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Effect of "aging" of ammonium-exchanged forms of zeolite Y by IR spectroscopic data

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The changes in the structures of ammonium-exchanged forms of zeolite Y under conditions of prolonged exposure in air are studied by IR spectroscopy. It is established that the cation distribution in freshly prepared samples is nonequilibrium: the cations migrate with time to the most energetically stable sites. In addition, partial decomposition (no more than 3 to 6%) of the NH_4^+-form is also observed, which results in a decrease in the ionic character of the framework bonds that is equivalent to an apparent increase in the framework silicate modulus.

Key words: zeolite NH_4Na—Y, aging in air, IR spectroscopy.

It has previously been established[1,2] that dealuminated zeolites (the systems with a cation distribution that is far from the distribution corresponding to a minimum of the free energy of crystals[3]) change their structures noticeably with time. The character of the changes depends on the states both of anion and cation sublattices, which are determined by the type of a dealuminating agent and conditions of its effect on the initial forms of zeolite. Ammonium forms, which are widely used as the initial forms of zeolite in various procedures of dealumination, are the products of structural chemical modification: the cationic exchange of Na^+ for NH_4^+. Therefore, it is reasonable to expect their structural transformations with time as well.

The purpose of this work is to study the effect of prolonged exposure in air on the structures of ammonium-exchanged forms of zeolite Na—Y by the changes in the IR spectra of the vibrations of the framework.

Experimental

Ammonium forms of synthetic zeolite Na—Y (Si/Al = 2.56), both as-prepared and exposed in air for four years, were studied. The exchange degrees of Na^+ for NH_4^+ of these samples were 50, 68, and 98 %. The cation exchange was carried out by treatment of Na—Y with a 1 *N* aqueous solution of NH_4NO_3 at 353 K. The completeness of the exchange was determined from the chemical composition of the samples

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estimated by standard procedures of analysis.

IR spectra of samples molded with dried KBr in a ratio of 1 : 300 were measured on a Bruker IFS-115c IR-Fourier spectrometer (1-cm^{-1} resolution in the 400 to 1500 cm^{-1} frequency range). Absorption spectra were normed by the zeolite content per unit surface area of the light beam.

Results and Discussion

A comparison of the IR spectra of freshly prepared and exposed-in-air zeolites NH_4Na—Y (see Fig. 1) makes it possible to reveal the characteristic changes in their structures, which are to a great extent common for samples with different degrees of exchange of Na^+ for NH_4^+. Aging results in high-frequency (HF) shift of the bands, which is 3 to 8 cm^{-1} for the most intense $\nu_{as}(TO_4)$ band of the antisymmetric vibrations of the tetrahedrons (T = Si, Al). Many factors affect the position of the absorption band (AB) maximum, which is determined by the known dependence of the $\nu_{as}(TO_4)$ frequency on the force constant of the T—O bond and the reduced mass of the nodal atoms of the framework,[4] in this IR spectral region of the vibrations of the alumosilicate framework. In addition to the type and coordination number *n* of nodal atoms, these factors are, in particular, the type of a cation, which compensates an excess negative charge of the framework (ENCF), and the packing density of the primary structural units of TO_n. In the general case, the HF shift of AB of the vibrations of a zeolite framework, which is most pronounced in the $\nu_{as}(TO_4)$ region, is an indicator of a decrease in ENCF.[5] It has previously been established[6] that the decrease in ENCF in the thermal decomposition of the most exchanged NH_4^+-form of zeolite Y (Si/Al = 2.37) under the given conditions, which rule out dealumination, corresponds to a 10 to 12 cm^{-1} HF shift of the $\nu_{as}(TO_4)$ band. It is also known[7] that noticeable decomposition of NH_4^+-exchanged faujasites occurs during dehydration *in vacuo* at room temperature. It can be assumed by analogy that ammonium forms of faujasites, which are exposed in air for a long time, also partially decompose due to fluctuations of relative moisture content imitating the conditions of dehydration *in vacuo*. It can be assumed that decomposition is also caused to a slight extent by oxidation processes.[8] However, at least a 30 % degree of decomposition should correspond[6] to the HF shift of the $\nu_{as}(TO_4)$ band observed with long exposure of NH_4Na—Y, while the data presented in Fig. 2 attest to considerably lower degrees of this process. In fact, a comparison of the values of the optical density at the maximum of the AB of the antisymmetric bending $\delta_{as}(NH_4^+)$ vibrations of the ammonium cation in the range of 1400 cm^{-1} (see Ref. 9) in the spectra of freshly prepared and exposed-in-air samples with degrees of exchange of Na^+ for NH_4^+ of 50, 68, and 98 % reveals decreases of the NH_4^+ content in these samples by only 6, 4, and 3 %, respectively. Therefore, in this case decomposition of the NH_4^+-forms cannot be a determining factor for the HF shift of AB observed.

