

SURFACE CHEMISTRY AND POROSITY OF NATURAL AND ACTIVATED ALUMINOSILICATE FROM MONTMORILLONITE AND CLINOPTILOLITE

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Influence of acid and alkaline activation on the surface characteristics of natural combined aluminosilicate sorbent $M_{45}C_{20}$ containing montmorillonite and clinoptilolite components has been studied by means of IR-spectroscopy and isopiestic method. The shifts of absorption bands in the IR-spectra proved that both acid and alkaline treatment caused opening of Si–O–Al bonds followed by dealumination of sorbent and formation of groups Si–OH. The formation of amorphous phase of silica was observed upon acid treatment as a result of the destruction of octahedral layers of montmorillonite. Isotherms of water vapor sorption by natural $M_{45}C_{20}$ (MCnat) and activated $M_{45}C_{20}$ by acid and alkali (MCAc and MCAlk) have been studied. BET-theory was successfully applied for calculation of the specific surface area. The sorption capacity for water increases in the order: MCnat < MCAc < MCAlk. It has been found that the specific surface area of natural combined aluminosilicate sorbent increases under acid and alkaline treatment by 1.3 and 1.5 times, respectively.

Keywords: aluminosilicate, activation, acid and alkaline treatment, surface characteristics

INTRODUCTION

Natural aluminosilicates are widely used in processes of sorption purification of gaseous and liquid substances [1, 2], catalytic conversion of various compounds [3], production of porous silicas and catalyst supports [4, 5], fillers of different composite materials and in many other fields. The reason for such wide applications lies in diversity of their mineral structure which reveals unique properties even in the natural state, as well as in their ability to acquire new tailor-made properties after modification and activation [6]. An advantage of industrial use of natural clay minerals in comparison with synthetic materials is their low cost which allows avoiding regeneration of waste sorbents and to utilize them as additives in building or other industries [7].

The structure of aluminosilicate materials can be represented by different components – clay layered (montmorillonite), hard-sphere framework zeolite (clinoptilolite) and others. Physicochemical and surface properties of clay minerals are

determined by their porous structure and different active sites on the surface such as exchangeable cations, coordinatively unsaturated ions Al^{3+} , Mg^{2+} , Fe^{3+} , acid/basic hydroxyl groups and oxygen anions [8, 9]. In order to produce tailor-made catalysts and sorbents, montmorillonite- and clinoptilolite-containing clays are activated by various methods of treatment, such as thermal treatment [10], ion exchange [11, 12], treatment with acids [13, 14] and alkalis [15, 16]. Currently, montmorillonite minerals are often modified in such processes as grafting [17], silylation [18] or intercalation [19, 20] due to their capability to swell.

The essence of activation is that the chemical composition of minerals is selectively modified, which results in an increase in the specific surface area, specific pore surface [14] and thermostability, changes in pH of the surface, interlayer charge density, surface hydrophilicity/hydrophobicity, etc. However, the presence of different structural components, including admixtures and impurities, in natural minerals causes the necessity of mineral purification and/or separation thus increasing

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production costs and limiting their applications. In addition, the response of various structural components of a mineral towards a modifying agent is different.

The present work is aimed at regulation and assessment of surface characteristics of natural composite aluminosilicate sorbent $M_{45}C_{20}$ containing clay and zeolite structural components using its acid and alkaline activation.

MATERIALS AND METHODS

Natural mineral sorbent $M_{45}C_{20}$ from the Sokymytsky deposit (Ukraine), which has nanosized pores (average pore diameter ~ 3 nm), was studied. The sorbent is a multicomponent porous system consisting of the clay component (montmorillonite (M) – 45 %) and the zeolite component (clinoptilolite (C) – 20 %). In addition to the above mentioned major structural components, such minerals as goethite (10 %), illite (15 %), and calcite (10 %) were also present in the sample [21]. The natural sorbent (particle fraction < 0.25 mm) was activated by treating it with 2.33 M H_2SO_4 (MCAc) and 2.0 M NaOH (MCAIk) solutions at a 1:5 ratio of solid phase / activator solution under constant stirring at 371 K for 6 h [14, 22]. The resulting pulp was filtered through filter paper. The solid deposit was washed with distilled water until the reaction of rinse waters was neutral and then dried to a constant weight at 378 K.

