DEVELOPMENT OF A BINDING-FREE METHOD FOR THE SYNTHESIS OF ALUMINOSILICATES NaA

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https://doi.org/10.5281/zenodo.10363393

Abstract. *The work shows that only at least 30% of the initial grains (granules) can be included, and after crystallization of the artificially obtained highly dispersed NaA aluminosilicate, a product with a degree of crystallinity close to 100% can be obtained, and in the absence of additives, a hydrosodalite phase can be obtained. A "sol-gel" method for the synthesis of mesoporous aluminosilicate has been developed. The gel for the two-stage synthesis of mesoporous aluminosilicate was prepared according to the following method: 50.0 ml of tetraethyl orthosilicate, kaolin, sodium hydroxide, ethyl alcohol, hexamethylenediamine and citric acid and 50.0 ml of ethanol solution were added to 50.0 ml of H2O solution. 12.0 ml of 0.1 M NaOH and 50.0 ml of hexamethylenediamine were added in a thin stream and the mixture was left with intensive stirring for 10 minutes. To increase the binding-free crystallinity of the artificially obtained mesoporous aluminosilicate NaA to ~100%, a method of loosening additives to a highly dispersed mesoporous artificially obtained aluminosilicate of the same structural type synthesized from highly active methacaolin has been developed. it is mixed with kaolin from the mine in a ratio of 30-70 /70-30%, respectively.*

The aim of the work is to develop a method for the synthesis of NaA aluminosilicate without binders.

Keywords: *NaA aluminosilicate, kaolin, metakaolin, sodium metasilicate, mesoporous.*

INTRODUCTION

Structural kaolins allow them to be modified to improve their surface properties and adsorption characteristics [1]. In the synthesis of porous materials, they try to increase the specific surface area, since with an increase in the specific surface area, the sorption properties of sorbents increase with a decrease in the average pore size. [2-7]. Today, the oil and gas industry is on the rise. As a result, a large number of toxic gases are released into the environment. This leads to the destruction of the environment and ecology. Based on the above, modern catalytic and sorption processes require the creation of sorbents and catalysts with controlled properties in all ranges from microporous to macroporous, increasing the mobility of molecules, and the use of catalysts and surface sorbents allows for increased efficiency [8-15].] . For the problems of effective use of zeolite adsorbents and catalysts on the surface of inclusion of an additional porosity system in the samples, it ensures the preservation of the crystal structure. There are two fundamentally different approaches to the synthesis of zeolites, the first of which offers additional pores in addition to micropores: the creation of pores due to the partial destruction or reorganization of the lattice of zeolite crystals, i.e. zeolite primary crystallization [19,20]. Today, aluminosilicates are widely used in various fields of the chemical industry. Along with the use of aluminosilicates as adsorbents, catalysts are being developed on their basis [21-34].

THE EXPERIMENTAL PART

For the synthesis of mesoporous aluminosilicate with different temperatures of "zol-gel" synthesis and standard synthesis of nanocrystals of mesoporous aluminosilicate, the gel was prepared according to the following method: 15.0 ml tetraethylortosilicate, kaolin, sodium hydroxide, ethyl alcohol, hexamethylenediamine and citric acid. and 15.0 ml of ethanol solution was added in a thin stream to a solution of 15.0 ml of distilled water and 15.0 ml of hexamethylenediamine at 100 ° C and the mixture was vigorously stirred for 20 minutes.

The gel for the two-stage synthesis of mesoporous aluminosilicate was prepared according to the following method: 50.0 ml of tetraethyl orthosilicate, kaolin, sodium hydroxide, ethyl alcohol, hexamethylenediamine and citric acid and 50.0 ml of ethanol solution were added to 50.0 ml of H2O solution. 12.0 ml of 0.1 M NaOH and 50.0 ml of hexamethylenediamine were added in a thin stream and the mixture was left with intensive stirring for 10 minutes.

From the main solution (from uterine plants) The preparation of the gels was carried out as follows. To 38 ml isolated from mesoporous aluminosilicate crystals synthesized at 100 ° C, 15.0 ml of tetraethylortosilicate, kaolin, sodium hydroxide, ethyl alcohol, hexamethylenediamine and citric acid were added in a thin stream.

