Effect of activation temperature on surface basicity of natural aluminosilicates

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Montmorillonite and nontronite are layered aluminosilicates of smectite group minerals widely demanded in many industries owing to their unique physical-chemical and other properties. By thermal activation of raw clays there are variations in their porosity, surface area and physical-chemical properties, including formation and redistribution of surface active site of acid-base or redox character. The aim of present studies included investigation of the effect of thermal activation on the character of distribution and a number of basic sites on the surface of natural layered aluminosilicates by means of the new method of inverse thermoprogrammed desorption of CO_2.

Samples of natural aluminosilicates rich in montmorillonite (Montmorillonite 67%, illite 5%, quartz 5%, feldspars 21%) and nontronite (nontronite 70%, illite 10%, kaolinite 5%, quartz 10%, feldspars 8%) were characterized by XRD, XRF, BET N_2 adsorption techniques. To probe surface basicity and determine the number of basic sites a new iTPD-CO_2 was used. Prior the iTPD-CO_2 measurement 100 mg of a sample was activated at 200, 300, 400°C, then cooled down and loaded with CO_2 (3ml/min flow rate of CO_2 for 30 min). Next, the reactor was flushed by 5 ml/min N_2-flow to desorb weakly sorbed CO_2. The iTPD-CO_2 profiles were recorded within 20-800°C at a 20°C/min heating rate and treated using ChemStation software.

The experimental profiles of CO_2 desorption for Mt and Nt samples observed two temperature regions. Low temperature peaks evolved around 80-90°C for Mt and between 110-127°C for Nt were most likely related to the weak basic sites, whereas high temperature peaks around 510 and 620°C for Mt and above 320°C for Nt testified to stronger ones. The reasoning of the obtained iTPD-profiles was done considering thermal behavior of layered aluminosilicates.

The total basicity of Nt and Mt samples was 359.2 and 209.9 μmol/g respectively. The 1.6 times higher basicity of Nt was, obviously, caused by its phase and chemical composition and developed surface area and porosity. At higher activation temperatures the number of weak basic sites related to hydroxyl groups of adsorbed water molecules gradually decreased, namely, by 21 times for Mt and by 2.8 times for Nt.
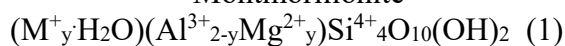
Dehydroxylation of structural Al-OH, Fe-OH, Mg-OH above 200°C, which becomes irreversible above 300°C, provided formation of residual oxygen atoms and their contribution to population of stronger basic sites. In accordance with thermal behavior of dioctahedral smectites, is assumed that strong basic sites of Mt are trans- and cis-vacant Al-OH groups dehydroxylating correspondingly at ~550 and 650°C. Fe-rich sample of Nt rapidly lost hydroxyls at rather lower temperatures that resulted in more heterogeneous distribution of strong basic sites of varying strength. At higher activation temperatures the ratio of stronger sites number to weak sites increased from 23 to 200 for Mt, whereas for Nt this ratio varied between 54-67 times. In general, total basicity of Mt and Nt decreased by 2.2-2.3 times as a result of their dehydration and dehydroxylation by thermal activation. The normalized values of basicity per unit surface area (B_Σ/S, μmol/m^2) were 1,5 times higher for Mt surface, testifying to higher occupancy and density of active sites for Mt than that of Nt.

Keywords: montmorillonite, nontronite, thermal activation, inverse TPD-CO_2, surface basicity.
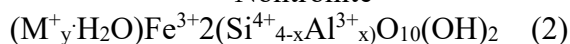
Introduction

Montmorillonite and nontronite are layered aluminosilicates belonging to smectite group minerals formed during weathering of igneous rocks in an alkaline media and constituting soil loams and sedimentary rocks [1-3]. The structure of monemotillonite and nontronite are represented by three-layer packages (T-O-T) of silica-oxygen tetrahedral and alumina-oxygen octahedra. Different extent of isomorphic substitutions of Si^{4+} for Al^{3+}, and Al^{3+} for Fe^{2+}, Fe^{3+} or Mg^{2+} in tetrahedral or octahedral sheets, respectively, leads to origin of 0.2-0.6 negative layer charge in smectites [1]. The chemical composition of octahedral sheet is the major difference of montmorillonite from nontronite that is revealed in their general chemical formulas [1, 3]:

Montmorillonite
$$(M^{+}_{y} \cdot H_2O)(Al^{3+}_{2-y}Mg^{2+}_{y})Si^{4+}_{4}O_{10}(OH)_2 \quad (1)$$
Nontronite
$$(M^{+}_{y} \cdot H_2O)Fe^{3+}_{2}(Si^{4+}_{4-x}Al^{3+}_{x})O_{10}(OH)_2 \quad (2)$$

Smectites are widely demanded in most of industrial productions owing to their unique physical, chemical, mechanical, rheological and other properties, as well as their rich and spread natural deposits making them environmentally compatible and safe [4-8]. For operation with gases or volatile compounds [9, 10] and, currently, by cement and concrete productions [11] to be used as a source of cementitious materials, raw clays need to be activated. Most often thermal activation is applied, as a result of which molecules of CO_2, H_2O and other substances leave the surface providing an increase in porosity and specific surface of a sorbent [9-12]. However, the exposure of high temperature can be destructive for aluminosilicates irreversibly changing their layered structure [1, 4, 12]. Processes of dehydroxylation at t>300ºC and amorphization at t>500ºC of layered aluminosilicates are the reasons for a decline of their internal surface, loss of ability to swell, ion-exchange and adsorb [10, 12, 13]. In addition, thermal exposure changes physical-chemical properties and, most often, increases free energy of the surface due to formation, redistribution or enhancing the accessibility of surface active site of acid-base or redox character [14, 15].

At ambient conditions, acid-base equilibrium of surface active site of natural clays is shifted towards their higher acidity [14-16]. The contribution of basic sites of the surface (structural hydroxyls, adsorbed water, edge OH-groups) becomes evident by the change of external conditions (pH, temperature), chemical [17-20] or physical [21-23] modification of aluminosilicates. In a number of processes basicity of catalyst or sorbent surface plays a decisive role [24, 25] that makes studies on basic properties of the surface under activation or modification of materials of current interest.

The aim of present studies included investigation of the effect of thermal activation on the character of distribution and a number of basic sites on the surface of natural layered aluminosilicates by means of the new method of inverse thermoprogrammed desorption of CO_2.

Table 1. Phase and chemical composition of natural and modified aluminosilicate samples [19]

Sample	Phase composition	Chemical composition, %								
		SiO_2	Al_2O_3	Fe_2O_3	Na_2O	MgO	K_2O	CaO	TiO_2	L.O.I.
Mt-0	Montmorillonite 67%, illite 5%, quartz 5%, feldspars 21%	59.48	23.34	2.89	2.09	2.38	1.14	1.62	0.24	6.61
Nt-0	Nontronite 70%, illite 10%, kaolinite 5%, quartz 10%, feldspars 8%	66.06	13.84	6.41	0.2	1.78	0.99	1.4	-	6.34

Materials and methods

Samples of natural aluminosilicates rich with montmorillonite (Mt-0) from Industrial Minerals GmbH, Germany, and nontronite, Nt-0 from Voronezh deposit "Podgornoe" were chosen as objects of investigation. Phase and chemical compositions of investigated natural aluminosilicates samples were determined by XRD and XRF techniques [19] and represented in Table 1.

Specific surface area of the samples was calculated from the N_2 adsorption-desorption isotherms obtained at -196°C using a TRISTAR 300 gas adsorption. Outgassing conditions included 2 h at 90°C followed by 8 h at 250°C. BET-method was applied for calculation of specific surface area (SSA); BJH method for mesopores volume, and t-plot analysis were used for assessment of micropores volume.

Inverse thermal programmed desorption of CO_2 (iTPD-CO_2) was used to probe surface basicity and determine the number of basic sites. The new iTPD-technique [26] TPD- is based on the FID-detection of CH_4 formed at an intermediate step of methanization of CO_2 desorbed from the surface of investigated sample by a GC. A specially designed sample loop (SL) of a fixed volume (250 μL) allows calibration of the FID-signal of GC received from the measurement and thus quantitatively determine volume of desorbed CO_2. For the iTPD-CO_2 measurement 100 mg of a sample was placed in to quartz U-tube reactor and activated at different temperatures (200, 300, 400°C) in the N_2-flow for 8 hours. After that samples were loaded with CO_2 in the 3ml/min flow of CO_2 for 30 min at ambient temperature. Next, the reactor was flushed by 5 ml/min N_2-flow to desorb weakly sorbed CO_2. At further step, the profile of iTPD-CO_2 was recorded within the 20-800°C temperature range at a heating rate of 20°C/min with a total duration of TPD of 90 min. The iTPD-CO_2 profiles were treated using ChemStation software.

