

INVESTIGATION METHODS FOR PHYSICO-CHEMICAL SYSTEMS

Characterization of the Alumino–Silico–Oxygen Clinoptilolite Framework and its Hydrogen Forms via IR Spectroscopy

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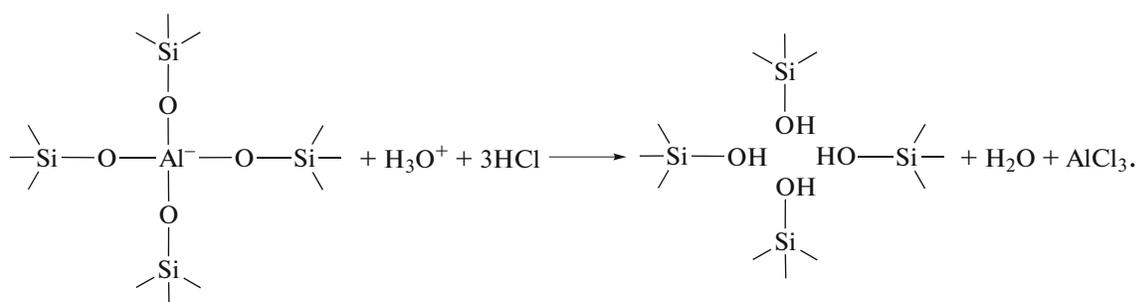
Abstract—In this work, clinoptilolite hydrogen forms are obtained from the Khonguruu zeolite locality (Republic of Sakha, Russia) using hydrochloric acid solutions of different concentrations. The chemical composition is identified via X-ray spectral microprobe analysis and thermogravimetry. IR vibrational spectra of the alumino–silico–oxygen framework are studied in its dealumination and decationization. The effect of the aluminum content in clinoptilolite hydrogen forms on the intensity change and frequencies of the principal vibrational bands of alumino–silico–oxygen framework is established as well.

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INTRODUCTION

Chemical modification of natural zeolites (the treatment with an acid, ion exchange and others) allows one to acquire their new forms with a set of the valuable properties [1–6]. Acid treatment of many natural zeolites is accompanied by their decomposition and the formation of gel or silica. However, acid exposure on clinoptilolite (Cl) allows one to obtain their hydrogen forms (H-forms). The interaction of hydrochloric acid

(HCl) solution with Cl is favored by simultaneous decationization and dealumination [7, 8]. According to Barrer's notions [2], a release of aluminum from the alumino–silico–oxygen Cl framework is accompanied by its substitution by an equal amount of H_3O^+ which compensates the negative charges in zeolites treated with acid, arising at the site of aluminum removed from the framework, as is shown below:



Despite the fact that the dealumination of zeolites with acids is poorly understood, and there are some works reporting other ways of aluminum removal [9, 10], most of authors hang upon the above dealumination stoichiometry.

IR spectroscopy of zeolites in the frequency range of 1400–400 cm^{-1} assigned to vibrations of alumino–silico–oxygen framework is widely used for structural

characterization of zeolite crystal lattices and quantitative evaluation of the changes therein which are caused by the external factors [11–19]. The effect of chemical modification of zeolites on the IR band intensity in the alumino–silico–oxygen framework is poorly studied, which is obviously due to the complexity of the selection of sample preparation conditions, a lack of a standard for natural zeolite and not entirely correct assumption of additivity of dipole moments.

According to Nakamoto [20], this can result in disagreement of the results or even their contradiction.

Comparing zeolite tuffs of various localities, many authors [11, 13–16] call attention to the IR band frequencies in the vibration range of the alumino–silico–oxygen framework, which depend on the $\text{SiO}_2/(\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3)$ ratio in zeolite, rather than the intensities of these bands. Here, the S–O–Si(Al) anti-symmetric valent vibration band with a maximum at $1050\text{--}1100\text{ cm}^{-1}$ is the most sensitive. Its shift toward the higher frequencies is observed in aluminosilicates with a decrease in the relative aluminum content. This phenomenon was first described by Mealkey in [21], where small deviations from the above law caused by sensitivity of this band to topology of the zeolite crystal structure were mentioned as well.