For the synthesis of mesoporous aluminosilicate microcrystals, the gel was obtained at room temperature as follows: 15 g of kaolin and 7.6 g of SiO2 were slowly added to an aqueous solution of 0.72 g of NaOH and 3.18 g of citric acid and stirred for 25 minutes.

The synthesis products were separated from the mother liquor by particle size filtration and washed with distilled water to pH = 7. The nanocrystals were washed in three purification stages, consisting of adding water, dispersing in an ultrasonic bath, centrifugation and separation of liquids. The synthesis products were then dried at 120 ° C for 12 hours. Some of the mesoporous aluminosilicate nanocrystals formed a set of loose and dense particles, respectively, in the form of a suspension of nanocrystals, and the other in the form of monoliths obtained after centrifugation. The dried samples, in turn, were regularly heated at a temperature of 550 ° C for 6 hours.

Half of the samples of nanocrystals and microcrystals of mesoporous aluminosilicate were activated in a thermostatically controlled reactor equipped with a magnetic stirrer. Mesoporous aluminosilicate powders were added to a 1 M hydrochloric acid solution and then mixed at 60 ° C for 40 minutes. The powders were then separated by filtration and washed with copious amounts of water, dried at 120 ° C for 10 hours, and then calcined at 550 ° C for 4 hours. The resulting powders were ground in a mortar and the fraction <0.25 mm was separated through a sieve.

THE RESULTS OF THE EXPERIMENT AND THEIR DISCUSSION

The work shows that only at least 30% of the initial grains (granules) can be included, and after crystallization of the artificially obtained highly dispersed NaA aluminosilicate, a product with a degree of crystallinity close to 100% can be obtained, and in the absence of additives, a hydrosodalite phase can be obtained. At the same time, the artificially obtained aluminosilicate in granules (granules) simultaneously acts as a crystalline filament that accelerates crystallization, as well as an additive that promotes the formation of a secondary porous structure developed in them.

Considering that granular artificial aluminosilicate cannot be synthesized without a binder with high properties, artificially obtained highly dispersed NaA aluminosilicate in granules (granules) only from kaolin, we have proposed kaolin as the main source of silicon and aluminum. synthesis of dispersed NaA aluminosilicate. For this purpose, we have developed a method for producing artificially obtained highly dispersed NaA aluminosilicate.

The practice of industrial application of absorbers of gases and liquids containing mesoporous, artificially obtained aluminosilicates has shown that one of the main conditions is . Powdered mesoporous, artificially obtained aluminosilicate X is pre-synthesized, then it is formed using kaolin from the Karnab Ota mine and additives, which turns into granules (granules) of the desired shape and size. The obtained granules (granules) are subjected to heat treatment in order to convert the kaolin of the Karnab Ota deposit into methacaolin, and in a solution of sodium hydroxide it turns into a solid under the conditions provided for artificially obtained mesoporous alumosilicate NaA without a preliminary binder.

The charred granules (granules) obtained in this way turn into a solid at the following molar ratios of the components forming the solid in the reaction mixture in a solution of sodium hydroxide: (2.0-2.2) Na2O • Al2O3 • 6 SiO2 • (40 -70) H2O. An increase in the Na2O/SiO2 ratio in the reaction mixture contributes to an increase in the hardness and adsorption capacity of the artificially produced mesoporous aluminosilicate. However, with an increase in the amount of sodium hydroxide per unit mass or volume, the transition to SiO2 solution increases, the strength of granules (granules) decreases and the molar ratio of SiO2/Al2O3 in mesoporous synthetic aluminosilicate decreases. The amount of SiO2 in the finished mesoporous, artificially obtained aluminosilicate decreases to a greater extent than during the crystallization of granules (granules) formed using NaOH. An increase in the SiO2/Al2O3 ratio in the reaction mixture slows down the crystallization process. Table 1 shows the properties of granulated (granules) Y mesoporous artificially produced aluminosilicates obtained in both variants. As can be seen from Table 1, samples without binders of granular (granules) Y-mesoporous artificially obtained aluminosilicates are similar in adsorption capacity to highly dispersed Y-mesoporous artificially obtained aluminosilicates.

