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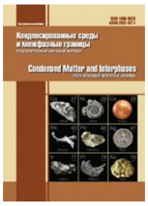

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Composition, structure, and electrophysical properties of natural zeolite clinoptilolites subjected to mechanical activation with potassium hydrosulfate

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Abstract

Objectives: The mechanochemical modification of zeolites with the addition of acidic salts causes an increase in the defectiveness of their structure, a change in the dispersion of the powder, and the conductivity of tableted samples. The aim of the study was to obtain mineral samples with improved conductivity using a mechanochemical method from air-dry mixtures of clinoptilolite-stilbite, clinoptilolite rocks and, potassium hydrosulfate in different ratios.

Experimental: The shape and size of particles, chemical and phase composition of powders, and their physical properties were studied using electron microscopy, energy-dispersive X-ray spectrometry, X-ray phase analysis, differential scanning calorimetry, infrared spectroscopy, sieve analysis, gravimetry, and air permeability. The electrical conductivity of the tableted samples was measured using a three-electrode circuit in the temperature range from 25 to 100 °C.

Conclusions: The results of the study demonstrated that mechanical treatment of mixtures of zeolites with an acidic salt leads to the amorphization of stilbite and feldspar, polymorphic transformations of quartz into cristobalite and tridymite, and an increase in structural defects. The interaction of components occurs via the silanol groups of clinoptilolite and hydrosulfate groups through the formation of hydrogen bonds and with the involvement of water molecules. It was also established that the electrical conductivity of a mineral tablet sample based on clinoptilolite rock and potassium hydrosulfate in an equimass ratio, subjected to shock-shear action with a mechanical energy dose of 2.16 kJ/g, amounted to $4.26 \cdot 10^{-4}$ $S \cdot m^{-1}$ at 100 °C. Electrical conductivity values of the same order were obtained earlier for the mechanochemical activation of natural zeolites with potassium hydrophosphates. Consequently, the hydrosulfate anion does not make a significant contribution to the conductivity of zeolite samples compared to the hydrophosphate anion.

Keywords: Natural zeolites, Clinoptilolite, Stilbite, Mechanochemical activation, Electrical conductivity, Potassium hydrosulfate

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1. Introduction

Zeolites are used as adsorbents, catalysts, and ion exchangers [1–4], in electrochemical devices, for example, for lithium-ion batteries due to the unique microporous structure and ion-exchange properties [5–7]. Low ionic conductivity limits the use of natural zeolites as solid electrolytes [8, 9]. The ionic conductivity can be increased by chemical modification, thermal treatment, and mechanical activation in high-energy devices [10–13]. Mechanical treatment of a solid substance leads to the reduction and deformation of particles without the use of high temperatures and aggressive chemical reagents [14–16]. The resulting defects and impairments in the crystal lattice create additional vacancies and interstitials and contribute to an increase in the concentration and mobility of charge carrier ions [8, 10]. Moreover, the formation of an amorphous phase can provide higher ionic conductivity compared to the crystalline phase [10, 17, 18].

The mechanical treatment of zeolites in the presence of acidic alkali metal salts leads to complex structural changes [11]. Intense mechanical action causes a decrease in the size of crystallites, an increase in the specific surface area, and the introduction of alkali metal ions from the acid salt into the zeolite structure [19]. The electrical properties of mechanically activated zeolites containing acidic salts of alkali metals differ significantly from the properties of the original materials [11, 19]. Ionic conductivity increases by several orders of magnitude depending on the type of zeolite, acid salt, mechanical activation conditions, and temperature [19]. In mechanically activated zeolites, an increase in the concentration of alkali metal ions and the formation of defects contribute to an increase in ionic conductivity [8, 12]. The control of the amount of defects in zeolites is crucial for energy storage applications [20]. It was demonstrated [19] that the electrical conductivity of pressed samples obtained by joint mechanochemical activation of clinoptilolite-stilbite or clinoptilolite rocks with potassium hydrophosphate is ~ 10^{-5}–10^{-6} S·m^{-1} at 25 °C. Potassium hydrosulfate is a good ionic conductor (Fig. 1) with the ability to stabilize the amorphous state [21], but it is brittle and not chemically stable. Properties of potassium hydrosulfate in nanocomposite solid electrolytes (1–x) $KHSO_4$-xSiO_2 depend on the particle size and pores of silicon dioxide [21]. Highly porous and microporous zeolites are mechanically and thermally stable and are also suitable matrices for encapsulating conductive components [5, 6]. Guest ions can influence proton conductivity due to the synergistic effect of pore characteristics and ion concentration [7]. The structure, dispersion, morphology, physical, and electrophysical properties of the resulting composite will be affected by the joint mechanical activation of natural zeolite with potassium hydrosulfate.

This study aimed to obtain mineral powders with improved electrophysical properties using short-term mechanical activation of mixtures of natural zeolite clinoptilolites with potassium hydrosulfate in different ratios.

2. Experimental part

2.1. Materials

Natural zeolite rocks [22], clinoptilolite-stilbite (I) and clinoptilolite (II) (Kholinsky and Shivyrtuisky deposits, Russia) were pre-crushed using a crusher, and potassium hydrosulfate (d) (pure for analysis grade, GOST 4223) was used without any processing.

The assignment of absorption bands in the IR spectrum of $KHSO_4$, ν, cm^{-1} was: 2978; 2884; 2834; 2484; 2417 (H_2O; OH in HSO_4); 1767; 1701 (OH bound with HSO_4); 1651; 1620 (H_2O); 1454;

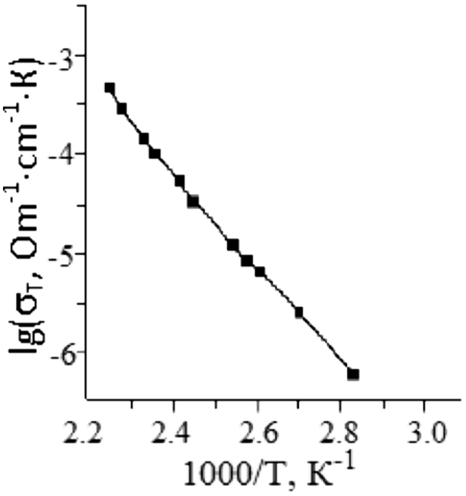

Fig. 1. Temperature dependences of potassium hydrosulfate conductivity (complex impedance method, impedance meter BM-507, *n* = 5 Hz–500 kHz, silver electrodes, cooling mode, air, 2 K/min) [21]

1317; 1284; 1175 (S-O-H); 1071; 1007; 883; 853 (SO_4); 665; 614; 577 (SO_4); 453. The conductivity of tableted mechanically activated samples of clinoptilolite-stilbite and clinoptilolite rocks at 25 °C varied from ~ 10^{-6} to10^{-9} S·m^{-1} [23].

Modified mineral samples were obtained by mixing clinoptilolite powders with a particle size not exceeding 0.5 mm with 25, 33, and 50 wt % potassium hydrosulfate and subsequent mechanical activation for 3, 5, and 7 min in a vibratory bowl grinder IVCh-3 according to the method described in detail in the study [19].

2.2. Research methods

The shapes and sizes of particles were examined using electron microscopy (scanning electron microscope JSM-6510LV JEOL, Japan). The elemental composition was determined using an INCA Energy 350 X-ray energy dispersive spectrometer (Oxford Instruments, UK).

The phase composition was investigated using powder diffraction (DRON-3 diffractometer, CuK_α-radiation, Ni-filter, $U = 25$ kV, $I = 20$ mA, $2\theta = 3–55°$, 1°/min). Semi-quantitative analysis was carried out using the corundum number method. The relative degree of crystallinity of clinoptilolite (k_{rel}) was calculated as described in [19].

