Hydrothermal synthesis of zeolite HSZ-30 based on kaolin

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Abstract. We were the first to study natural kaolin and, on its basis, obtained a zeolite of the HSZ-30 type. As samples of selected Pakhtachinsky kaolin containing 68.8% mordenite (Ca₂₂Na₂K₉Al₉Si₄₂O₉₈•36H₂O) and 31.2% quartz (SiO₂), the sample was thoroughly washed with distilled water and dried at 120 °C for 6 days. Hydrothermal synthesis was carried out in Mori type autoclaves with a volume of 20 cm³. Optimal conditions for obtaining zeolite of the HSZ-30 type: temperature 120 °C, concentration of thermal solution 2 N, processing time 6 days. IR spectroscopic studies were carried out on a Nicolette IS-10 IR spectrometer (Thermo Scientific, USA) in the frequency range 400...5000 cm⁻¹. The phase and chemical composition of the initial and final products was determined by X-ray (2D PHASER «Bruker» (CuKα-radiation, 2θ = 20–80°) and elemental (Launch of Triton XL dilution refrigerator – Oxford instrument) methods of analysis. The article presents the results of a study of the influence of the conditions of hydrothermal synthesis (H₂O/Si ratios in precursor mixtures and synthesis temperatures) HSZ-30 for crystal size and morphology.

1. Introduction
The development of the oil refining and petrochemical industries requires new types of products with high quality indicators. In this regard, highly efficient catalysts are needed, including those based on zeolites. The enterprises of the petrochemical and oil refining industry, producing the main types of hydrocarbon raw materials, cannot be imagined without the development of the production of catalysts, in particular, synthetic zeolites. A lot of works are devoted to the study of zeolites. Zeolites are microporous substances with a regular crystal structure and a controlled pore size not exceeding 2 nm [1-4]. Zeolite frameworks are lattices consisting of tetrahedral T-atoms (T = Si, Al, etc.) connected by oxygen atoms. The usual “building blocks” of zeolite scaffolds are composed of 3-, 4-, 5-, and 6-membered rings (n-membered). Each n-membered ring consists of n T-atoms enclosed in a ring of oxygen atoms, and therefore actually has 2n atoms; thus, the 6-membered ring has a total of 12 atoms. The structures are ordered so that they form large rings that represent molecular pores — usually 8-, 10- and 12-membered, although structures with 9-, 14-, 18- and 20-membered rings are also known. Zeolites containing 8-, 10- and 12-membered rings are better known as microporous, medium-porous, and large-porous. On microporous zeolites n-paraffins are sorbed, and on large-porous ones - branched paraffins. Sorption of some not strongly branched paraffins is possible on medium-porous zeolites [5]. Thus, zeolites are part of a large class of materials called 'molecular sieves' used to separate mixtures of different molecular structures. Obtaining zeolites of various structural types [6-9], creating a wide range
of molecular sieves [10], practical implementation based on local mineral resources are an urgent problem in the chemistry of zeolites and silicates of large cations. Chemical modification has a significant effect on the physicochemical properties of zeolites [11-14], with the help of which it is possible to influence the structure of zeolites, to obtain minerals of the zeolite group and aluminosilicates with the required parameters.

The purpose of this work — carrying out hydrothermal treatment of a natural sample of kaolin to obtain an adsorbent and catalyst.

2. Experimental part
The synthesis of HSZ-30 (high-silica zeolite) was carried out under hydrothermal (HT) conditions. To study the effect of synthesis conditions on the size and morphology of zeolite crystals, the H2O/Si ratio was varied, synthesis temperature, various molecular templates were used - tetrapropylammonium hydroxide and bromide (TPAOH and TPABr), silicon sources – SiO2 and tetraethylorthosilicate (TEOS). The influence of the texture and structural properties of the samples on the state of the catalytically active component was studied by a number of physicochemical methods: X-ray phase analysis (XPA), dynamic light scattering, laser diffraction, low-temperature adsorption of N2 and Ar, transmission and scanning electron microscopy (TEM and SEM), thermost programmed desorption of ammonia (TPD NH3) and electron diffuse reflectance spectroscopy (EDS).