Table 1

Properties of granulated (granules) Y mesoporous aluminosilicates obtained artificially without binders

Indicator	The first method	The second method	Mesoporous synthetic aluminosilicate with high silica content
Total density g/cm3	0,75	0,70	-
Molar ratio of SiO2/Al2O3 in mesoporous synthetic aluminosilicate	4,9	4.3	4,5
Adsorption capacity for water vapor at 20 °C (N/PS), (cm3/g) 0.1	0,25	0,27	0,29
0,5	0,26	0,28	0,30

The dynamic capacity of water vapor in absolute mass or volume corresponding to the dew point minus 70 °C, mg/cm3*	155	150	-
Mechanical crushing force kg/mm2	2.2	0,8	-

- The indicators of 20-25 0C of the air mixture in the flow mode, atmospheric pressure and artificially obtained gas-liquid absorbing substance with a volume of 150 cm3 were determined. The air-steam flow rate according to C(W) is 4.0 ± 0.25 dm3/min, the vapor content per unit mass or volume is 12-15 mg/dm, N2O and CO2 and mercaptans (thiols) are 6.0 ± 0 in vapor, 25 dm3/min. Their amounts per unit of mass or volume are 13-15 mg/dm, 10 mg/dm and 10 mg/m, respectively.

There is very little information about the patterns of formation of highly dispersed mesoporous aluminosilicates artificially obtained from the kaolin of the Karnab Ota mine. This paper describes options for the synthesis of granular mesoporous, artificially obtained aluminosilicates using kaolin from the Karnab Ota mine as the main source of aluminum oxide and silicon oxide (IV). At the same time, mesoporous synthetic aluminosilicate A, obtained without a binder, has a low degree of hardness (70-80%), has no phase purity (5% admixture of the sodalite phase), but has the same structure as mesoporous. synthetic aluminosilicate, which is granulated with a binder, made of aluminosilicate is at the level of its adsorption capacity. Despite the high quality of the resulting mesoporous, artificially obtained aluminosilicate materials, these methods are unpromising for industrial use due to the complexity and multi-stage technology, as well as a large volume of environmentally harmful wastewater.

Taking into account that it is impossible to synthesize granular (granular) mesoporous, artificially obtained aluminosilicate without adding finely dispersed mesoporous, artificially obtained aluminosilicate A to the granulate (granules) obtained only from the kaolin of the Karnab Ota mine, without the highly characteristic binder silicon (IV) . We have made a proposal to develop the synthesis of finely dispersed mesoporous artificially obtained aluminosilicate A using kaolin obtained at the Karnab ota mine as a source of aluminum oxide oxide and as the main material. For this purpose, we have developed a method for obtaining a highly dispersed mesoporous artificially obtained aluminosilicate A. It was previously established that in order to obtain a granulate (granules) of mesoporous, artificially obtained aluminosilicate A from aluminosilicate X-ray amorphous granules (granules), it is necessary to carry out their initial low-temperature (25-30 °C) thermochemical treatment. in a crystallization solution. Granulate (granules) without a binder, based on experimental data, the technology of mesoporous artificial extraction of aluminosilicate has been developed (Fig. 1).

The crystallization process is non-linear due to the transformation of granules (granules) containing a mechanical mixture of mesoporous, artificially obtained aluminosilicates and solid methacaolin substances with high activity into granules (granules) with single mesoporous, artificially obtained aggregates (granules) of aluminosilicate polycrystalline substance with a change in the secondary porous structure will appear. The following methods of organizing a secondary porous structure were studied in experiments:

- the change in the ratio of mesoporous, artificially obtained aluminosilicate/kaolin obtained from the Karnab Ota deposit during the formation of granules;