Weight changes of 20 mg of mineral samples heated in platinum crucibles in the range of 30 to 850 °C were studied in a dynamic argon atmosphere at a heating rate of 10 °C/min using a synchronous thermal analyzer (STA 449F1, NETZSCH, Germany). The apparent activation energy of dehydration (E_A) in the temperature range from 50 to 150 °C was calculated using the Arrhenius equation according to the study [24].

The specific area was determined using the T-3 (Tovarov) device [14]. The granulometric composition of the powders was studied using sieve analysis, and their bulk density (ρ_b) was measured using gravimetry. True density (ρ_{tr}) was determined by the pycnometric method using TS-1 kerosene as the working fluid. Layer porosity (ε_{la}) was calculated using the equation [19]:

$$\varepsilon_{la} = [1 - (1/\rho_b \cdot \rho_{tr})] \cdot 100\ \%, \qquad (1)$$

The mineral structures were analyzed using a SHIMADZU FTIR-8400S Fourier transform infrared spectrometer in the frequency range of 4000–400 cm^{-1} in tablets with KBr.

The samples were prepared in tablet form (diameter 10 mm and thickness 3–4 mm) using the IP-1A-1000 press. The volume conductivity was measured using an E6-13A teraohmmeter (air humidity 26 %, $U = 100$ V, three-electrode circuit, $t = 25–100$ °C; error: 5 %) [19]. The activation energy of conductivity (E_{act}) was calculated graphically based on the linear dependence of the natural logarithm of electrical conductivity on the reciprocal temperature.

The parameters and properties of clinoptilolite zeolites modified with potassium hydrosulfate and subjected to mechanical activation were compared with similar characteristics of natural zeolites processed under identical conditions without additives and with potassium hydrophosphate. [19]. The marking of the samples includes the type of rock (I, II), salt content (dx, where $x = 25, 33, 50$), and the exposure time (3, 5, 7 min, corresponding to energy doses equal to 2.16, 3.60, 5.04 kJ/g), with its components separated by a dash.

3. Results and discussion

3.1. Study of morphology and chemical composition

Clinoptilolite-stilbite rocks modified with potassium hydrosulfate were characterized by a complex surface relief formed by polydisperse aggregates of irregularly shaped particles (Fig. 2). After three minutes of mechanical treatment, micron-sized aggregates with the size of 46×23, 44×21, 42×33 (Id33-3), and after seven minutes aggregates with the size of 29×23, 25×21, 24×30 (Id33-7) were revealed on SEM images of the powder surface. The replacement of clinoptilolite-stilbite with clinoptilolite rock in the composition did not have a significant effect on the surface morphology, but the size of the largest aggregates increased to 41×53, 30×27, 26×17 (IId33-7). A doubled increase of salt content had practically no effect on the sizes of particle aggregates – 40×44, 21×25, 17×23 (IId25-5), 45×25, 25×14, 16×22 (IId50-5), without excluding the possibility of the formation of quasi-spherical agglomerates in the case of a potassium hydrosulfate content of 25 wt %. The image of the surface of the Id50-7 powder was significantly different, with large, rounded, agglomerated particle formations measuring 60×95, 57×81, 54×42 μm revealed. Electron microscopy data showed that mechanical

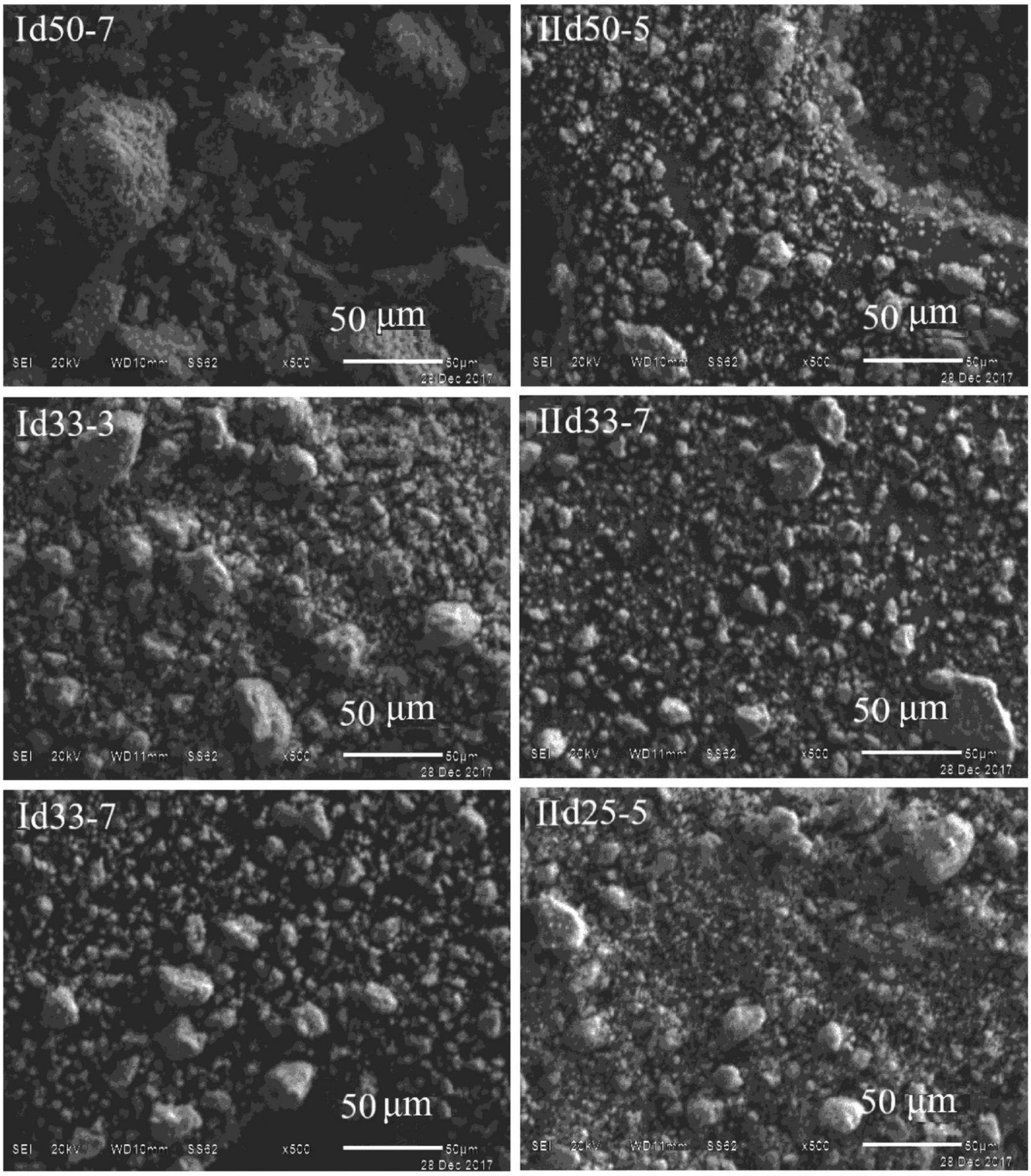

Fig. 2. SEM images of selected samples: I, clinoptilolite-stilbite rock; II, clinoptilolite rock; 25, 33, 50, potassium hydrosulfate (d) content, wt %; 3, 5, 7, duration of mechanical treatment, min

shock-shear action in an air environment promoted both dispersion and the formation of aggregate-agglomerate structures of mineral particles. In order to obtain high-quality powder for pressing, the duration of mechanical processing should be 7 minutes. This time corresponds to an energy dose of 5.04 kJ/g.

