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The Properties of Strongly Dealuminated Y Zeolites

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By combining thermal treatment and extraction of aluminium with hydrochloric acid, we have succeeded in reducing the content of Al atoms in Zeolite Y from 57 to 5 per elementary cell, without destroying the faujasite structure. The properties of the zeolite have been tested by sorption methods, by gas chromatography, and by ir and NMR spectroscopy.

INTRODUCTION

The modification of zeolitic crystals is important for the preparation of selective adsorbents and catalysts. The faujasites have attracted much attention and the preparation of various types of this material has been achieved by ion exchange, decationization, and dealumination of the lattice (*1*, *2*). The aim of our work was to prepare a zeolite of type Y with a maximal degree of dealumination and decationization. We tried to prepare a zeolite with a faujasite structure consisting as far as possible only of Si and O atoms. Such a siliceous zeolite could represent a very interesting model because after removing all cations and Al atoms from the lattice, the electrostatic field intensity should decrease substantially. This fact enables us to neglect the electrostatic term in the sum of sorption potentials.

EXPERIMENTAL

It is well known that the direct extraction of Al from Y zeolites with acids is possible only as far as 50% removal of Al without any loss of the crystallinity of the lattice (*3*). In order to avoid loss of crystallinity by direct extraction we have used a combination of the method for the preparation of the ultrastable faujasites according to McDaniel and Maher (*4*), together with a subsequent extraction with a solution of HCl. The content of Al in this sample was lower than $\frac{1}{10}$ of the original content in the NaY zeolite.

It was verified (*5*) that during the stabilization process the lattice loses a fraction of the Al atoms which migrate into the cavities of the zeolite, where an Al–O compound is found (*6*). The stabilization is accompanied by partial replacement of the Al vacancies by Si atoms (*1*, *2*). In the second step of our preparation procedure the above-mentioned "extralattice" Al atoms were extracted together with a certain fraction of the framework Al with the HCl solution. The preparation procedure of our US-Ex zeolite is systematically described in Table 1. The chemical com-

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TABLE 1

Scheme for the Preparation of US-Ex Zeolite

Description of the operation	Abbreviated nomenclature of the zeolite
1. Commercial NaY zeolite	NaY
2. Ion exchange: 20 g NaY in solution of 300 g $(NH_4)_2SO_4$ in 1500 ml H_2O, 15 min at 100°C	$NaNH_4Y$-I
3. Ion exchange: solution of 100 g of $(NH_4)_2SO_4$ in 1500 ml H_2O, 15 min at 100°C	$NaNH_4Y$-II
4. Activation in muffle furnace, 3 hr, 540°C	NaHY
5. Ion exchange: solution 300 g $(NH_4)_2SO_4$ in 6000 ml H_2O, 1 hr, 100°C	NH_4HY-I
6. Ion exchange: solution 300 g $(NH_4)_2SO_4$ in 6000 ml H_2O, 1 hr, 100°C	NH_4HY-II
7. Activation in a tube furnace in a stream of water vapor	US-w
8. Aluminum extraction with dilute HCl (0.1 *N*), washing in H_2O drying at 100°C	US-Ex

position of the original zeolite was $Na_{54} \cdot (AlO_2)_{57} \cdot (SiO_2)_{135}$. Other data for completely dehydrated samples are presented in Table 2.

Adsorption measurements were carried out on a microbalance of the McBain type. ir spectra were recorded on a Perkin-Elmer 621 spectrometer by a technique described elsewhere (*7*), where details of the chromatographic measurements are also presented. NMR spectra were recorded using a wide line spectrometer of the bridge type KRB 35/62 at 21 and 62 MHz as described previously (*8*). Calorimetric data were obtained with a microcalorimeter of the Calvet type similar to that used by Sichhart *et al.* (*9*).

RESULTS AND DISCUSSION

During the dealumination process no significant destruction of the lattice took place. This conclusion is supported by the following experimental results.

