Synthesis of Zeolite NaA with Facets through the Sol-Gel Technology

Dimitar Georgiev[1], Ivan Petrov[2], Todor Michalev[3] and Ivan Pejchev[4]

Abstract – **We examined the possibility of obtaining pure synthetic crystals of zeolite NaA with the chemical composition $Na_{12}[(AlO_2)]_{12}(SiO_2)_{12}.27H_2O$ by sol-gel methods. What we received was a product with the proven structure of zeolite NaA, confirmed by studies conducted using the methods of XRD, IR spectroscopy and SEM. The technology for the preparation of zeolite NaA was developed using the method of the sol-gel process comprised of preparation of two sol-gel solutions (at temperature up to 90°C for the reflux), and synthesis of the final product (washing, drying and activation of the zeolite).**

Using the methods of IR, XRD and SEM was studied the structure of the obtained synthetic product, and the results were compared to those of zeolite NaA, prepared through hydrothermal synthesis. It was found that the synthetic product obtained by sol-gel technology is in its pure crystalline phase, the obtained crystalline entities are 2-3μm in dimension; single crystals are cubes with symmetrical facet form.

Keywords – **Zeolite NaA, Synthetic zeolite, Sol-gel technology, Structure of zeolite.**

I. Introduction

Zeolites are materials, which have many applications, such as in household products, aquacultures, agriculture, water treatment, etc., due to their absorption abilities, ion exchange and size selectivity properties. Zeolite NaA has also been used in gas separation membranes to enhance the selectivity of the support. Commercial Zeolite NaA is synthesized through conventional techniques and silicates and aluminates are mostly used as starting materials [1-4].

Convenient synthesis procedures for pure Zeolite NaA by sol-gel methods were developed so that microcrystals of high chemical quality, good crystalline and size homogeneity can be obtained.

This method for the preparation of Zeolite NaA is preferred by many authors [5-11], because it uses pure raw materials, the obtained products are homogeneous and the synthesis is performed at lower temperatures.

[1]Dimitar Geotgiev is with the Technical Faculty of Assen Zlatarov University in Burgas, 1 Prof. Iakimov str., Bourgas 8010, Bulgaria, E-mail: dgeorgiev@btu.bg.

[2]Ivan Petrov Ph.D. is a student at the Technical Faculty of Assen Zlatarov University in Burgas, 1 Prof. Iakimov str., Bourgas 8010, Bulgaria, E-mail: bulmarine@abv.bg.

[3]Todor Michalev Ph.D. is a student at the Technical Faculty of Assen Zlatarov University in Burgas, 1 Prof. Iakimov str., Bourgas 8010, Bulgaria, E-mail: *rl_burgas@abv.bg.*

[4]Ivan Pejchev Ph.D. is a student at the Technical Faculty of Assen Zlatarov University in Burgas, 1 Prof. Iakimov str., Bourgas 8010, Bulgaria, E-mail: peichev.ivan@gmail.com.

II. Experimentals

The synthesis procedure leads to crystals with the chemical composition of $Na_{12}[(AlO_2)]_{12}(SiO_2)_{12}.27H_2O$.

Used raw materials: Tetraethoxysilane Si(OC2H5)4, Aldrich, purity> 99%, Aluminum powder, purity 99.9%, Sodium Hydroxide (NaOH), pellets, Merck, purity> 99%, Deionized water.

In Figure 1 is the projects scheme for the preparation of zeolite NaA using the sol-gel technology.

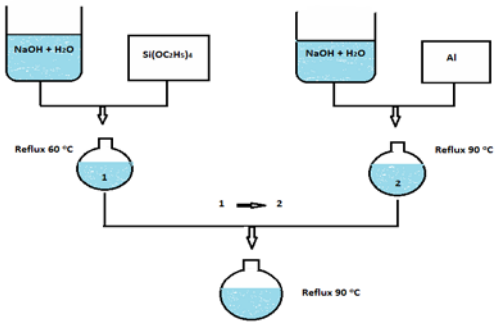


Fig. 1. Scheme of the synthesis procedure for zeolite NaA

For this purpose we prepared a starting gel, which was a combination of two working solutions. The starting compositions are prepared in a suitable vessel with constant stirring at a temperature of 60 to 90°C, and then refluxed. The solutions and the gel are prepared in the following sequence, which is shown in Table 1.