In this work, we study the effect of the chemical composition of H-form CIs on their IR spectra in order to clarify the ability to apply IR spectroscopy for description of structural and chemical modifications of alumino–silico–oxygen CI framework during the treatment of zeolite with HCl hydrochloric acid.

EXPERIMENTAL

The Characteristics of the Precursor

The precursor used in this work was zeolite tuff from the Khonguruu location (Sakha, Russia). In accordance with X-ray diffraction (XRD) with a Ritweld semiquantitative estimation of phases, the CI content in the natural sample was $87 \pm 5\%$, the quartz content was $13 \pm 5\%$, and no other minerals were detected from these data, which testifies to their quite low content (below 5%). With respect to this, the use of the chosen material for synthesis of H-form CI is justified by its high content in tuff and rather low concentration of impurity minerals, which are expected to bring an insignificant error to the experimental results.

The principal component concentrations in the Khonguruu natural tuff calculated relative to the sample dried at 378 K are shown in Table 1.

Preparation of Hydrogen Forms of Clinoptilolite

Before treatment, the ground tuff precursors were subjected to additional grinding in a Pulverisette 7 planetary mill (Fritsch Corp., Germany) with the agathe balls and were then sieved on vibrational bolters, allowing the selection of a fraction with grain sizes of $6 \times 10^{-5}\text{--}9 \times 10^{-5}\text{ m}$ (60–90 μm).

The samples were exposed in 0.1, 0.5, 1.0, 2.0, and 5.0 M/L HCl hydrochloric acid high-purity solutions at constant intensive stirring. The tuff : solution weight ratio was 1 : 25, the contact time with solutions was 24 h, and the temperature was 353 K.

After this time, zeolites were separated from solutions via decantation and were washed with distilled water on a vacuum filter until a negative qualitative

Table 1. Chemical composition of natural CI and its modifications

Form	Chemical composition, %				
	Na ₂ O	K ₂ O	MgO	CaO	
Natural	4.03	3.00	1.13	0.45	
0.1 CI	0.59	1.24	0.80	0.37	
0.5 CI	0.16	1.05	0.50	0.27	
1.0 CI	0.05	0.95	0.28	0.22	
2.0 CI	0	0.68	0.15	0.14	
5.0 CI	0	0.07	0.07	0.07	
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	H ₂ O	SM
Natural	67.72	15.61	1.07	6.99	4.06
0.1 CI	76.89	10.36	0.70	9.05	6.95
0.5 CI	86.27	3.46	0.56	7.73	21.46
1.0 CI	88.79	2.61	0	7.10	34.02
2.0 CI	90.35	2.34	0	6.34	38.61
5.0 CI	93.42	0.91	0	5.46	102.66

SM—silicate modulus ($\text{SiO}_2/[\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3]$ ratio).

reaction for Cl^- chloride ions with AgNO_3 silver nitrate solution. They were then dried in air to achieve the air-dry state.

In accordance with the described technique, the following H-forms were obtained: 0.1, 0.2, 0.5, 1.0, 2.0, and 5.0 CI (here and hereinafter, we use designations of CI, where a coefficient corresponds to the molar concentration of HCl solution used in their synthesis).

Methods of Characterization

Pretreatment. To remove hygroscopic water, CI and its modifications were heated for 2 h at 383 K and

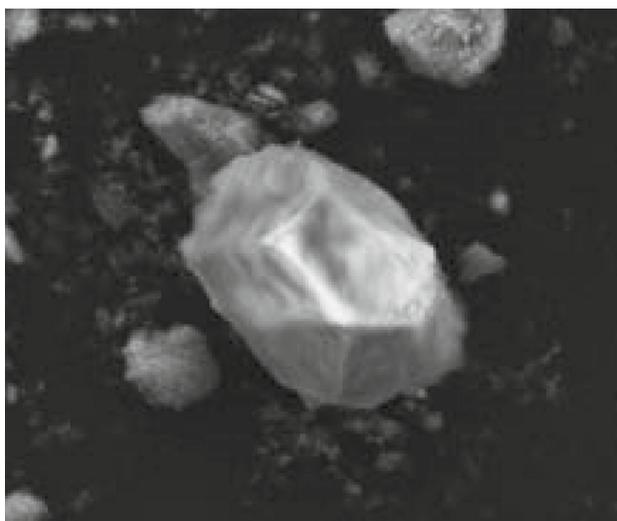


Fig. 1. Clinoptilolite particle after grinding of Khonguruu tuff (1000 \times magnification).