(1) From the X-ray diffractograms presented in Fig. 1 for NH_4Y and US-Ex it follows that the structure of US-Ex zeolite is well preserved. The changes of the intensities of the diffraction lines are connected with the different chemical composition of the elementary cell. The shifts of the lines demonstrate the reduction of the lattice parameter to 2.417 nm. From electron microscope pictures it could be concluded that during the dealumination process neither the size nor the shape of crystals has been changed. Channels of the order of about 10 nm indicated that surface corrosion could be observed on the surfaces of the crystals.

(2) Infrared spectra in the region of the skeletal vibrations of the zeolite (400 to 1200 cm^{-1}) presented in Fig. 2 indicate a well-developed crystalline structure. With

TABLE 2

Structural Data for NaY, NaHY, and US-Ex

Sample	Chemical analysis of dehydrated zeolite	Number of Al atoms per cavity		Lattice parameter (nm)
		In T position	In extra lattice position	
NaY	$0.2Na_2O \cdot 0.21Al_2O_3 \cdot SiO_2$	7	0	2.472
NaHY	$0.1Na_2O \cdot 0.21Al_2O_3 \cdot SiO_2$	5	2	2.454
US-Ex	$0.005Na_2O \cdot 0.013Al_2O_3 \cdot SiO_2$	0.5	0	2.427

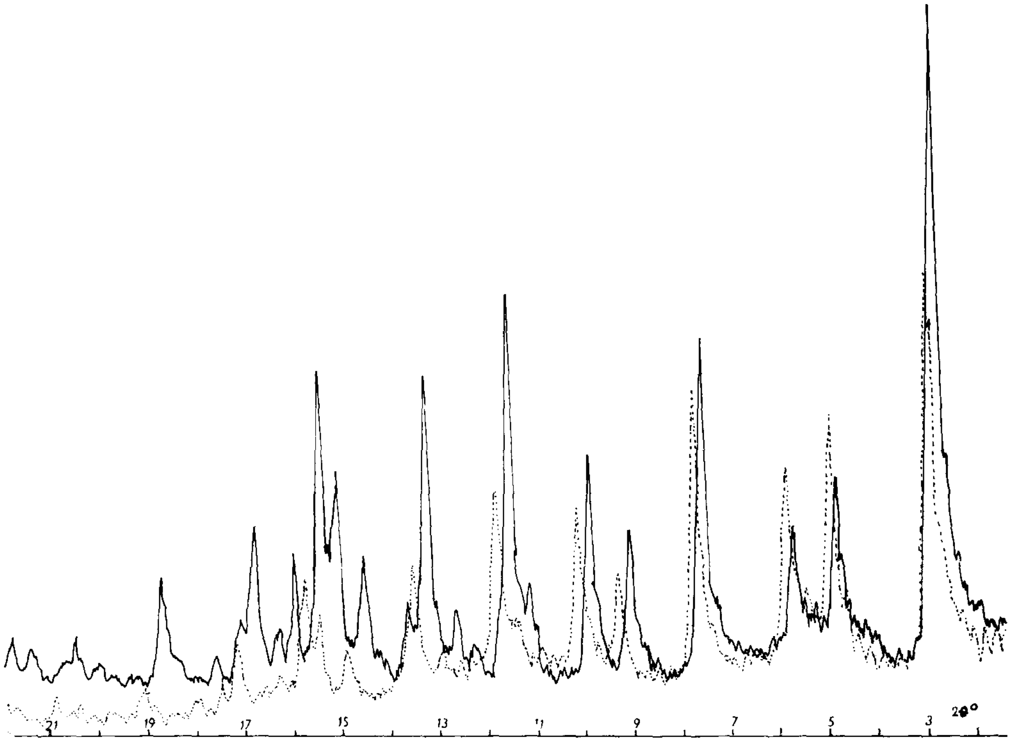


FIG. 1. X-Ray powder diagrams of NH_4Y (——) and US-Ex (- - -) zeolite.

increasing dealumination the absorption bands become sharper, probably due to a more isotropic character of the vibration of T atoms. The observed linear dependence of the wavenumbers of the skeletal vibrations on the amount of Al atoms in the framework described by Pichat *et al.* (*11*) and verified by us allows us to determine the amount of Al atoms which have left the T positions in the lattice. The results are presented in Table 2.

