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# Adsorption of Industrial Pollutants by Natural and Modified Aluminosilicates

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Additional information is available at the end of the chapter

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## Abstract

The adsorption ability of natural clay minerals and zeolites is a structurally caused distinguished feature, which determines their physical–chemical properties and almost each area of application. The type of surface active sites responsible for adsorption behavior differs for various structural types of aluminosilicates and varies under modifying agents. The present chapter illustrates the effect of the acid and base modification of natural aluminosilicates on their adsorption behavior in respect to a number of pollutants present in aqueous media. For this, the change of adsorption-structural characteristics of natural clay samples containing representatives of the main groups of clay minerals under activation is considered. Further, the chapter focuses on characterization of surface active sites by means of a new method of a catalytic conversion of 2-methylbut-3-yn-2-ol. The presence of both acid and basic sites on the aluminosilicates surface as well as variations of surface acidity and basicity for different structural types of aluminosilicates under varying conditions of modification is discussed. The third highlight of the chapter encompasses adsorption processes taking place in aqueous solutions of formaldehyde, acetic acid, and ammonium chloride on the surface of natural and activated aluminosilicates. The activating effect of a number of inorganic acids and bases on adsorption equilibrium is compared. The considered mechanism of the adsorption of electrolytes and polar molecules from aqueous media may comprise hydrogen bonding, chemisorptions, or ion-exchange reactions.

**Keywords:** Clay minerals, zeolites, acid and base activation, surfaceactive sites, methylbutynol conversion, adsorption

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## 1. Introduction

The adsorption ability of natural aluminosilicates, e.g., clay minerals and zeolites, is inseparable from humans from the times of their first existence till the present days. The use of clays

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for making ceramic wares and their use in households, industry, engineering, and in creating the art articles, etc., is based on the unique properties of their surfaces to absorb/adsorb molecules of water, organic substances, inorganic cations, and anions, leading to a partial or complete swelling of the layered structure of minerals followed by a sliding of clay layers relative to each other. Nowadays, ceramic materials, both traditional and advanced, are of extreme significance in the fields of electronics, communications, optics, transportation, medicine, energy conversion and pollution control, aerospace, construction, and recreation [1, 2]. Each of the specified fields of application exploits some single or several distinguished properties of ceramic materials, but despite this, the general feature of all these areas is the phenomenon of adsorption (lat. *sorbeo*—capture or uptake), which, in the nature of the case, is realized by the contact of two or more different phases. The adsorption properties of materials are determined by the state and chemical activity of surface, porosity, and external conditions; they assign the conditions for material production and further exploitations.

The present chapter considers adsorption phenomena and physical–chemical properties of surface of natural aluminosilicates, which are the base of traditional ceramic materials, in natural state and under effect of reagent treatment (acid and alkaline activation). Noteworthy, that natural aluminosilicate samples are always a mixture of different phases, i.e., clay and nonclay minerals, mixed phases, oxides, organic matter, etc., formed under varied geological conditions. Depending on the application field, one may employ separation and purification of natural polymineral phases in order to enrich the content of a definite mineral phase or to eliminate admixtures. Nevertheless, under no specific treatment or purification, raw aluminosilicate samples are confirmed to comprise enhanced physical–chemical characteristics and, hence, significant adsorption, ion-exchange, or catalytic ability, which are proportional to the content of a rock forming clay mineral or a zeolite in the natural sample [3–6]. Hereinafter, physical–chemical behavior of raw aluminosilicate samples is considered with the aim of further application as low cost and effective adsorbents of industrial pollutants.

The first part of the chapter illustrates the effect of a chemical exposure (acid and base activation) on the chemical composition of aluminosilicates and their surface properties (porosity and specific surface area), including chemical reactions of aluminosilicates during activation.

The second part is focused on a new characterization method for identification of the type and activity of surfaceactive sites by means of catalytic reaction of 2-methylbut-3-yn-2-ol (MBOH) conversion. It is shown hereinafter that depending on the crystal structure of a mineral present in natural raw sample, as well as on the chemical modification applied, the acidity and basicity of the surface is changed, providing various sites to be active in adsorption or catalytic process.

The possibility of a diverse adsorption mechanism (physical, chemical adsorption, and ion-exchange) realized during uptake of various substances from aqueous media will be illustrated for formaldehyde, acetic acid, and ammonia chloride solutions in the third part of the chapter.

The background considered in this chapter will be a correlation of the structural type and physical–chemical properties of the surface of natural aluminosilicates to the type of activating effect of an inorganic modifier and to the mechanism of adsorption process in systems with

industrial toxicants. The examined information will improve the knowledge and understanding of the professionals on the specific properties of natural aluminosilicates used in ceramics, as well as on the methods of their investigation and application for elaboration of environmentally safe materials and technologies.

## 2. Surface properties of natural aluminosilicates and their modification

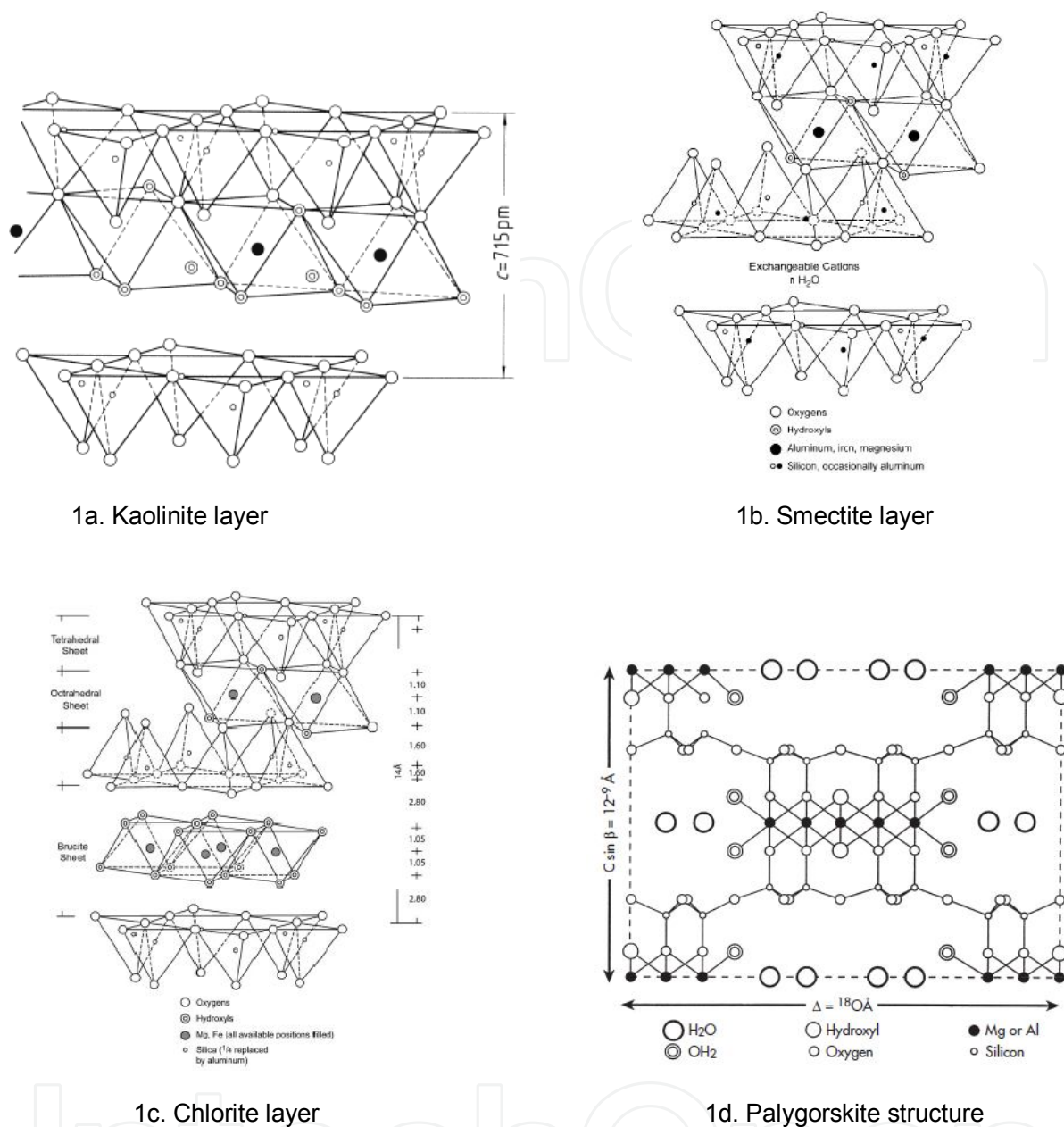
### 2.1. Structural features and classification of natural aluminosilicates

Among a rich variety of natural aluminosilicates, the most remarkable adsorption properties are typical for clay minerals and zeolites owing to the features of their structure and chemical composition.

Clay minerals are a group of hydrous aluminum, magnesium, and iron silicates that form the bases of clays and soils. Most of clay minerals have layered or semilayered structure. The main structural elements of the most natural aluminosilicates are tetrahedra of  $\text{SiO}_4$  (T) and/or octahedra of  $\text{AlO}_6$  (O) joint by the vertices and forming the planar sheets, i.e., tetrahedral and octahedral sheets, respectively. A combination of T- and O-sheets constitutes an elementary layer and attributes a mineral to a specific structural type or a group according to the last recommendations of the nomenclature committee of AIPEA (International Association for the Study of Clays) [7]. For instance, as for planar phyllosilicates, a combination of T- and O-sheets (Fig. 1a) forms the elementary layer of 1:1 mineral type (kaolinite, dickite, etc.), whereas in the extensive 2:1 mineral type (talc, montmorillonite, vermiculite, etc.), an octahedral sheet is sandwiched between two T-sheets (T-O-T layer, Fig. 1b). The type of interlayer material, i.e., water molecules, exchangeable cations of alkali/alkaline earth metals, and hydroxides (Fig. 1c), and the layer charge ( $x = 0\sim 2$ ) allow further subdivision of minerals into subgroups. Additionally, there is a group of nonplanar minerals, previously named “quasi-layered silicates,” observing a modulated structure (strips, islands, ribbons, etc). Unlike the planar ones, discontinuous chains of T-sheets are inverted, linking adjacent 1:1 or 2:1 sheets (Fig. 1d) and producing the zeolites like channels [8].

The layers are combined into elementary packages, the aggregate of which forms a mineral particle with the size finer than  $4\text{ }\mu\text{m}$ . The isomorphic substitutions of  $\text{Si}^{4+}$  for  $\text{Al}^{3+}$  in T-sheets and  $\text{Al}^{3+}$  for  $\text{Fe}^{2+}/\text{Fe}^{3+}$  in O-sheets impart a negative charge of aluminosilicate framework, which is balanced by cations from the surrounding environment and explains cation-exchange properties of aluminosilicates. The most remarkable cation-exchange capacity (CEC) is typical for clay minerals of 2:1 group, layered-chain minerals (sepiolite, palygorskite), whereas members of kaolinite group possess the lowest CEC as well as low swelling due to weak isomorphic substitutions.

Apart from layered minerals, the high CEC and adsorption ability is a characteristic feature of natural zeolites, aluminosilicates with a three-dimensional hard-sphere framework structure. The structural elements of zeolites are  $\text{SiO}_4$  and  $\text{AlO}_4$  tetrahedra joint by vertices in the way that cavities and channels are formed, in which hydrated cations, water, and other molecules may diffuse.



**Figure 1.** Structural types of planar (a–c) and nonplanar silicates (d): (a) 1:1 mineral group [9], (b) 2:1 mineral group (exchangeable cations and water in the interlayer) [10], (c) 2:1 mineral group (chlorite and hydroxides in the interlayer) [10], and (d) 2:1 nonplanar (modulated) silicate (palygorskite) [11].

Numerous investigations in the field of chemistry of aluminosilicates specify that the structure of clay minerals as well as their chemical composition, approximately expressed by the formula  $M_{2/n}O \cdot Al_2O_3 \cdot ySiO_2 \cdot zH_2O$ , determines the following active sites, which will be responsible for the adsorption behavior of natural clay minerals or zeolites: (i) exchangeable cations ( $K^+$ ,  $Na^+$ , and/or  $Ca^{2+}$ ); (ii) hydroxyls of acid/basic character ( $SiOH$ ,  $SiO(H^+)Al$ ,  $Al-OH$ , and  $OH$  or  $Mg-OH$ ); (iii) coordinatively unsaturated ions of  $Al^{3+}$ ,  $Mg^{2+}$ , and/or  $Fe^{3+}$ ; and (iv) oxygen anions  $O^-$ . Such reactivity of the surface and structural elements of silicates is obviously realized in their ability to physical adsorption, realized by van der Waals interactions or hydrogen



bonding with surface OH groups, coordinately unsaturated cations, oxygen anions, etc. Additionally, there is a good and proved opportunity for chemisorptions due to a stronger interaction between the surface and the molecules followed by formation of chemical bonds [12, 13]. Of course, ion-exchange reactions (involving exchangeable cations or OH groups) are important and will readily contribute to the adsorption process, as well as catalytic ability in specific processes and conditions [14]. However, to be competitive to the other commercial materials and adsorbents, clay minerals should meet the same requirements as for other adsorbents (Table 1).

Requirement	Characteristic of clay mineral	Compliance
High specific surface area and porosity	Mesoporous, $S = 20\text{--}150 \text{ m}^2/\text{g}$	+/- Activation needed
Chemical affinity to adsorbates	Polar, hydrophilic surface of clay minerals—affinity toward polar substances	+/- Modification needed
Chemical and thermal stability	Low chemical and thermal stability in natural form	Modification needed
Ability to regeneration	Possible	Modification needed
Availability	Widely available	+

**Table 1.** Compliance of natural aluminosilicates to general requirements for industrial adsorbents

As shown in Table 1, porosity, surface area, and surface physical–chemical affinity of natural aluminosilicates need to be improved to meet general requirements. For this, various methods of activation and modification have being applied

## 2.2. Chemical modification of clay minerals and its influence on surface properties

Natural aluminosilicates are able to interact easily with chemical reagents, modifying through this their surface and structural properties and, as a sequence, their physical–chemical activity. Along with the chemical exposure, aluminosilicates can significantly vary their properties under mechanical, thermal, and recently under physical exposure of magnetic field of different types (ultrahigh frequency (UHF), weak pulse field) [15, 16]. This behavior enables scientist unlimited opportunities in varying and targeting the properties of materials, produced based on or involving clay minerals and other silicates.

Despite the manifold means applied and being currently improved for the activation or modification of aluminosilicates properties, it is still possible to consider the following general groups of methods for clay minerals activation: mechanical (grinding of kaolinite), thermal, chemical (acid, alkali, salt, etc.), and physical (exposure of magnetic field) activations or a combination of them, e.g., mechanochemical and thermochemical activation.

