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СИНТЕЗ ГРАНУЛИРОВАННЫХ НИЗКОМОДУЛЬНЫХ ЦЕОЛИТОВ ИЗ МЕТАКАОЛИНА С ИСПОЛЬЗОВАНИЕМ УЛЬТРАЗВУКОВОЙ ОБРАБОТКИ

Исследованы процессы синтеза низкомодульных гранулированных цеолитов из смесей $6Al_2Si_2O_7$:12NaOH и $6Al_2Si_2O_7$:12NaOH:$12SiO_2$ с использованием ультразвуковой обработки водных суспензий. Для контроля процессов синтеза использовали рентгенофазовый анализ, сканирующую электронную микроскопию и инфракрасную спектроскопию. Показано, что после термической обработки смеси $6Al_2Si_2O_7$:12NaOH при 650 °C синтезируются СОД цеолит ($|Na_6|[Al_6Si_6O_{24}]$) и алюмосиликат натрия($Na_8Al_4Si_4O_{18}$). Прокалка смеси $6Al_2Si_2O_7$:12NaOH:$12SiO_2$ не приводит к образованию новых кристаллических фаз. После гидротермальной кристаллизации смеси $6Al_2Si_2O_7$:12NaOH в 2М растворе NaOH синтезируется ЛТА цеолит ($|Na_{12}|[Al_{12}Si_{12}O_{48}]$). Было установлено, что $Na_8Al_4Si_4O_{18}$ является прекурсором ЛТА цеолита. Гидротермальная кристаллизация смеси с избытком SiO_2 в 2М растворе NaOH приводит к образованию ПХИ цеолита $|Na_6|[Al_6Si_{10}O_{32}$. Было показано, что после кристаллизации обеих смесей в 6М растворе NaOH только СОД цеолит образуется как конечный продукт.

Ключевые слова: синтез, СОД цеолит, ЛТА цеолит, ПХИ цеолит

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SYNTHESIS OF GRANULATED LOW-MODULUS ZEOLITES FROM METAKAOLIN USING ULTRASONIC TREATMENT

The synthesis processes of the low-modulus granulated zeolites from mixtures of $6Al_2Si_2O_7$:12NaOH and $6Al_2Si_2O_7$:12NaOH:12SiO_2 were studied using ultrasonic treatment of the aqueous suspensions. To control the synthesis processes, X-ray diffraction, scanning electron microscopy and infrared spectroscopy were used. It was shown that after thermal treatment of the mixture of $6Al_2Si_2O_7$:12NaOH at 650 °C, SOD zeolite ($|Na_6|[Al_6Si_6O_{24}]$) and sodium aluminosilicate ($Na_8Al_4Si_4O_{18}$) are synthesized. The calcination of the mixture of $6Al_2Si_2O_7$:12NaOH: 12SiO_2 does not result in a formation of new crystalline phases. After the hydrothermal crystallization of the mixture of $6Al_2Si_2O_7$:12NaOH in 2M NaOH solution LTA zeolite ($|Na_{12}|[Al_{12}Si_{12}O_{48}]$) is synthesized. It was established that $Na_8Al_4Si_4O_{18}$ is a precursor of LTA zeolite. Hydrothermal crystallization of the mixture with SiO_2 excess in 2M NaOH solution results in a formation of zeolite PHI ($|Na_6|[Al_6Si_{10}O_{32}]$). It has been shown that after crystallization of the both mixtures in 6M NaOH solution, only SOD zeolite is the final product of the synthesis.

Key words: synthesis, SOD zeolite, LTA zeolite, PHI zeolite

INTRODUCTION

Zeolites are the porous framework aluminosilicates which have the regular cavities [1]. As the starting material for the synthesis of zeolites, sols and gels of Si and Al compounds as well as kaolin are used [1-3]. The sol-gel synthesis allows obtaining the crystals of zeolites with a high degree of crystallinity, but only in the form of powders. For industrial applications, it is necessary to have pellets. For this reason, a metakaolin is widely used in industry as a starting material [3, 4]. The disadvantage of these methods is the multistage hydrothermal crystallization.

