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Preparation of Carriers for Hydro-Cleaning Catalysts Based on Palygorsk Clay

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ABSTRACT: This article presents the results of studying the composition, structure and properties of carrier based on carbonate palygorskite and alkalinebentonite clays of the Nurata deposit for catalysts used in the hydrocleaning of diesel fuel. In order to obtain a carrier, carbonate-palygorskite clay of the Navbahor deposit was chosen; to increase activity, it was subjected to acid activation.

KEY WORDS: Absorption, X-ray diffraction, hydrotreating, carbonate-palygorskite, alumina-silicates, alumina-cobalt-molybdenum.

I. INTRODUCTION

In hydro cleaning catalysts, the main constituent component is the support (more than 80%). The use of natural aluminosilicate raw materials as a carrier opens up great opportunities for organizing the production of catalysts in our republic. The activation of natural aluminosilicate raw materials with mineral acids is one of the important ways to obtain activated supports for catalysts. Finding out the reasons for the change in the catalytic properties of natural aluminosilicates during acid treatment is of great scientific interest. These changes are undoubtedly associated with changes in the physicochemical and structural properties of natural aluminosilicates. The method of acid activation of natural raw materials consists in treating them with solutions of sulfuric, hydrochloric, phosphoric and nitric acid in a certain period of time with heating and stirring.

II. SIGNIFICANCE OF THE SYSTEM

Replacement of an expensive alumina carrier with available ones, carriers not inferior in physicochemical properties, is an urgent task.

III. LITERATURE SURVEY

The possibility of using natural clays as a catalyst or a carrier of the active components of various catalysts has been noted in the literature [1-2]. A comparison of the physicochemical and absorption characteristics of local natural clays and active alumina shows [4] that the clays studied can be used as carriers for hydrocleaning catalysts.

IV. METHODOLOGY

The acid activation of carbonate-palygorskite clay was carried out in this way, 2 liter of an acid solution (T: W = 1: 2) was added to 800 g of the sample, stirred at room temperature for 4-6 hours. Then it was filtered, dried, crushed and sieved through a 0.10 mm sieve. To clarify the structural changes occurring during acid activation, DTA, IR spectra, and X-ray diffraction patterns of the samples were studied.

V. EXPERIMENTAL RESULTS

IR spectra (Fig. 1.) Of absorption were recorded in the region of 400–4000 cm^{-1} on a Nicolet AVATAR-360 spectrophotometer. To take the spectra, we used the technique of pressing a sample with potassium bromide. IR - absorption spectrum of sample No. 2 (Fig. 1.) is characterized by frequencies at 3478, 3434, 3407, 3367, 3304, 3251, 3130, 3083, 2983, 2950, 2914, 2873, 2833, 2787, 2747, 3674, 2582, 2464, 1640, 1540, 1384, 1095, 1038, 918, 877, 793, 519, 473, and 422 cm^{-1} . Sample No. 3 (Fig. 1.) in the IR absorption spectrum has the following frequencies: 3519,

