Colloidal-Chemical Characteristics of Intercalated Aluminosilicates

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ABSTRACT: The processes of intercalation of montmorillonite and kaolin have been investigated. The intercalation process was fulfilled in three main stages: hydrolysis of Cr3+ and Al3+ salts with the formation of polynuclear hydroxocomplexes; ion exchange of aluminosilicate cations; heat treatment of the intercalated material. As it turned out, the stability and nature of both the layered material and the pillaring cation will affect the intercalation yield. The consumption of polyhydroxocation correlates well with the CFU values of kaolin and, at the same time, the yield of the process for Cr-; Al- and Cr/Al of kaolin is not less than 87; 92 and 88.6%, respectively. Experiments to study the dependence of pH and ζ-potential showed differences in this dependence for the initial layered systems and pillar materials based on them. At the same time, pillaring reduces the polydispersity values of montmorillonite and kaolin by more than 1.3±0.1 and 2.5 times, respectively. A change in the surface charge and thermal stability of pillar materials suggests a change in their acidity, which makes them promising in various adsorption and catalytic processes.

KEYWORDS: Montmorillonite clay, kaolinite, intercalation, chromium, aluminium, methylene blue, congo red, adsorption.

I. INTRODUCTION

In the crystal lattices of layered materials, there is a strong bond of atoms inside the layers, however, the layers themselves are connected by weaker forces, because of Van der Waals. Additional atoms or molecules can be introduced into such matrices, pushing apart the layers of the mineral. As a result, modified structural units are formed, consisting of alternating initial and new layers of embedded particles. A similar process of introducing groups of atoms between layers of layered materials is called intercalation [1, 2]. Aluminosilicate layers are capable of incorporating (intercalating) inorganic (pillaring), organic molecules with macrosizes, as well as oligomeric compounds [3, 4]. The main ideas about the structure of pillar clays were formulated in the studies of Barrer and MacLeod [5], Bergaya [6], Gil [7], Kloprogge [8], Pinnavaia [9], Sterte [10] and other scientists.

Regardless of some peculiarities, the process of this type of modification can be reduced to three main stages: 1) hydrolysis of metal ions with the formation of polynuclear hydroxo complexes - pillaring solution, 2) ion exchange, 3) heat treatment of the intercalated material [2; 11]. Thermal treatment is accompanied by dehydration and dehydroxylation of the introduced polyhydroxocations, as a result of which metal oxide clusters (supports, columns, pillars) are formed in the interlayer space of montmorillonite, which are firmly connected to the aluminosilicate layers through oxygen bridges. These clusters prevent the layers from approaching, forming a stable two-dimensional microporous structure, in which the interlayer distance is significantly increased compared to the original layered mineral [12]. Along with an increase in the number of micropores, in this process, due to the delamination of aluminosilicate layers, additional formation of mesopores occurs and due to this, the specific surface area of the obtained nanomaterials reaches values of 200-300 m^2/g and more. At the same time, the physicochemical characteristics of the obtained materials and their stability in various

Of particular interest are studies aimed at introducing active nanocomponents into the structure of layered aluminosilicates, leading to the creation of supported heterogeneous catalysts. The intercalation of polyvalent metal ions and their mixtures capable of undergoing reversible redox transformations opens up great potential for the use of pillar clays as oxidation catalysts, in particular, for the oxidative degradation of organic matter impurities in industrial effluents [13, 14].

Many scientists theorists and practitioners in the process of introducing large inorganic cations into layers of aluminosilicates sought to maximize the textural characteristics of the initial matrix, as well as to include and fix a catalytically active component in the structural unit of the layered material [15, 16, 17, 18, 19]It is interesting to know the degree of modification caused by pilling in terms of surface area, pore size and surface acidity. The determination of surface properties will be of great help in the development of acid-controlled clay catalysts for various organic reactions and molecular sieve type materials based on these clays. It is in this context that the present study was carried out, aimed at the intercalation of

montmorillonite and kaolin with polyoxocations with different concentrations and establishing the influence of these processes on the surface characteristics of pillar materials media also change.

II. SIGNIFICANCE OF THE SYSTEM

The processes of intercalation of montmorillonite and kaolin have been investigated. The intercalation process was fulfilled in three main stages: hydrolysis of Cr^{3+} and Al^{3+} salts with the formation of polynuclear hydroxocomplexes; ion exchange of aluminosilicate cations; heat treatment of the intercalated material. The study of methodology is explained in section III, section IV covers the experimental results of the study, and section V discusses the future study and conclusion.

III. METHODOLOGY

As layered aluminosilicates, bentonite clay (NB) purchased from Bentonite LLC (bentonite of the Navbakhor deposit, Uzbekistan) and enriched kaolin (EK) (Pakhtachinsk deposit, Uzbekistan) were chosen.

Before use, bentonite was subjected to enrichment in order to increase the main component - montmorillonite - more than 90%. Enriched kaolin was used in the form in which it was received from Alliance LLC.

