IR and ^{29}Si NMR investigation of the influence of alkaline modification on the structure of hydrothermally dealuminated Y zeolites
2.* Highly dealuminated zeolites

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Using IR and ^{29}Si NMR spectroscopy the influence of alkaline modification on the structure of samples obtained by steaming the ammoniated form of NH_4NaY zeolite (53 % NH_4^+, Si/Al = 2.37 pretreated under a moist atmosphere at 873 K) at 973 and 1073 K has been studied. Highly dealuminated forms of faujasite arise in the course of hydrothermal treatment as a result of the transfer of Al from the framework to extraframework hydroxide species accompanied by the formation of silica-type disiloxane bonds. The treatment of highly dealuminated samples with an aqueous solution of KOH at 353 K results in the partial regeneration of the crystallographic positions of Al in the framework. The structure of the sample modified with the alkali is identical to that of silicaalumina gel (Si/Al ≈ 2.2) "aged" in air for a long period of time.

Key words: zeolite Y; hydrothermal dealumination; alkaline modification; IR spectroscopy; ^{29}Si NMR spectroscopy.

The presence of disiloxane bonds[1] in which the electron configuration of the bridge oxygen is characteristic of crystalline modifications of silicon dioxide,[2] is one of the feature of the structure of highly dealuminated Y zeolites. These zeolites are obtained by steaming (at $T > 873$ K) ammoniated forms of NH_4NaY zeolites preliminarily calcinated at $T \leq 873$ K. The formation of these bonds, which occurs during the detachment of silanol groups from the dealuminated nodes, results in a considerable decrease in the elementary cell parameter a (by ~0.4—0.5 Å as compared with the initial) and causes an increase in hydrophobicity[2] and thermal stability.[3]

The treatment of such samples with alkaline solutions results in their realumination,[4—6] which is accompanied, however, by noticeable depolymerization of the highly siliceous framework.[6—8] The realuminating action of the alkaline treatment is considered[7] to be not the result of regeneration of normal bridge bonds of faujasite[6] in such a medium, but the sequence of copolymerization of silicate and aluminate ions formed during the dissolution of the silicon- and aluminum-oxygen parts of the framework in the alkali. In this process, structured silicaalumina gel with a lower Si/Al_{fr} modulus than that of alkaline untreated dealuminated zeolites.

The aim of the present work is to evaluate the influence of an aqueous solution of KOH on the structure of highly dealuminated Y zeolites obtained by steaming using IR absorption and ^{29}Si NMR spectroscopy.

Experimental

Highly dealuminated forms of the synthetic NaY zeolite (Si/Al = 2.37) (sample **1**) were studied. They were obtained* by steam treatment of the ammoniated form of a moderately dealuminated zeolite at 973 K (sample **2**) and 1023 K (sample **3**). The products of the treatment of **1—3** with a 0.25 *N* aqueous solution of KOH for 24 h at 353 K were also studied. The product of the calcination of NH_4NaY (53 % of NH_4^+) in a moist atmosphere at 873 K was used as the moderately dealuminated zeolite.

IR spectra of the samples (pellets with KBr) were registered on a Bruker IFS-115c IR-Fourier-spectrometer in the frequency range from 400 to 1250 cm^{-1}. The ^{29}Si NMR spectra were measured on a Bruker MSL-400 spectrometer with the use of the techniques of the fast rotation of the sample at the magic angle. The δ values of the isotropic chemical shift of the individual components of the ^{29}Si signal were measured relative to TMS. The conditions of the registration of the spectra have been described previously.[4,7]

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* For part 1, see *Russ. Chem. Bull.*, 1994, **43**, 346.

* The samples and corresponding ^{29}Si NMR spectra were presented by W. Lutz (Central Institute of Physical Chemistry, former GDR Academy of Sciences).