We were the first to study natural kaolin and, on its basis, obtained a zeolite of the HSZ-30 type. Pakhtachinsky kaolin was taken as samples [15-18], containing 68.8% mordenite (Ca2Si2Al2O10·6H2O) and 31.2% quartz (SiO2). The sample was thoroughly washed with distilled water and dried at 120 °C for 6 days. Hydrothermal synthesis was carried out in Mori type autoclaves with a volume of 20 cm3. Experiments on hydrothermal crystallization were carried out without creating a temperature gradient ΔT = 0 and without stirring the reaction mixture. The ratio of solid to liquid is 1:10. Experiments on the hydrothermal synthesis of zeolite of the HSZ-30 type were carried out for 4–7 days at a temperature of 110–200 °C. The concentration of the thermal solution of NaOH is 1–3 N. The optimal conditions for obtaining zeolite of the HSZ-30 type are: temperature 120 °C, concentration of thermal solution 2 N, processing time 6 days.

The identification of zeolite phases was carried out by methods of X-ray phase, elemental, IR spectroscopic and thermal analysis. To study the effect of synthesis conditions on the size and morphology of zeolite crystals, the H2O/Si ratio was varied, synthesis temperature, various molecular templates were used - tetrapropylammonium hydroxide and bromide (TPAOH and TPABr), silicon sources - SiO2 and tetraethylorthosilicate (TEOS). The influence of the texture and structural properties of the samples on the state of the catalytically active component has been studied by a number of physicochemical methods: X-ray phase analysis (XPA), dynamic light scattering, laser diffraction, low-temperature adsorption of N2 and Ar, transmission and scanning electron microscopy (TEM and SEM), thermostprogrammed desorption of ammonia (TPD NH3) and electron diffuse reflectance spectroscopy (EDS).

IR spectroscopic studies were carried out on a Nicolet IS-10 IR spectrometer (Thermo Scientific, USA) in the frequency range 400 ... 5000 cm⁻¹. Samples were prepared by pressing tablets with potassium bromide in air at a ratio of 1–2 mg of zeolite to 300 mg of KBr. Determination of the volume of micropores was carried out by comparison with a standard on a “Sorbtometer M” device. The reference standard is the adsorption isotherm measured on a non-porous material with a regular surface. The adsorption isotherm was used for non-carbon materials (0.05 <P / P0 <0.30 where P, P0 are the pressure values of the measured and saturated vapor of the adsorbate gas, respectively). Comparison with the reference standard is carried out by plotting a graph in which each adsorption value measured in the current experiment is assigned a value for the reference standard at the same P/P0 value.

In the range of filling a monolayer (0.05 <P / P0 <0.3), the corresponding graph is linear. The tangent of the slope of the graph line in this area is proportional to the specific surface area outside the micropores, and the size of the segment cut off by the straight line along the ordinate corresponds to the volume of micropores filled long before the formation of a monolayer on the mesopore surface. The
specific surfaces and the specific volume of the obtained HSZ were determined from the thermal desorption of nitrogen by the multipoint BET method. And although this method does not take into account the specifics of filling micropores, the data obtained can be valuable as a means of comparative analysis, due to the uniformity of the studied samples of high-silica zeolites. Electron microscopic studies of the morphology of zeolite crystals and iron nanoparticles were carried out on a JEOL JSM-6490LV scanning electron microscope (Japan). The preparations were fixed on analytical aluminum tables using conductive carbon tape and were sprayed with platinum. The image was obtained in the secondary electron mode (SE detector). The working magnification range varied from 200 to 13000 times. The accelerating voltage was 20 kV.

