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Comparison of surface acidity/basicity of natural and modified aluminosilicates by conversion of 2-methylbut-3-yn-2-ol

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Аннотация

Surface acidity/basicity of natural and acid/alkali activated aluminosilicates of layered (nontronite, Nt, glauconite, Gla), framework (clinoptilolite, C₉₅) and a mixed layered type (M₄₅C₂₀) structure were studied by means of catalytic conversion of 2-methylbut-3-yn-2-ol. Conversion over natural samples decreases in the order C₉₅ > M₄₅C₂₀ ≈ Nt > Gla. Acidic active sites are dominant on the surface of both natural and acid treated samples. Acid activation strongly reduced the catalytic activity of zeolite C₉₅ while in case of M₄₅C₂₀ and Nt the conversion slightly increased. The yield of products formed on acid sites decreased by 62% for C₉₅ and increased by 25; 30 and 100%, respectively for M₄₅C₂₀, Nt and Gla. Catalytic activity of all studied minerals was significantly suppressed after alkaline activation except for M₄₅C₂₀ for which the increasing activity of basic sites was observed. The changes in conversion and surface acidity of minerals were explained by the changes in a ratio of acidic and basic sites induced by surface modification.

Keywords: catalytic test reaction, natural aluminosilicates, acid and alkaline treatment, basic and acidic sites

Кислотность и основность поверхности природных, кислотно- и щелочноактивированных алюмосиликатов слоистой (нонтронит, Nt, глауконит, Gla), каркасной (клиноптилолит, C₉₅) и смешаннослойной структуры изучена методом каталитической конверсии 2-метилбутин-3-ола-2. Для природных образцов конверсия снижается в ряду C₉₅ > M₄₅C₂₀ ≈ Nt > Gla. Кислотные активные центры доминируют на поверхности как природных, так и кислотноактивированных образцов. Кислотная активация существенно снижает каталитическую активность цеолита C₉₅, в то время как для M₄₅C₂₀ и Nt она повысилась. Выход продуктов, образованных при участии кислотных центров, для цеолита C₉₅ понизился на 62%, а для M₄₅C₂₀, Nt and Gla повысился на 25; 30 и 100%, соответственно. Каталитическая активность всех исследуемых минералов была значительно подавлена, за исключением M₄₅C₂₀, для которого обнаружено возрастание активности основных центров. Изменения в конверсии и поверхностной кислотности минералов объясняется изменением в соотношении кислотных и основных центров при модификации поверхности.

Ключевые слова: каталитическая тестовая реакция, природные алюмосиликаты, кислотная и щелочная обработка, основные и кислотные центры

Introduction

Aluminosilicates can be considered as inorganic polymers, the structure of which is represented by continuous tetrahedral and/or octahedral sheets formed as a result of condensation of silica-oxygen tetrahedra SiO₄ and/or octahedral AlO₆ [1, 2]. Such

groupings (tetrahedral and octahedral) are the repeating units of an inorganic heteropolymer. The strongly marked adsorption properties of many natural aluminosilicates can be successfully applied to reduce the concentration of toxic components in both aqueous and gaseous media as well as by their addition into the paint or adhesive composition [3, 4]. Addition of activated natural aluminosilicates (zeolites, clay minerals) significantly decreases emission of toxic components (formaldehyde, acetone, butylacetate, styrene) containing in free form in gluing compositions that allows producing the environmentally friendly materials [3, 4]. However, it is necessary to take in to account that the activated surface of aluminosilicates is able to exhibit a catalytic effect owing to polarized Si-OH or Si-O(H⁺)-Al groups, exchangeable cations and polarized by them molecules of water or the coordinately unsaturated interlayer cations. As a consequence, the rate of curing of a gluing composition can be significantly changed that results the properties of a material.

In the present paper, the catalytic properties of natural, acid and alkali activated aluminosilicates of different structures were studied by the method of methylbutynol (MBOH) conversion.

Experimental

The objects under investigation were natural aluminosilicates having various structure: C₉₅ - clinoptilolite, 95% - hard framework structure; M₄₅C₂₀ - 45% montmorillonite (layered) and 20% clinoptilolite; Nt - nontronite (ferrous montmorillonite) - layered structure; Gla - glauconite - spherulites of layered minerals illite and smectite.

