Synthesis of Zeolite NaA as pellets of bulgarian kaolin

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Synthesis of Zeolite NaA as pellets of bulgarian kaolin: *Production of synthetic zeolites constantly escalate worldwide. This is explained by the increased needs of zeolites with certain qualities in the manufacture of detergents, paper works and especially for catalysts and adsorbents in the chemical industry. In comparison with natural, synthetic zeolites have significant advantages, such as: homogeneity of phase composition, a high degree of purity, uniform size of the crystalline forms and the pores and better ion-exchange properties.*

This report looks at issues relating to study the possibility of obtaining synthetic zeolite NaA, in the form of granules. The main feedstock material is bulgarian kaolin (type "BoExtra"), from "Kaolin AD". For our purposes, this kaolin is preferred due to appropriate the content of its main components - SiO_2 and Al_2O_3.

For the purposes of this study were prepared by a series of master batches containing the appropriate amounts of kaolin synthesized zeolite NaA, and aqueous NaOH. On the thus prepared ceramic mixtures are formed beads (2-4 mm), the method of the "fluidized bed", a specially designed and constructed for this purpose, a granulating system. Established the conditions for the next hydrothermal crystallization received raw granules previously worked in isothermal mode.

In the methods of XRD and SEM was investigated structure of the obtained synthetic zeolite products. It was found that the synthetic product obtained with the main raw material bulgarian kaolin by a process of hydrothermal synthesis of pellets has proven structure of Zeolite NaA.

Key words: *zeolite A, kaoline, synthesis of zeolites, granulation, fluidized bed, hydrothermal method.*

INTRODUCTION

Zeolites are widely used in adsorption, separation, catalysis, ion exchange and other processes. Some authors [1-7] have already studied the preparation of various zeolites from kaolin or other fly ashes and have made great progress in synthesis of zeolite A, mordenite, X, Y zeolites, etc.

Of interest is that kaolin possesses the Si-O or Al-O octahedral and tetrahedral sheets which create a charge imbalance in the 1:1 layer. There is very little substitution in the structural lattice, and thus it has a minimal layer charge and a low exchange capacity. Its surface area and absorption capacity is relatively low, but many of the properties of kaolin can be improved by proper treatment. The main applications of kaolin are for coating paper, functional fillers, plastics, rubber, glass fiber and other materials used in fine chemical engineering. Unfortunately, all of these materials are low value-added products. It is necessary to create a suitable method to utilize kaolin in an environmentally friendly manner that has high commercial value.

This report looks at issues relating to study the possibility of obtaining synthetic zeolite NaA, in the form of granules. The main feedstock material is bulgarian kaolin (type "BoExtra"), from "Kaolin AD" [2,3]. For our purposes, this kaolin is preferred due to appropriate the content of its main components - SiO_2 and Al_2O_3.

EXPERIMENTAL PART AND RESULTS

The technology for the synthesis of zeolite NaA with the form of granules having the following process steps: preparation of suitable starting ceramic mixture; fforming granules of a certain size (diameter 2-4 mm); tthermal activation of the obtained granules; ccrystallization (zeolitization) of the granules; final treatment of the zeolite granules.

With current technology for the preparation of zeolites, often the final product is in the form of granules with particular characteristics (geometry, size, bulk density, etc.). This requires granulation as a necessary and basic technological operations in technological schemes for the synthesis of zeolites.

For the purpose of the study was prepared starting powder mixtures to granulate with a composition according to Table 1 The components were mixed under continuous propelirane. That takes place in a suitable mixer with a homogenizer under vigorous stirring (shearing) of the mixture at a temperature of 50-70 °. Dry mixtures.