then were exposed in an excicator until cooling. Because of the expected natural inhomogeneity of the tuff precursor and its modifications with respect to the phase composition, the samples were selected via quartering.

Analysis of Chemical Composition. The chemical composition of Cl samples was determined via X-ray microprobing analysis. The Cl samples were applied on a conductive carbon tape fixed on a brass substrate. N₂ was purged to remove the particles firmly fixed on the tape. The samples were afterward put into the chamber of a JSM-7800F raster electron microscopy (JEOL Corp., Japan) and were subjected to vacuum up to a residual pressure of 9.6×10^{-5} Pa. The element analysis was implemented via a X-MAX-20 X-ray spectral console (Oxford Corp., United Kingdom) on an area of $2 \times 10^6 \mu\text{m}^2$ at an accelerating voltage of 20 kV and emission current of the absorbed electrons of 70 μA . The reference samples were natural and synthesized materials that were used in the analysis of the following minerals tested for homogeneity: albite (detection of Na), MgO (analysis for Mg), Al₂O₃ (detection of Al), SiO₂ (detection of Si), feldspar (detection of K), wollastonite (detection of Ca), and Fe (detection of Fe). Quantitative analysis was done in the Energy software via calculation of the peak intensities, determining the best match of the reference peaks on the basis of the least squares method with background suppression. The numerical content of each element was evaluated via averaging the data from the analysis of five independent samples.

The losses in the samples during ignition were estimated via thermal gravimetry on an STA 449C Jupiter device (Netzsch Corp., Germany). The samples were heated with a rate of 10°C/min in an argon environment at a standard pressure of 298–1173 K in Pt/Rh bowls with an Al₂O₃ substrate. The weight losses in Cl samples over the range of 383–1173 K were calculated from the obtained thermogravigrams on Proteus Analysis software (Netzsch Corp.).

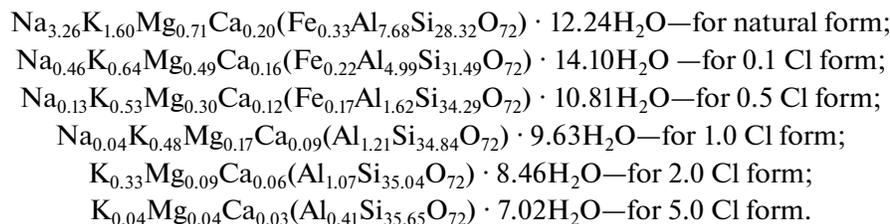
IR Studies. To perform IR studies, pellets were prepared via pressing at 20 MPa of a Cl + pure KBr (1 : 500) mixture carefully rubbed in the agate mortar for 10 min. IR spectra were recorded at room temperature on a Varian 7000 FT-IR spectrometer in the frequency range of 4000–300 cm⁻¹ with a resolution of 8 cm⁻¹. The number of scans for each sample was 16. The spectra were processed in the range of 1400–400 cm⁻¹ with subsequent calculation of the peak intensities and frequencies by means of the built-in fitting functions in the Varian Resolutions Pro™ software.

RESULTS AND DISCUSSION

Element Analysis

The quantitative chemical composition of natural Cl and its modifications, evaluated via the element analysis, is shown in Table 1.

The following formulas (calculated per a unit cell) were obtained for these modifications:



In synthesis of 0.1 Cl, tuff was taken in excess, and hydrochloric acid was thus completely consumed. This is indicated by the decreasing amount of Al₂O₃ during production of 0.1 Cl from natural Cl, which is equimolar to the quantity of HCl in its initial 0.1 M/L solution. For preparing other H-form Cl, hydrochloric acid was taken in excess.

