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Original article

# Clinoptilolite zeolite mechanochemically modified with polyethylene glycol for the preparation of oil sorbents

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ABSTRACT The effect of 'soft' mechanochemical activation in an air atmosphere of a mixture of clinoptilolite zeolite rocks with 10 and 20 wt % polyethylene glycol PEG-4000 on structure, physical properties, and oil adsorption properties was investigated. The doses of the applied mechanical energy were 2.16 and 5.04 kJ·g$^{-1}$. It is shown that clinoptilolite rock modified by 10 wt % polyethylene glycol with a mechanical energy dose of 5.04 kJ·g$^{-1}$ and clinoptilolite rock modified by 20 wt % of this polymer with an energy dose of 2.16 kJ·g$^{-1}$ have an oil capacity on the solid surface of 1.4 g·g$^{-1}$. We compared our results with similar data for polymer modifiers such as polyvinyl alcohol and polyacrylamide. We identified regular changes in the structure that can be used as a predictive assessment for the expected increase in the oil capacity of organomineral sorbents. It was found that in the IR spectra of these samples the ratio of intensities of absorption bands due to valence vibrations of siloxane and hydroxyl groups is not less than 3.2, and the porosity is not less than 72 %. The correlation between oil capacity and polymer content, porosity, and structural changes was revealed.

KEYWORDS clinoptilolite zeolite, mechanochemical activation, polymer, polyethylene glycol, oil capacity

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## 1. Introduction

The most common zeolite is clinoptilolite $(Na,K)_6Al_6Si_{30}O_{72} \cdot 20H_2O$, which belongs to the group of Heulandites (HEU) and has high porosity and absorption capacity [1–3]. Its framework of tetrahedral $SiO_4$ and $AlO_4$ units is formed by the intersection of three sets of channels with apertures of 0.31 × 0.76 nm, 0.36 × 0.46 nm, and 0.26 × 0.46 nm [4]. Using a top-down approach and mills, nanozeolites with particle sizes ranging from 50 to 200 nm [5–8] with improved catalytic activity [9, 10] and sorption properties [11, 12] can be obtained. The mechanochemistry of natural zeolites is poorly studied [13–15], however, it is a very promising area of research [16, 17]. To improve the physicochemical properties of clinoptilolite, its surface is modified with surfactants and polymers such as hexadecyltrimethylammonium chloride and n-cetylpyridinium bromide [8], chitosan [18–20], alginate [21], polyacrylamide [22], polydopamine [23], polypropylene [24], polyacrylonitrile [25], polypyrrole [26], polydimethylsiloxane [27], polyvinylpyrrolidone [28], poly-[5-(p-nitrophenylazo)-8-methacryloxyquinoline] [29], poly($\varepsilon$-caprolactone), poly(ethylene glycol), poly($\varepsilon$-caprolactone) [30], poly(ethylene glycol) and poly(vinylpyrrolidone) [31], nanohydroxyapatite, and chitosan and gelatin [32]. Modified polymer-zeolite materials are used for adsorption of heavy metal ions [18,21,22,24,26,29], aromatic hydrocarbons [7,25], methyl tert-butyl ether [2], dyes [18], and as catalytic [9] and photocatalytic [10] materials, as well as composite materials for bone tissue engineering [30, 32]. Zeolite-containing sorbents are characterized by their availability, environmental friendliness, low cost of purchase, and the possibility of recycling, which allows them to be considered for the removal of petroleum compounds [11, 33, 34]. For this, mineral substances are poured onto an (land-based) oil spill, spread onto the surface mechanically, and then collected together with the absorbed substance and transferred for recycling [35]. However, the process of surface modification of clinoptilolite with organic surfactants may not improve its sorption properties [36]. The important factor here is the diffusion of organic liquid into the mesopores. Modification of natural zeolites clinoptilolites by readily available inexpensive polymers solves the problem of increasing the hydrophobicity of the mineral matrix surface, which can contribute to the increase in oil capacity of materials.

The use of mechanical activation of solid substances leads to the formation of nanostructured porous materials. It also leads to the formation of defects in crystal lattices, which affects the number of active centers and adsorption. Modification of clinoptilolite with synthetic polymers, on the one hand, and application of mechanochemical activation, on the other hand, open prospects for obtaining efficient hybrid organomineral sorbents [37, 38]. Obtaining chitosan/zeolite sorbents by two-hour mechanochemical synthesis [39] requires significant energy consumption. Methods of 'soft' mechanical activation using short processing times are of interest. Previously, the authors have used polyvinyl alcohol [38] as well as polyacrylamide [40] as modifying polymers. The mechanochemical air-dry modification of clinoptilolite in the mild impact-abrasion regime with polyvinyl alcohol and polyacrylamide increased [38] and decreased [40] oil capacity, respectively. The use of polyethylene glycols as zeolite modifiers is known [41, 42]. This environmentally safe, biodegradable synthetic polymer has surface-active and sorption properties [43], is able to bind with porous materials by hydrogen bonds [41], so it is of interest to apply it to create oil sorbents.

