Effect of aging of highly siliceous Y- and ZSM-5-type zeolites by IR spectroscopic data

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The changes in the structure of highly siliceous Y- and ZSM-5-type zeolites during prolonged aging in air have been studied by IR spectroscopy. At relatively low (<20) Si/Al ratios, gradual improvement of the zeolite structure is observed, which is related to ordering of the cationic and anionic sublattices. As a rule, this is accompanied by symmetrization of the tetrahedral framework units and decrease of the excessive negative charge of the framework. At higher Si/Al ratios, the zeolite structure transforms into stable crystalline silica modifications, α-cristobalite (in the case of highly siliceous analogs of Y zeolite) and α-quartz (in the case of ZSM-5-type zeolites).

Key words: highly siliceous Y- and ZSM-5-type zeolites, aging in air; IR spectroscopy.

It has long been supposed that the structure of synthetic zeolites that have no natural analogs is metastable.[1] At the same time, it is known[1] that synthetic analogs of natural zeolites have a more disordered structure than that of natural ones. The ordering of their structure occurs gradually with time,[2,3] accompanied by symmetrization of tetrahedral units and decrease of the excessive negative charge of the framework (ENCF).

Storage in air results in more pronounced changes in the products of structural chemical modification of zeolites than those for their initial forms. It is assumed[3] that the main factor of ordering the structure of the products of cationic substitution is the migration of cations to the most energetically favorable crystallographic sites. This migration is difficult in the case of cations, which are capable of strong donor-acceptor interaction with the anionic framework, for example, Mg^{2+} (see Ref. 4) and NH_4^+ (see Ref. 3). Another, more powerful method of structural chemical modification of zeolites, namely, dealumination, also noticeably changes the structure of modified products.[2,5]

Since dealuminated zeolites are very valuable in practice as highly efficient adsorbents and catalysts of organic and petrochemical synthesis,[6] study of the stability of the structure of representatives of this class as well as of the class of highly siliceous (HS) zeolites, pentasils,[7] being valuable in the same respect, is an urgent problem. The purpose of this work is the study of the changes in the structure of dealuminated zeolites Y and ZSM-5 and silicalites during their prolonged storage in air on the basis of the IR lattice vibration spectra.

Experimental

We studied synthetic zeolite Y (Si/Al = 2.4), its dealuminated forms (the products of subsequent hydrothermal and acidic treatment of NH_4Na—Y (Si/Al = 18 and 31, respectively) and the treatment of Na—Y with an aqueous solution of ethylenediaminetetraacetic acid (EDTA) (Si/Al = 4.3)) and samples of synthetic zeolite ZSM-5 (Si/Al = 14) and silicalite-1 (Si/Al = 600)* obtained by hydrothermal synthesis using tetrapropylammonium hydroxide (TPA) as an organic template. Aluminum was extracted from Na—Y by EDTA using the procedure described previously.[8] The conditions of preparation of the samples are presented in Table 1.

The unit cell parameter (a_0) for faujasites was determined by a Siemens D-500 X-ray diffractometer. The values of atomic Si/Al ratios in crystals were obtained from the data of chemical analysis and ^{29}Si NMR spectroscopy.

IR spectra of samples molded with dried KBr in a 1 : 300 ratio were recorded on a Bruker IFS-115c FT-spectrometer with 2-cm^{-1} resolution in the range of 400—1250 cm^{-1}. Integral intensities of bands in IR spectra were measured by the procedure described previously.[5]

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Table 1. Crystal-structural parameters of the samples studied and conditions of their treatment

Sample	Conditions of treatment of samples	a_0/Å
1	Zeolite Na—Y, without treatment	24.67
2	Treatment of sample 1 with EDTA at 373 K	24.53
3	Subsequent treatment of sample 1 with an 0.2 *N* solution of NH_4NO_3 at 293 K (53 % Na^+/NH_4^+ substitution), with vapor for 3 h at 873 K, with a 1 *N* solution of NH_4NO_3 at 353 K (98.7 % Na^+/NH_4^+ substitution), with vapor for 3 h at 1023 K	24.30
4	Treatment of sample 3 with a 0.1 *N* solution of HCl at 323 K	24.27
5	ZSM-5, without thermal and/or acidic treatment	—
6	Silicalite-1, without thermal and/or acidic treatment	—
7	Calcination of sample 6 for 6 h at 873 K and treatment with a 0.6 *N* solution of HCl at 293 K	—

