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Effect of acid and alkaline treatment on physical-chemical properties of surface of natural glauconite

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Physical-chemical properties of the structure and the surface of natural (Glt-Nat) and modified by 2M H₂SO₄ (Glt-Ac); 2M NaOH (Glt-Alk) aluminosilicate samples containing glauconite were studied by means of XRD, SEM, BET-methods and catalytic conversion of methylbutynol (MBOH). It was observed that investigated sample was a mixture of mixed layered minerals of illite-smectite (I-S) series, having a I:S ratio of 50:50 and 80:20. The content of the mixed-layer mineral phase (I:S=50:50) changed as follows: 30-35% for Glt-Nat; 20-25% for Glt-Ac and 10-15% for Glt-Alk. The elemental composition did not significantly change after both types of treatment, whereas a twofold increase in specific surface area of Glt-Ac was observed. The catalytic conversion of MBOH after 10 min of reaction changed in the order: Glt-Ac (25.4%) > Glt-Nat (23.5%) > Glt-Alk (5.7%). The product yields distribution confirmed presence of both acid and basic sites on the surface, with the major contribution of acid sites. According to experimental yields of products formed over acid pathway of the reaction, acidity of unit surface area varied in the order: Glt-Nat > Glt-Ac > Glt-Alk. The chemical modification of natural sample caused an alteration of its surface acidity/basicity as observed from the ratio ($R_{a/b}$ values) of product yields normalized per unit area of surface. The highest $R_{a/b}$ was found for Glt-Ac (97.5), which was 3 times higher as for Glt-Nat (33.1) and 7.7 times that for Glt-Alk (12.6).

Keywords: natural glauconite, acid/alkaline activation, surface and characterization, surface active sites, catalytic conversion of methylbutynol

Влияние кислотной и щелочной обработки на физико-химические свойства поверхности природного глауконита

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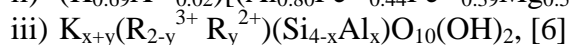
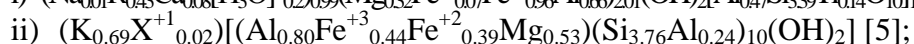
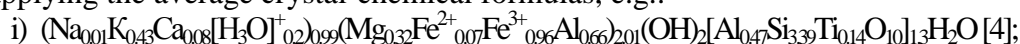
Физико-химические свойства структуры и поверхности природного (Glt-Nat) и модифицированного растворами 2M H₂SO₄ (Glt-Ac); 2M NaOH (Glt-Alk) алюмосиликатного образца, содержащего глауконит, изучены методами XRD, SEM, BET и каталитической конверсии

метилбутинола (МВОН). Обнаружено, что исследуемый образец является смесью смешаннослойных минералов ряда иллит-сметтит (I-S) с соотношениями слоев I:S равными 50:50 и 80:20. Содержание фазы I:S=50:50 изменилось следующим образом: 30-35% для Glt-Nat; 20-25% для Glt-As и 10-15% для Glt-Alk. Элементный состав значительно не изменился после обоих типов химической обработки, тогда как двукратное увеличение удельной поверхности было обнаружено для кислотно-активированного минерала. Каталитическая конверсия МВОН после 10 мин. реакции изменялась в ряду: Glt-As (25.4%) > Glt-Nat (23.5%) > Glt-Alk (5.7%). Распределение продуктов реакции подтвердило присутствие как кислотных, так и основных центров на поверхности, при наибольшем вкладе кислотных центров. Согласно экспериментальным значениям выхода продуктов, образуемых с участием кислотных центров, кислотность единицы поверхности минерала изменялась в порядке: Glt-Nat > Glt-As > Glt-Alk. Химическая модификация природного образца привела к вариациям в его кислотности/основности поверхности, как следует из значений отношения ($R_{a/b}$) выхода продуктов, нормализованных на единицу площади поверхности. Наибольшее значение $R_{a/b}$ было обнаружено для Glt-As (97.5), что в три раза выше, чем таковое для Glt-Nat (33.1) и в 7.7 раз выше, чем для Glt-Alk (12.6).