The phase and chemical composition of the initial and final products was determined by X-ray (2D PHASER "Bruker" (CuKα - radiation, 2θ = 20–80°) and elemental (Launch of Triton XL dilution refrigerator - Oxford instrument) analysis methods. Thermogravimetric analysis of the samples was carried out on a "Q-Derivatograph 1500-D" Hungarian company MOM in a dynamic mode in the temperature range of 20-1000 °C. Shooting mode: heating rate 10 °/ min; paper speed 2.5 mm / min; the sensitivity of DTA, TG is 500 mV; ceramic crucibles; reference – Al₂O₃. Elemental analysis was performed with a Launch of Triton XL dilution refrigerator - Oxford instrument (Oxford Instrument, UK). A weighed portion of the test sample was homogenized by fusion, then they were prepared in the form of pressed disks with a diameter of 40 mm on a boric acid substrate. A mixture of chemical reagents Al₂O₃ and SiO₂ was used as a reference sample, an X-ray tube, high voltage up to 8 kV, helium purge, a sample rotator, a Focus S selective filter system, which improves the effective resolution and provides lower detection limits, were used as an excitation source.

3. Experimental results and their discussion

Primary macroscopic kaolin from Angren appears to be an oily gray clay ore, weakly chlorinated, containing grains of quartz, bionite fragments of granular quartz, and feldspar. The Sultan-Uwais mine is located in the Sultan Uwais Mountains of the Republic of Karakalpakstan, from which primary and secondary kaolin are extracted. These ores are yellow-gray in shape and contain fragments of glauconitokvartz sand, muscovite, feldspar and crystalline ores. As a result of complex studies, the chemical, mineral and granulometric properties of kaolins from the Angren and Sultan-Uwais mines were studied, and their physicochemical and technological properties were determined, both natural and enriched. IR absorption spectra of the samples were studied on a Specord-IR-75 spectrophotometer (Germany). To carry out the tests, the samples were pressed with a mixture of potassium bromide in powder form and the object of study was studied in a ratio of 300:1 by bringing the powder samples to disk shape. Measurement error ± 0.2%. Typically, IR spectra are studied in the range of 100–10000 cm⁻¹, while the study of the desired spectra of clays and kaolins lies in the range of 400–4000 cm⁻¹. IR spectroscopy provides interesting information about the internal structure of clay-layered aluminosilicates.

Results and their discussion The first figure 1 shows the IR spectra in the area of 400-4000 cm⁻¹ of natural and enriched kaolins of Angren (Republic of Uzbekistan) as well as the famous Pakhtachi (Republic of Uzbekistan, Samarkand region).

In the study of kaolin IR spectra, it can be divided into two main areas. In the first high-frequency field (above 300 cm⁻¹) lies the O-H group valence oscillation (a - band), which is due to the hydrogen bond between the layers of clay-forming minerals belonging to the octahedral cation as well as the water molecule. The second area (400-1400 cm⁻¹) belongs to the absorption bands of minerals in the silicate structure.

As can be seen from figure 1, the IR spectrum of Pakhtachi kaolin shows clear absorption bands at 3620 and 3695 cm⁻¹. The inner OH group, surrounded by layers of aluminum and oxygen (octahedral), has a band corresponding to valence oscillation at 3620 cm⁻¹. As a quantitative criterion for characterizing the degree of perfection of the structure of kaolins (index Hinkley), the intensity ratios of 3696 and 3620 cm⁻¹ bands are taken, the greater the relationship, the more perfect the structure.
According to the experimental results, the Hinkley index is 1.33 in Pakhtachi kaolin, the magnitude of this value indicates that kaolin has an excellent crystalline structure.

![Figure 1. IR spectra of Angren and Pakhtachi kaolins. Angren-1 (natural); 2 (enriched); 3- Pakhtachi kaolins.](image_url)

Deformation vibration of the Al-OH bond (S - band) is observed in the low frequency region of the band shadows. For cotton kaolin, it appears as a single intensive strip at a frequency of 914 cm\(^{-1}\). In layered minerals, the absorption bands of water adsorbed molecules between the layers are observed in the area 1637-1625 cm\(^{-1}\) (deformation vibration). When comparing the IR spectra of cotton kaolin and Angren natural kaolin, low-intensity bands at 3695 and 3620 cm\(^{-1}\) and dyed (размиты) bands at frequencies of 3400 and 3500 cm\(^{-1}\) are observed in the high frequency field. The crystalline index of natural kaolin in Angren is 0.94, in addition, the IR spectrum of natural kaolin shows an absorption band of 1890 cm\(^{-1}\) at low intensity.