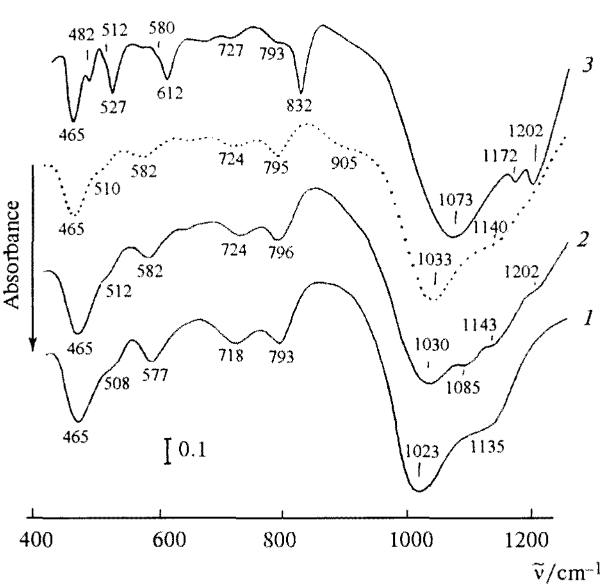


Fig. 1. IR lattice vibration spectra of samples 1—3. Spectra (*1*—*3*) correspond to the numeration of the samples in Table 1. The dotted line shows the spectrum of sample 1 treated with a 0.1 *N* aqueous solution of HCl at 293 K.

Results and Discussion

It has been shown previously[2,5] that the changes in the structure of dealuminated zeolites during prolonged storage in air are determined by the peculiarities of their structural chemical state, which are closely related to the nature of the dealuminating agent and the conditions of its action on the initial forms of zeolites.

The dependence of the structural chemical state of dealuminated zeolite Y on the type of the agent used for removal of Al from the framework is demonstrated clearly by the IR lattice vibration spectra (Fig. 1).

The formation of the chelate complex $NaAl(EDTA) \cdot H_2O$ upon extraction of aluminum from faujasite by EDTA accompanied by the deformation of SiO_4 tetrahedrons at the sites of removal of Al results[9] in a decrease in symmetry of the latter. This is manifested clearly in the IR lattice vibration spectrum (see Fig. 1, curve *2*) as a more complex absorption contour in the range of $\nu_{as}(TO_4)$ (T = Si, Al) due to the appearance of new bands at 1085 and 1202 cm^{-1}. The removal of OH groups occurring in the process of dealumination[2] is evidenced by the absence of the corresponding absorption ν(T—O(H, Na)) in the range of 900—950 cm^{-1} in the spectrum of the dealuminated sample. Recovering of hydroxyl and alkoxyl defects prevents to a certain extent depolymerization of the framework and, hence, a decrease in the crystallinity of zeolite. It can be assumed that this is one of the reasons for the fact that the spectrum in the range of characteristic vibrations of the framework Si—O—Al bonds (500—800 cm^{-1}) changes slightly compared to the spectrum of the initial zeolite (see Fig. 1, curve *1*).

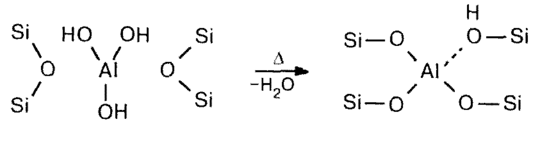
Unlike this situation, the framework is depolymerized even at low degrees of dealumination (~18 %) of zeolite Y with HCl (see the dotted curve in Fig. 1). The framework depolymerization is manifested as the appearance of the absorption band at 905 cm^{-1} corresponding to the vibrations of the terminal bonds, whose intensity is comparable to those of the characteristic bands in the range of 500—800 cm^{-1}, and as a decrease in the intensity of the latter compared to the corresponding bands in the spectrum of Na—Y. The decrease in the intensity of the bands can be partially caused[10] by decationization of crystals under the action of mineral acids. However, the retention of the form of the spectrum (the number of bands and the ratio of their intensities) in the range of $\nu_{as}(TO_4)$ testifies that no local deformation of tetrahedrons accompanied by the change in their vibrational symmetry occurs upon dealumination with HCl. In this case,[11] the a_0 parameter is unchanged due to the absence of recovering defects as a result of dehydroxylation of terminal groups. On the contrary, dealumination by EDTA or thermal vapor treatment results in a decrease in a_0 (see Table 1).