We found that mechanical activation for 7 minutes increases the oil capacity of clinoptilolite-stilbite rock on solid and water surfaces by 10 and 16 %, respectively. An increase of oil capacity on solid and water surfaces for clinoptilolite rock is achieved by 7 and 10 %, respectively, after mechanical activation for 3 minutes [11]. The aim of the present work was to mechanochemically prepare polymer-zeolite sorbents based on clinoptilolite rocks and high molecular weight polyethylene glycol and evaluate the role of the organic modifier in changing their physical and sorption properties.

## 2. Experimental

### 2.1. Materials

The natural zeolites used in this work are clinoptilolite and clinoptilolite-stilbite rocks of Shivyrtuy and Kholinsky deposits, respectively (Transbaikal Territory, Russia). Their phase and chemical composition were studied earlier [11]. Polyethylene glycol (PEG-4000, NORPEG$^{TM}$, TU 2483-008-71150986-2006, Russia) was chosen as a polymer modifier. The kinematic viscosity of this polymer at 99 °C is 130 mm$^2$·s$^{-1}$, density at 20 °C is 1.2 g·cm$^{-3}$, melting range is 58 – 62 °C, water content does not exceed 1 wt%.

IR spectrum of PEG-4000, $\nu$, cm$^{-1}$: 3460 (O–H); 2880 (C–H); 1470 and 1340 (C–H); 1280 and 1110 (C–O–C); 963 and 842 (C–O–C) [44].

Crude oil (technical, Cherkasy Chemicals Plant) for oil refineries (GOST 9965-76) was used in the study. Oil characteristics, presented as mean ± standard deviation, are as follows: density determined by the pycnometric method is 0.8411 ± 0.0011 g·cm$^{-3}$, the kinematic viscosity determined by a viscometer VPZh-2 is 8.35 ± 0.07 mm$^2$·sec$^{-1}$.

### 2.2. Modification of natural zeolites

The technological scheme for producing organomineral sorbents [38, 40] and the effects observed during mechanical activation of clinoptilolite zeolites with polymers are shown in Fig. 1.

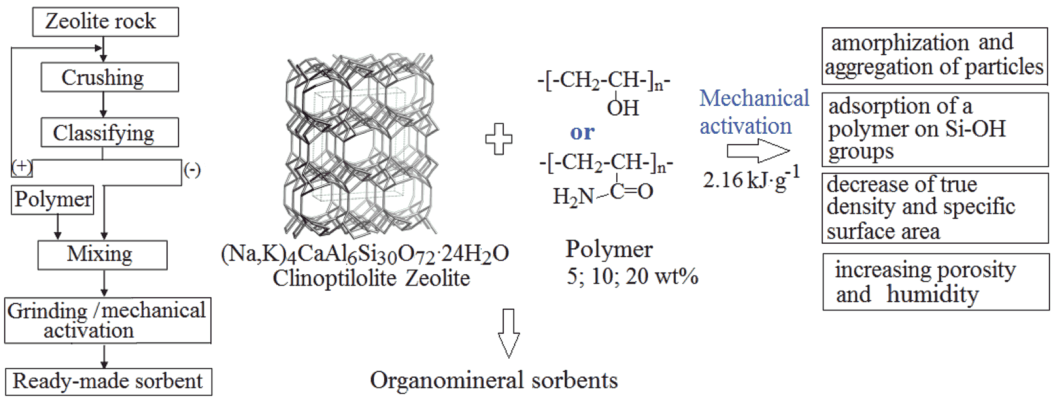


FIG. 1. Technological scheme for producing organomineral sorbents and the effects observed during mechanical activation of mixtures of clinoptilolite zeolites with polymers

Organomineral sorbents were obtained in a vibrating mill Retsch MM 400 (grinding principle is impact and attrition, max. speed 30 Hz; up to 8 mm feed size and 5 $\mu$m final fineness; power 0.9 kW; energy intensity 13 W·g$^{-1}$) by mechanoactivation of air-dry mixture of zeolite rocks: clinoptilolite-stilbite (I) and clinoptilolite (II) with additions of 10 wt % (I10, II10) and 20 wt % (I20, II20) of PEG-4000 for 166 s (superscript $'$) and 388 s (superscript $''$), which corresponds to doses of mechanical energy [11] equal to 2.16 and 5.04 kJ·g$^{-1}$.

### 2.3. Methods of characterization

IR spectra were obtained using a SHIMADZU FTIR-8400S FTIR spectrometer in the region from 4000 to 400 $cm^{-1}$ in potassium bromide tablets. The ratio of intensities ($I_2/I_1$) of absorption bands (a.b.) at 1045 – 1070 and 3430 – 3450 $cm^{-1}$ was calculated by measuring the length of each band to the zero line.

The true density ($\rho_{tr}$, $g{\cdot}cm^{-3}$) was determined by the pycnometric method (working fluid – kerosine KO-25 $d_{20}{}^{\circ}C = 0.795$ $g{\cdot}cm^{-3}$), and the bulk density ($\rho_b$, $g{\cdot}cm^{-3}$) and hygroscopic humidity content ($W$, %) were determined by the gravimetric method.

The porosity of the zeolite and organo-zeolite powder ($P$, %) was calculated using the following equation:

$$P = \left( \frac{\rho_{tr} - \rho_b}{\rho_{tr}} \right) \cdot 100\ \%. \tag{1}$$

The oil capacity of the sorbent on the solid surface was calculated as in [11, 38, 40], taking into account the blank sample after placing the powder in a tea bag, immersion in crude oil (GOST 9965-76), and incubation in it for 15 minutes.

