

STUDY OF THE SYNTHESIS OF HIGH SILICON ZEOLITE FROM BENTONITE

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Abstract: *The study examined the physicochemical and textural characteristics of natural bentonite in the Navbahor region (Uzbekistan), the methods of their enrichment and activation, as well as the possibility of using high-silica zeolite in the catalytic aromatization of oil gases and natural gas. The obtained zeolites with a high silicon content were treated MoO_3 to form two mononuclear and single binuclear complexes, and therefore, the obtained catalyst showed high catalytic activity in the catalytic aromatization of petroleum gases and natural gas. The monofunctional and bifunctional mechanisms of the Langmuir-Hinshelwood reaction were also considered and kinetic equations describing this process were deduced.*

Keywords: *high silicon zeolite(HSZ), Langmuir-Hinshelwood, mesoporous, montmorillonite.*

INTRODUCTION

Despite the growing interest of researchers in the problems of chemical processing of hydrocarbon raw materials, the choice of highly selective adsorption and catalytic systems is still relevant. The selectivity of the action of adsorbents and catalysts depends on their composition, structure, conditions of use and many other factors. Therefore, it is important to obtain highly selective adsorbents and catalysts and create perfect technological processes based on them.

The development of a scientific basis for the preparation and use of zeolites has become an independent area of fundamental research [1,2].

In practice, the most common zeolites are NaA and KA zeolites used to dry liquids and gases. The latter is also used to dry bioethanol [2,13]. Interestingly, the more hydrophobic the adsorbate, the deeper the purification. At a temperature of 20⁰ C and compressed air humidity of 10%, the equilibrium adsorption of water in zeolites reaches a zeolite value of about 10 mmol/ g for NaA and NaX. NaX is also used to separate hydrocarbons, purify methane from hydrogen, and enrich the air with 95% oxygen. CaX and CaY are used to separate stereoisomers, e.g., glucose /fructose, while NaX and CaX zeolites are used to separate olefins from paraffin [3,14].

The selectivity and acidity of hydrophobic microporous molecular sieves are widely used in heterogeneous catalytic processes. For example, microporous molecular sieves are active catalysts for isomerization that occur in the presence of hydrogen at high pressure [4-7]. At present, the main issue is the ability to obtain nanoparticles and clusters that have a high resistance to external influences over time.

There is a lot of work in the modern literature on the stabilization of metal nanoparticles in polymer matrices [8-9]. However, aluminosilicate matrices have several advantages, they have high heat and chemical resistance and special surface properties, which allows them to be considered the most promising materials. It is known that when forming nanoparticles, a series of intermediate stages of formation of unstable small clusters usually begin. During their sequential synthesis, larger particles than ever before are formed up to quasimetallic and then nanoscale particles [10-11, 15-16]. Aromatic hydrocarbons, mainly benzene, toluene, ethylbenzene and xylenes, are important chemical products in the petrochemical industry [17-20]. At present, aromatic compounds are obtained by catalytic reforming and cracking of oil fractions. But at a time when oil reserves are dwindling, there is a growing demand to find alternative sources of aromatic hydrocarbons. One of the alternative sources of aromatic hydrocarbons is natural gas and petroleum gases [21-23].

One of the promising methods of processing natural gas and petroleum gases is their catalytic aromatization [24-25]. Mo-retaining catalysts modified by intermediate metal ions have high catalytic activity in the aromatization reaction of natural and petroleum gases without oxidizers [26-27].

MATERIALS AND METHODS

In the laboratory, the synthesis of zeolites was carried out in vessels with a volume of 250 cm³. The chemical composition of zeolites is as follows: the mass fraction of sodium oxide was determined on a flame photometer PAJ-2 flame emission photometry. The molar relations of SiO₂/Al₂O₃ were on formula $M = \frac{SiO_2}{Al_2O_3}$.

An important characteristic of zeolites is their statistical capacity, which was determined by the values of the complete saturation of the zeolite with steam and heptane. Before analysis, the zeolite sample was heated at 500-550 °C for 3 hours. Before acid treatment, the soil was ground to 0.08 mm. To 10 g of ground, the soil was added 40 g of heated H₂SO₄ and heated by stirring in a water bath.