In the case of hydrothermal dealumination, the strongest changes in the spectrum (see Fig. 1, curve *3*) occur in the range of both the characteristic absorption of the zeolite framework vibrations (500—800 cm^{-1}) and the vibrations of tetrahedral units $\delta(TO_4)$ and $\nu(TO_4)$. It has been shown[5,8,12] that the distinctive feature of the spectra of highly dealuminated products of the hydrothermal treatment of zeolite Y is the presence of the bands at ~525, 610, and 830 cm^{-1}, which are mainly caused by the absorption of vibrations of extraframework oxygen-containing aluminum species. Their another peculiarity is the presence of the bands[12] in the range of $\delta(TO_4)$ and $\nu(TO_4)$ assigned to disiloxane bonds of various configurations, close to linear (468 and 1200 cm^{-1}) and nonlinear (476 and 1170 cm^{-1}), which are formed subsequently at the sites of extraction of Al at various stages of the hydrothermal treatment of crystals. The a_0 parameter decreases more considerably under this method of modification of zeolite Y than for dealumination with chelating agents or acids.

Since structural chemical states of zeolites dealuminated by various methods differ substantially, the routes of their structural transformations, including both spontaneous and thermally activated transformations, are also unequal.

The ability of Na$^+$ cations concentrated near deformed SiO_4 tetrahedrons in the sites of extraction of Al by EDTA (at 373 K)[2,9] to shift easily from these sites and thus affect the state of the anionic framework is clearly demonstrated by the spectra presented in Fig. 2. Thus, after the treatment of freshly prepared sample 2 (see Fig. 2, curve *1*) with water, its spectrum is simplified noticeably in the range of $\nu_{as}(TO_4)$ (see Fig. 2, curve *2*) and looks like the spectrum of the initial Na—Y zeolite (see Fig. 1, curve *1*). However, after a short storage in air, the form of the spectrum is completely recovered and corresponds to the state typical of the freshly prepared dealuminated form. (The reversibility of the changes in the spectra is shown in Figs. 2 and 3 by bilateral arrows.) Unlike this situation, extended treatment of sample 2 with vapor at ~370 K irreversibly eliminates local deformations of the SiO_4 tetrahedrons (see Fig. 2, curve *3*), which is similar to the situation observed previously[2] for prolonged storage of these samples in air (see Fig. 2, curve *4*). The normalization of the state of the cationic sublattice of zeolite reached under certain conditions under the action of water molecules facilitates recovery of the normal symmetry of tetrahedral units of the framework and results in a decrease in ENCF, which appears distinctly in the high-frequency (HF) shift of the bands. The latter is 5—7 cm^{-1} for the bands in the range of $\nu_{as}(TO_4)$.

The different situation is observed for the products of hydrothermal dealumination of zeolite Y. The presence of extraframework oxygen-containing aluminum species in these products exerts a substantial effect on the character of the changes in the structure with time and in the process of thermal treatments. The changes are caused[5,12] by the partial recovery of the initial structure of faujasite due to the transfer of Al from extraframework Al^{VI} compounds to the alumosilicate framework. The changes upon prolong storage of samples in air are related, as in the case of samples dealuminated by EDTA, to the action of water molecules,[2] while the changes caused by calcination are also related to the probable high-temperature reaction of extraframework Al compounds with siloxane bridges, which results in recovering hydroxyl defects[13] and regeneration of aluminosilicate bridging bonds:



The removal of extraframework aluminum species from crystals of highly dealuminated zeolites by acidic treatment, which increases the Si/Al ratio to 20 and higher, modifies the physicochemical properties of zeolites,[6] and affects substantially the routes of transformation of their structure. The partial removal of Al^{VI} species appears in the IR spectrum of the framework vibrations as a decrease in the intensities of the bands at 527, 612, and 832 cm^{-1} (Fig. 3, curve *1*) compared to the corresponding bands in the spectrum of the initial

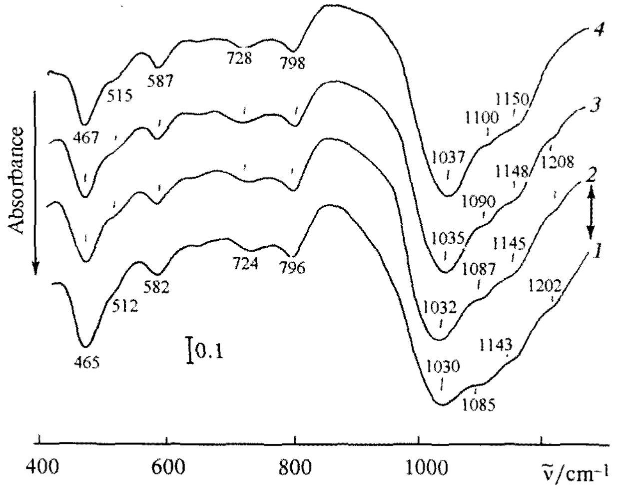


Fig. 2. IR lattice vibration spectra of initial sample 2 (*1*), after its treatment with water at 293 K (*2*), after prolonged treatment with water vapor at ~370 K (*3*), and after aging in air for more than 10 years (*4*).