Correlation coefficients ($r_{xy}$) between oil capacity and porosity, oil capacity and ratio of absorption band intensities, oil capacity and polymer content were calculated using MS Excel.

The characteristics of the PEG-modified clinoptilolite-stilbite and clinoptilolite rocks were compared to those of the rocks mechanically activated under the same conditions, but without polymer, as well as with samples modified with other polymers under the same conditions.

## 3. Results and discussion

It was found previously that the supplied dose of mechanical energy affects the structure and oil-sorption properties of clinoptilolite rocks [11]. Thus, the samples exhibit maximum oil capacity after their mechanical treatment for 3 and 7 minutes for clinoptilolite and clinoptilolite-stilbite rocks, respectively (Fig. 2).

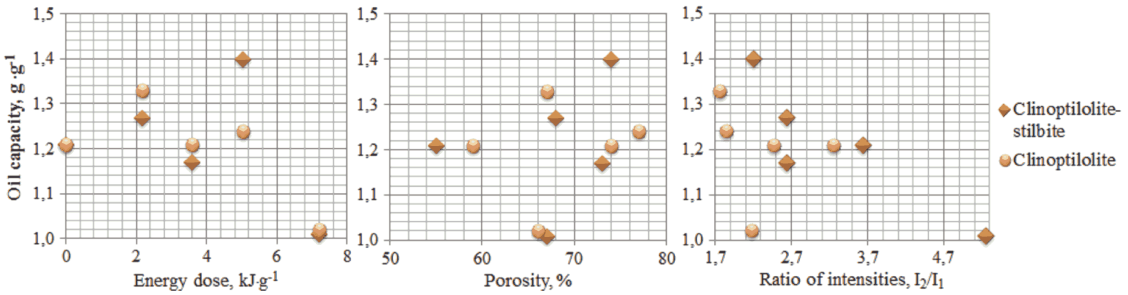


FIG. 2. Dependence of sorption of crude light oil by clinoptilolite zeolites on the dose of mechanical energy, porosity and ratio of intensities of absorption bands at 1045 – 1070 and 3430 – 3450 $cm^{-1}$ (based on materials [11])

These samples have oil capacity values equal to 1.40 and 1.33 g/g and porosity, calculated using formula (1), equal to 74 and 67 %, respectively. In addition, the ratio of the intensities of the absorption bands caused by the stretching vibrations of siloxane bonds and silanol groups is on average $I_2/I_1 \sim 2$. However, the highest correlation coefficients were obtained only for the dependence of oil capacity on the ratio of the intensities of the absorption bands ($r_{xy} = -0.8766$) and porosity ($r_{xy} = -0.6565$) for clinoptilolite-stilbite and clinoptilolite rocks, respectively.

Figures 3 and 4 show IR spectra of samples of zeolite and polymer-zeolite sorbents resulting from the mechanochemical method with energy doses of 2.16 and 5.04 $kJ{\cdot}g^{-1}$, respectively.

The samples of mechanically activated clinoptilolite-stilbite (samples I′, I″) and clinoptilolite rocks (samples II′, II″) are characterized by typical absorption bands in the infrared region of the spectrum [11]. The absorption bands with the highest intensities with maxima in the region from 1045 to 1069 $cm^{-1}$ belong to the valence vibrations of Si–O–Si groups, and the absorption bands in the frequency region from 3599 to 3622 $cm^{-1}$ belong to the valence vibrations of OH-groups of intra-complex water [11, 45].

The presence of polyethylene glycol in the modified organomineral samples is confirmed by the presence of absorption bands with maxima at 2882, 1451 (1462), 1343 (1346), 833 (845, 849) $cm^{-1}$, which are due to valence and scissor vibrations of $CH_2$ groups, vibrations of C–O–C groups, respectively [44]. The low-frequency shift and disappearance of the absorption bands of hydroxyl groups with maxima in the region of 3580 – 3630 $cm^{-1}$ in the IR spectra of samples I10′ and I20′ (Fig. 3), I10″ and I20″ (Fig. 4), respectively, indicate the interaction between silanol groups of clinoptilolite and hydroxyl groups of polyethylene glycol.

Shifts of absorption bands of valence vibrations of hydroxyl groups are observed both in the long-wave region (samples II10′, II20″) and in the short-wave region (samples I10′, II20′, II10″) and indicate the rearrangement of the hydrogen