(3) The sorption capacities measured by argon at $-195°C$ (a = 8.5 mmol g^{-1}) and by benzene at 70°C (a = 2.48 mmol g^{-1}) are only slightly lower than the data for NaY. The form of the adsorption isotherm is also not as sharply rectangular as is usually observed on cationic forms of zeolites. After repeated hydration at 20°C and dehydration at 350°C *in vacuo* no changes in sorption capacities were observed. This result together with X-ray diffraction data confirms that US-Ex zeolite is stable under hydrothermal conditions in contrast to the normal shallow bed HY zeolite (*12*).

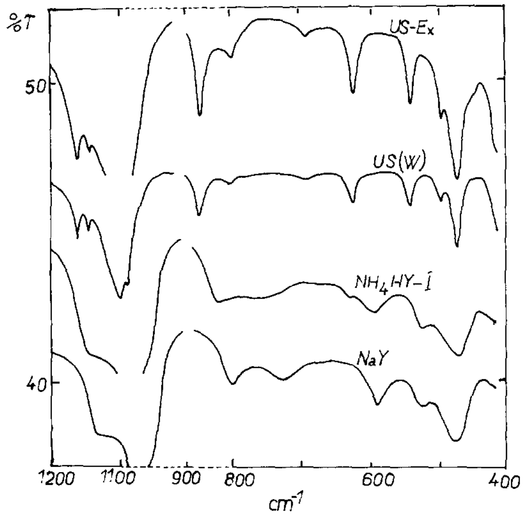


FIG. 2. ir spectra of the investigated zeolites in the region of skeletal vibrations.

During the stabilization process of McDaniel and Maher nearly 25% of the Al atoms are released from T positions and therefore a significant amount of vacancies in T positions should be created. X-Ray analysis of the ultrastable zeolite shows that all T positions are occupied (*13*, *14*). The vacancies are eliminated due to the migration of Si atoms under the influence of hydrothermal conditions during the stabilization process.

In our investigations infrared spectroscopy and NMR technique were used to obtain information about the nature of the structural OH groups found after the extraction of Al from the lattice. In Figs. 3a and b spectra of the stretching vibrations of structural OH and OD groups are plotted. No bands indicating the presence of adsorbed water molecules have been found in the region of deformation vibrations of HOH and DOD, respectively. Therefore all the absorption bands presented in Fig. 3 correspond to structural OH groups. All hydrogen atoms are exchangeable with deuterium. The strong and narrow band at 3735 cm^{-1} and at 2749 cm^{-1} in the OH and OD regions corresponds to isolated OH and OD groups, respectively. These groups are not very sensitive to the adsorption of water (see Fig. 3b) and they are relatively stable up to almost 700°C (see Fig. 3a, curve 4). The wavenumber of these groups is near to the wavenumber of the terminal –Si–OH groups (*15*, *16*). We suppose that the abovementioned groups in US-Ex zeolite have the same character. The high intensity of their absorption band compared with the same band in HY zeolites is probably connected with the high roughness of the surface of crystals. However, a similar type of OH groups could be located also at the Al vacancies. In the ir spectrum of OH groups two other weak bands at 3630 and 3540 cm^{-1} are detected. Both bands are very sensitive to the adsorption of water (see Fig. 3b) and we suppose that the corresponding protons are located in the vicinity of the remaining Al atoms in T positions. In the region 3300 to 3700 cm^{-1} a broad band appears, characteristic of OH groups in mutual interaction with hydrogen bonds, as in the case of silica gel (*16*). The