According to the analysis, the treatment of Cl with HCl hydrochloric acid leads to decationization and dealumination. Using 5 M/L acid solution washes away completely Na⁺ and Fe³⁺ and almost completely (until 94 wt %) washes away the framework Al, leaving a small amount of K⁺, Mg²⁺, and Ca²⁺ ions (0.07 wt % for each ion type).

To calculate the degree of substitution, let us express the cationic composition of Cl modifications

through the nominal formulas, where the indices indicate the equimolar fraction of the corresponding cation in the unit cell, assuming that complete removal of cations will provide a pure H-form of Cl. In this case, the nominal formulas of the obtained Cl modifications can be expressed as follows:

0.49 Na	0.24 K	0.21 Mg	0.06 Ca	— Cl	Natural Cl
0.63 H	0.07 Na	0.10 K	0.15 Mg	0.05 Ca	— Cl
0.77 H	0.02 Na	0.08 K	0.09 Mg	0.04 Ca	— Cl
0.84 H	0.01 Na	0.07 K	0.05 Mg	0.03 Ca	— Cl
0.90 H		0.05 K	0.03 Mg	0.02 Ca	— Cl
0.97 H		0.01 K	0.01 Mg	0.01 Ca	— Cl

These nominal formulas are widely used in the literature dedicated to H-forms of zeolites, and we think

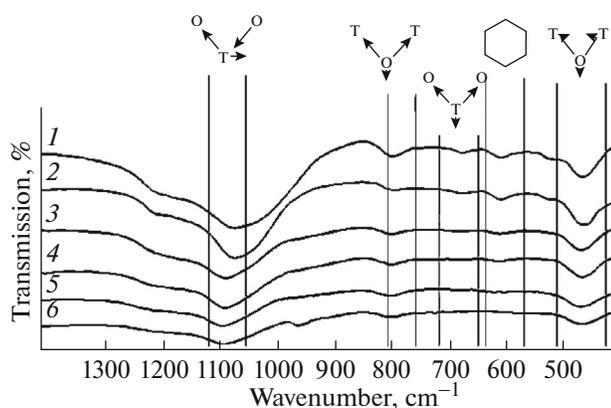


Fig. 2. IR spectra of natural Cl (1) and its modifications: (2) 0.1, (3) 0.5, (4) 1.0, (5) 2.0, and (6) 5.0 Cl.

they best express the degree of cation substitution (in our case, Na^+ , K^+ , Mg^{2+} , and Ca^{2+} by H^+).

Analysis of IR Spectra

Figure 2 displays IR spectra of Cl precursor and its H-forms in the range of 1400–400 cm^{-1} . The general profiles of IR spectra of Khongururu Cl match those of Cl from other locations described in [1, 2, 11, 13, 14, 18, 19].

As is seen, an increased degree of dealumination of Cl leads to blurring of the bands assigned to the aluminosilico-oxygen framework, i.e., to a decrease in their intensity, which indicates amorphization of zeolite structure.

In accordance with IR spectroscopic data, degradation of the aluminosilico-oxygen framework strongly increases with the increasing HCl content starting from 2 M/L (“2.0 Cl” in Fig. 2). This is confirmed by the disappearance of the bands in the frequency range of 610–600 and 680–670 cm^{-1} , which are attributed to the vibrations of double rings between tetrahedra and symmetric valent vibrations inside tetrahedra. Moreover, a band at 959 cm^{-1} assigned to (Si–O) strain vibrations of Si–OH silanol group is amplified in the IR spectrum of Cl treated with 5 M/L HCl solution (“5.0 Cl” in Fig. 2), while its intensity was low in the previous spectra, this being caused by the growing defects in the nests between tetrahedra instead of aluminum removed from the framework.