IR-spectra of natural and activated aluminosilicate samples were recorded on a "Vertex 70" spectrometer in a frequency range 400–4000 cm^{-1} . Prior to analysis 2.5 mg of sample and 250 mg of dried KBr were stirred in an agate mortar for 10 min, and then compressed for 30 min under pressure of 0.8–1.0 $\cdot 10^4$ kg/cm².

The water vapor sorption by the investigated sorbents was studied by means of isopiestic method. Relative water vapor pressure was varied within 0.07...0.98 range using saturated solutions of NaOH and salts with known activity values at 295 \pm 1 K. Samples of sorbents (0.0700 \pm 0.0002 g) dried at 378 K till a constant weight were placed into desiccators, filled with saturated solutions, then placed into a thermostat (295 K). The time for reaching isopiestic equilibrium depended on relative pressure of the solvent being between 20 and 30 days. Reaching constant weight of a sorbent indicates attaining equilibrium.

The specific surface area of the samples was calculated isopiastically from the water vapor sorption isotherm of the samples [23].

The true and apparent densities of the adsorbents were determined using the procedures described in [23]. The porosity structure of the samples was calculated using formulas proposed in [24].

RESULTS AND DISCUSSION

IR-spectra of natural and activated samples of aluminosilicate sorbent $M_{45}C_{20}$ are given in Fig. 1. Assignment of absorption bands was done according to [25, 26].

In the IR-spectrum of the natural sorbent MCnat (Fig. 1, line 1) it is possible to distinguish three characteristic regions of absorption.

1. Absorption bands of hydroxyl groups of water molecules in a range of frequencies 3700–3000 cm^{-1} . A broad absorption band with two maxima at 3610 and 3408 cm^{-1} testifies to the presence of free hydroxyl groups on the surface, in an interlayer and canals cavities (first maximum) and those bound in different ways by hydrogen bond OH-groups in structural constructions like Al–OH, Si–OH with molecules of H₂O (second maximum).

2. Absorption in a frequency range 1700–1300 cm^{-1} . A characteristic absorption band at 1624 cm^{-1} arises from bending vibrations of OH-groups of hydrate water adsorbed by the exchanged cations. A medium intensity absorption band at 1421 cm^{-1} is a consequence of superposition of absorption due to bending vibrations of OH-groups in structures Si–OH, Al–OH, Mg–OH, and Fe–OH present in octahedral sheets of montmorillonite.

3. The region of stretching and bending vibrations of Si–O groups at 1300–400 cm^{-1} . For the natural sorbent $M_{45}C_{20}$ in this region there is typical an absorption band of sufficient intensity at 1030 cm^{-1} , which can be attributed to intra-tetrahedral and intra-octahedral stretching vibrations of Si–O–Si and Si–O–Al bonds. Medium and weak intensity absorption bands at frequencies 707, 580, and 462 cm^{-1} correspond to combined vibrations: bending vibrations of Si–O bonds and stretching vibrations of Al–O bonds, which form the structure of the natural sorbent. In this region there is also an absorption band at 874 cm^{-1} attributed to C–O bond vibrations in carbonates [27]. Both acid and alkali chemical activation of sorbent $M_{45}C_{20}$ led to structural changes in its IR-spectrum.

