General and Inorganic Chemistry

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

1. Moderately dealuminated zeolites

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The change in the structure of NH_4NaY zeolite (53 % NH_4^+, Si/Al = 2.37) after hydrothermal treatment at 873 K followed by modification with aqueous KOH solution at 353 K was studied by IR and ^{29}Si NMR spectroscopy. It has been shown that hydrolytic cleavage of the Al—O bond of the deammoniated zeolite sites by hydrothermal treatment predominates in the framework groups $Si(OAl)_n(OSi)_{4-n}$, n = 2, 3. Molecular water adsorbed on such a sample exists as hydrogen-bonded associates with hydrogen bonds of various strengths reaching that in ice-like structures (the band at 2468 cm^{-1}). Treatment with an alkali results in partial regeneration of the normal bridge bonds. The exchange of the protons of the terminal silanol groups with the alkaline cation prevents those groups from participating in the regeneration process.

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

The double action of KOH on hydrothermally dealuminated zeolites Y has been established on the basis of IR spectroscopy.[1,2] On one hand, realumination occurs,[1—5] *i.e.*, regeneration of the Al—O bonds of the original structure of faujasite. On the other hand, there are processes which do not favor this realumination: the exchange of the protons of the terminal silanol groups of dealuminated nodes with K^+ (in the case of $Si/Al_{fr} \leq 6—10$ [1] and the elementary cell parameter $a = 24.50 \div 24.60$ Å) and depolymerization of the framework[2,6] due to cleavage of the disiloxane bonds formed in the dehydroxylation of the silanol groups of the dealuminated nodes (in the case of samples with $Si/Al_{fr} \geq 10$ and $a = 24.50 \div 24.40$ Å).

The goal of this work is to estimate the influence of aqueous KOH solutions on the structure of moderately dealuminated zeolite Y obtained by hydrothermal treatment[7] with the use of IR spectroscopy and ^{29}Si NMR.

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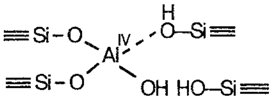
Experimental

The studied samples* were obtained from synthetic zeolite NaY (Si/Al = 2.37) (sample **1**): the potassium-exchanged form (sample **2**) was prepared by the treatment of sample **1** with an aqueous solution of KNO_3; the dealuminated form (sample **3**) was prepared by deep-bed calcination of the ammonium-exchanged (53 % NH_4) form of sample **1** at 873 K in a moist atmosphere; alkali-modified zeolite (sample **4**) was obtained by the treatment of sample **3** with a 0.25 N aqueous solution of KOH at 353 K for 24 h.

IR spectra of the samples (pellets with KBr, 1:300) were registered on a Bruker IFS-115c IR-Fourier-spectrometer with a resolution of 2 cm^{-1} in the frequency range from 400 to 1250 cm^{-1}. ^{29}Si NMR spectra were obtained on a Bruker MSL 400 spectrometer with the use of the technique of the fast rotation of a sample at the magic angle. The isotropic chemical shifts δ of the individual components of the ^{29}Si NMR signal were measured relative to the TMS signal. The conditions of the recording NMR spectra were similar to those used previously.[3,6]

Results and Discussion

The hydrothermal treatment of NH_4-exchanged forms of the zeolite NaY at $T_{tr} < 873$ K is not accompanied by the formation of extraframework hydroxide species of hexa-coordinated aluminum, but only causes the hydrolysis of the most ionic Al—O bonds at the deammoniated nodes[1,8] resulting in the fragments



The decrease in the number of Al—O—Si bonds is accompanied by a decrease of the excess negative charge of the framework (ENCF). The acidic and hydrolytic stability of the framework is thus increased due to the decrease in the proton-acceptor ability of the oxygen atoms of the nonhydrolyzed bridges. Therefore, more drastic treatment conditions are needed for the deeper hydrolysis of the Al—O bonds at the deammoniated nodes.[2] The general high-frequency (HF) shift of the absorption bands (AB) in the IR-spectrum of the framework corresponds to the decrease in the ENCF and, hence, in the ionic character of the framework bonds T—O (T = Si, Al). The maximum shift, by ~20 cm^{-1}, is registered in the range of asymmetric vibrations of the TO_4 tetrahedrons (Fig. 1, *a*, curves *1, 3*).