Aluminosilicates were activated by 2M solutions of H₂SO₄ and NaOH at 100°C with a ratio of *adsorbent* /activator = 1:4 for 6 h. The slurry washed until neutral reaction was filtered, dried, milled and sieved into fractions (200-315 microns).

Catalytic reaction of 2-methylbut-3-yn-2-ol (MBOH) was carried out in a U-shaped reactor at 250°C, likewise in [5].

Before the reaction the catalyst was activated in the flow of nitrogen at 400°C for 8 h. The reaction mixture (substrate) composed of MBOH (95%) and toluene (5%) used as an internal standard. Depending on the type of active sites, acidic, basic or coordinatively unsaturated ions, MBOH was converted into various products [5]. The analysis of the reaction products was carried out by gas chromatography. The equations for calculating the MBOH conversion and yield of products were described in detail in [5].

Results and discussion

Dependence of MBOH conversion on reaction time for natural aluminosilicates is represented in fig. 1.

The highest value of conversion were observed for clinoptilolite C₉₅, gradually decreasing in the order C₉₅ > M₄₅C₂₀ ≈ Nontronite > Glauconite. In the first 30 min of reaction there was a sharp decline in the conversion over all studied aluminosilicates indicating at deactivation of the surface sites of catalysts. The possible reason of this is adsorption of reaction products on the catalyst surface resulting in blocking of the active sites.

In order to compare the extent of influence of acidic and alkaline activation of aluminosilicates on their catalytic activity in reaction of MBOH conversion it is necessary to address to the results given in table 1.

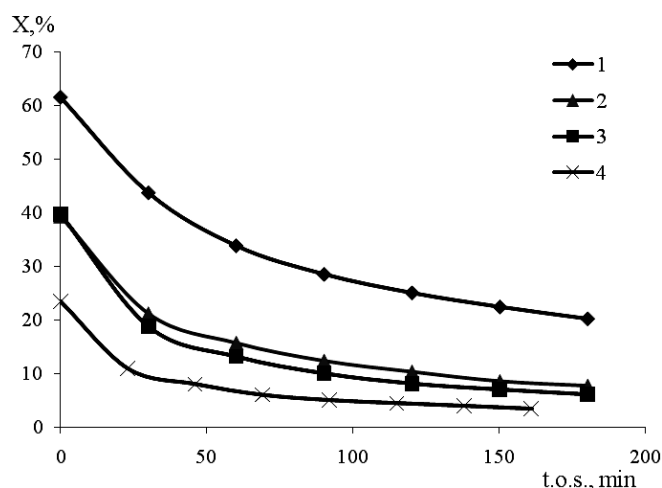


Fig. 1. Dependence of the MBOH conversion on the reaction time (t.o.s.) for natural aluminosilicates: 1 – C₉₅; 2 – M₄₅C₂₀; 3 – Nontronite; 4 – Glaucanite

Table 1. Values of MBOH conversion for natural, acid and alkali activated aluminosilicates (reaction time 30 min)

Sample	Type of treatment		
	Natural	Acid	Alkaline
C ₉₅	43.7	17.3	14.7
M ₄₅ C ₂₀	21.1	25.7	35.3
Nt	18.8	22.2	15.3
Gla	10.9	11.8	3.6

As shown in table 1, the acid activation of the zeolite C₉₅ significantly reduced its catalytic activity, while in the case of M₄₅C₂₀ and nontronite there was a slight increase in MBOH conversion, weakly expressed for glaucanite.

Alkaline activation sharply weakened catalytic activity of the zeolite and glaucanite, decreasing the value of MBOH conversion by a factor of three, except for M₄₅C₂₀. For alkali treated M₄₅C₂₀ the rise of MBOH conversion by 60% was observed as compared with the natural sample.

Using the data of fig. 2, one compares the yield of products and the type of active sites on the surface of the natural and activated aluminosilicates.