A treatment with hot sulfuric acid resulted in a broadening of the absorption band at 1030 cm^{-1} (Fig. 1, line 2), which also shifted to the higher frequency of 1140 cm^{-1} reflecting an increasing

number of Si–O–Si groups in the structure of MCAc sample. Furthermore, it indicates an increasing molar ratio $\text{SiO}_2/\text{Al}_2\text{O}_3$ due to dealumination of minerals by acid activation [9]. A shoulder appeared at 943 cm^{-1} in the broad band in the region $900\text{--}1100\text{ cm}^{-1}$, corresponding to vibrations of Si–OH bonds, which compensate excess of the negative charge of a framework due

to a removal of structural Al and a breakup of Si–O–Al bonds [25]. An absorption band at 580 cm^{-1} is mostly sensitive to presence of residual Al^{3+} -ions in octahedral layer, and after sulfuric acid treatment shifts to a higher frequency of 590 cm^{-1} , which also confirms dealumination of octahedral layers [28].

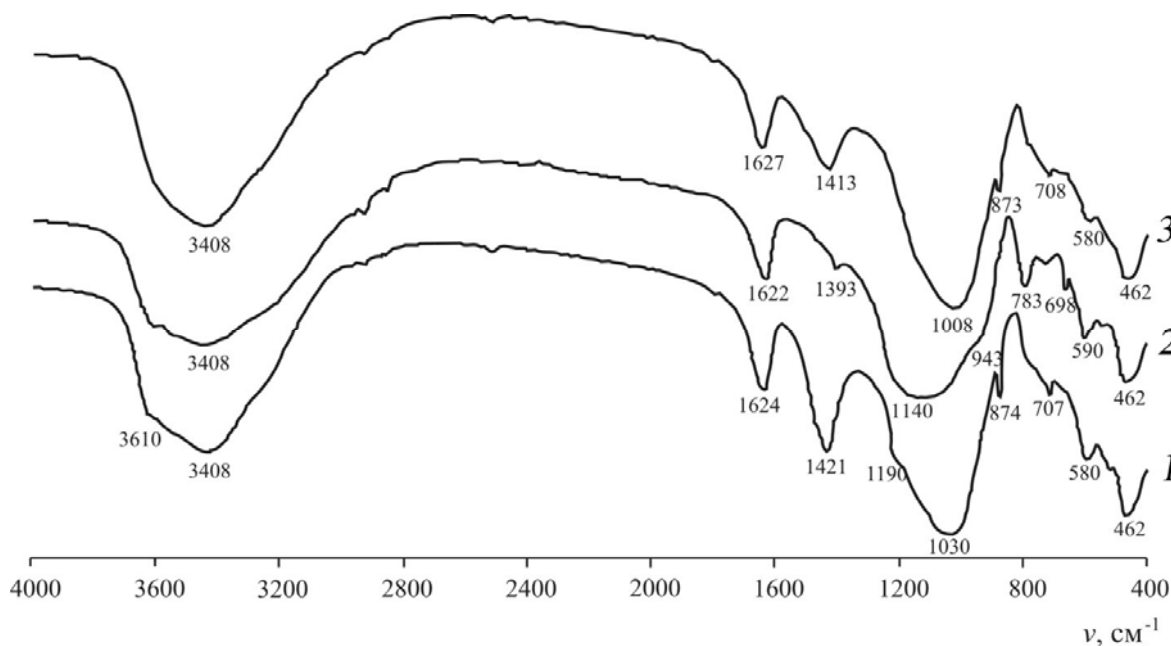


Fig. 1. IR-spectra of natural MCnat (1) activated by acid MCAc (2) and activated by alkali MCAk (3) aluminosilicate $\text{M}_{45}\text{C}_{20}$

The formation of the amorphous silica by acid treatment of sorbent is confirmed by appearance of a basic band at 783 cm^{-1} among three absorption bands of bending vibrations Si–O, which is characteristic to silica gel [29].

Destruction of the octahedral sheet of clay components (montmorillonite and illite) of MCAc sorbent due to formation of an amorphous silica [9] along with a decrease in water content, filling sorbent pores, lead to a decrease in relative intensity of the absorption band in the region of $3700\text{--}3000\text{ cm}^{-1}$ and in a drastic reduction of the absorption band at 1421 cm^{-1} .