Analyzing the IR spectrum of Angren-enriched kaolin, it can be said that in the high frequency field it has the same spectrum as Pakhtachi kaolin, but also the peak intensity ratios at 3670 and 3620 cm\(^{-1}\) (Pakhtachi kaolin -1.33, in Angren enriched kaolin - 1.12) this indicates that they are close to the degree of crystallization. It is known that the absorption bands of the silicate structure of kaolins are mainly in the low frequency region, the number of waves is in the area of 300-1400 cm\(^{-1}\). Valence vibration on the Si - O bond has an absorption band in the area of 800-1300 cm\(^{-1}\), and deformation vibration has an absorption band in the area of 500-400 cm\(^{-1}\). The maximum absorption state [SiO\(_4\)] in the 900–1300 cm\(^{-1}\) region depends on the degree of polymerization of the tetrahedrons. The higher the level of interconnection of tetrahedrons, the higher the base maximum will shift to the higher frequency range. Along the “condensation” series of [SiO\(_4\)] tetrahedrons, exactly the isolated [SiO\(_4\)] - [Si,O\(_2\)] groups - [SiO\(_3\)] chain [Si_3O_8] layer is a three-dimensional carcass structure, the absorption peaks shifting towards the high frequency range.

As can be seen from figure 1, the above kaolin samples have wide absorption bands in the area of 950–1150 cm\(^{-1}\). They are observed at peaks 1010 and 1100 cm\(^{-1}\), Si-O-Si bond valence oscillation can be considered as a classification of the layered structure of the disilicate group. Angren natural kaolin is painted in 797 and 778 cm\(^{-1}\) double absorption strips, and the wide payoff is due to the presence of a large amount of quartz mixture in this sample. Kaolins of Pakhtachi and Angren-enriched kaolin have a single peak at 797 cm\(^{-1}\) in the IR spectrum, while the second 778 cm\(^{-1}\) peak shifts to a lower frequency (759 cm\(^{-1}\)) in Pakhtachi kaolin, possibly due to the presence of [SiO\(_4\)] tetrahedrons with three bands, as well as [AlO\(_3\)] structure grouping is associated with the formation of a silicon cation tetrahedral layer.
The low-frequency absorption bands of 432, 470, 540 cm\(^{-1}\), where the peaks are clearly visible, are associated with the deformation vibration of the Si-O-Si bond. These bands are present in the IR spectra of kaolins tested together, only in the Angren natural kaolin the intensity of these peaks is low. It should also be noted that when Al\(^{3+}\) is replaced by Me\(^{2+}\) in the octahedral layer, the intensity of the absorption bands 541–538 cm\(^{-1}\) (Si-O-Al) decreases, and the frequency also decreases due to the decrease in Me-O-Si distance. Due to the reduced bond strength, Angren is observed in the IR spectrum of natural kaolin. The 396 and 366 cm\(^{-1}\) intensive absorption bands are unique to Angren natural kaolin due to the mixing of this.

O-Si-O deformation vibration quartz. Preliminary studies show that kaolin from the Sultan-Uwais mine differs from kaolin from the Angren deposit in chemical-mineralogical granulometric composition due to its structural specificity, which can be examined by IR spectroscopy. Figure 2 shows the IR absorption spectra of natural and enriched kaolin in Sultan Uwais (Republic of Uzbekistan). The data show that strong absorption bands of 3696 and 3620 cm\(^{-1}\) were observed in the field of valence oscillations of the Sultan-Uwais natural and enriched kaolin OH, which were of the same intensity. The 3696 cm\(^{-1}\) band belongs to the OH group within the surface forming the OH-O bond between the packets, and the 3620 cm\(^{-1}\) band generally belongs to the inner OH group. These groups are more difficult to ON exchange because it is located in the area between the layers of the kaolinite pack. For Sultan-Uwais kaolin, the \(I_{3696}/I_{3620}\) ratio (according to Hinkley) increases from 0.98 to 1.04, for Angren kaolins from 0.94 and 1.11, respectively, to the naturally enriched state, the crystallization index is less than one. The Sultan-Uwais natural kaolins have a deformation vibration band belonging to the 914 cm\(^{-1}\) Al-OH bond, which shows a lower absorption than the enriched kaolin, while the peak intensity decreases further at 913 cm\(^{-1}\).