For *mechanical and/or mechanochemical activation*, different types of mills have been applied, i.e., planetary ball-mill, vertical jet (compressed air), cryogenic mills, etc. [17]. Grinding usually

starts from a reduction of particle size, promoting the deformation of crystal structure of minerals mainly along the *c*-axis, and a disruption of Si-OH, Al-OH, Al-O-Si, and Si-O bonds. Depending on the milling conditions, surface characteristics and colloid properties of clay minerals are changed [18]. In the first grinding stages, a decrease of particle sizes and an increase in clay surface area are observed, including variations of their porosity. Further grinding causes adhesion of the particles, followed by a decline of the specific surface area, amorphization of the structure, and change in plastic and dispersion properties of clays [19, 20]. Mechanical exposure is accompanied by the new active sites appearing at the boundaries of the particles faults and an increase in cation-exchange capacity of the mineral, as often observed for kaolinite and other clay minerals.

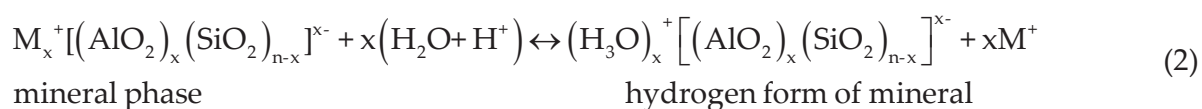
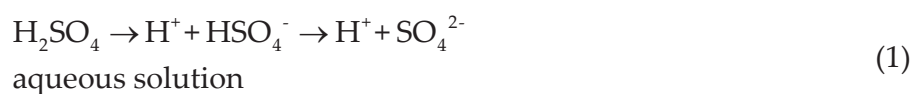
Severe changes of the structure and properties of minerals are reached by mechanochemical treatment in a definite chemical media (water, acid, alkaline solutions, and other substances) [21–23]. It is frequently used to enhance their catalytic activities, acid dissolution, or for the higher leaching of aluminum.

*Thermal activation* of clay minerals is based on the thermal treatment of natural clay sample at an elevated temperature resulting in desorption of adsorbed gases and water molecules and evolution of free surface. However, at rather high temperatures, which are different for each mineral type, crystal structure can undergo partial damage or entire structure collapse followed by a decrement of surface activity.

*Chemical activation or modification* usually provides the strongest affect on the structure and properties of materials due to chemical interactions of a modifying agent and the surface of material [24]. Despite numerous modifying agents exploited in recent decades for altering the properties of aluminosilicates, the activation by acid and alkaline solutions remains as the most frequently used in industrial or laboratory processing of clays [8, 25, 26].

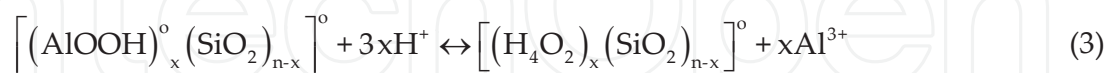
For acid activation or acid leaching, generally mineral acids (sulfuric or hydrochloric acids) are used [27–29]. The application of organic acids, e.g., acetic, formic acids, and oxalic, is rarer as their effect is weaker due to their low strength [30, 31].

The following chemical reactions take place during the contact of an aluminosilicate and acid solution. First, as most of the clay minerals possess ion-exchange ability, the ion-exchange reactions will occur. The exchangeable cations, usually cations of alkaline or alkaline earth elements, e.g.,  $\text{Na}^+$ ,  $\text{K}^+$ , or  $\text{Ca}^{2+}$ , located in the interlayer space will be substituted (cation-exchange) for protons resulted from dissociation of an acid:

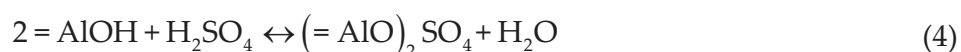


where  $M_x^+ = Na^+, K^+, Ca^{2+}, Mg^{2+}$ .

Along with the Ion-exchange reactions, there is an acid attack of the layered structure. Protons of the acid easily penetrate into the interlayer space and react mainly with cations of the octahedral sheet. This process is known as “dealumination” as it comprises substitution of octahedral  $Al^{3+}$  or  $Fe^{2+}/Fe^{3+}$  ions by protons and formation of additional Si-OH groups in the tetrahedral sheet:



In addition, one may expect anion-exchange reactions (Eq. (4)) between AlOH groups of basic character and  $SO_4^{2-}$  anions with the formation of sulfates:



The occurrence of these reactions of decationating and dealumination is confirmed by changes in the chemical composition of natural aluminosilicate samples (Table 2). Raw clay samples from several deposits in Russia, which phase composition involved presence of clay minerals of different layer type (1:1; 2:1 layered and 2:1 nonplanar), were crushed and sieved into grain fraction <0.25 mm and further subjected to acid activation by 2M  $H_2SO_4$  solution at 100°C for 6 h [4].

Aluminosilicate sample, deposit	Structural components	Chemical composition, %										SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>
		SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	FeO	MgO	CaO	Na <sub>2</sub> O+K <sub>2</sub> O	H <sub>2</sub> O	Loss on ignition	Total	
Palygorskite (Pal), Cherkassy, Russia	Palygorskite ~50%, quartz, zeolites, mica, feldspar	53,25 70,33	9,84 5,46	7,68 1,98	0,61 0,16	7,95 2,15	3,62 0,92	0,86 0,61	10,00 10,28	4,83 7,31	98, 64 99, 20	2,77 9,39
	Kaolinite ~60%											
Kaolinite (Kaol), Voronezh, Russia	mica ~30%	50,48 69,83	18,21 7,43	6,84 2,23	0,27 0,08	1,80 0,42	1,96 0,11	0,35 0,24	0,23 0,24	3,20 9,10	99,34 99,85	4,32 7,99
	montmorillonite ~10%											
Mixed samples (HdmCK), Voronezh, Russia	Hydromica ~30-35%, clinoptilolite ~5%, kaolinite ~5%, quartz, mica – traces	48,54 71,43	11,24 8,93	0,86 0,74	- -	1,10 0,38	9,78 0,62	4,12 0,96	- -	13,86 16,78	99,93 99,74	5,41 12,88

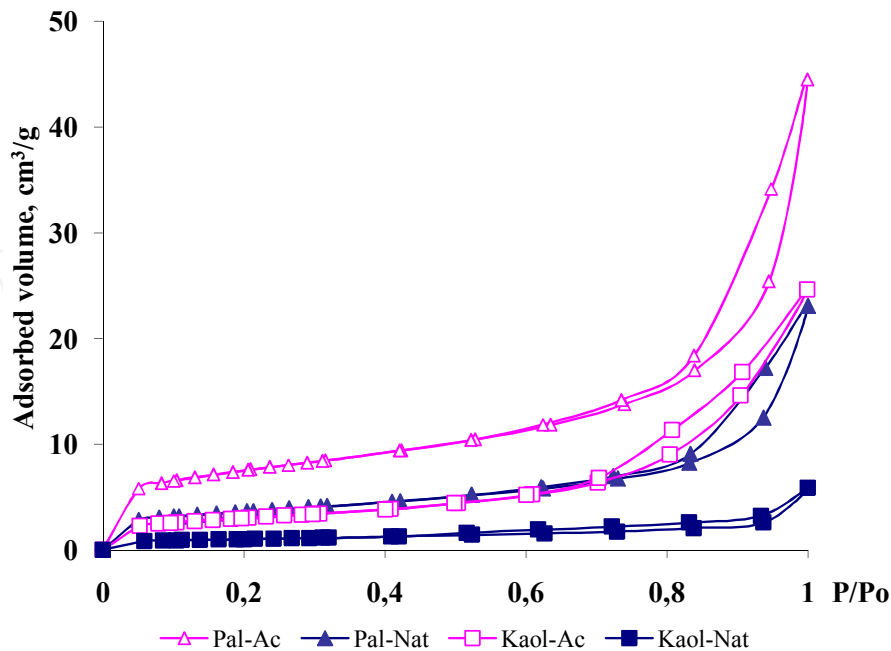
**Table 2.** Chemical composition of natural aluminosilicate samples before and after acid activation by 2M  $H_2SO_4$  at 100°C for 6 h [4]; size fraction of grains < 0.25 mm



It follows from Table 2 that the content of metal oxides was markedly reduced after acid activation, namely,  $\text{Al}_2\text{O}_3$  (by 1.3–2.5 times),  $\text{Fe}_2\text{O}_3$  (1.2–3.8 times),  $\text{FeO}$  (3.4–3.8),  $\text{MgO}$  (2.9–4.3 times),  $\text{CaO}$  (3.9–17.8 times),  $\text{Na}_2\text{O}$ , and  $\text{K}_2\text{O}$  (1.4–4.0 times), except for  $\text{SiO}_2$ . This fact clearly testifies to the occurrence of the Cation-exchange reactions (Eqs. (2) and (3)) during acid leaching. As a result, the content of silica oxides as well as silica module ( $\text{SiO}_2/\text{Al}_2\text{O}_3$ ) was increased.

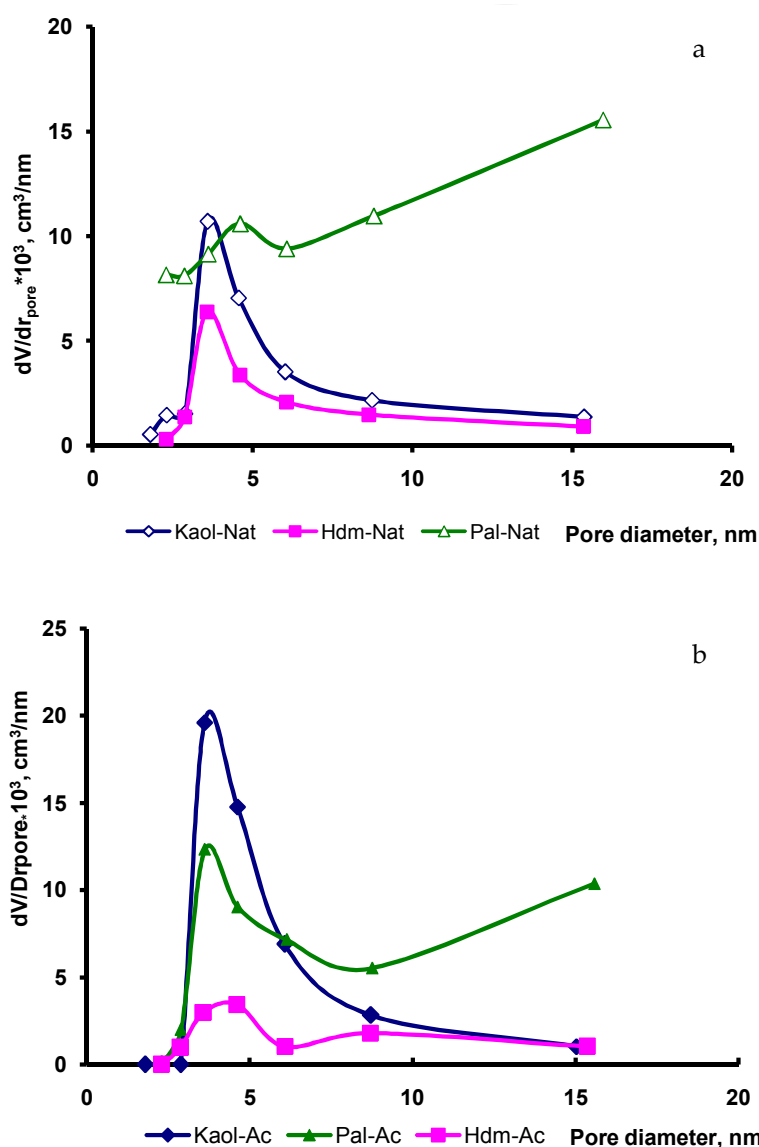
Moreover, due to changes of the chemical composition caused by acid treatment, serious variations of surface and structural characteristics of minerals have been observed [32, 33], which also strongly depend on the acid solution concentration and duration of the treatment. At shorter acid leaching times, mainly Ion-exchange reactions take place along with a slight destruction of the layered structure. This is followed by an increase in pore size of aluminosilicates, transformations of the micro pores into mesopores, and rise of specific surface area of the mineral [34]. However, by durable acid treatment, the crystal structure of minerals is more profoundly damaged, which finally lead to the falling of surface area as well as the adsorption capacity of aluminosilicates.

Fig. 2 illustrates  $\text{N}_2$  adsorption/desorption isotherms obtained to characterize surface properties of porous materials applying the BET method [4]. Here, the S-shape forms of  $\text{N}_2$  adsorption and desorption isotherms for natural and 2M  $\text{H}_2\text{SO}_4$ -treated samples, containing palygorskite (Pal) and kaolinite (Kaol) as major components, and hysteresis loops arose due to polymolecular adsorption and a capillary condensation of  $\text{N}_2$  molecules in the pores of adsorbent. According to the IUPAC classification, this isotherm type is attributed to mesoporous materials having pore diameter of 2–50 nm.



**Figure 2.** BET  $\text{N}_2$  adsorption isotherms for natural (Nat) and treated by 2M  $\text{H}_2\text{SO}_4$  (Ac) palygorskite (Pal) and kaolinite (Kaol).

The volumes of nitrogen adsorbed by Pal were higher than that for Kaol samples. Acid treatment of natural samples increased  $N_2$  adsorbed volume in two times that testified to development of additional free surface area and free pores volume of adsorbents. It follows from pore size distribution (Fig. 3) that pore diameters of investigated clay samples varied within 3–4 nm.



**Figure 3.** Pore size distribution of natural aluminosilicate samples before (a) and after (b) modification by 2M  $H_2SO_4$  [4].

It is remarkable that acid treatment practically did not change the pore diameters of clay samples, whereas the pore volume rose by two orders owing to additional formation/opening of mesopores (Fig. 3b). The highest growth of mesopores fraction observed for Kaol sample (Fig. 3b) testifies to the strongest acid attack of its structure (1:1 layer type), obviously due to easy accessible for protons octahedral sheet and octahedral cations of  $Al^{3+}$ . The crystal structure of palygorskite or illite minerals present in other natural samples, apparently more resistant

to acid as in their structure the octahedral sheet, is hidden between tetrahedral sheets as well as the stronger interactions between the layers occurs in mica/illite.

Experimental isotherms of  $N_2$  adsorption provide information on values of specific surface area of investigated clay samples (Table 3). The phase composition of natural samples (Table 2) along with the features of their structure determined the order in which specific surface area of samples decreased: Pal > Kaol > HdmCK.

Sample	S, m <sup>2</sup> /g		S <sub>acid</sub> /S <sub>nat</sub>
	Natural	Acid treated	
Pal	146	262	1.8
Kaol	27	64	2.4
HdmCK	24	31	1.3

**Table 3.** Specific surface area of natural and modified by 2M  $H_2SO_4$  aluminosilicate samples

The application of acid treatment for the modification of natural aluminosilicates increased their specific surface area in 1.3–2.4 times. The ratio of  $S_{acid}/S_{nat}$  pointed out that the effect of acid treatment on surface characteristics of investigated aluminosilicate samples, containing various structural components, weakened in the order Kaol > Pal > HdmCK.

