Synthesis of High Silicon of Zeolites and Their Sorption Properties

[1]I.I. Mamadoliev., [2]N.I. Fayzullaev, [1]K.M. Khalikov
[1]Samarkand Medical Institute,
[2]Samarkand State University
bekhruzjon_omanov509@inbox.ru

Abstract

During the study, the synthesis, structure, and physicochemical characteristics of high-silicon zeolites from bentonite and kaolin were studied. Adsorption isotherms are characteristic of type IV according to the de Boer classification and characterize the adsorption of mesocellular substances. In the isotherm in the range P/P_0 = 0-0.05, monomolecular adsorption in mesopores and adsorption in micropores are observed. At P/P_0 = 0.05, mono- and multimolecular adsorption is observed in mesocytes. P/P_0 = 0.05-0.4 represents the polymolecular adsorption field. Based on the results obtained, the adsorption of CO_2, H_2S, and NO_2 gases by absorption of a mixture of $CaCl_2 \cdot ZnCl_2 \cdot MnCl_2$/HSZ salts in a synthesized sorbent was studied. According to experimental results, the dynamic capacity of $CaCl_2 \cdot ZnCl_2 \cdot MnCl_2$/HSZ relative to hydrogen sulfide was 2.76% by mass. The total dynamic capacity of the adsorbent on H_2S was above 20-25%.
Keywords: bentonite, kaolin, colloid, ductility, adsorption capacity, meso and micropores, dynamic capacity.

1. Introduction

In recent years, natural and artificial zeolites have been widely used in thepurification of hydrocarbons. Adsorption methods for industrial hydrocarbon purification are one of the most common methods in the industry. Their use allows a number of valuable compounds to be returned to production in order to reuse. [1-2].Synthetic porous aluminosilicates with specified characteristics are promising materials for solving a whole range of urgent interdisciplinary tasks related to the development of new drugs, their delivery systems, new catalysts and sorbents. Natural layered silicates (clays) and silicates with a skeleton structure (zeolites) as materials with a number of unique properties, such as ion exchange ability, high cation exchange capacity, micro- and nanoporous structure, the presence of surface active centers of various nature, have long been widely used as highly efficient systems for the separation and purification of paraffin hydrocarbons, separation of mixtures of various gases and liquids, refrigerant dryers, for the extraction of radioactive isotopes from liquid waste the nuclear industry, to solve a number of problems of pharmacy and cosmetics.

The study of zeolites has been the subject of many works. Zeolites are microporous substances with a regular crystalline structure and a controlled pore size not exceeding 2 nm [3-6]. Zeolite frameworks are lattices consisting of tetrahedral T atoms (T = Si, Al, etc.) connected by oxygen atoms.At present, more than 200 types of synthetic zeolites of various structural types are known [7–9]. However, in industry no more than 10% of all known structures are produced, and only 5 structural types are actually used as catalysts [10-13].

The most important requirements for adsorption materials are: high specific surface area, selective responsiveness and easy regeneration [14-15]. In addition, the adsorbent should be cheap and harmless, with no corrosive properties, should retain its adsorption feature for a long time, and be highly mechanically durable. One of the most common adsorbents is activated carbon and is produced by various brands.

One of the most important areas for now is the development of environmentally friendly sorbents, catalysts and catalysts based on local raw materials [16 - 17].

ISSN: 2005-4297 IJCA

2. Experimental part

To determine the chemical and physicochemical characteristics, we placed sample granules in 100 g of mass in a 250-cm glass tube and poured 150 cm^3 of distilled water. The flask was stirred for 24 hours on the AVU-6 unit at 120 rpm. After drying, the adsorbent was passed through a sieve with 0.5- and 0.25-mm diameter, and the mechanical and physicochemical properties were studied. Before acid treatment, we grinded the soil samples until to reach particle size 0.08 mm. We added 40 ml H_2SO_4 heated to 10 g of grinded soil and stir in a water bath. After processing, the soil was filtered through a paper filter in the Buchner funnel and washed with distilled water at pH = 5.4-5.7. The soil was then dried with the filter paper in the dryer for 12 hours at 120ºC. Specific surface area and the distribution of pore sizes were found in the automatic adsorbometer ASAB 2010 by the low-temperature nitrogen desorption method. Sediment analysis was performed on water and glycerol mixture in different dispersion environments using the Oden method.