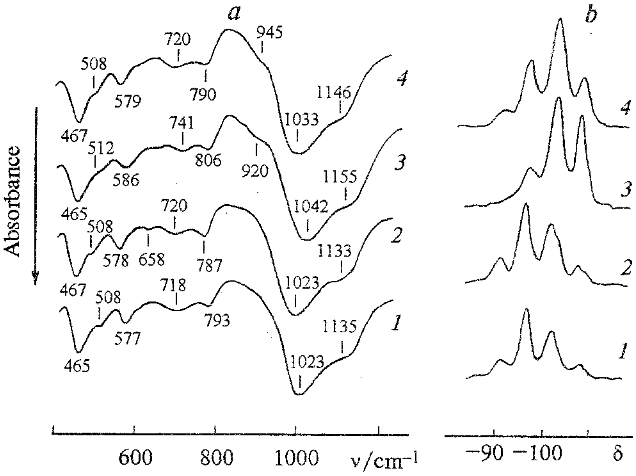
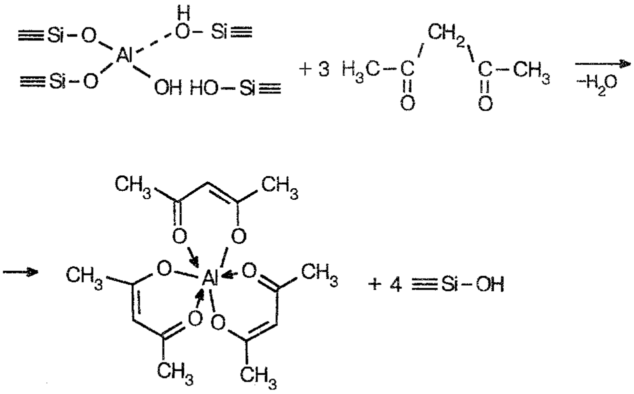


Fig. 1. IR absorption spectra of the framework (*a*) and ^{29}Si NMR spectra (*b*) of samples **1**—**4** (*1*—*4*).

The existence of hydrolyzed bonds in the structure of **3** is confirmed by the presence of AB at 880—950 cm^{-1}. The ν(OH) bands at 3620—3700 cm^{-1} are observed in the IR-spectra of the samples related to **3** ($Si/Al_{fr} \le 6$—10, $a = 24.50 \div 24.60$ Å) (see Refs. 9—11), and intense peaks at −101.0 and −90.5 ppm are observed in the ^1H—^{29}Si NMR spectra (see Ref. 12). These samples yield a considerable amount of "chemical" water.[13] The absence of bands at 520, 610, and 830 cm^{-1} in the IR absorption spectrum indicates that **3** has no near- or extraframework hydroxide species of Al^{VI} formed by the hydrolysis of more than two bonds of the deammoniated nodes of the structure.[2]

The broadening of the $^{27}Al^{IV}$ signal in the ^{27}Al NMR spectra of samples similar to **3** is explained[14] by the change in the coordination state of the Al atoms during the partial hydrolysis of Si—O—Al bonds (Al atoms remain in the framework). However, the appearance of the diffuse shoulder of the Al^{IV} peak is not attributed to absorption of Al^{IV} in so-called[4] "violated" tetrahedral coordination, but to the Al^{VI} atoms in the extraframework species.[15,16] After impregnation of the sample with acetylacetone (AA), a narrow peak of Al^{VI} appears in the spectrum that is explained[15,16] by the transformation of "invisible" compounds, such as $Al(OH)_3$, $Al(OH)^{2+}$, and Al_2O_3, (broad signal) into "visible" compounds (narrow signal) represented by the mobile complex $Al(acac)_3$. However, the same complex



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

may also be formed by the chelation of the Al in the deammoniated or partially hydrolyzed nodes of the structure.

The disappearance of the $\mathrm{Al^{VI}}$ peak accompanied by the noticeable narrowing of the $\mathrm{Al^{IV}}$ peak after the aqueous treatment of the samples preliminarily impregnated with AA confirms the chemical modification of the structure of the dealuminated samples.