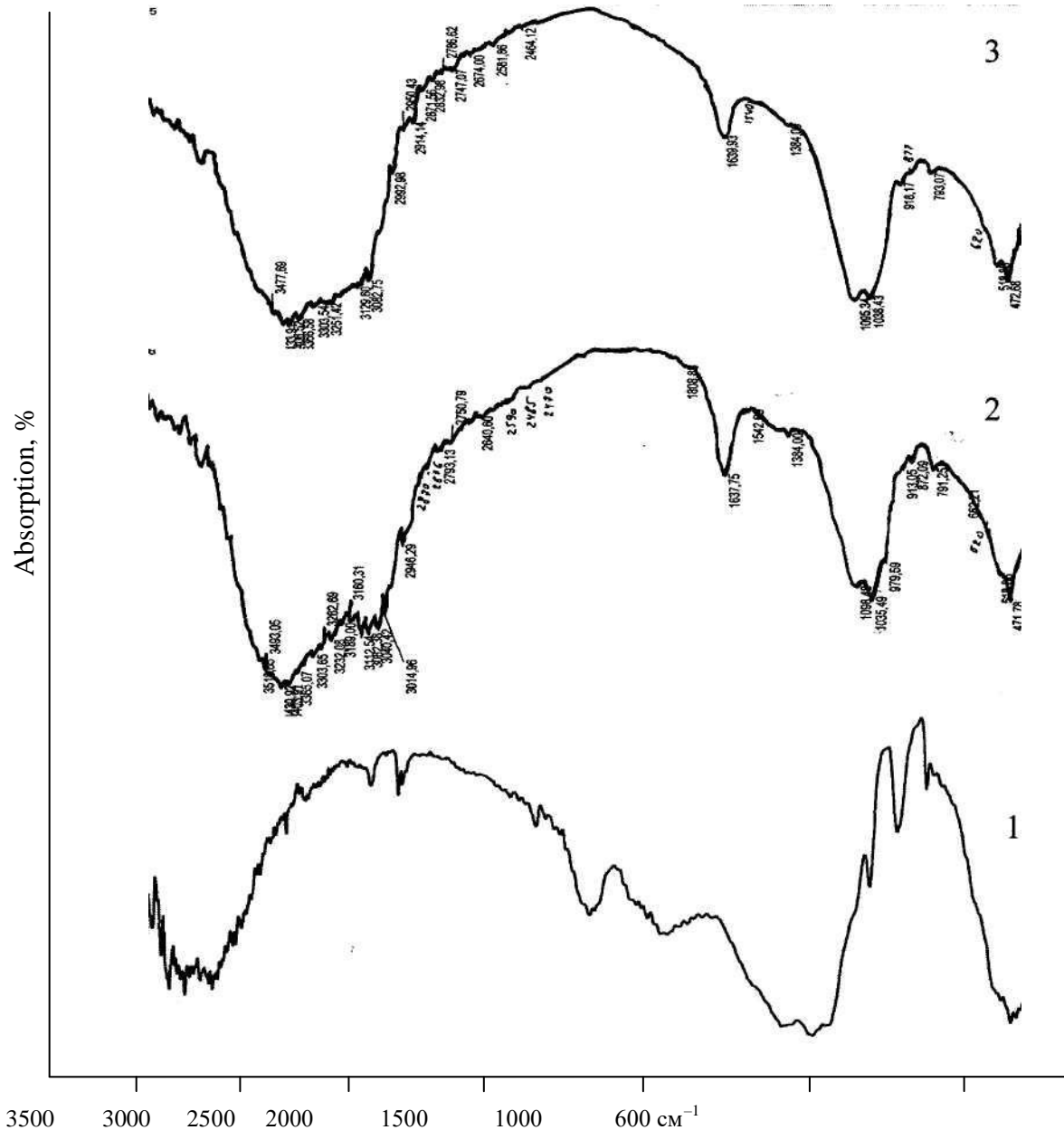


Fig. 1. IR spectra of the starting and activated carbonate palygorskite. 1-source carbonate palygorskite; 2- carrier based on carbonate palygorskite activated with 10% H₃PO₄; 3- carrier based on carbonate palygorskite activated with 5% H₃PO₄.

The frequencies found in the region of 3519–3100 cm⁻¹ correspond to stretching vibrations of the O–H bond of water molecules and phosphoric acid. The bands found in the range 1500-1200 cm⁻¹ correspond to the stretching vibration of the P=O bond of phosphoric acid. The frequencies observed in the region of 1638-1640 cm⁻¹ are consistent with the deformational vibration of the OH bond of water molecules and hydroxyl groups of phosphoric acid. The frequencies found in the region of 1100–850 cm⁻¹ correspond to stretching vibrations of the O – P – O bond of phosphoric acid. The bands found in the region of 650-400 cm⁻¹ correspond to deformation vibrations of the O-P-O bond of phosphoric

acid. The frequencies found are 1050- (3, 800- (1, 625- (4 and 500- (2 cm⁻¹) correspond to stretching vibrations of silicon oxide of the form [SiO₄]⁴⁻ [3].

Thus, an analysis of the IR spectra of samples treated with 5% and 10% phosphoric acid shows that the acid concentration has little effect on the structure of the samples. On this basis, the activation of carbonate-palygorskite clay with a 5% phosphoric acid solution can be considered sufficient for the preparation of catalyst supports.