As follows from fig. 2, that the higher yields of products of acidic pathway of the reaction (MBYNE, Prenal) are typical for all samples of natural and acid activated aluminosilicates, indicating at dominance of acidic active sites on their surface. The effect of acid activation is inequable for minerals with different structures. A significant decrease in the yield of acidic products (by 62%) is characteristic for the zeolite C₉₅, whereas for minerals possessing a layered structure, montmorillonite, nontronite, glaucanite, the yield of acidic products increased by 25; 30 and 100%, respectively.

The most probable reason for the decrease in catalytic activity of clinoptilolite C₉₅ is a dissolution of oxides Al₂O₃, Fe₂O₃, reducing polarization of surface bridging SiO(H⁺)Al groups and leading to a weakening of the Broensted acid sites.

The presence of a free acid in the structure of the rest minerals remaining after the activation is, probably, responsible for the increasing acidity and amplification of catalytic properties.

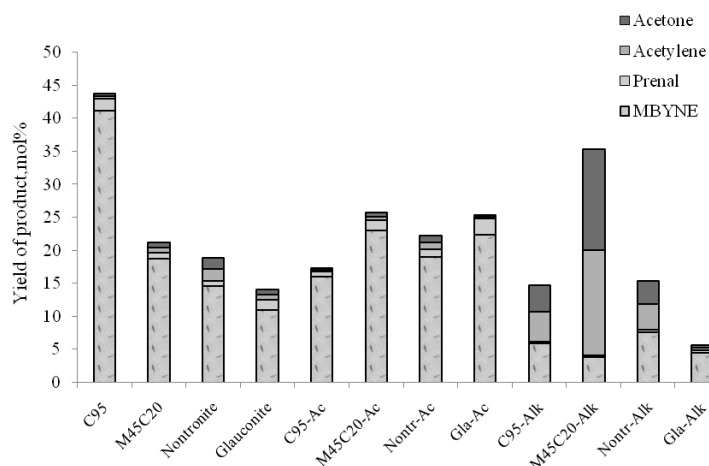


Fig.2. Yield of products by conversion of MBOH over natural, acid (Ac) and alkali activated (Alk) aluminosilicates. Reaction time 30 min

The alkaline activation significantly suppressed the catalytic activity of all studied minerals by reducing the yield of acidic products in 7 times for clinoptilolite, in 4,4-4,8 for glauconite and $M_{45}C_{20}$, and in 2 times for nontronite (fig. 2). At the same time, it should be noted the increasing yield of basic products (acetylene, acetone) formed on basic centers. The highest contribution of the basic sites in the MBOH conversion was found for a mixed mineral $M_{45}C_{20}$, which came in total to 31%, while for C_{95} , nontronite and glauconite the yields of basic product were equal to 8,50; 7,34 and 0,79% respectively.

The effect of alkali on the aluminosilicate structure is realized in a preferential destruction of silicon-oxygen tetrahedra due to chemical interaction of SiO_2 with sodium hydroxide forming sodium silicate. The contribution of ion-exchange processes between $AlOH$ groups of the tetrahedral sheet of layered silicates and Na^+ ions or a cation-exchange of Mg^{2+} for Na^+ is observed to a lesser extent [6]. These processes resulted in the changes of the surface properties such as surface area and porosity. A significant increase in specific surface area (ca. 2 times) and an increase in pore diameter after the alkaline activation were shown for $M_{45}C_{20}$. However, in the case of glauconite the alkaline treatment did not change the value of specific surface area, which apparently is caused by redistribution of the proportion of macro and micro pores in the mineral structure. The globular structure of glauconite favors the surface changes mainly in the outer layer of the spherulites, preventing penetration of the activator molecules, or a substrate in the case of a catalytic reaction, that ultimately affects the lower catalytic activity of the sample Gla-Alk.

Thus, the catalytic activity of natural aluminosilicates of a layered or a framework structure in the reaction of MBOH conversion is provided by acid active sites. The acid activation significantly decreases activity of clinoptilolite, and slightly increases activity of the minerals with the layered structural component. The alkaline treatment reduces acidity of catalyst and conversion of MBOH for all studied minerals except for a mixed mineral $M_{45}C_{20}$, due to a significant increase in its surface characteristics.

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