

## FORMATION OF HYDROXYL GROUPS AND EXCHANGE WITH DEUTERIUM ON NaHX AND NaHY ZEOLITES

L. KUBELKOVÁ and J. NOVÁKOVÁ

*J. Heyrovský Institute of Physical Chemistry and Electrochemistry,  
Czechoslovak Academy of Sciences, 121 38 Prague 2*

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The deammoniation and dehydroxylation of  $\text{Na}(\text{NH}_4)\text{X}$  and  $\text{Na}(\text{NH}_4)\text{Y}$  zeolites were compared. With the X type, both processes overlap and proceed more easily than with the Y type. Both H forms contain structural OH groups and hydroxyls denoted as SiOH, to which a  $3740\text{ cm}^{-1}$  band in the IR spectrum is assigned. The zeolite NaHX contains, in addition, OH groups characterized by  $3700$  and  $3600\text{ cm}^{-1}$  bands. Certain differences in the behaviour of NaHX and NaHY zeolites during deammoniation and dehydroxylation can be attributed to the presence of "non-localizable" H atoms. Active sites for the  $\text{D}_2$ -OH exchange are formed probably during dehydroxylation. Hydrogen in SiOH groups is replaced by deuterium with both zeolite types more slowly than H atoms of other OH groups, which influences the kinetic dependences in the gas phase. The presence of water in the gas phase influences the kinetics and can distort the determination of the number of H atoms bound in the zeolites.

In our previous work<sup>1</sup> we have shown the advantages of the combination of the IR spectroscopic solid phase analysis with the mass spectroscopic gas phase analysis in the study of the isotopic exchange of deuterium with hydrogen of OH groups (or with a differently bound hydrogen) in zeolites (further:  $\text{D}_2$ -OH exchange). The IR spectroscopy enables to follow the exchange rate of deuterium with hydrogen for every individual type of the OH groups and thus to obtain information about their possible heterogeneity elucidating the kinetic dependences in the gas phase. The same concentration of deuterium in the gas and solid phases indicates the attainment of an equilibrium, which is difficult to find out by only one of the methods. This quantity is important for the determination of the number of H atoms participating in the exchange in the given zeolite.

An important factor in the  $\text{D}_2$ -OH exchange can be the activation of  $\text{D}_2$  molecules catalysed by the zeolite. Information about this activation is obtained from the exchange of gaseous deuterium with gaseous hydrogen (further:  $\text{D}_2$ - $\text{H}_2$  exchange).

The present work deals with the  $\text{D}_2$ -OH exchange on NaHX zeolites with different degrees of dehydroxylation in comparison with NaHY zeolites studied previously<sup>1</sup>. To characterize the samples, the dehydroxylation of NaHX and NaHY zeolites and their formation from their ammonium forms were also followed.

## EXPERIMENTAL

## Chemicals

A zeolite of the type  $\text{Na}_{0.4}(\text{NH}_4)_{0.6}\text{-X}$  was prepared from its NaX form with a Si : Al ratio equal to 1.33 (Research Institute for Oil and Hydrocarbon Gases, Bratislava, ČSSR) by the usual cation exchange in an ammonium chloride solution at 70°C. Another zeolite,  $\text{Na}_{0.3}(\text{NH}_4)_{0.7}\text{-Y}$  with a Si : Al ratio equal to 2.5 was of the same origin.

For the measurement of IR spectra and weight analyses the samples were pressed at 700  $\text{kp}/\text{cm}^2$  into plates of a "density" of 5–20  $\text{mg}/\text{cm}^2$ . In the mass spectrometric measurements of the kinetics of the  $\text{D}_2\text{-OH}$  exchange, deammoniation, and dehydroxylation, powdered zeolites were used.

Deuterium was prepared by the reaction  $2 \text{D}_2\text{O} + 2 \text{Na} = 2 \text{NaOD} + \text{D}_2$  and purified by diffusion through a palladium tube. Its D content was 75–90 at. %.

## Apparatus and Measurement

*Solid phase analysis and IR spectra.* A zeolite sample was placed in a vacuum IR cell<sup>2</sup>, which was a part of a volume-calibrated vacuum apparatus. The sample was heated to the desired temperature in a small oven and after cooling to the laboratory temperature the IR spectrum was measured by a Perkin-Elmer 621 spectrophotometer in the interval 1200–4000  $\text{cm}^{-1}$ . In some cases a reference beam attenuator was used. During the measurement of the  $\text{D}_2\text{-OH}$  exchange the sample mass was 15–60 mg, the deuterium pressure 0.5–1 Torr, the reaction volume 720  $\text{cm}^3$ , and temperature 300 or 500°C. Besides the measurement of the IR spectrum of the zeolite, a sample of the gas phase was taken for mass spectrometry. The band heights in the IR spectra,  $A_v$  ( $\text{cm}^2 \text{mg}^{-1}$ ), were calculated as  $A_v = d^{-1} \log(I_0/I)_v$ , where  $d$  is the sample "density" in  $\text{mg}/\text{cm}^2$ ,  $I$  and  $I_0$  are transmittances at the wave number  $\nu$  of the given band and at a base line, respectively.

