



Thermal decomposition of the ammonium forms was performed in an electric furnace at 550 and 770° C, respectively. The sample geometry and the stabilization procedures used in this study were described previously [15].

The following denotation of the US samples is used: USC for samples stabilized at 550° C, USE for those at 770° C. These letters are followed by a number, giving the percentage of the residual Na cations in the US forms with respect to the original NaY form, e.g.; USC-87, USE-53.

The extraction of extralattice aluminium was effected by slurring 10 g samples of the stabilized zeolite in 1000 ml of 0.1 N NaOH solution for 24 hrs, filtering, washing with 500 ml of water, and drying. The same procedure was applied in the case of aluminium extraction with 1 N  $\text{NH}_4\text{OH}$  aqueous solution. In special experiments aliquots of the US samples were extracted with potassium-sodium tartarate ( $\text{KNaC}_2\text{H}_4\text{O}_6$ ) aqueous solution. The extracts were analyzed for aluminium and the composition of the sample calculated from the amount of aluminium extracted. The removal of only extralattice aluminium by all the above mentioned procedures was tested using  $\text{NaNH}_4\text{Y}$  zeolites as a blank. No traces of aluminium were found in the extracts of the blank.

Sorption capacity measurements and X-ray diffraction data were used to establish the degree of structural collapse of various materials and the contraction of the lattice of stabilized samples. The sorption capacities of Ar and  $\text{H}_2\text{O}$  were measured with a quartz balance. The details of the infrared measurements have been described previously [16]. The heats of adsorption of model adsorbates were calculated from the data obtained by gas chromatography. The treatment in hydrothermal conditions was realized by the repeating the following cycles: full hydration of the zeolite at room temperature followed by desorption of  $\text{H}_2\text{O}$  at 370° C *in vacuo* ( $10^{-4}$  torr).

Sorption capacities of Ar and water were established for all samples in order to test the possible changes of the volume of the zeolite cavities, which may be caused either by partial loss of crystallinity or by presence of voluminous cationic aluminium

Table I

Sorption capacities  $a_0$  of Ar at -198° C and  $\text{H}_2\text{O}$  at 25° C, the influence of repeated treatment in hydrothermal conditions (THTC) and Al extraction  $a_0$  mmole  $\text{g}^{-1}$

Zeolite	$a_0$ after THTC		$a_0$ after Al extr.		Relative increase of $a_0$ in %	
	Ar	$\text{H}_2\text{O}$	Ar	$\text{H}_2\text{O}$	Ar	$\text{H}_2\text{O}$
NaHY-31	5.08	—	—	—	—	—
USE-31	9.71	15.40	10.63	17.92	9	16
USC-31	10.70	16.68	11.32	18.53	5	11
NaHY-53	6.31	—	—	—	—	—
USE-53	9.75	15.29	10.50	17.57	8	15
USC-53	10.62	16.74	11.17	18.31	5	9
NaHY-67	6.11	—	—	—	—	—
USE-67	3.11	amorphous	—	—	—	—
USC-67	10.26	16.30	10.78	17.00	5	4
NaHY-87	5.34	—	—	—	—	—
USE-87	2.50	amorphous	—	—	—	—
USC-87	10.34	18.02	10.48	17.94	1	0

in the cavities. The respective data for all zeolites studied in this work are shown in Table I. Y zeolites containing 50% or less of the original Na cations can be stabilized also at 770° C. A higher content of Na<sup>+</sup> excludes the positive effect of stabilization at the temperature 770° C. The increment for water adsorption capacity after complete Al cation exchange in comparison to the increment for argon may be in connection with the fact, that sodalite cages are accessible for water but not for Ar molecules.