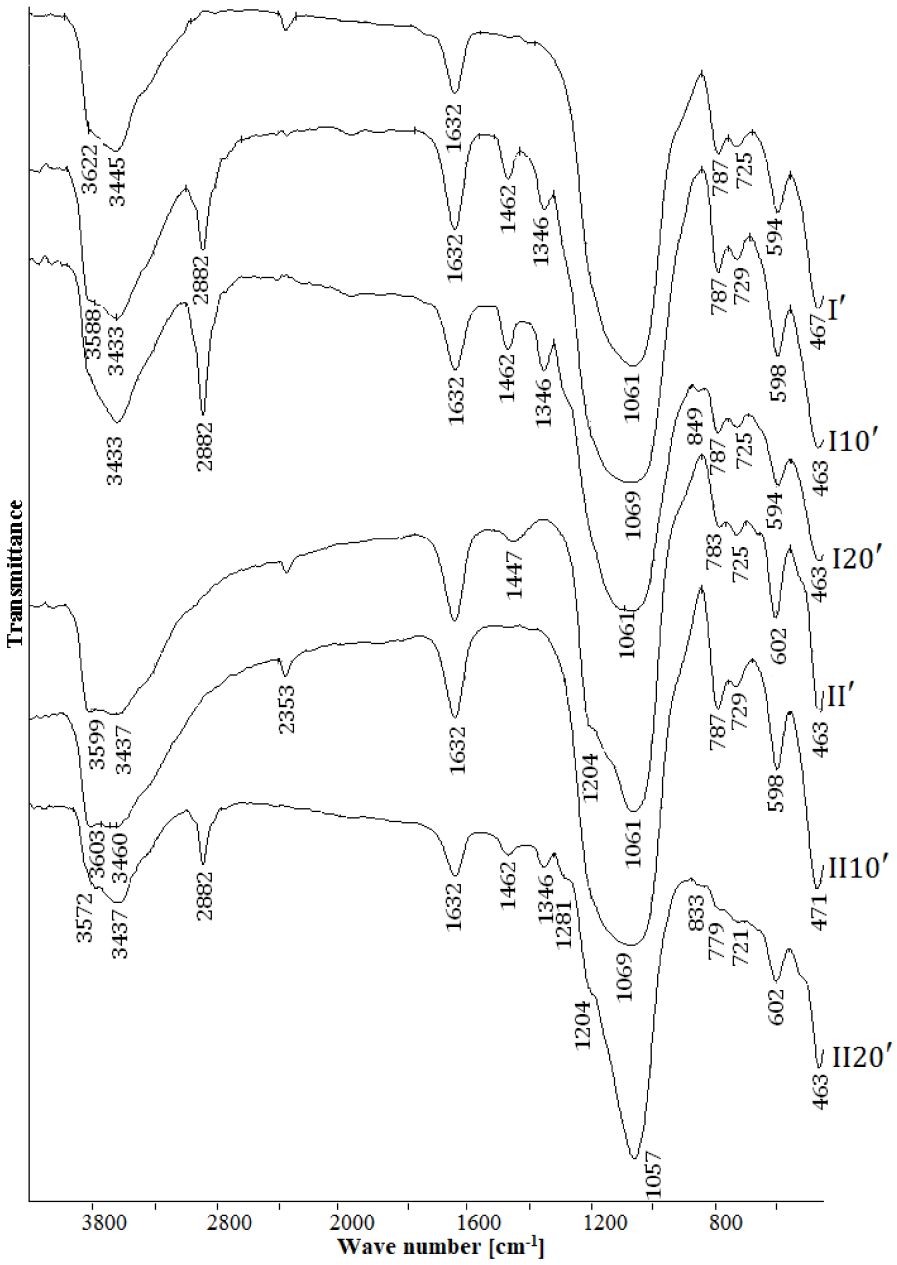


FIG. 3. IR spectra of the samples of the zeolite rocks mechanically activated with and without PEG as a modifier: I – clinoptilolite–stilbite rock, II – clinoptilolite rock; the subscripts 10 and 20 specify the weight percent of PEG in the samples; superscript ′ indicates the dose of induced mechanical energy 2.16 kJ·g$^{-1}$

bonding system due to modification of the mineral framework by polyethylene glycol. There are shifts of absorption bands corresponding to valence vibrations of siloxane bonds in the region of high frequencies (samples I10′, II10′), as well as in the region of low frequencies (sample II20′). A narrowing and an increase in the intensities of the absorption bands belonging to the valence vibrations of siloxane bonds and, at the same time, a decrease in the intensity of the absorption band corresponding to the valence vibrations of hydroxyl groups were observed (samples II20′, II10″). This pattern was also observed in the IR spectra of clinoptilolite rocks modified with 20 wt % of polyvinyl alcohol [38] with improved oil capacity.

The application of a higher dose of mechanical energy ($D = 5.04$ kJ·g$^{-1}$) is reflected in the IR spectrum of clinoptilolite-stilbite sorbent by a low-frequency shift of the absorption band maximum due to the valence vibrations of OH-groups at 3622 (sample I′, Fig. 3) to 19 cm$^{-1}$ (sample I″, Fig. 4). In addition, there are high-frequency shifts of absorption bands due to valence vibrations of Si–O–Si, deformation vibrations of $SiO_4$, vibrations of twin rings between