*Alkaline or soda activation* is often used for industrial processing of clays applied as drilling muds. Different substances have been used as an activating agent, i.e., alkalis (NaOH, KOH, and LiOH), salts of alkaline ( $Na_2SiO_3$ ,  $Na_2CO_3$ ) or alkaline earth metals ( $CaSO_4$ ), and oxides (MgO) of about 2–4 mass%. The most significant parameter, which affects the dispersing and rheological properties, is the  $Na^+$  content. As a result, the viscosities, swelling indices, and filtration losses of clay suspensions significantly vary until they fulfill the drilling mud standards or satisfy the requirements of paint industry [35], ceramic production [36], etc.

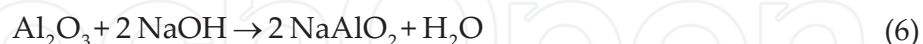
The alkaline activation of natural mineral sorbent  $M_{45}C_{20}$  (grain size < 0,25 mm) with the following phase composition: montmorillonite (45%), clinoptilolite (20%), goethite (10%), illite (15%), and calcite (10%) from Sokirnitsa deposit, Ukraine, was carried out by 2M solutions of NaOH or  $NH_4OH$  for 6 h at 100°C, followed by washing of the sample till neutral pH. The observed changes in the chemical composition of the aluminosilicate were mainly due to the reduction of  $SiO_2$  (6%) and MgO (1%) oxides and an increase in content of  $Na_2O$  (Table 4).

Sorbent	Content (% per absolutely dry sample)								Loss on ignition	SiO <sub>2</sub> /R <sub>2</sub> O <sub>3</sub>
	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	Na <sub>2</sub> O	K <sub>2</sub> O	TiO <sub>2</sub>		
MCNat	56.65	14.32	7.03	8.12	1.62	0.79	2.78	0.63	7.9	2.74
MC-Alk	50.72	15.50	8.13	8.79	0.55	5.32	2.8	0.7	7.3	2.14

Note: R—Al, Fe; MCN—natural aluminosilicates  $M_{45}C_{20}$ ; MC-Alk—aluminosilicates  $M_{45}C_{20}$  treated with a 2M NaOH solution.

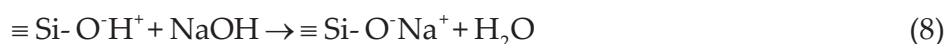
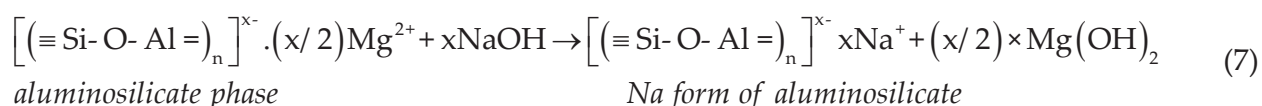
**Table 4.** Chemical composition of natural mineral sorbent  $M_{45}C_{20}$  treated by 2M NaOH [37]

Apart from the acid treatment, which affect to the most to octahedral cations, alkaline treatment selectively influences the tetrahedral sheets by means of the chemical dissolution of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  in the alkali forming sodium silicates and sodium aluminate, respectively [38]:

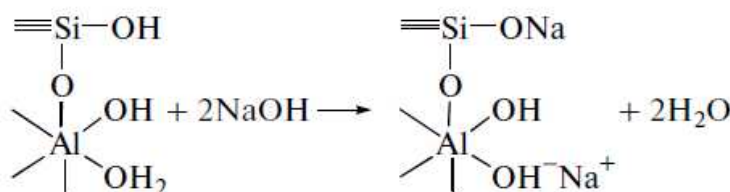


In the alkaline medium, the Si–O–Si bond is less stable than the Si–O–Al bond [39]; therefore,  $\text{Si}^{4+}$  easily transfers from aluminosilicate structure into the solution in comparison with  $\text{Al}^{3+}$ . This is evidenced by a decrease in  $\text{SiO}_2$  content, whereas that for  $\text{Al}_2\text{O}_3$  remained almost unchanged (Table 4).

Meanwhile, the  $\text{Na}_2\text{O}$  content increased abruptly (by a factor of 6.7), which along with a threefold decrease of  $\text{MgO}$  content, illustrated the occurrence of several ion-exchange reactions, involving (i)  $\text{Mg}^{2+}$  (or  $\text{Ca}^{2+}$ ) from the interlayer space or octahedral positions (7) and (ii) silanol groups (8) and  $\text{Na}^+$  ions from the external solution:

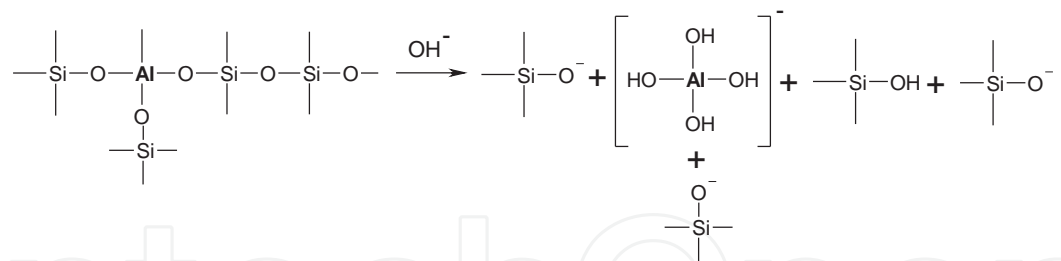


In the case of montmorillonite,  $\text{Na}^+$  ions can be exchanged for  $\text{H}^+$  ions of hydroxyl groups bound to aluminum atoms at the boundaries of the octahedral layer [37]:

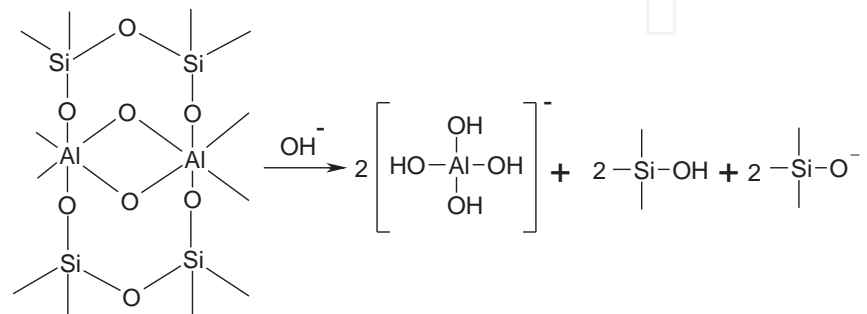


**Scheme 1** Exchange of  $\text{Na}^+$  for  $\text{H}^+$  ions of protonated Al–OH groups

All in all, the action of  $\text{NaOH}$  solution is destructing for silicon skeleton of aluminosilicate via the disruption of  $-\text{Si}-\text{O}-\text{Si}-$ ,  $-\text{Si}-\text{O}-\text{Al}-$ , and  $-\text{Al}-\text{O}-\text{Al}-$  bonds followed by formation of low polymeric aluminate and silicate anions, and anions of silicon acids. Schemes 2 and 3 demonstrate this action of alkali on clinoptilolite and montmorillonite structural components, respectively:



**Scheme 2.** Transformations of the aluminosilicate structure of the clinoptilolite component under alkaline conditions



**Scheme 3** Transformations of the aluminosilicate structure of the montmorillonite component under alkaline conditions

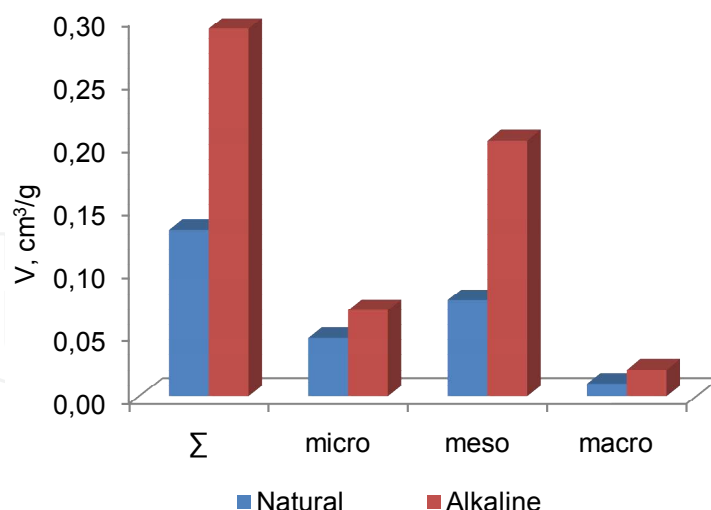
As aluminate and silicate are accumulated in the alkaline medium, the polycondensation reaction is likely to occur between aluminate and silicate ions, either yielding an amorphous aluminosilicate phase or followed by the crystallization of the amorphous phase and formation of new zeolite phases [37, 40, 41]. This reaction is the basic one for the production of geopolymers by means of alkaline activation of natural clays that have been frequently used for manufacturing the building materials [42].

For the case of a combined aluminosilicate sorbent  $M_{45}C_{20}$ , the alkali activation contributed to transformation of the original aluminosilicate structure into a zeolite structure of heulandites [37]. The surface characteristics of aluminosilicates, including  $M_{45}C_{20}$ , were significantly changed after alkaline exposure (Table 5). Porosity, pore diameter, and specific surface area raised in about 1.5 times. Fig. 4 testified that total pore volume increased by a factor of 2.2 mainly due to a significant increase in mesopore volume (by a factor of 2.6).

Sample	Porosity, %	Average pore diameter, $D_{av}$ , nm	Adsorption capacity of monolayer, $am(H_2O)$ , mmol/g	Specific surface area, $S$ , $m^2/g$
$M_{45}C_{20}$ -Nat	36,0	2,6	2,55	197
$M_{45}C_{20}$ -Alk	48,8	3,9	3,77	297

**Table 5.** Surface characteristics of the natural (Nat) and alkali-treated (Alk) sorbent  $M_{45}C_{20}$





**Figure 4.** Pore volumes of natural (Nat) and alkali-treated (Alk) sorbent  $M_{45}C_{20}$ . (Adopted from Belchinskaya et al. [43].)

Summarizing this section, one should emphasize that the extent of acid/alkaline modification of aluminosilicates chemical composition, and hence, their surface properties depends strongly on (i) structural features of the major aluminosilicate phase in the sample and (ii) type of modifying agent and conditions. Octahedral sheets of 1:1 layer type mineral phase are easily accessible for acid attack as compared to 2:1 planar (montmorillonite and illite) or 2:1 nonplanar (palygorskite) mineral phases. Tetrahedral sheets of all mineral types undergo chemical interaction with alkaline solution yielding either an amorphous or crystalline aluminosilicate phase.

Variations in chemical composition as well as in the structure of modified aluminosilicate samples affect the activity of the surface. In the next section, one will consider the nature of surfaceactive sites of natural aluminosilicate samples and the effect of surface modification by acid and basic solutions on their distribution and the strength. It is of high importance to characterize the surfaceactive centers, which impart the material adsorption, catalytic, or other surface activity.

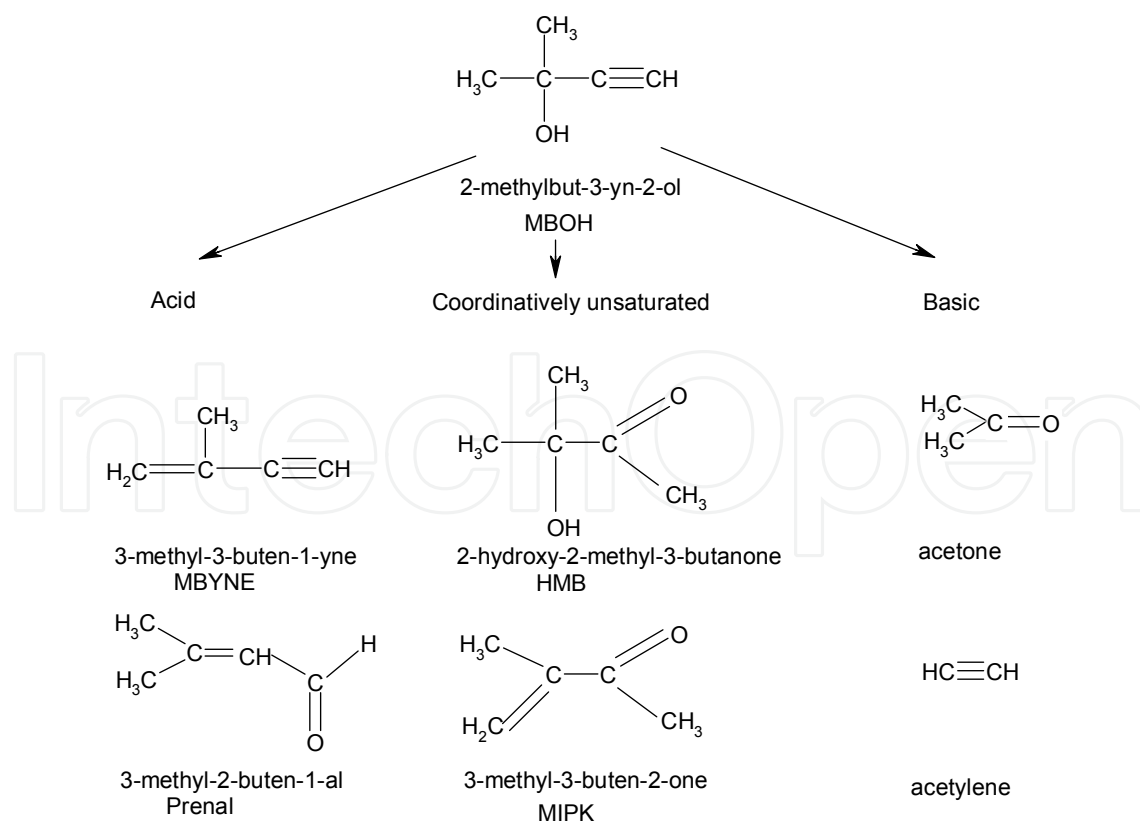
### 3. Characterization of surfaceactive sites of natural aluminosilicates by catalytic conversion of methylbutynol

Surface acid–base properties of solid materials are essential for almost each of their application. The use of aluminosilicates as adsorbents, binders, fillers, ion-exchangers, emulsifiers, catalysts or catalysts supports, etc., requires knowledge of their surface activity. To this belongs surface ability to donate/accept a proton (Broensted sites) or an electron pair (Lewis sites). Natural clay minerals and other aluminosilicates, like no other materials, comprise both Broensted acid (protons of polarized SiOH groups or water molecules, bridge hydroxyls Si-O(H<sup>+</sup>)-Al), Broensted basic sites (hydroxyls of structural MeOH groups,