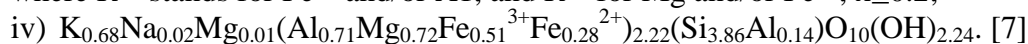
Ключевые слова: природный глауконит, кислотная и щелочная активация, характеристика структуры и поверхности, активные центры поверхности, каталитическая конверсия метилбутинола

Introduction

Natural layered aluminosilicates are represented not only by lamellar, but also by globular species, to which belong glauconites – the globules of a bright green color, as well as other mixed-layer minerals with a high iron content. Spherulite-like particles of these minerals consist of illite and smectite layers (2:1 layer type), which have uneven and unequal ratio between them along the volume of granules [1]. Glauconite is a typical marine mineral, being formed as a result of co-coagulation of Fe, Al and Si gels (products of decomposition of ash particles/volcanic glasses) in the interface of oxidative and reductive zones around fragments of organic matter and particles of Fe-Al smectite. Marine and sludge waters are the main sources of K^+ and Mg^{2+} , which diffuse to reductive micro systems [2-4]. Intensive involvement of K^+ -cations into mineral structure increases the number of mica packages that results in the more ordered mineral structure typical for more mature glauconites. The chemical composition of glauconite is commonly characterized by a higher content of Fe^{3+} ($Fe_2O_3 \sim 6,1-27,9\%$), to a lesser extent by Fe^{2+} ($FeO \sim 0,8-8,6\%$) and other micro elements. Depending on the age and a degree of maturation, glauconites significantly vary their chemical composition that is expressed by applying the average crystal-chemical formulas, e.g.:



where R^{3+} stands for Fe^{3+} and/or Al, and R^{2+} for Mg and/or Fe^{2+} ; $x \geq 0.2$;



Nevertheless, the geological age (Cretaceous or Tertiary glauconites) has little to do with the composition of glauconites. Of greater importance in determining the composition of a glauconite, is the specific environment, in which the glauconite was formed, particularly, the degree of iron concentration, its Red-Ox state and opportunities of iron oxidation and/or K^+ -fixation [10, 11].

The type of a cation, which is generally occupying the octahedral positions (more than a half of the total sum of octahedral cations, e.g. about 1.0 f.u.(formula unit), attributes minerals of the glauconite group to one of the three types [8]: ferrous (Fe^{3+}), aluminium or magnesium glauconite [7]. The changes in the composition of octahedral cations cause an alteration of the ratio of tetrahedral cations as well as anions, mainly OH^- and F^- , i.e. the generally ferric minerals have a higher Si content along with a lower

tetrahedral Al^{3+} content, whereas aluminium and magnesium glauconites comprise higher F content, reaching about 1.8% (or 0.4 f.u.) [8].

The high layer (~0.35 in tetrahedral; ~0.47 in octahedral sheet [9]) and the interlayer (0.46-1.23 [9]) charges, as well as the fraction (<5-10% [12]) of swelling (smectite) layers present in glauconite samples, determine their physical-chemical properties, namely, lack or almost no swelling, high cation-exchange capacity (CEC~6-14 mg-eq/100 g [12, 14, 15], low specific surface and porosity [16, 17]. Owing to a high CEC, glauconites are widely applied in processes of ion-exchange treatment of water from hardness ions [18-20], as well as heavy metal ions and radionuclides [21, 22].

Nevertheless, weak porosity and low specific surface area of natural glauconites may constrain their use for a sorption extraction of larger molecules and ions, assuming their modification or activation. Commonly, natural aluminosilicates on the base of layered, layered-band and/or framework minerals have been activated by thermal, chemical (acid, alkaline, [23, 24], salt [19, 20, 25, 26]), mechanical [27], field (microwaves, magnetic fields [28, 29]) modifications. Recent, though a few studies of natural glauconites illustrated that they were able to vary their sorption properties under mechanical [30], chemical (exposure of acid [16, 19], manganese oxides [31], salts [18, 20]), and microwave exposures [32], however, the detail behavior and mechanism of transformations of the structure and properties of glauconites (globular structure) are still faintly studied.

The present work investigates surface characteristics, nature and type of surface active sites of natural (Glt-Nat), acid- (Glt-Ac) and alkali-treated (Glt-Alk) glauconite in order to elucidate the mechanism of the structure and surface properties transformation under effect of reagent modification.