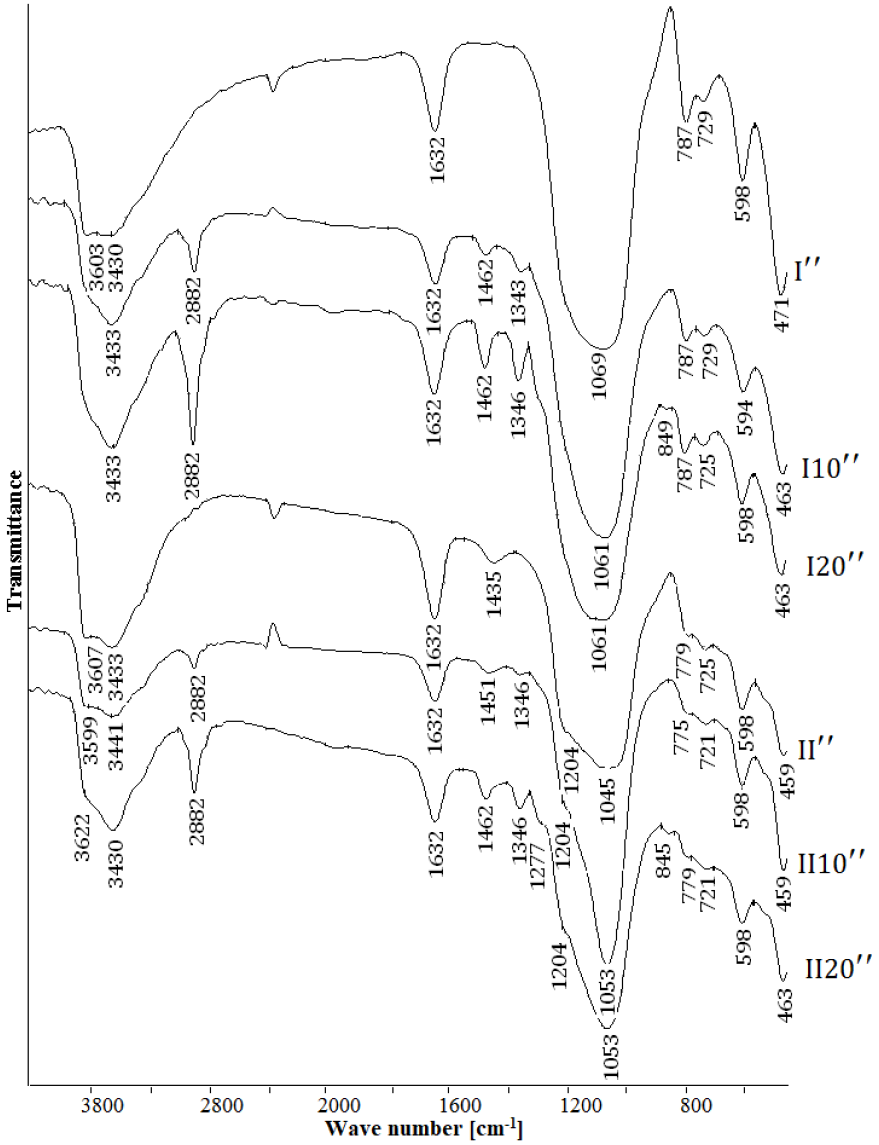


FIG. 4. IR spectra of the samples of the zeolite rocks mechanically activated with and without PEG as a modifier: I – clinoptilolite–stilbite rock, II – clinoptilolite rock; the subscripts 10 and 20 specify the weight percent of PEG in the samples; superscript ″ indicates the dose of induced mechanical energy 5.04 kJ·g$^{-1}$

(Si, Al)–O–Si tetrahedra, and deformation vibrations of Si–O–Si with maxima at 1061 and 725, 594, 467 cm$^{-1}$, respectively (sample I′, Fig. 3) by 8 and 4, 4, 4, 4 cm$^{-1}$ (sample I″, Fig. 4). Structural changes in clinoptilolite rock under the action of the same dose of mechanical energy are manifested by a high-frequency shift of the absorption band with maximum at 3599 cm$^{-1}$ (sample II′, Fig. 3) by 8 cm$^{-1}$ (sample II″, Fig. 4) and low-frequency shifts of absorption bands with maxima at 1061 and 783, 602, 463 cm$^{-1}$ (sample II′, Fig. 3) by 16 and 4, 4, 4, 4 cm$^{-1}$, respectively (sample II″, Fig. 4).

In the IR spectra of the modified organomineral samples, the increase in the dose of the applied mechanical energy is reflected by the following changes:

— disappearance of the absorption band of valence vibrations of free OH-groups, low-frequency shifts at 3, 8 and 4 cm$^{-1}$ of the absorption bands of $CH_2$, Si–O–Si and (Si, Al)–O–Si groups, respectively (sample I10″, Fig. 4);
— high-frequency shift by 4 cm$^{-1}$ of the absorption band belonging to vibrations of the twin rings between (Si, Al)–O–Si tetrahedra (sample I20″, Fig. 4);
— low-frequency shifts at 4 and 19 cm$^{-1}$ of the absorption bands of valence vibrations of free and OH-groups bound to water molecules, low-frequency shifts at 16, 12, 4 and 12 cm$^{-1}$ of the absorption bands of valence vibrations of Si–O–Si, Si–O groups, deformation vibrations of $SiO_4$ and Si–O–Si groups, respectively (sample II10″, Fig. 4);

— high-frequency shift by 50 $cm^{-1}$ of the absorption band of valence vibrations of free OH-groups; low-frequency shift by 7 $cm^{-1}$ of the absorption band of valence vibrations of OH-groups bound to water molecules, low-frequency shift by 4 $cm^{-1}$ of the absorption band of valence vibrations of C–O–C; valence vibrations of Si–O–Si, vibrations of twin rings between (Si, Al)–O–Si tetrahedra, and a high-frequency shift of the absorption band of deformation vibrations of C–O–C bonds (sample II20″, Fig. 4).