Results and discussion

iTPD-CO_2 profiles of montmorillonite and nontronite samples treated at different temperatures are given in Fig.1.

As follows from the Fig.1, there were two temperature regions of the CO_2 desorption in the profiles of Mt and Nt samples. Low temperature peaks evolved around 80-90°C for Mt and between 110-127°C for Nt were most likely related to the weak basic sites [27], whereas high temperature peaks around 510 and 620 °C for Mt and above 320°C for Nt testified to stronger ones. To reason the obtained iTPD-profiles one should consider thermal behavior of layered aluminosilicates [28] as dehydration state and products will determine surface properties. It is well confirmed by thermal analysis that smectites and dioctahedral 2:1 layered silicates loose water in three temperature ranges: i) dehydration at <220°C involving loss of H_2O from the interlayer space of expandable clays; ii) OH groups
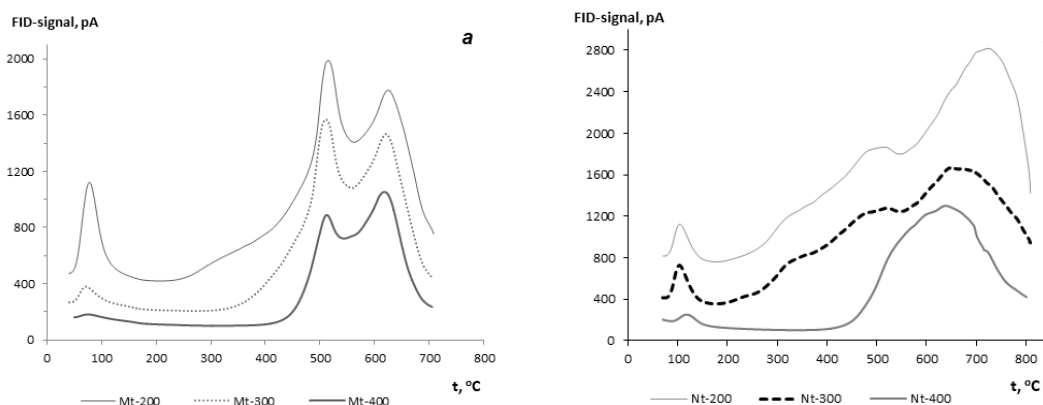

Fig. 1. iTPD-CO_2-profiles of montmorillonite (1a) and nontronite (1b) activated at 200, 300 and 400°C

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bound to the surface between 220-350°C, and iii) dehydroxylation between 350-1000°C resulting from the reaction between the octahedral hydroxyls. Due to this, gradual decrease in the intensities of the low temperature peaks at higher activation temperatures testified to a decrease in the weak basic sites related to hydroxyl groups of adsorbed water molecules. As shown for Na-Mt [27] 23% of basic sites were weak and caused desorption between 20 and 110°C, whereas at 140-200°C CO_2 desorption was caused by medium strength basic sites accounting for 42%.

Elevation of activation temperature from 200 to 400°C caused further dehydration of the samples and a decrease in the number of weak surface sites. Moreover, at temperatures above 200°C there is a process of dehydroxylation of structural hydroxyls Al-OH, Fe-OH, Mg-OH, which becomes irreversible above 300°C due to damage of the 2:1 layered structure of aluminosilicates. As shown in [29], mainly octahedral hydroxyls dehydroxylate according to a scheme 2 $(OH^-)=H_2O+O^{2-}$, providing formation of residual oxygen atoms in the structure and their contribution to population of stronger basic sites along with octahedral hydroxyls. As dehydroxylation of dioctahedral smectites typically has a duplet on DTA curve due to earlier dehydroxylation of trans-vacant (tv) Al-OH groups (~550°C), while that for cis-vacant (cv) Al-OH appears at higher temperature (~650°C) [30], it is similarly assumed that strong basic sites of Mt sample are represented by correspond-

ingly trans- and cis-vacant Al-OH groups. The distance between the adjacent OH-OH-groups is shorter in tv- (2.45 A [30]) then in cv- (2.85 A [30]) dioctahedral 2:1 layer minerals that facilitates dehydroxylation of tv-Al-OH groups and, hence, determines variations in the strength of basic sites formed. Redistribution of A1-O and Al-OH bond strengths due to migration of Al cations to empty five-coordinated sites testifies to heterogeneity of aluminous cv-layers dehydroxylation [30, 31].

