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Research of zeolite catalysts for the process of alkylation of aromatic hydrocarbons

Abstract: The experience of studying the process of alkylation of toluene with butene in the presence of a catalyst based on natural zeolite shows the high fundamental importance of toluene to butene ratio in the reaction zone with a uniform concentration distribution of butene over the entire surface of the catalyst. Such process conditions differ in activity, selectivity, as well as the duration of the solid catalystoperation. The synthesis of a catalyst based on natural zeolite was effectively carried out by the absorption method. The range of values of the main parameters and general properties of the catalyst synthesis that ensure the effective conduct of the alkylation reaction is determined. The study of acid centers was carried out by the method of direct registration of OH groups of catalysts based on natural zeolite and IR spectroscopy. Subsequently, the acidic properties of decationized and heat-treated zeolite, and catalysts based on it were investigated. X-ray structural analysis was performed in the laboratory of physical and chemical research methods to determine the mineral and chemical composition of Koskuduk amorphous rock clays. The 5 phases were identified based on the results of X-ray analysis of the studied kaolinite clay: α-quartz- SiO_2, calcite $CaCO_3$, mica R_1R_{2-3} $[AlSi_3O_{10}](OH, F)_2$, R_1 = K, Na; R_2 = Al, Mg, Fe, Li; mixed-layer mineral and chlorite impurities.

Keywords: catalyst, natural zeolite, clay, amorphous porous rock.

Introduction

Catalytic processing of petroleum products in the presence of alumosilicates occupies a leading position in modern chemical production [1,2]. Currently, one of the main directions in the oil refining industry is the production of an effective catalyst that improves the quality of products with the systematic use of natural resources. For Kazakhstan, the issue of issuing alumosilicate catalysts in oil refining at the expense of reserves is considered as an urgent issue. To reduce the content of aromatic compounds, benzene, alkenes, sulfur, saturated steam pressure, as well as the boiling point in gasoline, it is necessary to increase the quality of alkylates and production volumes [3–5]. At the same time, the product of the alkylation process is a solution for improving the quality of gasoline without oxygen-containing compounds.

The modern industrial alkylation process is no different from the processes created in the 40s of the twentieth century, based on the use of liquid acids and sulfuric and hydrogen fluoride. The main disadvantage of these catalysts is considered to be the high unit cost, toxicity and corrosion activity, the difficulty of separating the catalyst from the resulting product. Despite the constant maturity of the liquid acid alkylation process, the industrial organization constantly maintains the efficiency and safety of operation of the existing plant with great difficulty. The hope that exists today is connected with the development of industrial alkylation, that is, with the use of solid catalysts that solve the above problems and have economic, technological advantages instead of a liquid catalyst.

Alkylation product-alkylate is a high-octane (according to the study, the octane number is not less than 90-94), less sulfur, a component that does not contain aromatic compounds and alkenes to produce high-octane gasoline. Alkylate has a high value in the world specification as a component of gasoline, which is a component of motor fuels [6,7].

The low environmental indicator of the process is associated with the use of catalysts necessary for the process to be carried out [8,9]. This makes it possible to search for a new catalytic system based on the same and at the same time heterogeneous catalysts based on $AlCl_3$: zeolites, alumosilicates, clays, cationites, the mentioned series of catalysts is distinguished by several advantages – environmental safety of production, high selectivity of the target product and easy separation processes [7]. Zeolites are aluminosilicate materials with complex, three-dimensional porous structures [10].

Materials and methods

The initial alumosilicates were pre-crushed, i.e. Semeitau zeolite and Koskuduk amorphous rock clay were crushed in a stupa and passed through a sieve with a diameter of 0.25 mm. To replace the acidic part of the catalyst with an active form, a 1M NH_4Cl solution was used. Decathion was carried out in a round-bottomed flask by triple mixing in a water bath for 6 hours.The treated samples were filtered and rinsed with distilled water until the ions contained in them were cleaned, cleaned of chlorine ions contained in them by rinsing with distilled water, and then the sample was dried to a constant weight at a temperature of 100 ºC. After drying, the column was subjected to heat treatment at a temperature of 100-500 ºC for 4.5 hours to change the ammonium form of zeolite to the H-form.

Heat-treated zeolite was mixed with amorphous clay in the ratio of zeolite/amorphous clay – 15/85 mass%. The resulting catalyst was mixed with a binder and molded into a cylinder-type mold with a diameter of 3 mm and a length of 10 mm.