To intensify the heterogeneous processes, the ultrasonic treatment may be used [5, 6]. In the review [7], it was shown that ultrasound allows reducing the hydrothermal crystallization time of the zeolites. In Ref. [8], we established that a preliminary ultrasound treatment of the suspension of metakaolin and aluminum oxide allows synthesizing the granulated LTA zeolites. In this case, the hydrothermal crystallization is carried out in one step. The zeolite type will be determined by the concentration of NaOH solution.

The zeolite type is also determined by the composition of the starting ingredients. In Refs. [8-10] for the synthesis of the LTA zeolite, the Al_2O_3 excess over the stoichiometry has been used. The purpose of this work is a study the synthesis of granulated low-modulus zeolites from the suspension of metakaolin with a SiO_2 excess. To intensify the processes of synthesis, ultrasonic treatment will be used.

EXPERIMENT

For metakaolin producing, the perfume kaolin was used. Kaolin was calcined at 700 °C for 4 h. The

silica gel and the solid aluminum hydroxide were also used. Two mixtures were prepared for the study:

(i) $6Al_2Si_2O_7$: 12NaOH;

(ii) $6Al_2Si_2O_7$: 12NaOH: $12SiO_2$.

Composition of the mixture (i) corresponds to the stoichiometry of the synthesis reaction of the LTA zeolite ($|Na_{12}|[Al_{12}Si_{12}O_{48}]$).

The ultrasonic treatment (UST) was carried out in an ultrasonic dispergator UD-20 with an oscillation frequency of 22 kHz and an amplitude at the end of the concentrator of 8 microns for 10 min. The suspension was then evaporated to a residual moisture content of about 20 wt%. The pellets with diameter 3 mm was molded from the received paste. The pellets were dried at 100-110 °C. The thermal treatment (TT) of dried pellets was carried out at 650 °C for 4 h. Hydrothermal crystallization (HTC) was carried out at 100 °C for 4 h in an aqueous solution with NaOH concentration of 2 and 6 mol/l. Conditions of TT and HTC were chosen based on the results of our earlier studies [10, 11]. After HTC, the pellets were washed with distilled water and were dried.

The reliable identification and characterization of the zeolite micro crystals requires the simultaneous use of various testing methods [12]. In this work, the following testing procedures were used:

• The powder X-ray diffraction (XRD) patterns were recorded on DRON-3M X-ray diffractometer. The CuKα radiation (k = 0,15406 nm, Ni-filter) was used with a power supply settings of 40 kV and 20 mA. The scan rate was 1 min^{-1}, and the scanning step was 0,01°.

• The Fourier transformed infrared (IR) spectra were measured by Avatar 360 FT-IR ESP spectrometer in the range of 4000-400 cm^{-1}. The samples were prepared by the KBr method with the sample-to-KBr ratio of 1:100.

• The scanning electron microscopy (SEM) measurements were taken with the JSM-6460 LV microscope.

The crystalline phases in the XRD patterns were identified by the comparison of the calculated interplanar spacings ($d = \lambda/2\sin\Theta$, where λ is the wavelength, and Θ is the diffraction angle) with those taken from the ASTM databases.

Since the LTA, SOD and PHI belongs to the cubic syngony, the lattice parameter was calculated from the equation of [13]

$$1/d^2 = (h^2 + k^2 + l^2)/a^2,$$

where h, k, and l are the Miller indexes.

To identify the absorption bands on the IR spectra, data of Ref [1, 14] were used.

RESULTS AND DISCUSSION

After UST of the mixture (i) on the XRD patterns, the halo and the reflex of quartz were detected (Fig. 1, *a*). After UST of the mixture (ii), an analogous pattern is observed (Fig. 2, *a*). This type of XRD patterns is characteristic for metakaolin.