A sample of bentonite purified from large mechanical impurities was dissolved in distilled water, taken in a volume ratio of 1:10. Calculated amounts of soda ash were added to the suspension (until the pH of the system reached 10) to convert all exchangeable cations into Na^+ forms. The optimal amount of the modifier was determined by the change in the pH values of the suspension after settling. After adding the soda modifier, the suspension was subjected to ultrasonic treatment to accelerate the process of dissolution - dispersion, which reduces the time of cation exchange and better enrichment of the original clay. Then the suspension was left alone for one day. After the suspension was well mixed, and the upper part of the suspension was separated from the bottom by decantation. The solid phase of the upper suspension was separated from the liquid by centrifugation (centrifuge DIAB DM0412) and dried at a temperature of 100 ± 2ºC. The dried clay was ground using a laboratory mill (knife mill, up to 20,000 rpm, universal, IKA M 20). For further purposes, samples of enriched bentonite sifted through No. 04 mm sieves (Vibrating Screen SY300) were used.

Al^{3+} and Cr^{3+} polyoxocations were synthesized as intercalating agents, for which $AlCl_3 \cdot 6H_2O$, $CrCl_3 \cdot 6H_2O$, NaOH brand (chemically pure) reagents were purchased from OOO KHIMREAKTIV INVEST were used.

Synthesis of polyoxocations was carried out in an aqueous solution by hydrolysis of salts using solutions of a hydrolyzing agent. The initial concentration of aluminum and chromium salts varied from 0.1 to 1 M, and of the hydrolyzing agent from 0.1 to 0.5 M. The molar ratio of Cr^{3+} and Al^{3+} ranged from 1:1 to 1:10, and the ratio $(Cr^{3+}+Al^{3+})/OH^-=(1\leq3)$ and at the same time the pH value of the system reached 5 ± 0.5. The duration of the synthesis varied from 30 minutes to 50 hours. The temperature of the polyoxocation synthesis system varied from 20 to 70°C.

For the synthesis of pillar materials, the values of the amounts of polyoxocations necessary to replace the exchange cations of enriched clay were established. For this purpose, the amounts of exchangeable Na^+ cations were first determined; K^+ (GOST 3594.3-93); Ca^{2+}; Mg^{2+} (GOST 3594.2-93) used layered systems

The synthesized pillaring solutions containing chromium and aluminum polyoxocations were heated to 60ºC and then a weighed portion of enriched clay was added to these solutions with constant stirring and a temperature of at least 50ºC, so that from 1 to 15 mmol of cations per 1 g of clay. After 2 hours of stirring, the resulting suspensions were kept at room temperature for 1-7 days. The suspension was stirred from time to time. After holding, the upper part of the suspension (the formation of a precipitate and partial clarification of the upper part was observed) was removed by decantation. The lower part was centrifuged and the precipitate was washed with distilled water. The washing water was examined for the presence of Cl^- ions and then only the precipitate was dried at room temperature or in an oven. The obtained samples were stored in a desiccator.

The crystallinity of the materials was studied by X-ray powder diffraction using an XRD Empyrean PANanalytical X-ray diffractometer with a minimum scan step of 0.0001° and angle setting reproducibility <0.0002°. CuK_α radiation was applied (β-filter, Ni, 1.54178 current mode and tube voltage 30 mA, kV) and the detector rotation speed was 4 deg/min with a step of 0.02 deg, and the scanning angle varied from 4 to 80º.

The chemical analysis of the samples was carried out on an Al 1200 atomic absorption spectrophotometer. At the same time, the determination of the oxide composition of the initial and intercalated samples was carried out in accordance with the methods of classical analytical chemistry (GOST 21216-2014).

IR spectra were taken on an Avatar 360 FT-IR Nicolet iS50 Thermo Fisher Scientific spectrometer with Fourier transform in the frequency range 400-4000 cm^{-1}. Thermogravimetric, differential thermal, and calorimetric analyzes were carried out on a Q-1500 D derivatograph in the range of 20-800°C in air at a heating rate of 5°/min.

Potentiometric titration was carried out using a pH-meter-millivoltmeter brand pH-410 with a combined electrode ESLK-01.7, the measurement error was 0.05 units.

The study of the electrokinetic potential was carried out by the method of macroelectrophoresis on a laboratory U-shaped tube, as well as on a Zetasizer Nano device (Institute of Physical Chemistry of Polymers). This device provides the ability to determine the hydrodynamic particle size.

