General and Inorganic Chemistry

Effect of thermal and acid treatment on the structure of NH_4Na—Y zeolite by IR data

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The structural transformations of ammonium-exchanged forms of Na—Y zeolite during thermal evacuation and acid treatment were studied using IR spectroscopy. The formation of the zeolite H-forms by shallow-bed evacuation of NH_4N—Y at 570 K is accompanied by a high-frequency shift of the bands in the IR lattice vibration spectra. In the formation of the H^+-forms resulting from the decationization of zeolite by treatment with an aqueous HCl solution, no shifts of the bands are observed. During deep-bed calcination in air the H^+-form, is transformed into the H-form completed by the formation of a highly-crystalline stabilized zeolite at 623 K. A rapid increase in the shallow-bed calcination temperature results in a collapse of the structure of the H- and H^+-forms followed by the formation of amorphous SiO_2.

Key words: IR spectroscopy, thermal and acidic decationization, NH_4Na—Y zeolite.

In the literature,[1—5] emphasis has been placed on the difference between the properties of decationized zeolites produced by thermal decomposition of ammonium forms and those produced by treatment with aqueous solutions of mineral acids. It has been shown[2,3] that the hydronium H^+-forms of zeolite Y produced by acidic decationization[4] exhibit stronger Brönsted acidity than the hydrogen H-forms produced by the thermal deammoniation of NH_4Na—Y.

The published data[4] also indicate that the hydronium forms have a higher ion-exchange capacity. However, the distinctive features of the decationized sites in their structure are still rather uncertain.

The aim of the present work is to clear up these features in the zeolite Y structure, based on the IR spectra in the region of lattice vibrations.

Experimental

In the present work, previously investigated[6] sodium-ammonium forms of zeolite Y (Si/Al = 2.37) with different degrees of Na^+/NH_4^+ substitution (λ) were studied. The samples were thermally-evacuated at 570 K until complete decomposition of the NH_4^+ ion. The acid decationization was carried out by the treatment of the zeolites at 293 K with an aqueous 0.01 *N* HCl solution at the ratio of 0.2 mmol of H^+ per 1 g of zeolite. The degree of NH_4^+ cation removal depending on the duration of the thermal or acidic treatment was assessed by the optical density at the maximum of the δ_{as} (NH_4^+) absorbance band at ~1400 cm^{-1} using a calibration plot of this value versus the amount of NH_4^+ in the zeolite.

The IR spectra of the samples pressed into pellets with dried KBr (1 : 300) were recorded on a Bruker IFS-115c FT-IR spectromener with resolutions of 1 and 4 cm^{-1} in the frequency ranges 400—1250 and 1400—4000 cm^{-1}, respectively.

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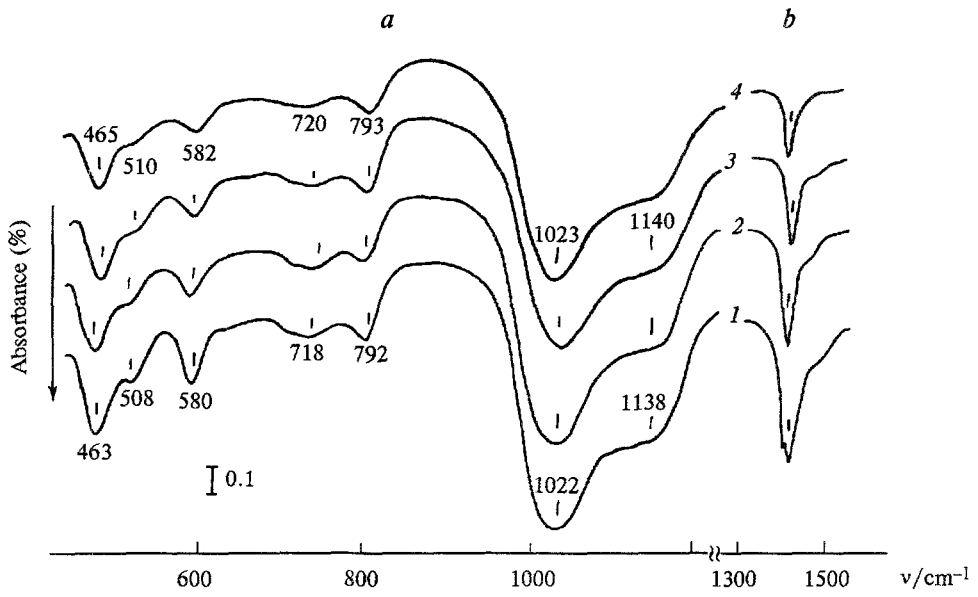
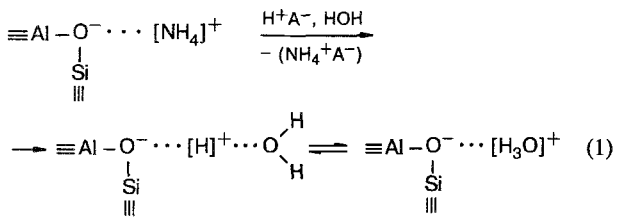