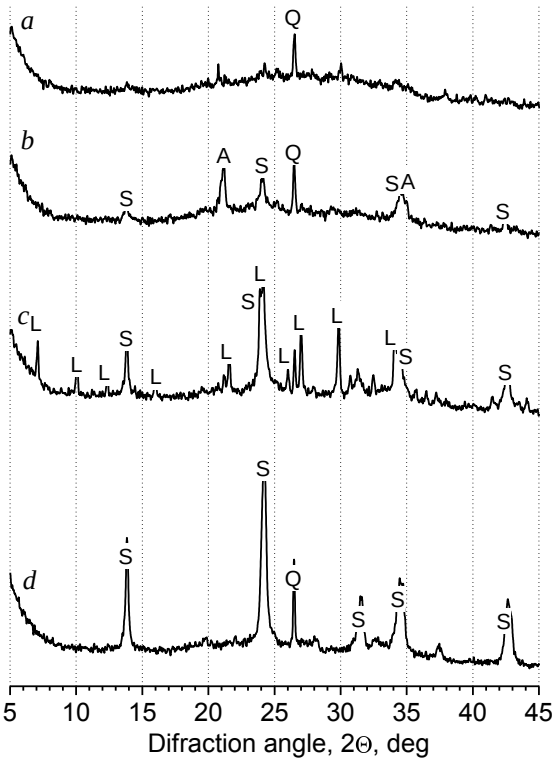

Fig. 1. XRD patterns of mixtures (i) $6Al_2Si_2O_7$: 12NaOH. a) after UST; b) after UST and TT; c) after UST, TT and HTC in solution with a concentration of 2 mol/l; d) after UST, TT and HTC in solution with a concentration of 6 mol/l. A is sodium aluminum silicate ($Na_8Al_4Si_4O_{18}$); L is LTA zeolite ($|Na_{12}|[Al_{12}Si_{12}O_{48}]$); Q is quartz ($SiO_2$); S is SOD zeolite ($|Na_6|[Al_6Si_6O_{24}]$)

Рис. 1. Рентгенограммы смесей (i) $6Al_2Si_2O_7$: 12NaOH. a) после ультразвуковой обработки (УО); b) после ультразвуковой и термической обработки (ТО); c) после ультразвуковой и термической обработки и гидротермальной кристаллизации (ГТК) в растворе с концентрацией 2 моль/л; d) после ультразвуковой и термической обработки и гидротермальной кристаллизации в растворе с концентрацией 6 моль/л

On the SEM images of the mixture (i), the particles with a size of 0.1-0.5 μm were detected (Fig. 3, *a*). These particles are combined into the aggregates with a size of 0.2-2 μm. There are also the particles with a size of 15 μm and the needle-shaped particles with a length of 2-3 μm. In the mixture (ii) after UST, there are the irregularly shaped particles, which are combined into aggregates with a size of 1-5 μm (Fig. 4, *a*).