X-ray diffraction analysis (Co-Kα-radiation) was performed on the DRON-4 diffractometer with a cobalt X-ray tube. The PDF-2 database of the International Center for Diffraction Data (JCPDS, 1999) was used for the analysis of diffractograms. The porosity of the samples was determined by Quantrome NOVA (USA) analyzer of low-temperature nitrogen desorption. Each sample was dehydrated for 2 hours at 250ºC under vacuum prior to measurement.

To determine the shear density, the sorbent weighed 500 g and was kept in the dryer for 600 h at 60ºC. 400 g of the dried sample was weighed and placed in a 500 ml cylinder, measured a volume V_1. We then densified th sorbent by light tapping under the cylinder and t and again measured a volume V_2.

The bulk density of the sorbent was determined by the following formula:

$$\gamma_1 = \frac{P}{V_1} \quad \gamma_2 = \frac{P}{V_2} \qquad [g/cm^3]$$

where P-is the mass of the sorbent; Density of γ_1, γ_2-sorbent and subsequent bulk density, g/cm^3.The subject of the study was the Navbakhor bentonite and Pahtachi kaolin [19-20].

High-silicon zeolite (HSZ) was synthesized as follows: mixing 30 g of bentonite in 300 ml of double-distilled water, a suspension was prepared by slowly mixing, during which the particles of minerals contained in bentonite were separated into fractions. The resulting suspension was left for a day. Then the sample was centrifuged at a speed of 7000 rpm for 5 minutes. The obtained fraction was dried in the open air at room temperature for 6 hours, and then at 65ºC for 12 hours. The sample was then activated in 1.5 M nitric acid at 80-90ºC for 2 hours. After activation, 200 ml of distilled water was added to the bentonite suspension and rapidly cooled. The resulting sample was then washed several times with distilled water, centrifuged and dried at room temperature for 12 hours, and then at 65ºC for 12 hours. Consequent chemical treatment with sodium carbonate and 25% nitric acid in the same order was carried out.

3. Results and discussion

In order to purify petroleum products from various gases, 20% solutions of $CaCl_2$, $ZnCl_2$, $MnCl_2$ on high-silicon zeolite obtained by the above method are absorbed for 2 hours with strong shaking. As a result, a sample was obtained with the composition $CaCl_2 \cdot ZnCl_2 \cdot MnCl_2$/HSZ. The chemical composition of the sample was analyzed by an energy dispersive spectrometer and X-ray spectroscopy