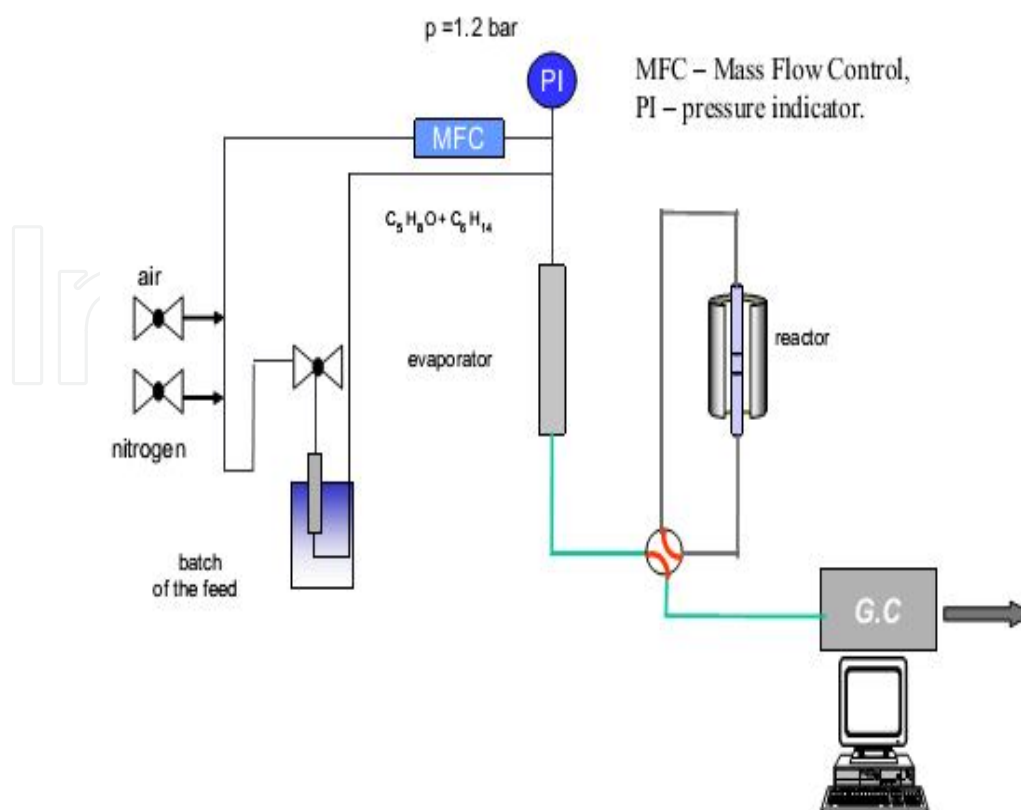
OH groups of polarized water molecules), Lewis acid (exchangeable cations, coordinative nonsaturated ions  $\text{Al}^{3+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Fe}^{3+}$  ions), and Lewis basic sites (oxygen anions of tetrahedral or octahedral sheets). Usually the number and the type of surface sites of different solids, including aluminosilicates, are determined by using the probe molecules. The nonreactive probe molecule is adsorbed on the surface and studied then by different physical–chemical methods (titration and spectroscopic techniques (FTIR, XPS, NMR), temperature-programmed desorption (TPD) of  $\text{NH}_3$  and  $\text{CO}_2$ , microcalorimetry, thermal analysis, etc.). On the other hand, in a number of catalytic reactions, reactive probe molecules have been applied, i.e., iso-propanol, cumene, benzene, etc., to characterize surface sites based on their reactivity under conditions close to real operation [44–46].

One of the catalytic test reactions, the catalytic conversion of 2-methylbut-3-yn-2-ol (MBOH), was recently applied for characterization of surfaceactive sites of natural clay minerals and nonclay aluminosilicates [4, 5, 47, 48]. A distinguished feature of this method is that it allows unambiguous determination of acidic, basic, and coordinative unsaturated (amphoteric) sites, which can be present simultaneously on the surface of the adsorbent or catalyst.

A substrate (probe) molecule of methylbutynol is converted into various reaction products depending on the type of active site (Fig. 5). Acidic sites are responsible for formation of 3-methyl-3-buten-1-yne (MBYNE) or 3-methyl-2-buten-1-al (Prenal), whereas basic sites generate acetone and acetylene [49].



**Figure 5.** Scheme of methylbutynol conversion.



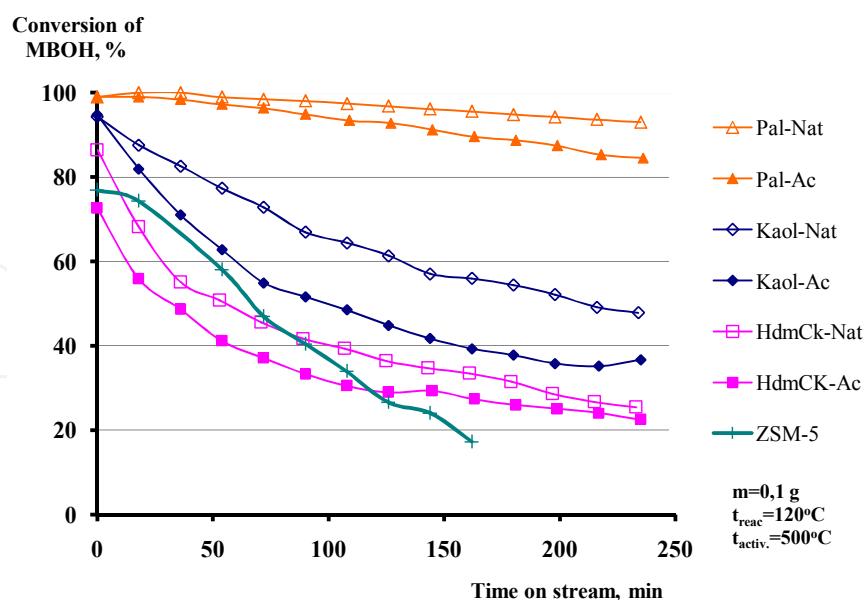
**Figure 6.** Experimental setup for test reaction of methylbutynol conversion [50].

The experimental setup for MBOH conversion is shown in Fig. 6. The reaction mixture of 95% of methylbutynol and 5% of toluene is fed applying static nitrogen pressure of 202.65 kPa into the evaporator and then into the reactor where 0.2 g of catalyst is placed. Prior to the reaction, the catalyst was sieved in to 215–300  $\mu\text{m}$  fraction and activated in a stream of nitrogen at 500°C during 4 h in order to remove water and  $\text{CO}_2$  from the surface. The catalytic conversion of MBOH is carried out at 120°C applying GC method for on-line product analysis.

Fig. 7 displaces conversions of MBOH over natural and acid modified aluminosilicate samples discussed in Section 2.1–2.2.

The highest conversion of MBOH was observed for palygorskite-containing sample (Pal), and the lowest for hydromica (HdmCK) and a synthetic zeolite ZSM-5 ( $\text{SiO}_2/\text{Al}_2\text{O}_3 = 45$ ) used as a reference. The gradual decrease of MBOH conversion on time testifies to deactivation of the catalyst, especially in the case of HdmCK and zeolite ZSM-5, which underwent the strongest deactivation from the initial stage of reaction, apparently, due to its microporous structure and irreversible adsorption of reaction products [50].

The catalytic activity of natural aluminosilicate samples for the conversion of MBOH under applied conditions declined in the order  $\text{Pal} > \text{Kaol} > \text{HdmCK}$ , which is in accordance to their specific surface area changed as 146, 35, and 24  $\text{m}^2/\text{g}$ , correspondingly [5]. It is essential to note that proportion of clay mineral in a raw clay sample directly affects its catalytic activity in the conversion of MBOH. For instance, the conversion of MBOH over samples with content of



**Figure 7.** Conversion of MBOH over natural (Nat) and treated by  $2\text{MH}_2\text{SO}_4$  (Ac) aluminosilicate samples.

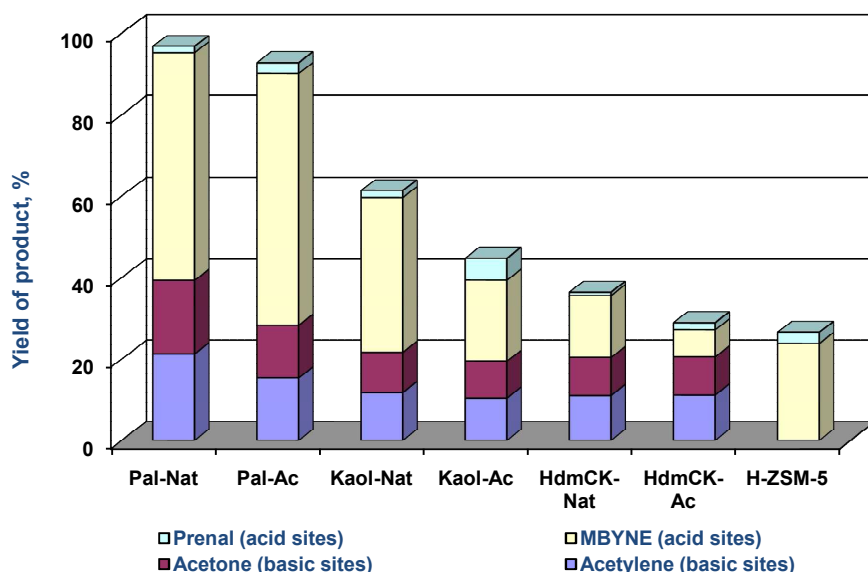
montmorillonite varied as 10%, 30%, 60%, and 80% amounted respectively to 52%, 85%, 87%, and 95% after 200 min of reaction [5]. Hereby, an increasing contribution of both acidic and basic sites into the conversion of MBOH was observed at higher proportions of the mineral in the raw sample.

After acid treatment of these aluminosilicate samples by 2M solution of  $\text{H}_2\text{SO}_4$ , the conversion of MBOH was lower than that in the case of natural minerals. This was caused by the changes of the chemical composition of aluminosilicates, considered above in Section 2.2, resulted in the dissolution of Al and Fe oxides followed by the weakening of silanol groups  $\text{Si-OH}$  polarization and reduction of a number of bridge hydroxyls  $\text{Si-O(H}^+)-\text{Al}$  acting as Brønsted acid sites.

To identify the types of surface-active sites, one should address to the yields of reaction products shown in Fig. 8.

The typical products of MBOH conversion over natural aluminosilicate samples were MBYNE and Prenal formed via acid pathway of the reaction as well as acetone and acetylene, confirming the presence of basic centers on the surface. Indeed, many authors [51–53] proved there is no clay having only acidic or basic properties because both types of sites are present on the surface and transforms to each other under definite conditions such as water content, pH, etc.

The ratio between the acidic and basic products differs from the type of major aluminosilicate component in the sample. Thus, yields of MBYNE and Prenal exceed yield of acetylene and acetone during the MBOH conversion over Pal, Kaol, and H-ZSM-5 (entirely acidic products). This fact shows, apparently, that the number or the strength of acid centers on the surface of given aluminosilicates exceeds the number/strength of basic centers. However, the contribution of basic centers to the general concentration of surface centers is essential. Additionally, TPD- $\text{NH}_3$  and  $\text{CO}_2$  studies of acidity and basicity distribution for natural and ion-exchanged



**Figure 8.** Yields of products formed during MBOH conversion over natural and acid-treated aluminosilicate samples.

montmorillonites revealed that acidity level is 2–3 times higher than that for basicity, regardless to the cation introduced on the clay surface [52]. Alkaline cations confer to clays low acidity and weak acid strength, in comparison with alkaline earths.

In the case of kaolinite-rich sample (Kaol), the contribution of acidic and basic sites should be comparable due to its weak natural structural acidity caused by low isomorphous substitution of low valence cations for higher valence cations mainly in the tetrahedral sheet. AlOH groups of basic character located at side edges of crystals cover about 45% of total kaolinite surface [51] resulting in its ability to adsorb both acidic and basic molecules almost equally [53]. However, the presence of montmorillonite (10%) and mica (30%), as referred to in Table 1, in the natural sample containing kaolinite explains higher yield of acidic products.

In the case of the sample containing natural hydromica (HdmCK), the yields of acid and basic products were practically identical that evidenced of comparable concentration or the strength of acid and basic sites on its surface. Natural hydromicas, as nonexpanding clay minerals, possess low Brønsted acidity due to absence or very low hydration of interlayer exchangeable cations. Its catalytic activity originates from cation sites on the external basal surfaces [54] as well as from surface sites of clinoptilolite and montmorillonite present in the samples.

The origin of basic properties of natural clay minerals, for which acidic properties are more characteristic, is related to formation of Lewis basic sites during dehydroxylation process taking place at catalyst activation at 500°C. Upon heating, silanol groups Si-OH transform into siloxane one Si-O-Si, in which O<sup>-</sup> ions are able to act as Lewis bases. Other reactions, such as carbonates decomposition, take place as well, yielding MgO and CaO and providing additional basic sites.

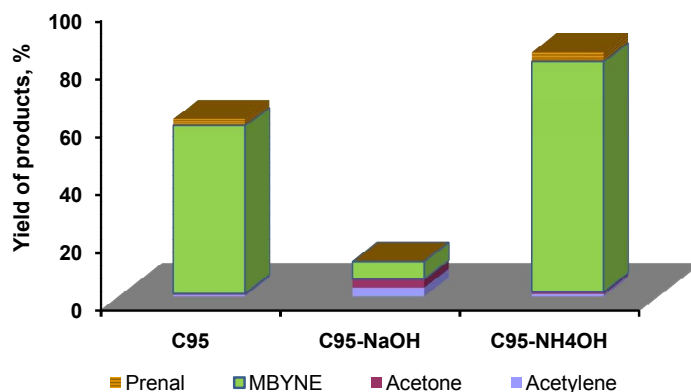
Acid treatment of samples containing kaolinite and hydromica resulted in a reduced yield of acid products. This was mainly due to the dissolution of metal oxides, loss of cations from the



interlayer space ( $\text{Ca}^{2+}$ ,  $\text{Na}^{+}$ ) and from octahedral positions ( $\text{Al}^{3+}$ ,  $\text{Mg}^{2+}$ ) that provided lower polarization of structural Si-OH groups and/or water molecules in hydrated shells, and consequently weaker surface acidity. Nevertheless, the yields of basic products for MBOH conversion over Kaol-Ac and Hdm-Ac were almost not affected, indicating the same basicity of the surface before and after acid activation.

On the contrary, the higher basicity of the sample containing natural palygorskite caused by its higher content of MgOH and AlOH groups was markedly reduced after acid treatment, obviously on the same reason (dissolution of octahedral cations of  $\text{Mg}^{2+}$  and  $\text{Al}^{3+}$ ), providing higher yields of acidic products at the same time.

In the case of alkaline treatment of natural aluminosilicates, different effects were observed depending on the base used as a modifying agent. Fig. 9 illustrates yields of products for MBOH conversion over natural clinoptilolite sample (C95, 95% of clinoptilolite, 5% illite; grain size, 215–300  $\mu\text{m}$ ) treated by 2M solutions of NaOH and  $\text{NH}_4\text{OH}$ .