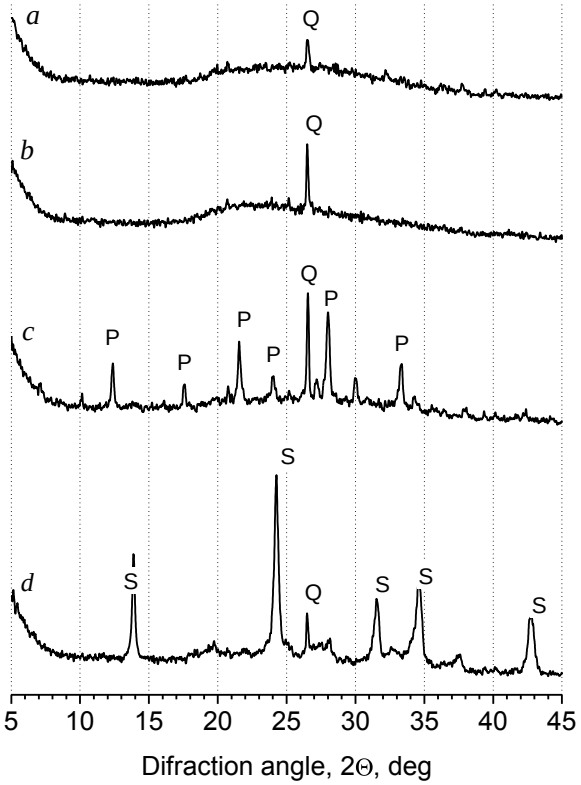

Fig. 2. XRD patterns of mixtures (ii) $6Al_2Si_2O_7$: 12NaOH: $12SiO_2$. a) after UST; b) after UST and TT; c) after UST, TT and HTC in solution with a concentration of 2 mol/l; d) after UST, TT and HTC in solution with a concentration of 6 mol/l. P is PHI zeolite ($|Na_6|[Al_6Si_{10}O_{32}]$); Q is quartz ($SiO_2$); S is SOD zeolite ($|Na_6|[Al_6Si_6O_{24}]$)

Рис. 2. Рентгенограммы смесей (ii) $6Al_2Si_2O_7$: 12NaOH: $12SiO_2$. a) после УО; b) после УО и ТО; c) после УО, ТО и ГДК в растворе с концентрацией 2 моль/л; d) после УО, ТО и ГДК в растворе с концентрацией 6 моль/л. Р – ПХА цеолит($|Na_6|[Al_6Si_{10}O_{32}]$); Q – кварц ($SiO_2$); S – СОД цеолит($|Na_6|[Al_6Si_6O_{24}]$)

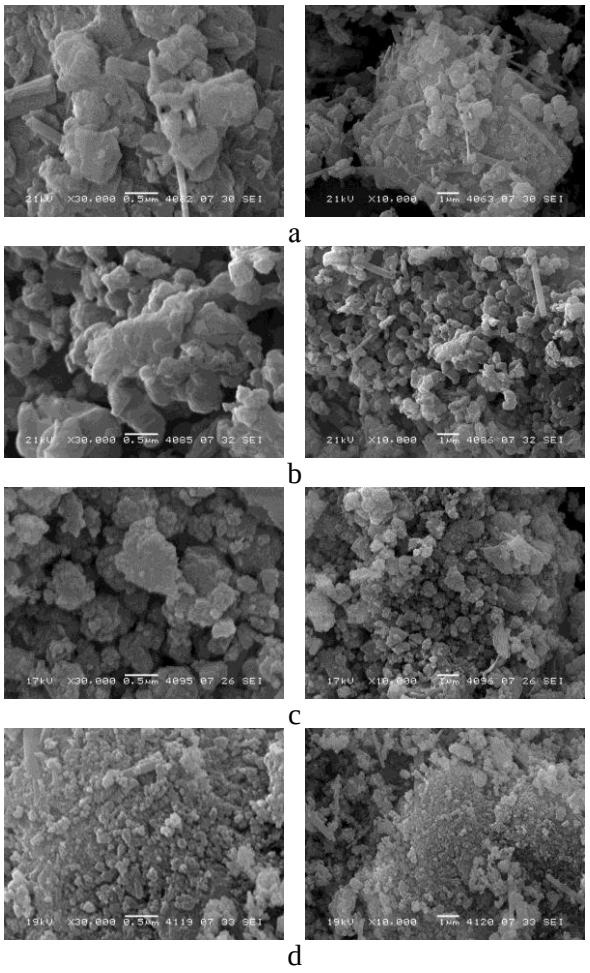

Fig. 3. SEM images of mixtures (i) $6Al_2Si_2O_7$: 12NaOH. a) after UST; b) after UST and TT; c) after UST, TT and HTC in solution with a concentration of 2 mol/l; d) after UST, TT and HTC in solution with a concentration of 6 mol/l

