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INVESTIGATION OF THE ADSORPTION PROPERTIES OF THE SORBENT OBTAINED IN THE PROCESS OF MODIFICATION OF CLINOPTILOTHITE IN THE PURIFICATION OF NATURAL GAS FROM SULFUR COMPOUNDS

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Abstract: The study of the possibility of using modified clinoptilolite as an adsorbent and the adsorption properties of zeolite in the purification of natural gas supplied to gas processing plants from sulfur compounds contained in it is an urgent task. In the experimental study, the adsorbent fraction was chosen as 0.5÷1.0 mm, density - 0.8 g/cm³, adsorbent layer height - 600 mm. Optimal conditions are selected in such a way that the pressure in the experimental process is 0.2-5.0 MPa, the amount of mercaptans in the purified natural gas is 50÷400 mg/nm³, the temperature is 20÷25°C, the gas flow rate is 0.2÷0.25 m/s. The intensity and accuracy of desorption of sulfur compounds adsorbed on clinoptilolite at 250°C, the same results were obtained on NaX zeolite at 320°C. The catalytic activity of regeneration of clinoptilolite at lower temperatures than that of NaX zeolite, although small, made it possible to minimize the decomposition of mercaptans. Adsorption of 200 mg/nm³ of mercaptans in modified clinoptilolite in less than 30 minutes, this figure was recorded for 150 minutes in zeolite NaX. It was studied that adsorption did not change after 90 minutes in clinoptilolite and after 500 minutes in zeolite NaX.

Keywords: clinoptilolite, zeolite, modification, dealumination, regeneration, sorbent, mercaptan, hydrogen sulfide.

Introduction. The study of the structure and properties of existing and widely used natural raw materials - the class of layered bentonites obtained from clay rocks, is an important scientific task aimed at creating new multifunctional materials [1,2]. This is mainly due to the specificity of the physicochemical properties of layered bentonites, their ability to have active centers of various natures, adsorption and ion exchange. This opens up wide opportunities for their use, for example, in the creation of new effective materials for water treatment and wastewater treatment, sorbents in pharmacology, anti-migration and filtration barriers for long-term storage of hazardous waste. [3-8]. Layered silicates are minerals common in nature. They make up to 75% of sedimentary rocks of the earth's crust. The most famous representatives of layered silicates are clays. Clay has long been used in various areas of human activity. The scope of their application is very wide: production of ceramic and construction products, oil extraction and processing, metallurgy, chemistry, paper, pharmaceuticals, food and other industries [9].

They are also known as natural sorbents, ion exchangers, catalysts and catalyst carriers [10 - 13]. The development of new methods for changing the structure of layered silicates and changing their physicochemical properties is constantly expanding the scope of their use.

Recently, intensive research has been conducted to create and study multifunctional inorganic 2D nanomaterials related to intercalated layered substrates. Among them are columnar (or columnar) materials, distinguished by a unique texture and physicochemical properties. They are characterized by a specific surface area, a regular distribution of micro- and mesopores, thermal stability and the presence of active centers of various natures. Therefore, they are used to obtain effective sorbents, molecular sieves, catalyst carriers, etc.

Currently, a large number of high-quality (columnar) materials are known based on bentonite matrices, the chemical formulas of which are unknown, cross-linked with hydrolysis products of various metals [11]. Among the modification methods, pilling is of great interest to researchers; this technological method opens up broad prospects for the functional application of natural clays in various fields of science and technology. Pilling is a process of preserving a layered system while simultaneously transforming it into a heat-resistant micro- or mesoporous material. The basic concepts of the structure of elephant clays were formed in the studies of Pinnaway, Sterte and other scientists.

Regardless of its specific properties, this process can be described by three main stages: 1) hydrolysis of metal polyhydroxo complexes, 2) ion exchange (intercalation) of interlayer cations of layered bentonite, 3) heat treatment (firing) of layered bentonite. It should be noted that intercalation is the main stage of clay preparation. Intercalation is a process based on changing the structure of the sludge by expanding the interlayer space due to the introduction of large inorganic complexes. This method was invented in 1977 by scientists from the Brindley sample [12]. During the intercalation of layered silicates, a developed microporous structure is formed, the specific surface area increases and access to the active centers located on the inner surface becomes possible. The most well-known main molecule of aluminum hydroxide is the Al 13 ion, which was originally isolated in the form of sulfate and selenate salts [13-14].