The presence of a doublet strip at 913–930 cm\(^{-1}\) indicates the presence of simple dikkite in Angren natural kaolinite and Sultan-Uwais kaolinite (figures 1 and 2). The hydroxyl OH group is bound to the Al\(^{3+}\) octahedral cation in the hydrosilicate structure, probably due to its direct effect on the surface of Sultan-Uwais unenriched kaolin, which is characterized by 920–926 cm\(^{-1}\) absorption (figure 2).

**Figure 2.** IR spectrum of Sultan-Uwais kaolin: 1-natural; 2 enriched.
In the study of Sultan-Uwais kaolin in the natural and enriched state, absorption bands with peaks 1009, 1033, 1100 cm\(^{-1}\) were observed in the 950-1150 cm\(^{-1}\) areas, which are classified by Si-O-Si bond valence oscillations in the disilicate group layered structure. Silicon oxygen bonding differs sharply from ordinary ionic bonding between metal and oxygen, so the [SiO\(_4\)] tetrahedron represents a set of ionic complexes with a common structure with other silicate metal atoms in a geometric landscape surrounded by only four oxygen atoms of the silicon atom. Two peaks are observed in the IR spectrum of Sultan-Uwais enriched kaolin at 794 and 755 cm\(^{-1}\), indicating the presence of a three-component ring in the tetrahedron [SiO\(_4\)] when the silicon cation is replaced, and the structural grouping [AlO\(_4\)]. The complexity of the IR spectrum band is explained by the fact that silicon-oxygen tetrahedrons cause the ring chain and other radicals to bend the tetrahedron and reduce their symmetry. The high strength of silicon radicals does not make them hard, on the contrary, they cause other elements of the gabitush-mineral to break down and deviate from the hardness. For the Sultan-Uwais natural kaolins, the fundamental oscillation of the Si-O-Si bond in the silicon oxygen tetrahedron increases the intensity by shifting the absorption band 728 and 777 cm\(^{-1}\) to the right.

The intensive absorption bands 695, 397, and 370 cm\(^{-1}\) are unique to Sultan-Uwais natural kaolin, which is associated with the O-Si-O deformation vibration of the quartz mixture.

Kaolins from the Angren and Sultan-Uwais deposits are not well formed and have a different kaolinite group.

Crystallization rates in Angren and Sultan-Uwais kaolins are less noticeable than in kaolinite compared to Pakhtachi kaolin: in the kaolinite group, these values differ from each other by the specificity of the deformable structural OH-O bond between the packets. Enriched kaolins are characterized by a well-formed structure, mainly due to the fact that they are located in a single layer of kaolinite.

As an object of study, we took kaolin from Pakhtachi (Uzbekistan, Samarkand region) and studied the possibility of changes in chemical composition in the activated state relative to the natural state, analyzing and comparing natural (figure 3) and "acidic" kaolin (figure 4) to 7000°C. A comparison of the results obtained shows that a loss of Tg mass was observed from the curve (figures 3 and 4). It can be assumed that since natural kaolin contains many components, this can be seen from the fact that the temperature decreases from 0 to 3500°C in the sample by 10% by mass. In kaolin treated with an aqueous solution of sulfuric acid (figure 4), the mass loss is 10% when the temperature rises from 0 to 5000°C.

Figure 3. Derivatogram of chemically untreated (primary) Pakhtachi kaolin.
The article presents the results of a study of the effect of hydrothermal synthesis conditions (H₂O / Si ratio in mixtures of precursors and synthesis temperature) of HSZ-30 on the size and morphology of crystals.