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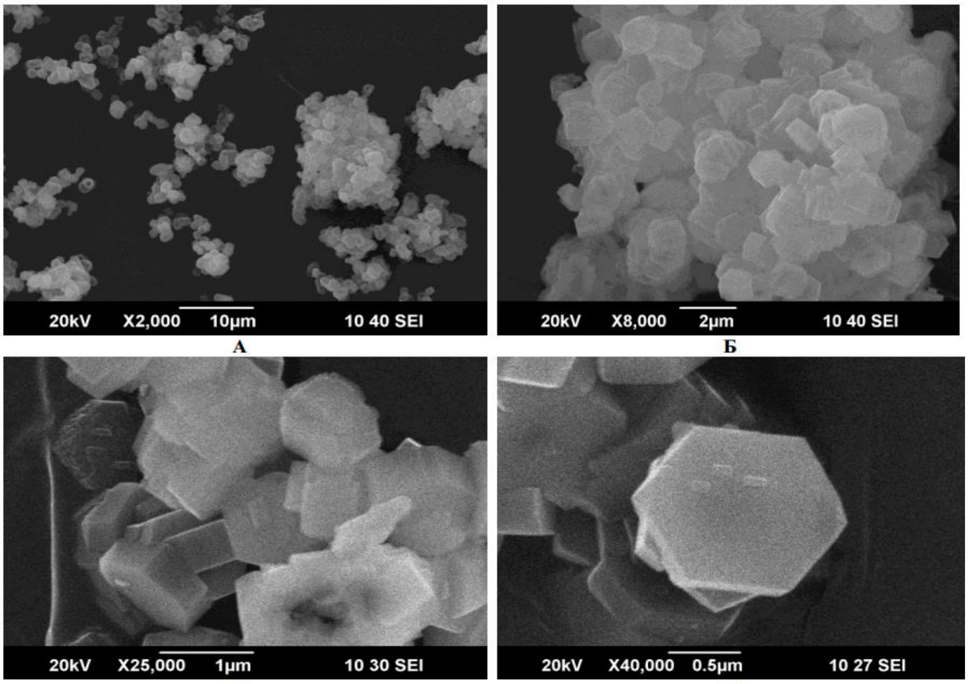

Figure 1. Microphotographof HSZ obtained in scanning electron microscope: (*up*) (A) ×2000 magnification; (B) ×8000 magnification; (*bottom*) (A) ×25000 magnification; (B) ×40000 magnification.

Adsorption isotherms are typical of type IV according to the de Bour classification and characterize the adsorption of mesoporous materials. In the isotherm, monomolecular adsorption in the shells and $P\text{-}P_0$ = 0-0.05, as well as adsorption in microwave microwaves are observed. At P/P_0 = 0.05, mono- and multimolecular adsorption in the pores is observed. Area P/P_0 = 0.05–0.4 is the polymolecular adsorption that is used to compare surface surfaces (S_{sol}) in the BET equation. Adsorption isotherms characterize capillary condensation in the intermediate shells P/P_0 = 0.4-1.0.

The paper presents the results of the influence of thermal activation factors on zeolites with different cationic composition. Silicon enriched zeolite obtained from Navbakhar bentonite was used as sorbent.

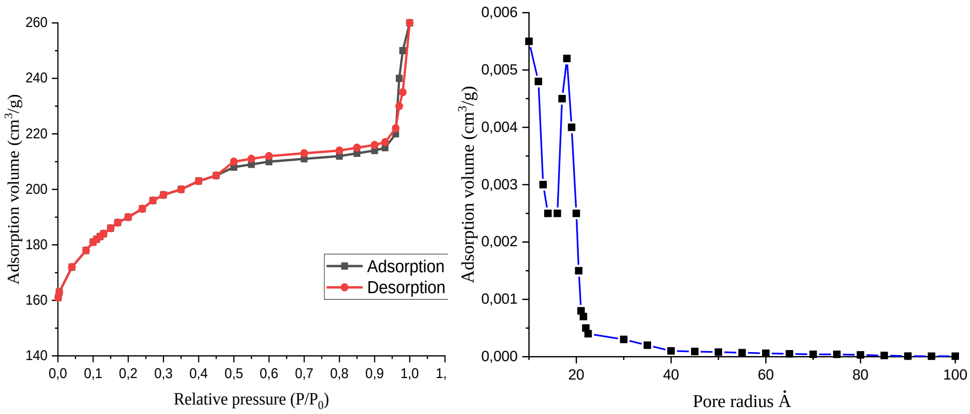

Figure 2. Adsorption-desorption isotherms and pore size distribution differential curves related to radius of synthesized sorbents.