The least structural changes affected sample I20″; therefore, no change in its physical and sorption properties should be expected. The most significant changes with increasing dose of mechanical energy are observed in the IR spectrum of sample II10″ and therefore it may show improved sorption properties.

Hygroscopic humidity, bulk and true densities, porosity, oil sorption capacity of the investigated zeolite and polymer-zeolite samples are given in Table 1.

The increase in moisture content of the samples with the increase in the content of polymer in the compositions of the samples is explained by the high content of hydroxyl groups. Maximum values of moisture content $\sim$ 3.5 wt % are observed in modified samples I20′ and II20′ (Table 1). The bulk density of polymer-zeolite sorbents is non-monotonically dependent on the PEG content. It increases by 2 to 4 % (samples I10″, I10′, II10′, II20′) and 17 % (sample II10″), and decreases by 3 % (sample II20″) and 9 to 12 % (samples I20″, I20′) compared to the values of the same characteristic of mechanically activated zeolites (samples I′, I″, II′, II″).

The bulk density of clinoptilolite-stilbite (sample I′) and clinoptilolite rocks (sample II′) decreases with increasing dosage of applied mechanical energy by 4 % (sample I″) and 6 % (sample II″). The true density of mechanically activated zeolite samples I″ and II″ increases by 7 and 3 % with increasing the mechanical energy dose by 2.88 $kJ \cdot g^{-1}$, which is explained by obtaining more compact pelletised particles and is in agreement with the data of [11]. The true density of PEG-zeolite sorbents decreases by 8 % (sample II20″), 14 % (samples I20′, II20′), 21 % (sample I20″) with the addition of 20 wt % polymer modifier, also observed in case of modification with polyvinyl alcohol [38], as well as polyacrylamide [40]. The oil capacity of PEG/clinoptilolite-stilbite sorbents with the addition of 20 wt % polyethylene glycol increases by 14 and 6 % in samples resulting from the application of energy doses of 2.16 and 5.04 $kJ \cdot g^{-1}$, respectively. The oil capacity of PEG/clinoptilolite sorbents also increases by 10 % with application of energy dose 2.16 $kJ \cdot g^{-1}$ and does not increase with application of energy dose 5.04 $kJ \cdot g^{-1}$ (Table 1). The maximum value of oil capacity resulting from the modification of clinoptilolite rock with polyethylene glycol is 1.4 $g \cdot g^{-1}$.

TABLE 1. Physical and sorption properties of zeolite and PEG/zeolite samples

| Samples | Content, wt% | | Time, $t$, s | Energy dose, $D$, $kJ \cdot g^{-1}$ | Humidity, W, % | Density, $\rho$, $g \cdot cm^{-3}$ | | Oil capacity, SC, $g \cdot g^{-1}$ |
|---|---|---|---|---|---|---|---|---|
| | Zeolite | PEG | | | | Bulk | True | |
| Clinoptilolite – stilbite rock | | | | | | | | |
| I | 100 | 0 | 0 | 0 | 5.5 | 0.950 | 2.090 | 1.23 |
| I′ | 100 | 0 | 166 | 2.16 | 2.6 | 0.635 | 2.258 | 1.12 |
| I10′ | 90 | 10 | 166 | 2.16 | 2.6 | 0.651 | 2.141 | 1.19 |
| I20′ | 80 | 20 | 166 | 2.16 | 3.5 | 0.558 | 1.932 | 1.28 |
| I″ | 100 | 0 | 388 | 5.04 | 1.1 | 0.613 | 2.418 | 1.20 |
| I10″ | 90 | 0 | 388 | 5.04 | 2.3 | 0.624 | 2.391 | 1.23 |
| I20″ | 80 | 20 | 388 | 5.04 | 2.4 | 0.557 | 1.903 | 1.27 |
| Clinoptilolite rock | | | | | | | | |
| II | 100 | 0 | 0 | 0 | 6.4 | 0.869 | 2.136 | 1.23 |
| II′ | 100 | 0 | 166 | 2.16 | 1.3 | 0.518 | 2.218 | 1.27 |
| II10′ | 90 | 10 | 166 | 2.16 | 2.7 | 0.538 | 2.309 | 1.37 |
| II20′ | 80 | 20 | 166 | 2.16 | 3.5 | 0.534 | 1.898 | 1.40 |
| II″ | 100 | 0 | 388 | 5.04 | 2.0 | 0.489 | 2.275 | 1.38 |
| II10″ | 90 | 0 | 388 | 5.04 | 3.0 | 0.571 | 2.142 | 1.40 |
| II20″ | 80 | 20 | 388 | 5.04 | 3.3 | 0.474 | 2.095 | 1.38 |

It was previously studied [11, 38] that the absorption bands corresponding to the valence vibrations of the siloxane bond are the most sensitive to mechanical effects. To evaluate the influence of the modifier (PEG) on the structural changes in the organomineral sorbent, the ratio of the intensities of the two most intense and susceptible to changes absorption bands due to the valence vibrations of siloxane and hydroxyl groups was calculated from the IR spectra. In addition, the porosity was calculated using formula (1). This is significant because of the existing relationship 'solid structure – sorption properties'. The final results of the calculations are summarized in Table 2.