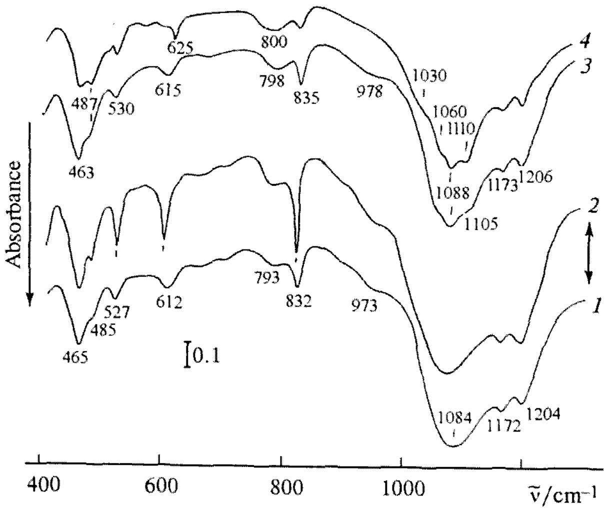


Fig. 3. IR lattice vibration spectra of initial sample 4 (*1*), after its calcination at 1173 K (*2*), after aging in air for more than 10 years (*3*) followed by subsequent calcination at 1173 K (*4*).

highly dealuminated sample (see Fig. 1, curve *3*) as well as the appearance of the distinct absorption band of asymmetric stretching vibrations of the Al^{VI}—O bonds[14] at 973 cm^{-1}. The isolation of this band from the total ν(T—O) absorption contour due to the considerable decrease in its intensity after acidic treatment[14] can be one of the reasons for the HF shift of the maximum of the most intense band in this range.[15]

Calcination of this sample results in an increase in the relative intensity of the absorption bands in the range of 400—1000 cm^{-1}, which is especially drastic for the bands at 527, 612, and 832 cm^{-1} (see Fig. 3, curve *2*) that do not shift noticeably. This testifies about the change in the electrooptical properties of zeolite, which is likely related to the change in the crystal-chemical state of Al of extraframework species upon calcination. However, the spectrum of zeolite recovers to a great extent its form after storage of the calcinated sample in air and repeated calcination. This does not result in an increase in the intensity of the bands typical of the structure of the initial zeolite, especially the D6R band at 580 cm^{-1} (which is observed[5] upon calcination of highly dealuminated faujasites unmodified by acidic treatment) and indicates that after removal of Al^{VI} species soluble in acids, aluminum-containing compounds remain in the structure, which are nonreactive toward the interaction with HS-framework and cannot participate in the reversible transitions $Al^{VI} \rightleftharpoons Al^{IV}$.

The IR spectrum of sample 4 modified by acidic treatment (see Fig. 3, curve *3*) after prolong storage in air exhibits a decrease in the intensity of the bands at 530, 615, 835, and 978 cm^{-1} compared to the corresponding bands in the spectrum of the initial sample. This is accompanied by an increase in the relative intensity of the $\delta(SiO_4)$ band at 487 cm^{-1} and so-called ring band at 798 cm^{-1} associated[16] with the absorption of $[Si_6O_{18}]$ rings of the silica matrix and by the appearance of the distinct $\nu_{as}(SiO_4)$ band at 1105 cm^{-1} typical of the spectra of α-quartz and/or α-cristobalite.[17] These changes testify clearly about the beginning of transformation of the structure of HS-faujasite into the structure of crystalline SiO_2. Calcination of the aged sample results in the increase in these changes (see Fig. 3, curve *4*). The appearance of the band at 625 cm^{-1} typical of the spectrum of α-cristobalite[17] allows one to draw a conclusion that the structure of HS-faujasite is rearranged into the structure of this stable crystalline modification of silica. It can also be assumed that the appearance of the bands at ~1060 and 1030 cm^{-1} in the range of $\nu_{as}(TO_4)$ in the spectrum of the calcinated sample is due to the formation of the silicate and, probably, aluminosilicate phases.[17]

Gradual transformation into one of the stable crystalline modifications of silica was also observed for representatives of another class of HS-zeolites, pentasils, which, unlike faujasites, have no natural analogs.[18] The comparison of the spectrum of freshly prepared zeolite ZSM-5 in the Na—TPA-form with the spectrum of the same sample stored in air for about 10 years (Fig. 4, curves *1* and *1'*) reveals the general HF-shift of the bands. This indicates to a decrease in ENCF of zeolite. It is noteworthy that the most intense $\nu_{as}(TO_4)$ band is structurized due to isolation of the HF-component at 1108 cm^{-1}, whose position is close to that of the corresponding absorption band in the spectrum of α-quartz (see the dotted curve in Fig. 4). However, the total changes in the spectrum are insignificant.