In the IR-spectrum of an alkali-treated sample (Fig. 1, line 3) the absorption in the region of $1200\text{--}900\text{ cm}^{-1}$ increases its intensity so decreasing the width and structuring of a band. The band maximum at 1030 cm^{-1} is shifted to the low frequency region, indicating the diminution of molar ratio $\text{SiO}_2/\text{Al}_2\text{O}_3$ owing to alkaline treatment. The dominant contribution to the absorption of shorter bonds Si–O caused by the break of Si–O–Al

and Si–O–Si bonds by alkaline activation [27] is confirmed by a shift of the maximum to 1008 cm^{-1} as well as by the decrease in the band intensity at 707 and 580 cm^{-1} .

For quantitative analysis of the influence of acid activation of $\text{M}_{45}\text{C}_{20}$ on its clay and zeolite components, water vapor sorption has been studied and the surface characteristics of sorbents have been determined.

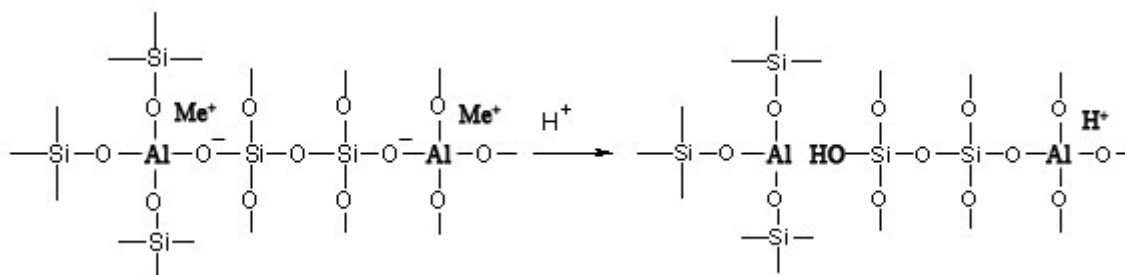
Isotherms of water sorption by different $\text{M}_{45}\text{C}_{20}$ samples are shown in Fig. 2, representing a dependence of the amount of absorbed water (a , mmol/g) on the relative pressure of water vapor (P/P_s).

Water vapor adsorption isotherms on natural and activated samples have S-shape, indicating polymolecular sorption of water. In the region of low relative pressures ($P/P_s < 0.35$) there is a rise of the isotherm caused by interaction of water molecules with the most active sites – exchangeable cations, oxygen atoms of silica and aluminum tetrahedral of the framework and

polarized hydroxyl groups of the sorbents. A plateau in the region of medium values of $P/P_s = 0.35 \dots 0.60$ corresponds to formation of the monomolecular layer of adsorbed water molecules. Further increase in the relative pressure of water vapor ($P/P_s > 0.60$) causes an increase in the amount of adsorbed water due to formation of the second and subsequent layers of the adsorbed water molecules [30].

As a result of acid and alkaline activation, the sorbent capability for hydration in the whole region of relative pressure has increased. Sorption capacity of $M_{45}C_{20}$ samples towards water molecules increases in a following row: $MCnat < MCAc < MCAlk$.

Change of hydration parameters of the sorbent due to acid and alkaline treatment in the region of low values of relative pressure of water vapor ($P/P_s < 0.35$) is caused by a change in the number and type of sorption active sites. Acid treatment removes cations and aluminum [29, 31]



Formation of new active sites, including acid sites to the amount of 0.79 mmol/g, increases the capability of $M_{45}C_{20}$ mineral sorbent towards hydration.

The increase in the adsorption capacity of alkali activated sample at relative pressure $P/P_s < 0.35$ is related to the increase in its cation-exchange capacity due to accumulation of Na^+ -ions in the ion-exchange complex.

For activated samples, vapor sorption isotherms show a steeper rise at $P/P_s > 0.80$; an increase in the amount of adsorbed weakly bound water in this pressure range caused by formation of new microcavities interconnected inside the framework.