TABLE I
SEQUENCE OF PREPARATION OF THE BASIC COMPOUNDS

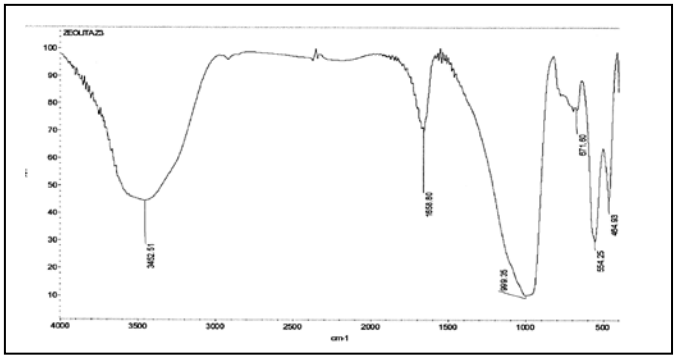
Composition	Procedures	Specifications
A.	1. [150 ml H_2O + 5.97 g NaOH]; 2. [(1) + 7.85 g $Si(OC_2H_5)_4$].	Temperature - 60°C, 60 min, reflux.
B.	3. [150 ml H_2O +5.97 g NaOH]; 4. [(3) + 2. 15 g Al.	Temperature - 90°C, 120 min, reflux.
Total	5. [A → B].	1. Temperature - room, 30 min, reflux. 2. Temperature – 90°C, 12 h, shear, reflux.

The next stage is the finalization of the synthesis of the zeolite. This stage is very important and includes washing, drying and activation of the final product. The washing was performed with water, and is done to eliminate the excess of soluble sodium compounds. Practically this is done by repeated subsequent washing with deionized water heated at 90°C and with continuous stirring of the slurry. After each wash centrifugation should be done (4500 rpm, 10 min). This continues until the system reaches a pH of 7-8. The drying is done in vacuum at 100°C for 120 min. The activation of the zeolite is performed by a heat treatment in a muffle furnace at a temperature of 550-600°C for 3 hours.

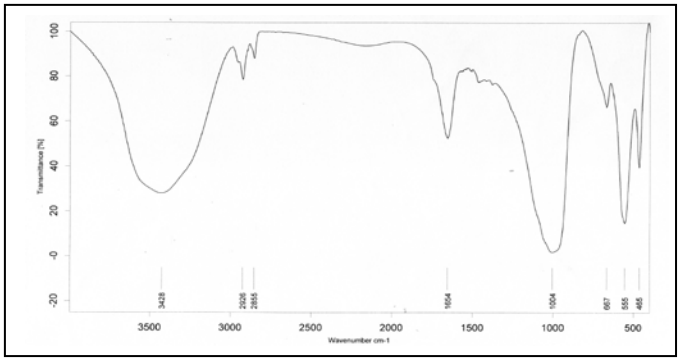
III. RESULTS AND DISCUSSIONS

The obtained product was tested using the methods XRD, IR spectroscopy and SEM. This was done in order for the structural features of the synthetic zeolite, that was received as a product, to be identified and compared with similar data obtained from the zeolite received through the hydrothermal method [12-14].

In Figure 2 are compared the IR studies of the NaA zeolite prepared by hydrothermal method and the one prepared by a sol-gel technology.



(a)



(b)

Fig. 2. IR specter of the Zeolite NaA prepared by: (a)- hydrothermal method, (b) - sol-gel technology

In Table 2 is shown the comparative data on the IR vibrational frequencies of the experimental results for the zeolite synthesized by the method of the sol-gel technology and the one prepared through the hydrothermal method.

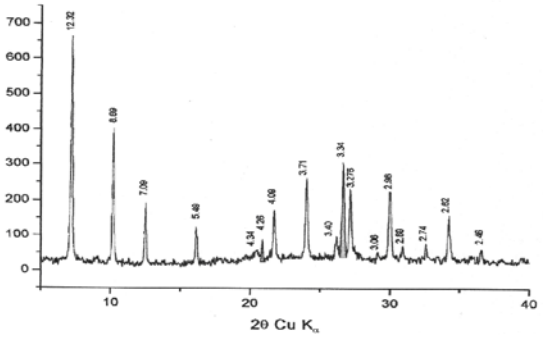
TABLE II
Most intense bands

Zeolite NaA- (sol-gel), Frequency, cm^{-1}	Zeolite NaA -(hydrothermal), Frequency, cm^{-1}
3228	3452
1654	1658
1004	999
667	671
555	554
465	464

