OBTAINING HIGH-SILICON ZEOLITES FROM KAOLIN

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ПОЛУЧЕНИЕ ВЫСОКОКРЕМНИСТЫХ ЦЕОЛИТОВ ИЗ КАОЛИНА

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ABSTRACT

Extraction of high-silicon zeolites (HSZ) from kaolin "Qarnab ota" was carried out on the technology "Sol-gel" with the participation of various organic compounds (templates). For this purpose, crystals were formed by adding hexamethylenediamine and an alcohol fraction to the liquid glass (29% SiO_2, 9% Na_2O, 62% H_2O) as $Al(NO_3)_3 \cdot 9H_2O$ template. At the end of the crystallization process, the solid phase was separated from the solution using a Büchner funnel. It was dried in the ShSU-m1 drying cabin to 120 ℃. And to lose the template, the SNOL30/1100 muffle furnace was heated at 550 ℃ for 8 hours. With the increase in the silicate modulus of HSZ, not only did the total specific surface area and porosity correspond to micro-and mesopores, but also increased the surface area and the volume.

АННОТАЦИЯ

Извлечение высококремнистых цеолитов (ВКЦ) из каолина «Карнабота» проводили по технологии «Золь-гель» с участием различных органических соединений (темплатов). Для этого формировали кристаллы путем добавления к жидкому стеклу (29% SiO_2, 9% Na_2O, 62% H_2O) в качестве темплата $Al(NO_3)_3 \cdot 9H_2O$ гексаметилендиамина и спиртовой фракции. По окончании процесса кристаллизации твердую фазу отделяли от раствора с помощью воронки Бюхнера. Высушивали в сушильном шкафу ШСУ-м1 до 120 ℃. А для потери темплата прогревали в муфельную печь (SNOL30/1100) при 550 ℃ в течение 8 часов. Рентгенофлуоресцентный анализ образцов элементного и оксидного содержания (масс., %) ВКЦ, в которых кристаллизация каолина проводилась в течение 8-9 часов. С увеличением силикатного модуля ВКЦ увеличивались не только общая удельная поверхность и пористость, соответствующие микро- и мезопорам, но и площадь поверхности и объем.

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Keywords: Qarnab ota, Sol-gel, template, kaolin, specific surface area, surface area, micro and meso pores.
Ключевые слова: Карнаб ота, Зол-гель, темплат, каолин, удельная поверхность, площадь поверхности, микро- и мезопоры.

Introduction

Today, among the technologies for purification of oil and natural gas from water vapour and sulfur compounds, the adsorption processes of drying and purification using zeolites with high absorption properties at low partial pressures, selectivity of adsorption of polar substances, etc. play an important role [1,2,3]. Their disadvantage is the loss of activity of adsorbents in a relatively short period when there are large amounts of thiols in the purified gas (up to 500 mg/m^3) [4]. Therefore, the creation of a new generation of silica gels with a large volume of pores and mechanical strength and their application independently or in combination with zeolites in the drying and purification of oil and natural gas from sulfur compounds, in this regard, the research and development of such a process is a topical issue [5,9]. There are a large number of bentonite deposits in the country, and the demand for bentonite and its products is growing in various industries, such as agriculture, machinery, chemical and petrochemical industries, and construction. In this regard, based on the creation of modern technologies for the processing of low-quality bentonite raw materials, it is necessary to obtain products with improved technological parameters and physicochemical and mechanical properties. One of the promising directions to solve this problem is to introduce nano dispersed components into raw materials using these nanotechnology advances [6,7,8]. Demand for bentonite and its products is growing in various industries where they are used, such as agriculture, machinery, chemical and petrochemical industries, and construction. In this regard, on the basis of the creation of modern technologies for the processing of low-quality bentonite raw materials, it is necessary to obtain products with improved technological parameters and physicochemical and mechanical properties. One of the promising directions to solve this problem is to introduce nano dispersed components into raw materials using these nanotechnology advances [10]. Demand for bentonite and its products is growing in various industries where they are used, such as agriculture, machinery, chemical and petrochemical industries, and construction. In this regard, based on the creation of modern technologies for the processing of low-quality bentonite raw materials, it is necessary to obtain products with improved technological parameters and physicochemical and mechanical properties. One of the promising directions to solve this problem is to introduce nano dispersed components into raw materials using these nanotechnology advances [1,7,10]. it is necessary to obtain products with improved technological parameters and physicochemical and mechanical properties. One of the promising directions to solve this problem is to introduce nano dispersed components into raw materials using these nanotechnology advances [10]. it is necessary to obtain products with improved technological parameters and physicochemical and mechanical properties. One of the promising directions to solve this problem is to introduce nano dispersed components into raw materials using these nanotechnology advances [7].