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Results and Discussion

The transformation of the original Y zeolite into a highly dealuminated one through the process of the stepwise steaming of the NH_4^+-form as illustrated in the IR absorption spectra in the range of the framework vibrations and in the ^{29}Si NMR spectra are presented in Fig. 1. The transition from the original sample (Fig. 1, *a*, curve *1*) to the highly dealuminated forms (Fig. 1, *a*, curves *2, 3*) (Si/Al_{fr} values are 14 and 18, respectively)[9] is caused, as is known, by the transfer of Al from the framework into the extraframework hydroxide species of Al^{IV}. In the IR spectrum this is manifested as the appearance of absorption bands[9] (AB) at ~520, 610, and 830 cm^{-1} characteristic of hydroxide species of aluminum[10,11] (near-framework species with at least one covalent bond with the framework and extraframework species). At the same time, AB at 460—490 and 1170—1200 cm^{-1}, assigned to the bending and asymmetric stretching vibrations, respectively, of the nonlinear and close to linear disiloxane bonds formed on the detachment of the terminal silanol groups from the dealuminated nodes at $T > 873$ K, appear in the spectra. The considerable decrease in the number of framework Al—O bonds in the composition of the Si—O—Al bridges after dealumination is accompanied by a decrease in the intensity of the AB at 700—780 cm^{-1} characteristic of such bonds.[9] Thus, only weak AB at 740 and 727 cm^{-1}, whose intensities decrease as the degree of dealumination increases, are observed in the spectra of the dealuminated samples (Fig. 1, *a*, curves *2, 3*), while the spectrum of the original sample (Fig. 1, *a*, curve *1*) has a broad AB with the maximum at ≈ 718 cm^{-1} in this range. The decrease in the excessive negative charge of the framework (ENCF) manifested in the IR spectra[2,12] as a total high-frequency (HF) shift of the AB, is the consequence of the decrease in the content of normal Al—O bonds in the framework.

Table 1. Values of δ of the components of the ^{29}Si signal for the samples studied

Sample	δ*				
	Si(0 Al)	Si(1 Al)	Si(2 Al)	Si(3 Al)	Si(4 Al)
1	−103.9 (−104.6)	−98.6 (−99.3)	−93.1 −(94.7)	−87.6 (−88.4)	−83.6 (−83.6)
2	−107.7 (−106.2)	−101.7 (−100.3)	— (−94.7)	— (≈−89.7)	— (≈−83.9)
3	−107.4	−101.0	—	—	—
	(blurred continuum at ≈ −93.4 ppm)				

* Before the alkaline treatment, in parentheses — after the treatment.

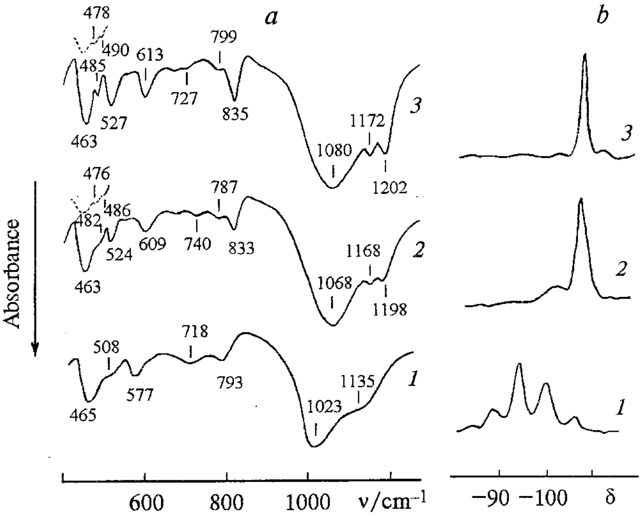

Fig. 1. IR absorption (*a*) and ^{29}Si NMR (*b*) spectra of **1—3** (*1—3*). Dotted line in Fig. 1, *a* indicates spectra of **2** and **3** measured at dilution of KBr 1:1000.

Figure 1

Changes in the crystal chemical state of the silicon-oxygen nodes of the framework resulted from dealumination are clearly demonstrated by the ^{29}Si NMR spectra. The removal of Al from the framework of the original zeolite leads to the disappearance of the components of the ^{29}Si signal attributing to the absorption of Si of the framework $Si(OAl)_n(OSi)_{4-n}$ groups briefly designated as Si(n Al), for n = 4, 3, and 2, and to a decrease in the intensity of the component for n = 1. In addition, a drastic increase in the intensity of the Si(0 Al) component (Fig. 1, *b*, curves *2, 3*) is observed. This component becomes narrower as the degree of dealumination increases due to the enhancement of the uniformity of the surrounding of Si atoms, which causes the crystal chemical equivalency of the silicon-oxygen nodes of the framework of the dealuminated zeolite.[13]

The presence of weak components of Si(1 Al) with δ −101.7 and −101.0 ppm (Table 1) in the ^{29}Si NMR spectra of **2**, **3** attests to a definite but insignificant content of the Al—O—Si bridge bonds in the framework. The existence of weak bands at 740 and 727 cm^{-1} in the corresponding IR spectra (see Fig. 1, *a*, curves *2, 3*) also indicates this. The lower-frequency (LF) position of the AB of vibrations involving the Al—O bond in the framework of **3** attracts one's attention. This position correlates to the lower-field (LF) position of the corresponding component of the ^{29}Si signal. Such a difference attests[14] to less covalency of the Al—O—Si bond in the framework of **3**, which causes lower acidic stability of its framework. The presence of AB of terminal siloxane bonds in the range of 900—950 cm^{-1} in the IR spectrum of the analog of **3** treated with an HCl solution and their absence for the analog of **2** after the same treatment[10] confirm this conclusion.