Table 1: Composition of the feed mixtures for granulation

Components	Composition, mass. %				
	Z_1	Z_2	Z_3	Z_4	Z_5
Kaoline	80.0	79.0	73.0	71.0	65.0
Zeolite NaA	15.0	15.0	20.0	20.0	25.0
Aqueous solution - 2% of NaOH	5.0	6.0	7.0	9.0	10.0

The introduction of pre-prepared, powdery zeolite NaA to 25 wt.% to the basic starting material, as well as certain amounts Aqueous solution - 2% of NaOH, aims at obtaining granules of a certain size, which after drying and heat treatment corresponding to possess a sufficiently developed porosity. The bonus of pre-synthesized powder zeolite NaA, appears also as nucleating for subsequent crystallization.

Granulation was carried out the installation with "fluid bed". To this end, fformula granules of 2 to 4 mm. The system has a system for automatic separation of the granules with preset dimensions [8,9]. These were dried at 100°C, in terms of "fluid bed". This is done to obtain the initial strength of the granules (known as the "green strength"). The granules thus obtained were subjected to the thermal activation in a muffle furnace at a temperature 720°C for 3 h. Best results were obtained with samples from the composition Z_3.

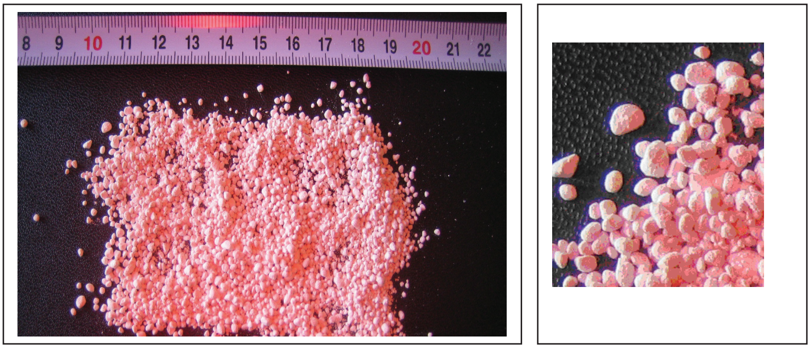


Fig. 1. Photography granules Zeolite NaA

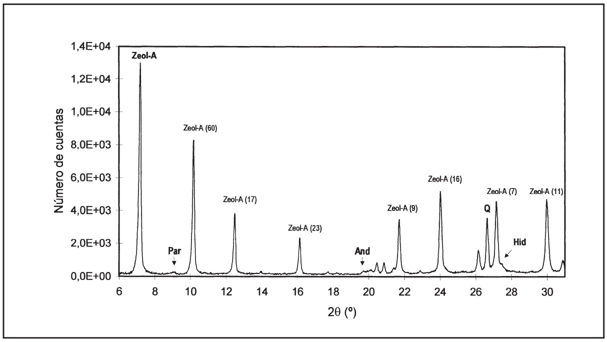
Fig. 1 shows a photograph of granules (composition Z_3), derived from the plant with a "fluidized bed". Very clearly seen that the resulting granules are of type "Blackberry" - i.e. relatively irregular spherical shape without a lot of dust.

The next responsible operation of technology is hydrothermal crystallization of the resulting granules. It was held in the autoclave reactor hydrothermal conditions at temperatures up to 90°C and continuously propelirane the granules in an aqueous solution of NaOH, having a concentration in terms of Na_2O - 95 g / l.

The crystallization process is performed in autoclave conditions, with continuous homogenization of the granules at lower speeds propelirane so as not to disturb the integrity of the granules, and not to form a "dead" areas in the crystallization solution.

For this purpose was held etc. isothermal crystallization under the following temperature conditions: 8-12 hours at 20-40°C; 8-12 hours at a temperature of 60-70°C and 12-24 hours at 90°C.

It repeatedly washing the beads with deionized water to remove excess unreacted alkali (to pH 7-8), drying - 12 h at 90°C and packaged.



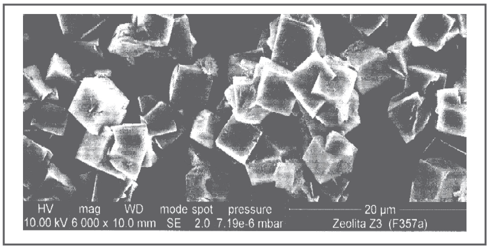


Fig. 2. XRD and SEM of zeolite NaA (composition Z_3, granules)

On fig.2 shows the results of surveys of XRD and SEM of the final product as described above technology. It is seen that the major crystalline phases are zeolite A and small quantities of quartz.

