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THE POSSIBILITY OF HYDROTHERMAL SYNTHESIS OF NaY ZEOLITE USING DIFFERENT MINERAL ACIDS

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Abstract- ***NaY Zeolite was synthesized from sodium-aluminate solution from the Bayer process, water glass and mineral acids HCl, H_2SO_4, HNO_3 and H_3PO_4 acids were used in order to reduce the concentration of Na^+ ions to the mole ratio that will enable the formation of NaY Zeolite. The reaction mixture for the synthesis of NaY Zeolite had the following composition: $2Na_2O : Al_2O_3 : 6{,}5SiO_2: 120H_2O$. The synthesis was conducted with the addition of "seed gel" using hydrothermal method. Crystallization lasted 24 hours at the temperature of 100°C. The samples obtained were subjected to mineralogical and chemical analysis. Mineralogical analysis, obtained by x-ray diffraction, showed that, for the identical conditions of synthesis, NaY zeolite was obtained in those sytheses in which H_2SO_4, HNO_3 and H_3PO_4 were used, whereas the synthesis using HCl resulted by occurrence a transitient amorphous phase without the presence of NaY zeolite crystals.***

Keywords: crystallization, hydrothermal method, NaY Zeolite, mineral acids.

I. INTRODUCTION

Zeolites are microporous hydrated alumosilicates of the elements of the first two groups of the periodic system, with the following general empirical formula:

$$M_{x/n}[(AlO_2)_x(SiO_2)_y] \bullet mH_2O \qquad (1)$$

Where M is an alkaline or alkaline earth cation, n is cation valency, m is the number of water molecules in the unit cell, x and y is the total number of aluminium and silicon tetrahedrons[1,2].The basic structural cells of the threedimensional zeolite structure are aluminium and silicon atoms (even phosphorus atoms at some places) lying at the centre of tetrahedron with oxygen atoms at its vertices in the Fig. 1.

Tetrahedra, being basic building units of the structure, can be combined in different ways, forming four-membered or six-membered rings.

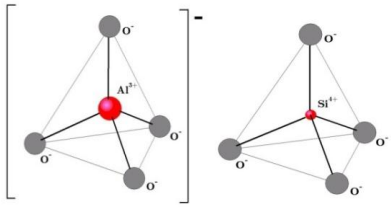

Fig. 1 Aluminium$(AlO_4)^{5-}$and Silicon $(SiO_4)^{4-}$ tetrahedra[1]

Combining tetrahedra into different structural forms results in the so-called secondary building units (SBU). Different secondary units are joined with each other producing different forms of polyhedra and long chains.[1-4]For example, mutual combination of eight six-membered rings and four four-membered rings can build a cuboctahedron (known as β-cage or sodalite unit). Clustering of cuboctahedron in space forms three types of zeolite (sodalite, zeolite A and zeolite X/Y). Faujasites form a singificant group of minerals within zeolite. Both natural and synthetic faujasite zeolites are composed of a unit cell produced by the clustering of 9 sodalite units through hexagonal prisms. Synthetic faujasite zeolites, depending on the mole ratio of SiO_2 and Al_2O_3, are classified as X and У. Type X zeolites have SiO_2 /Al_2O_3 mole ratio of two to three, whereas that of type У is above three.[3,4]

Nowadays, synthetic zeolites are more and more commonly used when compared to the natural ones, primarily owing to their purity, unified morphology, particle size, and other properties. Synthetic zeolites are prepared under conditions similar to those with natural zeolites. The time of preparation required is reduced using higher temperature and pH value. The oldest and the most commonly used method for the synthesis of zeolite is the so-called hydrothermal crystallization of alumosilicate gel in a closed system, or autogenous pressure, during appropriate period of time. Alumosilicate gel is most commonly obtained by mixing the raw materials which contain aluminium (aluminate, aluminium nitrate, aluminium sulphate and other) and silicon (water glass, kaolinite, colloid SiO_2 , and other, till suitable mole ratio is obtained. The composition of the reaction mixture is vital for the synthesis of zeolite, and is expressed as oxide ratio :