Methodology empirical analysis. In our republic, synthetic zeolite NaX is widely used as an important adsorbent in the purification of natural gas from sulfur compounds. The pressures at the stages of natural gas purification can be found using their values in the ranges. At low partial pressures, which are not high in value, modified clinoptilolite does not have significant differences in adsorption properties from synthetic zeolite NaX:

$$H_2S\ P < 2.82\ MPa;\ RSH\ P < 0.52\ MPa$$

Along with the adsorption of ethyl mercaptans on modified clinoptilolite and synthetic zeolite NaX, the processes of its desorption (regeneration) were also carried out [15]. We know that natural gas supplied to gas processing plants contains high-sulfur compounds - hydrogen sulfide, carbonyl sulfide and mercaptans. Initially, it is purified from impurities containing natural gas, for which an aqueous solution of diethanolamine is used. The total content of natural gas and the proportion of mercaptans (10÷20%) when cleaning mixtures using the above method, the residual content in terms of sulfur in the gas is about 400 mg/nm^3. After cleaning with an aqueous solution of diethanolamine, the humidity of natural gas drops to a dew point of - 10/-15°C and a pressure of 5.0 MPa. Synthetic zeolite NaX is used in the adsorption method for the process of additional purification of natural gas from mercaptans. The residual content of mercaptans in natural gas is not less than 36 mg/nm^3 in terms of sulfur. Adsorption of mercaptans in modified clinoptilolite as a result of acid treatment was carried out in the experimental setup described below.

The adsorber is made of stainless steel and has a cylindrical device with an internal diameter of 11 mm and a height of 1 m. The pressure in the process is controlled by a sampling pressure gauge, and the gas flow from the adsorber is measured by a RS-5 rotameter.

In this experiment, the adsorbent fraction was 0.5 ÷ 1.0 mm, the lift was 0.8 g/cm^3, the adsorbent layer height was 600 mm, and zeolite NaX was used.

Optimum conditions were selected so that the pressure in the experimental process was 0.2-5.0 MPa, the amount of mercaptans in purified natural gas was 50 ÷ 400 mg/nm^3, the temperature was 20 ÷ 25°C, and the gas flow was 0.2 ÷ 0.25 m/s. During the experiments, the composition of the gas entering and leaving the adsorber was studied by analyzing mercaptans over a certain period of time. The amount of mercaptans was determined by the argentometric method. During the experiments, after the adsorption phase was completed, the adsorbent was purified by blowing the bed with purified heated natural gas for 4 hours, and then regenerated. The velocity of the purified (regenerated) gas is 0.025 m/s, the order of the purification temperature was selected based on the kinetics of water desorption, which is best adsorbed in zeolites from additives in the purified gas. During the regeneration of clinoptilolite, the temperature of natural gas at the inlet to the adsorber is 220°C, when carried out with zeolite NaX - 320°C. The reason for the difference in temperatures during the regeneration process is explained by the difference in energies due to the interaction of water molecules on the zeolite surface, which is less than NaX for clinoptilolite.

The amounts of hydrogen sulfide and mercaptans in the natural gas leaving the adsorber during purification were compared. The regeneration process was considered complete when the amount of mercaptans in the purified natural gas decreased to 20 mg/m^3.

II.Results. The output curves of the adsorption process are shown in Figure 1. As can be seen from the figure, the output curves have a high value, which is typical for the adsorption process of a mixture of substances as a result of the displacement of one substance from one adsorbed phase to another.