The average oxide content in mass percentage and the calculated silicate modulus indicated that natural zeolites belong to the high-silica group (Table 1). The silicate modulus of samples from clinoptilolite-stilbite rock was 10–11, while for samples from clinoptilolite rock it was 8–9. As a result of increasing the energy dose from 2.16 to 5.04 kJ/g (Id33-3 and Id33-7), the silicate modulus increased slightly, indicating that the strength and number of acid centers decreased. An increase in the content of potassium hydrosulfate in the sample compositions expectedly led to an increase in the concentration of K_2O and SO_3, as well as a decrease in the concentration of Na_2O. An increase in the dose of mechanical energy will lead to an increase in the mobility of extra-framework hydrated cations in the aluminum-silicon-oxygen framework system. This is possible not only due to the increase in the concentration of K^+ cations, but also due to changes in the degree of their hydration, caused by the conversion

Table 1. Average oxide content and silicate modulus for selected samples

Samples	Average content of main components in mineral samples, wt %										M_c = Si/Al
	SiO_2	Al_2O_3	Na_2O	CaO	Fe_2O_3	K_2O	SO_3	MgO	CuO	ZnO	
Id33-3	52.2±7.4	8.8±0.9	1.3±0.2	1.2±0.2	0.7±0.2	15.6±2.1	18.4±1.8	0	1.1±0.5	0.8±0.3	10.1
Id33-7	47.1±7.6	7.6±0.4	1.1±0.3	1.0±0.3	0.8±0.5	19.4±5.2	19.6±2.5	0	2.1±1.4	1.2±0.6	10.5
Id50-7	34.3±1.6	6.0±0.4	0.9±0.2	0	0.5±0.1	25.3±2.9	31.5±3.4	0	0.9±0.6	0.6±0.5	9.7
IId25-5	63.8±2.9	13.2±0.7	1.6±0.2	2.2±0.2	2.0±0.4	6.8±1.9	7.6±2.9	1.0±0.1	1.0±0.2	0.7±0.1	8.2
IId33-7	47.9±4.6	9.6±0.7	1.2±0.1	2.1±0.3	1.9±0.2	14.3±1.6	19.5±1.8	0.8±0.1	1.6±0.7	1.1±0.5	8.4
IId50-5	37.3±4.0	7.3±0.6	0.8±0.1	1.7±0.2	1.9±1.1	20.3±2.0	26.1±2.1	0.8±0.1	2.3±2.3	1.5±1.5	8.7

I, clinoptilolite-stilbite rock; II, clinoptilolite rock; 25, 33, 50, potassium hydrosulphate (d) content, wt %; 3, 5, 7, duration of mechanical treatment, min

of mechanical energy into thermal energy as a result of local heating during mechanochemical activation.

3.2. Study of phase composition

X-ray diffraction patterns of mechanically activated (I5, I7, II5, II7) and mechanochemically modified with potassium hydrosulfate clinoptilolite rocks (Id50-7, Id33-7, IId50-5, IId33-7, IId25-7) are shown in Fig. 3. Changes in the intensities and positions of diffraction peaks reflect transformations in the crystal structure of clinoptilolite after mechanical treatment. In the X-ray images of clinoptilolites mechanically activated with acid salt, compared to those mechanically activated without additives, an increase in the intensity of reflections by 1.3–1.9 times was observed. Disorder of the crystal structure was indicated by an amorphous halo in the region 2θ = 10–35° (Id33-7, IId33-7). Mechanochemical treatment of natural zeolites together with salt led to a change in their phase composition (Fig. 3). Thus, in the diffraction patterns of Id50-7, Id33-7, and IId50-5 samples, reflections of high-temperature phases of cristobalite and tridymite were recorded instead of the expected impurity quartz (Table 2). This indicates a polymorphic transition of quartz into cristobalite and is consistent with the data on the products of mechanical activation of quartz raw materials [25]. The relative degree of crystallinity of clinoptilolite increased in Id33-7 and IId25-5 samples and decreased in Id50-7, IId50-5, and IId33-7 samples. It was revealed that salt is present after mechanical activation, together with stilbite-clinoptilolite and clinoptilolite rocks in the form of $K_3H(SO_4)_2$ and $KHSO_4$, respectively. It is known that the disordering of the hydrogen bond system during phase transitions and high proton conductivity is the characteristic feature of the first of the mentioned salts [26]. In addition, the diffraction patterns of clinoptilolite-stilbite samples modified with potassium hydrosulfate did not contain crystalline phases of stilbite and microcline. The increase in electrical conductivity was associated with amorphization, which was confirmed by a decrease in the relative degree of crystallinity of clinoptilolite (Id50-7, IId33-7, IId50-7 samples). At the same time, the crystalline nanoporous structure of clinoptilolite provided channels for the efficient diffusion of metal cations and the necessary mechanical strength. Obviously, the optimal values of the degree of crystallinity of clinoptilolite in the samples, rather than the maximal values, are important.

3.3. Thermal stability study

On the DSC curves of mechanically activated zeolites, endothermic effects were observed in the temperature range of 172–202 °C [22], which are explained by the removal of sorption water. Similar curves of zeolites mechanically activated together with potassium hydrosulfate in equimass ratios contain several endothermic effects (Fig. 4). During thermal decomposition of potassium hydrosulfate, reactions (2)–(4) may occur.

$$2KHSO_4 \xrightarrow{240\ ^{\circ}C} K_2SO_4 + H_2SO_4, \tag{2}$$

$$2KHSO_4 \xrightarrow{320\text{–}340\ ^{\circ}C} K_2S_2O_7 + H_2O, \tag{3}$$

$$K_2S_2O_7 \xrightarrow{>600\ ^{\circ}C} K_2SO_4 + SO_3. \tag{4}$$

According to the results of X-ray phase analysis, samples contained crystals of $K_3H(SO_4)_2$ (Table 2). Then the endothermic effects at 386 and 392 °C (IId50-3, Id50-3) can be attributed to the phase transition of $K_3H(SO_4)_2$ into the high-temperature tetragonal phase [26]. The endothermic effects at