**Figure 9.** Yields of products formed during MBOH conversion over natural clinoptilolite (C95), treated by 2M NaOH (C95-NaOH) and  $\text{NH}_4\text{OH}$  (C95- $\text{NH}_4\text{OH}$ ) solutions.

The treatment of clinoptilolite sample by a NaOH solution strongly inhibited the conversion of MBOH, providing higher basicity and scarce acidity of the surface. Considering variations in chemical composition and porosity [37,43] by alkaline modification, the possibility of both rising and falling specific surface area, and the low stability of Si-O-Al bond in the alkaline media, it is obvious that not only the surface-active sites but also the structure and textural properties were changed [55].

The effect of  $\text{NH}_4\text{OH}$  treatment on surface activity of clinoptilolite was completely different. The catalytic activity of C95- $\text{NH}_4\text{OH}$  for the conversion of MBOH was significantly higher as for natural one, mainly due to high surface acidity, which arisen from the dissociation of  $\text{NH}_4^{+}$  ions by thermal effect under reaction conditions. The  $\text{NH}_4^{+}$  ions adsorbed during  $\text{NH}_4\text{OH}$  treatment acted as strong proton donors (Broensted acid sites) upon the reaction.

In addition to the above-considered application of the MBOH conversion method for characterization of surface-active sites of aluminosilicates, it is necessary to illustrate the ability of

this method to assess the strength of surface-active sites attracting other independent method (TPD-NH<sub>3</sub> technique) for surface acidity/basicity analysis. For the series of natural aluminosilicate samples originated from several deposits in Jordan (J) and Russia (R), it was possible to compare the acidity/basicity of the surface. The phase compositions of investigated aluminosilicate samples are given in Table 6. Experimental yields of products from MBOH conversion and surface acidity determined by TPD-NH<sub>3</sub> for various natural aluminosilicate samples are summarized in Table 7. To compare the surface activity of the investigated samples, the values of A<sub>s</sub> and B<sub>s</sub> (Table 7) were introduced as yields of products normalized by specific surface area (S<sub>BET</sub>) or by surface acidity of aluminosilicates.

Sample	Phase composition	Chemical composition (mass%)								
		SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	FeO	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	TiO <sub>2</sub>
Zeolite, Tell Rmah, Jordan (Zeol-J)	(Major—phillipsite, chabazite, faujasite)	42.0	12.8	12.1	-	10.1	8.5	4.0	0.8	0
Bentonite, Al-Azraq, Jordan (Bent-J)	Smectite 10%, illite, feldspar, quartz	55.7	20.1	1.5	-	3.5	2.1	0.1	2.4	2.5
White kaolinite, Al-Azraq, Jordan (W-Kaol-J)	(Minor—quartz, mica, feldspar, gypsum)	48.0	36.3	1.0	-	0.3	0.1	0.1	1.8	0
Red kaolinite, Batn el Ghoul, Jordan (R-Kaol-J)	(Minor—quartz, mica, feldspar, gypsum)	47.6	24.9	6.1	-	1.0	0.5	0.8	2.3	0.7
Diatomite, Al-Azraq, Jordan (Diat-J)	Traces of kaolinite, illite, and quartz	72.0	11.8	5.8	-	1.5	7.2	0	0	0
Palygorskite, Cherkassy, Russia (Pal-R)	Plg-R ~50%, quartz, zeolite, mica, feldspar	53.2	9.8	7.7	0.6	7.9	3.6	Na <sub>2</sub> O+K <sub>2</sub> O 0.9		0
Kaolinite-R, Voronezh, Russia (Kaol-R)	Kaolinite ~60%, hydromica ~30%, montmorillonite ~10%	50.5	18.2	6.8	0.3	1.8	1.9	0.3		0
Hydromica-R, Voronezh, Russia (Hdm-R)	Hydromica ~30–35%, clinoptilolite ~5%, kaolin ~5%, quartz, mica—traces	48.5	11.2	0.9	-	1.1	9.8	4.1		0

**Table 6.** Chemical and phase composition of the aluminosilicate samples from deposits in Jordan (J) and Russia (R)

As shown in Table 7, the highest acidity per unit area was observed for kaolinite sample (Kaol-R). For the other aluminosilicate samples, the acidity of unit surface area varied in the following order: Kaol-R > Hdm-R > Bent-J = R-Kaol-J > Zeol-J = Pal-R > W-Kaol-J > H-ZSM-5 = Diat-J. This

is in agreement with the confirmed fact of an extremely high acidity of thermally treated Kaol, acidic surface of which at 0% moisture is equivalent in acidity to a solution of 90% sulfuric acid [14]. Additionally, as confirmed by Liu et al. [56], the major acidic sites on the edges of minerals particles are  $\equiv\text{Si-OH}$  and  $\equiv\text{Al-OH}_2\text{OH}$  groups, which had  $\text{pK}_a$ s of 6.9 and 5.7 for kaolinite and  $\text{pK}_a$ s of 7.0 and 8.3 for montmorillonite (Mt), respectively.

Regarding the surface sites of other clay minerals samples, Voronchak et al. [57] confirmed that 48% of surface sites of Pal were weak acid sites, whereas that for Bent was only 21%.

According to the values of  $A_m$  (Table 7), the strength of acid sites available after 116 min of the MBOH conversion was distributed among the studied samples in a following way: Kaol-R > Pal-R > Bent-J > R-Kaol-J > W-Kaol-J > Zeol-J > Diat-J > H-ZSM-5.

Catalyst	S <sub>BET</sub> , m <sup>2</sup> /g	Acidity, μmol/g	Acidity/ S <sub>BET</sub> , μmol/m <sup>2</sup>	Yields of reaction products, mol%				A <sub>s</sub> , mol	B <sub>s</sub> , mol	R <sub>a/b</sub>	A <sub>m</sub> , mol
				Acid sites (Y <sub>a.s.</sub> )		Basic sites (Y <sub>b.s.</sub> )		%/	%/	mol/m	%/
				MBYNE	Prenal	Acetone	Acetylene	(m <sup>2</sup> /g)	(m <sup>2</sup> /g)	ol	(mmol/g)
Zeol-J	96 <sup>[43]</sup>	130.0 <sup>[43]</sup>	1.3	42.5	1.1	6.5	5.9	0.4	0.1	6.7	336
Bent-J	70 <sup>[43]</sup>	59.4 <sup>[43]</sup>	0.8	33.9	0.0	15.2	5.6	0.5	0.2	2.2	571
R-Kaol-J	45 <sup>[43]</sup>	56.9 <sup>[43]</sup>	1.3	17.9	5.2	4.5	4.2	0.5	0.1	5.1	407
W-Kaol-J	41 <sup>[43]</sup>	14.1 <sup>[43]</sup>	0.3	10.0	0.0	11.2	1.1	0.2	0.3	0.9	346
Diat-J	39 <sup>[43]</sup>	29.0 <sup>[43]</sup>	0.7	1.4	1.2	4.5	4.4	0.1	0.1	0.6	186
Pal-R	146 <sup>[27]</sup>	73.0	0.5	55.8	1.6	18.0	21.3	0.4	0.1	3.2	786
Kaol-R	27 <sup>[27]</sup>	48.0	1.8	37.9	1.7	9.9	11.8	1.5	0.4	4.0	825
Hdm-R	24 <sup>[27]</sup>	-	-	15.1	0.8	9.4	11.1	0.7	0.4	1.9	-
H-ZSM-5 (t.o.s.= 116 min)	370 <sup>[27]</sup>	240.0	0.6	23.8	2.8	0.0	0.0	0.1	-	-	111
H-ZSM-5 (t.o.s.= 17 min)				73.1	0.0	0.0	0.0	0.2	-	-	304

$A_s$ —yield of products formed on acid sites normalized to  $S_{\text{BET}}$ ,  $\text{mol}\% / (\text{m}^2/\text{g})$ ;  $B_s$ —yield of products formed on basic sites normalized to  $S_{\text{BET}}$ ,  $\text{mol}\% / (\text{m}^2/\text{g})$ ;  $R_{a/b} = A_s/B_s$ ,  $\text{mol}/\text{mol}$ ;  $A_m$ —yield of products formed on acidic sites normalized to surface acidity,  $A_m = Y_{a.s.}/C_{a.s.}$ ,  $\text{mol}\% / (\text{mmol}/\text{g})$ ;  $C_{a.s.}$ —surface acidity (TPD- $\text{NH}_3$ ),  $\text{mmol}/\text{g}$ ; t.o.s.—time on stream.

**Table 7.** Yields of reaction products in MBOH conversion over natural aluminosilicates (t.o.s. = 116 min)

The evidence of a strong and fast deactivation of H-ZSM-5 follows from its values of  $A_m$  at early (17 min) and late (116 min) stages of reaction (Table 7). At the same time, it is obvious that the strength of active sites for natural Zeol and H-ZSM-5 is comparable, while the latter undergoes significant deactivation due to its microporous structure.

The values of  $B_s$ , characterizing the basicity of unit surface area of aluminosilicate samples, changed in the following order: Kaol-R > Hdm-R > W-Kaol-J > Bent-J > Pal-R > Zeol-J > Diat-J. It follows that for Kaol-R and Hdm-R samples, the higher basicity of unit area of surface is typical despite the high values of surface acidity  $A_s$ . As shown Alsawalha et al. [50], the energy of activation for the basic pathway was slightly higher than that for the acidic one ( $E_A = 79.4$  kJ/mol and  $E_A = 45.8$  kJ/mol, respectively) as calculated for the conversion of MBOH on silica-alumina and hydrotalcite. The reaction mechanism considered in detail by the same authors indicated that SiOH groups were the acidic centers and oxygen anions O<sup>-</sup> were the basic centers on the surface of the catalyst. As expected from the structure of zeolite H-ZSM-5 and from its high value of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio, equal to 45, only products of the acidic pathway were formed. In the case of clay minerals, the Broensted acid sites are mainly represented by the water molecules polarized by interlayer cations during an activation procedure.

The lowest conversion and product yields were observed for Diat-J, probably due to its low acidity [47] as a result of partial condensation of surface silanols to siloxane groups during the thermal treatment [58].

Thus, it was proved by the MBOH conversion method that surface of natural aluminosilicate samples comprise both acidic and basic sites, which can be responsible for the catalytic or adsorption ability of the material surface. The application of acid or alkaline modification changes not only the structure but also the texture and surface sites activity and a ratio between various active sites. Surprisingly, the highest surface acidity of kaolinite-containing samples was proved by several methods, although this mineral has the lowest isomorphic substitution and cation-exchange ability.

In the next paragraph, the adsorption ability of natural aluminosilicate samples is considered, which developed in aqueous solutions of various substances considered as industrial toxicants.

## 4. Adsorption of industrial pollutants by natural and modified aluminosilicates

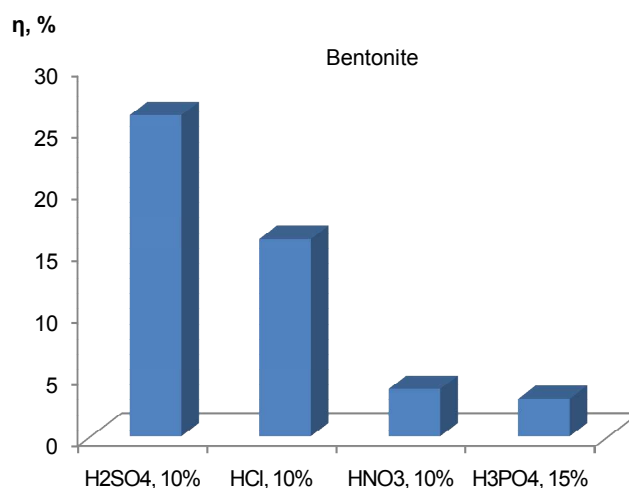
### 4.1. Natural and acid/base-treated clay minerals and zeolite as adsorbents of formaldehyde from aqueous solutions

Formaldehyde is an organic substance (the simplest aliphatic aldehyde), a colorless gas with a pungent odor, soluble in water, alcohols, and polar solvents. It causes a negative impact on the genetic material, reproductive organs, respiratory tract, eyes, and skin, as well as seriously affects the central nervous system and has been considered and officially proved as a potentially carcinogenic to humans and living organisms by the Hygienic Standards of Russian Ministry of Health and the International Agency for Research on Cancer. However, for the last decades, such materials and goods as resins, plastics, paints, textiles, disinfectants, and preservatives were manufactured using formaldehyde and its derivatives. Among them are urea-formaldehyde resins frequently used as a base for adhesives and gluing mixtures for manufacturing of the furniture, lacquers, building paints, gluing materials, composites, etc.

By the production of urea-formaldehyde resins (UFR), polycondensation reaction between urea and formaldehyde is not usually brought to the end in order to get the resin in liquid form and vary the structure of the polymer resin. As a result, there is always free formaldehyde in the end-product of UFR synthesis, which is released into the atmosphere of the working zone during synthesis, preparation of gluing composition, gluing and drying of wood products (cheap boards, furniture, etc.), and washing of the gluing equipment, while exploiting the new furniture itself.

The amount of formaldehyde in wastewater coming from washing of gluing equipment may reach 500 mg/L [3, 16], which is 10 times higher than the concentration of formaldehyde in wastewater taken for treatment and 10,000 times higher than the MPC of water (0.05 mg/dm<sup>3</sup>). To eliminate formaldehyde pollution, modern water treatment technologies combine various physical–chemical methods, among which adsorption is the major one and the development of effective, low cost, recyclable, and environmentally benign adsorbent is of current interest.

Natural clay minerals and zeolites revealed high adsorption capability toward formaldehyde both from aqueous and from gaseous phases [3], which can be further increased by applying acid treatment or physical (thermal, electromagnetic field exposure) activation. The activation effect of mineral acids (Fig. 10) on adsorption capacity toward formaldehyde of natural bentonite samples decreased in the order  $\text{H}_2\text{SO}_4 > \text{HCl} > \text{HNO}_3 > \text{H}_3\text{PO}_4$ , which did not fully matched the change of mineral acid dissociation constants.

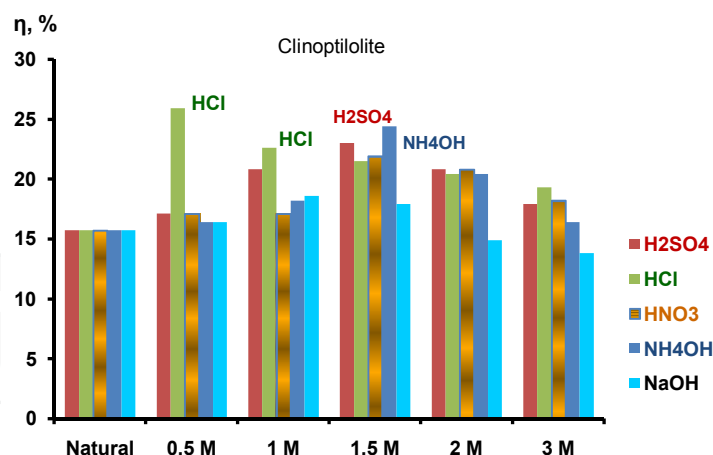


**Figure 10.** The rate of purification of model wastewater containing formaldehyde by acid-treated bentonite (deposit from Voronezh area, Russia).