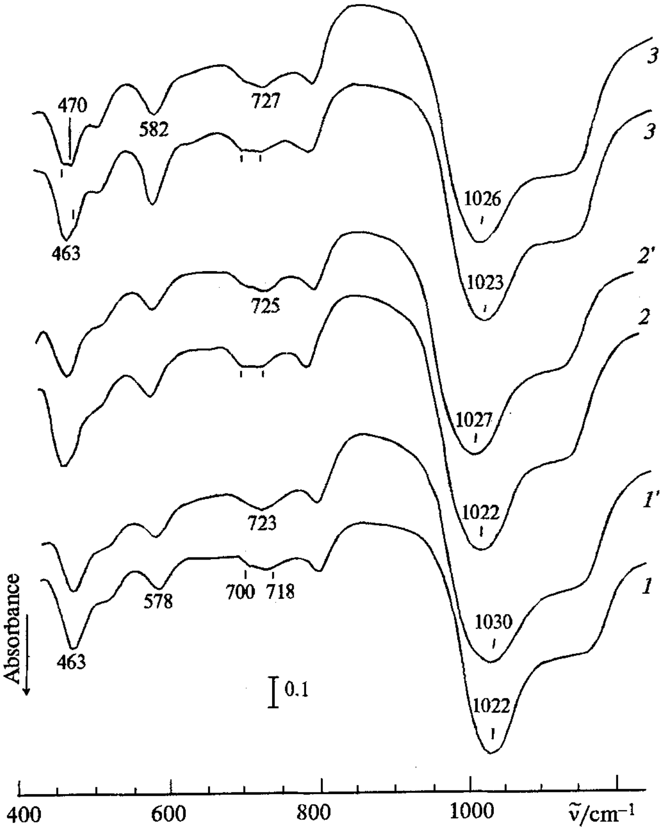

Fig. 1. IR absorption spectra of the framework vibrations of as-prepared samples (*1—3*) and the same samples exposed in air for four years (*1'—3'*) of zeolite NH_4Na—Y with degrees of exchange of 50 % (*1, 1'*), 60 % (*2, 2'*), and 98 % (*3, 3'*).

A possible stabilization of the structure due to hydrolytic breaking of the most ionic alumooxygen bonds,[5] which would cause a noticeable HF shift of bands, should also be ruled out as a reason, because no absorption of the stretching ν(T—O(H)) vibrations of hydrolyzed bonds are observed in the spectra of "aged" samples at 880 to 920 cm^{-1}.

This absorption is not observed in the spectra of the freshly prepared samples either, which indicates that the structure is perfect in this case: there is an absence of the so-called hydroxyl defects of the synthesis. "Curing" the defects, which results in the formation of normal bridge bonds at room temperature in the case of a favorable arrangement of the hydroxyl groups,[10] also could affect the position of the $\nu_{as}(TO_4)$ band due, in particular, to a considerable difference in the order of terminal and bridging bonds.[11]

It is known[2] that migration of cations to the sites corresponding to optimum compensation of the negative charge of the AlO_4 tetrahedrons is one of the reasons for a decrease in ENCF of dealuminated faujasites in the process of their aging in air.