Experimental Part

High-silicon zeolites (HSZ) from kaolin "Qarnab ota" were made on the technology "Sol-gel" with the participation of various organic compounds (templates). High-silicon zeolites were synthesized in a stainless steel autoclave at 175-200 ℃ for 6 days according to the following method. The initial reaction mixture was prepared by rapid mixing with the addition of hexamethylenediamine and an alcohol fraction as an $Al(NO_3)_3 \cdot 9H_2O$ template to a liquid glass (29% SiO_2, 9% Na_2O, 62% H_2O). At the end of the crystallization process, the solid phase was separated from the solution using a Büchner funnel and dried for 12 hours in a drying oven at ShSU-m1 to 120 and fired at 550 ℃ in a SNOL 30/1100 muffle furnace for 8 hours to lose template. For the decathionization of the resulting high-silicon zeolite, 10 g of zeolite was treated with the addition of 100 g of 25% ammonium chloride. The solution was held in a water bath at 90-100 ℃ for 2 hours with constant stirring. Then the sediment (NH_4^+/zeolite) was filtered, washed with distilled water, dried and burnt for an hour at 550 ℃. Then the cationized zeolite powder was pressed and analysed.

Results and Discussion

Kaolin has a layered structure, consisting of tetrahedral and alumina-oxygen octahedral layers of repetitive silicon-oxygen. When kaolin is heated to 550-600 ℃, it turns into amorphous metakaolin, and above 925 ℃ it turns into a defective aluminium-silicon spinel in the crystalline state. When the temperature is raised to 1050 ℃, the following changes occur:

$$2Al_2Si_2O_5(OH)_4 \xrightarrow{55-600^0C} 2Al_2Si_2O_7 + 4\,H_2O$$

kaolin metakaolin

$$2Al_2Si_2O_7 \xrightarrow{925-950^0C} Si_3Al_4O_{12} + SiO_2$$

metakaolin spinel

$$3Si_3Al_4O_{12} \xrightarrow{1050^0C} 2Si_2Al_6O_{13} + 5SiO_2$$

spinel mullite cristobalite

The chemical composition and texture characteristics of samples of Nurobot kaolin and synthesized HSZ (elements and oxides) are shown in Figures 1 and 2 (analysis of X-ray fluorescence spectrometry).

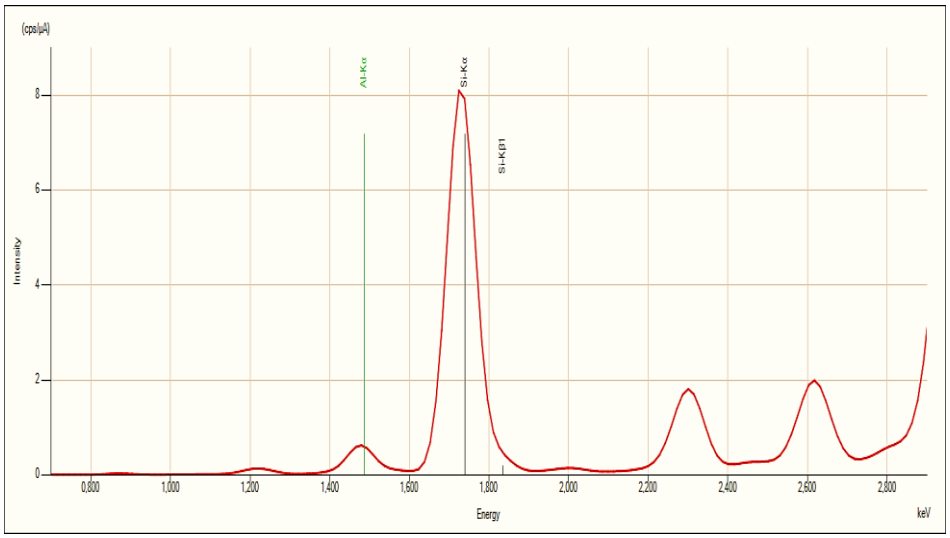

Figure 1. X-ray fluorescent results of samples of chemical composition (mass,%) of HSZ synthesized by crystallization of kaolin "Qarnab ota" for 8 hours

Table 1.