Рис. 3. СЭМ изображения смесей (i) $6Al_2Si_2O_7$: 12NaOH. a) после УО; b) после УО и ТО; c) после УО, ТО и ГТК в растворе с концентрацией 2 моль/л; d) после УО, ТО и ГТК в растворе с концентрацией 6 моль/л

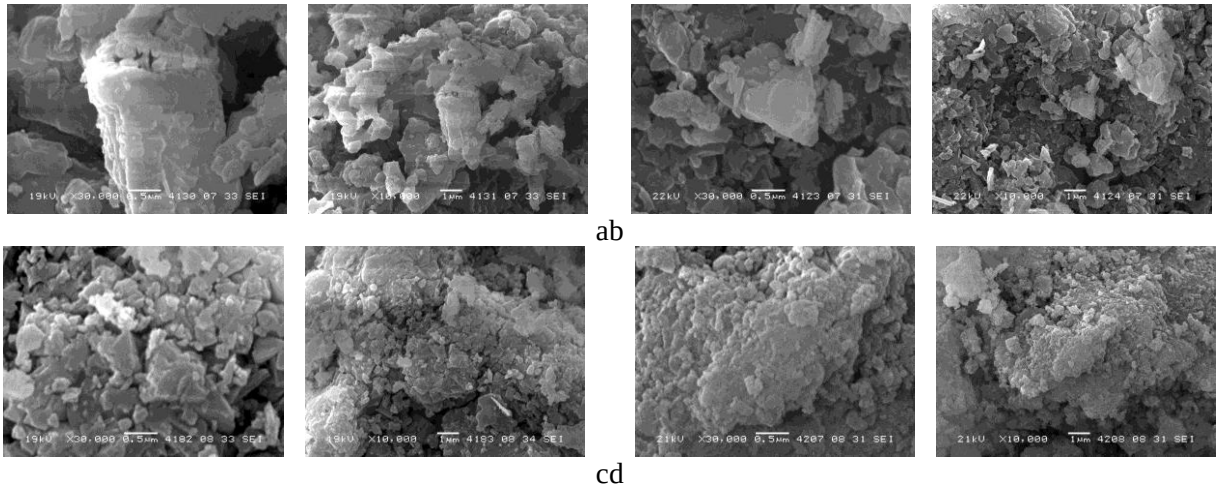

Fig. 4. SEM images of mixtures (ii) $6Al_2Si_2O_7$: 12NaOH: $12SiO_2$. a) after UST; b) after UST and TT; c) after UST, TT and HTC in solution with a concentration of 2 mol/l; d) after UST, TT and HTC in solution with a concentration of 6 mol/l

Рис. 4. СЭМ изображения смесей (ii) $6Al_2Si_2O_7$: 12NaOH: $12SiO_2$. a) после УО; b) после УО и ТО; c) после УО, ТО и ГТК в растворе с концентрацией 2 моль/л; d) после УО, ТО и ГТК в растворе с концентрацией 6 моль/л

On the IR spectrum of the mixture (i), the band at 1000-900 cm^{-1} is attributed to the bending vibrations of Si–O and Al–O(H), and bands at 757, 698 and in the range 1200-1000 cm^{-1} correspond to the stretching vibrations of Si–O and Al–O (Fig. 5, *a*). The bands at 1490 and 1450 cm^{-1} are attributed to vibrations of the surface OH groups and band at 1600 cm^{-1} is ascribed to condensed molecular water. A set of bands in the range 3700-2800 cm^{-1} responds to the external and internal vibrations of OH groups. On the IR spectrum of the mixture (ii), a similar set of absorption bands was detected (Fig. 6, *a*), but there are differences. Firstly, there is the band at 540 cm^{-1} which corresponds to the deformation vibrations of Si–O. Second, all absorption bands have a higher intensities.

All above differences are explained by the presence of a SiO_2 excess in the mixture (ii).