In case of Nt sample, the distribution of strong basic sites is more heterogeneous as follows from the shoulder and overlapped peaks at 350-650°C. Variation of chemical composition of Nt from Mt, mainly, in the octahedral sheet strongly affects their surface sites distribution, thermal behavior and CO_2 sorption ability. It was confirmed for Fe-rich smectites (nontronites) and micas (glauconites, celadonites) consisting of tv 2:1 layers that they rapidly loose hydroxyls at significantly lower temperature as compared to Al-rich samples [30, 32]. Indeed, iTPD-CO_2 profiles of Nt samples (Fig. 1b), rich in Fe, differs from those of Mt samples by the broad and insufficiently resolved high temperature region. Apart from week basic sites, formed around 100°C, formation of stronger basic sites started above 300°C and resulted in heterogeneous distribution of various strength basic sites. One may distinguish three different basic sites attributed to i) shoulders around 315-320°C (Nt-200, Nt-300), ii) maxima at 480°C (Nt-200, Nt-300) and iii) maxima at 700°C (Nt-

Table 2. Volume of desorbed CO_2 (V_{CO2}, µL/g) and surface basicity of montmorillonite and nontronite activated at various temperatures

Sample	T_{act}, °C	S, m²/g	Volume of desorbed CO_2, µL/g		Total V_{CO2} desorbed, µL/g	Total number of basic sites, B_Σ, µmol/g	Specific basicity of surface, B_Σ/S, µmol/ m²
			Weak basic sites	Strong basic sites			
Mt-0	200	43	19.4	450.8	470.2	209.9	4.9
	300		3.8	363.3	367.1	163.9	3.8
	400		0.9	207.9	208.8	93.2	2.2
Nt-0	200	105	14.6	790.0	804.6	359.2	3.4
	300		14.0	561.5	575.5	256.9	2.5
	400		5.1	341.8	346.9	154.9	1.5

200) and 640°C (Nt-300), and testifying to their strength enhancement.

It follows from table 2 that total basicity of Nt samples 1.6-1.7 times that of Mt, obviously, due to its phase and chemical composition from one side and developed surface area and porosity as well. At the same time, Mt samples had slightly higher number of weak sites as Nt, which are easily lost by rising temperature from 200 to 300°C as compared to Nt. As activation temperature rose from 200 to 400°C, the number of weak sites for Mt decreased by 21 times whereas for Nt by 2.8 times. Moreover, the ratio of stronger sites number to weak sites significantly increased (from 23 to 200) for Mt activated at higher temperatures, whereas for Nt this ratio varied between 54-67 times for the applied activation temperatures. In general, total basicity of both Mt and Nt decreased by 2.2-2.3 times at thermal activation as a result of their dehydration and dehydroxylation.

To compare the basicity of unit area of the minerals surface, one may normalize the obtained basicity value B_Σ, μmol/g, per unit surface area and produce values of B_Σ/S, μmol/m^2, given in Table 2. The values of B_Σ/S testified that basicity of the unit area of Mt surface was 1.5 times higher than that of Nt surface obviously due to a higher occupancy and density of active sites for Mt.

Conclusion

Applying the iTPD-CO$_2$ technique it was shown that surface of natural and thermally treated layered aluminosilicates of smectite group possesses one type of weak basic sites and a spectrum of strong basic sites. The number of weak basic sites for both Mt and Nt strongly depended on activation temperature applied and fast decreased due to the loss of loosely bound water molecules at elevating temperature. The distribution of strong basic sites was bimodal for Mt surface and, presumably, was primarily caused by presence of cis-vacant and trans-vacant Al-OH groups in octahedral sheet of the mineral. The Nt sample observed heterogeneous distribution of stronger basic sites represented by Fe^{3+}-OH-Al^{3+} and Fe^{3+}-OH-Fe^{3+} in the octahedral sheets proving thermal sensitivity of Fe-rich smectites. The total basicity and total volume of CO$_2$ adsorbed by Nt samples exceeds that of Mt in 1.6-1.7 times. Nevertheless, the determined value of specific basicity of unit area of Mt surface was 1.5 times higher than that of Nt obviously due to variations in chemical and phase composition of samples that resulted in a higher density of active sites of Mt containing sample. The rise of activation temperature from 200 to 400°C resulted in a 2.2-2.3 times drop of total basicity of both Mt and Nt samples as a consequence of their dehydration and dehydroxylation.

