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IR spectroscopic study of structure—chemical aspects of the Na–Y zeolite dealumination with ethylene diamine tetraacetic acid

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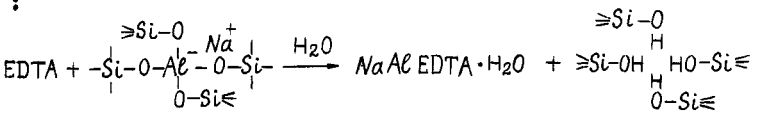
Abstract

Dealumination (DA) of Na-Y zeolite with EDTA was studied by means of the IR lattice vibration spectroscopy. Spectral criteria of DA are considered and a mechanism for DA is proposed as based on the structure-chemical peculiarities involved in chelating of framework Al with EDTA. This produces lowering of the symmetry of terminal $SiO_3O(H,Na)$ tetrahedra forming at the sites of Al expulsion, which are dehydroxylated under disiloxane bonds formation on DA at 373 K. Prolonged aging of the samples dealuminated at 373 K, unlike those dealuminated at 293 K, results in the regeneration of the initial symmetry of SiO_4 tetrahedra.

Dealumination (DA) of zeolites with ethylene diamine tetraacetic acid (EDTA) has become a matter of much research and practical application. However, the structure-chemical peculiarities involved in the DA of zeolites with this reagent are far from being completely studied. In accordance with the widely accepted mechanism for the DA of sodium zeolite Y with EDTA (ref. 1), it is water molecules that are considered dealuminating a framework through the hydrolysis of Al-O-Si bonds under the formation of $Al(OH)_2^+$, while EDTA molecules are considered playing the role of cationic sublattice modifiers due to the decationization by those of $(AlO_4)^-Na^+$ sites and the formation of Na_2EDTA which then exchanges one Na^+ cation for $Al(OH)_2^+$ to yield $NaAlEDTA \cdot H_2O$ removable from crystals. The summation equation of the process, which is easily deduced on the basis of the equations presented in (ref. 1) as :



does not reveal the "personality" of EDTA as dealuminating agent, for it closely corresponds to the equations reported (ref. 2) for the DA of zeolites with other different chemical agents. Hitherto, little attention has been paid to investigating the role of the temperature factor of DA with EDTA, with the latter being proposed in (ref. 1) to perform by a rapid-addition technique, i.e., by stirring for 6 h the

mixture of EDTA and a slurry of zeolite in water, and by a slow-addition one, i.e., by addition of EDTA to a boiling zeolite slurry during 18 h using Soxhlet extractor. The greater crystallinity, cyclohexane sorptive capacity and thermostability of the slow-addition products as compared to the same of the rapid-addition ones was interpreted as a result of different rate of addition of EDTA to sodium zeolite Y without consideration of the temperature factor of DA.

In the present work, an attempt was made to contribute to the clarification of these questions using the IR lattice vibration spectroscopy as a method providing valuable information on the crystal structure local rearrangements occuring in very early stages of different structure-chemical modification processes, i.e., when the "patches" of changed structure are of only 2-5 Å in size (ref. 3), while X-ray method needs "patches" of 80 Å in size to be able to start with detecting crystal structure rearrangements (ref. 4).
IR spectra were recorded using 0.3% KBr platelets on a Bruker IFS-115c Model FT-IR spectrometer over the range of 400 - 1250 cm^{-1} under a resolution of 2 cm^{-1}. The samples investigated were dealuminated forms of a synthetic Na-Y zeolite obtained by treating this with EDTA under the conditions proposed in (ref. 1). Additionally, a "rapid" DA at 373 K was performed due to stirring reagents in a thermostat for 6 h. Characteristics of the samples investigated are collected in Table as determined for freshly prepared samples.

TABLE. Characteristics of the samples investigated.

Sample	The DA technique	Chemical composition, in moles per 1 mole of Al_2O_3				Degree of DA,%	Unit cell parameter, [b] a_o, Å
		Na_2O	SiO_2	[a] H_2O	H_2O/SiO_2		
1	Na-Y	1.03	5.13	9.12	1.78	0	24.67
2	rapid, 293 K	0.91	9.14	12.59	1.38	44	24.64
3	slow, 373 K	0.95	9.42	11.90	1.25	45	24.53
[c] 4	rapid, 293 K	1,08	9.05	14.22	1.53	43	[d] 24.62 (24.63)
[c] 5	slow, 373 K	0.98	10.09	11.20	1.08	49	[d] 24.54 (24.49)

[a] measured for the samples dealuminated at 293 and 373 K after exposition of those to the same atmospheric ambient.