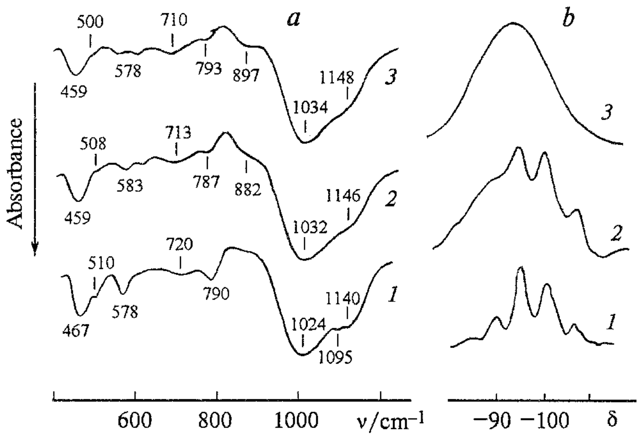

Fig. 2. IR absorption (*a*) and ^{29}Si NMR (*b*) spectra of **1—3** (*1—3*) treated with KOH.

The treatment of **2** and **3** with an aqueous solution of KOH results in the realumination of the framework with the restoration of the Al—O—Si bridge bonds due to the interaction[6] of the aluminate ion with the terminal siloxane bonds formed during dissolution of the extraframework hydroxyl Al compounds in the alkali and cleavage of the disiloxane bonds at the dealuminated nodes, respectively. This is manifested in the IR spectra (see Figs. 1, *a* and 2, *a*, curves *2, 3*) as the disappearance of AB of hydroxide species of Al^{VI} and the simultaneous increase in the intensity of the AB of the vibrations involving the Al—O bond attributive of the framework Al—O—Si bridges, especially the characteristic AB at 578—583 cm^{-1}. The increase in the intensity of the AB at 710—713 cm^{-1} attests to the increase in the total content of Al—O bonds in the framework in the course of the alkaline treatment. The structure of the zeolite modified with the alkali possesses, however, a low degree of crystallinity, which results in the diffusion of the AB at 460 and 1030 cm^{-1} related to the bending and stretching vibrations of the TO$_4$ tetrahedrons and in the appearance of the AB of the terminal T—O(H) bonds at 882 and 897 cm^{-1}. The total LF-shift of AB of the framework[4,6,7,12] observed on the realumination is the result, as has been already mentioned,[12] not of the cationic substitution for K$^+$, which causes only an insignificant shift of the AB in the IR spectrum (see Figs. 1, *a* and 2, *a*, curves *1*) but of the increase in ENCF due to the increase in the content of bridge Al—O—Si bonds in the framework.

The regeneration of the components of the Si(*n* Al) signal, *n* = 1, 2, 3, and 4 (see Figs. 1, *b* and 2, *b*, curves *2*) characteristic of the original structure (see Figs. 2, *b*, curve *1*) in the spectrum of **2** treated with alkali also attests to the partial regeneration of the crystallographic positions of aluminum in the structure of the modified sample. The low degree of crystallinity of the samples treated with the alkali is manifested in a noticeable broadening and overlapping of the components of the ^{29}Si signal resulting in the case of **3** in the completely diffused continuum with the maximum at δ ≈ −93.4 characteristic of the spectrum of zeolite Y after its loss of crystallinity.[15] However, crystallinity estimated by the ratio integral intensities of the ν(D6R) IR-band in the spectra of the modified and original zeolites is ~20 % for **3**.