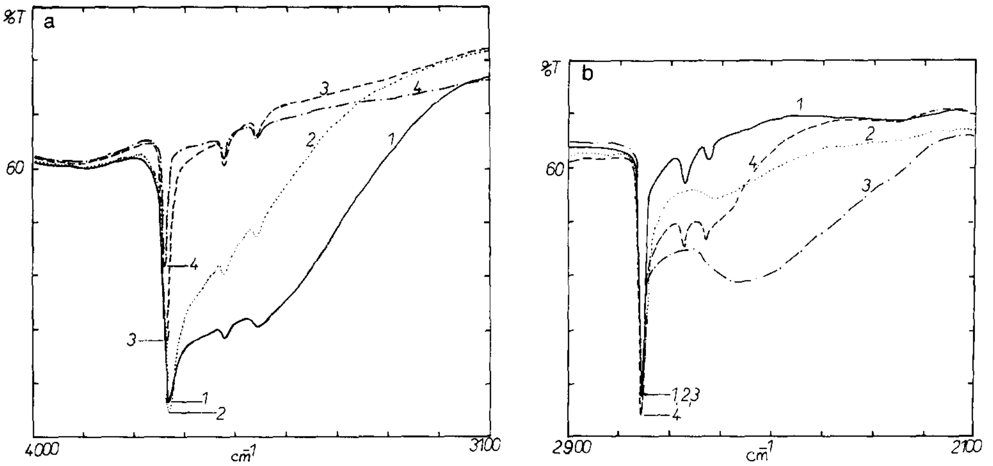
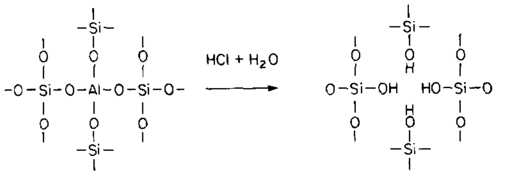


FIG. 3. (a) ir spectra of US-Ex zeolite in the region of the OH stretching vibrations after treatment *in vacuo* at (1) 150°C for 24 hr, (2) 350°C for 24 hr, (3) 550°C for 6 hr, and (4) 700°C for 20 hr. (b) ir spectra of the US-Ex zeolite in the region of OD stretching vibrations: (1) After treatment *in vacuo* at 650°C for 20 hr; (2) after the adsorption of D_2O at 5 Torr pressure and 25°C; (3) after the adsorption of D_2O at 16 Torr and 25°C; (4) after the desorption of D_2O into the cooling trap.

treatment of the zeolite with an acid solution produces Al vacancies (*17*). The existence of OH groups capable of mutual interaction may be expected first of all at these vacancies as follows from the scheme



where $(OH)_4$ "nests" are created. The distance between oxygen atoms in the undisturbed SiO_4 tetrahedron is about 0.27 nm Using the empirical relation between wavenumber of the stretching mode ν(OH) and the distance between oxygen atoms in the hydrogen bond R (O–H...O) given in the literature (*26*), we obtain from the observed wavenumbers 3200 to 3600 cm^{-1} the O...O distances of 0.27 to 0.35 nm, respectively.