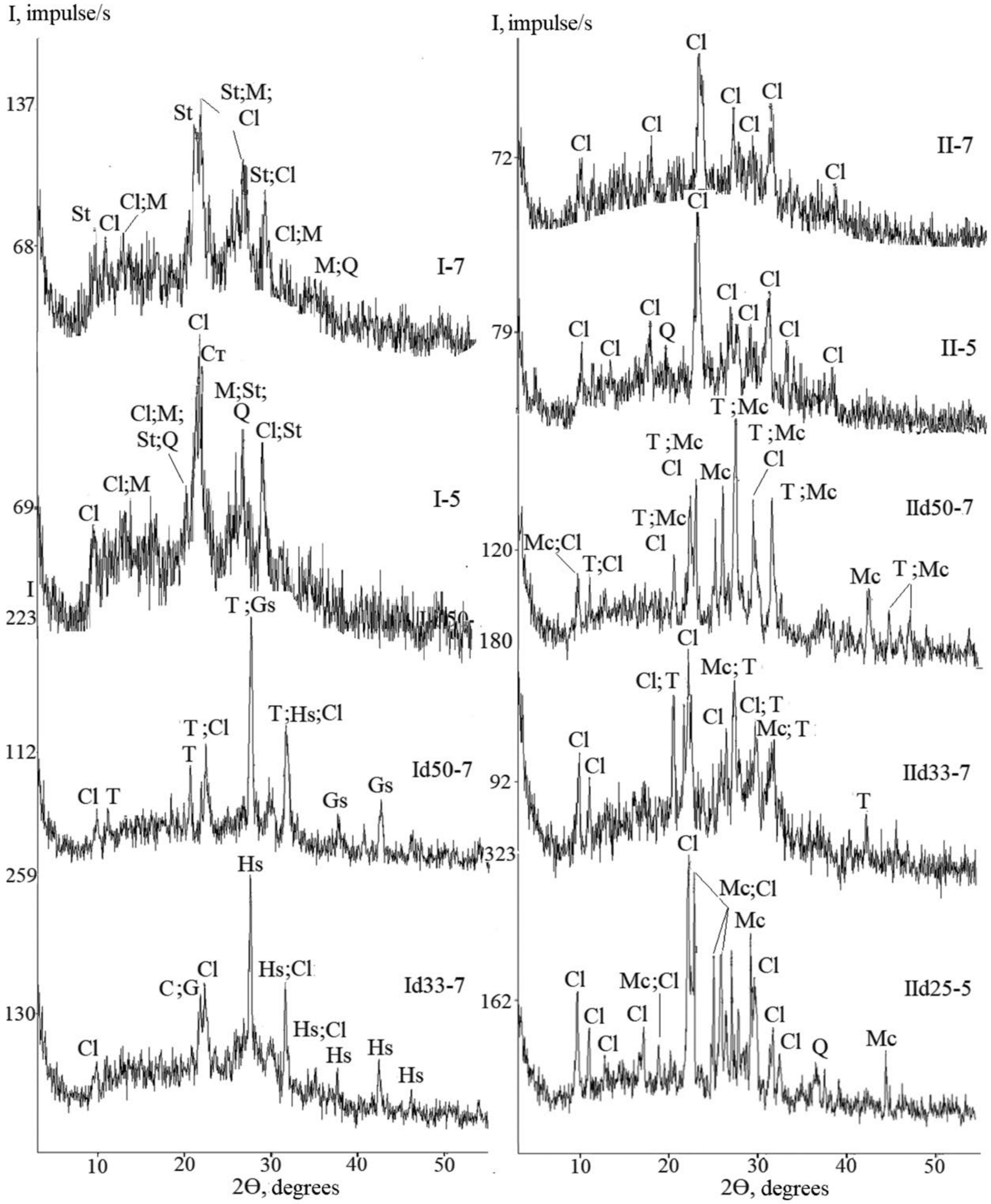

Fig. 3. X-ray diffraction patterns of zeolite samples: I, clinoptilolite-stilbite rock; II, clinoptilolite rock; 25, 33, 50, potassium hydrosulfate (d) content, wt %; 3, 5, 7, duration of mechanical treatment, min.; Cl, clinoptilolite; G, heilandite; St, stilbite; M, microcline; Q, quartz; C, cristobalite; T, tridymite; Ms, mercallite; Hs, potassium hydrosulfate

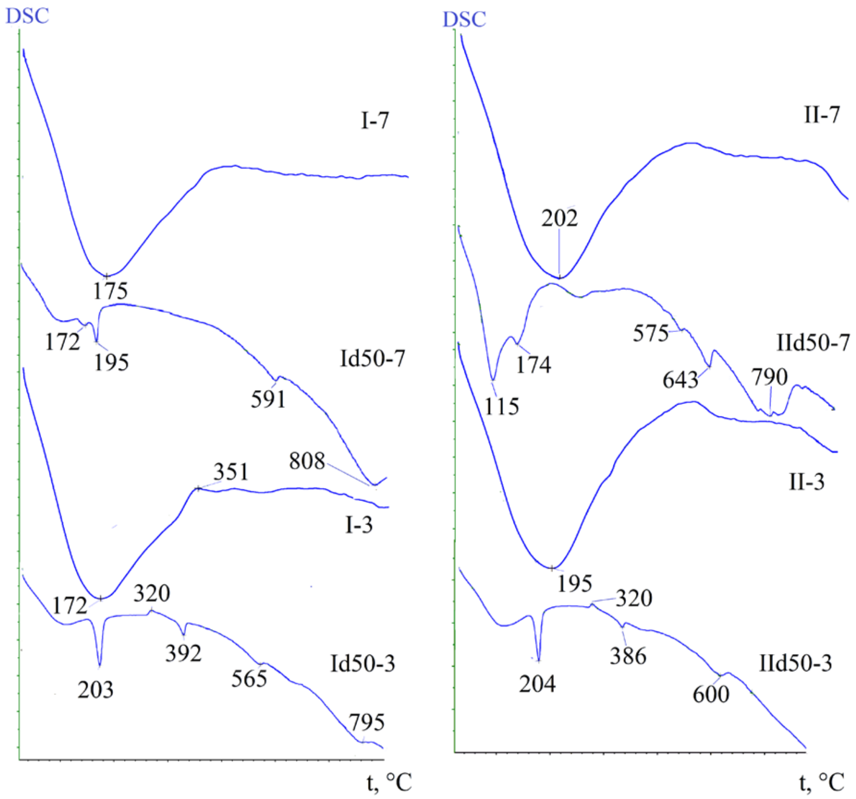

Fig. 4. Differential scanning calorimetry curves of selected samples: I, clinoptilolite-stilbite rock; II, clinoptilolite rock; 50, potassium hydrosulfate (d) content, wt %; 3, 7, duration of mechanical treatment, min

Table 2. Composition of phases, interplanar distances (d) in the region 2θ = 22–26°, relative intensities of diffraction reflections (I/I_0) of clinoptilolite and relative degree of its crystallinity (k_{rel})

Samples	Crystalline phases*	d, Å			I/I_0			k_{rel}, %
I7	St; Cl; M; Q	3.975	3.786	3.427	253	137	171	100
Id33-7	Hs; Cl; G; C	3.974	–	3.320	402	0	268	119
Id50-7	Hs; T; Cl	3.981	3.869	3.426	209	90	49	62
II5	Cl	3.971	3.780	3.419	1000	297	484	100
IId25-5	Cl; Mc; Q	3.979	3.862	3.417	1000	465	427	106
II7	Cl	3.982	–	3.434	1000	0	579	100
IId33-7	Mc; T; Cl	3.962	3.787	3.411	941	202	334	94
IId50-7	Mc; Cl; T	3.972	3.863	3.342	369	169	74	39

Cl: [00-025-1349] $(Na,K,Ca)_6(Si,Al)_{36}O_{72}\times 20H_2O$; [00-019-0211] $CaAl_2Si_7O_{18}\cdot 7.5H_2O$

St: [00-022-0518] $Ca_4Al_9Si_{27}O_{72}\cdot 32H_2O$; M: [00-019-0932] $KAlSi_3O_8$; Q: [01-085-0794] SiO_2; C: [01-082-0512] SiO_2; T: [01-083-1339], [00-016-0152] SiO_2; Mc: [01-072-1247] $KHSO_4$; Hs: [00-052-0406] $K_3H(SO_4)_2$; I, clinoptilolite-stilbite rock; II, clinoptilolite rock; 25, 33, 50, potassium hydrosulphate (d) content, wt %; 5, 7, duration of mechanical treatment, min

195–204 °C with a clear shape were caused by the structural phase transition and disorder in the crystal lattice of $KHSO_4$ [27]. They can be attributed to the process of salt melting in a mechanically activated zeolite matrix. After seven minutes of mechanical treatment, an obvious inclusion of the hydrosulfate anion in the hydrogen bond system was observed, and the indicated endothermic effect in the region of 381–390 °C was no longer recorded. Moreover, endothermic effects were reduced by a factor of 2–3 at 195 °C (Id50-7) and 174 °C (IId50-7) . It should be noted that the endothermic effects were preserved in the temperature range from 560 to 650 °C in all zeolite samples with potassium hydrosulfate additives.