The IR spectroscopic information about the local changes in the structure is supplemented by the ^{29}Si NMR data presented in Fig. 1, *b*. The values of δ of the individual components of the ^{29}Si signal due to the resonance absorption of the Si atoms in $\mathrm{Si(OAl)}_n\mathrm{(OSi)}_{4-n}$ (designated for brevity as Si(n Al), where n = 0, 1, 2, 3, and 4 corresponds to the number of framework Al atoms in the nearest surroundings of a particular Si atom) and the relative values of the integral intensities of the corresponding components of the $I_{\mathrm{Si}(n\ \mathrm{Al})}$ signal separated from the general absorption profile assuming the Gaussian form of the individual lines are listed in Table 1. For the calculation of $I_{\mathrm{Si}(n\ \mathrm{Al})}$, the integral intensity of the extended ^{29}Si signal $\sum_{n=0}^{4} I_{\mathrm{Si}(n\ \mathrm{Al})}$ was assumed to be 100. The values of $\mathrm{Si/Al_{fr}}$ listed in Table 1 were calculated by the formula:[17,18]

$$\mathrm{Si/Al_{fr}} = \sum_{n=0}^{4} I_{\mathrm{Si}(n\ \mathrm{Al})} \Big/ \sum_{n=0}^{4} 1/4 I_{\mathrm{Si}(n\ \mathrm{Al})}.$$

As can be seen from Fig. 1, *b* and Table 1, the change in the state of aluminum, going from **1** to **3**, is manifested in an increase in δ of the individual components of the ^{29}Si signal, which causes the general high-field (FH) shift of its centroid.[19,20] Reflecting the tendency of the T—O—T angles of tetrahedrons to increase[21,22] and, hence, of the proton-acceptor ability of the bridge oxygen to decrease, this shift indicates, similarly to the HF-shift of the bands in the IR-spectrum of the framework oscillations, the change in the electron state of the framework bonds T—O due to the decrease in their ionic character because of the hydrolytic cleavage of some of the bridge bonds in the deammoniated nodes. The redistribution of the values of the integral intensity of the components (decrease in $I_{\mathrm{Si}(n\ \mathrm{Al})}$ for n = 4, 3, and 2 and increase in $I_{\mathrm{Si}(n\ \mathrm{Al})}$ for n = 1, 0) points to easier hydrolytic cleavage of those framework bonds where the silicon atoms have no less than two Al atoms in their nearest neighborhood. This fact has been previously mentioned[23] and correlates with the conclusion[24–26] that the extraction of Al atoms from the secondary units of a zeolite structure is easiest when their number is greatest.

As can be seen from Table 1, the redistribution of $I_{\mathrm{Si}(n\ \mathrm{Al})}$ in the ^{29}Si NMR spectrum of **3** corresponds to an increase in $\mathrm{Si/Al_{fr}}$ from 2.37 to 3.1. As the formula used for the determination of this value is derived for the standard state of the structure, when each $\mathrm{Al^{IV}}$ atom is linked by normal bridge bonds with silicon atoms, the $\mathrm{Si/Al_{fr}}$ value calculated from the NMR spectrum is of a formal character for the case of samples with cleaved bridge bonds. In fact, it reflects the change in the ionic character of the framework bonds as the result of the change in the amount of normal Si—O—Al bridge bonds in the framework. The $\mathrm{Si/Al_{fr}}$ ratio calculated from the ^{29}Si NMR spectra for products of the hydrothermal dealumination of zeolite Y seems to be understated,[12] because the framework groups $\mathrm{(SiO)_3SiOH}$ and $\mathrm{(SiO)_2Si(OH)_2}$, with the corresponding peaks at −101.0 and −90.5 ppm in the ^{1}H—^{29}Si NMR spectra, are responsible for a certain contribution to the Si(1 Al) and Si(2 Al) components of the signal.

If one proceeds from the simplified concept of the mechanism of hydrothermal dealumination as the simultaneous hydrolysis of four Al—O bonds of the deammoniated node with the subsequent migration of silicon to vacant sites (this contradicts the real experimental data[1,2,27]), the change in $\mathrm{Si/Al_{fr}}$ from 2.37 to 3.1—3.9 corresponds to a removal of 25—40 % of the Al from the framework. If one proceeds from the more realistic concept of the mechanism of this process as the stepwise hydrolysis of the Al—O bonds of the deammoniated nodes[1,2,28] accompanied by a progressive decrease in the ENCF and terminated with the formation of disiloxane bonds with the electron configuration of the bridge oxygen characteristic of crystalline modifications of silica,[2] this change in $\mathrm{Si/Al_{fr}}$ corresponds to the hydrolysis of 1—1.6 of the four bonds in a deammoniated node.