The one of the promising methods was used – X-ray phase analysis, which allows to determine the qualitative and quantitative composition of the clinker with high accuracy to control the quality of the obtained sorbent [11]. X-ray phase analysis of the flask was performed on a diffractometer D2 Phaser Bruker. The sorbent under study was averaged, and a sample of 20-25 g was taken from it, which was crushed into fine grits in a metal mortar. After averaging the grits, 5-7 g of material was taken from it, which was crushed in the agate composition of the raw mixture and clinker was carried out in a powder mortar by periodic screening on a 006sieve using a soft brush. The remaining residue on the sieve was ground again and sieved until the initial sample of the material was completely passed. The test substance sample was stuffed into a cuvette made of organic glass and having a diameter of 20-25 mm with a recess on one of the planes up to 3 mm. The stuffing was carried out gradually, in layers, until the recess in the cuvette was completely filled, after which the surface of the material under study was carefully aligned so that the material planes and the collar of the cuvette ring coincided. A cuvette filled with material was installed in a goniometer sample holder, where the material was irradiated with X-rays with a certain wavelength at a variable angle of incidence.

Results and discussion

Most of the primary Semeitau zeolite consists of mordenite Ca, Na, $K_2Al_2Si_{10}O_{24}\cdot 7H_2O$, formed by a rhombic lattice, with parameters: a=18.11 Å, b=20.55 Å, c=7.53 Å. Zeolite also contains a small amount of clinoptilolite. The total number of two phases is 60%. The remaining composition: quartz – 15%, crystallobolite-15 and albite – anorthite solid solution-10%. Heat treatment of Semeitau zeolite reflects its structure and properties. X-ray analysis of zeolite shows a change in the structural deformation of the crystal lattice, in which the loss of water in the composition leads to a slight compression. Dehydration, which breaks the bonds of the water molecule from the cation and oxygen skeleton, disrupts the sequence of zeolite construction, and therefore the cations exchange occurs. These structural changes indicate that there is a change in values in lattices a, b and c. The stronger compression in the grid is more common on the b axis: a=18,10 Å, b=20,50 Å, c=7,51 Å.

The study of the phase composition of natural alumosilicate does not fully reflect the constituent components of the original mineral, so its chemical composition was studied.

The results of chemical analysis on the alumosilicate content of primary and activated Semeitau zeolite are shown in Table 1.

IR spectroscopy through the chemical composition of primary and decathionated Semeitau zeolite can provide direct information about the surface and adsorption forms of various compounds in nature. In addition, the data obtained allows to describe not only those or primary substances of the zeolite surface, but also individual molecules or groups of atoms.The spectroscopic method allows to describe it as a surface intermediate product in nature, describe changes in its properties in various reactions, and determine which structural surface groups are involved in the interaction.It was found that the primary Semeitau zeolite contains ion exchange cations: Na^+, K^+, Ca^{2+}, Mg^{2+} and Fe^{3+}. Three times treatment with 1M NH_4Cl reduces the amount of ions contained in zeolite. The SiO_2 / Al_2O_3 ratio is 6.8.

Table 1 – Chemical composition of primary and decathionated Semeitau zeolite

Sample	Composition of basic oxides, mass %						
	Al_2O_3	SiO_2	Na_2O	K_2O	CaO	MgO	Fe_2O_3
Primary zeolite	10.63	72.80	1.18	5.04	1.61	0.35	1.50
Decathionated zeolite	10.52	74.70	0.12	5.34	3.85	0.05	2.01

Clays are kaolinite, hydroslud, montmorillonite, etc.a type of rock consisting of clay materials with a diameter of no more than 0.01 mm. The main chemical composition of clay rock consists of SiO_2, Al_2O_3, H_2O. The adsorption capacity of clay is the property of clay material to adsorb ions and molecules on its surface.An amorphous structure is one of the physical conditions of a solid body, characterized by two features. The first, under normal conditions, the properties of such substances do not depend on the chosen direction, that is, they are isotropic. Secondly, when the temperature increases, there is a softening and gradual transition of amorphous substances to a liquid state. The actual melting point is not accepted.

Clay rocks are of particular importance in petrochemical and oil refining industries. In this work, domestic Koskuduk amorphous rock clay was used as clay.

Analysis of Koskuduk amorphous rock clays by X-ray analysis is shown in Figure 1.