As shown in Fig. 10, hydrochloric acid, as a stronger electrolyte compared with  $\text{H}_2\text{SO}_4$ , caused lower activating effect on bentonite adsorption capacity. However, one should consider the more severe structural and surface changes caused by HCl and expect, therefore, the shorter times needed to enhance the surface and adsorption characteristic of minerals.

In the case of clinoptilolite-rich sample containing C95 (95% of clinoptilolite), the activating effect observed for various mineral acids and bases was in a strict compliance with their

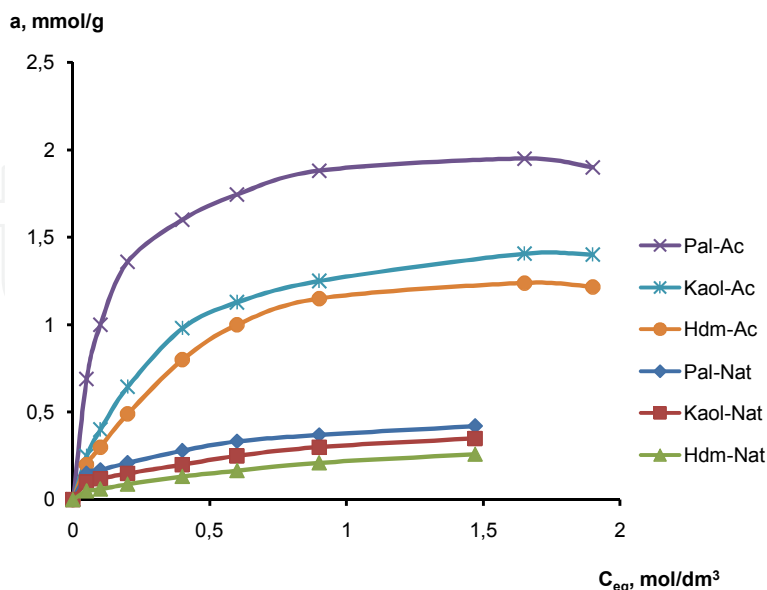




**Figure 11.** The rate of purification of model wastewater containing formaldehyde by clinoptilolite C95 (95% of clinoptilolite, Slovak deposit) treated by varied concentrations of mineral acids and bases.

strength determined by the dissociation constants (Fig. 11). The adsorption capacity of clinoptilolite activated by mineral acids decreased in the order  $\text{HCl} > \text{H}_2\text{SO}_4 > \text{HNO}_3$  [29], which is the order for the decrease of their  $K_d$  values. Moreover, the weaker the acid, the higher the concentration necessary to activate the sample and reach the same adsorption capacity as for the sample treated by a stronger mineral acid. The activation effect of acids observes a maximum, when at lower and moderate concentrations there is a rise of surface characteristics (specific surface area, porosity, and adsorption capacity) and then, at higher concentrations, a decline due to severe destruction of the mineral structure.

Adsorption isotherms of formaldehyde from aqueous solutions by natural and acid-treated samples containing kaolinite, hydromica, and palygorskite are shown in Fig. 12.



**Figure 12.** Isotherms of formaldehyde adsorption from aqueous solutions by natural (Nat) and acid-treated (Ac) aluminosilicate samples rich in palygorskite (Pal); kaolinite (Kaol), and hydromica (Hdm).

The obtained adsorption isotherms have a convex shape, which is similar to isotherms of the Langmuir's type. The isotherms for acid-treated samples lie much higher than that for natural ones, specifying the activation affect of acid. The highest adsorption ability was observed for Pal, and the lowest for Hdm, obviously, due to the changes of their specific surface area and porosity considered earlier (Table 3).

The adsorption parameters (Table 8) obtained from the isotherms were satisfactorily described applying the Langmuir equation (Eq. 9)):

$$a = a_{\max} \frac{K_{\text{ads}} \cdot C_{\text{eq}}}{1 + K_{\text{ads}} \cdot C_{\text{eq}}} \quad (9)$$

$$\text{or} \dots \frac{1}{a} = \frac{1}{a_{\max}} + \frac{1}{a_{\max} \cdot K_{\text{ads}} \cdot C_{\text{eq}}},$$

where  $a$  is the adsorption ability of a sorbent, mmol/g;  $a_{\max}$  is the maximal adsorption ability of a sorbent, mmol/g;  $K_{\text{ads}}$  is the constant of adsorption equilibrium; and  $C_{\text{eq}}$  is the equilibrium concentration of a substance in solution, mol/dm<sup>3</sup>.

Sample	$a_{\max}$ mmol/g		$\frac{a_{\max}(\text{Ac})}{a_{\max}(\text{Nat})}$	$K_{\text{ads}}$		$\frac{K_{\text{ads}}(\text{Ac})}{K_{\text{ads}}(\text{Nat})}$	$R^2$	$-\Delta G_{293\text{K}}$ kJ/mol	
	Nat	Ac		Nat	Ac			Nat	Ac
Pal	0.67	2.36	3.5	3.60	11.70	3.25	0.999 0.961	2.94	5.98
Kaol	0.37	1.60	4.3	2.20	5.90	2.70	0.998 0.986	1.92	4.32
Hdm	0.39	1.10	2.8	1.70	7.40	4.35	0.987 0.913	1.29	4.87

$R^2$ —correlation coefficient; numerator—natural; denominator—activated by H<sub>2</sub>SO<sub>4</sub>.

**Table 8.** Adsorption characteristics of natural (Nat) and modified by 2M H<sub>2</sub>SO<sub>4</sub> (Ac) clay minerals samples

The equilibrium parameters ( $a_{\max}$  and  $K_{\text{ads}}$ ) were maximal for both natural and activated Pal sample, owing to its well-developed surface, porosity, and high activity of surface sites. Acid treatment enhanced the adsorption capacity of aluminosilicates more than 3 times (Table 8), having the most significant effect on Kaol sample, containing kaolinite, illite, and montmorillonite (Table 2). Apparently, this was the feature of the layered structure of the Kaol components, which was less stable against acid attack, unlike that for Pal and Hdm.

The adsorption equilibrium constants ( $K_{\text{ads}}$ ) were also maximal for Pal, changing in the order Pal > Kaol > Hdm for adsorption on natural samples and as Pal > Hdm > Kaol for adsorption on acid-activated samples. Evidently, the acid activation caused not only the surface area and porosity variations but also the type and/or the strength of active sites. As a result, the highest

value of  $\frac{K_{\text{ads}}(\text{Ac})}{K_{\text{ads}}(\text{Nat})}$  found for Hdm sample (4.35) indicated the strongest shift of the adsorption equilibrium toward adsorption products due to more significant changes in the surface sites activity. The ratio of Gibbs free energy,  $\Delta G$  (thermodynamic potential), calculated as  $\Delta G = -RT \ln K_{\text{ads}}$ , was the highest for Pal samples as well. However, the ratio of  $\Delta G$  before and after acid treatment was the highest for Hdm, which means that the higher energy gain was obtained due to increased activity of surface sites of Hdm. To explain this fact, the adsorption parameters from Table 8 were normalized per unit of surface area of the samples (Table 9).

Sample	$a'_{\text{max}}$ mmol/m <sup>2</sup>		$\frac{a'_{\text{max}}(\text{Ac})}{a'_{\text{max}}(\text{Nat})}$	$-\Delta G'_{293\text{K}}$ kJ/mol/m <sup>2</sup>	
	Nat	Ac		Nat	Ac
Pal	0.0045	0.009	2.0	0.02	0.022
Kaol	0.013	0.025	1.9	0.071	0.067
Hdm	0.0162	0.035	2.1	0.053	0.157

**Table 9.** Adsorption parameters of aluminosilicate samples normalized per unit area

As shown in Table 9, there is an inverted order of adsorption capacity for investigated aluminosilicate samples: Hdm > Kaol > Pal. The maximal adsorption occurs on the unit surface of Hdm sample, while the minimum one occurs on the unit surface of Pal. Apparently, it points at the higher number and/or the stronger active sites on the surface of Hdm sample, and the weaker one or in a fewer amount on the surface of Pal.

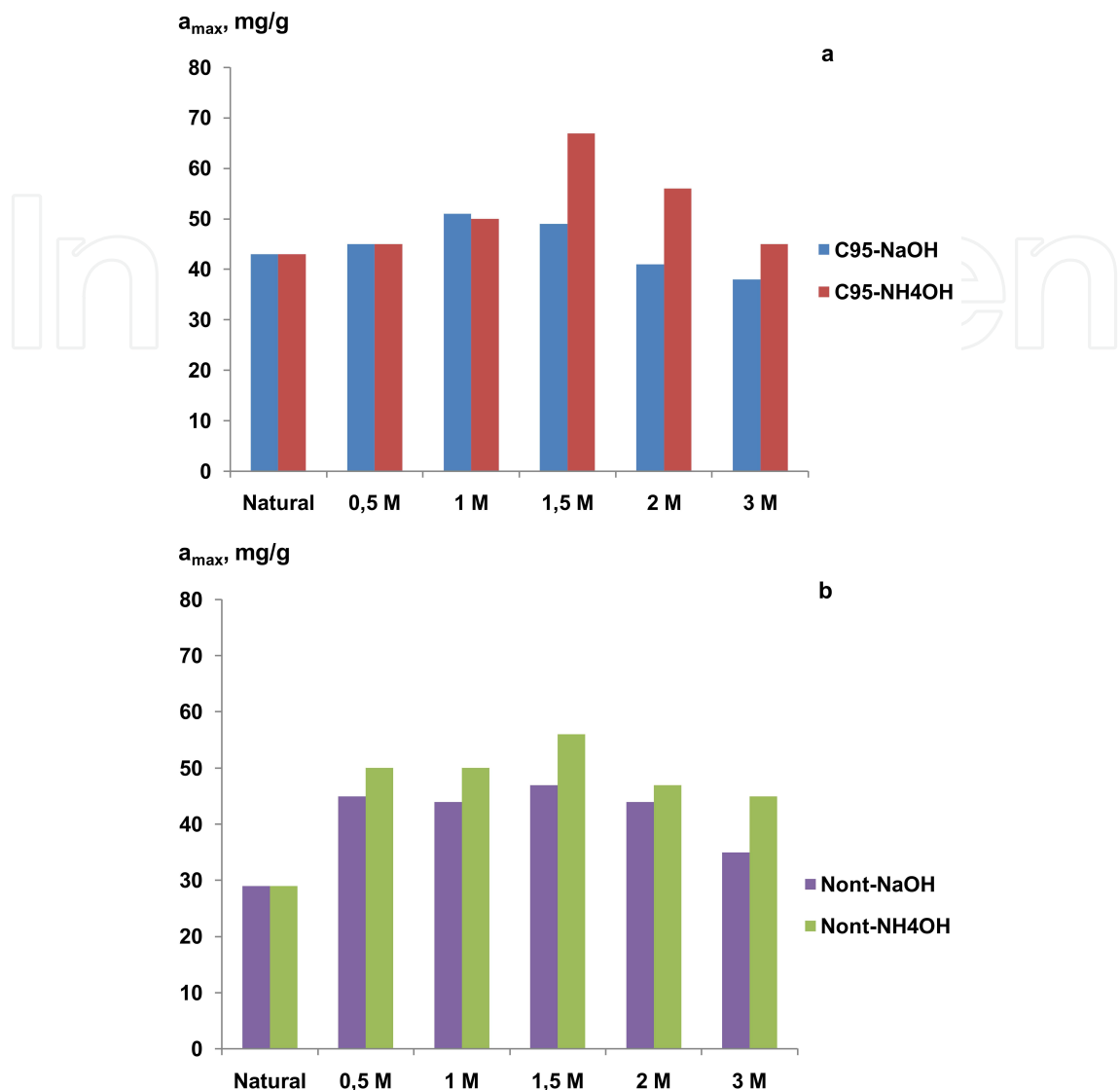
According to the ratio of  $a'_{\text{max}}$  before and after acid treatment, this type of activation almost equally influenced the surface properties of investigated aluminosilicates and caused a twofold increase in their adsorption capacity.

Higher values of Gibbs free energy for adsorption per unit area were obtained for Hdm, and the lowest values were for Pal. Therefore, one may assume the stronger adsorption interaction on Hdm surface than on other minerals that is apparently related to the strength of the adsorption sites and in good agreement with MBOH characterization data considered in Section 3.

The effect of alkaline activation of the adsorption capacity of natural aluminosilicates was weaker in the case of NaOH solutions compared with NH<sub>4</sub>OH (Fig. 13a and b) or mineral acids solutions (Fig. 12).

As confirmed in Fig. 13 for natural samples rich in clinoptilolite (C95, 95%) and nontronite (Nont; 58% nontronite, 7% kaolinite, 15% illite, and 20% quartz), treatment by NaOH (6 h, 100°C) brought up to 15% and 38% gain in adsorption capacity, respectively, while acid treatment gave 32–65% excess in formaldehyde adsorption for C95 and more than twofold excess for Nont treated by 2M H<sub>2</sub>SO<sub>4</sub>.

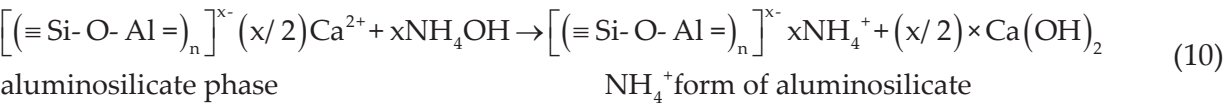
The use of NH<sub>4</sub>OH solutions as activation agent was more effective than NaOH, providing 35–50% rise in formaldehyde adsorption by C95 and Nont samples. Moreover, the effect of

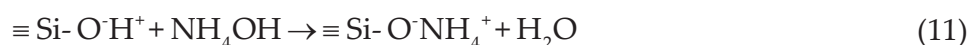


**Figure 13.** Adsorption capacity of samples containing natural clinoptilolite (C95,(13a)) and nontronite (Nont, (13b)), modified by varied bases (NaOH, NH<sub>4</sub>OH) concentrations, determined in aqueous solutions of formaldehyde.

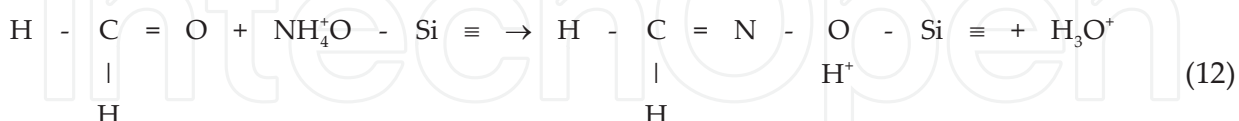
NH<sub>4</sub>OH treatment was comparable to that for mineral acids or even higher than the treatment with 2–3M H<sub>2</sub>SO<sub>4</sub>, HCl, and HNO<sub>3</sub>.