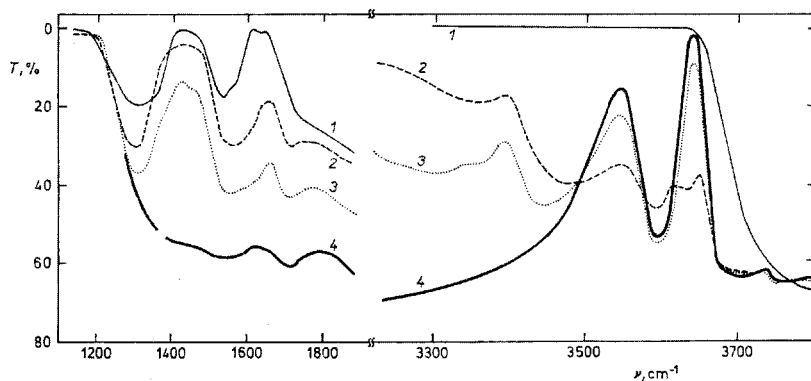


FIG. 1

IR Spectra of  $\text{Na}(\text{NH}_4)\text{Y}$  Zeolite

1 On the air; 2 after evacuating at 120°C for 15 min, 3 18 h; 4 after evacuating at 300°C for 30 min.

*Gas phase analysis.* The gas phase kinetic dependences in the  $D_2$ —OH and  $D_2$ — $H_2$  exchanges were measured continually with a MCH 1302 type mass spectrometer (USSR). Its sensitivity was the same for  $D_2$ , HD, and  $H_2$ . The quantity of the samples was 100 mg, the reaction volume  $700\text{ cm}^3$ , pressure of deuterium 0.5 Torr was constant during the exchange, temperature during  $D_2$ —OH exchange was 300 or  $500^\circ\text{C}$ , for  $D_2$ — $H_2$  exchange  $200^\circ\text{C}$ . During the study of the dehydroxylation of the H forms of the zeolites and their formation from the  $NH_4$  forms, the decomposition products were led directly into the mass spectrometric cell without the use of leaks. The sample quantity had to be very small, 0.1 mg or less, hence the obtained values have in this case only a qualitative character.

*Weighing.* The weight decrements during dehydroxylation of the H forms of the zeolites were determined on a spiral balance<sup>3</sup> with a sensitivity of 1.042 or 1.625 mg/mm. The sample quantities taken into work were 100—300 mg.

In the measurements of IR spectra, weight decrements, and in mass spectrometry measurement the vacuum attained in the apparatus was  $10^{-5}$ — $10^{-6}$  Torr. The  $D_2$ —OH exchange is under our experimental conditions influenced neither by external diffusion nor by diffusion into the large cavities of the zeolite<sup>1</sup>.

## RESULTS

### *Formation of NaHX and NaHY Zeolites and their Dehydroxylation*

The change of the  $NH_4$  form of the zeolites to the H form is accompanied by *a*) loss of the adsorbed water (dehydration), *b*) escapement of gaseous ammonia and formation of hydroxyl groups (deammoniation), and *c*) splitting off of water at the expense of OH groups formed by deammoniation. This process will be termed "dehydroxylation" to distinguish it from the case *a*). (The term "dehydration" in the literature

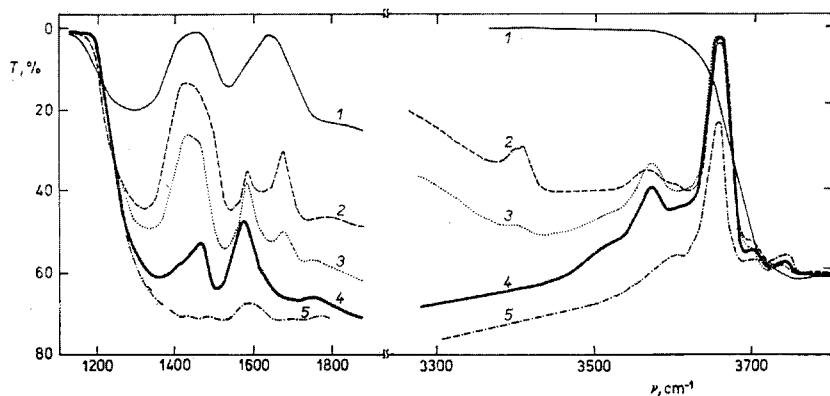


FIG. 2

IR Spectra of  $Na(NH_4)X$  Zeolite

1 On the air; 2 after evacuating at  $120^\circ\text{C}$  for 15 min, 3 18 h; 4 at  $300^\circ\text{C}$  for 30 min; 5 at  $500^\circ\text{C}$  for 30 min.