Experimental

Natural probes collected on the area of Voronezh anticline [2] were consequently prepared by precipitation and electromagnetic separation on the SIM-1 in order to obtain 90-95% content of glauconite in the sample. For acid and alkaline treatments samples of glauconite were correspondingly exposed of 2M solutions of H_2SO_4 or NaOH at 371K for 6 h [22]. Afterwards, samples were washed to neutral pH, dried, crashed and sieved into fraction 200-315 μm .

XRD-method was used to characterize phase composition and structural transformations of the samples using Ultima-IV diffractometer (Rigaku, Japan). The following working mode was applied: 40 kV; 40 mA, Cu-X-ray target, Ni-filter, 2 θ measuring range - 5-65 $^\circ$ 2 θ , Minimum step size 0.02 $^\circ$ 2 θ , fixed system of focus slits.

The samples were studied both in non-oriented (in the plane of the substrate support for XRD-analysis) and oriented states, prepared from a diluted suspension, in air-dried state and after saturation in vapours of ethylene glycol for 48 h.

The diagnostics of mineral composition was done by comparing the experimental and reference spectra from the database PDF-2 using software package PDXL, Rigaku. For the quantitative analysis, the method of full-profile processing of X-ray patterns from the non-oriented samples [36] was used applying a RockJock software [37]. Well-crystallized zincite (ZnO-10%) was applied as an internal standard.

Mathematical modeling of X-ray patterns [38] obtained for the oriented samples in air-dried and ethylene glycol saturated states were carried out using software Sybilla (Sevron). The primary task was to choose a model of a mixed-layer structure of illite-smectite type and clarification of structural features.

SEM-measurements were carried out using Scanning electron microscope Hitachi SEM S3200-N and a supplement EDX-system Oxford Inca X-act with a SDD on the INCA-software.

BET-nitrogen adsorption. Surface characteristics of glauconite samples were determined by BET-method using the Quantachrome Autosorb-1. For this, 0.3 g of the sample was out gassed at 300 °C for 90 min. The BJH-method was applied for pore size distribution assessment.

Catalytic conversion of methylbutynol (MBOH) was applied to characterize the type and activity of surface sites [5]. A 150 mg charge of sample was placed in a steel reactor and activated at 400 °C consequently in the flow of air (4h) and N₂ (4h) with a flow rate of 50 L/h. After cooling down the reactor to reaction temperature $t_{\text{reac}}=250^{\circ}\text{C}$, the reaction mixture of 95% of 2-methylbut-3-yn-2-ol (MBOH) and 5 % of hexane was allowed to contact to the catalyst applying a static pressure of N₂. Reaction products formed on acid (Prenal, MBYNE), basic (acetone, acetylene) or coordinately unsaturated (HMB, MIPK) sites were analysed by a Hewlett-Packard Model 5890 series II gas chromatograph connected on-line to the reactor outlet and equipped with a capillary column (Optima Wax, Macherey-Nagel) [34].

Results and discussion

Effect of acid and alkaline activation on the structure of glauconite.

X-ray diffraction patterns of natural and activated glauconite samples are shown in Fig. 1. It follows from the analysis of the XRD- patterns from non-oriented samples (Fig. 1) that dioctahedral layered aluminosilicates of 2:1 layer type group predominated in all investigated samples. These aluminosilicates include minerals of the next series: illite-smectite, smectites and mixed-layered clay minerals of illite-smectite (I-S) series. The rather distinct non-basal reflexes obviously testified to a well-ordering of a micaceous component of the polytype 1M as a part of mixed-clay minerals. This ordering is due to a natural bias of the layers relative to each other by $\pm 120^{\circ}$. The admixture of non-clay minerals (quartz) was less than 3-5% according to the full-profile quantitative analysis.

The similarity of XRD-patterns of the powders of mixed-clay minerals and defect mica minerals required their analysis in oriented state. The most significant differences of clay minerals from each other are in their parameter C, which is strongly affected by the type of packages in the mineral structure and the nature of their alternation. Mathematical modeling of the diffraction patterns of oriented samples in air-dry state and after the saturation allowed clear distinguishing between the discrete minerals (illite-glauconites and smectites) and mixed-layered clay minerals of illite-smectite series (Fig. 2).