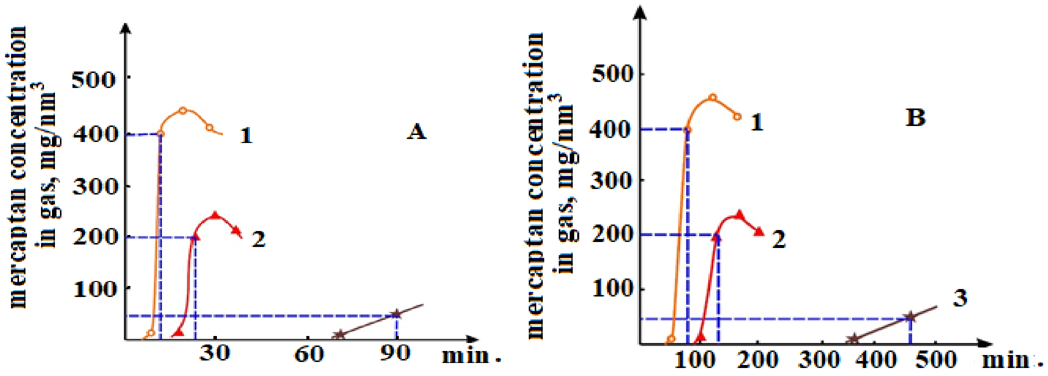

Fig. 1. Curves of mercaptan adsorption yield in modified KP (A) and synthetic zeolite NaX (B)

From the output curves of the adsorption state, a,g, wt%. From the mercaptans (1), it is possible to calculate the dynamic activity of the zeolite and the maximum activity a_max, wt%. (2).

We take τpr and τr as follows:

out is the amount of mercaptan in the natural gas leaving the adsorber, Cout = 10 mg/nm^3 out is the time until the amount of mercaptan in the natural gas entering and leaving the adsorber is equalized, Cout = C_0

As can be seen from the figure, mercaptans adsorb 200 mg/nm^3 in less than 30 minutes in modified clinoptilolite, which can be observed in 150 minutes in zeolite NaX. As the process rate decreases over time, it is clear that the adsorption has not changed by 90 min in clinoptilolite and by 500 min in zeolite NaX.

From the data presented in Table 1, it is known that the dynamic activity of modified clinoptilolite obtained by acid treatment at high concentrations of mercaptans in natural gas is approximately six times smaller than the size of zeolite NaX. But at average concentrations this difference is equal. The data in the table are consistent with the experimental data in the laboratory.

Table 1. Dynamic and equilibrium adsorption activity of ethyl mercaptan at different concentrations by clinoptilolite and synthetic zeolite NaX

№	Experimental conditions		Adsorbent			
			NaX		Modified clinoptilolite	
	Pressure, MPa	Mercaptans at the entrance concentration, mg/nm^3	a_g,% mass.	a_{max},% mass.	a_g,% mass.	a_{max},% mass.
1	5,0	400	3,2	4,3	0,52	0,64
2	5,0	200	2,8	3,7	0,50	0,63
3	5,0	50	2,6	3,2	0,50	0,62
4	1,0	400	2,6	3,2	0,48	0,60
5	1,0	200	2,4	3,0	0,40	0,52
6	1,0	50	2,0	2,6	0,38	0,51
7	0,5	400	2,4	3,0	0,46	0,59
8	0,5	200	1,7	2,1	0,40	0,52
9	0,5	50	0,6	0,7	0,43	0,54
10	0,2	400	1,4	1,6	0,40	0,50
11	0,2	200	0,8	1,0	0,40	0,50
12	0,2	50	0,4	0,5	0,40	0,45

Based on the results of the regeneration process study, kinetic curves are formed that characterize the presence and rate of movement of sulfur-containing substances (Fig. 2).

As can be seen from Fig. 2, when using clinoptilolite as an adsorbent with a maximum amount of mercaptans in the regeneration gas of 6 g/m^3, it is possible to achieve a gas temperature of 150°C leaving the adsorber. It is known that the main component of mercaptans, i.e. 80%, is desorbed in one hour. The temperature curve (3) has a parametric horizontal section as follows: for 20 minutes the temperature is equal to 150°C. These values correspond to the temperature and time of intensive desorption of mercaptans adsorbed on zeolite.

As can be seen from Figure 2, hydrogen sulfide is formed in the regeneration gas at a temperature of 140°C (curve 2), which indicates the possibility of calculating the product of the thermocatalytic process of mercaptan decomposition. When calculating the material balance, it was found that after four hours, the mercaptans are desorbed, i.e. only 2% of them are cracked. When using zeolite NaX, the maximum amount of mercaptans in the regeneration gas is 14 g/nm^3, and these results can be achieved at a temperature of gases leaving the adsorber of 150°C. After three hours, 90% of the mercaptans are desorbed, about 10% of which we can observe cases of decomposition.