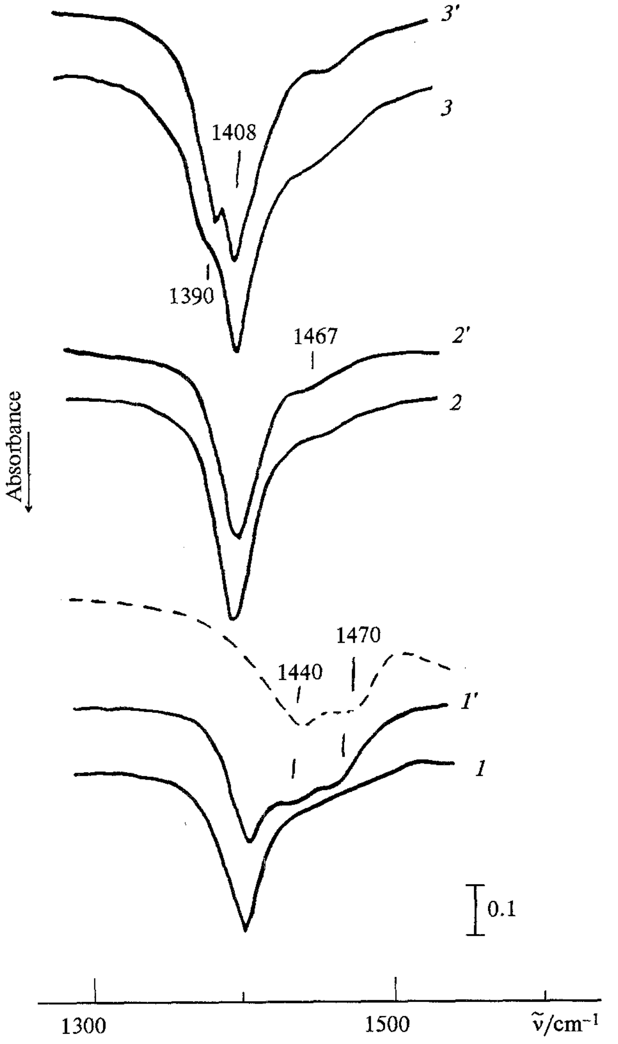

Fig. 2. IR spectra in the $\delta_{as}(NH_4^+)$ absorption region of as-prepared samples (*1—3*) and samples exposed in air for four years (*1'—3'*) of zeolite NH_4Na—Y with a degree of exchange of 50 % (*1,1'*), 68 % (*2,2'*), 98 % (*3,3'*) (dashed line indicates the spectrum of Na—Y after treatment with 0.001 *N* HCl for 3 min at 293 K).

Changes in the states of the cationic sublattice are also observed with aging of the studied NH_4^+-exchanged forms of zeolite Y, which is evidenced indirectly by the changes in the 500 to 800 cm^{-1} region. Vibrations of the bridging bonds involving Al—O, which are typical of this zeolite structure, are observed in this region. One of such characteristic changes is a decrease in the integral intensity of the ν(*D6R*) band of the stretching vibrations of double six-membered rings at ~580 cm^{-1}, which is the most pronounced in the spectrum of the most exchanged NH_4^+-form. This behavior of the spectrum in the range of ν(*D6R*) points out the changes in the localization of the cations at S_I sites.[12—14] For example, the migration of the cations to the S_I sites corresponding to a minimum of the Coulomb energy of dehydrated crystals[15] accompanied by redistribution of the cations to S_I, S_I', S_{II}, and S_{II}'[12] effects to a great extent a decrease in the intensity of the band of the stretching vibrations of double rings.