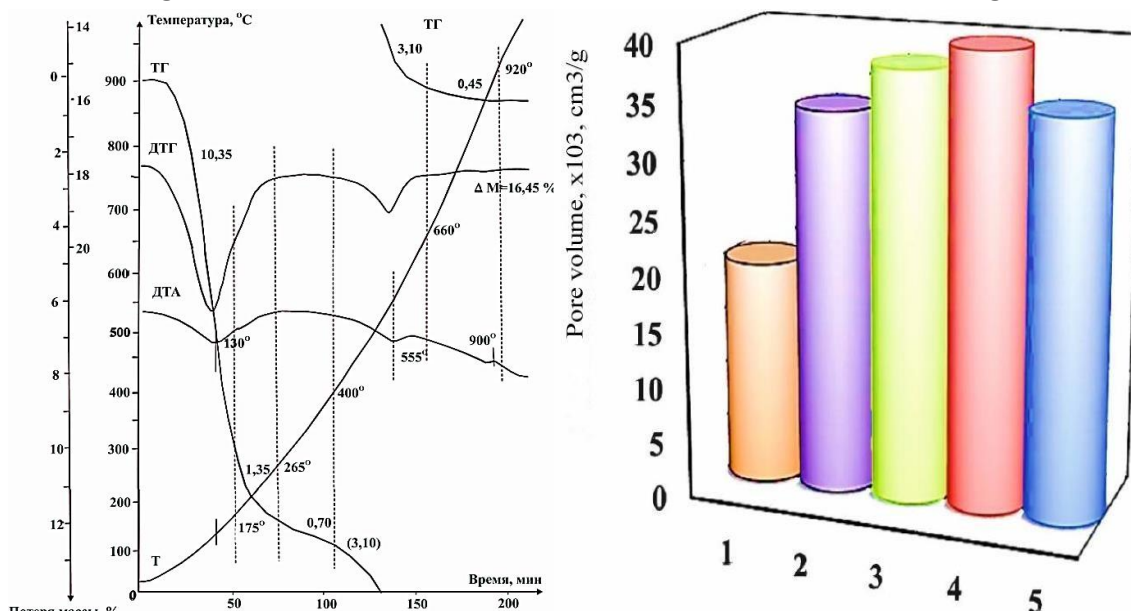
The solution was kept in a water bath at 90-1000 °C for 2 hours under constant stirring, then the precipitate (NH₄⁺/zeolit) was filtered, washed with distilled water, dried and calcined at 550-6000 °C for 8 hours. The decanted zeolite powder was then compressed into tablets and cut into granules. The catalytic methane aromatization reaction was carried out under the following conditions. The non-oxidative conversion of methane (purity 99.9%) was carried out by changing the temperature in the flow reactor in the range 600-800

$^{\circ}\text{C}$, at $P = 0.1 \text{ MPa}$, the ratio methane: argon = 1:1, with a space velocity of 200-1000 h^{-1} . In the quartz reactor (reactor diameter 12 mm), the catalyst volume was 1 cm^3 . Catalyst particle size 0.5-1.0 mm. Before the start of the experiment, the catalyst was heated under helium flow at $7500 \text{ }^{\circ}\text{C}$ for 20 minutes. The reaction products were analyzed by gas chromatography every 10 minutes. The state, dispersion and structure of the active catalyst centres were examined by electron microscopy and electron diffraction. The composition of the starting and forming compounds was analyzed chromatographically.

ANALYSIS AND RESULTS

The distribution of pores by specific surface area and size was detected on the automatic absorptiometer

“ASAB 2010” by low-temperature nitrogen desorption. Sedimentation analysis was carried out by the Oden method in water and an aqueous glycerol mixture in various dispersion media. Physicochemical and textural characteristics of natural bentonite imported from Navbahor district (Uzbekistan), which was originally used for the production of high-silicon zeolite, were studied. The results are shown in Figures 1-4.



1-primary bentonite; 2-20 minutes; 3-30 minutes; 4-40 minutes; Bentonite treated for 5 to 50 minutes.