[b] calculated by diffractograms obtained on a "Simens" D-500 Model diffractometer.

[c] were dealuminated 12 years ago.

[d] determined for the aged samples.

Dealumination of Na-Y zeolite with EDTA at 293 and 373 K is seen from Fig. 1 (spectra 1 - 3) to produce the structure changes which are essentially similar between the corresponding samples 2 and 3, and are detected by following spectral features;

- the HF-shift of the framework modes, with the $\nu_{as}TO_4$ one, (T=Si,Al) exhibiting the shift by ≈ 10 cm^{-1} as a result of lowering the excessive negative charge of the framework (ENCF) (ref. 5),

- the decrease in intensity of the Y-type zeolite structure characteristic modes at 509 - 512 cm^{-1} (ref. 6), 582 - 583 cm^{-1} (ref. 7) and that

of the band at 720–726 cm^{-1} attributable to Al-O vibrations in Si-O-Al bridges (ref. 8),

– emergence of the band at 652 cm^{-1} attributable to $\nu_s SiO_4$ (ref.9),

– complication of the $\nu_{as} TO_4$ region due to arising of new bands at 1085 – 1090 and 1202 – 1208 cm^{-1}.

The first three criteria of faujasite DA are universal (ref. 10), while the latter is specific for the DA with EDTA, hence needs a detailed consideration to provide information on the role of EDTA as a dealuminating agent.

Arising of new bands in the T-O stretching vibration region is well known to evidence the formation of a new crystalline phase and/or lowering of the symmetry of TO_4 tetrahedra (ref. 11). Since the position of newly formed bands closely corresponds to that of the $\nu_{as} SiO_4$ bands in crystalline SiO_2 polymorphs spectra (ref. 11), it is reasonable to assume that such phase is present in the dealuminated samples. But the absence in the δTO_4 region of the bands at 470 – 480 cm^{-1} characteristic of such phase (ref. 11) provides evidence for no foreign phase formation in these samples. Therefore, the observed complication of the $\nu_{as} TO_4$ region is to be ascribed to lowering of the symmetry of a part of SiO_4 tetrahedra which might result from local structure deformations on DA with EDTA.

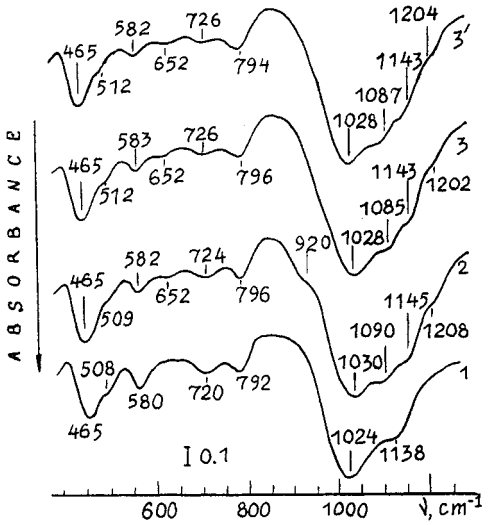


Fig. 1

Spectra of the samples 1 – 3 and of the product of rapid DA at 373 K of Na-Y zeolite to the degree of 45% (3′).

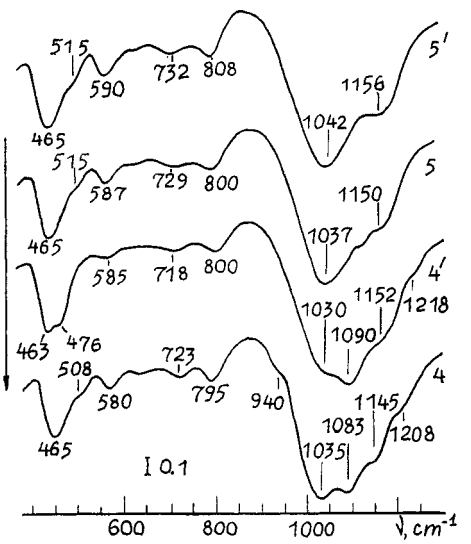
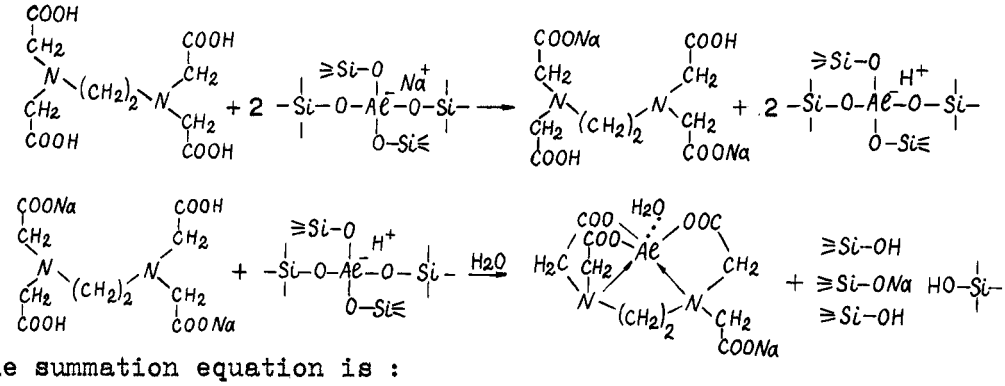