The treatment of aluminosilicates with NH<sub>4</sub>OH solution comprises the occurrence of ion-exchange reactions (Eqs. (7) and (8)) considered above for the case of NaOH treatment:



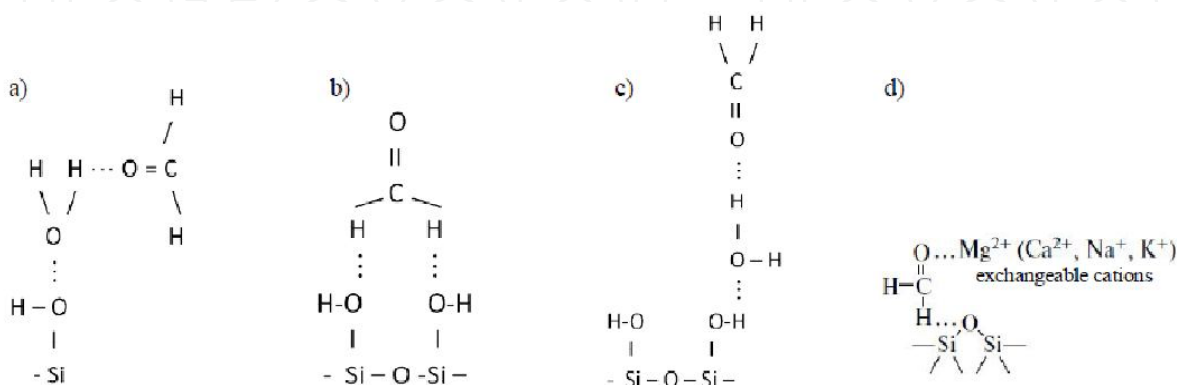


Also, there is a possible adsorption of  $\text{NH}_4\text{OH}$  molecules due to H-bonding to the surface polar groups. The consequences of such enrichment of the silicate surface with ammonia ions is a possibility of chemisorptions of formaldehyde molecules due to their interaction with  $\text{NH}_4^+$  ions resulting in formation of imine



The occurrence of this reaction was observed and confirmed for the amine-functionalized mesoporous silica [59]. Thus, reaction (12) concerns one of the possible mechanisms of formaldehyde adsorption, which is likely to occur via surface functional amine groups.

Nevertheless, the surface of acid and alkali-treated aluminosilicate samples supposes another adsorption mechanism, comprising the most likely allocation of the formaldehyde molecules (associates) on the adsorbent surface. The FTIR spectroscopy applied to elucidate the mechanism of adsorption from the aqueous phase met some obstacles. Under the competitive adsorption of water molecules on the highly hydrophilic and hydroxylated surface of aluminosilicate, the main changes observed are the intensities of the absorption bands of the hydroxyl groups of water, whereas the absorption bands of carbonyl group  $\text{C}=\text{O}$  are superimposed on the oscillations of OH group and was hard to determine unambiguously the presence of formaldehyde in the spectra. In this regard, the following adsorption mechanism for formaldehyde molecules was suggested (Fig. 14). The molecules of formaldehyde, which exist in the form of hydrates ( $\text{HO}-\text{CH}_2-\text{OH}$ ) in aqueous solutions, are bound to the surface, mainly via hydrogen bonding. Various actives sites, e.g., Broensted ( $\text{Si}-\text{OH}$ ,  $\text{Si}-\text{O}(\text{H}^+)-\text{Al}$ ,  $\text{AlOH}_2^+$ ) and Lewis (exchangeable and structural cations, oxygen anions of the lattice) sites, are expected to contribute to H-bonding of formaldehyde.



**Figure 14.** Adsorption of formaldehyde on the surface of aluminosilicates [3, 29].



Additionally, it is necessary to take into account that formaldehyde molecules are highly reactive; they easily oxidize and polymerize, undergoing hydrolysis in an acidic media to the starting monomer formaldehyde, whereas in alkaline media, the reaction of Kannitsarro may take place.

Thereby, the above-mentioned behavior of the aluminosilicate samples allows one to conclude that, depending on the structure of clay minerals or a zeolite presenting in the investigated natural samples, the adsorption of formaldehyde may occur (i) on the surface and in the interlayer space of layered aluminosilicates (montmorillonite and other clay minerals), (ii) on the lateral facets of clay mineral crystals, (iii) inside and outside of zeolite channels of clinoptilolite, and (iv) in the transport channels of palygorskite.

**4.2. Base-treated natural aluminosilicate as adsorbents of acetic acid from aqueous solutions**

Acetic acid along with formic and other organic acids comes into the wastewater of wood-working industry on the stages of the hot steam treatment of wood before the production of plywood and fiber boards. Cellulose and hemicelluloses undergo hydrolysis yielding these acids and other organic substances, which are released then into the atmosphere and get into wastewater amounting up to 3000 mg/L for acetic and up to 500 mg/L for formic acids. Anaerobic wastewater treatment allows reducing organic acid content to 100 mg/dm<sup>3</sup>, whereas the maximal permissible concentration (MPC) for acetic acid in water is 0.01 mg/dm<sup>3</sup>.

The adsorption of acetic acid on acid-treated clay minerals do not occur [60], whereas natural and alkali-activated clay minerals proved adsorption ability toward acetic acid.

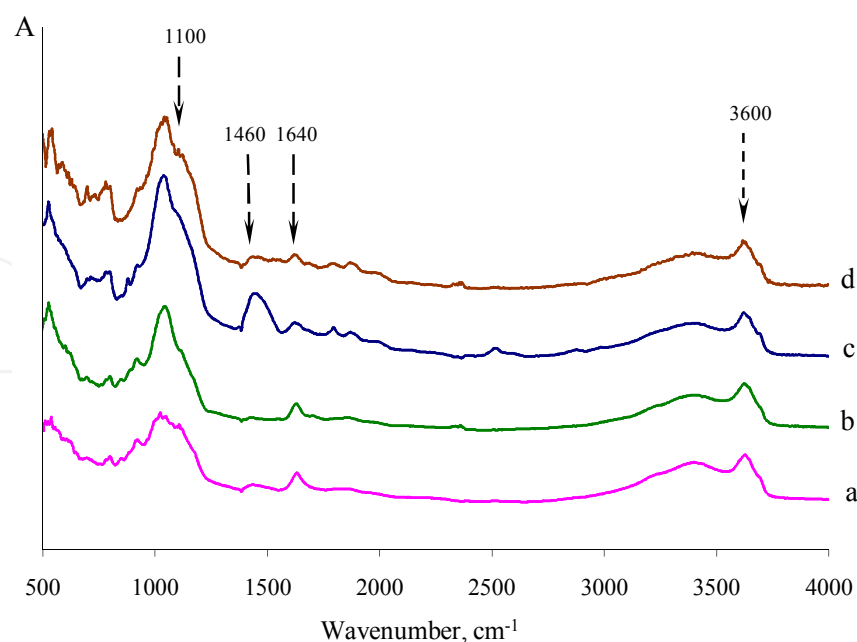
The isotherms of the adsorption of acetic acid by natural and alkali (2M NaOH)-treated sample of montmorillonite M95 (95% of montmorillonite) had typical form of the Langmuir type isotherms, indicating at monolayer adsorption within the chosen concentration interval (0.1–2.0 mol/dm<sup>3</sup>). The equilibrium parameters of adsorption assessed applying Langmuir equation are given in Table 10.

Adsorbent	$a_{\max}$ , mmol/g	$K_{\text{ads}}$	$R^2$	$-\Delta G$ , kJ/mol
Mont-Nat	2.1	3.0	0.989	12.5
Mont-Alk	2.9	6.5	0.999	14.3

**Table 10.** Adsorption parameters of natural and alkali-treated montmorillonite M95

Alkaline treatment increased the maximal adsorption capacity of montmorillonite in 1.4 times, obviously, due to additional hydroxylation of the aluminosilicate surface, which contributed to a higher adsorption of acetic acid molecules. The increase in adsorption equilibrium constant,  $K_{\text{ads}}$ , and the change of thermodynamic potential testify to a higher thermodynamic probability and a higher energy gain for the adsorption process on alkali-treated clay mineral.

The FTIR spectra of natural and alkali-activated montmorillonite (Fig. 15) allowed the elucidation of the mechanism of the adsorption of acetic acid.



**Figure 15.** FTIR spectra of montmorillonite (M95) before and after the adsorption of acetic acid: (a) natural montmorillonite (MM), (b) natural MM after the adsorption of acetic acid, (c) alkali-treated MM, and (d) alkali-treated MM after the adsorption of acetic acid.

As shown in Fig. 15, all the spectra comprise the bands of the aluminosilicate lattice, i.e., Si-O ( $1050\text{ cm}^{-1}$ ), Si-O-Si ( $804\text{ cm}^{-1}$ ), O-Si-O ( $540\text{ cm}^{-1}$ ), and Si-O-Al ( $1100\text{ cm}^{-1}$ ) [61, 62]. Under alkaline exposure, there was partial change of montmorillonite structure evidenced by the broadening of the  $1050\text{--}1110\text{ cm}^{-1}$  band in spectra c and d (Fig. 15). This has likely facilitated the access of hydroxyls to lattice  $\text{Mg}^{2+}$  and  $\text{Al}^{3+}$  ions and resulted, therefore, in a significant absorption at  $1460\text{ cm}^{-1}$  (overtones of Mg-OH and Al-OH groups [62]). The band about  $1640\text{ cm}^{-1}$  was caused by adsorbed water molecules and practically did not change the intensity. Also, the stretching vibrations of OH groups ( $3600\text{ cm}^{-1}$ ) as well as a band at  $3400\text{ cm}^{-1}$  due to hydroxyls of interlayer water did not change from samples to sample.

After the adsorption of acetic acid, the FTIR spectra observed no bands corresponding to neutral or ionized carboxylic group as well as bands of methyl group of acetic acid. However, the absorption band at  $1460\text{ cm}^{-1}$  was found to substantially reduce its intensity for the case of alkali-activated montmorillonite and almost completely disappeared from the spectrum of natural sample. This fact allows one to conclude that hydroxyl groups of Al-OH and Mg-OH were involved in the binding of acetic acid. Adsorptive interaction may be due to the hydrogen bonding between the hydroxyl groups of montmorillonite ( $=\text{SiOH}$ ,  $\text{-MgOH}$ ,  $\text{-AlOH}$ ) and the carboxyl group of acetic acid. The mechanism of acetic acid adsorption on the surface of montmorillonite shown in Fig. 16 was proposed after Tanaka et al. [61], who confirmed it for the adsorption of acetic acid on hydroxyapatite.

Furthermore, the reaction of neutralization is possible between hydroxyl groups of montmorillonite and molecules of acetic acid.

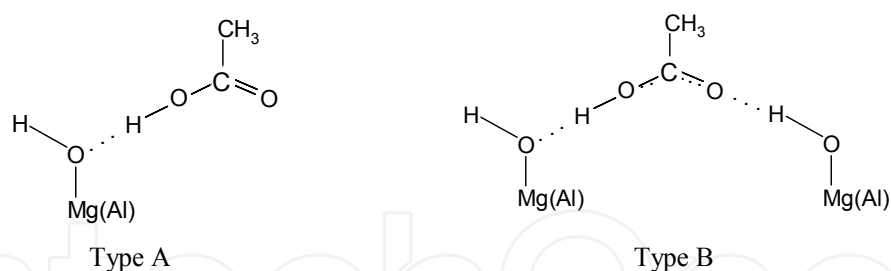


Figure 16. Mechanism of the adsorption of acetic acid [61].

Thus, the above-mentioned examples of alkaline and ammonium hydroxide activation illustrated that depending on the nature of the activating agent and the chemical nature of the adsorbate, the adsorption phenomenon may occur via various interactions, e.g., hydrogen bonding, chemical reaction (chemisorption), and/or ion-exchange.

#### 4.3. Contribution of ion-exchange reactions to the adsorption of ammonia ions

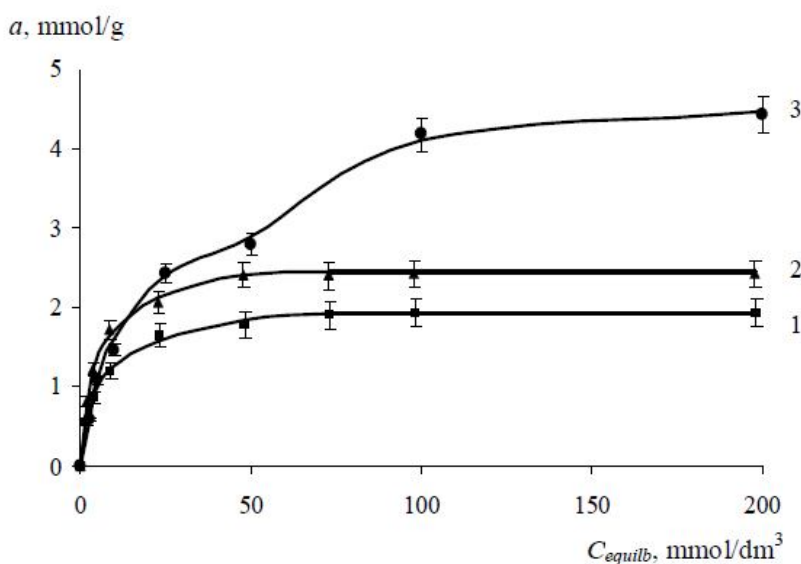
In solutions of electrolytes, the substances that dissociate into ions by dissolution, ion-exchange processes significantly contribute to the adsorption process if the adsorbent exhibits ion-exchange ability. This is illustrated hereinafter, on the features of ammonium ions adsorption, which is a major toxicant of industrial, domestic, and agricultural wastewater. For the treatment of wastewater from ammonium ions, adsorbents on the base of natural and synthetic zeolites as well as other aluminosilicates are frequently used.

The main mechanism for  $\text{NH}_4^+$  sorption by zeolites is ion-exchange. Extra framework cations  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$ , balancing the negative charge of the framework, are being replaced stoichiometrically for  $\text{NH}_4^+$  ions [64–66] in the order of selectivities for clinoptilolite  $\text{K}^+ > \text{NH}_4^+ > \text{Na}^+ > \text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  [64]. The  $\text{NH}_4^+$  sorption capacities of zeolites vary about 6.8–7.2 mmol/g.