$$a\ M_{2/n}O : Al_2O_3 : b\ SiO_2 : d\ H_2O \qquad \textbf{(2)}$$

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where M represents cation with electrical charge *n*, which is usually sodium ion. In order to obtain a shorter period of time for zeolite preparation, particularly with the synthesis of Y zeolite, certain organic compounds can be added into the reaction mixture to serve as a template or seed gel obtained from aluminate solution and water glass under particular conditions, having a particular mole ratio of the oxide of aluminum, silicon, alkaline or earth alkaline metals, as well as water molecule [5-7].

When it comes to Y zeolite commercial production, NaY has a significant role. It is transformed, by further treatment (transformation and calcination processes) into other forms that are more suitable for manufacture. Commercially available NaY zeolites possess SiO_2 /Al_2O_3 mole ratios ranging from 5 to 6, and constant efforts are made to obtain even greater mole ratios.

II. EXPERIMENTALS

The experimental research, the results of which are presented in this paper, involved using aluminium hydroxide, sodium hydroxide, water glass, sodium-aluminate solution (synthetic and from the Bayer alumina production process) and HCl, H_2SO_4, HNO_3 and H_3PO_4 acids (Table 1.).

TABLE 1. PROPERTIES OF RAW MATERIALS IN NaY ZEOLITE

	Raw material	Properties
1.	aluminum hydroxide	Content: Al_2O_3=64,83%;SiO_2=0,009%; Fe_2O_3=0,012%; Na_2O_{uk}=0,22%; CaO=0,017%; loss by heating 1000°C 34,89%
2.	Sodium hydroxide	48,78%, ρ=1,514 g/ cm^3
3.	Water glass	Content: Na_2O=159,3 g/dm^3; SiO_2=380,4 g/ dm^3; ρ=1,430 g/ cm^3
4.	Aluminate solution from the Bayer alumina production process	content: Na_2O_k = 155 g/dm^3; Al_2O_3 = 161,2 g/ dm^3; ρ=1,310 g/ cm^3
5.	HCl	37%, ρ=1,190 g/ cm^3
6.	HNO_3	65%, ρ=1,391 g/ cm^3
7.	H_3PO_4	85%, ρ=1,710 g/ cm^3
8.	H_2SO_4	96%, ρ=1,840 g/ cm^3

The water glass used in synthesis is produced in "Alumina" factory with content of Na_2O and SiO_2 given in table 1. The process of manufacturing water glass was by hydrothermal dissolution of quartz sand with sodium hydroxide in an autoclave, and obtained module (SiO_2/ Na_2O) was 2,47, witch is typed as alkaline glass.

Aluminate solution used in synthesis also was from the Bayer alumina production process in Factory „Alumina" Zvornik. Aluminate solution was obtained after leaching of bauxite and separation of leaching products with content given in table 1.

Aluminum hydroxide and sodium hydroxide were used as raw materials for the preparation of synthetic aluminate. Synthetic aluminate was obtained by dissolving aluminum hydroxide with sodium hydroxide at the boiling temperature of the solution; its concentration was Na_2O = 395,6 g/ dm^3 and Al_2O_3 = 81,9 g/ dm^3 .

The basses raw materials used in synthesis are products of factory "Alumina" and they have very high content of Na_2O and H_2O. Also the water glass isn't so rich on SiO_2, so the synthesis could give as a result of other tipe of zeolite witch in his structure have more content of Al_2O_3, Na_2O. In this work mineral acids HCl, H_2SO_4, HNO_3 and H_3PO_4 were used in order to reduce the concentration of Na^+ ions to the mole ratio that will enable the formation of NaY Zeolite. The presence of acids during synthesis may also influence the course of the reaction.

Additionally, the results obtained during the process of synthesis were compared to the commercial zeolite CBV 100.