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Влияние температуры активации на основность поверхности природных алюмосиликатов

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Монтмориллонит и нонтронит представляют слоистые алюмосиликаты группы смектита, которые широко востребованы во многих промышленных производствах благодаря своим физико-химическим и многим другим свойствам. Термическая активация глинистого сырья изменяет пористость, удельную поверхность и физико-химические свойства поверхности, включая образование и перераспределение поверхностных активных центров кислотно-основного или окислительно-восстановительного характера. Целью данного исследования явилось изучение эффекта термической активации на характер распределения и количество основных центров поверхности природных слоистых алюмосиликатов с помощью усовершенствованного метода обращенной термопрограммированной десорбции CO_2.

Образцы природных алюмосиликатов, богатые монтмориллонитом (монтмориллонит 67%, иллит 5%, кварц 5%, полевой шпат 21%) и нонтронитом (нонтронит 70%, иллит 10%, каолинит 5%, кварц 10%, полевой шпат 8%) были охарактеризованы методами XRD, XRF, BET адсорбции N_2. Для исследования основности поверхности и определения количества основных центров был использован новый метод iTPD-CO_2. Перед измерением iTPD-CO_2 100 мг образца активировались при 200, 300, 40см^3/мин, 30 мин). Далее, реактор промывался потокам азота при скорости 5 см^3/мин для десорбирования слабо связанного CO_2. Профили iTPD-CO_2 снимали в интервале 20-800ºC при скорости нагрева 20ºC/мин и обрабатывали в программе ChemStation.

Экспериментальные профили десорбции CO_2 для образцов Mt и Nt характеризовались присутствием двух температурных участков. Низкотемпературные пики, обнаруженные около 80-90ºC для Mt и около 110-127ºC для Nt, скорее всего связаны со слабыми основными центрами, тогда как высокотемпературные пики около 510 и 620ºC для Mt и выше 320ºC для Nt указывают на более сильные основные центры. Объяснение полученных профилей iTPD проведено с учетом термического поведения слоистых алюмосиликатов.

Общая основность образцов Nt и Mt составила 359.2 и 209.9 мкмоль/г соответственно. Основность Nt, превышающая в 1.6 раза таковую для Mt, очевидно связана с его фазовым и химическим составом и более развитой удельной поверхностью, и пористостью. При повышении температуры активации число слабых основных центров, связанных с гидроксильными группами воды, постепенно снижалось, составив уменьшение в 21 раз для Mt и 2.8 раза для Nt.

Дегидроксилирование структурных Al-OH, Fe-OH, Mg-OH выше 200ºC, переходящее в необратимое при температурах выше 300ºC, привело к образованию остаточных атомов кислорода и их вкладу к общее количество более сильных основных центров. В соответствии с термическим поведением диоктаэдрических смектитов, предполагается, что сильными основными центрами образца Mt являются trans- и cis-вакантные Al-OH группы, дегидроксилирующие соответственно при ~550ºC и 650ºC. Образей Nt, с повышенным содержанием железа, быстро терял гидроксилы при более низких темпартурах, что при отразилось в более гетерогенном распределении основных центров различной силы. При повышении температуры активации отношение числа сильных основных центров к слабым повысилось с 23 до 200 для образца Mt, тогда как для Nt это отношение составило 54-67 раз. В целом, общая основность Mt и Nt снизилась в 2.2-2.3 раза в следствие их дегидратации и дегидроксилирования при термической активации. Нормализованные значения основности на единицу площади поверхности (B_Σ/S, мкмоль/м^2) оказались в 1.5 раза выше для образца Mt, что очевидно указывает на более высокую занятость поверхности и плотность расположения активных центров для Mt в сравнении с Nt.

Ключевые слова: монтмориллонит, нонтронит, термическая активация, обращенная термопрограммированная десорбция CO_2, основность поверхности.

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