The intensities and second moment data of the NMR curves measured for the samples with different temperatures of activation are listed in Table 3. After treatment in a vacuum of 10^{-4} Torr (1 Torr = 133.3 Pa) for 12 hr at 60°C no adsorbed water has been found, in agreement with the ir results within the experimental sensitivity (an amount of water lower than 0.5 molecule per cavity was not detectable). The second moment of the resonance curve of the structural OH groups in the "shallow bed" HY zeolites is about 1 G^2 (1 G = 0.1 mT) and is nearly independent of the temperature of activation (*19*). The second moment of the structural OH groups of silica gel exhibits values of about 0.1 G^2 under the same conditions of activation. The values of the second moment for various treatment temperatures given in Table 3 demonstrate that most of the OH groups present in the US-Ex zeolite are not in interaction with Al nuclei and that they are similar to the OH groups of silica gel. Also by spin echo measurements as in the work of Freude *et al.* (*24*) it could be shown that there is no magnetic H...Al interaction for the OH protons. After the treatment of the zeolite at 60°C and also at 200°C they exhibit relatively intense magnetic proton–proton interaction. Only a small fraction of the groups mentioned is probably located, in agreement with the ir spectroscopic results at the Al vacancies. During the extraction process of the zeolite US-w (having 1.5 Al atoms per cavity) one atom of Al per cavity is dissolved and extracted from the zeolite lattice so that 0.5 Al atoms per cavity remain in the lattice (see Table 2). If the mechanism presented in the scheme described above is valid, one Al atom should be replaced by four protons in the lattice. The value of 4.8 OH groups per cavity determined after the treatment at 60°C agrees relatively well with the above-mentioned consideration. Supposing a tetrahedral configuration of protons at the Al vacancy we derive from the measured second moment of 0.54 G^2 a proton–proton distance of about 0.35 nm. For two protons at a distance of 0.35 nm we calculate a second moment of 0.18 G^2. Therefore our estimated amount of OH groups and their second moments may be explained by OH pairs after partial dehydroxylation of OH at Al vacancies. The $(OH)_4$ "nests" described by Breck and Skeels (*25*) are not present at high temperatures as follows

TABLE 3

The Amount of Structural OH Groups of US-Ex Zeolite Determined by NMR

Temperature of activation *in vacuo* (°C)	The number of OH groups per cavity	Second moment (G^2)
60	4.8 ± 0.3	0.54 ± 0.05
200	2.3 ± 0.2	0.40 ± 0.04
300	1.0 ± 0.2	0.20 ± 0.04
400	0.9 ± 0.2	0.17 ± 0.04
500	0.5 ± 0.2	—

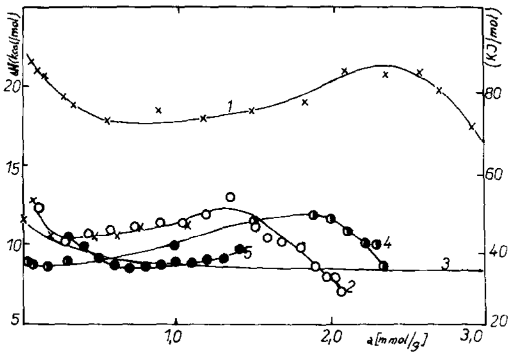


FIG. 4. Heats of adsorption as a function of the amount of adsorption: (1) Benzene–NaX; (2) benzene–US-Ex; (3) benzene–SiO_2 (according to Ref. 20); (4) butane–NaY; (5) butane–US-Ex.

TABLE 4

Chromatographic Heats of Adsorption on Zeolites[a]

Adsorbate	US-Ex	NaY
CH_4	17.6 ± 1.1	18.1 ± 0.6
C_2H_6	23.6 ± 0.9	26.0 ± 1.5
C_3H_8	29.5 ± 0.4	34.0 ± 1.2
C_2H_4	Activated adsorption	47.1 ± 1.5
$-CH_2-$	6.0	8.0

[a] kJ mol^{-1}.

from our ir spectra and NMR calculations. In our opinion the $(OH)_4$ "nests" have a relatively poor stability. From the NMR measurements it is evident that after dehydroxylation at 400°C and hydration at 25°C three OH groups per cavity (from 3.9 OH per cavity) are created again. The same conclusion follows from the ir spectra in Fig. 3b. The OH groups remaining after the treatment at 500°C and represented by the band at 3735 cm^{-1} are the terminal OH groups located partly on the surface of the crystals and partly at the vacancies of Al after the dehydroxylation.