The experimental part of the paper was conducted in the laboratory of the Alumina Factory "Alumina" in Zvornik and the laboratories at the Faculty of Technology Zvornik. The syntheses of zeolite involved using the following:

- apparatus for hydrogel preparation consisiting of: thermostated burettes for dosing raw materials, reaction vessel and high/speed dispersers,
- 500 cm^3 polypropylene reactor for crystallization,
- air thermostat for obtaining the desired temperature of crystallization.

In order to reduce the period of time for the preparation of NaY zeolite and to accelerate the sythesis, the seed gel of 16 Na_2O : 1,2 Al_2O_3 :15 SiO_2 : 320 H_2O mole compositions was used. The seed gel was obtained by mixing water glass with synthetic aluminate solution at room temperature. It was left for 48h at room temperature and then used as such for the preparation of reaction mixture. The reaction mixture for zeolite synthesis had oxide ratio of 2 Na_2O : Al_2O_3 : 6,5 SiO_2 : 120 H_2O and it was obtained in the following way: seed gel was added to a reaction vessel and mixed with distilled water, afterwards, a certain amount of water glass was added to the vessel till 6,5 SiO_2: Al_2O_3 mole ratio was obtained and the mixture was stirred. Then, aluminate solution from the process of alumina production was added drop by drop till the mentioned mole ratio was obtained by constant and intensive stirring. Acids were added the last with intensive stirring; distilled water was added in such an amount as to reach the mole ratio of the reaction mixture. The reactor was

then closed and left in the thermostat at the temperature of 100°C for 24 h.The obtained suspension was filtrated, the deposit was rinsed and then dried at 105°C , it was ground and subjected to further analysis. The powder obtained in such way underwent chemical analysis, x-ray diffraction analysis, and we determined its granulometric compostion, specific surface area, ion-exchange capacity and water absorption.

Chemical analysis of the resulting powder determined the following parameters:

- The content of Na_2O, by means of atomic absorption spectroscopy on Perkin-Elmer 4000 device.
- The content of Al_2O_3 ,by means of potentiometric titration on "TITRIPOL" device.
- The content of SiO_2 , it is determined using the cassic gravimetric method.

The size and distribution of particles in the zeolite suspension and powder was determined on a laser apparatus for size particle VA INSTRUMENTS, "MICROSIZER-201S" within the range of sizing of 0-50μm and for 30 seconds and 50W power of ultrasound.

Specific surface area of the powder was determined using a low temperature nitrogen adsorption (BET method of one spot), on the Micromeritics, FlowsorbII 2300 device.

Mineralogical analysis of the powder was conducted using X-ray diffraction analysis on X-ray diffractometer PHILIPS, PW1710, using Cuanticathodes (40V, 50 mA, Kα = 0,15405μm).

Ion exchange capacity (IEC) was determined using a method based on the classic volumetric analysis for determining Ca^{2+} ions left in the solution after a 10 minute exchange.

Water absorption was determined gravimetrically based on the difference in mass of the sample after it had been saturated with water vapour (the sample which had been previously annealed at 500°C) and the mass of the same sample prior to saturation.

III. RESULTS AND DISCUSSION

The paper presents the results of the synthesis of NaY zeolite sodium aluminate solution from Bayer process, water glass and mineral acids. Acids H_2SO_4 (synthesis 1), HCl (synthesis 2), HNO_3 (synthesis 3), and H_3PO_4 (synthesis 4), were used in order to decrease the concentration of Na^+ions to the mole ratiothat will enable the formation of NaY zeolite. The reaction mixture for the synthesis of NaY zeolite had the following composition $2Na_2O : Al_2O_3 : 6{,}5SiO_2 : 120H_2O$.The results obtained were compared to the commercial zeolite sample designated as NaY.

Chemical analysis of the powders obtained after syntheses (Table 2.) indicates that, under the same conditions of synthesis, synthesis 1 had the nearest mole ratio SiO_2 /Al_2O_3 to that of the commercial zeolite.

It can also be seen that greater deviation of SiO_2 /Al_2O_3 mole ratio from that of the commercial zeolite occured in synthesis 2 and that powdered SiO_2 is present in larger quantities, which can also be evidence of incomplete reaction or separation of amorphous SiO_2.