Table 2 shows the assignment of the bands from IR spectra of Khongururu Cl over the range of 1400–400 cm^{-1} in comparison with the IR spectroscopy data for natural zeolite from the Kaimanes location (Cuba) [14], where the Cl content is also 87%. There are also some differences in the frequencies between zeolites from both locations. A lack of data on the line at 680–670 cm^{-1} in the IR spectrum of Cl from Cuba, which seems to be overlapped by more intense neighboring components, calls attention to itself. The effect

Table 2. Assignment of IR bands of Cl from Kaimanes and Khongururu, and its modifications

		T–O strain vibrations	Intertetrahedral vibrations of double rings	Intratetrahedral symmetrical valent vibrations
Kaimanes (Cuba) [14]		459	608	?
Khongururu (Russia)	ν , cm^{-1}	462	604	671
	<i>I</i> , %	38	4	3
0.1 Cl	ν , cm^{-1}	460	603	673
	<i>I</i> , %	37	4	2
0.5 Cl	ν , cm^{-1}	464	606	674
	<i>I</i> , %	36	3	1
1.0 Cl	ν , cm^{-1}	463	607	677
	<i>I</i> , %	22	1	<1
2.0 Cl	ν , cm^{-1}	463	–	–
	<i>I</i> , %	19	–	–
5.0 Cl	ν , cm^{-1}	464	–	–
	<i>I</i> , %	17	–	–
		Intertetrahedral symmetrical valent vibrations	Si–O strain vibrations	Intratetrahedral antisymmetrical valent vibrations
Kaimanes (Cuba) [14]		795	–	1062
Khongururu (Russia)	ν , cm^{-1}	794	–	1070
	<i>I</i> , %	10	–	55
0.1 Cl	ν , cm^{-1}	788	–	1072
	<i>I</i> , %	9	–	46
0.5 Cl	ν , cm^{-1}	795	–	1085
	<i>I</i> , %	5	–	32
1.0 Cl	ν , cm^{-1}	795	–	1086
	<i>I</i> , %	3	–	21
2.0 Cl	ν , cm^{-1}	793	–	1087
	<i>I</i> , %	2	–	11
5.0 Cl	ν , cm^{-1}	797	959	1091
	<i>I</i> , %	2	1	11

of the chemical treatment on the band intensity in the IR spectra of Cl was not analyzed in [14].

Statistical IR Data Processing

In zeolites, SM (silicate modulus) is considered to be a $[\text{SiO}_2/(\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3)]$ ratio that is expressed through the weight fractions of the appropriate oxides

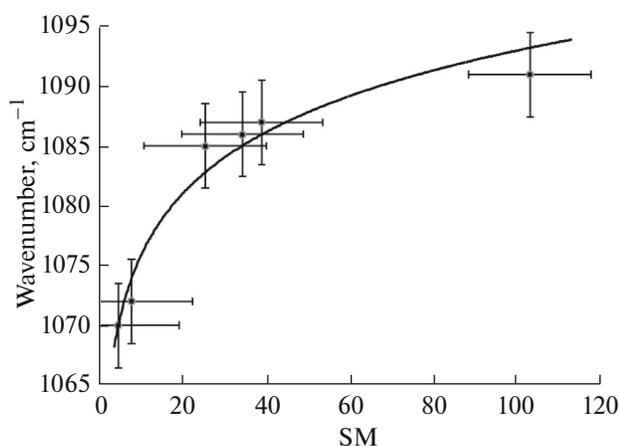


Fig. 3. The frequency of the band assigned to antisymmetrical valent vibrations inside an alumino-silico-oxygen tetrahedron as a function of silicate modulus of the studied CI samples.

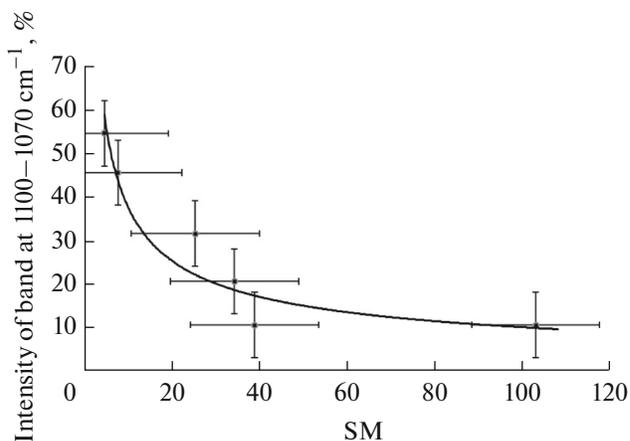


Fig. 4. The intensity of the band assigned to antisymmetrical valent vibrations inside alumino-silico-oxygen tetrahedron as a function of silicate modulus of the studied CI samples.