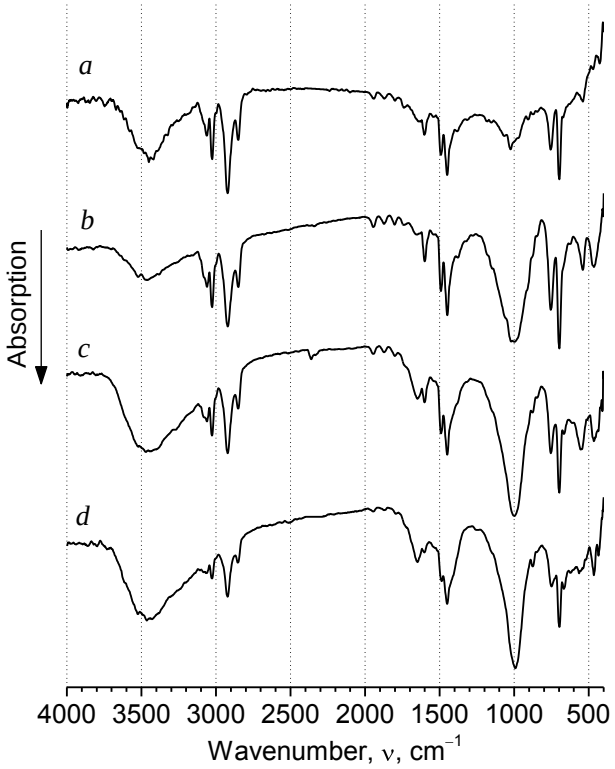

Fig. 5. IR spectra of mixtures (i) $6Al_2Si_2O_7$: 12NaOH. a) after UST; b) after UST and TT; c) after UST, TT and HTC in solution with a concentration of 2 mol/l; d) after UST, TT and HTC in solution with a concentration of 6 mol/l

Рис. 5. ИК спектры смесей (i) $6Al_2Si_2O_7$: 12NaOH. a) после УО; b) после УО и ТО; c) после УО, ТО и ГТК в растворе с концентрацией 2 моль/л; d) после УО, ТО и ГТК в растворе с концентрацией 6 моль/л

After TT of the mixture (i), the new reflexes were detected on the XRD pattern (Fig. 1, *b*). These reflexes have been identified as the SOD zeolite ($|Na_6|[Al_6Si_6O_{24}]$) and the sodium aluminum silicate ($Na_8Al_4Si_4O_{18}$). Thus, the main reactions of solid phase synthesis can be represented as

$$3Al_2Si_2O_7 + 6NaOH \rightarrow |Na_6|[Al_6Si_6O_{24}] + 3H_2O, \quad (I)$$

$$2Al_2Si_2O_7 + 8NaOH \rightarrow Na_8Al_4Si_4O_{18} + 4H_2O. \quad (II)$$

The presence of the halo and the small intensities of the reflexes suggest that the solid phase reaction doesn't proceed completely. TT of the mixture (ii) does not result in the formation of new crystalline phase (Fig. 2, *b*).