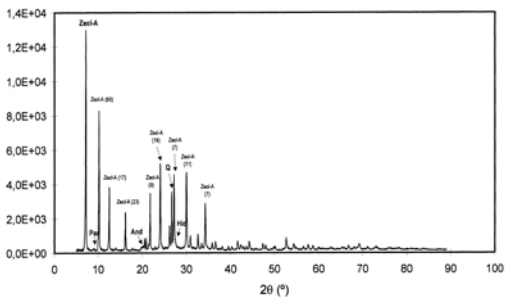
It is clear from the data shown that the synthesized zeolite has intense groups of IR vibrational frequencies comparable to those of the zeolite prepared by the Hydrothermal Method, and to the literature values for the same zeolite. The vibrational frequencies of the Al-O groups are observed up to 667 cm^{-1}. And after 1000 cm^{-1} are observed the ones that show the Si-O-Al relationship in the TO_4 tetrahedra (T = Si or Al). On the left side of the IR spectrum there are clearly shaped peaks at around 3428 cm^{-1} and 1654 cm^{-1} which characterize the zeolitic water. The experimentally obtained IR spectrum proves that the formed product is zeolite NaA, as there is coincidence in the IR waves at 1004, 667, 555 and 465 cm^{-1} in the IR spectrum of zeolite NaA with the data from the literature consulted [15].

Figure 3 shows the diffractograms of Zeolite NaA obtained by sol-gel technology (a) and the one produced through the hydrothermal method (b). It is obvious that the zeolite prepared by the sol-gel process does not contain additional crystalline phases. This results from the fact that it is produced from pure starting materials. The products received from kaolin through the hydrothermal method [12-14], are displayed below:

Major phases**:** Zeol-A = Zeolite A ($NaAlSi0_4$);
Q = Quartz ($Si0_2$).
Minor phases: Hid = Hydroxycancrinite - $(Na_8(AI_6Si_6O_{24})(OH)_{2.04}(H_2O)_{2.66})$**;**
Par = Paragonite -$(NaAI_2(Si,AI)_4O_{10}(OH)_2)$;
And = Andalusite ($AI_2(Si0_4)0$).



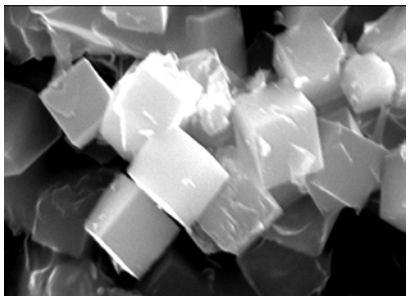
(a)



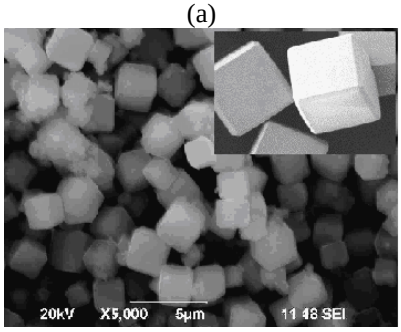
(b)

Fig. 3. XRD of Zeolite NaA: (a) - sol-gel technology, (b) - hydrothermal method

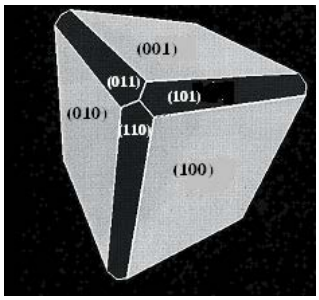
In Figure 4 are shown photographs from scanning electron microscopy of Zeolite NaA - synthesized by hydrothermal method (a), synthesized by sol-gel technology (b), and a single crystal of zeolite NaA, synthesized by sol-gel technology. The resulting crystal formations synthesized by the both methods are clear cubes measuring about 2-3 μm. You can see the cube's facet edges of Zeolite NaA synthesized by sol-gel technology. This is probably due to the use of optimal conditions in the crystallization process.



(a)



(b)



(c)

Fig.4. SEM of Zeolite NaA: (a) - synthesized through hydrothermal method, (b)- synthesized through sol-gel technology, (c)- scheme of a single crystal, received through sol-gel technology

IV. CONCLUSION

The studies conducted through scientific work give reason for the following important conclusions:

• We examined the possibility of obtaining a synthetic Zeolite NaA with the chemical composition pf $Na_{12}[(AlO_2)]_{12}(SiO_2)_{12}.27H_2O$ through the method of sol - gel technology and we received a product with the proven structure of Zeolite NaA, which was confirmed by studies conducted through the methods of XRD, IR and SEM.

• The technology that has been developed for the preparation of Zeolite NaA under the method of sol - gel technology comprises of the following stages: obtaining two compositions (at temperature of 60-90 °C, with continuous vigorous stirring and reflux), and final treatment (washing, drying and activation) of the zeolite.

• Using the methods of IR, XRD and SEM was studied the structure of the obtained synthetic product, and the results were compared to those from Zeolite NaA, prepared by hydrothermal synthesis. It was found that: the synthetic product obtained by sol - gel technology is in pure crystalline phase, it was compared with the one obtained through hydrothermal method from natural Bulgarian kaolin, and the resulting crystalline entities are of the same size (2-3 μm); the single crystal is a regular cube with facet edges.

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