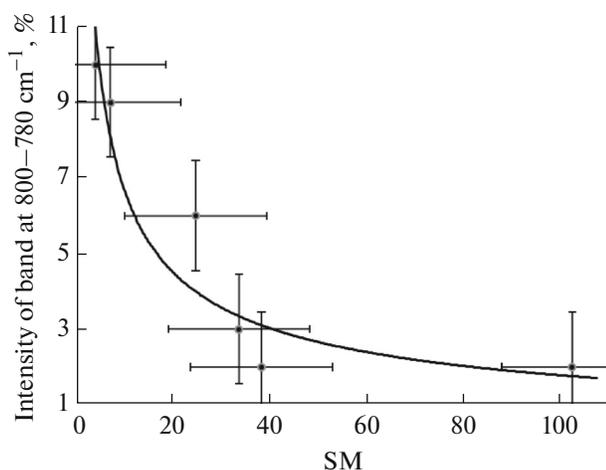


Fig. 5. The intensity of the band assigned to symmetrical valent vibrations between alumino-silico-oxygen tetrahedra as a function of silicate modulus of the studied CI samples.

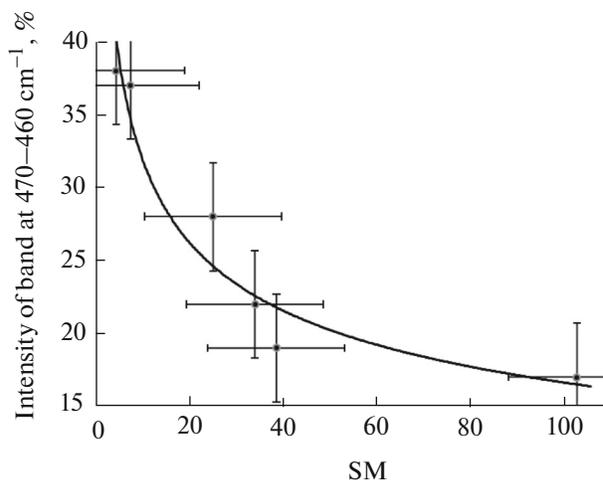


Fig. 6. The intensity of the band assigned to T-O strain vibrations as a function of silicate modulus of the studied CI samples.

in the zeolite composition. As a rule, the SM magnitude is comparable with the main properties (chemical, catalytic, sorption, and others) of natural and synthetic zeolites [4, 7, 9–11, 15].

In our opinion, a statistical relationship between the chemical composition and IR data for zeolites over the vibration range of alumino-silico-oxygen framework can be established via its comparison with SM value.

Figures 3–6 display the dependences of SM on the frequency of a characteristic band at 1010–1070 cm^{-1} (Fig. 3) and the intensity of the characteristic bands at

470–460, 680–670, and 800–780 cm^{-1} (Figs. 4–6) with indication of the standard construction error. A correlation analysis via calculation based on a method described in [22] revealed a correlation between the compared magnitudes (at a confidence probability of $P = 0.95$).