Analyzing the XRD-patterns in Fig.2, it is observed a significant amount of a swelling component by a clear shift of basal reflexes and a change in their intensities ratio. The main phase component was a disordered mixed-layered formation of I-S series with a prevailing of I-S interlayers (ratio ~ 20:80). The main basal reflections are shown in Fig. 2. The low intensities of even reflexes illustrated a high amount of isomorphic iron in the structure of micaceous component. This phase may be attributed to glauconite-smectites; however, the term «illite-smectite» is more common for the mixed-layered minerals.

The swelling mineral was represented as a disordered mixed-layered mineral illite-smectite with almost the same ratio of illite and smectite interlayers (50:50). This phase appeared distinctly as a shift of the first reflex within the 12-15 Å range in air-dry state towards 17-18 Å in ethylene glycol saturated state. The amount of I-S (50:50) phase changed for different samples. The highest content of this phase, nearly 30-35%, was

reached in natural sample Glt-Nat, followed by its decrease to 20-25% after acid treatment and to 10-15% after alkaline treatment.

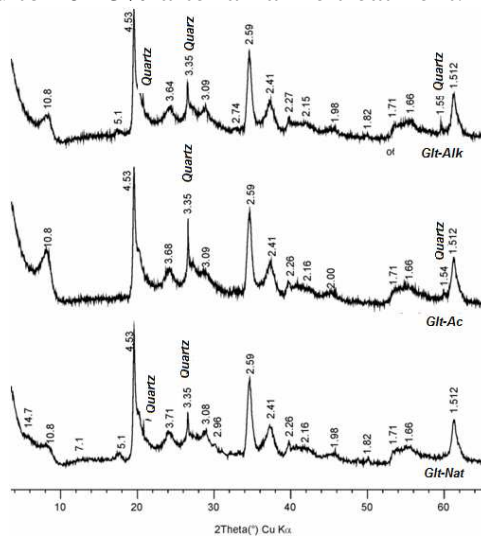


Fig. 1. X-ray diffraction patterns of non-oriented samples of natural (Glt-Nat), acid- (Glt-Ac) and alkali- (Glt-Alk) treated glauconite

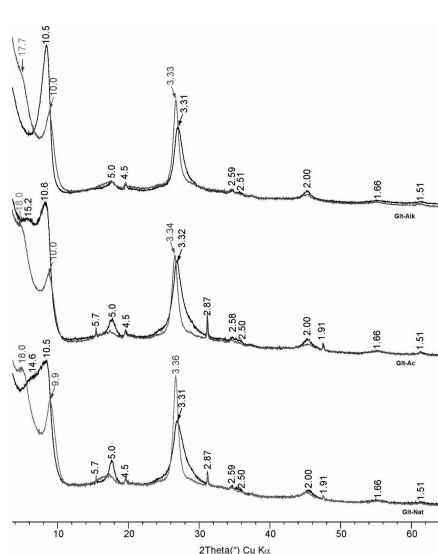


Fig. 2. XRD-patterns of oriented samples of natural (Glt-Nat), acid- (Glt-Ac) and alkali- (Glt-Alk) treated glauconite

Due to the fact that investigated samples are a mixture of mixed-layered clay minerals of glauconite-smectite and illite-smectite series, they can not be attributed to «glauconites». According to the recommendations of the International Committee on Clay minerals (AIPEA), there should be no swelling interlayers in the structure of true glauconites and illites [35], otherwise, the samples are attributed to the mixed-layered formations [39, 40]. Hereinafter, the investigated samples are referred as mixed-layered mineral (MLM) of I-S series.

The relief of the particle surfaces of the investigated MLM before and after chemical treatment is shown in Fig.3.

The particles of natural MLM-sample are represented by the granules of an elongated shape with a slightly expressed layered morphology. The agglomerates with a fine flaky shape found in natural samples confirmed, apparently, the presence of smectite. After acid and alkaline treatment the form of granules did not significantly change, although a more layered relief was observed. The elemental composition of natural and activated MLM are given in Table 1.

As follows from Table 1, the elemental composition of natural and activated MLM was represented by i) Si, Al, O atoms in the mineral structure forming a tetrahedral sheet of the crystal; ii) atoms of Al, Fe, Mg, O, included in the octahedral grids. The exchangeable cations of natural sample are represented, mainly, by potassium and calcium ions. In small quantities found Cr and Ti, apparently in the form of the respective oxides due to the presence of impurities in natural sample.