often means both the loss of the adsorbed water and the dehydroxylation.) These processes, especially the first two, cannot be easily experimentally separated. The dehydration and deammoniation take place partly already at the laboratory temperature. In the present work the behaviour of X and Y zeolites in vacuum at 120, 300, and 500°C, always at least for 18 h, was studied by analysis of the gaseous (mass spectroscopy) and solid (IR spectra) phases.

In Figs 1–3 are shown the IR spectra of the starting  $\text{Na}(\text{NH}_4)\text{Y}$  and  $\text{Na}(\text{NH}_4)\text{X}$  zeolites in contact with the air and further after evacuation at 120 and 300°C for different time intervals. Figs 1 and 2 give information about  $\text{NH}_4^+$  ions ( $1430\text{ cm}^{-1}$  band), and adsorbed water ( $1640\text{ cm}^{-1}$  band), which, however, overlaps with the  $1670\text{ cm}^{-1}$  band assigned to the vibration of  $\text{NH}_n$ . In this way the possibilities of the determination of water in the sample are limited.

The spectrum of OH groups is shown also in Figs 1–3. The most important bands are  $3640$  and  $3550\text{ cm}^{-1}$  for the Y zeolite,  $3650$  and  $3565\text{ cm}^{-1}$  for the X zeolite. They are assigned to the stretching vibrations of OH groups containing O atoms of the regular zeolite lattice (structural OH groups). A comparison of the contents of water and ammonia in the gas phase during evacuation at 120 and 300°C is seen from Fig. 4a,b for the X and Y zeolites. Prior to this measurement the samples were evacuated at room temperature.

*Evacuation at 120°C.* It follows from the IR spectra that at this temperature both the dehydration and a gradual loss of  $\text{NH}_4^+$  ions (deammoniation) with the formation of structural OH groups take place. For the Y zeolite, after 15 min of evacuation a new  $3620\text{ cm}^{-1}$  band was found (Fig. 1, curve 2), which disappeared after evacuating for 18 h (curve 3). This new band probably bears a relation to the presence of adsorbed water. We found namely the same band in the spectrum of the NaHY zeolite after adsorption of small amounts of water; after its desorption this band also disappeared. After evacuating for 18 h, both zeolite types contain also  $\text{NH}_4^+$  ions (Fig. 1, curve 3). The difference between the X and Y zeolites is clear from the gas phase analysis (Fig. 4a): at 120°C deammoniation prevails with the X type, dehydration with the Y type.

*Evacuation at 300°C.* At 300°C the decomposition of the  $\text{NH}_4^+$  ions continues: after evacuating for 30 min we did not find the  $1430\text{ cm}^{-1}$  band in the spectrum (Figs 1 and 2, curve 4). With the Y zeolite the loss of  $\text{NH}_4^+$  ions was accompanied by the formation of further structural OH groups (Fig. 1, curve 4). With the X zeolite, however, we did not observe an increase of the  $3650$  and  $3565\text{ cm}^{-1}$  band heights (Fig. 2, curve 4) although the decrease of the  $1430\text{ cm}^{-1}$  band height was so large that (in analogy to the Y zeolite) the expected change should be noticeable. Evacuating for 18 h did not cause a change of the bands of the stretching vibrations of the OH groups with the Y zeolite, whereas with the X zeolite their height decreased and a slow dehydroxylation started to proceed (Fig. 3).

According to the gas phase analysis (Fig. 4b), ammonia is set free in a larger extent from the Y than from the X zeolite. With both samples, water was found in the gas phase. We have probably to deal with the finishing of its desorption; with the X zeolite also dehydroxylation makes a contribution.

Deammoniation is at 300°C with both zeolite types essentially finished. In the gas phase a relatively very small amount of ammonia was found even at 500°C, however no corresponding changes were found in the IR spectra.

The NaHY and NaHX zeolites formed at 300°C contain besides structural hydroxyls also small amounts of OH groups (further denoted as SiOH) manifested by a 3740  $\text{cm}^{-1}$  band in the spectrum. This band is in the literature<sup>4</sup> assigned to terminal OH groups of zeolite particles, OH groups of silica impurities, or hydroxyls formed as a result of structural changes of the zeolite lattice due to the action of water. The zeolite NaHX contains, in comparison with NaHY, some more OH groups that are manifested by a weak 3700  $\text{cm}^{-1}$  band and a broad band with a center at about 3600  $\text{cm}^{-1}$ . Both these bands were found also by other authors<sup>5,6</sup>.