The treatment of **3** with a 0.25 *N* aqueous solution of KOH at 353 K results in insignificant dissolution of the crystals and $\mathrm{Na^+/K^+}$ substitution (see Ref. 6), exchange of the protons of some Si—OH terminal groups for $\mathrm{K^+}$, and regeneration of the Si—O—Al normal bonds from those in which such an exchange has not occurred.[1] The regeneration of the Si—O—Al bridge bonds is manifested in the IR spectrum (see Fig. 1, *a*, curves *3, 4*) as

Table 1. Parameters of ^{29}Si NMR signals (δ, I (rel. units)) of the samples studied

Sample	$\mathrm{Si/Al_{fr}}$	Si(4 Al)		Si(3 Al)		Si(2 Al)		Si(1 Al)		Si(0 Al)	
		δ	I	δ	I	δ	I	δ	I	δ	I
1	2.37	−83.6	1.5	−87.6	12.3	−93.1	40.1	−98.6	37.1	−103.9	9.1
2	2.37	−83.6	1.5	−88.5	14.1	−94.0	39.8	−99.3	37.6	−104.6	7.1
3	3.1	−86.0	1.2	−90.2	4.7	−95.2	16.7	−101.0	43.4	−105.9	33.4
4	2.8	−87.2	2.0	−89.8	8.4	−95.1	27.6	−101.2	44.9	−105.7	17.1

a low-frequency (LF) shift of the AB of the framework by 10—12 cm^{-1}. The LF-shift of AB of the framework is accompanied by an increase in the intensity of AB corresponding to vibrations involving the Al—O bond (508, 579, and 720 cm^{-1}). The exchange of a proton for a K^+ cation results in the HF-shift of ν(Si—O(H)) AB from 920 to 945 cm^{-1} and its simultaneous narrowing due to the homogenization of the composition of the terminal groups.

The LF-shift observed for the AB of the framework after the alkaline treatment of the dealuminated sample is explained[6] solely by the influence of cationic substitution. However, a comparative analysis of the IR spectra of zeolites NaY and KY (see Fig. 1, *a*, curves *1, 2*) reveals that the differences between them are insignificant, especially in the $\nu_{as}TO_4$ range.

The peculiarities of the cationic substitution are observed more distinctly in the ^{29}Si NMR spectrum due to its higher sensitivity to the type of cation[21] in the zeolite crystals. Actually, the exchange of Na^+ for K^+ in the original sample causes, as can be seen from Table 1, a noticeable HF-shift of the components of the ^{29}Si signal. Therefore, one may suppose that the low-field (LF) shift of the signal components expected in the regeneration of the normal bridge bonds from the hydrolyzed bonds will be cancelled out by the HF-shift caused by cationic substitution. Indeed, the alkaline treatment of **3** results in a LF-shift of the ^{29}Si signal components (see Table 1, samples **3**, **4**), whose relative value is insignificant compared with that of the LF-shift of the AB of the framework in the IR-spectra (see Fig. 1, *a*, curves *3, 4*). The redistribution of the relative values of the integral ntensity of the ^{29}Si signal components, which is observed after the alkaline treatment, relates to the decrease in Si/Al$_{fr}$ from 3.1 to 2.8. As is clear from the data given above, this decrease corresponds not to Al "reinsertion"[3] into the framework from the composition of the extraframework species, but to the increase in the Si—O—Al bridge bonds content in the framework. The greater relative value of the HF-shift of the Si(1 Al) signal, compared with other components of the signal, and the less considerable change in the value of its ntegral intensity[3] indirectly attest to the occurrence of cationic exchange in the $(SiO)_3SiOH$ silanol groups of he dealuminated nodes. The insignificant change in the ntegral intensity of the Si(1 Al) peak after the alkaline reatment of the sample indicates that the contribution of the absorption of Si in $(SiO)_3SiOH$ is considerable.