Chemical composition of HSZ (mass,%) synthesized by crystallization of "Karnab ota" kaolin for 8 hours

Component	Result	Unit	Detection limit
Al_2O_3	19	mass%	0,0682
SiO_2	81	mass%	0,017
[Intensity]			
Measuring condition	Element line	Intensity(cps/μA)	BG intensity(cps/μA)
Low-Z	Al-Kα	3,60248	0,45173
Low-Z	Si-Kα	48,08134	0,24949
Component	Result	Unit	Detection limit
Al	14,4	mass%	0,0517
Si	61	mass%	0,0127
K	4,65	mass%	0,059
Na	ND	mass%	
Ca	4,9	mass%	0,0382
Fe	13,6	mass%	0,0018
Mn	0,0713	mass%	0,0039
Zn	0,0316	mass%	0,0006
Ti	1,35	mass%	0,0124

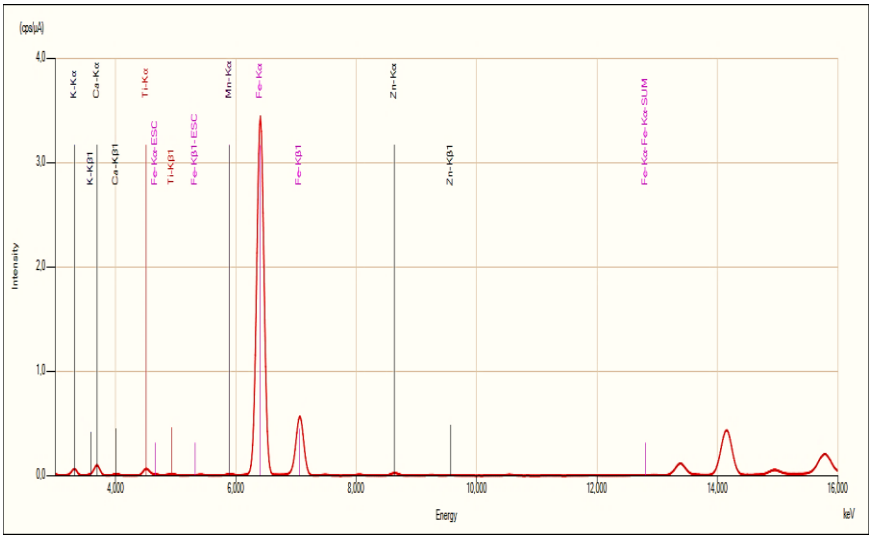

Figure 2. X-ray fluorescence analysis of samples of HSZ oxides (mass,%) for 9 hours crystallization of "Karnab ota" kaolin

Table 2.

Analysis of samples of HSZ oxide content (mass,%) by crystallization of kaolin "Qarnab ota" for 9 hours

Component	Result	Unit	Detection limit
Al_2O_3	17,2	mass%	0,0609
SiO_2	69,6	mass%	0,0143
K_2O	2,47	mass%	0,0306
CaO	2,82	mass%	0,0221
MgO	ND	mass%	
TiO_2	0,869	mass%	0,0081
Fe_2O_3	7,03	mass%	0,0009
MnO	0,0313	mass%	0,0018
[Intensity]			
Measuring condition	Element line	Intensity(cps/μA)	BG intensity(cps/μA)
Low-Z	Al-Kα	3,69886	0,45502
Low-Z	Si-Kα	49,23903	0,24893
Mid-Z	K-Kα	0,47517	0,09365
Mid-Z	K-Kβ1	0,07997	0,46481
Mid-Z	Ca-Kα	0,80453	0,11619
Mid-Z	Ti-Kα	0,58645	0,09405
Mid-Z	Mn-Kα	0,1055	0,11278
Mid-Z	Fe-Kα	34,89019	0,06255

In subsequent experiments, experiments were performed to determine the surface area of synthesized zeolite samples.

Table 3.

Texture characteristics of freshly prepared and heat-treated HSZ

Parameters	Freshly prepared	700 ℃	760 ℃	800 ℃	Balanced
Specific surface area, m^2 / g	207,6	198,8	198,5	184,8	89,8
The volume of the pore, cm^3 / g	0,165	0,156	0,156	0,146	0,065
Microactivity,%	90,3	87,5	85,2	84,85	42,4

The results of the analysis of the data in Table 3 show that with the increase of the silicate modulus of HSZ, not only the total specific surface area and porosity but also the surface area and volume, which corresponds to micro-and mesopores, increases. Adsorption testing in the equilibrium model allows to determine the maximum amount of adsorbed substance and to calculate the thermodynamic parameters of adsorption in the low-temperature range. It is accepted to determine the adsorption equilibrium using the experimental construction of adsorption isotherms. In the literature, it is common to express adsorption using Langmuir and Freundlich models:

$$\frac{\Gamma}{\Gamma_\infty}=\frac{K_L\cdot C^0}{1+K_L\cdot C^0};\ \ \Gamma=K_F\cdot C^{on};\ \ \frac{\Gamma}{\Gamma_\infty}=\frac{K_L\cdot C^{0n}}{1+K_L\cdot C^{0n}};$$

$$\frac{C/C^0}{\Gamma\left(1-\frac{C}{C^0}\right)}=\frac{1}{\Gamma_\infty\cdot C}+\frac{k-1}{\Gamma_\infty kC^0}$$