IV. EXPERIMENTAL RESULTS

The preparation of intercalating agents is considered an important step in the intercalation process. Thus, one of the criteria for high yields of pillar materials is the stability of the modifying polycation itself. It is known that the stability of polyhydroxocations is greater for the ion that exists in solution at wide pH ranges [20]. The influence of the concentration and nature of the hydrolyzing agent, the temperature and duration of cation formation on the change in the pH of the medium of solutions of polyoxocations Cr^{3+}, Al^{3+} and Cr^{3+}/Al^{3+} were studied. The results obtained are consistent with the known literature data [21] and there are some distinctive points. A 1 molar solution of $CrCl_3 \cdot 6H_2O$ differs from this solution of $AlCl_3 \cdot 9H_2O$ in lower pH values. However, when solutions of a hydrolyzing agent (NaOH) are added at the same molar ratios (1:1), the pH values of the chromium salt solution system increase more. At the same time, the change in pH for more dilute solutions is contradictory, and the pH of 0.1 M solutions of Cr^{3+} and Al^{3+} increases from 2.8 and 3.5 to 4.5 and 4.2, respectively, when 1 M NaOH solution is added. The range of pH changes for the Al^{3+} salt solution is about 0.7, while for the Cr^{3+} solution it is about 1.7 units. For precipitation from solutions of Cr^{3+} and Al^{3+}, the necessary amounts of hydrolyzing agent are Me^{3+}/OH^- 2.65 and 2.6, respectively, while the solution has pH values of 5.3 and 5.1. The stability of Cr^{3+} polyoxocations is greater when they are synthesized in dilute solutions. Increasing the concentration narrows the range of pH values at which polyoxocation sols exist in solution. Heteronuclear polycations based on Cr^{3+} and Al^{3+} ions should be synthesized in a solution with an initial concentration of at least 0.5M. Probably, in this case, it is Al^{3+} ions that participate in the synthesis of polycation nuclei, and the larger the Al/Cr ratio, the wider the pH range of existence of polyoxocations in solution. The study of the influence of the ratio of these cations showed that the optimal concentrations of salts of the two metals is not less than 1:10±1 (Cr/Al). It is at such ratios that the highest values of the stability index are achieved, and this is evidenced by the wide ranges of pH (3.2≤5.2) for the existence of cations in solution. The study of the effect of temperature and the duration of the formation of polycations on the change in the pH of the medium showed that during aging at room temperature, the pH of the system changes little, and no visual changes are observed. And increasing the temperature of the system with Al^{3+} (0.5M Al^{3+}, $Al^{3+}/OH=2.4$) to 53-56ºC helps to reduce the pH of the system from 4.5 to 3.87 within 1-1.5 hours. These changes are associated primarily with the formation of sols of larger cations, due to which the concentration of OH ions in the solution decreases significantly and a decrease in pH is observed. Probably, at lower temperatures, the formation of sols of larger cations from smaller ones, which have already formed in the composition of the solution at the initial moment of potentiometric titration, does not occur. Judging by the change in the pH of the system, the mononuclear polycation based on Cr^{3+} ions is characterized by higher formation temperatures and the temperature range at which the pH decreases are 74-76ºC. From the results of the experiments, it is clear that the joint cation of Cr^{3+} and Al^{3+} ions conducts better at a temperature of 50ºC at the initial moment.

Experiments have established that the amount of intercalated cation has a direct dependence on the cation exchange capacity (CEC) (Table 1) of the original kaolin and the availability of these cations. In the case of montmorillonite, the amount of Me^{3+} cations intercalated into its layers is more than 3 times higher than the required calculated amounts. It is likely that this is due to the relatively easy expansion of montmorillonite layers in one medium and possibly the formation of a more complex structure than conventional periodic columns, such as in the case of [22]. This assumption, of course, will affect the results of X-ray phase analysis (Fig. 1)hours), then increase the temperature to 70ºC (within a day).

Table 1
The composition of the cation-exchange complex of the studied samples and their amounts

Sample	Na⁺	K⁺	Ca²⁺	Mg²⁺	Σ_cation
	мг экв/100 г				
NB	62,2	23,7	23,6	12,6	122,1
ЕК	4,4	9,1	6,1	5,8	25,4

In this way, numerous samples were obtained at various ratios of MM and pillaring cations. As it turned out to be the most optimal in terms of the largest amounts of the intercalated active component, i.e. the column between the MM layers and its stability in various media, the ratios of the Me^{3+} cation and montmorillonite (mmol/g) are considered to be 5.6 ± 0.2 mmol/g. The resulting samples were conventionally named Cr-MM, Al-MM and Cr/Al-MM. The calculated amounts of Me^{3+} polyoxocations per exchange cations EK are about 0.7-0.8 mmol per g EK, therefore, to achieve high yields of the process, the consumption of polycations was more than 1 mmol/g

To rachieve high yields of the ion exchange process, i.e. intercalation, their specific time and temperature conditions exist. Despite the low CEC values for EK, the process of polyoxocation incorporation takes quite a long time (at least 4 days), which is also affected by the size of the polyoxocation. An important role is also played by the stability of both the metal cation itself and the initial matrix. The rather long time course of the process of intercalation of kaolin is probably primarily due to the inaccessibility of exchange cations due to the stability of its structure in the aquatic environment. On the contrary, montmorillonite with an expanding structure easily exchanges interlayer cations and it takes about 18-22 hours to achieve equilibrium in the polyoxocation:montmorillonite system, depending on the nature of the starting material. Monovalent cations are more easily exchanged than polyvalent ones, which is primarily due to the stability of the bonds between the tetrahedral network and the interplanar cation. At the same time, the consumption of polyhydroxocation correlates well with the values of CEC of kaolin and, at the same time, the yield of the process for Cr-EK; Al-EK, and Cr/Al-EK is not less than 87; 92 and 88.6%, respectively, as evidenced by the results of the spectral analyzes performed (Fig. 2). In this case, the outputs are calculated from the total consumption of the pillaring cation