For the samples treated by acid (Glt-Ac) there were no significant changes in the elemental composition found, in the contrast to the montmorillonite containing samples studied before [41]. This demonstrated a relative stability of the structure of the investigated MLM against the acid attack. Obviously, a stronger interaction of the layers in the I-S mixed layered mineral resulted in the lack of layer and interlayer swelling, thus,

preventing the penetration of the acid and its interaction with the elements of the crystal lattice.

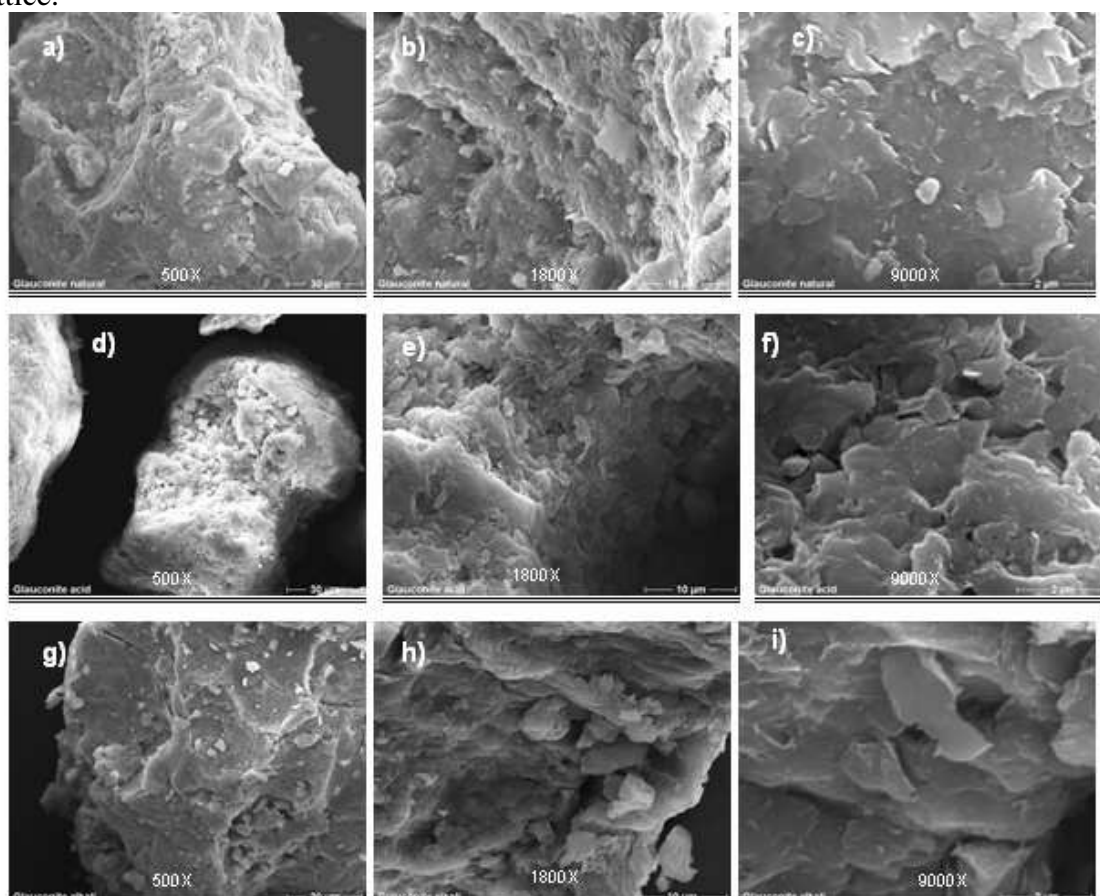


Fig. 3. SEM-images of investigated glauconite samples: natural (a)-(c); acid-treated (d)-(f); alkali-treated (g)-(i). Resolution: 9000x, 1800x, 500x.