Figure 2. The duration of acidic activation of bentonite depends on the size of the pores.

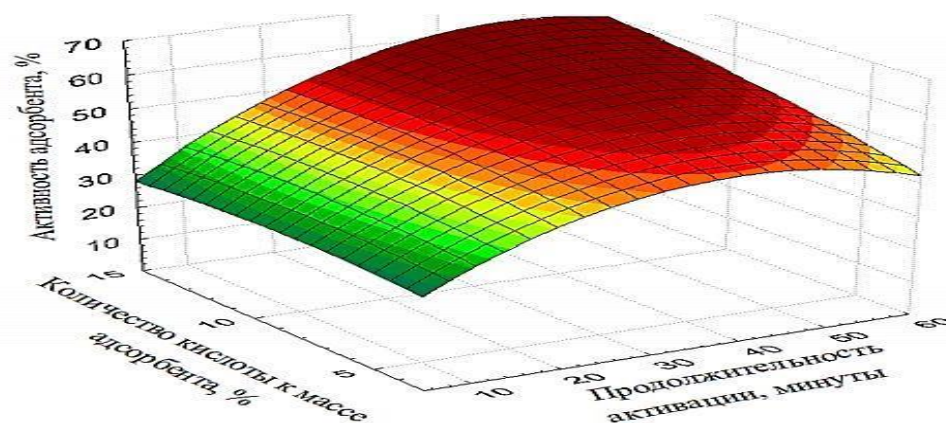


Figure 3. Dependence of the adsorption activity of the adsorbent synthesized from bentonite on the acid activation regime.

The main component of bentonite is montmorillonite. The structure of Montmorillonite can be thought of as follows: a single layer of silicate consists of two layers of tetrahedrons joined together by their edges. Since the bonds between them are weakly high molecular distance is large, different particles enter the intermolecular space: ions, molecules, nanoparticles can enter. This explains why bentonite soils have high sorption, swelling and ion exchange properties. The elemental cell of bentonite contains 3 plates, which form packets, with $[AlSiO_4]$ –tetrahedrons. The three-layer package will be negatively charged:

To determine the acidic properties of the catalysts, the method of temperature-programmed desorption was used. This makes it possible to determine the nature of the catalysts, the strength and concentration of active sites. For this, HSZ catalysts were prepared, promoted with oxides of zinc, zirconium, galley, and scandium (the content of metal oxides 1.5%), which were divided into samples with a particle size of 4: 3: 2 mm in a ball vibration mill. The measurement results are shown in Table 1.

Table 1. Acidic properties of catalysts.

Granule size, mm	Peak temperature, °C		The concentration of desorbed NH_3 , $\mu mol / g$			Activation energy, kJ/mol	
	T_1	T_n	C_1	C_n	C	E_1	E_n
4	190	420	205	168	383	29,5	108,9
3	190	380	194	130	334	28,7	95,2
2	190	380	185	126	321	-	-

Table 2. Specific surface area porosity of HSZs samples.

Example	Mezo-porous		Micro-porous		Relative proportion of micro-pores,%
	SMezo-porous, м ² /г	VMezo-porous, см ³ /г	S microporous, м ² /г	V micro-porous, см ³ /г	
HSZ	167	0,068	96	0,041	37,6
HSZ+1%Mo	221	0,081	101	0,046	36,2
HSZ+2%Mo	196	0,061	95	0,042	40,8
HSZ+5%Mo	182	0,066	107	0,047	41,6

CONCLUSIONS AND RECOMMENDATIONS

Thus, the physicochemical and texture characteristics of natural bentonite in Navbahor district (Uzbekistan), methods of their enrichment and activation, as well as the possibility of using high-silica zeolite in the catalytic aromatization of petroleum gases and natural gas were studied. The calculated size distribution of the pores along the isothermal hysteresis cycles (loops) was $r \approx 8.5$ nm. The volume of sorbent porosity by capillary filling with water was determined as $V_n = 0.135$ sm³/g. It has been proved that the shape and size of the crystals formed by the sorbents vary depending on the nature of the structure-forming ones.

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