However, an increase in the Me^{n+}:MM ratio from the corresponding CEC values does not reduce the yields of the intercalation process, which is associated not with the exchange of interplanar cations, but with the adsorption of polycations in accessible pores and active sites of aluminosilicates. This conclusion was reached by studying the degree of leaching of active ions, as it turned out, intercalated polycations are resistant to temperature and other influences, and the degree of leaching into the aquatic environment is practically zero.
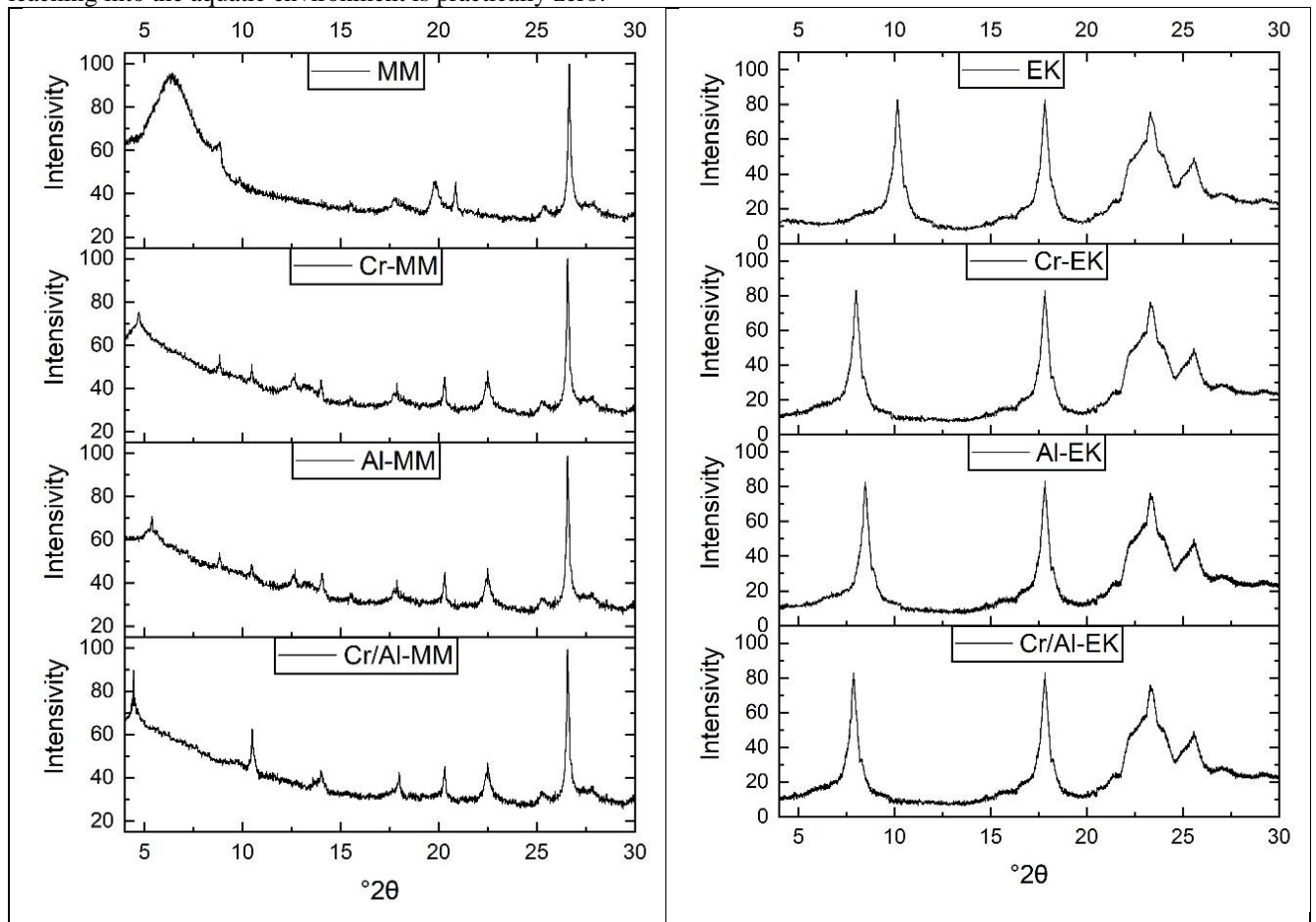

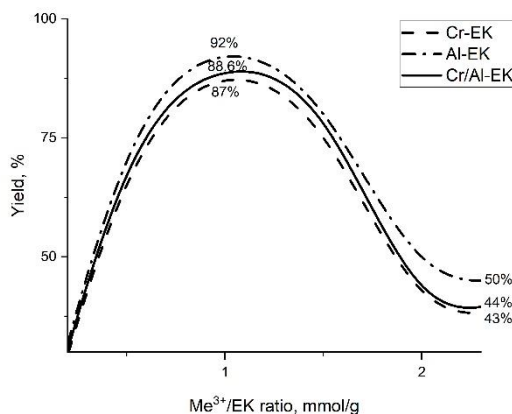**Fig.1. Segment of X-ray diffraction patterns of samples: (left) NB; (right) ЕК; 3)**

Fig.2. Influence of Me^{3+}/clay ratio (mmol/g) on the yield of the intercalation process

It is important to note that in the process of implementation or at early and late stages of modification, the use of mechanical action (ultrasound, microwaves, disintegrator grinding) can radically change the results of modification, especially, which is noticeable when used as a matrix for EK intercalation. In this case, an increase in CEC and EK dispersion is observed. However, such serious changes for MM are not observed, but still by controlling the process it is possible to increase the yield of the process by another 1-2%, which increases the economic effect of the process and reduces the water consumption for the needs of the process.