Table 1. Elemental composition of natural and activated mixed-layer mineral of illite-smectite series

Element	Content, atom%		
	<i>Glt-Nat</i>	<i>Glt-Ac</i>	<i>Glt-Alk</i>
O	72.10	72.58	72.12
Na	-	-	1.21
Mg	1.54	1.51	1.49
Al	3.66	3.45	3.35
Si	15.86	15,39	14.39
K	1.74	1.75	1.64
Ca	0.42	0.40	0.98
Cr	0.05	-	-
Fe	4.48	4.75	4.46
Ti	0.11	0.18	0.36
S	0.05	-	-
Total	100.00		

In the case of alkaline treatment, the content of Si has slightly decreased as a result of its chemical interaction with alkali forming sodium silicate. As a consequence, Na content increased in the elemental composition of the Glt-Alk sample. Besides, a non-

exchange uptake of Na^+ -ions was possible as well as, to a lesser extent, an ion-exchange of K^+ for Na^+ could occur.

Surface characteristics of natural and activated MLM of illite-smectite series.

Fig. 4 shows nitrogen adsorption and desorption isotherms on natural and activated by solutions of sulfuric acid and sodium hydroxide MLM-samples. The resulting isotherms are characterized by a presence of hysteresis loop caused by a capillary condensation of nitrogen. According to the IUPAC classification, this type of isotherm indicates at the presence of meso pores in an adsorbent. For the Glt-Nat and Glt-Alk samples, the isotherms were practically identical that indicated at the small changes in the surface properties of the sample due to the alkaline treatment. The isotherms obtained for the Glt-Ac sample lie higher, providing the volume of N_2 -adsorbed twice as high as for the natural sample. Hence, the acid treatment of natural sample promoted an activation of its surface and adsorption properties due to a partial destruction of the mineral structure, dissolution of its swelling smectite layers, which are less resistant to acid exposure.

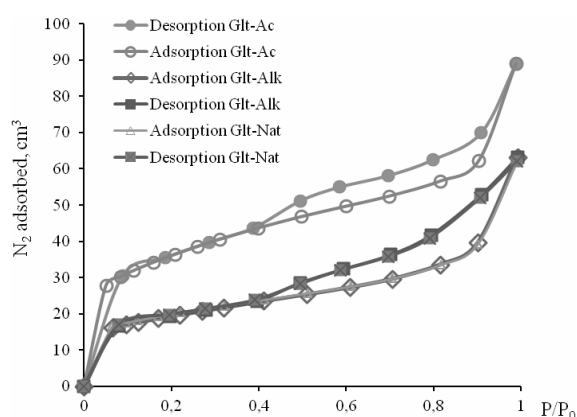


Fig. 4. Isotherms of adsorption and desorption of nitrogen by natural (GltNat), acid- (Glt-Ac) and alkali- (Glt-Alk) treated MLM mineral

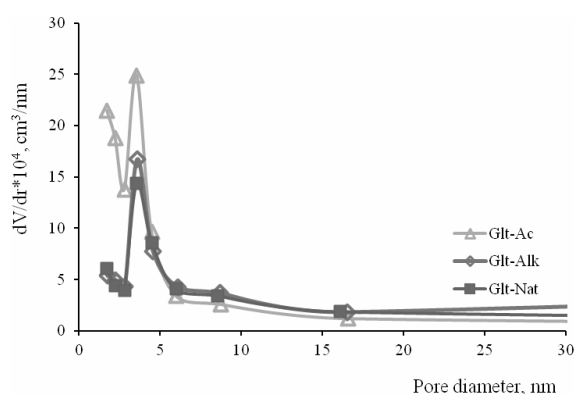


Fig. 5. Pore size distributions of the natural (Glt-Nat), acid- (Glt-Ac) and alkali- (Glt-Alk) treated investigated MLM of illite-smectite series

Pore size distributions of the investigated samples calculated from the BET-desorption isotherms are shown in Fig. 5.

It follows from Fig. 5, that the pore size of investigated samples varied mainly within the 2.8-5.9 nm range, which corresponds to diameter of meso pores. The mean pore diameters and specific surface area values of the natural and modified samples are summarized in Table 2. As a result of acid treatment the fraction and the volume of meso pores increased approximately in two times by a slight decrease of the mean pore diameter. By the alkaline treatment the fraction (~14%) and the diameter of meso pores slightly increased.