Besides OH groups, both the zeolite types contain after evacuation at 300°C

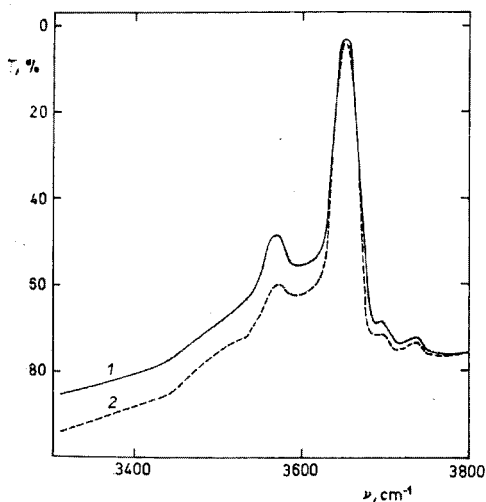


FIG. 3

## IR Spectra of NaHX Zeolite

1 After deammoniation at 300°C for 30 min  
2 after further evacuation at the same temperature for 18 h.

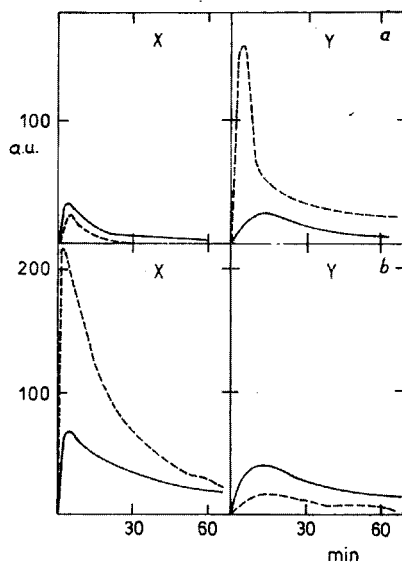


FIG. 4

Decomposition of  $\text{Na}(\text{NH}_4)\text{X}$  and  $\text{Na}(\text{NH}_4)\text{Y}$  Zeolites Followed by Mass Spectrometric Analysis

----- Evolution of ammonia and ———— water at 120°C (b) and 300°C (a).

traces of organic impurities and adsorbed carbon dioxide, which can be easily removed at 500°C. Their presence was indicated by gas phase analysis during evacuation at 500°C. With the X zeolite, 1585 and 1475  $\text{cm}^{-1}$  bands in the IR spectrum, which disappear at 500°C (Fig. 2, curve 5), can be assigned to adsorbed  $\text{CO}_2$  in the form of carbonate complexes. With the Y zeolite, no similar bands were observed.

*Dehydroxylation of NaHX and NaHY zeolites at 500°C.* A partial dehydroxylation of the NaHX zeolite takes place already at 300°C. By increasing the temperature gradually and analysing the gas phase we found that this process begins with the NaHY zeolite only at 450°C. To compare both types of zeolites, we therefore chose a temperature of 500°C. Fig. 5a,b shows the influence of the duration of the dehydroxylation at 500°C on the height of the IR spectral bands assigned to structural hydroxyls and SiOH groups. The starting samples were treated by evacuating for 18 h at 300°C. It is obvious that the dehydroxylation proceeds more easily with the NaHX than with the NaHY zeolite. With both these types, the number of SiOH groups increases, and this still more with the latter. The OH groups of the NaHX zeolite that are characterized by the 3600  $\text{cm}^{-1}$  band are at 500°C also removed but more slowly than the structural hydroxyls, to which a 3565  $\text{cm}^{-1}$  band is assigned (Fig. 2, curve 5). The 3700  $\text{cm}^{-1}$  band occurs in the IR spectrum of the NaHX zeolite even after 18 h of evacuation but is overlapped by higher 3740 and 3650  $\text{cm}^{-1}$  bands.

#### $\text{D}_2\text{—OH}$ Exchange at 300°C

In the preceding work<sup>1</sup> we found that the capability of exchange of the hydroxyl H atoms (or differently bound H atoms) of the NaHY zeolite with gaseous deuterium proceeds substantially more easily with increasing degree of dehydroxylation. We now found the same, although weaker effect in the case of the NaHX zeolite. At 300°C the equilibrium is not reached after 18 h and only a portion of the solid phase H atoms participates in the  $\text{D}_2\text{—OH}$  exchange. This quantity is indicated in Table I (B), where the NaHX and NaHY zeolites treated by 18 h evacuation at 300°C (denoted as  $Z_{300}$ ) and the same samples dehydroxylated for 18 h at 500°C (denoted as  $Z_{500}$ ) are compared. The total number of H atoms (C) indicated in the table was calculated from equilibrium data for the  $\text{D}_2\text{—OH}$  exchange at 500°C. It is obvious that with the  $Z_{300}$  samples a smaller fraction of all H atoms participates in the  $\text{D}_2\text{—OH}$  exchange at 300°C than with the  $Z_{500}$  samples. The dehydroxylation effect is at the same time much more pronounced with the Y than with the X zeolite.