A study of the X-ray diffraction pattern shows (Fig. 2.) that when activated with strong acids, a partial destruction of the clay mineral crystal occurs, therefore, when activated, bonds between clay crystals break. This led to a deterioration in the swelling capacity of clay, i.e., to a decrease in the expansion of the mineral crystal as a result of the penetration of water molecules into the interplanar space. Acid activation leads to a change in the structure of palygorskite clay. This can be seen from the disappearance of some and the appearance of new reflexes in the X-ray diffraction patterns of the samples. As shown by the analysis of X-ray diffraction patterns (Fig. 2) of the initial carbonate-palygorskite clay and activation products in various mineral acids, with an increase in the activator concentration and

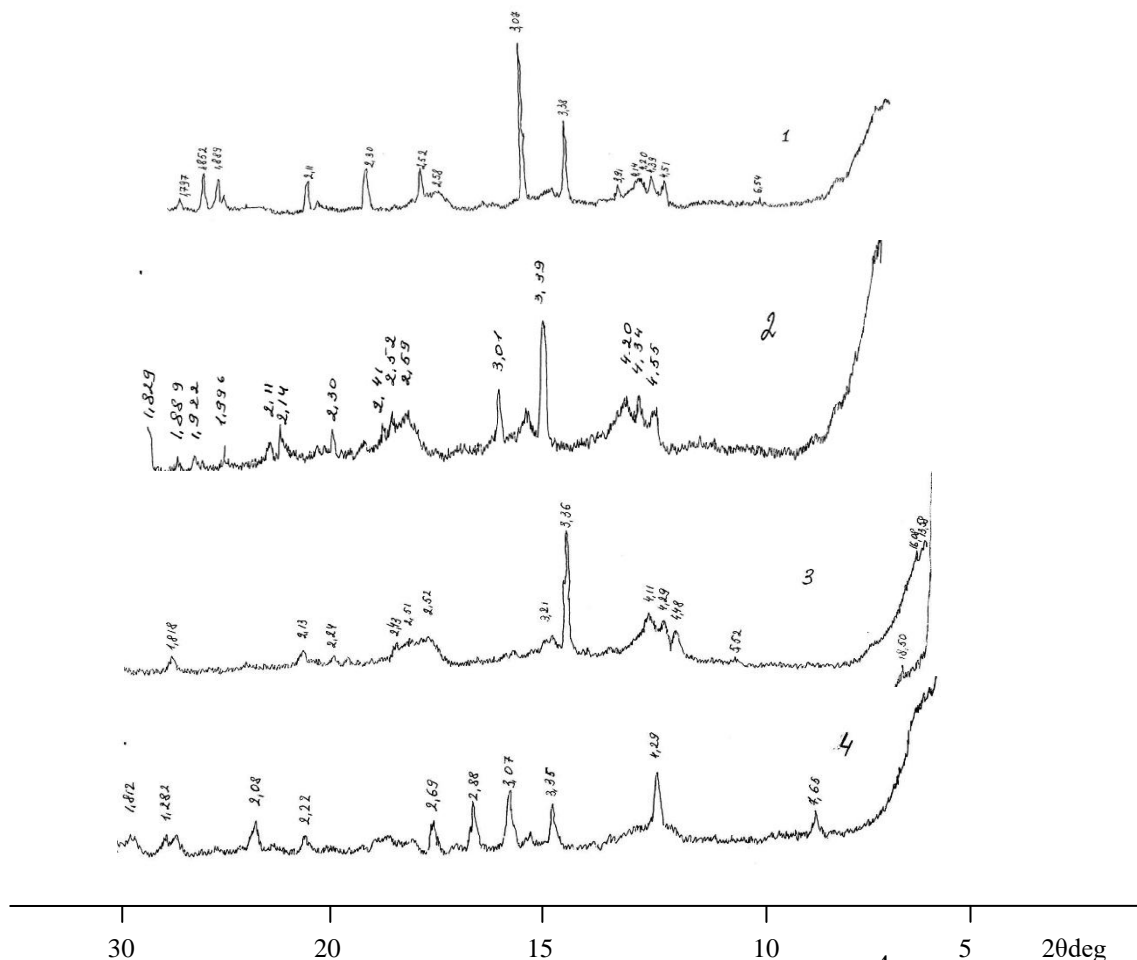


Fig.2. X-ray diffraction patterns of activated carbonate-palygorskite clay samples in 4 d solutions: 1 - initial carbonate-palygorskite clay; 2 - treated with 8% HNO₃; 3 - treated with 15% H₂SO₄; 4 - processed with 15% HCl.