The smooth course of thermogravimetric curves of mechanically activated zeolites is characteristic of the mineral clinoptilolite

[19]. The TG curves of zeolites modified with potassium hydrosulfate, as in the case of modification with potassium hydrophosphate trihydrate [19], had two to three stages of weight loss (Fig. 5). It was found that the residual mass of mechanically activated equimass compositions of clinoptilolites with the addition of acid salt at 850 °C reaches 76–79 % (Table 3). The process of evaporation of sorption water from the studied powders with high determination coefficients ($R^2 \geq 0.94$) can be described by the formal Broido's kinetic equations and diffusion models (Table 3). The apparent activation energy of dehydration in the temperature range of 30–150 °C for samples mechanically activated together with potassium hydrosulfate for 3 and 7 minutes was comparable

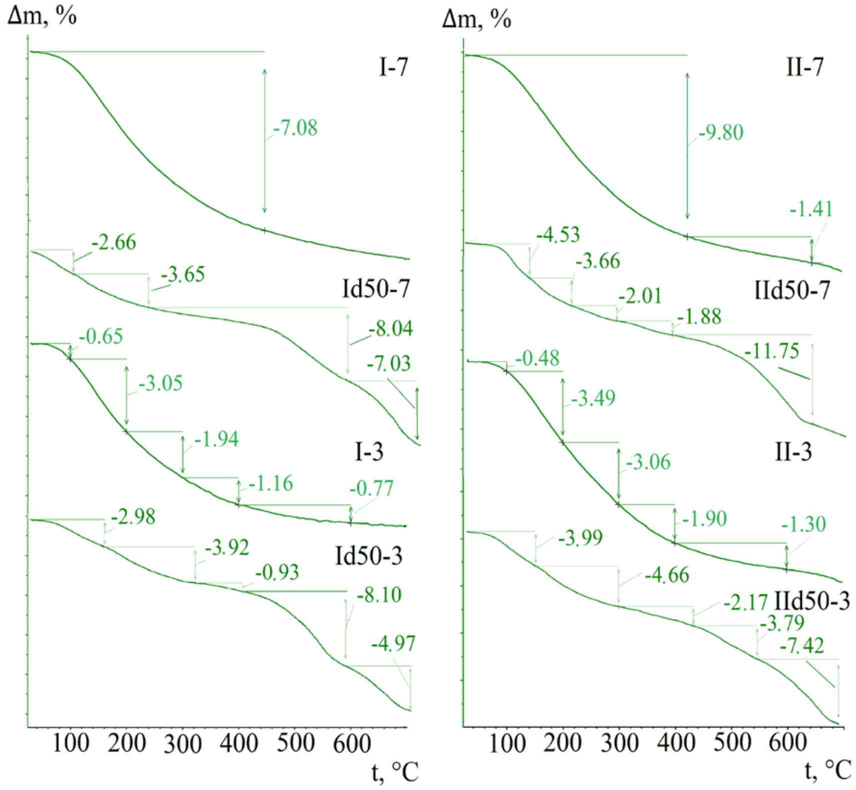

Fig. 5. Thermogravimetric curves of selected samples: I, clinoptilolite-stilbite rock; II, clinoptilolite rock; 50, potassium hydrosulfate (d) content, wt %; 3, 7, duration of mechanical treatment, min

Table 3. Minima of DTG curves, mass loss at 850 °C, apparent activation energy of dehydration in the Arrhenius equation according to selected formal kinetics: models one-dimensional diffusion (D1), Ginstling–Brownstein (D4),

Samples	DTG$_{min}$, °C	Δm_{850}, %	Model D1		Model D4		Broido*	
			R^2	E_a, kJ·mol^{-1}	R^2	E_a, kJ·mol^{-1}	R^2	E_a, kJ·mol^{-1}
Ic50-3	93; 144; 307	9.95*	0.9688	34.19	0.9774	36.58	0.9883	30.74
Id50-3	119; 218	21.04	0.9936	43.20	0.9932	43.59	0.9994	32.17
Ic50-7	110; 142; 309	8.39*	0.9971	49.49	0.9955	51.27	0.9976	37.42
Id50-7	117; 169	21.40	0.9962	51.12	0.9960	51.60	0.9999	36.25
IIc50-3	140; 303	9.31	0.9983	45.48	0.9971	47.05	0.9978	35.10
IId50-3	121; 207	22.03	0.9760	42.20	0.9751	42.71	0.9938	31.84
IIc50-7	140; 293	10.00	0.9998	43.08	0.9994	44.94	0.9983	34.35
IId50-7	115; 174	23.57	0.9908	55.04	0.9902	55.79	0.9980	38.62

* – mass losses are given at 700 °C [19], activation energy of dehydration of samples with potassium hydrophosphate trihydrate (c) was calculated by us earlier [19]; I, clinoptilolite-stilbite rock; II, clinoptilolite rock; 50, potassium hydrosulphate (d) content, wt %; 3, 7, duration of mechanical treatment, min

to similar indicators for zeolites modified with potassium hydrophosphate trihydrate [19]. In addition, the E_A values were approximately 50 % and 10-17 % lower compared to the same indicators for control samples (I3, I7, II3, II7).

3.4. Analysis of the structure

The IR spectra of the studied samples (Fig. 6) had characteristic absorption bands associated with vibrations of the Si-O-Si, Si-O-Al, and O-H bonds, as well as the presence of water molecules in the zeolite channels [22]. Absorption bands with maxima in the regions of 1283–1287 and ~ 850 and 885 cm^{-1} belong to the stretching vibrations of the S-O and S-O-H groups [27, 28], and deformation vibrations of O-S-O and scissor vibrations of S-O-H groups at 577–579 cm^{-1} [27]. An increase in the acid salt content in the compositions of mineral samples was accompanied by an increase in the number of absorption bands in the region of 3050–2450 cm^{-1}, associated with sulfate groups, and an increase in the intensity of absorption bands belonging to OH groups linked by hydrogen bonds. In the IR spectra of samples from clinoptilolite-stilbite rocks containing 25 wt % potassium hydrosulfate, an increase in the dose of mechanical energy was accompanied by a shift in several absorption bands. A shift to the short-wave region of the bands of the stretching vibrations of OH groups and to the long-wave region of the absorption bands of asymmetric stretching vibrations of SO_4 were observed at 1169 cm^{-1} (Id25-x, where x = 3, 5, 7), and the shift of the absorption bands of the Si-O-Si stretching vibrations (IId25-x, where x = 3, 5, 7) to the long-wave region was also revealed.