- introduction of pore-forming additives

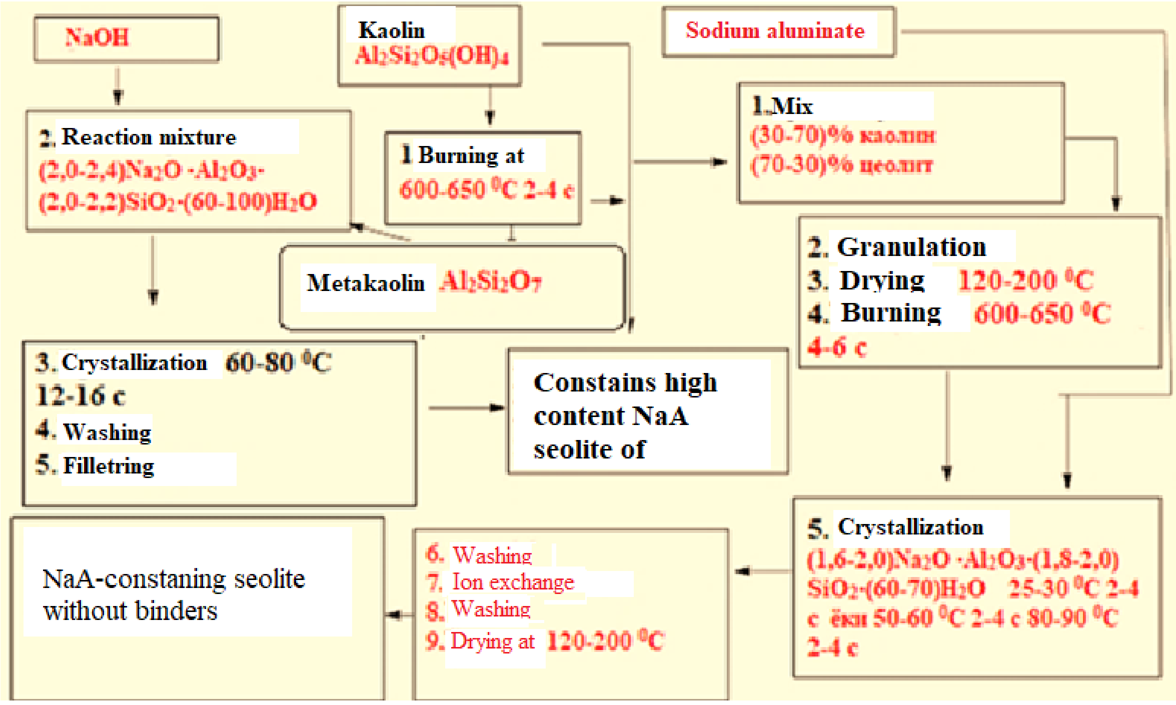

Figure 1. The main structural diagram of the processes for obtaining artificially obtained aluminosilicate A with highly dispersed and non-binding mesoporous granulate (granules) from kaolin extracted at the Karnab Ota mine.

The method developed by us to increase the binding-free crystallinity of mesoporous synthetic aluminosilicate A to ~100% was synthesized from highly active methacaolin as a loosening additive to highly dispersed mesoporous synthetic aluminosilicate of the same structural type of the Karnab Ota mine. mixtures with kaolin in a ratio of 30-70 / 70-30%, respectively. The introduction of a mesoporous artificially obtained aluminosilicate not only increased the purity of the phase, but also significantly reduced the synthesis time.

A significant acceleration of crystallization is achieved, apparently, due to a highly dispersed mesoporous, artificially obtained aluminosilicate. A solid substance that is part of the granules (granules), acting as an initiator. A change in the secondary pore structure due to the transformation of granules containing a mechanical mixture of mesoporous synthetic aluminosilicate and highly active methacaolin particles into single aggregates of mesoporous synthetic aluminosilicate solids.The NaA comes with

CONCLUSION

Thus, the work shows that only at least 30% of the initial grains (granules) can be included, and after crystallization of the artificially obtained highly dispersed NaA aluminosilicate, a product with a degree of crystallinity close to 100% can be obtained, and in the absence of additives, the hydrosodalite phase.

The resulting charred granules (granules) turn into a solid at the following molar ratios of the components forming the solid in the reaction mixture in a solution of sodium hydroxide: (2.0-2.2) $Na_2O \cdot Al_2O_3 \cdot 6\ SiO_2 \cdot (40\text{-}70)\ H_2O$.

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