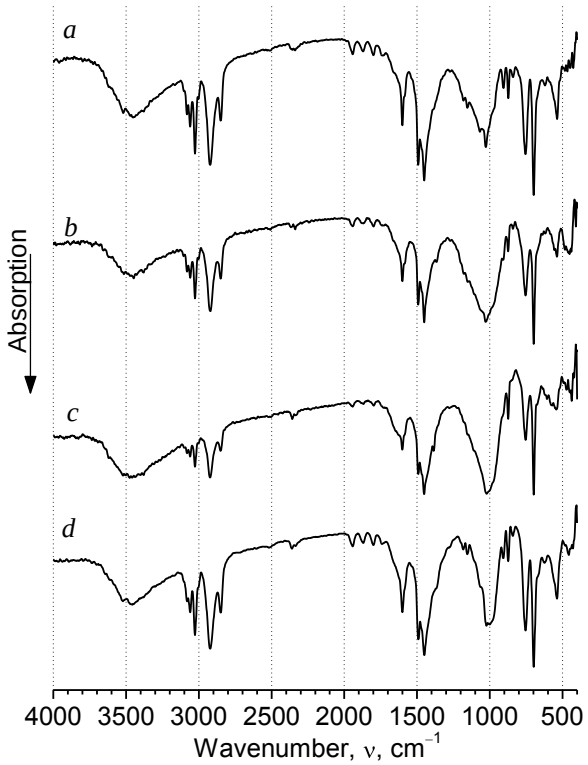

Fig. 6. IR spectra of mixtures (ii) $6Al_2Si_2O_7$: 12NaOH: $12SiO_2$. a) after UST; b) after UST and TT; c) after UST, TT and HTC in solution with a concentration of 2 mol/l; d) after UST, TT and HTC in solution with a concentration of 6 mol/l

Рис. 6. ИК спектры смесей (ii) $6Al_2Si_2O_7$: 12NaOH: $12SiO_2$. a) после УО; b) после УО и ТО; c) после УО, ТО и ГТК в растворе с концентрацией 2 моль/л; d) после УО, ТО и ГТК в растворе с концентрацией 6 моль/л

On the SEM images of the mixture (i) after TT, the particles with a size of 0.1-0.5 μm were discovered (Fig. 3, *b*). It should be noted that the particles have a clear-cut faceting. This is explained by the formation of the new crystalline phases. In the mixture (ii) after TT, the essential changes were not detected (Fig. 4, *b*).

On the IR spectrum of the mixture (i) after TT, an increase in intensity of all absorption bands is observed (Fig. 5, *b*). It should be noted the appearance of the new band in the range of 500-435 cm^{-1}, which corresponds to the asymmetric and bending vibrations

in the TO_4 tetrahedron (where T is Si or Al). A similar pattern is observed on the infrared spectrum of the mixture (ii) (Fig. 6, *b*). These phenomena confirm proceed of solid state reactions (I) and (II).

HTC of the mixture (i) in 2M NaOH solution leads to an increase in the content of SOD zeolite and to the formation of a new phase of the LTA zeolite ($|Na_{12}|[Al_{12}Si_{12}O_{48}]$) (Fig 1, *c*). The parameter *a* of the crystal lattice of the SOD zeolite is 9.042 Å, and the parameter *a* of LTA zeolite is 24.763 Å (Table). The experimental values slightly exceed ASTM database data (8.848 and 24.555 Å, respectively). After HTC of the mixture (ii) in 2M NaOH solution, the phase of PHI zeolite ($|Na_6|[Al_6Si_{10}O_{32}]$) is formed (Fig. 2, *c*). The lattice parameter *a* of PHI zeolite is 10.078 Å (10 Å is ASTM data). On XRD pattern, there are also the reflexes of quartz.

The SEM images (Fig. 3, *c*) demonstrate that the mixture (i) after HTC in 2M NaOH solution consists of particles with a size of 0.1-0.2 μm, that are combined into aggregates with a size of 0.5 to 1.5 μm. HTC of the mixture (ii) in 2M NaOH solution gives the formation of the clearly faceted crystals with a size of 0.2-0.5 μm, which constitute the solid agglomerates with a size from 1 to 5 μm (Fig. 4, *c*).

On the IR spectrum of a mixture (i), the band in the range of 600-500 cm^{-1} is shifted to the high frequency region from 543 to 560 cm^{-1} (Fig. 5, *c*). This indicates the formation of double 4-membered rings which are the structural units of the LTA zeolite framework. On the IR spectrum of the mixture (ii), the appearance of new bands in the range of 630-570 cm^{-1} is detected (Fig. 6, *c*). These bands correspond to the bending vibrations of the 8-membered rings, which are the basis of the PHI zeolite framework.