On the basis of water sorption isotherms obtained, the specific surface area and monolayer capacity were determined using the BET-equation in a linear plot [32]

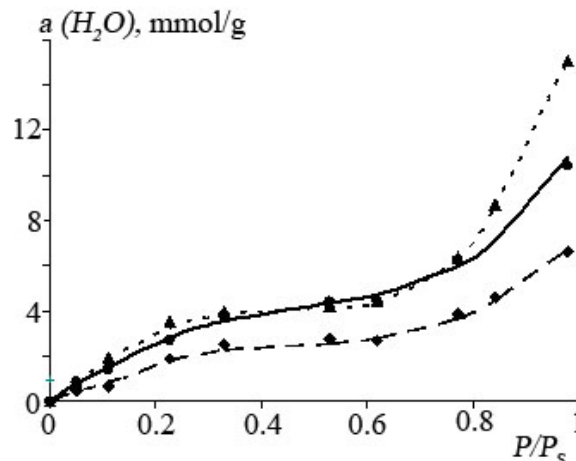


Fig. 2. Isotherms of water vapor sorption by $MCnat$ (\blacklozenge), $MCAc$ (\bullet) and $MCAlk$ (\blacktriangle) sorbents

accompanied by a breakup of Si–O–Al bond and formation of new sorption sites – silanol groups, three-coordinated Al-atoms as well as Brønsted sites in accordance with the scheme:

$$\frac{P/P_s}{a(1-P/P_s)} = \frac{1}{Ka_m} + \frac{K-1}{Ka_m} \cdot P/P_s, \quad (1)$$

where P/P_s – relative pressure of water vapor; a – amount of adsorbed water, g/g; a_m – adsorption capacity of saturated monolayer, g/g; K – factor dependent on the energy of inter-molecular interaction in the adsorption layer.

From the slope of the straight line in the coordinates $\frac{P/P_s}{a(1-P/P_s)}$ vs. P/P_s , which is

equal to $\frac{K-1}{Ka_m}$, and the intercept of the axis

$\frac{P/P_s}{a(1-P/P_s)}$ equals to $\frac{1}{Ka_m}$, values of a_m and

K were calculated in the range of relative pressures $P/P_s < 0.35$.

Values of specific surface area S (m^2/g) of natural and activated samples were calculated using the equation

$$S = a_m \cdot N_a \cdot \omega_m \cdot 10^{-17}, \quad (2)$$

where a_m – capacity of a water monolayer, mmol/g ; N_a – Avogadro's number, $6.023 \cdot 10^{23} \text{ mol}^{-1}$; ω_m – area occupied by an adsorbate molecule in a tight layer on the surface of adsorbent (the surface area covered by a water molecule $\approx 12.8 \pm 5.4 \text{ \AA}^2$).

Hydration and structural characteristics of $\text{M}_{45}\text{C}_{20}$ sorbent determined from isotherms of water sorption as well as from true and apparent densities are shown in Table.

As the data of Table show, natural $\text{M}_{45}\text{C}_{20}$ sorbent has a relatively high porosity (36.0%) in the pore range with an average diameter of 2.6 nm. In the porous structure macro-, micro- and mesopores are present, with a domination of the last type.

It has been found that acid activation of natural $\text{M}_{45}\text{C}_{20}$ sorbent is accompanied by an increase in its specific surface area (by 1.3), pore volume (by 1.6), pore diameter (by 1.3) and porosity (by 1.3 times) and decrease in its true and apparent density. This fact is caused by removal of interlayer cations broadening of intercrystalline space, and as a result of partial destruction of an octahedral layer (removal of Al^{3+} , Fe^{3+} , and Mg^{2+} ions from sorbent matrix).