The  $\text{D}_2\text{—OH}$  exchange is in the IR spectrum accompanied by a decrease of the intensity of the OH groups bands and by the formation of the corresponding OD groups bands as discussed in detail in ref.<sup>1</sup>. Both with the NaHY and NaHX zeolites it was found that the SiOH groups are transformed to SiOD more slowly than other hydroxyl groups.

To judge the influence of the dehydroxylation of a zeolite on the activation of  $D_2$  molecules, we studied also the  $D_2$ — $H_2$  exchange at  $200^\circ C$ , *i.e.*, under conditions where the  $D_2$ —OH exchange did not proceed. In the case of the NaHX zeolite, the  $D_2$ — $H_2$  exchange was found both with the  $Z_{300}$  and  $Z_{500}$  samples, whereas in the case of NaHY only with the  $Z_{500}$  sample.

### $D_2$ —OH Exchange at $500^\circ C$

During the  $D_2$ —OH exchange at  $500^\circ C$  a partial dehydroxylation of samples with a high content of OH groups takes place. This dehydroxylation is under our experimental conditions not influenced by the pressure of deuterium. The process is much more rapid and the amount of evolved water much larger with the NaHX than with the NaHY zeolite. For illustration, in Fig. 6 is shown the IR spectrum of the  $Z_{300}$  sample of the zeolite NaHX before (curve 1) and after 18 h heating in a closed apparatus at  $500^\circ C$  and cooling (curve 2). The decrease of the heights of the  $3650$  and  $3565\text{ cm}^{-1}$  bands, which are assigned to structural hydroxyls, is accompanied by the formation of new bands, which are shown — besides a  $1640\text{ cm}^{-1}$  band — in Fig. 6. These correspond to vibrations of water, which was adsorbed on the sample after cooling to the laboratory temperature; after evacuating at  $300^\circ C$  they disappear from

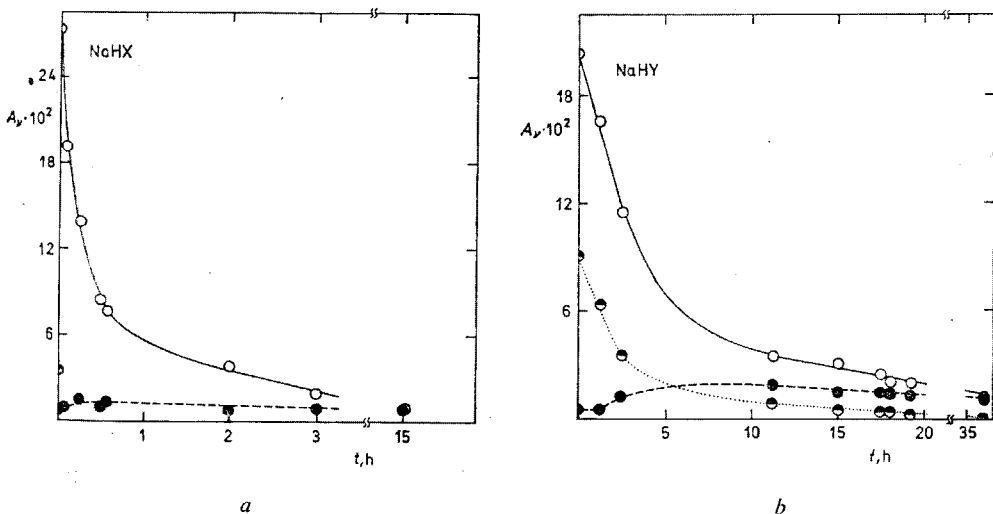


FIG. 5

Dependence of Band Heights on Dehydroxylation Time at  $500^\circ C$

*a* Zeolite NaHX: ●  $3740\text{ cm}^{-1}$ , ○  $3650\text{ cm}^{-1}$ , ●  $3565\text{ cm}^{-1}$ . *b* Zeolite NaHY: ●  $3740\text{ cm}^{-1}$ , ○  $3640\text{ cm}^{-1}$ , ●  $3550\text{ cm}^{-1}$ . The samples were prepared by 18h-decomposition at  $300^\circ C$ .