TABLE 2. CHEMICAL ANALYSIS OF THE OBTAINED POWDERS

synthesis	Na_2O [%]	Al_2O_3 [%]	SiO_2 [%]	Loss by annealing at 800°C [%]	Mole ratio SiO_2 /Al_2O_3
1.	13,97	21,76	63,00	24,70	4,92
2.	1,9	16,86	79,84	39,80	8,05
3.	14,61	22,03	62,72	24,74	4,84
4.	14,40	23,48	60,50	19,59	4,38
NaY	12,49	21,39	64,69	23,39	5,14

Granulometric analysis of the powders obtained showed that the average diameter of 50% of particles for Synthesis 1, was 4,33 μm; Synthesis 2., 6,41 μm; Synthesis 3., 3,57 μm; Synthesis 4., 2,38 μm; and NaY 2,90 μm (Table 3.)

Granulometric analysis of the powders obtained showed that the average diameter of 50% of particles for Synthesis 1, was 4,33 μm; Synthesis 2., 6,41 μm; Synthesis 3., 3,57 μm; Synthesis 4., 2,38 μm; and NaY 2,90 μm (Table 3.) These results indicate that the smallest particles were obtained in the synthesis using H_3PO_4 , whereas the largest ones were the result of HCl synthesis. Moreover, the obtained histograms show a significant presence of 19,9 μm fractionin a declining order-Synthesis with HCl (Figure 4.), HNO_3(Figure 5.), H_2SO_4 (Figure 3.) and the smallest presence in synthesis with H_3PO_4 (Figure 6.). The best distribution of particles, under the same conditions of synthesis was achieved by H_3PO_4 synthesis (Figure 6.).

The powders obtained also underwent X-ray diffraction analysis in order to achieve phase identification of the samples, and the diffractograms were compared to the diffractogram of the commercial NaY zeolite (Figure 7.). Diffraction analysis showed that NaY zeolite was presentin syntheses with H_2SO_4, HNO_3 and H_3PO_4(Figure 8,10 and 11.), where as synthesis with HCl had an amorphous base as its result without NaY zeolite crystals present.

TABLE 3.GRANULOMETRIC COMPOSITION OF THE POWDER

P,%	10	20	30	40	50	60	70	80	90	100
Synthesis 1.(μm)	1,5	2,26	2,90	3,57	4,33	5,36	6,95	9,71	16,9	50
Synthesis 2.(μm)	2,49	3,39	4,24	5,18	6,41	7,96	10,8	15,2	20,4	50
Synthesis 3.(μm)	1,34	1,89	2,40	2,94	3,57	4,47	6,41	12,8	19,1	50
Synthesis 4. (μm)	1,09	1,43	1,75	2,06	2,38	2,74	3,19	3,88	6,13	50
NaY(μm)	1,37	1,84	2,22	2,56	2,90	3,27	3,72	4,35	5,55	50
D (μm)	1	2	4	6	10	15	20	30	40	50
Synthesis 1.(%)	4	16,3	45,9	64,5	80,6	87,6	93,4	98,9	100	100
Synthesis 2. (%)	0,7	5,5	27,2	46,9	68	79,6	89,4	98,2	99,8	100
Synthesis 3. (%)	4,7	22,1	55,3	68,6	76,9	83,4	91,2	98,6	100	100
Synthesis 4. (%)	7,8	38,2	81,2	89,8	91,1	92,9	96,2	99,4	100	100
NaY(%)	4,4	24	74,9	92	95,5	96	97,8	99,6	100	100