The dynamic activity of the adsorbent is always lower than the static activity and is associated with the condition of the adsorbent. The dynamic activity of the adsorbent is the main indicator of the size of the adsorbent and the time of the sorption cycle. Adsorption experiments were carried out as follows. The $CaCl_2 \cdot ZnCl_2 \cdot MnCl_2$/HSZ system was heated in a muffle furnace for 2 hours at 400℃, then cooled on a desiccator.

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Purification of natural gas was carried out in a wired device. Dynamic activity was determined by the formula:

$$A_g = C_o \cdot W \cdot \tau$$

whereC_o– initial concentration of H_2S, CO_2, NO_2in a solution, g/100 g;

W- gasflowrate, m/s;

τ–protective action time of adsorbent.

Adsorption isotherms of H_2S, CO_2, NO_2were studied on activated charcoal (C_{act}; NaX zeolite and $CaCl_2 \cdot ZnCl_2 \cdot MnCl_2$/HSZ.

Table 1. Adsorption isotherms on activated charcoal CO_2, H_2S and NO_2 (C_{act}); results on zeolite NaX and $CaCl_2 \cdot ZnCl_2 \cdot MnCl_2$/HSZ

Adsorbents	Activated charcoal (C_{act})			ZeoliteNaX			$CaCl_2 \cdot ZnCl_2 \cdot MnCl_2$/HSZ		
Components	H_2S	CO_2	NO_2	H_2S,	CO_2	NO_2	H_2S	CO_2	NO_2
Static, g/100 g	9.22	7.23	7.02	12.78	10.95	9.95	16.46	13.98	12.84
Activity, g/100 g	7.02	5.36	5.03	9.96	8.74	8.06	14.6	11.64	10.92

ForadsorptiononasystemCaCl$_2 \cdot$ ZnCl$_2 \cdot$MnCl$_2$ /HSZthe following mixture:

Table 2. $CaCl_2 \cdot ZnCl_2 \cdot MnCl_2$ / HSZcontent of model compounds to study adsorption to the system

Content	Mass content, %		
	No 1	No 2	No 3
Hydrogen sulfide	2.85	3.05	2.80
Carbon dioxide	-	2.90	5.93
Nitrogen	97.15	94.05	91.25

Experiments were carried out at the Bukhara petroleum refinery in a semi-industrial complex with a mass fraction of hydrogen sulfide of 2.9% and a mass fraction of sulfur in mercaptanes of 0.5%. The absorption process was carried out by supplying petroleum gases to the adsorber with an adsorbent height of 100 cm and a diameter of 5 cm. For potentiometric determination of sodium sulfide and mercaptides, a Drexel flask filled with a 10% sodium hydroxide solution was installed at the outlet of the reactor.

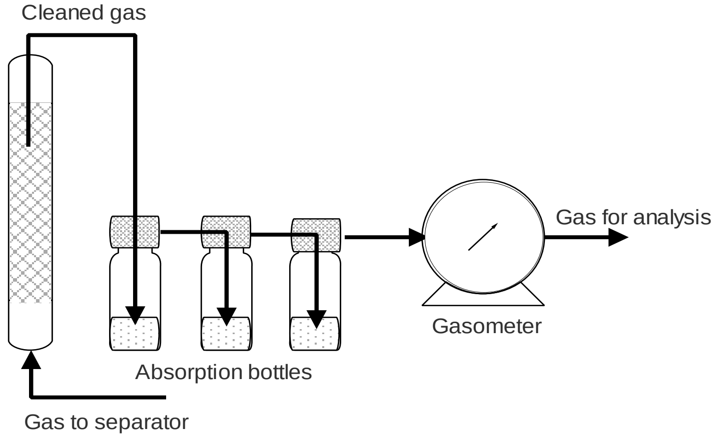

Figure 3. Experimental adsorber device for the purification of petroleum gases from hydrogen sulfide.

Studies have shown that the total sulfur content in $CaCl_2 \cdot ZnCl_2 \cdot MnCl_2$/HSZ in hydrogen sulfide is 14.3% (mass). The dynamic sulfur capacity is 11.3% at 1000 ppm. From experimental data, we can conclude that in a device with a gas flow of 4000 m^3/day, this sorbent can be used continuously for 1.5 weeks.