Fig. 2

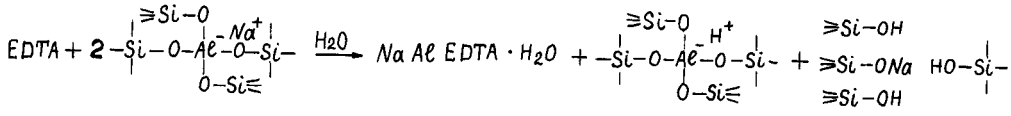
Spectra of the samples 4 and 5 calcinated at 873 K (4′,5′).

Originating of structure deformations seems realistic when taking into account the specific properties of EDTA and its chelates with Me^{3+} cations. Indeed, to form a chelate $NaAlEDTA \cdot H_2O$ (ref. 1), the cyclic structure of which is constrained due to the strong deformation in the plane $-N-(CH_2)_2-N-$ of a chelatic cycle, including two rings -N-CO-O- with their angles exhibiting a significant deviation from normal values, EDTA molecules have to undergo a trans-cis conformational transition facilitated by the substitution of carboxyl groups protons for Na^+, to be able to chelate polyvalent cations (ref.12)

In this respect, it seems reasonable to represent the zeolite DA procedure as follows. When entered a large cavity, EDTA molecule decationizes two $(AlO_4)^- Na^+$ sites, thus changing configuration and dealuminates thereafter one (ref. 1) of the decationized sites:



The summation equation is :



Due to the scheme proposed, the formation of NaAlEDTA·H_2O molecule, with its $-COO^-$ groups being sterically constricted on "holding" aluminium, is preceded by the proper orientation of three corresponding framework bonds at the decationized sites, in order that a geometrical and energetical fitting of interacting groups was achieved. After the extraction of Al those framework bonds remain deformed to a certain extent, thus causing the above mentioned lowering of terminal $SiO_3O(H,Na)$ tetrahedra symmetry. The latter is supported by the ^{29}Si NMR data revealing that on DA of sodium zeolite Y with EDTA, an appreciable broadening of the signals along with the change in their profiles occur as indicating of the distortion in the short range environment of tetrahedral Si atoms at the dealuminated sites of the zeolite framework (ref. 13). The formation of terminal Si-O(H,Na) groups at the dealuminated sites is identified by the emergence of a LF-shoulder on the most intensive ν T-O band with its maximum at ≈ 920 cm^{-1} (spectrum 2) characteristic of ν Si-O(H,Me^+) vibrations (ref. 9). The absence of such absorbance bands in the spectra of the samples dealuminated at 373 K, either by the slow-addition technique (spectrum 3) or by the rapid-addition one (spectrum 4), enables one to conclude that the interaction of terminal groups under the Si-O-Si bridges formation is the case during the DA process at elevated temperatures. Additionally, a close similarity between the spectra 3 and 3 argues in favour of that fact that the rate of EDTA addition to a zeolite at a given temperature is hardly likely to influence the structure of final products.

The formation of siloxane bridges on DA at 373 K brings about a markedly pronounced hydrophobization of the products obtained. As is seen from Table, the content on molecular adsorbed water on the samples dealuminated at 373 K is in average by 15 - 20% lower than that on the samples obtained at 293 K. It appears that it is the exchange of terminal siloxane bonds for bridging ones, known to make the framework T-O bonds of stronger covalent character, i.e., to decrease the proton accepting capability of oxygen hence to increase the hydrophobicity and acidic resistance of the samples (ref. 9), that limits the degree of DA at 373 K to the observed value of 50% (ref. 1). Furthemore, the samples dealuminated at 373 K are seen from the same Table to demonstrate a greater reduction of a_o as compared with the samples dealuminated at room temperature, thus providing another argument in favour of the disiloxane bonds formation at the sites of Al expulsion on DA at elevated temperature.