The XRD results showed that the value of d001, which determines the size of slit-like micropores, depends on the method of clay intercalation. The X-ray diffraction pattern of enriched bentonite is characterized by reflections at $2\theta=7.22°$ (I/I0=82%), which indicates an alkaline form of montmorillonite. During intercalation with Cr^{3+} polycations, the main reflection shifted towards smaller angles ($2\theta=4.75°$), which corresponds to an increase in the interplanar distance MM from 12.27 to 18.59 Å. It should be noted that the greatest value of the basal distance is achieved with the introduction of mixed polyoxocations (19.8 Å), which is probably due to the large size of the pillaring agents and their stability. As it turned out, mononuclear polycations based on Al^{3+} have a lower ability to push apart layers of montmorillonite and the d_{001} reflection corresponds to 5.36°. Meanwhile, the intensity of reflection (001) in this sample is somewhat weakened. At the same time, reflections characteristic of impurity phases (calcite) weaken or completely disappear, which is associated with the distance from the MM system during the modification processes.

Analysis of X-ray diffraction patterns of kaolin samples showed a slight shift during intercalation. The initial EK is characterized by a peak at $2\theta=9.5°$ and, upon intercalation, it shifts to a lower region of angles and becomes equal to 8.01; 8.5 and 7.9°, respectively, for Cr, Al and Cr/Al intercalated kaolin.

The results of X-ray phase analysis show an increase in micropores in the system of MM and kaolin as a result of pillaring. It is known that the introduction of metal oxide pillars causes a change in the magnitude of the surface charge of the layered system. In general, the pH of clay suspensions changes, and the point of zero charge (PZC) changes. This change is especially noticeable for MM, which is associated with a large number of introduced polyoxocations, which contribute to a change in the surface charge.

The relationship between pH and ζ-potential for the initial MM was positive in the pH range of 2–9.3 (Fig. 3). The pH of the medium affects the mobility of exchangeable cations adsorbed on the side faces and interplanar cations (mainly Na in our case), which causes a sharp increase in the electrokinetic potential.

The values of the ζ-potential for particles of intercalated MM in 0.1% suspension are practically similar. In our opinion, these values are not related to the conservation of the thickness of the electrical double layer; on the contrary, due to pillaring, the metal oxide columns should form an immovable part of the colloidal particle. However, despite this, the retention of negative values of the ζ-potential is associated with an increase in negative charges in oxide clusters. If the metal oxide clusters were not characterized by a large number of negative charges, pillaring would lead to an increase in the values of the electrokinetic potential due to a decrease in the electrical double layer. These assumptions are proved by the results obtained in the modification of MM with monomeric Al^{3+} ions.