TABLE I

Numbers of H Atoms for NaHX and NaHY Zeolites Participating in  $D_2$ —OH Exchange at  $300^\circ C$  after 18 h (B), Total Numbers of H Atoms Determined from Exchange at  $500^\circ C$  (C), and Band Heights of OH Groups in IR ( $A_v$ )

Sample	B H/g . $10^{-20}$	C H/g . $10^{-20}$	$A_v \cdot 10^{+2}, \text{cm}^2 \cdot \text{mg}^{-1}$			
			$3\ 740\ \text{cm}^{-1}$	$3\ 640\ \text{cm}^{-1}$ (Y) $3\ 650\ \text{cm}^{-1}$ (X)	$3\ 550\ \text{cm}^{-1}$ (Y) $3\ 565\ \text{cm}^{-1}$ (X)	
NaHX	Z <sub>300</sub>	2.6	$41 \pm 6$ (18.4) <sup>a</sup>	0.6	27	3.1 <sup>b</sup>
	Z <sub>500</sub>	3.5	$11.7 \pm 3$	0.8	0.9	—
	Z <sub>300</sub>	0.1	$31 \pm 0.8$ (14) <sup>a</sup>	0.5	20.5	8.8
NaHY	Z <sub>500</sub>	2.0	$6.5 \pm 2$	1.5	3	0.5

<sup>a</sup> Calculated from the chemical composition; <sup>b</sup> the band overlaps with a broad  $3600\ \text{cm}^{-1}$  band.

the spectrum (curve 3). The same, but much smaller effect was found also with the Z<sub>300</sub> sample of the zeolite NaHY. Adsorbed water was found also in a sample of NaHY predehydroxylated at  $500^\circ C$  for 2.5 h, but not in the Z<sub>500</sub> samples of the NaHX and NaHY zeolites.

The kinetics of the  $D_2$ —OH exchange depends on the dehydroxylation of the X and Y zeolites (Fig. 7a,b). With increasing dehydroxylation the deviation from the kinetic dependence of the first order increases (with respect to the deuterium concentration in the gas phase). This deviation is probably caused by the presence

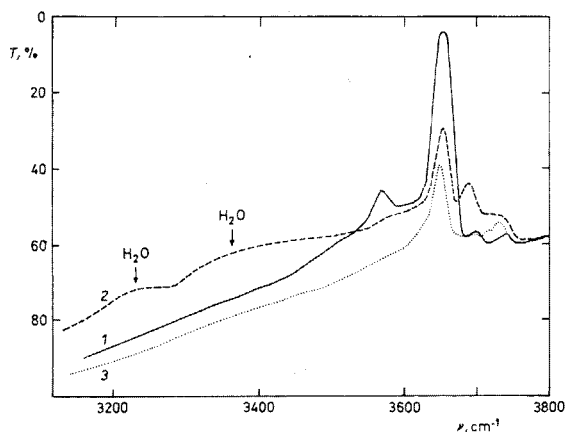


FIG. 6

IR Spectra of NaHX Zeolite Prepared at  $300^\circ C$

1 Original sample; 2 after heating in a closed apparatus at  $500^\circ C$  for 18 h and cooling; 3 after evacuation at  $300^\circ C$  for 18 h.



of SiOH groups whose H atom is exchanged with deuterium more slowly than the H atoms of other OH groups and whose fraction in both zeolite types increases with the dehydroxylation (Fig. 5*a,b*). However, the SiOH fraction is about the same with the  $Z_{300}$  samples of the NaHX and NaHY zeolites, nevertheless with the X type the  $D_2$ —OH exchange at 500°C is practically of the first order in contrast to the Y type (Fig. 7*a,b*). This difference can be attributed to the influence of water vapour whose content in the gas phase was found to be much higher with the X than with the Y zeolite.

The number of H atoms in the zeolite determined from the composition of the gas phase after attainment of equilibrium during the  $D_2$ —OH exchange can be also influenced by the presence of water vapour. The number of H atoms in the  $Z_{300}$  samples of the NaHX and NaHY zeolites, calculated from the chemical composition, and the mean experimental values found from the  $D_2$ —OH exchange are given in Table I. The experimental values are about twice as large as the theoretical ones. By measuring the weight loss on a spiral balance between 250 and 500°C, the quantity of  $1.55 \cdot 10^{21}$  H atoms/g was derived for the NaHX zeolite, whereas from the  $D_2$ —OH exchange between 300 and 500°C the corresponding result was  $2.9 \cdot 10^{21}$  H atoms/g. Similar differences were found for the NaHY zeolite between 300 and 500°C; spiral balance:  $1.4 \cdot 10^{21}$ ,  $D_2$ —OH exchange:  $2.3 \cdot 10^{21}$  H atoms/g.