Fig. 1. IR spectra of NH_4Na—Y zeolite (98 % NH_4^+) in the regions of lattice vibrations (*a*) and bending vibrations of the ammonium ion $\delta_{as}(NH_4^+)$ (*b*), taken before (*1*) and after decationization (*2*—*4*) by HCl-treatment (λ = 30.45 and 70 %).

Results and Discussion

As can be seen from Fig. 1, the decrease in the NH_4^+ content when zeolite Y is treated with an aqueous HCl solution with concentration $[H^+]$, which is insufficient to dealuminate the crystals,[1,7] is accompanied by almost no high-frequency (HF) shift of the lattice vibration bands. The acid treatment of the Na^+-form of zeolite Y under the same conditions also causes[8] no shift in most of the absorbance bands in this region of the IR spectrum,[8] which is analogous to observations made in the acid treatment of mordenite[5] and A- and X-type zeolites.[9]

These facts testify that the exchange of the cation that balances the excess negative charge of the framework (ENCF) for a proton during acidic treatment, causes no decompensation of ENCF, which, in turn, indicates that there is no drastic change in the structural-chemical state of the aluminium-oxygen nodes of the framework.

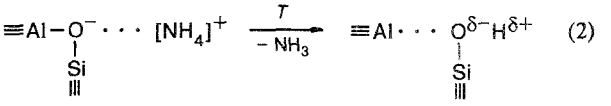


(1)

It appears that the dynamic character of the hydronium ion in the zeolite structure[10] results in the broadening and diffusion of the specific lattice vibration bands in the 500 to 800 cm^{-1} range, that are observed as the degree of acid decationization increases.

Unlike this, a gradual increase in the temperature of the NH_4Na—Y evacuation from 293 to 570 K followed by evacuation for 3 h at the final temperature, *i.e.*, under the conditions required[11,12] for the complete decomposition of the NH_4^+ cation, but insufficient for the initiation of dehydroxylation,[11,13,14] (and, hence, for the dealumination of the zeolite framework by the water formed)[11] results in the high-frecuency (HF) shift of the bands, which is the most pronounced in the region of the asymmetric stretching vibrations of the tetrahedrons. The corresponding dependence of the shift of the maximum of the $\nu_{as}(TO_4)$ (T = Si, Al) band on the NH_4^+ content in the zeolite evacuated is given in Fig. 2.

The HF shift of the zeolite lattice vibration bands indicating the lowering in the ENCF[6,8] is the result of the weakening of the aluminum-oxygen bonds during deammoniation accompanied by the formation of bridging OH groups:



(2)

As can be seen from Fig. 2, the maximum value of the shift of the $\nu_{as}(TO_4)$ band during deammoniation is far less than that observed[6] in the hydrolysis of aluminum-oxygen bonds resulting from the hydrothermal dealumination of NH_4Na—Y.