Thus, studying the IR absorption and ^{29}Si NMR spectra leads to the conclusion of the existence of a certain, although far from complete, reversibility of the tructural changes caused by the hydrolysis of framework bonds during hydrothermal treatment due to the action of the alkali.

The reversibility of the structural changes is also clearly reflected by the IR spectra of the studied samples n the range of hydroxyl-containing vibrations. As can be seen from Fig. 2, the hydrolytic cleavage of the Si—O—Al bonds in the sample of the ammonium-exchanged form of the original zeolite results in the increase in the integral intensity of the AB of the stretching vibrations of the hydroxyl groups νOH with the maximum at ~3420 cm^{-1} (see Fig. 2, curves *1, 2*). The main contribution is made by the diffuse continuum with the absorption maximum at ~3200 cm^{-1} spread to the LF-range up to ~2600 cm^{-1}. This is characteristic of the absorption of hydrogen-bonded associates of hydroxyl-containing structures with different hydrogen bond strengths[29] (in particular, of molecularly adsorbed water). The considerable increase in the intensity of AB at ~3620 cm^{-1}, which is assigned[9—11] to the vibrations of OH groups in ≡Al—OH bonded with the framework, clearly attests to the existence of hydrolyzed bonds in the structure of **3**.

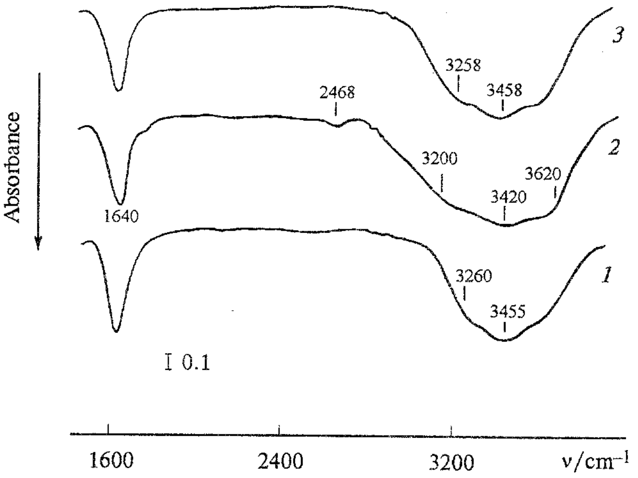
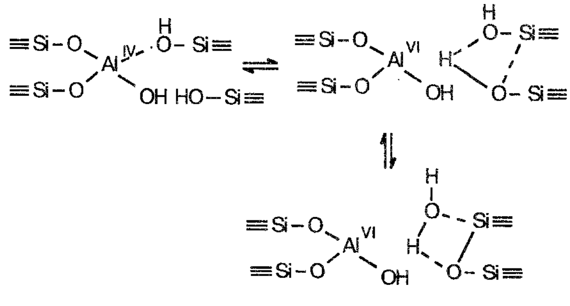


Fig. 2. IR spectra of samples **1** (*1*), **3** (*2*), and **4** (*3*) in the range of the appearance of oscillations of hydroxyl-containing structures.

The AB at 2468 cm^{-1} observed in the spectrum of this sample is assigned to the combination tone of the bending and libration vibrational modes of water molecules in the ice-like state[30] and indicates the existence in the structure of **3** of special forms of molecularly adsorbed water, which are characteristic of ice-like structures.[31] Apparently, these special states of water are realized when a hydrogen bond forms between the bridge and terminal silanol groups.



Disiloxane bonds[2] are formed when the sample is heated under water deficient conditions[32] (shallow-bed calcination) even at relatively low temperatures (~773 K).

The treatment of sample **3** with an aqueous KOH solution (see Fig. 2, curve *3*) results in (reversible to a large extent) changes in the spectrum in the range of vOH, which appear as a decrease in the absorption at ~3258 cm^{-1} and the disappearance of the absorption at 2468 cm^{-1}. However, as can be seen from Fig. 2, the reversibility of the changes in this spectral range is also far from complete. Apparently, the replacement of the proton of the silanol group by K^+ prevents not only regeneration of a normal bridge bond from those hydrolyzed, but also the formation of a disiloxane bond, resulting in an increase in the thermal and hydrothermal stability of the structure.

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