An increase in the H₂O / Si ratio in mixtures of HSZ-30 zeolite precursors leads to an increase in the average crystal size and an increase in the yield of the target product (figure 5) due to a decrease in the nucleation rate and nucleation concentration. An increase in the temperature of hydrothermal synthesis leads to an increase in the average crystal size and crystallinity of the samples.

Crystal morphology also depends on the H₂O / Si ratio in the precursor mixture (figure 6). At H₂O / Si = 10 and H₂O / Si = 300, smooth lamellar crystals are formed. In the 25< H₂O / Si <100 range, aggregate-like ellipsoidal crystals are formed. In the transition region at H₂O / Si = 150, a mixture of smooth lamellar and aggregate-like crystals of various shapes is observed. According to TEM data, aggregate-like crystals are single crystals (figure 7). The crystal morphology is apparently associated with different mechanisms of crystal growth, depending on the state of the silicate precursors. TEM images of HSZ-30 samples synthesized from mixtures of precursors with a H₂O / Si ratio of 25 and 50 (figure 7) show mesoporous and hollow crystals due to their partial dissolution in an alkaline medium.
Figure 6. SEM images of HSZ-30 zeolites synthesized from mixtures of precursors with different H₂O / Si ratios.

The tendency of aggregate-like crystals to dissolve can be associated with the defectiveness of their structure due to the growth of crystals by the mechanism of aggregation of nanoparticles. The formation of hollow zeolites is usually associated with a decrease in the concentration of lattice-stabilizing aluminum from the surface of the crystals towards the center. Thus, methods have been developed for the synthesis of crystals of HSZ-30 zeolites with the required morphology and size in the range from 30 to 5000 nm.

To form hierarchically porous materials by structuring nanocrystals, suspensions of well-crystallized HSZ-30 particles with a narrow crystal size distribution and an average hydrodynamic diameter of 80 and 180 nm, respectively, were used. Crystal structuring was carried out by centrifuging the suspensions followed by drying, or directly by drying at 50 °C. As a result, particles with a size of 2-5 mm were obtained (figure 8), which were then thoroughly ground in a mortar or left unchanged and calcined to remove the molecular template and bond the crystals due to the dehydration reaction with the participation of Si – OH groups of neighboring particles. Calcination of opalescent particles and powder promoted the formation of aggregates with dense and loose packing of crystals, respectively (figure 8). As a reference sample, HSZ-30 microcrystals of various morphology with an average size of 5 µm were obtained (figure 8). The size distributions of mesopores for the synthesized materials are shown in figure 9. The size distribution of mesopores depends on the packing of crystals in aggregates (figure 9). In the case of close packing of HSZ-30 crystals, most of the mesopores are in the range 10–40 nm; the size distributions of mesopores exhibit maxima at 25–30 nm for HSZ-30. For aggregates with loose packing of HSZ-30 crystals, a wide pore size distribution is seen in the range from 10 to 80 nm, most of the mesopores are in the range of 40 - 70 nm. A sample of microcrystals HSZ-30 contains a small amount of mesopores 10 - 20 nm in size, which, apparently, represent structural defects.
Figure 7. TEM images of zeolites synthesized from mixtures of precursors with different $\text{H}_2\text{O} / \text{Si}$ ratios.

Figure 8. Photo and SEM images of various kaolin samples.
Thus, porous zeolites with high crystallinity can be obtained by structuring nanocrystals, the size of crystals and their packing determine the textural characteristics of materials.

All zeolite samples are well crystallized, have a large specific BET surface area (480–650 m$^2$/g), mesopore surface area (180–350 m$^2$/g), and pore volume (0.50–0.75 cm$^3$/g).

The use of Pakhtachi kaolin makes it possible, without auxiliary components (organic medium, mineralizers, binders) and under moderate conditions, to carry out the hydrothermal synthesis of zeolite HSZ-30. The diffractogram of the initial sample is shown in figure 10.