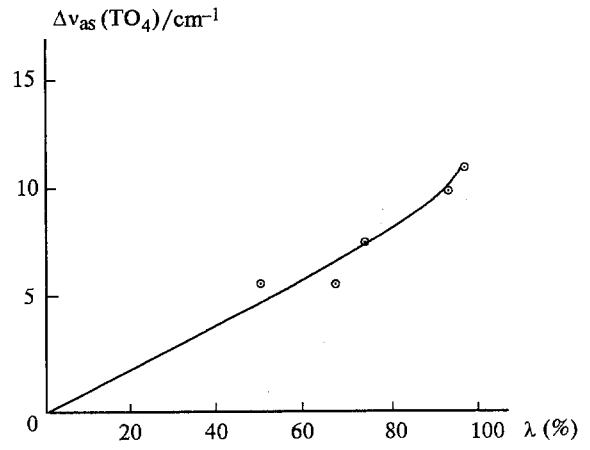


Fig. 2. Relationship between the HF shift of the $\nu_{as}(TO_4)$ band observed in the IR spectra of NH_4Na—Y after heat-evacuation at 573 K, and the value of λ.

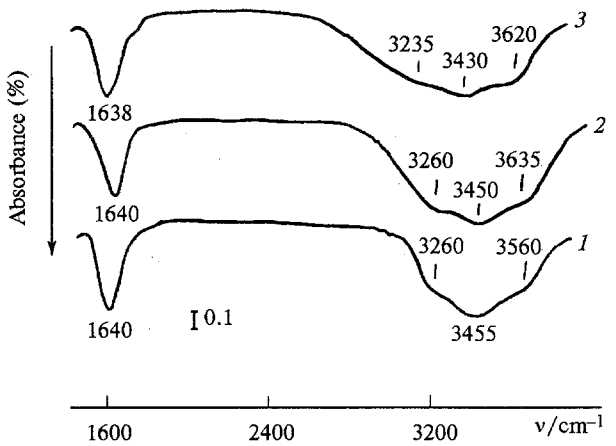


Fig. 3. IR spectra in the region of OH-modes of zeolite Na—Y (*1*), zeolite Na—Y decationized by HCl-treatment at 293 K (*2*), and zeolite NH_4Na—Y (98 % NH_4^+) deammoniated by heat-evacuation (573 K, 3 h) (*3*).

The strength of the aluminium—oxygen bond in the —Al···O(H)—Si≡ fragment, whose absolute value is comparable to that of a coordination bond, has been shown previously to determine to some extent, the acidity of the bridging hydroxyl groups[15]. In its turn, the strength of the Al—O bonds in these fragments is dependent on the composition of the surroundings of the Al atom. Those silanol groups of the ≡Al···O(H)—Si≡ fragments whose Al atoms do not contain other Al atoms within the first coordination sphere have the highest acidity.[12]

The presence of weak acidic groups in the structure of the thermally deammoniated Y zeolites is the reason for the incomplete replacement of the proton with alcaline[4] or ammonium[16] cations. In the case of the zeolites decationized by acid treatment, completely reversible ion exchange can be achieved.[4]

The spectra of the OH modes of Y zeolites thermally deammoniated or decationized by acid treatment are also different. As can be seen from Fig. 3, the spectrum of the acid-decationized Na—Y zeolite (curve *2*) is much more similar to that of the initial Na—Y sample than that of the thermally deammoniated zeolite (curve *3*). Instead of the band at 3260 cm^{-1} observed in the spectra of the sodium and hydronium forms (assigned[17] to the overtone of bending vibration of molecular-adsorbed water enhanced by Fermi resonance with the stretching vibration of water molecules symmetrically perturbed by a hydrogen bond),[17] a diffused continuum with the maximum at 3235 cm^{-1} characteristic of the absorbance of hydrogen-bonded OH associates with various degrees of hydrogen bonding appears in the spectrum of the thermally deammoniated sample. A diffused continuum is the common feature of the spectra of the NH_4Na—Y samples deammoniated by thermal evacuation and those treated by the hydrothermal dealumination at $T \leq 873$ K. The latter proceedure results in deammoniation followed by partial hydrolysis of the Al—O bonds giving rise to a further, more pronounced decrease in the ENCF.[18] Due to the presence of weakened bonds between Al and the framework O atoms, the thermally deammoniated zeolites can be also considered to be slightly dealuminated.