Major phases: Zeol-A = Zeolite A ($NaAlSi0_4$) ; Q = Quartz ($Si0_2$).

Minor phases: Hid = Hydroxycancrinite -

$(Na_8(Al_6Si_6O_{24})(OH)_{2.04}(H_2O)_{2.66})$;

Par = Paragonite -($NaAl_2(Si,Al)_4O_{10}(OH)_2$);

And = Andalusite ($Al_2(Si0_4)0$)

CONCLUSIONS

The possibilities for obtaining synthetic zeolite NaA in the form of granules with the main raw material - Bulgarian kaolin оф company "Kaolin AD", type "BoExtra". Technology involves pre-forming pellets of ceramic powders, made of multifunctional installation method "fluidized bed", in which the following results:

• Studied the conditions and the technological regime to obtain granules with a preset sizes (2-4 mm) specially designed and manufactured for this purpose installation method "fluidized bed".

• There are conditions for hydrothermal crystallization (zeolitization) of granules with the following temperature regime: 10 h at a temperature of 40 °C; 12 h at a temperature of 60 °C and 18 h at a temperature of 90 °C.

• With the methods of XRD and SEM was investigated structure of the obtained synthetic product. It was found that the synthetic product obtained with the main raw material Bulgarian kaolin, method hydrothermal synthesis granules is shown a structure of Zeolite NaA.

REFERNCES

[1] Georgiev, D., B.Bogdanov, Y. Hristov, I. Markovska, I.Petrov, Synthesis of NaA zeolite from natural kaolinite, Book of Zeolite 2010, 8th international conference, july 2010, Sofia, Bulgaria, 2010, 95-97.

[2] Georgiev, D., B. Bogdanov, Y. Hristov, I. Markovska, K. Angelova, Synthesis of NaA zeolite, Proc. of 12^{th} Int. Conf. on Mechanics and Technology of Composite Materials, 22-24 Sept. 2009, Varna, Bulgaria, 41-46.

[3] Georgiev, D., B. Bogdanov, Y. Hristov, I. Markovska, Synthesis of NaA Zeolite from Natural Kaolinite, Oxidation Communications, 34, No 4, 2011, 812–819.

[4] Rocha, J. , Klinowski J. and Adams, J.M. Synthesis of zeolite Na-A from metakaolinite revisited, Journal of the Chemical Society, Faraday Transactions 87, 1991, 3091-3097.

[5] Gualtieri, A., Norby, P., Artioli, G. and Hanson J., Kinetics of formation of zeolite Na-A [LTA] from natural kaolinites, Journal Physics and Chemistry of Minerals, 24, 1997, 191-199.

[6] Covarrubias, C., Garcia R., Arriagada R., Yanez J., and Garland T. Cr(III) exchange on zeolites obtained from kaolin and natural mordenite, Microporous and Mesoporous Materials 88, 2006, 220-231.

[7] Basaldella, E.I., Boneno R.D. and Tara J.C. Synthesis of NaY zeolite on preformed kaolinite spheres. Evolution of zeolite content and textural properties with the reaction time, Industrial and Engineering Chemistry Research 32, 1993, 751-757.

[8] Rusev D.R., Method for technological calculation and constructive design of fluidized bed devices, Annual of Univ. ”Prof.Dr.A.Zlatarov”- Bourgas, v. XXXIV, No1, 2005.

[9] Bogdanov , B., D Rusev, Y. Hristov, I. Markovska , D.Georgiev, Design of a Grid for Preparation of high Density Granules from Dispersed Materials, World Academy of Science Enginering and Technology, Issue 59, Venice, Itali, 2011, 2650-2653, ISSN 2010- 376X, eISSN , 1042-1045.

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This paper has been reviewed