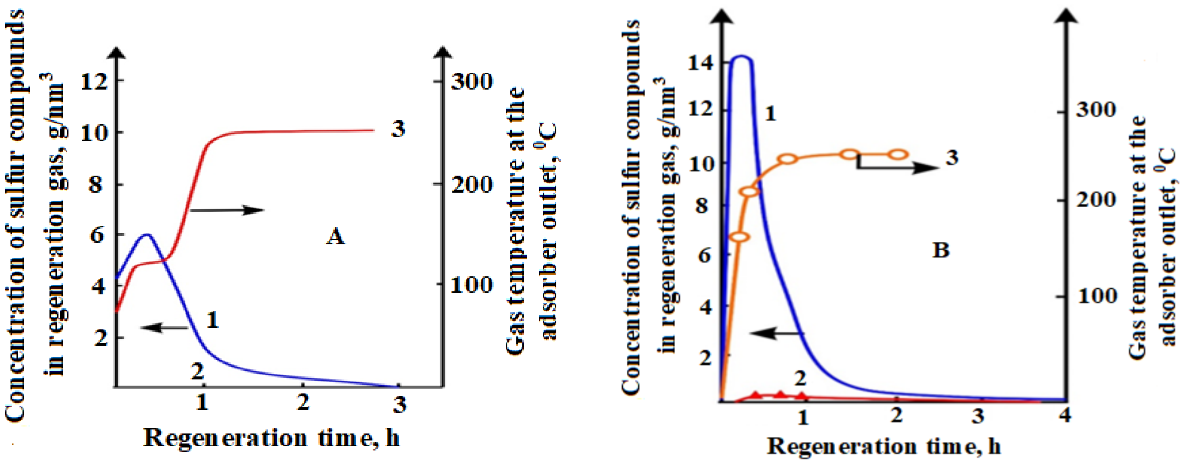

Fig. 2. Kinetic curves of regeneration of CP (A) and zeolite NaX (B):
1 - concentration of mercaptans; 2 - concentration of hydrogen sulfide;
3 - gas temperature at the outlet of the adsorber.

Comparison of the data in the figures above showed that the same results can be achieved in terms of intensity and accuracy of desorption of sulfur compounds adsorbed on clinoptilolite at 250°C as on zeolite NaX at 320°C. The catalytic activity of clinoptilolite regeneration at lower temperatures than that of zeolite NaX, although small, allows minimizing the decomposition of mercaptans. This factor is of great practical importance, on which the service life of the zeolite mainly depends. During the decomposition of mercaptans, olefin hydrocarbons are formed along with hydrogen sulfide, which polymerize in small quantities at high temperatures with the formation of carbon-like layers in the zeolite, thereby causing its deactivation. The results of the experiments show that the use of modified clinoptilolite obtained by acid treatment in combination with synthetic zeolites in sulfur removal processes leads to positive results: the first layer is synthetic zeolite at the input of purified natural gas, in the connecting layers - clinoptilolite. Since the processing speed of the adsorbent in the connecting layers is low, replacing the synthetic zeolite with clinoptilolite has little effect on the overall absorption of sulfur by the layer. Also, the use of a mixed layer in counter-current regeneration in cracking processes contributes to an increase in the service life of adsorbents, taking into account the high thermal stability of clinoptilolite, i.e. thermochemical stability and very low catalytic activity.

III. Conclusions. 1. The degree of dealumination of modified clinoptilolite used as an adsorbent for purification of sulfur compounds present in natural gas was 36%, and the adsorption properties of zeolite NaX were studied.

2. Adsorption of 200 mg/nm^3 of mercaptans in modified clinoptilolite in less than 30 minutes, this figure was recorded for 150 minutes in zeolite NaX.

3. It was studied that adsorption did not change after 90 minutes in clinoptilolite and after 500 minutes in zeolite NaX.

4. It was established that the same results can be achieved in terms of intensity and accuracy of desorption of sulfur compounds adsorbed on clinoptilolite at 250°C as on zeolite NaX at 320°C.

5. Considering the high thermal stability of clinoptilolite in cracking processes, i.e. thermochemical stability, the use of a mixed layer in counter regeneration led to an increase in the service life of the adsorbents.

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