Despite the mentioned difference in the structural-chemical states of the samples of thermally and acid-deammoniated zeolite Y (Fig. 4, *a* and *b*, curve *1*), the samples exhibit a noticeable similarity in their behavior during various calcination procedures.

Thus, at the rapid temperature rise up to 623 K and shallow-bed calcination of the samples at this temperature in air, *viz.*, under conditions that almost rule out hydrothermal dealumination,[19,20] amorphization of the structure is observed (Fig. 4, *a* and *b*, curve *2*). This fact is indicated by a drastic decrease in the intensity of the bands at ~510, 580, and 720 cm^{-1} characteristic of the vibrations of the framework bonds involving Al—O. The observed increase in the intensity of the TO_4 bending vibration band (accompanied by its HF shift from 463—465 to 467—470 cm^{-1}) attests to a decrease in the degree of bonding between the tetrahedra[21] due to the local disodering of the zeolite structure. This effect is known[22] to precede the total transformation of the structure at higher temperatures. These changes are more pronounced for the acid-decationized sample (Fig. 4, *b*, curve *2*). The residual Na^+ cations contained in its structure seem to have a destabilizing rather than a stabilizing effect on the structure during thermal treatments. This is probably caused by localization of the cations at those sites of the zeolite structure that do not correspond to optimal compensation of the AlO_4 negative charge.[23] If this is so, the Na^+ cations could act as nuclei for mineralization resulting in the degradation of the zeolite structure[24] and the elimination of SiO_2.

The higher stability of the structure of the H-form of the zeolite compared to the H^+-form stems from the

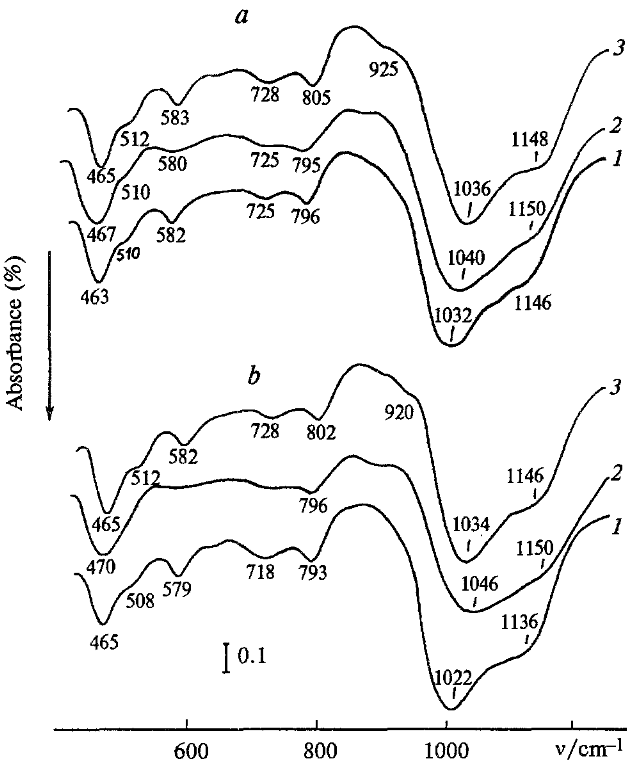


Fig. 4. IR lattice vibration spectra of NH_4Na—Y zeolite (98 % NH_4^+) deammoniated by heat-evacuation at 573 K (*a*), and of Na—Y zeolite decationized by HCl-treatment at 293 K (*b*): the initial samples (*1*), samples shallow-bed calcinated in air at 623 K (*2*), samples deep-bed calcinated in air with a slow increase in temperature from 293 to 623 K followed by exposure for 3 h at 623 K (*3*).

fact that the structure of the first form is stabilized even during its preparation *via* thermal deammoniation (see Scheme 2) owing to weakening of some of the Al—O bonds and, hence, lowering of the ENCF.