In Table I are also compared the band heights in the IR spectra assigned to structural OH and SiOH groups in the  $Z_{300}$  and  $Z_{500}$  samples with the number of H atoms for both zeolite types. With the  $Z_{300}$  samples, the ratio of the heights of the 3650

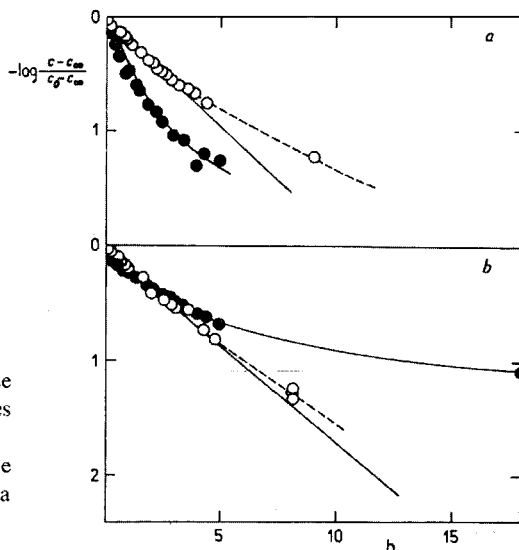


FIG. 7

$D_2$ —OH Exchange in Gaseous Phase with NaHX (*b*) and NaHY (*a*) Zeolites as Function of Time at 500°C

●  $Z_{500}$ ; ○  $Z_{300}$ ;  $c$ ,  $c_0$  and  $c_\infty$  denote atomic concentrations of deuterium at a time  $t$ ,  $t = 0$  and  $t \rightarrow \infty$ , respectively.

$\text{cm}^{-1}$  band for the NaHX zeolite to the  $3640 \text{ cm}^{-1}$  band for NaHY corresponds to the ratio of their total number of H atoms. The  $3565 \text{ cm}^{-1}$  band for NaHX is, however, much lower than the  $3550 \text{ cm}^{-1}$  band for NaHY (and this even when the X zeolite was evacuated at  $300^\circ\text{C}$  for only half an hour). The X zeolite contains further more OH groups to which the  $3700$  and  $3600 \text{ cm}^{-1}$  bands are assigned (Figs 1 and 2). With the  $Z_{500}$  samples, the band heights of the OH groups are smaller for the X than for the Y zeolite although their number of H atoms is higher.

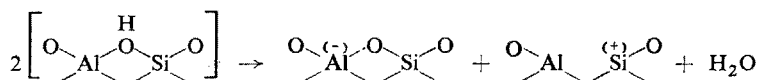
## DISCUSSION

Deammoniation and dehydroxylation of Y zeolites has already been studied in detail by other authors<sup>4</sup>. Less attention has been paid to the X type, whose deammoniation proceeds reportedly more easily than with the Y type and coincides with dehydroxylation (whereas with the Y type these two processes are separated)<sup>7</sup>.

Our results are in accord with these findings. The deammoniation is essentially finished with the X and Y zeolites at  $300^\circ\text{C}$ . With the X type, dehydroxylation begins at this temperature, whereas with NaHY only after increasing the temperature to  $450^\circ\text{C}$ . Accordingly, the dehydroxylation at  $500^\circ\text{C}$  is slower with NaHY than with NaHX.

Besides checking the results of the previous studies, it was found that during deammoniation of  $\text{Na}(\text{NH}_4)\text{X}$  the OH groups bands in the IR spectrum do not become higher toward the end of this process although it still proceeds. With the Y zeolite, the decomposition of  $\text{NH}_4^+$  ions is accompanied by the formation of structural hydroxyls: the weakening of the  $1430 \text{ cm}^{-1}$  band is proportional to the increase of the  $3640$  and  $3550 \text{ cm}^{-1}$  band intensities. The explanation of the mentioned anomaly of the X zeolite may be that at  $300^\circ\text{C}$  dehydroxylation proceeds together with, although much more slowly than deammoniation. It is hence possible to propose another explanation: The NaHX zeolite contains H atoms that are bound to its skeleton in such a way that the vibration of the skeleton-hydrogen is not manifested in the spectrum by a pronounced maximum — „nonlocalizable“ H atoms. It should be pointed out, that it has not yet been possible to locate all  $\text{Na}^+$  ions in the NaHX zeolite<sup>8</sup>.

The elimination of structural hydroxyls during dehydroxylation proceeds according to the simple known concept<sup>4</sup> so that an O atom is removed from the lattice and two units with opposite charges (Si, Al) are formed:



The atomic Si : Al ratio is equal to 1.33 for the zeolite NaHX and 2.5 for NaHY.