In addition to the difference between the spectra of corresponding samples 2 and 3 (or 3′) in the ν Si-O(H,Na) region, a somewhat lower intensity of the above discussed newly formed bands at $\approx$1080 and 1200 cm^{-1} in the $\nu_{as}TO_4$ region of the spectrum 3 (or 3′) as compared to the same of the spectrum 2 is observed, what may be considered a result of the reduction of local structure deformations giving rise to the regeneration to some extent of the symmetry of SiO_4 tetrahedra at the dealuminated sites, at elevated temperatures of DA.

So, the samples dealuminated to equal degrees at 293 and 373K demonstrate a structure-chemical non-identity which is most distinctly pronounced on the aged samples, the spectra of which are shown in Fig. 2. Comparing of the spectrum 2 of Fig. 1 to the spectrum 4 of Fig. 2 reveals that aging of the sample dealuminated at 293 K, due to exposing it for 12 years under atmospheric ambient, produces closing in frequencies of the two most intensive ν T-O bands as well as redistribution of their relative intensities i.e., the changes characteristic of the reduction of accidental degeneracy of corresponding vibrations. In line with these changes in the spectrum 4 there occurs a decrease in intensity of the band at $\approx$ 920 cm^{-1} accompanied by its narrowing and HF-shift to $\approx$ 940 cm^{-1}. The decrease in absorbance in this region bears evidence for terminal groups at dealuminated sites to be dehydroxylated on a prolonged aging of the sample, while narrowing and HF-shift of it indicate of the unification of the state of these groups and of the increase in the relative content on Si-O(Na) groups, with the latter known to absorb at higher frequencies than Si-O(H) ones (ref. 14). It is noteworthy that the absence of frequency shifts of most lattice vibration bands in the spectrum 4 of Fig. 2 with respect to the spectrum 2 of Fig. 1 suggests that aging of the sample dealuminated at 293 K produces very slight changes, if any, in its ENCF, what correlates with the X-ray diffraction data revealing no pronounced change in the value of a_o (see Table).

Unlike this, the sample dealuminated at 373 K demonstrates drastic changes on aging, which are evident from the spectra 3 and 5 of Fig.1 and 2. The changes consist in the submergence of the bands at $\approx$1085 and $\approx$1200 cm^{-1} under the fundamental bands at 1037 and 1150 cm^{-1}, thus giving rise to the regeneration of the initial $\nu_{as}TO_4$ region "appearance", on the one hand, and in the HF-shift of the lattice vibration modes, with the $\nu_{as}TO_4$ ones exhibiting the shift by 7 - 10 cm^{-1}, on the other hand. As far as the first of these indicates of the reduction of local structure deformations, the second, of the decrease in the ENCF of the sample. The latter correlates with the observed reduction of the unit cell parameter from 24.54 to 24.49 Å (see Table). Calcination of such sample in air at 873 K for about 6 h enhances both these effects thus yielding a high-silica (Si/Al = 5.02) faujasite sample (Fig. 2, spectrum 5′), the structure of which is much more similar to that of the initial Na-Y zeolite than the structure of freshly dealuminated samples 3 or 3′.

Calcination of the aged sample 4 (Fig. 2, spectrum 4′) results not in the perfection of the zeolite structure, as was observed in the case of the sample 5, but in the degradation of this due to the formation of SiO_2 polymorph crystallites detected by arising of the band at 476 cm^{-1} attributable to δ SiO_4, accompanied by the noticeable increase in intensity of the $\nu_{as}SiO_4$ band at 1090 cm^{-1}, i.e., by the changes known to precede the entire transformation of a zeolite structure into that of a SiO_2 polymorph occuring at higher temperatures of heat treatment (ref. 15). A similar pattern of thermal transformation of the crystal structure was demonstrated by both of the freshly dealuminated samples 2 and 3, unlike the initial Na-Y sample revealing no silica polymorph formation under the same conditions of heat treatment. The reason for this is that the situation of sodium cations at the sites of Al expulsion, as is readily demonstrated by the summation equation of the presented DA scheme, causes a mineralization of the dealuminated samples structure at the temperatures at which the structure of

initial Na-Y zeolite possessing a lower crystalline modulus, Si/Al, but a normal situation of sodium cations near AlO_4 tetrahedra, is stable.

One can assume that a prolonged exposition to atmosphere of the samples dealuminated at 373 K results in the migration of sodium cations from dealuminated sites to their normal crystallographic positions near AlO_4 tetrahedra bringing about the regeneration of the initial short range ordering of both the SiO_4 and AlO_4 tetrahedral units thus yielding a high silica faujasite-like structure. As to the samples dealuminated at room temperatures, no suchlike regeneration of the structure under the same conditions appears to account for trapping sodium cations by the disiloxane bonds being formed on the dehydroxylation of terminal groups, which creates mineralization nuclei (ref. 16).

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