Here $k=e^{\frac{Q-\lambda}{RT}}$, Q-λ- adsorption heat

$$\frac{\Gamma}{\Gamma_\infty}=\frac{K_R\cdot C^0}{1+\Gamma\cdot C^{0\beta}}$$

α,β - Parameters of the redmix –Peterson equation

There is a link between the equilibrium coefficient of adsorption and the change of adsorption enthalpy and Entropia as follows:

$$K_{adc}=e^{\frac{\Delta S_{adc}}{R}}\cdot e^{\frac{\Delta H_{adc}}{RT}}$$

Comparative Surface-Surface determination of solid samples. The comparative surface-surface of kaolin and the high-silicon zeolites obtained based on it was calculated by the method of Branauer-Emmet-Taylor (BET), which according to the following equation:

$$\frac{1}{w\cdot(\frac{P_0}{P}-1)}=\frac{1}{W_m\cdot C}+\frac{C-1}{W_m\cdot C}\cdot\frac{P}{P_0}$$

Where W-P/P_0 is the mass of gas absorbed at absolute pressure, W_m - is the mass of substance adsorbed on the surface coating to form a monolayer; C- adsorbents are BET constants indicating the value of the adsorbate interaction, representing the dependence of the first adsorption layer on the adsorption energy. The method Barrett-Joyner-Halenda (BCH) was used to determine the distribution of porridges by volume and size.

Conclusion

High-silica zeolites (HSZ) were prepared from gel soil from "Karnab ota" kaolin of Nurabad district of Samarkand region, which was chemically treated. Several technological processes have been carried out to prepare HSZ. The resulting high-silicon zeolite was treated with 25% ammonium chloride for decantation and washed several times in distilled water and then fired at 550 ℃ for 8 hours. The decanted zeolite powder was then pressed into a tablet and made into granules. The chemical composition and texture characteristics of samples of Nurobot kaolin and synthesized HSZs (elements and oxides) were analyzed by X-ray fluorescence spectrometry. The results were presented.

The chemical composition of the synthesized HSZ samples was studied by mass%, changes in heating and texture characteristics of zeolites (total specific surface area and volume of pores, surface area, volume, crystallization conditions and physicochemical properties of samples corresponding to micro-and mesopores). Data will be provided on a scheduled basis. The comparative surface calculation was performed by the BET (Brunauer-Emmett-Teller) method, and the calculation of the distribution of pores by size was performed by the BJH (Barreett-Jouner-Hallend) method. A technological scheme for the synthesis of high-silicon zeolite from natural raw materials has been developed. To do this, modified zeolite catalysts were prepared by ingestion of certain salts or acids.

References:

1. Fayzullayev N.I. et al. Kinetics and mechanism of the reaction of the catalytic oxycondensation reaction of methane // Austrian Journal of Technical and Natural Sciences. – 2019. – №. 5-6. – С. 62-68.
2. Ibodullayevich F.N., Ilkhomidinovich M.I., Bo'riyevna P.S. Research of sorption properties of high silicon zeolites from bentonite //ACADEMICIA: An International Multidisciplinary Research Journal. – 2020. – Т. 10. – №. 10. – С. 244-251.
3. Ilkhomidinovich M.I. Study of the sorption and textural properties of bentonite and kaolin //Austrian Journal of Technical and Natural Sciences. – 2019. – №. 11-12. – С. 33-37.
4. Mamadoliev I.I., Fayzullaev N.I. Optimization of the activation conditions of high silicon zeolite // International Journal of Advanced Science and Technology. – 2020. – Т. 29. – №. 3. – С. 6807-6813.
5. Mamadoliev I.I., Khalikov K.M., Fayzullaev N.I. Synthesis of high silicon of zeolites and their sorption properties // International Journal of Control and Automation. – 2020. – Т. 13. – №. 2. – С. 703-709.
6. Mamadoliyev I. Synthesis of high-silicone zeolites //Збірник наукових праць ΛΌΓΟΣ. – 2020. – С. 16-20.
7. Копылов А.Ю. и др. Современныежидкофазные методы сероочистки газового сырья // Известия высших учебных заведений. Химия и химическая технология. – 2010. – Т. 53. – №. 9. – С. 4-8.
8. Лютоев А.А., Смирнов Ю.Г., Ивенина И.В. Извлечение эмульгированных примесей нефти из воды при помощи высокодисперсных частиц магнетита //Защита окружающей среды в нефтегазовом комплексе. – 2014. – №. 4. – С. 40-45.
9. Серых А.И. Формирование, природа и физико-химические свойства катионных центров в каталитических системах на основе высококремнеземных цеолитов //Изв. дисс. док. – 2014. – С. 6.
10. Файзуллаев Н. и др. Каталитическая дегидроароматизация нефтянного попутного газа //Збірник наукових праць ΛΌΓΟΣ. – 2020. – С. 122-126.