Table II

Zeolite	SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> mole ratio	% Al removed	Unit cell nm
NaNH <sub>4</sub> Y-31	5.24	—	2.468
USE-31	5.97	12.18	2.453
USC-31	5.72	8.35	2.457
NaNH <sub>4</sub> Y-53	5.11	—	2.467
USE-53	5.70	10.41	2.452
USC-53	5.49	6.85	2.456
NaNH <sub>4</sub> Y-67	5.84	—	2.463
USC-67	6.11	4.46	2.454
NaNH <sub>4</sub> Y-87	5.84	—	2.463
USC-10	5.85	0.27	2.459

Table II summarizes the analytical data of cationic aluminium content and unit cell sizes for our US zeolites. Besides a general decline in cationic aluminium content with the increasing Na<sup>+</sup> content in a sample, the data also show the positive influence of temperature on the formation of Al cations for zeolites with Na<sup>+</sup> ≤ 50%. The data also show a unit cell shrinkage proportional to the extralattice aluminium content.

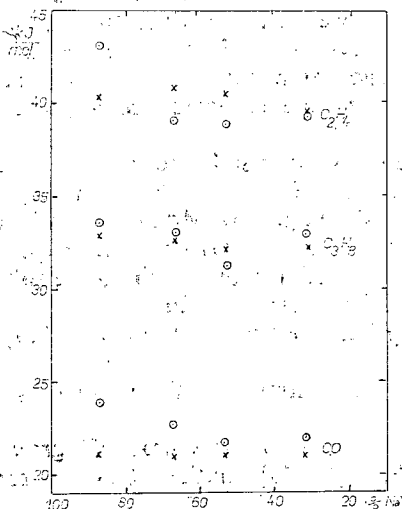


Fig. 1. Dependence of the adsorption heats for US and HY zeolites [17] on the Na<sup>+</sup> cation content. Adsorbates: ethene, propane, and carbon monoxide

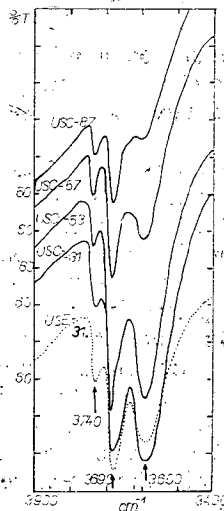


Fig. 2. Infrared spectra of the US samples

Dependences of differential heats of adsorption on the  $\text{Na}^+$  content in stabilized Y zeolites are plotted in Fig. 1. When comparing these results with the former ones [17] obtained with nonstabilized NaHY zeolites, the influence of Na cations on the energy of adsorption for adsorbates possessing the ability of specific interaction is lowered by the process of stabilization.

The stabilization of Y zeolites is connected with the formation of structural OH groups whose wavenumbers are shifted to higher values in comparison to OH groups of the nonstabilized forms [18, 19]. The IR spectra of our US zeolites investigated

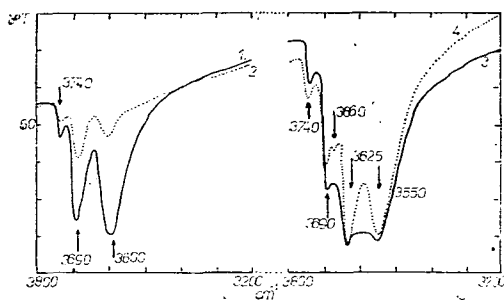


Fig. 3. Infrared spectra of the US samples after treatment with  $\text{NH}_4\text{OH}$  and potassium-sodium-tartrate solutions

curve 1 USE-31  
 curve 2 USC-31, both after the treatment with tartarate salt solution  
 curve 3 USE-31  
 curve 4 USC-31, both after the treatment with  $\text{NH}_4\text{OH}$  aqueous solution

in the OH stretching region are presented in Fig. 2, the wavenumbers correspond to the data of the quoted literature. The intensities of high frequency (HF) and low frequency (LF) bands are proportional to the degree of decationation and inversely to the temperature of stabilization. Fig. 3 represents the OH stretching spectrum of USC-31 and USE-31. Both samples were treated with 1 N  $\text{NH}_4\text{OH}$  (aqueous solution). Two new types of OH groups are observed, nearing to the HF and LF bands in HY zeolites. Even these materials are stable after repeated hydrothermal treatment. In the same figure the IR spectra of USC-31 and USE-31 are shown, the samples were treated with sodium-potassium

tartarate solution in order to remove the extralattice aluminium. In the OH stretching region no changes, corresponding to the absence of possible OH groups connected with Al cations, were observed. The stability of these extracted samples was preserved.