Similarly, the ion-exchange sorption of  $\text{NH}_4^+$  ions from aqueous solutions occurs on natural clays [67–69]. Both exchangeable cations and pH-influenced hydrolyzed Si-OH or AlOH groups from the edges of clay particles contribute to cation-exchange for  $\text{NH}_4^+$  ions, mainly in dilute solutions. The CEC of natural clays for  $\text{NH}_4^+$  is lower compared with zeolites, varying within 1–2 mmol/g. The  $\text{Na}^+$  form of natural clays enhances the adsorption of  $\text{NH}_4^+$  ions, the process of which obeys Langmuir-type adsorption. At high  $\text{NH}_4^+$  content, the retaining capacity of natural adsorbent materials decreases, providing contribution of the nonion-exchange sorption of  $\text{NH}_4^+$  ions.

In more detail, the contribution of ion-exchange reactions as major processes related to ammonium ions adsorption as well as the effect of acid/alkaline modification were studied for the mixed natural silica-alumina sorbent  $\text{M}_{45}\text{C}_{20}$  (45% of montmorillonite and 20% clinoptilolite) [63]. The isotherms of  $\text{NH}_4^+$  ions adsorption were obtained for natural and activated

M<sub>45</sub>C<sub>20</sub> sorbent from 0.0025 to 0.2 M solutions of NH<sub>4</sub>Cl at 295 K with an equilibration time of 3 h (Fig. 17).



**Figure 17.** Isotherms of NH<sub>4</sub><sup>+</sup> ions sorption on natural (1), acid-treated (2), and alkali-treated (3) M<sub>45</sub>C<sub>20</sub> sorbent.

The obtained isotherms have a convex shape with a saturation region that was satisfactorily described by the Langmuir equation. The adsorption capacity ( $a_{\max}$ , mmol/g) of natural and activated M<sub>45</sub>C<sub>20</sub> sorbent increased in the order MCN (1.9) < MCAc (2.4) < MCAIk (4.1) observing the highest value for alkali-activated sample.

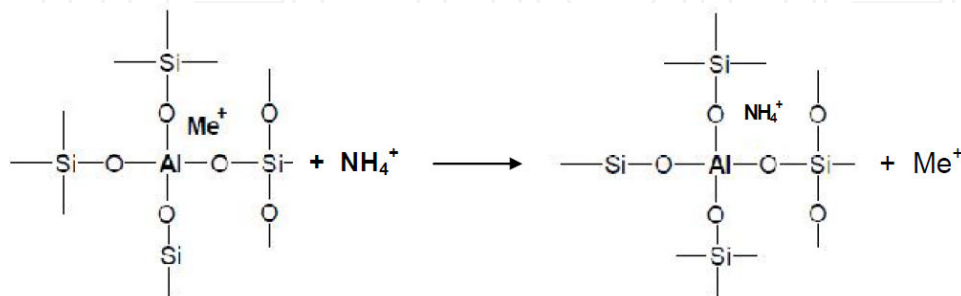
The quantities of exchangeable cations of Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, and Mg<sup>2+</sup> displaced by NH<sub>4</sub><sup>+</sup> ions during sorption process are summarized in Table 11.

$C_{eq}(\text{NH}_4^+)$ , mmol/dm <sup>3</sup>	Quantity of desorbed cations, mmol/g				$\Sigma \text{Na}^+, \text{K}^+, \text{Ca}^{2+},$ $\text{Mg}^{2+}$ , mmol/g	$a_{\text{NH}_4^+}$ , mmol/g	CEC, <sup>a</sup> mmol/g	CEC/ $a_{\text{NH}_4^+}$
	Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>				
1.950	0.085	0.020	0.370	0.092	0.567	0.550	1.029	1.9
4.143	0.115	0.025	0.481	0.208	0.829	0.857	1.518	1.8
8.806	0.134	0.029	0.741	0.301	1.207	1.194	2.249	1.9
23.363	0.154	0.035	0.952	0.395	1.536	1.637	2.883	1.8
48.228	0.160	0.039	1.105	0.453	1.757	1.772	3.315	1.9
73.108	0.170	0.041	1.180	0.509	1.901	1.892	3.590	1.9
98.076	0.170	0.041	1.180	0.509	1.901	1.924	3.590	1.9

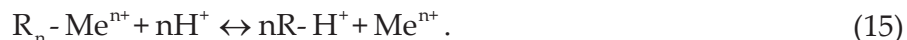
<sup>a</sup>CEC assessed as total amount of exchangeable 1<sup>+</sup> cations considering equivalent exchange of bi- and monocharged cations.

**Table 11.** Quantity of exchangeable cations desorbed from natural M<sub>45</sub>C<sub>20</sub> (MCN) sorbent by sorption of NH<sub>4</sub><sup>+</sup> ions (changed after Belchinskaya et al. [63])

It is seen from Table 11 that the total number of displaced exchangeable cations was almost equal to the amount of absorbed  $\text{NH}_4^+$  ions on natural sorbent in the whole range of external solution concentration. This fact testifies to cation-exchange reactions (Scheme 4) (and (Eq. 13)) taking place between the  $\text{NH}_4^+$  ions in aqueous solution and exchangeable cations ( $\text{Me}^{z+} = \text{Ca}^{2+}, \text{Mg}^{2+}, \text{Na}^+, \text{K}^+$ ;  $\text{R}_n$  is the framework of a silicate with a charge “n.”) in the sorbent phase. Moreover, the hydrolysis reaction (Eq. (14)) of  $\text{NH}_4\text{Cl}$  in aqueous solution should be considered, resulting in a significant contribution of protons to cation-exchange reactions (Eq. (15)).



**Scheme 4.** Cation-exchange reaction between  $\text{NH}_4^+$ -ions in solution and exchangeable cations in sorbent phases



The intensity of  $\text{NH}_4^+$  ions exchange for cations decreased in the order  $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{Na}^+ > \text{K}^+$ , which was mainly determined by the chemical content of respective metal oxide except for  $\text{K}^+$  ions. However, despite the higher  $\text{K}_2\text{O}$  content in the mineral phase, the exchange of  $\text{K}^+$  for  $\text{NH}_4^+/\text{H}^+$  was weaker compared with  $\text{Na}^+$ , although it had lower amount of  $\text{Na}_2\text{O}$ .

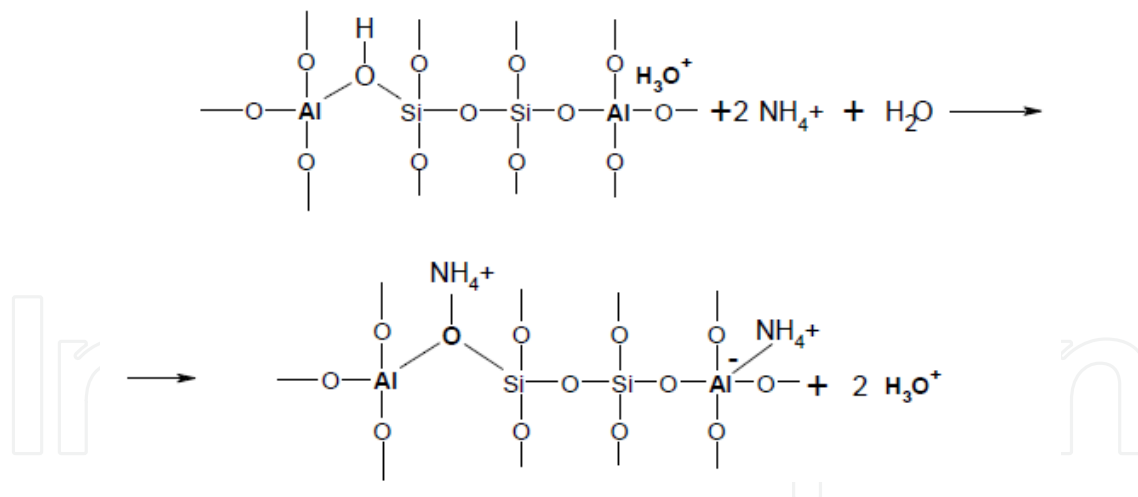
Taking into account the equivalent ion-exchange between 2+ and 1+ ions, the values of sorbent CEC available for  $\text{NH}_4^+$  capturing confirmed the significant contribution of protons ion-exchange (Eq. (15)) to the adsorption of  $\text{NH}_4^+$  ions by natural  $\text{M}_{45}\text{C}_{20}$  sorbent. As a consequence, the ratio of  $\text{CEC}/a_{\text{NH}_4^+}$  (Table 11) was twice as amount of ammonia adsorbed.

As shown in Table 12, the amount of  $\text{NH}_4^+$  ions adsorbed by acid-activated samples MCAC exceeds about twice the total amount of desorbed cations  $\text{Na}^+, \text{K}^+, \text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$ . This is explained by the transition of natural sorbent into  $\text{H}^+$  form by the acid treatment. As a result, the composition of the cation-exchange complex of MCAC to a greater extent was determined by the exchanged protons (or hydronium ions  $\text{H}_3\text{O}^+$ ), which has a quantity of  $\sim 0.79 \text{ mmol/g}$ , as estimated from a difference in the amount of desorbed cations from MCN and MCAC samples during the  $\text{NH}_4^+$  adsorption.

$C_{eq}(\text{NH}_4^+)$ , mmol/dm <sup>3</sup>	Quantity of desorbed cations, mmol/g				$\Sigma \text{Na}^+, \text{K}^+, \text{Ca}^{2+}, \text{Mg}^{2+}$ , mmol/g	$a_{\text{NH}_4^+}$ , mmol/g	CEC, mmol/g	CEC/ $a_{\text{NH}_4^+}$
	$\text{Na}^+$	$\text{K}^+$	$\text{Ca}^{2+}$	$\text{Mg}^{2+}$				
1.695	0.029	0.013	0.504	0.036	0.581	0.805	1.121	1.4
3.787	0.040	0.015	0.677	0.058	0.790	1.213	1.525	1.2
8.288	0.048	0.017	0.909	0.071	1.046	1.712	2.186	1.3
22.951	0.053	0.017	0.949	0.093	1.112	2.049	2.578	1.2
47.607	0.053	0.019	0.949	0.093	1.113	2.393	2.800	1.2
72.592	0.053	0.019	0.949	0.093	1.113	2.408	2.944	1.2
97.589	0.053	0.019	0.949	0.093	1.113	2.411	2.944	1.2

**Table 12.** Quantity of exchangeable cations desorbed from acidly treated  $\text{M}_{45}\text{C}_{20}$  (MCAc) sorbent by sorption of  $\text{NH}_4^+$  ions (changed after Belchinskaya et al. [63])

Therefore, the main ion-exchange reactions that took place were (i) ion-exchange of  $\text{NH}_4^+$  for exchangeable cations including  $\text{Ca}^{2+}$  и  $\text{Mg}^{2+}$  according to Eqs. (13) and (15), (ii) ion-exchange of  $\text{NH}_4^+$  for exchangeable protons, and (iii) exchange between  $\text{NH}_4^+$  and hydronium ions as well as protons of Si-OH groups located close to three-coordinated aluminum atoms, formed after acid treatment according to Scheme 5.



**Scheme 5.** Ion-exchange reaction between  $\text{NH}_4^+$ -ions and protons

In the case of alkali-treated aluminosilicate  $\text{M}_{45}\text{C}_{20}$  (Table 13), which was converted mainly in to  $\text{Na}^+$  form during treatment, the main adsorption mechanism was provided by ion-exchange of  $\text{Na}^+$  for  $\text{NH}_4^+/\text{H}^+$  ions from external  $\text{NH}_4\text{Cl}$  solution:





$C_{eq}(NH_4^+)$ , mmol/dm <sup>3</sup>	Quantity of desorbed cations, mmol/g				$\Sigma Na^+, K^+,$ $Ca^{2+}, Mg^{2+}$ , mmol/g	$a_{NH_4^+}$ , mmol/g	CEC, mmol/g	CEC/ $a_{NH_4^+}$
	Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>				
1.915	0.397	0.018	0.351	0.052	0.817	0.585	1.22	2.1
3.916	0.554	0.024	0.521	0.096	1.195	1.084	1.812	1.7
8.545	0.773	0.029	0.721	0.166	1.690	1.455	2.577	1.8
22.579	0.923	0.034	0.994	0.209	2.160	2.421	3.363	1.4
47.213	1.202	0.041	1.061	0.223	2.524	2.787	3.808	1.4
95.831	1.260	0.042	1.204	0.250	2.782	4.169	4.236	1.0
195.580	1.291	0.042	1.202	0.265	2.797	4.420	4.264	1.0

**Table 13.** Quantity of exchangeable cations desorbed from alkali-treated  $M_{45}C_{20}$  (MCalk) sorbent by sorption of  $NH_4^+$  ions (changed after Belchinskaya et al. [63])

The ratio  $CEC/a_{NH_4^+}$  (Table 13) illustrated that the joint ion-exchange of  $NH_4^+/H^+$  ions from external solution for exchangeable cations of mineral phase occurred till the higher concentrations. Starting from 95 mmol/dm<sup>3</sup> of  $NH_4Cl$ , the ion-exchange was determined mainly by  $NH_4^+$  ions providing  $CEC/a_{NH_4^+} = 1$ .

## 5. Conclusion

The physical–chemical properties of natural aluminosilicate samples containing mineral phases of various structural types (layered planar and nonplanar silicates, zeolites) and considered in this chapter illustrated that the structure of the natural aluminosilicate phases in the sample determined its surface characteristics and surface activity toward a modifying agent and adsorbate molecules, namely, higher content of kaolinite phase (1:1 layer type mineral with a lack of isomorphic substitutions) in the natural sample comprised lower surface parameters (specific surface area, porosity) and weaker population of the surface with active sites, according to its activity in MBOH conversion. Despite this, the surface of the sample containing kaolinite underwent severe changes under acid modification due to its higher reactivity, which results, obviously, from the easier access of the modifier to octahedral sheets in the 1:1 layer type of mineral structure. Moreover, as confirmed here by the method of MBOH conversion and that is in agreement with the observations done by other physical–chemical methods, including the quantum modeling, the surface of the sample containing kaolinite (Kaol) is characterized by the strongest acid sites along with the highest basicity of the unit area of the surface.

For the cases of palygorskite (Pal) or hydromica (Hdm)-rich natural samples, the effect of acid treatment on their surface parameters was weaker, which obviously referred to a higher resistance of the structure against acid attack resulting from the features of 2:1 layer type in both planar and nonplanar silicates. The well-developed surface of the sample containing

palygorskite, although it is populated by the weaker acid and basic sites, is another sequence of its structure.

Despite the variations in surface activity observed for different aluminosilicate types, one must underline the general mechanism of the adsorption of electrolytes and polar molecules by the surface of natural aluminosilicates. Owing to the similarity of the building elements of the considered natural silicates (tetrahedral/octahedral sheets), isomorphic substitutions, and a negative layer charge, they possess similar surface-active sites, involving OH groups, exchangeable cations, coordinately unsaturated cations, and surface oxygen anions. This allows natural aluminosilicates revealing similar adsorption behavior and the occurrence of the following several mechanisms of adsorption: hydrogen bonding, ion-exchange, or chemisorptions. The physical–chemical nature of the adsorbate is a determining factor for the contribution of a specific mechanism of sorption.

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