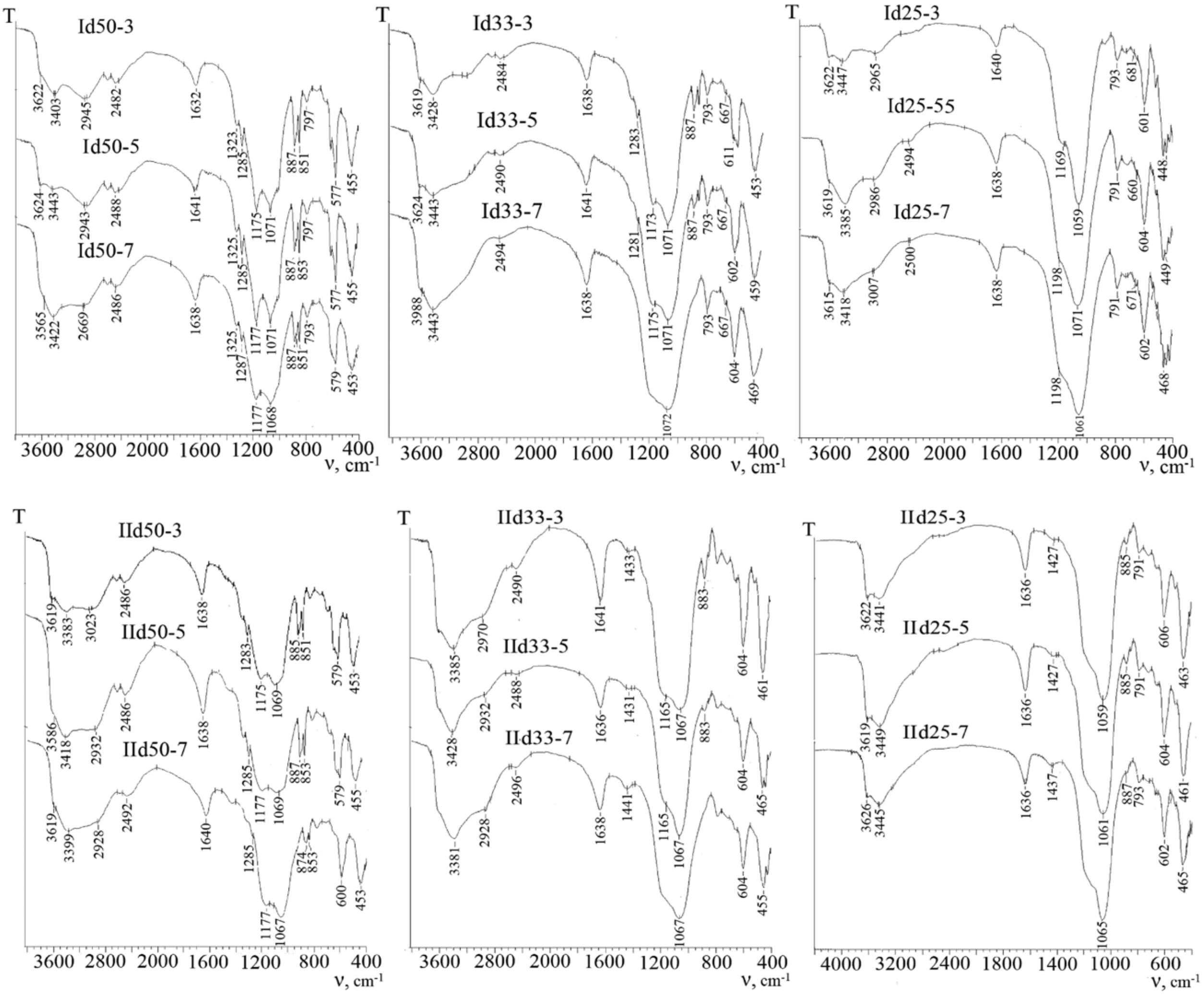

Fig. 6. Infrared spectra of zeolite samples: I, clinoptilolite-stilbite rock; II, clinoptilolite rock; 25, 33, 50, potassium hydrosulfate (d) content, wt %; 3, 5, 7, duration of mechanical treatment, min

In the IR spectra of samples from clinoptilolite rock (II), hydrosulfate absorption bands appeared with a maximum at 885–887 cm^{-1}, and small shifts of absorption bands to the long-wavelength region were observed. An increase in the acid salt content in the zeolite matrix led to significant changes, primarily in the infrared region of OH group vibrations. Hydrogen bonds of the polymer HSO_4^- chain play a significant role in the conductivity process and in the polymorphic behavior of $KHSO_4$ [29]. Doses of mechanical energy of 2.16 and 3.60 kJ/g caused similar structural changes, and already seven minutes of mechanical treatment (D = 5.04 kJ/g) led to more significant shifts of the absorption bands. The highest number of hydrogen-bonded OH groups was found in the IR spectra of powders with an equimass composition of potassium hydrosulfate and zeolite (Id50-x, IId50-x, where x = 3, 5, 7). In these cases, a transformation of the absorption band at 883–887 cm^{-1} into doublets, for example, 887 and 851 cm^{-1} (Id50-3) was observed. Absorption bands belonging to clinoptilolite at 604–601 cm^{-1} gave way to salt absorption bands at 579–577 cm^{-1} (Id50-x, where x =3, 5, 7, IId50-x, where x =3, 5). Considering the proton conductivity of potassium hydrosulfate and the important role of hydrogen bonds in the formation of conductivity channels, improved electrophysical properties can be expected in mineral samples with an equimass composition.

3.5. Study of physical properties

It is known that the presence of water molecules in natural zeolites contributes to an increase in conductivity [30]. When shock-shear mechanical action is applied to air-dry clinoptilolite rocks, local heating, is observed which activates the process of water desorption from the internal pores of zeolites [19]. This explains the decrease in humidity by ~ 9 % for mechanically activated natural zeolites (I3, I7, II3, II7) (Table 4). An increase in the dose of mechanical energy from 2.16 to 3.60 kJ/g causes a change in the crystalline structure of clinoptilolite, in which the constitutional water from the silanol groups, released during their interaction with potassium hydrosulfate, is converted into sorption water. As a result, the moisture content increases (W, %) in all acid salt-modified zeolite samples except Id50-5. With a further increase in the energy dose to 5.04 kJ/g, a decrease in hygroscopic moisture was observed, with the exception of IId50-7. The reduction of the salt concentration from 50 to 25 wt % in modified zeolites increased hygroscopicity, except for IId25-7. This can be explained by the formation of a new system of H-bonding of salt anions and silanol groups with the participation of water molecules, namely: S-O-H...H-O-H...H-O-Si.

Increasing the dose of supplied specific mechanical energy by 2.88 kJ/g contributed to an increase in the bulk density of the samples by ~ 6 % (IId33-7) and 13-14 % (Id50-7, IId50-7, IId25-7). The true density of powders changed or remained practically unchanged (Id25-7, IId50-7, IId25-7), or increased by 5-6 % (Id50-7, Id33-7), or decreased by 12 % (IId33-7). In this case, the porosity of the layer ranged from 40 % (IId25-3) to 64–65 % (IId50-7, Id50-5, Id50-7). Such changes are explained by the dispersion-agglomeration processes, the formation of an amorphous phase, dehydration, and the restructuring of

Table 4. Physical characteristics of modified zeolite samples

Samples	ρ_b, g·cm^{-3}	ρ_{tr}, g·cm^{-3}	ε_{la}, %	W, %	S_{sp}, cm^2·g^{-1}	Samples	ρ_b, g·cm^{-3}	ρ_{tr}, g·cm^{-3}	ε_{la}, %	W, %	S_{sp}, cm^2·g^{-1}
Id50-3	1.16	2.06	44	3.3	4870	IId50-3	1.10	2.18	58	3.4	5410
Id50-5	1.28	2.16	41	3.0	5950	IId50-5	1.19	2.11	60	4.3	3950
Id50-7	1.33	2.17	39	3.0	2630	IId50-7	1.25	2.22	64	4.5	3840
Id33-3	1.15	2.10	45	3.7	4710	IId33-3	0.88	2.37	52	4.8	10140
Id33-5	1.15	1.96	41	4.5	3480	IId33-5	0.98	2.04	50	5.0	6480
Id33-7	1.09	2.23	44	3.7	6200	IId33-7	0.93	2.08	48	5.0	7140
Id25-3	1.05	2.05	49	4.6	6950	IId25-3	0.78	2.14	40	4.7	13300
Id25-5	1.08	2.09	48	5.5	7120	IId25-5	0.81	2.14	42	4.9	13800
Id25-7	1.03	2.09	51	4.2	8500	IId25-7	0.88	2.15	47	4.3	11650

I, clinoptilolite-stilbite rock; II, clinoptilolite rock; 25, 33, 50, potassium hydrosulphate (d) content, wt %; 3, 5, 7, duration of mechanical treatment, min the pore system as a result of mechanochemical activation. The specific surface area of salt-modified clinoptilolite rocks after 7 minutes of mechanical activation decreased by 1.4 times compared to 3 minutes of such exposure (IIdx-3 and IIdx-7, where x = 25, 33, 50, Table 4). The same characteristic of clinoptilolite-stilbite rocks, on the contrary, increased by 1.2–1.3 times (Id25-7, Id33-7), except for the Id50-7 sample, the specific surface of which decreased by 1.9 times in comparison with Id50-3.

The granulometric composition and electrophysical characteristics of individual mechanically strong potassium hydrosulfate-modified and mechanically activated zeolite samples are presented in Table 5. An increase in the time of mechanical activation exposure predictably led to an increase in the mass fraction of particles with sizes of 71, 80 (Id50-5) and 140, 320 μm (IId50-5).