The mordenite content was estimated by the intensity of its basic diffraction reflections with the values of interplanar spacings $d = 11.50, 5.76, 4.35, 2.88$ Å. The coincidence (within the experimental error) of the experimental and tabular values of $d$ and the relative line intensities unambiguously
indicates the dominant mordenite in the samples. The diffraction pattern (see figure 10) shows peaks corresponding to interplanar distances \( d = 3.34, 2.45, 2.28, 2.12 \) Å, which indicates the presence of \( \alpha \)-quartz in the indicated silicon oxide SiO\(_2\) sample.

X-ray diffraction data for synthetic zeolite VCC-30 are presented in table 1.

**Table 1.** X-ray data for synthesized zeolite HSZ-30.

| \( d \) Å  | 15.85 | 13.02 | 10.20 | 7.85 | 7.55 | 7.02 | 6.30 | 5.99 | 5.46 | 5.25 | 5.03 | 4.50 | 4.41 | 4.33 |
|------------|-------|-------|-------|------|------|------|------|------|------|------|------|------|------|------|
| I (Rel.)   | 60    | 50    | 10    | 20   | 60   | 15   | 40   | 20   | 30   | 15   | 25   | 80   | 70   | 30   |
| Rel. Units |       |       |       |      |      |      |      |      |      |      |      |      |      |      |

| \( d \) Å  | 3.87  | 3.64  | 3.54  | 3.44 | 3.40 | 3.30 | 3.22 | 3.15 | 3.10 | 3.04 | 2.89 | 2.73 | 2.70 | 2.55 |
| I (Rel.)   | 90    | 100   | 60    | 25   | 30   | 15   | 20   | 30   | 70   | 75   | 90   | 50   | 15   | 15   |
| Rel. Units |       |       |       |      |      |      |      |      |      |      |      |      |      |      |      |

According to the data of X-ray diffraction analysis, zeolite HSZ-30 crystallizes in a hexagonal system with the parameters \( a = 31.20 \) Å, \( c = 7.55 \) Å.

The X-ray diffraction pattern of HSZ-30 zeolite synthesized on the basis of Pakhtachi kaolin is shown in figure 11.

**Figure 11.** X-ray diffraction pattern of synthesized zeolite HSZ-30.

In the IR spectrum of zeolites, absorption bands in the frequency range of 250 ... 1400 cm\(^{-1}\) correspond to the main vibrations of the aluminum-silicon tetrahedra of the framework structure of zeolites. The observed absorption bands are attributed to two types of vibrations: 1) vibrations characterizing the primary structural units of TO\(_4\), where T = Si\(^{4+}\), Al\(^{3+}\); 2) vibrations of TO\(_4\) tetrahedra along external bonds. The second type of vibrations depends on the nature of the joining of the tetrahedra into secondary structural units and the characteristics of the zeolite cavities. The IR spectrum of zeolite HSZ-30 is shown in figure 12.
4. Conclusion
Physicochemical properties and structural-chemical transformation of Pakhtachi kaolin under conditions of hydrothermal treatment and zeolite HSZ-30 obtained on its basis were studied for the first time.

The optimal conditions for the synthesis of zeolite YuKTS-30 were established: temperature 120 °C, concentration of thermal solution 2 N, processing time 6 days. It was also found that the dehydrated sample of the obtained ZSM-5 zeolite is completely rehydrated. According to X-ray phase and IR spectroscopic analyzes, the obtained zeolite is characterized by high crystallinity and can be used as a catalyst.

To study the effect of synthesis conditions on the size and morphology of zeolite crystals, the H₂O / Si ratio and the synthesis temperature were varied; various molecular templates were used — tetrapropylammonium hydroxide and bromide (TPAOH and TPABR), silicon sources — SiO₂ and tetraethylorthosilicate (TEOS). The influence of the texture and structural properties of the samples on the state of the catalytically active component was studied by a number of physicochemical methods: X-ray phase analysis (XPA), dynamic light scattering, laser diffraction, low-temperature adsorption of N₂ and AR, transmission and scanning electron microscopy (TEM and SEM), temperature-programmed desorption ammonia (TPD NH₃) and electron diffuse reflectance spectroscopy (EDS).

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