Thus, in the HTC process of the mixture (i) in 2M NaOH solution, the formation reaction of SOD zeolite is continued. At the same time in alkaline medium, the zeolitization reaction of the sodium aluminosilicate and the metakaolin occurs. This process can be described by the gross reaction:

$$2Na_8Al_4Si_4O_{18} + 2Al_2Si_2O_7 + 2H_2O \rightarrow \rightarrow |Na_{12}|[Al_{12}Si_{12}O_{48}] + 4NaOH. \quad (III)$$

In the mixture (ii), HTC in 2M NaOH solution leads to the formation of the PHI zeolite. The process can be represented by the gross reaction:

$$3Al_2Si_2O_7 + 4SiO_2 + 6NaOH = =|Na_6|[Al_6Si_{10}O_{32}] + 3H_2O. \quad (IV)$$

HTC in 6M NaOH solution results in the formation of SOD zeolite only in both mixtures (i) and (ii) (Fig. 1, *d* and 2, *d*). On the diffraction patterns of the mixtures, there are reflexes of quartz. The SEM images of mixtures (i) and (ii) are also similar (Fig. 3, *d* and 4, *d*). In both cases, there are particles with a size of 0.1-0.2 μm, that are combined into larger aggregates with the size up to 15 μm. IR spectra of mixtures (i) and (ii) are typical for the SOD zeolite (Fig. 5, *d* and 6, *d*). In the range of 820-620 cm^{-1} there are bands that are attributed to the symmetric and asymmetric stretching vibrations of simple 4-membered rings. The band at 534 cm^{-1} on the spectrum of the mixture (ii) corresponds to the bending vibrations of SiO_2, which has been introduced into the mixture in excess. Thus, the result of the HTC in 6M NaOH solution is not dependent on the composition of the starting mixture and the final product is a SOD zeolite, that is formed by the reaction of (I). It should be noted that the lattice parameters of the SOD zeolite are close to ASTM data (Table).

Table

The lattice parameters for the crystalline phases after HTC
***Таблица*. Параметры решеток для кристаллических фаз после гидротермальной кристаллизации**

The composition of the starting mixture Состав исходной смеси	The concentration of NaOH solution, mol/l Концентрация раствора NaOH, моль/л	Crystalline phase Кристаллическая фаза	The lattice parameter, *a*, Å Параметр решетки, *a*, Å.
$6(Al_2O_3 \cdot 2SiO_2)$:12NaOH	2	LTA	24.763
		SOD	9.042
	6	SOD	8.925
$6(Al_2O_3 \cdot 2SiO_2)$:12NaOH: $12SiO_2$	2	PHI	10.078
	6	SOD	8.899

CONCLUSIONS

The synthesis processes of the low-modulus zeolite from mixtures $6Al_2Si_2O_7$:12NaOH and $6Al_2Si_2O_7$:12NaOH:$12SiO_2$ using of ultrasonic treatment was investigated by X-ray diffraction, scanning electron microscopy and infrared spectroscopy.

It was shown that ultrasonic treatment of suspensions does not result in a formation of new crystalline phases.

It was found that the thermal treatment of the mixture $6Al_2Si_2O_7$: 12NaOH at 650 °C results in the synthesis of SOD zeolite ($|Na_6|[Al_6Si_6O_{24}]$) and sodium aluminosilicate ($Na_8Al_4Si_4O_{18}$). The calcination of the mixture $6Al_2Si_2O_7$: 12NaOH: $12SiO_2$ does not give the formation of new phases.

It was shown that the hydrothermal crystallization of the mixture $6Al_2Si_2O_7$: 12NaOH in 2M NaOH solution results in the synthesis of LTA zeolite ($|Na_{12}|[Al_{12}Si_{12}O_{48}]$). It was established that the sodium aluminosilicate is a precursor for the synthesis of LTA zeolite. Crystallization of the mixture with a SiO_2 excess results in the formation of the PHI zeolite.

It was shown that in the process of the hydrothermal crystallization in a 6M NaOH solution in both mixtures, only SOD zeolite is formed.

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