There is a positive relationship between the percentage of clay, its fineness, and the ζ-potential of its suspension. Similar data were also obtained for EK. However, pillaring significantly affects the values of the ζ-potential of the EK suspension.
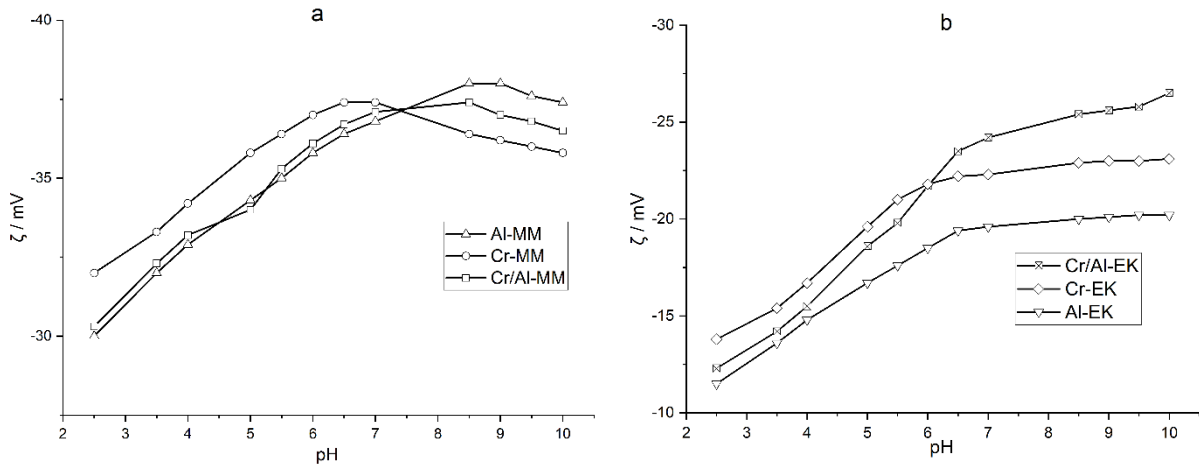
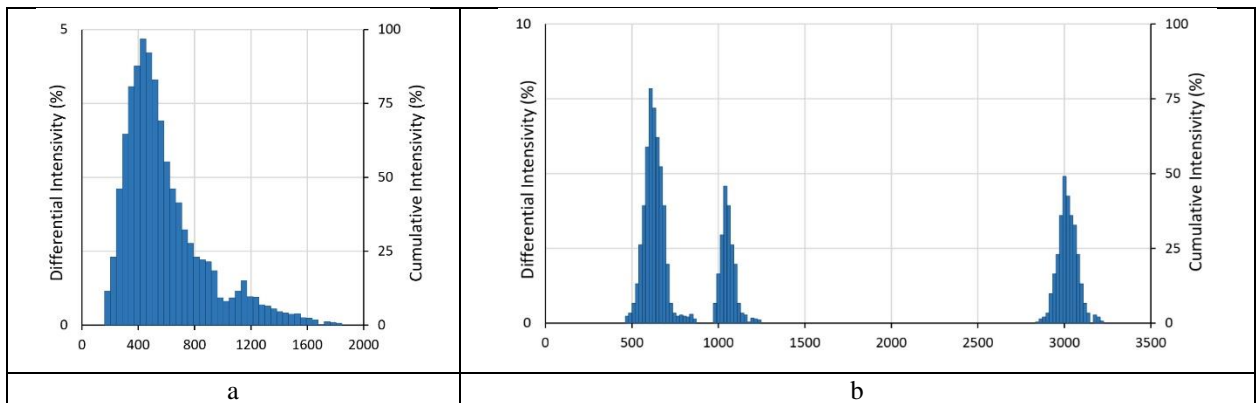**Fig.3. Dependence of ζ-potential on pH of 0.1% clay suspensions.**

Fig.4. Histogram of Particle size a) MM; b) EK.

Figure 4 shows data on the observation of particle sizes MM (a) and EK (b) in water. Thus, it can be seen from the figure that in the system under study, the size of MM particles varies from 0.1 to 1.8 µm, and in EK, within the range of 0.22–5.6 µm. montmorillonite (a) and kaolinite clay (b) in water (Fig. 4). The main part of MM clay is represented by particles with an average diameter of 300-450 nm. In the EK system, particles are observed with sizes of three different groups: 560-660; 1080-1100 and 3040-3200 nm.

Pillar materials are more uniform in terms of sample particle size, especially as seen with Al-MM. A noticeable change in the dispersion of particles is likely not only the result of modification, but also mechanical effects in the process of modification, which also leads to a decrease in the dispersion of the samples. The main part of Cr; Al and Cr/Al-MM are represented by particles with sizes of 180–220 nm, while for pillar kaolins, the characteristic particle sizes are about 500–600 nm. The system of pillar clays is more homogeneous, which is also confirmed by the values of the parameter of the degree of polydispersity (P), which have the following values (Table 2)

Table 2.
Polydispersity and average particle size values of samples (0.1% suspension)

Specifications	MM	Cr-MM	Al-MM	Cr/Al-MM
P	0,34	0,28	0,21	0,29
d_{avg}, µm	0,4±0,1	0,2±0,05	0,18±0,02	0,21±0,05

Table 3
Polydispersity and average particle size values of samples (0.1% suspension)

Specifications	EK	Cr-EK	Al-EK	Cr/Al-EK
P	1,20	0,44	0,53	0,39
d_{avg}, µm	1,2±0,1	0,5±0,05	0,5±0,05	0,5±0,05

The study of the surface characteristics of the synthesized materials showed that the point of zero charge of intercalated MM decreases by more than 0.8–1.2 units, while for EK the changes in the PZC are insignificant (Fig 5.). This indicates an increase in anionic centers on the surface of these materials, and the greater these changes, the greater the acidic properties of the intercalated ion itself ($Cr^{3+}>Al^{3+}$). In this aspect, the heteronuclear polyoxocations Cr+Al have average values. Therefore, the anion exchange activity and acidic properties of the resulting materials increase in this sequence.
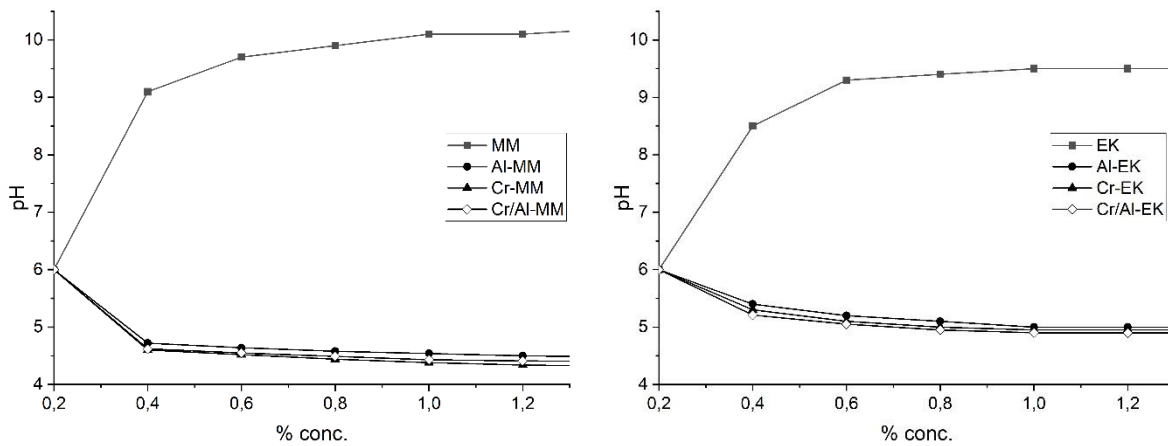