Heats of adsorption of *n*-butane and benzene are presented in Fig. 4 as a function of the adsorbed amount. For comparison, data of benzene–NaX, benzene–silica (20), and *n*-butane–NaX are presented as well. The character of the heat of adsorption of *n*-butane on US-Ex is typical for molecules without specific interactions with the adsorbent. It reflects the action of the dispersion forces which make the most important contribution to the adsorption energy. The heats of adsorption are therefore not substantially influenced by the chemical composition of the adsorbent and only intermolecular interaction causes a small increase of the heat of adsorption with the increasing adsorbed amount. The heats of adsorption decrease slightly only in the region of the small amounts of adsorbed butane due to the influence of the lattice defects. A similar heterogeneity is also pronounced in the case of benzene, the adsorption heats of which decrease by about 12.3 kJ mol^{-1}. The absolute values of the heats of adsorption in the systems benzene–US-Ex and benzene–porous silica are very close and

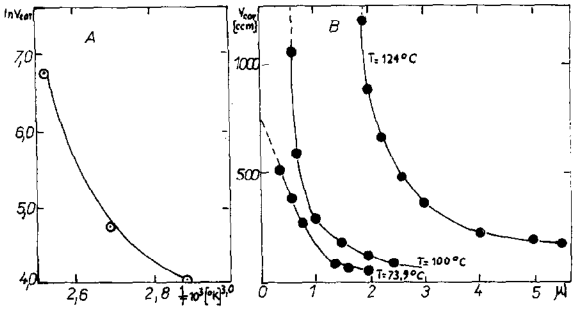


FIG. 5. (A) Dependence of the logarithm of the retention volume on the reciprocal temperature for ethylene–US-Ex. (B) Dependence of the retention volume of ethylene on the amount of adsorbate at different temperatures.

demonstrate that the expected reduction of the electrostatic components of the adsorption energy has been realized. On the other hand the heat of adsorption for benzene on NaX is higher, due to the specific interaction of benzene with cations. These results are in agreement with the chromatographic heats of adsorption for saturated hydrocarbons presented in Table 4. However, in the course of the chromatographic experiments with ethylene it has been found that activated adsorption takes place as follows from the dependence of retention volumes on temperature (Fig. 5a). A similar process in another system has been described by Ivanova and Zhuchovickii (*21*). The fraction of irreversibly adsorbed ethylene increases with temperature (see Fig. 5b). The products of polymerization were proved by mass spectrometry.

The acidity of the zeolite US-Ex measured with adsorbed pyridine at 300°C and $p = 6$ Torr was 0.04 mmol g^{-1} but without any measurable amount of irreversibly adsorbed (chemisorbed) pyridine. The ir spectra in the region 1700 to 1300 cm^{-1} for pyridine adsorbed at room temperature consist of three bands at 1437,1480, and 1585 cm^{-1} (with a weak shoulder at 1570 cm^{-1}). As is evident from this, mainly physically adsorbed species are present on US-Ex zeolite just as in the case of pyridine on Cabosil (*22*).

We tried to test the interesting experimental observation of activated adsorption of ethylene found in the chromatographic condition by ir spectra of adsorbed ethylene on US-Ex. It follows from the chromatographic measurements that the amount of irreversibly adsorbed ethylene is about 1 molecule per 2.5 to 7.0×10^3 cavities. The amount of the chemisorbed species of ethylene is so small that it was beyond the sensitivity of ir measurement to detect it. This is also in agreement with the fact that no detectable bands of Brønsted or Lewis type sites were found with pyridine. With respect to other published experiments (*23*) we suppose that the defects on the surface layer of crystals created during the treatment of the zeolite are probably the active sites initiating the activated adsorption of ethylene.

CONCLUSIONS

(1) A stable zeolite with the faujasite structure and containing only five Al atoms in the elementary cell can be prepared by extraction of Al from the stabilized Y zeolite with a solution of HCl.

(2) The resulting zeolite contains OH groups which are mainly of the terminal type, and whose behavior is similar to the OH groups of amorphous silica.

(3) This zeolite does not exhibit $(OH)_4$ "nests" at the Al vacancies after activation *in vacuo* at elevated temperatures.

(4) The amount of Al vacancies is lower than the expected amount (1 per cavity) as a result of some annihilation process.

(5) The US-Ex zeolite exhibits neither acid sites of the Brønsted type nor a significant amount of Lewis type sites.

(6) The field of the adsorption forces is substantially diminished due to minimal contribution of the electrostatic term.

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