The results of the presented study have shown that stable forms of a Y zeolite, containing up to 90% of the original Na cations present in NaY, can be prepared. This fact is in contradiction to the hypothesis developed by MCDANIEL and MAHER [1, 20] but in agreement with the results of KERR summarized in the review [21], and JACOBS and UYTTERHOEVEN [18]. All our treated Y zeolites exhibit the following common properties, which are characteristic for a stabilized form.

1. Structural stability, *i.e.* constant sorption capacity and full crystallinity after repeated hydration-dehydration treatment.

2. Shrinkage in the unit cell, resulting in a contraction of the lattice by about 0.3–0.6%.

3. The wavenumbers of the valence vibrations of structural OH groups are identical with those reported by other authors [18, 19] for the ultrastable form of Y zeolites.

4. A part of the aluminium atoms is extracted from its framework lattice positions and removable from the zeolite matrix with NaOH,  $\text{NH}_4\text{OH}$  or complex forming agent solution.

5. Lowered energetical inhomogeneity of the surface layers of our US zeolites has been found, resulting in different sorption and catalytical properties in comparison with those of nonstabilized NaHY zeolites.

From the quantitative point of view all these properties are influenced by the  $\text{Na}^+ \rightarrow \text{NH}_4^+$  cation exchange and by the temperature of the stabilization.

We have prepared stable structures differing significantly as to the intensities of the phenomena ( $\text{Na}^+$ ,  $\text{Al}(\text{OH})_x^{(3-x)+}$  content u. c. dimensions *etc*), accompanying the stabilization of the lattice. According to the X-ray spectroscopic study of KÜHL [22] such a structure may be formally taken for a hybrid form of the true HY and the USY, the ratio of both types depending on the concentration of cationic Al. Such a formal conception agrees with some results of our IR measurements, showing in Fig. 3 the presence of absorption bands in the hydroxyl stretching region characteristic for a HY zeolite [18]. Presuming, nevertheless, the validity of the conception of two independent parts of structure; a partial destruction must follow after treatment under hydrothermal conditions. But we have found that even these structures are stable as no decrease in adsorption capacities after the THTC was observed. According to this fact and to the observed independence of stability on the degree of stabilization we conclude that the changes during the stabilization process influence the properties of the whole structure. This conception agrees with the observed shrinkage of the whole zeolitic lattice.

The aluminium extraction from its lattice positions during the stabilization process is a necessary condition. But, as we have shown, its presence in the stabilized structure is unnecessary.

The formal comparison of the presented data of adsorption heats leads us to the conclusion that the stabilization process suppresses the sorption activity of the cationic adsorption centres. Nevertheless, we have to take into account the possible redistribution and the possibility of the removal of some  $\text{Na}^+$  due to the influence of water vapour during the stabilization process. This influence will be especially remarkable on the surface layer and will probably decrease towards the centre of the monocrystal. Under the dynamic conditions of the gas chromatographic method the information obtained refers mainly to the properties of the surface layers of zeolitic monocrystals where the adsorption equilibrium is attained. The hypothesis mentioned above accounting for the differences in the distribution of Na cations is supported by our results published earlier [15, 23] concerning the differences in sorption and catalytic behaviour of the surface layer and the bulk of the zeolite monocrystal.

Presented results of the X-ray photoelectron spectroscopy show that the content in silicon and aluminium at the surface can be widely different from the bulk composition of the NaY zeolite [24], and that the surface  $\text{NH}_4^+$  content in  $\text{NaNH}_4\text{Y}$  zeolites is about 1/2 of that of the bulk [25]. These observed differences in compositions confirming the heterogeneity of the structure may grow during the stabilization process.

To conclude: the study presented has shown the possibility of preparing a stable Y zeolite with high cation-exchange capacity. The stabilization process is considered to influence the whole structure of the zeolitic monocrystal.

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