Fig.5. Changes in the PZC of samples

The study of the effect of heat treatment on the thermal stability of the samples showed that the thermal behavior of materials is also determined by the nature of the intercalating cation. The heat treatment of the samples probably causes the transformation of the metal oxyhydrate columns.
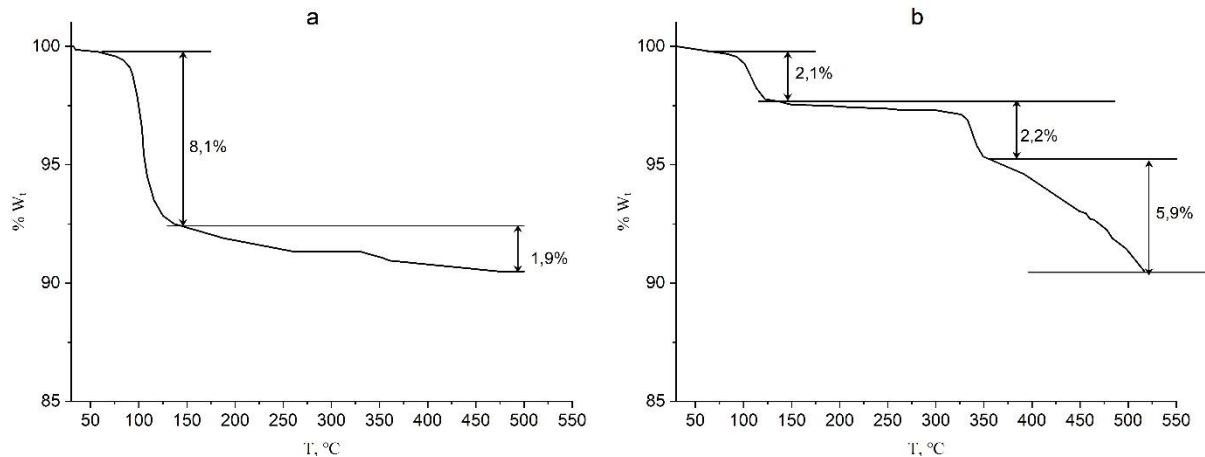

It is known that heat treatment of the original clay at temperatures above 100°C leads to irreversible adhesion of adjacent layers (especially at temperatures above 400°C) and deterioration of surface parameters. The results of TGA (Fig. 6) prove the removal of sorbed and chemically bound water at temperatures above 400°C. An increase in temperature to 500°C leads to further dehydroxylation of the montmorillonite surface and a decrease in the volume of interpacket slit-like pores. Further heating significantly affects the structure of the montmorillonite matrix

Fig.6. Thermogram of samples:a) MM; b) Cr-MM

For Cr pillarar MM, the thermal peak of the removal of physically adsorbed water and dehydroxylation was at 136 and 570°C, while for samples based on aluminum polyoxocations, the values of these peaks correspond to 121 and 497°C. In general, in all samples after modification, the total water content increased with a decrease in the amount of adsorbed water and an increase in its chemically bound form. The total heat treatment loss is about 10% for pillar MM and about 3.5% for pillar EK. The temperature of complete dehydration of kaolin pillars is higher than the corresponding MM pillars, which

shows the influence on the thermal stability of pillar materials not only of the nature of the pillaring agent, but also of the original matrix itself.

V. CONCLUSION AND FUTURE WORK

Thus, this study showed that the yield of the intercalation process is directly dependent on the CEC; therefore, minerals of the smectite group should have higher yields of the process. The intercalation of Cr and Al polyoxocations demonstrated an increase in the total volume of micropores, as evidenced by a change in the interplanar spacing. The results of the studies carried out make it possible to conclude that by regulating the process of introducing polyoxocations, it is possible to purposefully change the yield and surface characteristics of aluminosilicates. A change in the surface charge and thermal stability of pillar materials suggests a change in their acidity, which makes them promising in various catalytic processes.