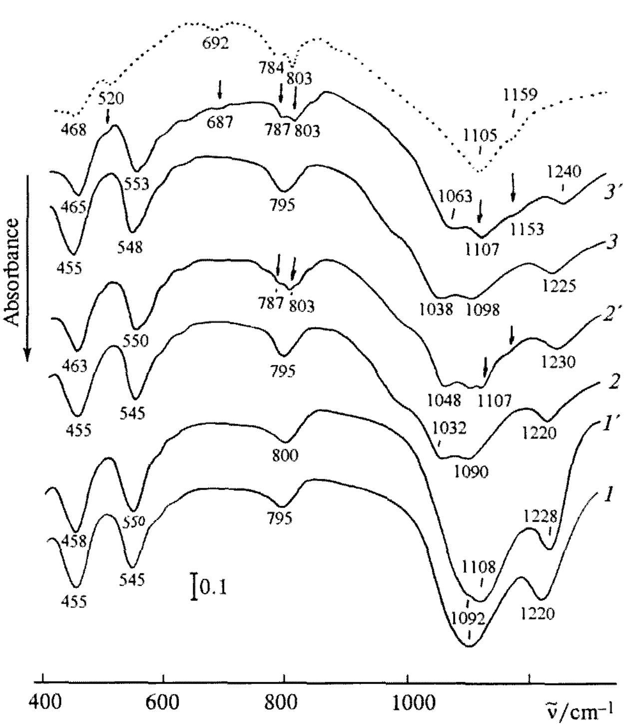


Fig. 4. IR lattice vibration spectra of samples 5, 6, and 7 (*1*, *2*, and *3*, respectively) after their aging in air for ~8 year (*1'*, *2'*, and *3'*, respectively). The dotted line indicates the spectrum of α-quartz (see Ref. 17).

More pronounced changes are observed with time in the spectra of the HS-analog of zeolite ZSM-5, silicalite-1. The spectra of silicalites are more complex in the range of $\nu_{as}(TO_4)$[19—21] than those of zeolites ZSM-5. The structure of the bands (see Fig. 4, curves *2* and *3*) is caused[21] by local distortions of tetrahedrons in the composition of flexible silicate chains, which occur under the action of cations in the process of crystal growth under the conditions of alkaline hydrothermal synthesis.

Aging of silicalites in air results in the changes in their spectra, which testify about gradual transformation of the initial structure into the structure of α-quartz, which is observed under certain conditions directly in the synthesis.[22,23] The spectra of aged silicalite samples resemble the spectrum of α-quartz in several absorption ranges (they are indicated by arrows in Fig. 4). The changed in the ranges of $\delta(TO_4)$ (463—465 cm^{-1}) and ν(T—O) (900—1250 cm^{-1}) are more noticeable in the spectrum of the sample preliminarily calcinated and treated by acid (see Fig. 4, curve *3'*). This can testify about the stabilizing role of tetraalkylammonium ions involved in the structure at early stages of crystallization of pentasils,[24] which, as known,[25] affect substantially the symmetry of crystals and the angular cell parameter. Extraframework octahedrally coordinated aluminum species[26,27] that are present in the structure of pentasils also can exert a stabilizing effect, which is of special significance for pentasils with Si/Al < 35.[28]

The gradual transformation into α-quartz is accompanied by a decrease in the degree of the "pentasilic" character of the structure identified by a decrease in the relative intensity of the characteristic absorption band of vibrations of the bonds in the five-membered rings at ~550 cm^{-1}. According to the estimation[29,30] by the ratio of the integral intensities of this band and the $\delta(TO_4)$ band at 450—460 cm^{-1}, the degree of the "pentasilic" character by ~15—20 % decreases for aged samples.

Thus, prolong storage results in the improvement of the structure of zeolites with a relatively low Si/Al ratio, while the structure of HS-zeolites is transformed into the structure of stable crystalline modifications of silica, independently of the fact whether they have natural structural analogs (faujasites or pentasils, respectively) or not.

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