the contact time of the sample with acid, a change in the structure of carbonate-palygorskite clay occurs. So, when clay is activated in a solution of an acid of relatively low concentration, substances that glue small particles dissolve and aggregates disintegrate, at high values of activator concentration and processing time, the clay structure is destroyed, significant quantities of sesquioxides are dissolved, i.e. removal of aluminum and iron oxides from the composition of palygorskite clay, as a result of which the clay surface increases. Alum-nickel-molybdenum and alumino-cobalt-molybdenum catalysts are used in the process of hydrocleaning oil distillates. As an active component in these catalysts, cobalt-molybdenum and nickel-molybdenum systems are used, their content in the catalyst is 18-20% by weight, the rest 80-82% is a carrier. Active alumina is used as a carrier. from the composition it follows that the main component

of the catalyst component is a carrier. Replacing an expensive carrier, aluminum oxide, with affordable, cheap carriers that are not inferior in their physicochemical properties, is an urgent task. The literature notes the possibility of using natural clays as a catalyst or carrier of the active components of various catalysts [1-2].

This article presents the results of studying the composition, structure and properties of the carrier based on carbonate palygorskite and alkaline bentonite clays from the Nurata deposit for catalysts used in hydrocleaning diesel fuel. In alkaline-bentonite and carbonate-palygorskite clay of the Nurata field, the average CaO content is 0.5 and 10.0%, respectively, which in terms of CaCO₃ is about 1.0–20.0%. As a part of these clays, an increased MgO value is observed (1.8–3.0%), which is associated with the presence of magnesite impurities. The ratio of the molecular amount of silica to the total content of molecular oxides in the rocks is from 46.8 to 58%. The chemical composition of the carbonate palygorskite of the Nurata deposit is given in Table 1.

The results of X-ray analysis showed that the carbonate palygorskite has a mineral composition. X-ray analysis revealed that the composition of carbonate clays Nurata

Table 1

№	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	SO ₃	Loss in heating	account
1.	46,79	-	8,63	-	3,44	2,74	10,08	-	1,60	1,99	-	24,33	99,94
2.	57,91	0,35	13,69	5,10	-	1,84	0,48	1,53	1,75	0,43	0,75	16,17	100,0

Comparative chemical composition of carbonate-palygorskite (1) and alkaline-bentonite clays (2) of the Nurata deposit, % mass.

There are palygorskite deposits (10.06 Å), calcite and montmorillonite (12.05, 3.12, 3.08 Å), which are rock-forming.