In this context, one can draw the conclusion that the state of the cationic sublattice of zeolite becomes non-equilibrium immediately after the cationic exchange, as it also takes place after dealumination, another more efficient method for structural chemical modification, which affects not only the cationic but the anionic sublattice of zeolite as well. It is known[16] that the occupation of the energetically stable sites in the faujasite structure (centers of hexagonal prisms) is especially difficult for the cations with high polarizing strengths due to a small size of the corresponding cavity. It is likely that the difficulties in the occupation of these sites are observed in the case of NH_4^+ cations due to their large sizes (1.43 Å) and ability (in addition to the pure Coulomb interaction) for donor-acceptor interaction with the oxygen atoms of the framework,[17] first of all with the O(1) atoms with the maximum negative charges.[18] The optimum arrangement of the cations in the prisms, which occurs with time, also results in noticeable changes in the states of the anionic sublattice. These changes manifest themselves in a specific way in the IR spectra of the vibrations of the zeolite framework. In addition to the HF shifts of the bands and the decrease in the integral intensity of the ν(*D6R*) band, these spectral manifestations also include characteristic changes (from 700 to 730 cm^{-1}) in the absorption region of the vibrations of the Al—O bonds of alumosilicates of the framework and layered structures.[19] The latter are very sensitive to the state of the cationic sublattice.[20] As can be seen from a comparison of spectra *1—3* and *1'—3'* in Fig. 1, the change in absorption occurs with time in this region due to a decrease in the relative intensity of its low-frequency edge (~700 cm^{-1}) in contrast to an increase in the intensity of the HF edge (~718 cm^{-1}) simultaneously with a shift of the latter from 723 to 727 cm^{-1}. These changes clearly attest to an increase in the covalent character of the Al—O bond and, hence, a decrease in the ionic character of the framework bonds as a whole, which appears as the HF shift of AB of the framework vibrations mentioned above. The increase in the covalent character of the Al—O bonds results in a decrease in the mobility of the alumooxygen tetrahedrons, which in turn decreases the relative intensity of the band of the bending $\delta(TO_4)$ vibrations of the tetrahedrons with an absorption maximum at ~463 cm^{-1} (see Ref. 21). In addition to these changes, in the spectrum of NH_4—Y with the 98 % degree of exchange an increase in the relative intensity of the HF shoulder of this band is observed simultaneously at 470 cm^{-1} (see Fig. 1, curves *3* and *3'*). The redistribution of the intensities of the individual bands in the total $\delta(TO_4)$ absorption contour, which is equivalent to the HF shift of its centroid, corresponds to an apparent increase in the Si/Al ratio.[22,23] In fact, the apparent increase in the silicate modulus, which is also identified to the same extent by the HF shift of AB in the $\nu(TO_4)$ range,[4] is related, as shown above, to the decrease in ENCF and ionic character of the framework bonds due to the partial decomposition of the NH_4^+-forms and migration of the cations to the optimum crystallographic sites.

The IR spectra in the $\delta_{as}(NH_4^+)$ absorption region also attest to the change in the state of the exchange cations in the structures of the ammonium forms exposed in air for a long time. As can be seen from Fig. 2, the spectra of zeolites with the 50 and 98 % degrees of cationic exchange change most of all. The intense bands at 1440, 1470, and 1390 cm^{-1}, which belong to carbonate-like species[24] (the products of sorption of atmospheric CO_2), appear in these spectra. In the spectrum of the 68 % NH_4^+-form, the changes in the 1467 cm^{-1} region are less drastic.

The bands at 1440 and 1470 cm^{-1} are identical to those observed in the spectrum of Na—Y after treatment with an HCl solution (see Fig. 2, dashed band), whose concentration is yet insufficient for dealumination,[6] and the duration of the treatment is not enough for a noticeable decationization of the crystals. The shift of the cation in the α-cavity due to this treatment or redistribution of cations caused by migration processes in aging favors the ion-dipole interaction of the exchange cations with CO_2, which results in the linear retention of CO_2 molecules.[25]

The absorption band at 1390 cm^{-1} observed in the spectrum of the 98 % NH_4^+-form corresponds to the absorption of carbonate-like species, which are products of the chemisorption of CO_2.[24] It is assumed[25] that the formation of the carbonate complexes tightly retained in the faujasite structure is caused by the interaction of CO_2 with the surface oxygen atoms adjacent to the exchange cations at the S_{III} sites, where the $-O^{\delta-}...Na^+$ distance is maximum.[26] It can be assumed in this connection that the change in the positions of the cations at the S_{III} sites, which causes delocalization of the negative charges of the O(3) and O(4) atoms, respectively, results in the observed increase in absorption at 1390 cm^{-1} in the spectrum of the aged 98 % NH_4^+-form.

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