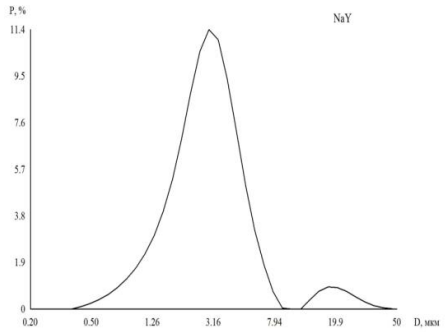

Figure 2. Granulometric composition of the commercial NaY zeolite

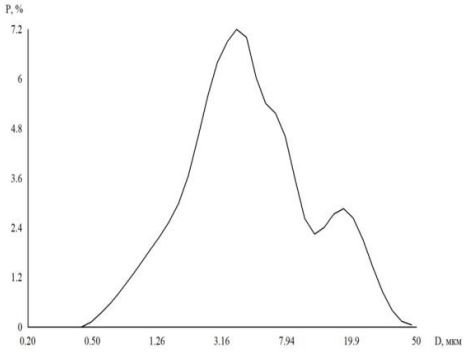

Figure 3. Granulometric composition of the powder Synthesis 1.

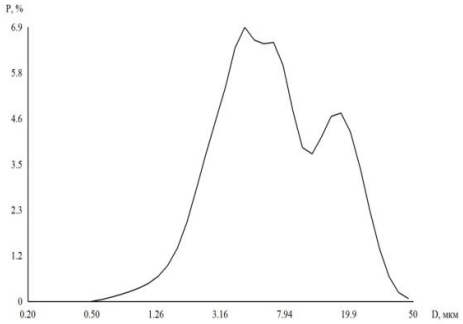

Figure 4. Granulometric composition of the powder Synthesis 2.

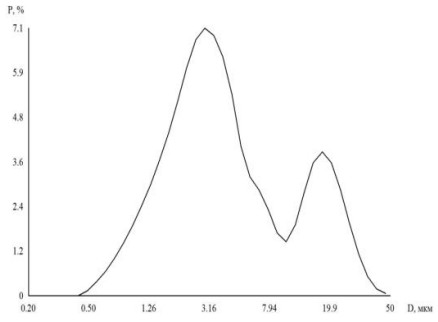

Figure 5. Granulometric composition of the powder Synthesis 3.

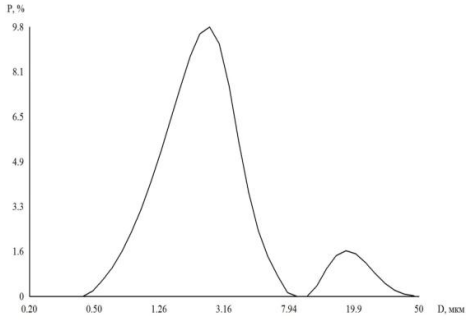

Figure 6. Granulometric composition of the powder Synthesis 4.

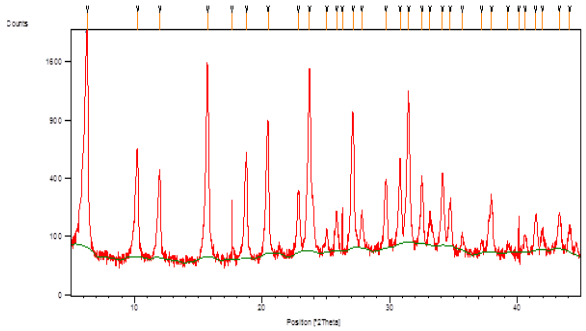

Figure 7. Diffractogram of the commercial NaY zeolite

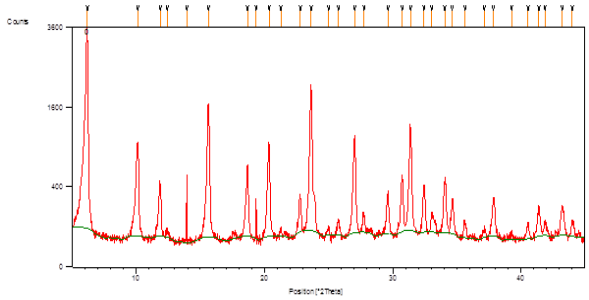

Figure 8. Diffractogram of the powder Synthesis 1.