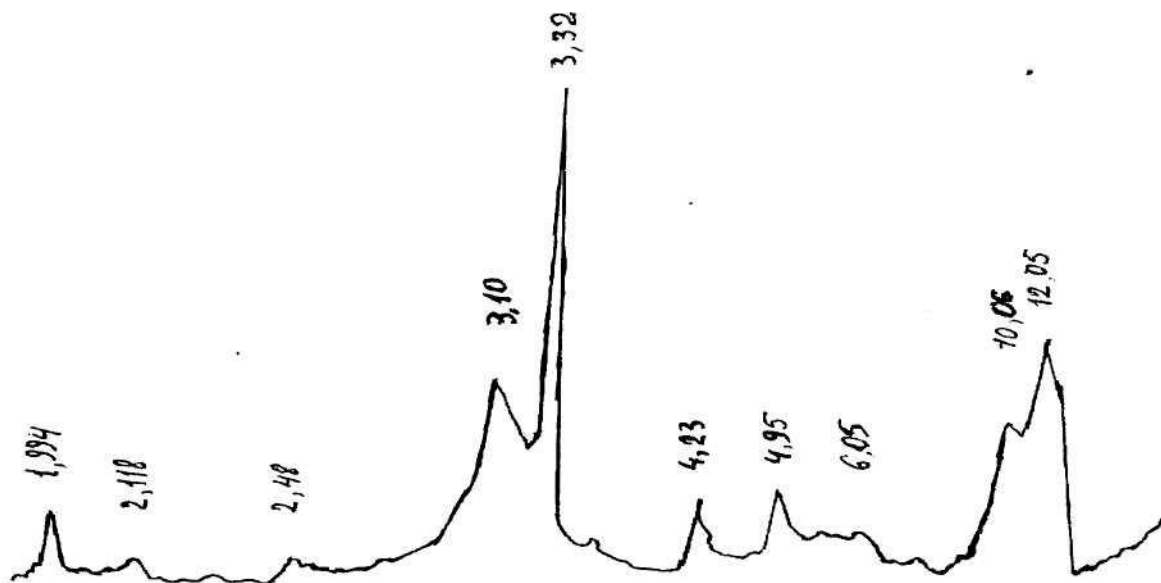


Fig.1. Diffractogram of carbonate palygorskite of the Nurata field.

Carrier properties for hydrocarbon hydrocleaning catalysts are determined by such characteristics as the specific surface area, pore size and volume, pore distribution over radii [3]. The porous structure of the carrier significantly affects the dispersion and distribution of the active components over the surface, the selectivity and the volumetric activity of the catalysts, due to the processes of transport of the reactants inside the granules. We have studied the adsorption properties of new carriers, obtained by various methods using a highly sensitive sorption unit with quartz spring weights of the type of Mac Ben. Sample No. 1 was obtained by treating carbonate-palygorskite clay with a solution of sulfuric acid, and Sample No. 2 was prepared by treating carbonate-palygorskite clay with water and then heated at 600 ° C for 2 hours. The results of the study of the adsorption of water vapor showed that the adsorption

isotherms of water vapor in the sample of carbonate palygorskites are S-shaped.

It is known that the treatment of clay minerals with mineral acids leads to a sharp change in their catalytic activity and other properties. In this regard, quite a lot of research has been carried out on the acid activation of clays and some considerations have been made about the mechanism of acid-clay reactions. Under the conditions of obtaining sample No. 1, partial dissolution of oxides naturally occurs, as a result of which the mesoporosity of the sample increases and the adsorption of water vapor increases. The results of the sorption of water vapor are shown in table 2.

When dehydrating natural minerals, meso- and micropores are released by heating; as a result, it absorbs the molecules of various inorganic substances. When carbonate palygorskite is heated to 400 ° C, its zeolite channels are reduced due to restructuring. The formation of a compressed form of minerals is completed at 450–500 ° C.

Table 2
Sorption characteristics of carbonate-palygorskite clay samples

Adsorbent , sample	1) capacity monolayer, a_m , mol/kg	2) Specific surface area $S \cdot 10^{-3}$, m^2/kg	3) Marginal adsorption, a_s , mol/kg	Maximum adsorption volume, $V_s \cdot 10^3$, m^3/kg
№1	4,81	319	20,2	0,36
№2	1,31	44,3	8,11	0,146

Thus, as evidenced by the data table. 2, the specific surface S_{arr} . No. 1 is 7.2 times the surface of the arr. No. 2, and the limiting sorption volume V_s , respectively, is 2.5 times greater. A comparison of the physicochemical, adsorption characteristics of local natural clays and active alumina [4] shows that the clays studied can be used as carriers for hydrocleaning catalysts.

Thus, the action of acids leads to the extraction of metal and water ions from the activated sample and creates larger voids, or cavities, accessible for most molecules with a larger size (for example, a benzene molecule) in those parts of the catalyst that they could not penetrate before.

VI. CONCLUSION AND FUTURE WORK

Thus, the analysis of the IR-spectra of the samples treated with 5% and 10% phosphoric acid shows that the acid concentration has little effect on the samples. On this basis, the activation of carbonate-palygorskite clay with a 5% phosphoric acid solution can be considered sufficient for the preparation of catalyst supports.

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