Due to mechanical activation with an energy dose of 2.16 kJ·g$^{-1}$, the porosity of zeolite sorbents increases by ∼31 % for clinoptilolite-stilbite and clinoptilolite rocks (samples I′ and I; II′ and II). After applying a mechanical energy dose of 5.04 kJ·g$^{-1}$, this textural parameter increases by 36 and 34 % for the above rocks (samples I″ and I; II″ and II). A slight decrease (from 1 to 5 % compared to control samples) in the porosity of sorbents after their joint mechanical activation with polyethylene glycol is associated with partial blocking of pores by the polymer. The Si–OH bands of organomineral samples appear red- and blue-shifted to the same bands of mechanoactivated clinoptilolite zeolites (Table 2). The same characteristics calculated for PVA/zeolite [38] and PAA/zeolite [40] sorbents are included in the same table for comparative analysis. For modifiers containing functional groups in the compound repeating link, polyvinyl alcohol and polyacrylamide, with increasing polymer content, an increase in the relative intensity of the absorption band, as well as an increase in the porosity are observed. The maximum values of these parameters ($I_2/I_1 = 5.5$, $P = 78$ %) are observed in a sample of clinoptilolitic rock modified with 20 wt % PVA by mechanochemical method (Table 2), and the maximum value of oil capacity equal to 1.55 g·g$^{-1}$ was registered in it [38]. The inverse regularity takes place for clinoptilolite-stilbite rock at its modification with polyethylene glycol. In this case, equal values of the ratio of the intensities of absorption bands and porosity (samples I20′; I20″, Table 2), as well as oil capacities (samples I20′; I20″, Table 1) were observed. This agrees with the conclusions described above based on the analysis of IR spectra of these samples.

TABLE 2. Relative intensity of a single absorption band in the IR spectra of polymer-modified zeolite samples and the porosity of the powder

| Samples | Content, wt% | | Time, $t$, s | Energy dose, $D$, kJ·g$^{-1}$ | Ratio of intensities $I_2/I_1$ | Shift a.b. $\Delta\nu_{\text{Si-OH}}$, cm$^{-1}$ | Porosity, $P$, % |
|---|---|---|---|---|---|---|---|
| | Zeolite | Polymer | | | | | |
| The modifier is polyethylene glycol | | | | | | | |
| I′ / I″ | Cl, St | — | 166 / 388 | 2.16 / 5.04 | 2.15 / 2.73 | 0 / 0 | 72 / *75* |
| I10′ / I10″ | Cl, St | 10 | 166 / 388 | 2.16 / 5.04 | 2.11 / 2.40 | −34 / — | 70 / *75* |
| I20′ / I20″ | Cl, St | 20 | 166 / 388 | 2.16 / 5.04 | 1.73 / 1.73 | — / — | 71 / 71 |
| II′ / II″ | Cl | — | 166 / 388 | 2.16 / 5.04 | 2.65 / 1.36 | 0 / 0 | *77* / *79* |
| II10′ / II10″ | Cl | 10 | 166 / 388 | 2.16 / 5.04 | 2.74 / *3.79* | +4 / *−8* | *77* / *73* |
| II20′ / II20″ | Cl | 20 | 166 / 388 | 2.16 / 5.04 | *3.18* / 1.86 | *−27* / *+15* | *72* / *77* |
| The modifier is polyvinyl alcohol [38] / polyacrylamide [40] | | | | | | | |
| I′ | Cl, St | — | 180 | 2.16 | 2.50 / 2.60 | 0 / 0 | 68 |
| I10′ | Cl, St | 10 | 180 | 2.16 | *3.33* / 2.78 | −3 / −13 | *72* / 66 |
| I20′ | Cl, St | 20 | 180 | 2.16 | *3.33* / *3.57* | −3 / *−7* | *78* / 69 |
| II′ | Cl | — | 180 | 2.16 | *1.78* / *1.72* | 0 / 0 | 67 |
| II10′ | Cl | 10 | 180 | 2.16 | *3.67* / 3.18 | *+5* / −2 | *73* / 69 |
| II20′ | Cl | 20 | 180 | 2.16 | *5.50* / 2.40 | *+9* / −6 | *78* / 71 |

Note. Cl – Clinoptilolite; St – Stilbite; $I_2/I_1$ – ratio of intensities of absorption bands with maxima at ∼ 1050 and ∼ 3620 cm$^{-1}$, corresponding to valence vibrations of Si–O–Si and OH-groups;

' — ' – there is no absorption band.

Modification of clinoptilolite-stilbite and clinoptilolite rocks by polyacrylamide and polyethylene glycol resulted in changes of porosity of samples by values from 2 to 5 %, and only addition of polyvinyl alcohol contributed to an increase of porosity by 9 % (I20) and 11 % (II20). It was calculated that the same high values of porosity ∼ 77 – 79 % are observed in samples of clinoptilolite rock mechanoactivated and modified with polyethylene glycol – II′; II10′, II20″, II″.

The relatively highest value of oil capacity $\sim 1.4$ g·g$^{-1}$ is registered. The revealed regularities agree with the opinion [36] that the sorption capacity towards oil is determined by the diffusion of organic liquid through mesopores.