With decreasing Al content the probability that two (Si, Al) units are separated by a Si atom increases. The dehydroxylation is easier with the X than with the Y type, possibly because of an easier formation of charge differences in the case of a closer distance of the (Si, Al) units. The proton mobility in both zeolite types is so large<sup>9</sup> that it cannot influence the dehydroxylation rate. This process is probably accompanied by small structural changes causing an increase of the number of SiOH groups. These changes are more profound with the NaHY than with the NaHX zeolite.

The NaHX zeolite contains, in contrast to NaHY, also OH groups which are characterized by a weak  $3700\text{ cm}^{-1}$  band and a broad  $3600\text{ cm}^{-1}$  band in the IR spectrum. Their occurrence is probably related to the existence of defects in the zeolite lattice. According to Heylen and Jacobs<sup>10</sup>, the  $3600\text{ cm}^{-1}$  band of NaH faujasites is an evidence of aluminium in the cation position (extra-lattice aluminium). However, in our opinion the mere coincidence of the positions of the  $3600$  and  $3700\text{ cm}^{-1}$  bands for the NaHX zeolite and the deep-bed calcinated zeolites obtained from the type Y is not sufficient to prove the presence of extra-lattice aluminium in the type X.

The  $3640\text{ cm}^{-1}$  band of the Y and  $3650\text{ cm}^{-1}$  band of the X zeolite are assigned to structural OH groups in large cavities of the zeolites. Their absorption coefficient is the same<sup>7</sup>. The absorption coefficient of the  $3565\text{ cm}^{-1}$  band of the X zeolite<sup>7</sup> is by about 25% higher than that of the  $3550\text{ cm}^{-1}$  band of the Y type; both these bands characterize the structural hydroxyls in small cavities. From the comparison of their intensities for the  $Z_{300}$  samples of both types with the total number of H atoms in the zeolites it could be concluded that hydroxyls that are characteristic for lattice defects in the X zeolite ( $3700$  and  $3600\text{ cm}^{-1}$ ) and possibly present "non-localizable" H atoms are formed at the expense of structural hydroxyls in small cavities.

The existence of "nonlocalizable" H atoms in the NaHX zeolite could be one of the reasons for the discrepancies which we found when comparing the total number of H atoms (determined from the  $D_2$ -OH exchange) with the intensity of the OH groups bands for the  $Z_{500}$  samples of X and Y zeolites.

According to our opinion, the  $D_2$ -OH exchange on NaHX as well as NaHY zeolites is catalysed by active sites formed by dehydroxylation. After evacuating at  $300^\circ\text{C}$ , the X zeolite is already partially dehydroxylated and therefore the rate of the  $D_2$ -OH exchange is higher than with the NaHY zeolite obtained under equal experimental conditions. Understandably, the exchange rate does not increase with further dehydroxylation of the X zeolite so markedly as in the case of the Y type. Besides the sites formed by splitting off oxygen from the lattice during dehydroxylation, also structural defects could function as active sites. With the NaHY zeolite, we showed<sup>1</sup> that the structural defects related to an increase of the  $3740\text{ cm}^{-1}$  band during dehydroxylation probably do not influence considerably the activation of  $D_2$  molecules. With the NaHX zeolite, however, we cannot exclude the activity

of defects for the  $D_2$ —OH exchange that are manifested by the 3700 and 3600  $cm^{-1}$  OH group bands.

The OH groups do not play an equal role in the  $D_2$ —OH exchange. The H atoms of the SiOH groups are in both zeolite types exchanged with deuterium more slowly than those of other hydroxyls and thus influence the kinetic dependences in the gas phase according to their fraction with respect to the total content of OH groups. The slower exchange of the H atoms of the SiOH groups can be due to both a stronger OH bond and a larger distance from the activation centers for deuterium.

The deviation from a first-order kinetic dependence in the gas phase decreases with the presence of water vapour. Its effect can be attributed to the fact that water acts as a deuteron-transferring agent, thus equalizing the rates of the  $D_2$ —OH exchange with different types of OH groups. It is namely known that the  $D_2O$ —OH exchange proceeds easily already at the laboratory temperature. Water can also weaken the OH bond by interaction with the OH group and thus contribute to the rise of the  $D_2$ —OH exchange rate.

The number of OH atoms determined from the  $D_2$ —OH exchange with the participation of water vapour may be increased by the OH groups on the walls of the apparatus, which react with  $D_2O$  but not with gaseous deuterium. Indeed the experimental value of the total number of H atoms in the  $Z_{300}$  samples is about twice as large as the theoretical or that found from the weight decrements. This increase is not essential for the conclusions as to the different behaviour of both zeolite types. However, the possible error due to the presence of water vapour in determining the total number exchangeable H atoms by the  $D_2$ —OH exchange should be considered in choosing the experimental conditions.

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