The functional dependences between the compared value pairs were plotted by means of the Microsoft Office software, and their equations were obtained as follows (1)–(4):

$$\nu = 1059\text{SM}^{0.007}; \quad (1)$$

Table 3. SM values calculated from IR spectroscopic data for natural and H-forms of Cl compared with the element analysis (EA) results

	SM _{EA}	SM _v	SM _{I1}	SM _{I2}	SM _{I3}
Natural form	4.06	4.38 (8)	4.47 (10)	4.92 (21)	4.84 (19)
0.1 Cl	6.95	5.71 (18)	6.02 (13)	5.86 (16)	5.29 (24)
0.5 Cl	21.46	31.98 (49)	11.01 (49)	11.52 (46)	13.4 (38)
1.0 Cl	34.02	36.47 (7)	22.23 (42)	36.57 (42)	29.95 (19)
2.0 Cl	38.61	41.6 (8)	65.3 (61)	71.87 (17)	48.82 (60)
5.0 Cl	102.66	70.3 (32)	65.3 (36)	71.87 (30)	70.73 (31)
Δ _{average} , %	—	20	35	29	32

$$I_1 = 135SM^{-0.6}; \quad (2)$$

$$I_2 = 26SM^{-0.6}; \quad (3)$$

$$I_3 = 61SM^{-0.3}, \quad (4)$$

where ν is the frequency of a band assigned to asymmetric valent vibrations inside tetrahedra, cm^{-1} ; I_1 is the intensity of assigned to asymmetric valent vibrations inside tetrahedra, %; I_2 is the intensity of assigned to symmetric valent vibrations between tetrahedra, %; I_3 is the intensity of a band attributed to T–O strain vibrations, %; and SM is the silicate modulus ($\text{SiO}_2/\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$).

The SM values calculated from IR spectroscopic data using formulas (1)–(4) and those determined via the element analysis are shown in Table 3; the error relative to the element analysis results is given in parentheses (%). The last line displays the average error of the SM values evaluated from IR spectroscopy data.

In accordance with the calculations, the lowest average relative error (20%) is obtained in the calculation of SM from the frequency of a band assigned to antisymmetric valent vibrations inside alumino–silico–oxygen tetrahedron.

The higher average relative errors of the SM calculations are obtained, when using the intensities of the bands attributed to antisymmetrical valent vibrations inside alumino–silico–oxygen tetrahedron (I_1), symmetric valent vibrations between alumino–silico–oxygen tetrahedra (I_2), and T–O strain vibrations (I_3), to be 35, 29, and 32%, respectively.

The calculation of the silicate modulus from the intensities of the bands that are attributed to intertetrahedral vibrations of the double rings and intratetrahedral symmetric valent vibrations is not possible because of the low values of the considered magnitudes.

CONCLUSIONS

In accordance with the element analysis, the treatment of Cl clinoptilolite with hydrochloric acid removes a significant (in the case of K^+ , Mg^{2+} , and

Ca^{2+}) or complete amount (for Na^+) of cations, as well as Al^{3+} and Fe^{3+} from the alumino–silico–oxygen framework, which results in decreasing intensities of all IR bands over the range of $1400\text{--}400\text{ cm}^{-1}$.

With increasing HCl concentration and, correspondingly, degree of dealumination and decationization, there is observed pronounced amorphization of Cl. This is indicated by the emergence of a band assigned to (Si–O) vibrations of the Si–OH group in the IR spectrum of 5.0 Cl and indirectly by a decrease in the mole quantity of H_2O per a unit cell, as follows: 0.1 Cl, 14.10; 0.5 Cl, 10.81; 1.0 Cl, 9.63; 2.0 Cl, 8.46; and 5.0 Cl, 7.02 M. This is, first, due to the accumulation of defects in the alumino–silico–oxygen framework and, consequently, its partial destruction. The degradation therein can be adequately determined via X-ray diffraction.

The plotted curves of SM as the functions of the intensities of the bands at $470\text{--}460$, $680\text{--}670$, and $800\text{--}780\text{ cm}^{-1}$ and the frequency of the component at $1100\text{--}1070\text{ cm}^{-1}$ enabled us to highlight their power behavior, which was proven via the correlation analysis, as well as to obtain its mathematical model.

The results of the inversely calculated SM give the ability to roughly determine the silicate modulus from formula (1). Formulas (2)–(4) ensure the calculation of the silicate modulus with a higher error.

The ability to use IR spectroscopy for quantitative description of structural and chemical transformations in the alumino–silico–oxygen Cl framework during the treatment of zeolite with HCl is thus confirmed in this work.

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