Porosity, in turn, is conveniently regulated by the mechanochemical method. It should be noted that the increase in porosity is accompanied by an increase in the ratio of intensities of absorption bands in the case of modification of clinoptilolite-stilbite and clinoptilolite rocks with polyvinyl alcohol and polyacrylamide (Table 2), and clinoptilolite rock with polyethylene glycol. However, such enhancement alone is not sufficient if, together with it, there is not a sufficient increase in the porosity of the organomineral sample. Consequently, in order for oil capacity to be approximately 1.4 g·g$^{-1}$ at modification of clinoptilolitic rocks with water-soluble polymers (polyvinyl alcohol, polyacrylamide, polyethylene glycol), it is necessary that the ratio of absorption bands of Si–O–Si and OH-groups in the IR-spectrum was not less than 3.2 and, at the same time, the porosity was not less than 72 %.

In order to find out the influence of such factors as polymer content, structural changes, and porosity, the correlation analysis was carried out. The correlation coefficients were calculated and summarized in Table 3.

Analysis of the data in Table 3 showed that there is very strong dependence of oil capacity of mineral samples modified with polyvinyl alcohol on all three parameters ($r_{xy} > 0.91$), namely, polymer content, structural changes (ratio of intensities of absorption bands $I_2/I_1$) and porosity.

TABLE 3. Correlation coefficients between oil capacity and polymer content, ratio of absorption band intensities, porosity of sorbent powders resulting from the mechanochemical method

| Polymers | Energy dose, $D$, kJ·g$^{-1}$ | Clinoptilolite-stilbite rock | | | Clinoptilolite rock | | |
|---|---|---|---|---|---|---|---|
| | | $r_{xy}$, where $y$ is a oil capacity and $x$ is ... | | | | | |
| | | weight of polymer | $I_2/I_1$ | Porosity ($P$) | weight of polymer | $I_2/I_1$ | Porosity ($P$) |
| PVA | 2.16 | 0.9959 | 0.9078 | 0.9880 | 0.9954 | 0.9957 | 0.9991 |
| PAA | 2.16 | 0.0368 | 0.3757 | 0.9789 | 0.0908 | −0.8392 | 0.0908 |
| PEG | 2.16 | 0.9974 | −0.9341 | −0.4364 | 0.9549 | 0.9605 | −0.6717 |
| PEG | 5.04 | −0.9803 | −0.9938 | −0.9632 | 0 | 0.9808 | −0.9449 |

When using polyacrylamide as a modifier, a very strong dependence of oil capacity on porosity is observed for clinoptilolite-stilbite rock, and a fairly strong inversely proportional dependence on structural changes (the ratio of absorption band intensities) for clinoptilolite rock. At modification with polyethylene glycol and the mechanical energy dose of 2.16 kJ·g$^{-1}$ for clinoptilolite-stilbite rock, there is a very strong direct dependence of oil capacity on the content of polyethylene glycol and its inverse dependence on structural changes and porosity. In this case, for clinoptilolite rock, there is a very strong direct dependence of oil capacity on the content of polyethylene glycol and on structural changes. In case of use of this modifier, an increase in mechanical energy dose from 2.16 to 5.04 kJ·g$^{-1}$, as a rule, contributes to approximation of correlation coefficients to the value $-1$ or $+1$. The exception is clinoptilolitic rock, the oil capacity of which does not depend on polymer content at all and is approximately 1.4 g·g$^{-1}$.

## 4. Conclusion

Organomineral sorbents based on clinoptilolite-stilbite and clinoptilolite rocks and safe synthetic polymer PEG-4000 were obtained by the method of 'soft' mechanoactivation in impact-attrition mode in an air atmosphere with processing times of 166 and 388 s, which corresponds to mechanical energy doses of 2.16 and 5.04 kJ·g$^{-1}$. The content of polyethylene glycol was 10 and 20 wt %.

It was found that mechanoactivation ($D = 2.16$ and 5.04 kJ·g$^{-1}$) of the powder leads to changes in bulk and true densities, hygroscopic moisture content of zeolite and PEG-zeolite sorbents. Infrared spectroscopy revealed that a more effective transformation of the structure, in the form of a decrease in the intensity and shift of the absorption band of free OH-groups and an increase in the intensity and shift of the absorption band of Si–O–Si groups, leads to a sorbent with improved sorption properties. Modification of clinoptilolitic rocks with polyethylene glycol leads to a decrease in bulk and true densities, an increase in hygroscopic humidity, and, as a rule, an increase in oil capacity. The oil capacity of clinoptilolite rock modified with 20 wt % PEG is $\sim 1.4$ g·g$^{-1}$, which is 8 – 15 % higher than that of analogues based on clinoptilolite-stilbite rock.

Comparative analysis of the data of mechanochemical modification of clinoptilolitic rocks with polyvinyl alcohol, polyacrylamide, and polyethylene glycol showed that organomineral samples having oil capacity not less than 1.4 g·g$^{-1}$ exhibit, in infrared spectra, a ratio of intensity of absorption bands caused by vibrations of siloxane and hydroxyl groups not less than 3.2, and a porosity not less than 72 %. Calculation of correlation coefficients confirmed that the determining factors affecting the oil capacity of organomineral sorbents are the content of polyvinyl alcohol, structural changes, and

porosity. However, the oil capacity of clinoptilolite-stilbite rocks modified with polyacrylamide is strongly dependent only on the porosity. In this case, the required value of porosity for oil capacity increase is not achieved under mild mechanical action.

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