Table. Adsorption-structural characteristics of natural and activated $\text{M}_{45}\text{C}_{20}$ sorbents

Sorbent	Density, g/cm^3			Porosity, P, %	Average pore diameter, D_{av} , nm	Volume, cm^3/g					Capacity of monolayer, a_m , mmol/g	S , m^2/g
	Bulk, ρ	Apparent, δ	True, d			Total pore, V_{Σ}	Micropores, V_{mi}	Mesopores, V_{me}	Macropores, V_{ma}	Adsorption pores, V_s		
MCnat	1.17	2.75	4.30	36.0	2.6	0.132	0.046	0.076	0.010	0.122	2.55	197
MCAc	1.09	2.18	4.08	46.6	3.3	0.214	0.061	0.134	0.019	0.195	3.38	261
MCAIk	0.81	1.70	3.32	48.8	3.9	0.292	0.068	0.203	0.021	0.271	3.77	297

As it is seen from Table, alkaline activation leads to an increase in the specific surface area of the natural sorbent to a higher extent than acid activation. The specific surface area increases from $197 \text{ m}^2/\text{g}$ for natural $\text{M}_{45}\text{C}_{20}$ to $297 \text{ m}^2/\text{g}$ for alkali-treated sample, with the total pore volume increasing from 0.13 to $0.29 \text{ cm}^3/\text{g}$. The main cause of such an increase in adsorption-structural characteristics of natural $\text{M}_{45}\text{C}_{20}$ sorbent as a result of alkaline treatment is, in our opinion, the formation of lattice crystals on the surface of particles so forming new micro and meso pores.

The observed rise of the pore volume in the process of alkaline treatment occurs due to transformation of montmorillonite with lamellar structure into a zeolite with hard framework structure, accompanied by formation of new pores.

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Хімія поверхні та поруватість природного і активованого алюмосилікату з монтморилоніту та кліноптілоліту

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З використанням ІЧ-спектроскопії та ізоп'єстичного методу вивчено вплив кислотної та лужної активації на хімію поверхні та поруватість природного комбінованого алюмосилікату $M_{45}C_{20}$, що містить монтморилоніт та кліноптілоліт. Зсуви смуг поглинання в ІЧ-спектрах підтверджують, що і кислотна, і лужна обробка обумовлюють розкриття зв'язків Si–O–Al, яке відбувається завдяки деалюмінації сорбенту та формуванню груп Si–OH. Утворення аморфної фази кремнезему спостерігається при кислотній обробці як результат деструкції октаедричних шарів монтморилоніту. Одержано ізотерми сорбції водяної пари на природному $M_{45}C_{20}$ (МСnat) та активованих $M_{45}C_{20}$ кислотою та лугом (МСAc і МСAlk) зразках. Для розрахунку питомої поверхні зразків успішно використана теорія БЕТ. Сорбційна ємність по воді зростає в ряду: МСnat < МСAc < МСAlk. Встановлено, що питома поверхня природного комбінованого алюмосилікатного сорбенту зростає після кислотної та лужної обробки, відповідно в 1.3 та 1.5 рази.

Химия поверхности и пористость природного и активированного алюмосиликата на основе монтмориллонита и клиноптилолита

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С использованием ИК-спектроскопии и изопьестического метода изучено влияние кислотной и щелочной активации на химию поверхности и пористость природного комбинированного алюмосиликата $M_{45}C_{20}$, который включает в себя монтмориллонит и клиноптилолит. Сдвиги полос поглощения в ИК-спектрах подтверждают, что и кислотная, и щелочная обработка обуславливают раскрытие связей Si–O–Al, которое происходит благодаря деалюминации сорбента и формированию групп Si–OH. Образование аморфной фазы кремнезема наблюдается при кислотной обработке как результат деструкции октаэдрических слоев монтмориллонита. Получены изотермы сорбции паров воды на природном $M_{45}C_{20}$ (МСnat) и активированных кислотой и щелочью $M_{45}C_{20}$ (МСAc и МСAlk) образцах. Для расчета удельной поверхности образцов успешно использована теория БЭТ. Сорбционная емкость по воде увеличивается в ряду: МСnat < МСAc < МСAlk. Установлено, что удельная поверхность природного комбинированного алюмосиликатного сорбента возрастает после кислотной и щелочной обработки, соответственно в 1.3 и 1.5 раза.

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