The dependence of the electrical conductivity of tableted samples on temperature in Arrhenius coordinates is shown in Fig. 7. The highest value of electrical conductivity among the studied samples at 25 and 100 °C was revealed for IId50-3 (Table 5). The activation energies of conductivity for mechanically activated clinoptilolite-stilbite rocks without additives and with potassium hydrosulfate were 0.17–0.18 [19] and 0.70–0.75 eV. For similar samples from clinoptilolite rock, the same characteristics were equal to 0.60–0.63 [19] and 0.66–0.91 eV. The determination

Table 5. Granulometric composition, specific conductivity at 25 and 100 °C, activation energies of conductivity, coefficient of determination of dependence ln (σ) = *f* (1/T)

Samples	Content of micrometer particle fractions, wt. %					Electrical conductivity at different temperatures (°C): $\sigma \cdot 10^6$, $S \cdot m^{-1}$		E_{act}, эВ	R^2
	≥ 630	320	140	80	≤ 71	25	100		
Id50-3	0.4	5.0	44.3	47.4	2.9	0.25	74.34	0.74	0.9379
Id50-5	1.9	7.9	29.7	50.4	10.1	0.34	88.84	0.75	0.9785
Id33-3	6.1	5.0	25.5	54.7	8.8	0.45	57.94	0.70	0.9280
IId50-3	0.5	4.9	54.6	35.6	4.3	0.85	426.47	0.73	0.8925
IId50-5	0.4	7.1	70.1	21.1	1.3	0.62	145.66	0.66	0.9063
IId33-3	1.1	4.9	81.0	10.3	2.8	0.08	71.48	0.91	0.9027

E_{act} is activation energy of conductivity in temperature ranges of 25–100 °C; R^2 is the coefficient of determination of the linear dependence $\ln\sigma = f(1/T)$; I, clinoptilolite-stilbite rock; II, clinoptilolite rock; 33, 50, potassium hydrosulphate (d) content, wt %; 3, 5, duration of mechanical treatment, min.

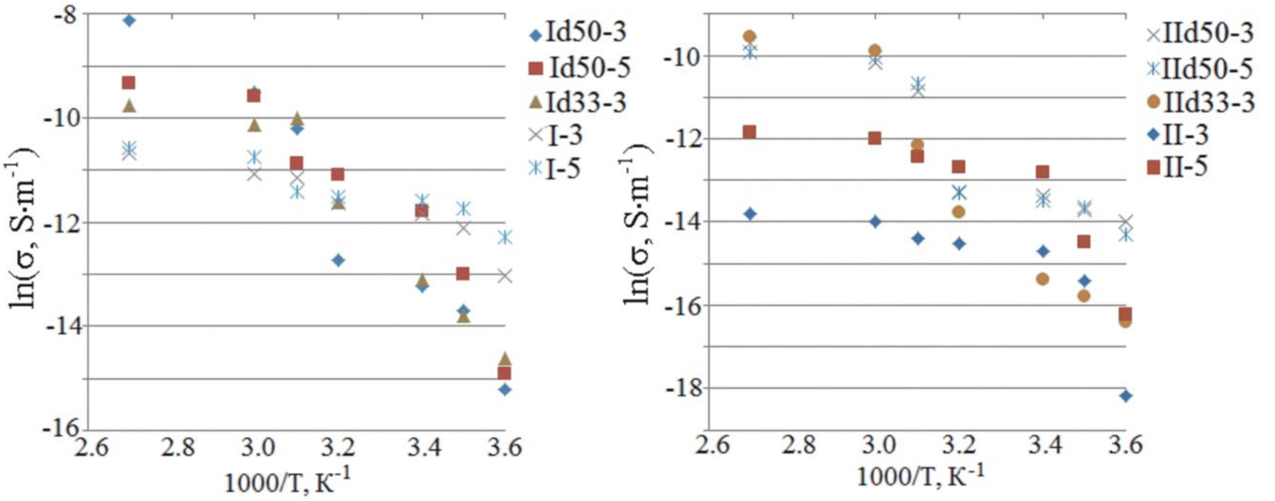

Fig. 7. Dependencies of the logarithm of specific conductivity on the inverse temperature for pressed samples: I, clinoptilolite-stilbite rock; II, clinoptilolite rock; 33, 50, potassium hydrosulfate (d) content, wt %; 3, 5, duration of mechanical treatment, min

coefficients of the linear dependencies $\ln\sigma = f(1/T)$ varied from 0.90 to 0.98. Clinoptilolite rock modified with potassium hydrosulfate in an equimass ratio after mechanical activation with an energy dose of 2.16 kJ/g had the highest specific electrical conductivity $\sigma = 4.26\cdot10^{-4}$ S·m^{-1}. This was comparable to the conductivity for a similar sample modified with potassium hydrogen phosphate trihydrate [19]. However, the activation energy of conductivity in the case of potassium hydrosulfate samples is almost 2 times higher.

4. Conclusions

From an air-dry mixture of clinoptilolite-stilbite (clinoptilolite) rocks and potassium hydrosulfate in ratios of 3:1, 2:1, and 1:1, mineral powders were obtained using a vibratory bowl grinder IVCh-3 with impact-shear action and an energy dose of 2.16, 3.60, and 5.04 kJ/g. Pressed samples at 25 °C had specific electrical conductivity values of about 10^{-6} S·m^{-1}. Short-term mechanical action on clinoptilolite rocks for 3–7 minutes together with salt led to the amorphization of stilbite and microcline, polymorphic transition of quartz into cristobalite and tridymite, as well as different phase states of the salts ($KHSO_4$, $K_3H(SO_4)_2$). The system of silanol groups and proton-containing hydrosulfate anions connected by hydrogen bonds, representing possible conduction channels, was formed with an equimass ratio of components and a dose of mechanical energy of 5.04 kJ/g. At 25 and 100 °C, the electrical conductivity of a sample based on clinoptilolite rock and potassium hydrosulfate of equimass composition with an energy dose of 2.16 kJ/g was $\sim8.5\cdot10^{-7}$ and $4.3\cdot10^{-4}$ S·m^{-1}, respectively. The results obtained earlier indicate that HPO_4^{2-} ions are better integrated into the zeolite structure and transfer charge more efficiently than HSO_4^-. Zeolites with the addition of potassium hydrosulfate, due to the presence of interaction and high hygroscopicity, are less promising for practical use in electrochemical devices compared to zeolites with the addition of potassium hydrogen phosphate trihydrate.

Contribution of the authors

Soloboeva T. P. – research concept, research implementation, writing and editing, and text conclusions. Dabizha O. N. – research concept, methodology development, text editing, conclusions, and scientific supervision. Batukhtin A. G. – research concept, resource provision for the research, participation in the discussion of results, assessment of research prospects.

Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

References

1. Lesiak P. Zeolites as catalysts: a review of the recent developments. *Jntes*. 2023;2: 065–073. https://doi.org/10.53412/jntes-2023-2-4.