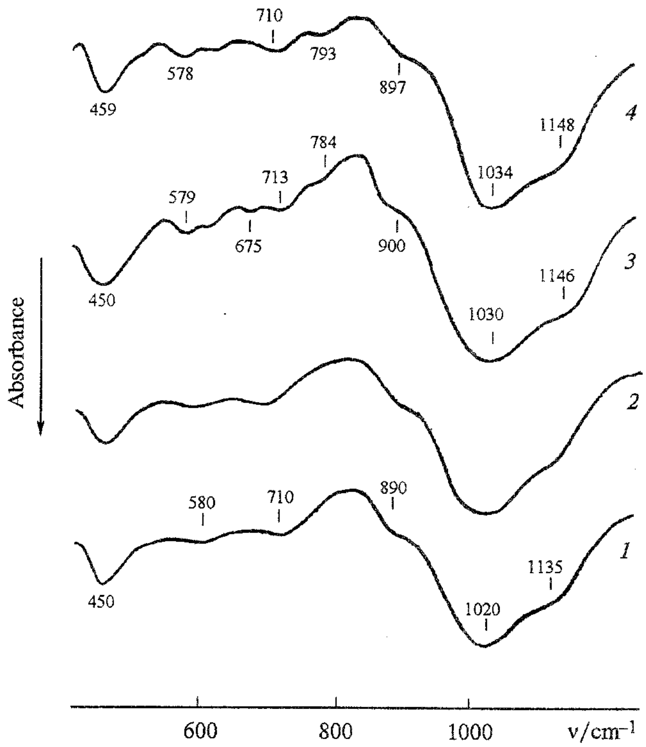

Fig. 3. IR absorption spectra of freshly prepared silicaalumina gel (*1*), treated with KOH (*2*), exposed in air for > 20 years (*3*), and of sample **3** treated with KOH (*4*).

In the ^{29}Si NMR spectra of silicaalumina gels with a partially ordered aluminosilicate lattice, unlike amorphous silicaalumina gels which have the same spectrum as that of **3** modified with alkali,[16] a discrete set of bands on the background of the diffused continuum is observed. This leads to the conclusion[7] that dissolution in the alkali and copolymerization of the silicate and dealuminate ions formed, and not realumination of the framework, is the result of the alkaline treatment of highly dealuminated products of hydrothermal treatment of Y zeolite. The partial ordering of the structure of silicaalumina gel obtained in this process is caused[7] by the elevated temperature, which accelerates crystallization of gels.[17,18]

However, as can be seen from Fig. 3, the treatment of freshly prepared silicaalumina gel* (used in the synthesis of Y zeolite) (curve *1*) with an aqueous solution of KOH for 24 h at 353 K (curve *2*) does not result in the formation of the bands characteristic of the structure of

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* The samples of silicaalumina gels were provided by N. N. Feoktistova (I. V. Grebenshchikov Institute of Chemistry of Silicates, Russian Academy of Sciences).

zeolite Y in the 450 to 700 cm^{-1} range, which is in accordance with the known fact that crystallization of this zeolite is impossible in a KOH medium (see Refs. 18, 19). Moreover it does not even result in noticeable changes in this spectral range, which would allow us to speak about the ordering of the alumosilicate lattice of the gel under these conditions.

Long exposure of silicaalumina gel in air results in the crystallization of zeolite Y, which manifests itself in the formation of the AB at 579, 713, 784 cm^{-1} characteristic of the zeolite Y structure (see Fig. 3, curve *3*). The HF-shift of AB of the framework, which is especially noticeable in the $\nu(TO_4)$ range attests to the decrease in the ENCF of the silicaalumina gel during the aging process. It is known that crystallization of faujasite in the solid phase due to the ordering of the aluminosilicate lattice of the silicaalumina gel with the proper composition[19] is observed after several weeks. Therefore, one can propose that in the case of silicaalumina gel "aged" for several years, the maximum degree of crystallinity of faujasite possible under such conditions is achieved. As can be seen from the comparison of the spectra of samples obtained during hydrothermal crystallization of silicaalumina gel in an alkaline solution (see Fig. 1, *a*, curve *1*) and during crystallization of the same gel in the solid phase (see Fig. 3, curve *3*), the crystallinity of the latter as estimated by the ν(D6R) band is ~5-fold lower. These data provide strong evidence that zeolites with perfect structures cannot be synthesized without direct participation of the liquid phase of silicaalumina gels and their components in the building of the crystals.[17,18]

The spectra of gel "aged" in air and of the highly dealuminated forms of zeolite Y treated with KOH (see Fig. 3, curves *3, 4*) are almost completely identical in the range of the characteristic vibrational modes of the zeolite Y framework at 500—800 cm^{-1} and the main tetrahedral units of the framework $\delta(TO_4)$ and $\nu(TO_4)$ at 450—459 and 1030—1148 cm^{-1}. At the same time, the more pronounced diffuseness of the $\delta(TO_4)$ and $\nu(TO_4)$ bands in the spectrum of the silicaalumina gel along with the appearance of the ν_s(Si—O) AB at 675 cm^{-1}, active in the Raman spectrum (see Ref. 20), attests to lower symmetry of the tetrahedral structural units of the framework of the silicaalumina gel as compared with the dealuminated samples modified with alkali.

Thus, the state of the faujasite framework achieved by long aging in air of the silicaalumina gel of the proper composition, can be easily reproduced by the alkaline treatment of highly aluminated products of the steaming of zeolite Y. In other words, the alkaline modification results in the reproduction of the structure of the original form of zeolite Y to only a minor extent. Therefore, in the case of highly dealuminated zeolites, there are fewer reasons to speak about the possibility of achieving complete reversibility of the structural changes caused by hydrothermal dealumination than in the case of moderately dealuminated zeolites.[12]

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