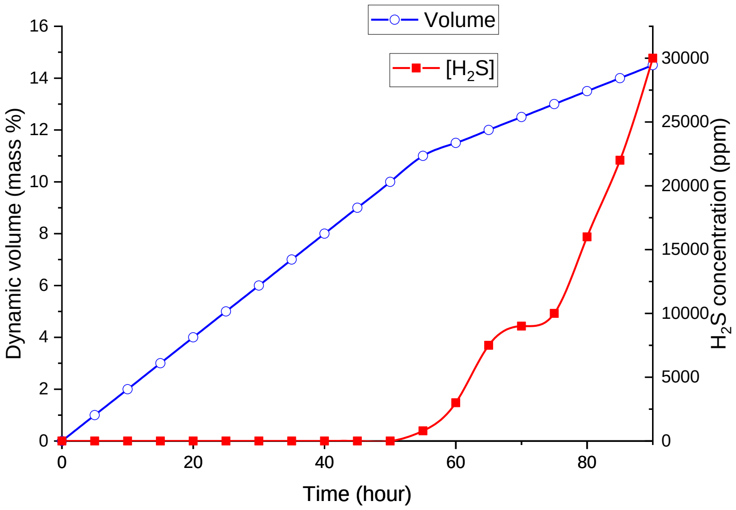

Figure 4. Changes in the dynamic capacity of the chemisorbent $CaCl_2 \cdot ZnCl_2 \cdot MnCl_2$/HSZ at the outlet of the adsorber with time.

To confirm the possibility of using $CaCl_2 \cdot ZnCl_2 \cdot MnCl_2$/HSZ, the experiment was conducted at a research industrial device in the Bukhara petroleum refinery filled with an adsorber with a diameter of 1.2 m, a height of 8 m and a mass of 2 tons.In the industrial apparatus of the mass fraction in the gas studied, 3.5% H2S after the beginning of the test, after 24 hours, the concentration of hydrogen sulfide released from the adsorber was 180 ppm. The results of the tests showed that the dynamic capacity of $CaCl_2 \cdot ZnCl_2 \cdot MnCl_2$/HSZ for hydrogen sulfide mass fraction was 2.76%. The full dynamic capacity of the adsorbent for H2S is less than 20-25%.Sorption isotherms were used to calculate the thermodynamic and equilibrium adsorption constants on the sorbent $CaCl_2 \cdot ZnCl_2 \cdot MnCl_2$/HSZ for CO_2, NH_3, H_2S.For this, linear Langmuir isotherms were obtained by calculating the inverse values of sorption (1/g) and concentration (1/s). Table 3 below shows the thermodynamic characteristics of the adsorption of CO_2, NH_3, H_2S on the sorbent $CaCl_2 \cdot ZnCl_2 \cdot MnCl_2$/HSZ at various temperatures.

Table 3. Thermodynamic characteristics of CO_2, NH_3, $H2_S$ adsorption on the sorbent $CaCl_2 \cdot ZnCl_2 \cdot MnCl_2$/HSZ at different temperatures

Sorbet	Temperature			-ΔH, kJ/mol	$-\Delta G_{295}$, kJ/mol	-ΔS, J/mol ·K	G, g/g
	295	323	335				
SO_2	1.0	3.70	20.0	61.50	1.129	17.05	0.64
H_2S	1.50	4.10	25.0	57.71	1.220	15.43	0.30
CO_2	1.10	3.95	23.50	62.66	11.52	174.03	0.38