2. Luzanova V. D., Rozhmanova N. B., Lanin S. N., Nesterenko P. N. Application of zeolites in high-performance liquid chromatography. *Sorbtsionnye I Khromatograficheskie Protsessy*. 2023;23(4): 691–704. (In Russ.). https://doi.org/10.17308/sorpchrom.2023.23/11576

3. Stocker K., Ellersdorfer M., Lehner M., Raith J. G. Characterization and utilization of natural zeolites in technical applications. *BHM Berg- Und Hüttenmännische Monatshefte*. 2017;162 (4): 142–147. https://doi.org/10.1007/s00501-017-0596-5

4. Grifasi N., Ziantoni B., Fino D., Piumetti M. Fundamental properties and sustainable applications of the natural zeolite clinoptilolite. *Environmental Science and Pollution Research*. 2024; 32:27805–27840. https://doi.org/10.1007/s11356-024-33656-5

5. Barbosa J. C., Gonçalves R., Costa C. M., … Lanceros-Méndez S. Metal-organic frameworks and zeolite materials as active fillers for lithium-ion battery solid polymer electrolytes. *Materials Advances*. 2021;2(12): 3790–3805. https://doi.org/10.1039/d1ma00244a

6. Li M., Chi X., Yu J. Zeolite-based electrolytes: a promising choice for solid-state batteries. *PRX Energy*. 2022;1(3): 1–16. https://doi.org/10.1103/prxenergy.1.031001

7. Shi H., Zhang J., Li J. The effect of guest cations on proton conduction of LTA zeolite. *RSC Advances*. 2021;11(10): 5393–5398. https://doi.org/10.1039/d0ra09917a

8. Kalogeras J. M., Vassilikou-Dova A. Molecular mobility in microporous architectures: conductivity and dielectric relaxation phenomena in natural and synthetic zeolites. *Crystal Research and Technology*. 1996;31(6): 693–726. https://doi.org/10.1002/crat.2170310602

9. Bolotin O. A., Goncharuk V. P., Bologa M. K., Mitina T. F., Polikarpov, A. A., Kostryukova, N. V. Activation of zeolite in a magnetic fluidized bed. *Electronic Processing of Materials*. 2024;60(3): 50–55. (In Russ.) https://doi.org/10.52577/eom.2024.60.3.50

10. Buzimov A. Y., Kulkov S. N., Gömze L. A., Géber R., Kocserha, I. Effect of mechanical treatment on the structure and properties of natural zeolite. *Perspektivnye Materialy*. 2018;9(5): 031–039. https://doi.org/10.30791/1028-978x-2018-4-31-39

11. Dabizha O. N., Soloboeva T. P., Khamova T. V., Shilova O. A. Mechanical activation of clinoptilolites with

sodium and ammonium hydrophosphates to improve their electrophysical properties. *Glass Physics and Chemistry*. 2023;49(3): 293–305. https://doi.org/10.1134/S1087659623600059

12. Astapova E. S., Pavlov S. S., Astapov I. A. Determination of structure characteristics and conductivity of Na-HS-zeolite with Mo, W and Ni nanopowders. *The Bulletin of the Adyghe State University, the series 4: Natural, Mathematical and Technical Sciences*. 2012;2(4): 31–39. (In Russ.) Available at: https://www.elibrary.ru/item.asp?id=18055827

13. Rainer D. N., Morris R. E. New avenues for mechanochemistry in zeolite science. *Dalton Transactions*. 2021;50(26): 8995–9009. https://doi.org/10.1039/d1dt01440d

14. Nikashina V. A., Streletskii A. N., Kolbanev I. V., ... Shumskaya L. G. Effect of mechanical activation on the properties of natural zeolites. *Inorganic Materials*. 2011;47(12): 1341–1346. https://doi.org/10.1134/S0020168511120144

15. Bebiya A. G., Gulyaev P. Y., Milyukova I. V. Change of physical and chemical properties clinoptilolite after mechanical activation. *Yugra State University Bulletin*. 2012;7-8: 7-13. (in Russ.). Available at: https://www.elibrary.ru/item.asp?id=24989138

16. Velichkina L. M., Zaikovskii V. I., Barbashin Ya. E., Ryabova N. V., Perevezentsev S. A., Vosmerikov A. V. Changes in the physicochemical properties of nickel-containing ZSM-5 zeolite under mechanical treatment. *Chemistry for Sustainable Development*. 2020;28 (4): 378–386. (In Russ.). https://doi.org/10.15372/khur2020242

17. Ovsyuk N. N., Goryaĭnov S. V. Amorphous-to-amorphous phase transition in zeolites. *JETP Letters*. 2006;83(3): 138–142. https://doi.org/10.1134/S0021364006030064

18. Buzimov A. Y., Eckl W., Gömze L. A., Kocserha I., Kurovics E., Kulkov A. S., Kulkov S. N. Effect of mechanical treatment on properties of Si-Al-O zeolites. *Epitoanyag - Journal of Silicate Based and Composite Materials*. 2018;70(1): 023–026. https://doi.org/10.14382/epitoanyag-jsbcm.2018.5

19. Dabizha O. N., Soloboeva T. P., Kalinina M. V., Shilova O. A. Structure formation and electrophysical properties of natural zeolites mechanically activated with potassium hydrophosphate to produce solid electrolytes. *Glass Physics and Chemistry*. 2024;50(4): 428–443. https://doi.org/10.1134/S1087659624600996

20. de Izarra A., Coudert F. X., Fuchs A. H., Boutin A. Molecular simulation of the impact of defects on electrolyte intrusion in zeolites. *Langmuir*. 2023;39(51): 19056–19063. https://doi.org/10.1021/acs.langmuir.3c03306

21. Ponomareva V. G., Lavrova G. The investigation of disordered phases in nanocomposite proton electrolytes based on MeHSO4 (Me = Rb, Cs, K). *Solid State Ionics*. 2001;145: 197–204. https://doi.org/10.1016/S0167-2738(01)00957-2

22. Dabizha O. N., Derbeneva T. V., Khamova T. V., Shilova O. A. Controlling the sorption activity of clinoptilolites with mechanical activation. *Inorganic Materials*. 2021;57(4): 399-408. https://doi.org/10.1134/s0020168521040038

23. Soloboeva T. P., Dabizha O. N. Investigation of electrical conductivity of mechanically activated clinoptilolite rocks. In: *Fundamental Bases of Mechanochemical Technologies: VI International conference, 21-24 November 2022, Novosibirsk*. Novosibirsk: ISSCM SB RAS, 2022. p. 46.

24. Rat'ko A. I., Ivanets A. I., Kulak A. I., Morozov, E. A., Sakhar I. O. Thermal decomposition of natural dolomite. *Inorganic Materials*. 2011;47(12): 1372–1377. https://doi.org/10.1134/s0020168511120156

25. Kosenko N. F., Smirnova M. A. Quartz polymorphic transformations stimulated by mechanical treatment. *Refractories and Industrial Ceramics*. 2012;7-8: 7–13. (In Russ.). https://elibrary.ru/item.asp?id=17889319

26. Selezneva E. V., Makarova I. P., Grebenev V. V., ... Choundhury R. R. The changes of thermal, dielectric, and optical properties at insertion of small concentrations of ammonium to $K_3H(SO_4)_2$ crystals. *Crystallography Reports*. 2018;63: 553–562. https://doi.org/10.1134/s1063774518040247

27. Swain D., Bhadram V. S., Pradhan G. K., Bhat S. V., Narayana C., Rao C. B. H. Superionic phase transition in $KHSO_4$: a temperature-dependent raman investigation. *Journal of Physical Chemistry A*. 2010;114(37): 10040-10044. https://doi.org/10.1021/jp103005g

28. Periasamy A., Muruganand S., Palaniswamy M. Vibrational studies of Na_2SO_4, K_2SO_4, $NaHSO_4$ and $KHSO_4$ crystals. *RASĀYAN Journal of Chemistry*. 2009;2 (4): 981–989. Available at: https://rasayanjournal.co.in/vol-2/issue-4/34.pdf

29. Payan F., Haser R. On the hydrogen bonding in potassium hydrogensulphate. Comparison with a previous crystal structure determination. *Acta Crystallographica Section B Structural Crystallography and Crystal Chemistry*. 1976;32(6): 1875–1879. https://doi.org/10.1107/s0567740876006572

30. Cura Ö., Ajjaq A., Çağırtekin A., Cavdar S., Acar S. Low-energy ball milling effect on the dielectric response and electrical transport mechanisms of natural clinoptilolite zeolites in a wide temperature range. *Materials Today Communications*. 2021;29: 102964. https://doi.org/10.1016/j.mtcomm.2021.102964

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