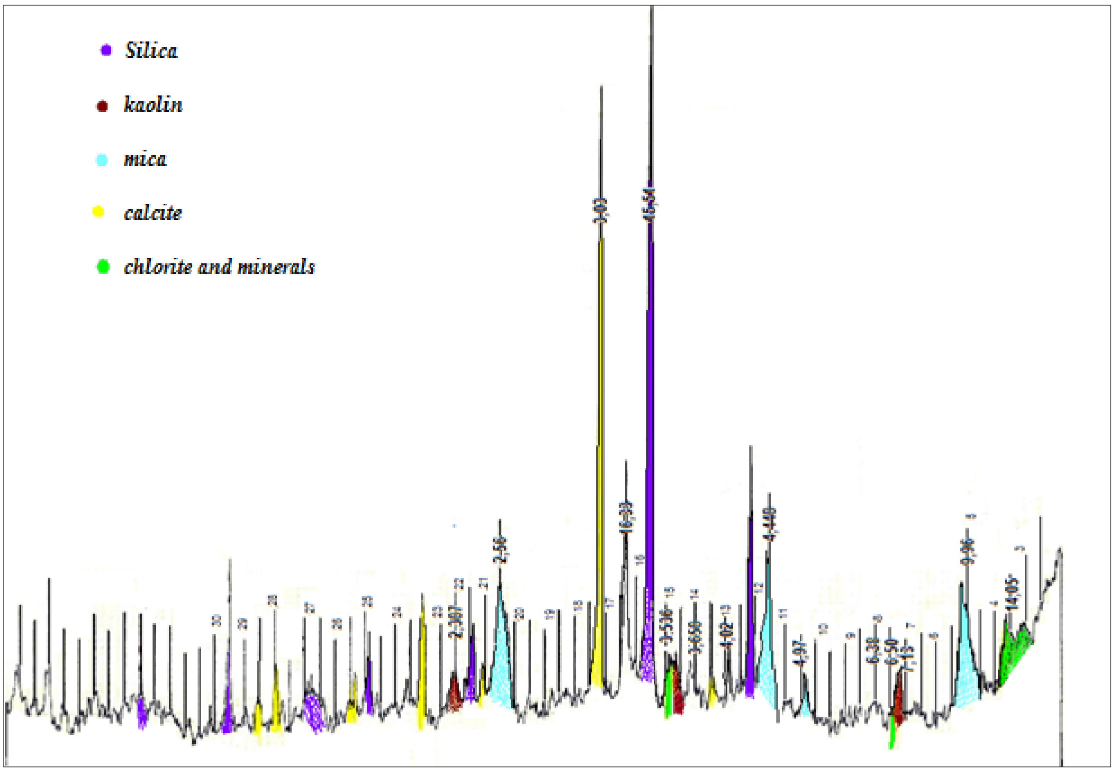

Figure 1– Phase composition of the amorphous rock of the Koskuduk deposit t

Radiophase and X-ray structural analysis were performed in the laboratory of physical and chemical research methodsto determine the mineral and chemical composition of Koskuduk amorphous rock clays.

The 5 phases were identifiedbased on the results of X-ray analysis of the studied kaolinite clay: α-quartz- SiO_2, calcite $CaCO_3$, mica $R_1R_{2\text{-}3}$ $[AlSi_3O_{10}]$ $(OH, F)_2$, R_1 = K, Na; R_2 = Al, Mg, Fe, Li; mixed-layer mineral and chlorite impurities. The basis of this mineral is $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$ – 79 % kaolinite.

X-ray structural analysis of kaolinite clayis shown in Table 2.

Table 2 –Chemical composition of Koskuduk amorphous clays

Component composition, %									
SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	H_2O	etc.	Total
30	13	6	15	4	2.3	4.3	24	1.4	100 %

An important role in assessing the activity of the catalyst in various processes is played not by the general geometric surface, but by the inner surface of the reagent molecule. The presence of macro-, meso – and microcirculation on the surface of a solid body affects the adsorption, diffusion, mechanical, capillary, etc.properties of the porous-dependent system, as well as determines the specifics of the course of catalytic and adsorption processes.

Semeitau natural zeolite and the catalyst based on it differ in porosity structure. Promotion of natural zeolite-based catalysts leads to an increase in the total pore volume by 2 times. This, in turn, increases the course of the catalytic process.

The presence of microcredit in catalysts leads to a slowdown in the components of the catalytic system. To determine the degree of surface permeability, it is necessary to have a value of the pore size in the catalyst.

Conclusion

In the presence of catalytic systems prepared and studied for the process of alkylation of toluene with butylene, it is established that an alkylate is formed that increases the octane number of gasoline:

the optimal composition of zeolite-containing catalysts was developed and its properties were determined;

in the process of alkylation of toluene with butene, active and selective catalysts were prepared, their physico-chemical properties were studied, and zeolite catalysts were produced.

The chemical composition and structure of Semeitau zeolite and Koskuduk amorphous rock clays were developed and the possibility of using them in the preparation of effective catalysts for alkylation process of aromatic hydrocarbons with olefin was demonstrated.

The range of values of the main parameters and general properties of the synthesis of the catalyst is determined, which ensures the effective conduct of the alkylation reaction.

The study of acid centers was carried out by the method of direct registration of OH groups of catalysts based on natural zeolite and IR spectroscopy, as well as by the method of molecular probe. Subsequently, decationized and heat-treated Semeytau zeolite and acidic properties of catalysts based on it were investigated.

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