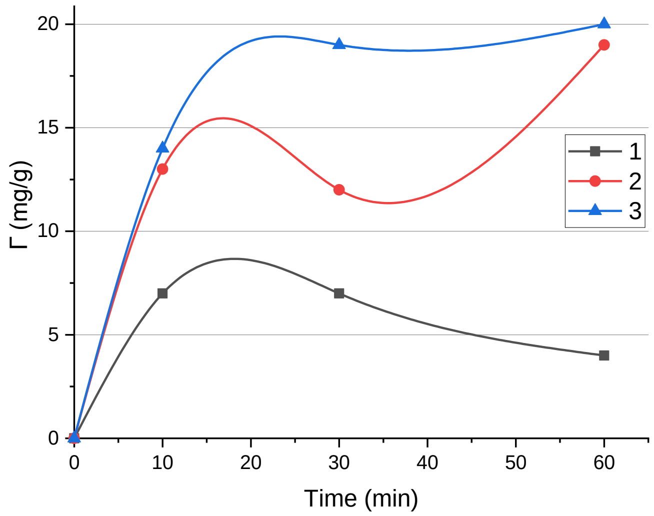

Figure 5. Kinetic curve of sorbentsto carbon dioxide, where: 1-natural bentonite; 2- high-silicon zeolite bentonite treated with a 1% solution of hydrochloric acid and sodium carbonate; 3 - high-silicon zeolite bentonite treated with a 10% solution of sulfuric acid and sodium carbonate.

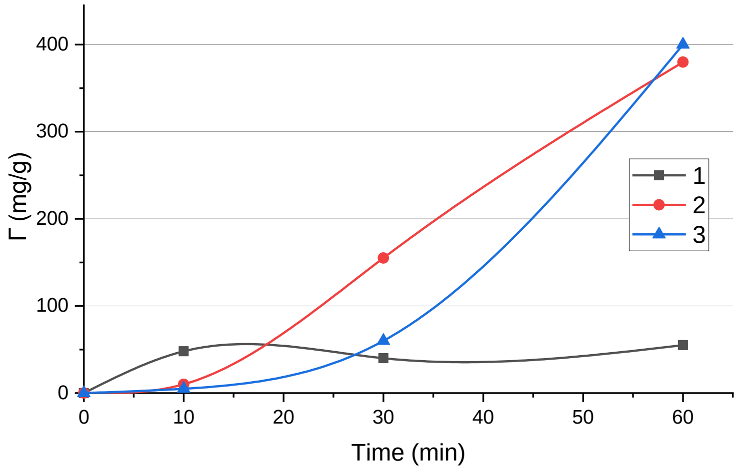

Figure 6. Kinetic curve of sorbents to hydrogen sulfide, where: 1-natural bentonite; 2- high-silicon zeolite bentonite treated with a 1% solution of hydrochloric acid and sodium carbonate; 3 - high-silicon zeolite bentonite treated with a 10% solution of sulfuric acid and sodium carbonate.

4. Conclusions

Thus, the sorption, textural and physicochemical characteristics of the high-silicon zeolite obtained from bentonite and kaolin were studied. Based on the results obtained, the adsorption of CO_2, H_2S and NO_2 gases by absorption of a mixture of $CaCl_2 \cdot ZnCl_2 \cdot MnCl_2$/HSZ salts in a synthesized sorbent was studied.According to experimental results, the dynamic capacity of $CaCl_2 \cdot ZnCl_2 \cdot MnCl_2$/HSZ relative to hydrogen sulfide was 2.76% by mass. The total dynamic capacity of the adsorbent on H_2S was above 20-25%.

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Authors

Mamadoliev Ikromjon Ilkhomidinovich
Education: Higher, on the specialty of "Inorganic Chemistry"
Scientific degree: -
Scientific title: -
Position: assistant Lecturer in the Department of Medicine and Biological
Total working experience: 16 years
Teaching experience: 14 years

Information about the author:
A bachelor of Chemistry, Samarkand State University in 2000-2004.
2004-2006 Samarkand State University, Master of Inorganic Chemistry.
Since September 18, 2018 he has been working in the Chair.