As a result of acid treatment the values of specific surface area of the mineral (Table 2) increased approximately two times. The main reason for this is the action of the acid mainly on the swelling illite-smectite layers (see above the results of XRD-studies), which resulted in the dissolution of the smectite component of an aluminosilicate and lead to an increase in the specific surface area of the sorbent. The proportion and the volume of mesopores increased by about two times, whereas the average pore diameter slightly decreased, apparently, due to an increased proportion of micropores formed during acid treatment. In case of alkaline treatment, the proportion (~5%) and the diameter of mesopores slightly increased.

Table 2. Specific surface area and pore diameter of natural and activated mixed-layered mineral «illite-smectite»

Sample	Specific surface area, m ² /g	Pore diameter, nm	Pore volume, cm ³ /g			Total pore volume, cm ³ /g
			Micro	Meso	Macro	
Glt-Nat	66	5.7	0.003	0.217	0.086	0.306
Glt-Ac	127	4.4	0.010	0.391	0.122	0.523
Glt-Alk	64	5.9	0.003	0.228	0.089	0.321

The action of the alkaline treatment practically did not change the specific surface area of the mineral. This is, probably, due to the simultaneous action of two factors: the dissolution of the swelling layers along the tetrahedral planes and an amorphization of the surface due to formation of insoluble sodium silicates.

Catalytic properties of natural and activated aluminosilicates.

Fig. 6 represents changes of the conversion of MBOH on time of the catalytic reaction over surfaces of the investigated mineral.

As follows from Fig. 6, the catalytic activity of Glt-Nat and Glt-Ac was comparable and approximately three times lower than that of a synthetic zeolite H-ZSM-5, which was used as a reference material. Conversion of MBOH on the surface of Glt-Alk proceeded with the lowest intensity. A decrease in the conversion on time indicated at the deactivation of the catalyst due to adsorption of reaction products [42, 43].

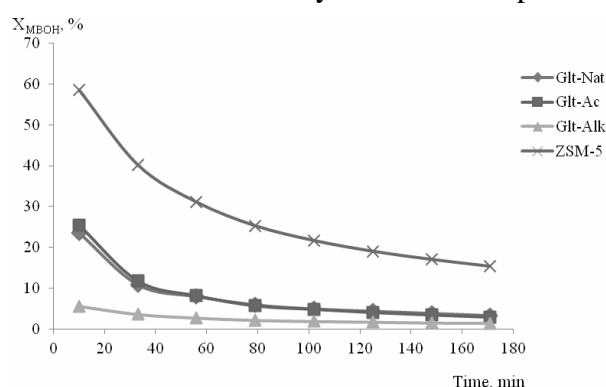


Fig. 6. Changes of MBOH conversions on time of catalytic reaction over the surfaces of Glt-Nat, Glt-Ac, Glt-Alk and a synthetic zeolite ZSM-5 (reference)

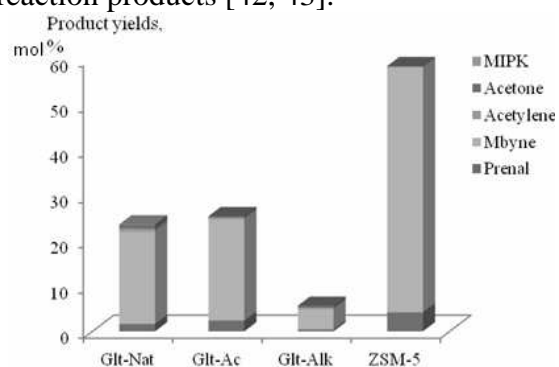


Fig. 7. Yield of products of MBOH conversion for Glt-Nat; Glt-Ac; Glt-Alk and ZSM-5 (reaction time is 10 min)

The yields of products formed during the catalytic reaction are summarized in Fig. 7. The major products of MBOH catalytic conversion MbyNE and Prenal formed over acidic pathway of the reaction. According to the reaction mechanism [33], acid sites of zeolites are represented mainly by bridged SiO(H⁺)Al hydroxyl groups (strong acid sites) and Si-OH groups (weak acid sites). For clay minerals, the protons of water molecules polarized by exchangeable cations within an interlayer space may significantly contribute to activity of acid sites. The source of the specific catalytic activity (SCA) of illite-smectite (I/S) clays is their Bronsted acidity resulting from the dissociation of water molecules bonded to exchangeable cations in the interlayers of the smectite and on the external basal surfaces of illite platelets [44]. Additionally, it was shown [44] that SCA of a cation site resulting from tetrahedral substitution of Al³⁺ for Si⁴⁺ was about 40 times greater than that of a site of octahedral origin. There was a linear relationship between the

SCA values and a platelet thickness of different micas and illites, confirming the major contribution of the external basal surfaces to the catalytic activity.