In order to achieve better characterization of the powders obtained, the syntheses also underwent specific surface area using BET single point method together with degasing the sample at 150 °C, as well as the commercial sample. The results show that NaY zeolites obtained by synthesis 1 and synthesis 4 had larger specific surface areas –respectively 519 m^2/g for the synthesis with $H_2SO_4$and 507m^2/g for the synthesis with H_3PO_4. Lower values for specific surface area were obtained for the synthesis with HNO_3, 340 m^2/g, which may suggest that although NaY zeolite occurs in this synthesis, its crystallinity is still very low, or the process of crystallization may not be completed. (Table 4.)

The obtained powders underwent ion exchange capacity , which was further compared to the commercial NaY zeolite. It can be seen that IEC of the powder obtained in synthesis 2 is extremely low, 9 mgCaO/g of zeolite, which confirms once again that NaY zeolite formation did not occur in this synthesis. Zeolite powder sobtained by syntheses 1 and 4 were similar to the commercial zeolite in IEC, which again conforms that these syntheses result in the zeolite with similar properties to those of the commercial one. Moreover,

these powders had nearly identical water absorption abilities, which indicates that the zeolites obtained have similar properties. Water absorption of the powders obtained in syntheses 2 and 3 was 21.43 and 19.68 % respectively, which is considerably lower than the previous samples; this means that crystallization was not complete, and the presence of amorphous phase is significantly high. (Table 4).

TABLE 4. SPECIFIC SURFACE AREA, ION EXCHANGE CAPACITY AND WATER ASORPTION OF THE OBTAINED POWDERS AND NaY ZEOLITES

Synthesis	Sp (m^2/g)	IEC (mgCaO/g of zeolite)	Water absorption (%)
Synthesis 1.	519	79	31.62
Synthesis 2.	300	9	21.43
Synthesis 3.	340	68	19.68
Synthesis 4.	507	84	32.16
NaY	626	80	-

Synthesis of NaY zeolite involved using the seed gel with 16 Na_2O : 1,2 Al_2O_3 :15 SiO_2 : 320 H_2O mole ratio obtained by mixing water glass with aluminate solution at room temperature, with a 48 h stagnation period.

Synthesis of NaY zeolite was conducted from the seed gel, water glass, aluminate solution and a mineral acid by hydrothermal method from the reaction mixture of 2 Na_2O : Al_2O_3 : 6,5 SiO_2 : 120 H_2O mole ratio, at 100°C and 24 h period of crystallization.

In order to reduce the concentration of Na^+ ions and to achieve the desired mole ratio of sodium, different mineral acids were used: HCl, H_2SO_4, HNO_3 and H_3PO_4.

Chemical analysis of the powders obtained shows that SiO_2:Al_2O_3 mole ratio closest to that of the commercial zeolite (5,1) was obtained using sulphuric acid for Na^+concentration decrease, which shows that the reactions with other acids were incomplete.

Granulometric analysis of the powders obtained shows a significant amount of 19.90 μm fraction with HCl and HNO_3 syntheses, somewhat lower with H_2SO_4 and the best distribution with H_3PO_4

X-ray diffraction analysis shows that the best crystallinity of NaY zeolite is achieved by H_2SO_4 synthesisin comparison with the commercial sample of NaY zeolite, whereas considerably lower crystallinity was achieved with HNO_3 and H_3PO_4 synthesis; HCl synthesis gave an amorphous phase without the presence of NaY zeolite.

IV.CONCLUSIONS

Specific surface area of the obtained powders using BET single-point method and degasing at 150°C, was the best with H_2SO_4 synthesis amounting to 519 m^2/g of zeolite, with H_3PO_4 it was 507 m^2/g, with HNO_3- 340 HNO_3. The lowest value was with HCl- 300 m^2/g of zeolite.

Ion exchange capacity of the obtained powders also shows that no NaY zeolite was obtained during HCl synthesis. H_2SO_4 and H_3PO_4 acid syntheses produced a good IEC (79 and 84 mgCaO/g of zeolite), and water absorption was significantly lower with HNO_3 and HCl synthesis which proves that crystallization was not complete or did not occur at all.

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