The considerable decrease in the intensity of the absorption bands at 510, 580, and 720 cm^{-1} (assigned to the framework bonds involving Al—O) in the specrtum of the deammoniated sample (Fig. 4, *a*, curve *2*), and the almost complete dissapearence of those bands from the spectrum of the decationized sample (Fig. 4, *b*, curve *2*) draw these spectra close to that of amorphous silica.[21] In addition, the low intensity of the bands or even their absence in the 400—800 cm^{-1} region, which is characteristic of Al—O absorbtion (both in the bridging bonds of the Y zeolite and in the crystalline aluminum hydroxide species),[25] suggests that the aluminum—oxygen part of the structure of the calcinated hydrogen- and hydronium zeolites exist as the amorphous Al-hydroxide species, which exhibit no bands in this IR region. These spectral changes are indicative of the phase segregation of the structure, *viz.*, the elimination of separate amorphous silica and alumina phases. The process appears to be similar to the natural process of the "weathering" of aluminosilicates to yield $SiO_2 \cdot xH_2O$ and amorphous Al hydroxide species as final products.

The phase segregation related to the process of the zeolite Y framework dealumination, that occurs during the shallow-bed calcination of the H^+- and H-forms with the participation of almost no water molecules, may be considered to be a result of the formation of Al_2O_3 according to the scheme:

$$2(Si{-}O)_3Al\cdots O(H){-}Si \rightarrow 3Si{-}O{-}Si + 2Si{-}OH + Al_2O_3$$

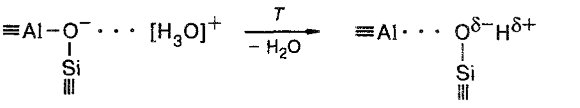
or the formation of AlOOH according to the Barrer scheme:[4]

$$(Si{-}O)_3Al\cdots O(H){-}Si \rightarrow 2Si{-}O{-}Si + AlOOH.$$

In contrast to this, when the temperature slowly increases to 623 K and the H- and H^+-forms of zeolites are calcined at this temperature in a deep-bed, *i.e.*, when the content on water vapor in the zeolite environment is below 40—50 %,[26] the stabilization of the structure occurs as a result of the gradual hydrolysis of the Al—O bonds in the $(Si{-}O)_3Al\cdots O(H){-}Si$ fragments and the decrease in the ENCF, which correlates with the HF shift of the lattice vibration bands. The corresponding changes in the spectra are similar to those occuring[6] during the hydrothermal treatment of the Y zeolite ammonium forms at $T \leq 873$ K. The close similarity between the spectra of the calcinated hydrogen and hydronium forms, which indicates the similarity of their structural-chemical states, should be noted.

This agrees with data[1] on the structural similarity of samples obtained by calcination at 623—873 K of the ammonium form of zeolite Y and calcination at 623—873 K of the form obtained by acid treatment of zeolite Y.

In the case of both the ammonium and hydronium forms, the stabilization of the zeolite structure due to the gradual hydrolysis of Al—O bonds and the rearrangement of the silicium—oxygen framework bonds during hydrothermal dealumination[27] seem to be preceeded by the formation of moieties with a weakened aluminum—oxygen bond:



(3)

1 **2**

Taking into account the relationship between the shift of the most intense $\nu_{as}(TO_4)$ band in the IR lattice vibration spectrum after the thermal deammoniation of NH_4Na—Y, and the degree of the replacement of NH_4^+ with Na^+ (see Fig. 2), which is 57 per unit cell at a Si/Al ratio of 2.37, it is easy to demonstrate that the transformation of **1** into **2**, *i.e.*, a strong acidic site into a weak one,[2] according to Scheme 3, is accompanied by the mean HF shift of the $\nu_{as}(TO_4)$ band by 0.2 cm^{-1}.

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