Acid activation of the investigated MLM aluminosilicate of illite-smectite series caused only a slight increase (less than 2 %) in the yield of products formed on acid sites despite a remarkable rise of SSA.

It should be noted that the products of the basic reaction pathway - acetylene and acetone, are also formed owing to surface basic groups. The low product yields testify to a weak basicity of the surface, which is further decreased after acid treatment due to dissolution of Al_2O_3 and Fe_2O_3 .

The alkaline activation of natural aluminosilicate sample caused a significant reduction in the yield of acidic products as well as in the overall conversion of MBOH. The main reasons for such effects of alkali are, obviously, a partial dissolution of Si, an amorphization of the surface and the absence of changes in the specific surface area of the sample.

To compare the effect of reagent modification on the physical-chemical activity of the surface of the investigated MLM, the values of MBOH conversions and product yields were normalized per unit surface area (Table 3).

Table 3. Values of MBOH conversion and yields of reaction products normalized per unit surface area

Sample	$X_{\text{MBOH, \%}}$ (10 min of reaction time)	Specific surface area, m^2/g	$X_{\text{MBOH}}/S_{\text{BET}}$, $\% / (\text{m}^2/\text{g})$	Product yields		$R_{\text{a/b}}$, mol/mol
				$A_s \cdot 10^3$, $\text{mol}\% / (\text{m}^2/\text{g})$	$B_s \cdot 10^3$, $\text{mol}\% / (\text{m}^2/\text{g})$	
Glt-Nat	23.5	66	0.4	331	10	33.1
Glt-Ac	25.4	127	0.2	195	2	97.5
Glt-Alk	5.7	64	0.1	76	6	12.6
ZSM-5	58.5	370	0.2	157	0	-

A_s – yield of products formed on acid sites normalized to S_{BET} , $\text{mol}\% / (\text{m}^2/\text{g})$; B_s – yield of products formed on basic sites normalized to S_{BET} , $\text{mol}\% / (\text{m}^2/\text{g})$; $R_{\text{a/b}} = A_s/B_s$, mol/mol.

It follows from Table 3, that the highest catalytic conversion of MBOH was observed for unit surface area of Glt-Nat, decreasing in the order: Glt-Nat > Glt-Ac=ZSM-5 > Glt-Alk. According to A_s values, the highest acidity, which provided the highest yield of products over acid sites, was found also for Glt-Nat comparing to the other samples. This can be caused either by stronger acid sites on the surface of Glt-Nat or by their higher concentration. The $R_{\text{a/b}}$ values testified to an alteration of surface acidity/basicity under exposure of acid or alkali during modification. The highest values of $R_{\text{a/b}}$ for Glt-Ac pointed out, obviously, to a weakening of surface basicity, moreover, A_s indicated about weakening of surface acidity for Glt-Ac as well. However, when comparing the $R_{\text{a/b}}$ values for Glt-Nat and Glt-Ac samples it follows that for Glt-Ac the contribution of acid sites to catalytic conversion of MBOH was 3 time higher than that for basic ones, although acidity of unit area of surface was reduced after acid treatment.

Conclusion

Study of the physical chemical properties of the surface and the structure of natural and modified aluminosilicate samples, containing glauconite, found out that the investigated sample should be attributed to a mixture of mixed-layer minerals of illite-

smectite series with a ratio of I:S=50:50 and 80:20. Acid and alkaline treatment did not significantly change the elemental composition of the sample. The twofold increase in specific surface area of the acid treated aluminosilicate sample was mainly caused by the dissolution of the smectite layers as confirmed by XRD-data, providing rise of mesopore volumes.

Catalytic conversion of MBOH revealed higher surface acidity of the natural and acid treated aluminosilicate sample as compared to alkali-treated one. Normalized values of product yields per unit area of surface testified to a decrease of surface acidity in the order: Glt-Nat>Glt-Ac>Glt-Alk, due to the changes in chemical composition and the strength/number of active sites.

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