REFERENCES

[1]. Gul N.R., Rutkov E.V., Tontegode A.Y., Usufov M.M. Atom and molecule intercalation of two-dimensional graphite film on metals. // Journal of Technical Physics. 1999. T. 69. . 9. P: 72-75. (In Russian)

[2]. Utashev E.I., Abdikalava A.B., Ashmetov I.D. Intercalated systems as adsorbents /Universum: chemistry and biology : electron. scientifically. 2020. 6/72. URL:https:///7universum.com/ru/nature/archive/item/9524 (In Russian)

[3]. Wang F., Li Z., Liu D., Wang G. Synthesis of magnetic mesoporous silica composites via a modified Stober approach // Journal of porous materials. 2014. V.21. P: 513-519.

[5]. Sinko K. Influence of chemical conditions on the nanoporous structure of silicate aerogels // Materials. 2010. V. 3. P: 704-740.

[6]. Barrer, B.R. Activation of montmorillonite by ion exchange and sorption complexes of tetra-alkyl ammonium montmorillonites / B.R. Barrer, D.M. MacLeod // Trans. Faraday Soc. – 1955. – Vol. 51. – P: 1290-1300.

[7]. Bergaya, F. Handbook of Clay Science / F. Bergaya, B.K.G. Theng, G. Lagaly // Elsevier: Amsterdam, Netherland – 2006. – Vol. 1. – P: 1224

[8]. Gil, A. Preparation and Characterization of Microporosity and Acidity of SilicaAlumina Pillared Clays / A. Gil, G. Guiu, P. Grange. M. Montes // J. Phys. Chem. –1995. – Vol. 99. – P: 301-312.

[9]. Kloprogge, J.T. Synthesis of Smectites and Porous Pillared Clay Catalysts: A Review / J.T. Kloprogge // J. Porous Mater. – 1998. – Vol. 5. – P: 5-41.

[10]. Pinnavaia, T.J. Intercalated Clay Catalysts / T.J. Pinnavaia // Science. – 1983. – Vol.220. – P: 365-371.

[11]. Sterte, J. Synthesis and properties of titanium oxide cross-linked montmorillonite /J. Sterte // Clays Clay Miner. – 1986. – Vol. 34. – P. 658-664.

[12]. Navalon S., Alvaro M., Garcia H. Heterogeneous Fenton catalysts based on clays, silicas and zeolites // Applied Catalysis B: Environmental. 2010. V. 99. P: 1-26.

[13]. J. Baloyi,T. Ntho and J. Moma. Synthesis and application of pillared clay heterogeneous catalysts for wastewater treatment: a review // RSC Adv., 2018, 8, p: 5197-5211.

[14]. Gil, A. Progress and perspectives on pillared clays applied in energetic and environmental remediation processes / A. Gil, A. Vicente // Curr. Opin. Green Sustain. Chem. – 2019. – Vol. 1. – P: 1-25.

[15]. Allouche, L. Al30: A Giant Aluminum Polycation / L. Allouche, C. Gerardin, T. Loiseau, G. Ferey, F. Taulelle // Angew. Chem. Int. Ed. – 2000. – Vol. 39. – №3. – P: 511-514.

[16]. Trewyn B.G., Slowing I.I., Giri S., Chen H.T. Synthesis and functionalizationof a mesoporous silica nanoparticle based on the sol-gel prosess and controlled release // Accounts of chemical research. 2007. V. 40. № 9. P: 846-853.

[17]. Santamaria E., Maestro A., Porras M., Gutierrez J.M., Gonzales C. Preparation of structured meso-macroporous silica materials: influence of composition variables on material characteristics // Journal of porous materials. 2014. V. 21. P: 263-274.

[18]. Hui, L. High performance photocatalysts: Montmorillonite supported-nano TiO2 composites / L. Hui, W. Zaiqin, L. Lingmin, C. Liang, L. Zhen, F. Jing // Optic. – 2017. – Vol. 136. – P: 44-51.

[19]. Hadjltaief, H.B. Photocatalytic degradation of methyl green dye in aqueous solution over natural clay-supported ZnO-TiO$_2$ catalysts / H.B. Hadjltaief, M.B. Zina, M.E. Galvez, P.D. Costa // J. Photochem. Photobiol. A. – 2016. – Vol. 315. – № 15. – P: 25-33.

[20]. Zuo, Q. Investigation on the thermal activation of montmorillonite and its application for the removal of U(VI) in aqueous solution / Q. Zuo, X. Gao, J. Yang, P. Zhang, G. Chen, Y. Li, K. Shi, W. Wu // J. Taiwan Inst. Chem. E. – 2017. – Vol. 80. – P: 754-760.

[21]. Kopylovich M.N., Kirillov A.M., Baev A.K. Formation of hydroxomplexes in the system Al3+-Cu2+-NO3-H2O /Journal of inorganic chemistry. 2000. T. 45. 5. C.888-891 (In Russian).

[22]. Burmistrova, N. N., Ivanova, E. N., Alekhina, M. B., Dudoladov, A. O., Konkova, T. V., & Maslova, O. A. (2018). Modification of montmorillonite clay for selective sorption of argon from mixture with oxygen. Sorption and chromatographic processes, 17(4), 657-666 (In Russian).

[23]. Mandalia, T., Crespin, M., Messad, D., and Bergaya, F. (1998) Large interlayer repeat distance observed for montmorillonites treated by mixed Al-Fe pillaring solutions. Chemical Communications, 19, 2111-2112.