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Obtaining The Structure of The Zeolite Synthesized from Floating Ashes Using Structural Methods

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Summary. Zeolites are microporous materials that can be synthesized from waste materials–floating ashes. As a start material we used floating ashes from place near by Bitola, Republic of Macedonia. The floating ashes are carrier of SiO_2, Al_2O_3 and Na_2O. Very characteristic is that the floating ashes contain 7.91% of Fe_2O_3.
For synthesis is applied low-temperature method (temperature from 363-373 K, time of crystallization is 6 hours). Additional quantity of Na_2O, Al_2O_3 and H_2O is added from $NaAlO_2$ and NaOH.
For synthesis of the Zeolites type NaA (synthetically obtained Zeolite) an appropriate mol ratio of oxides is chosen $SiO_2/Al_2O_3=1.3$; $Na_2O/SiO_2=3$; $H_2O/Na_2O=50$.
We conducted an assignation of the IR spectrum of the obtained zeolite. The IR spectrum is shown on the Figure 0.

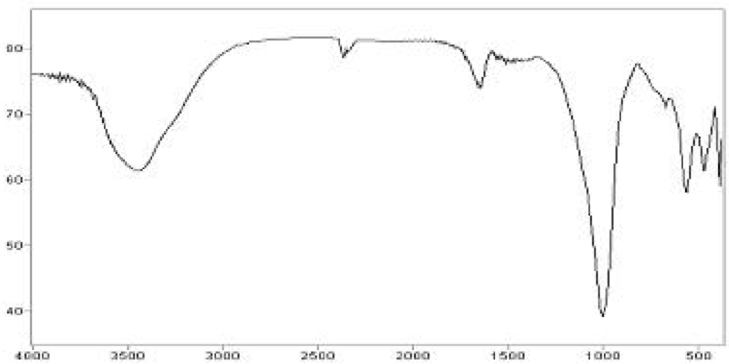

Figure 0. The IR spectrum of the obtained product

The peak values in the area of 3600-3400cm^{-1} with maximum value at 3500 cm^{-1} is a result of the vibrations of the OH^- groups from the water, while the peak at 1665 cm^{-1} is a result of the molecular water. In the area 1300-400 cm^{-1} there are the basic vibrations of the bond of Si(Al)-O zeolites.
The peak at 1000 cm^{-1} is antisymmetric and valent vibration, but the peak at 670 cm^{-1} is a valent vibration which is very weak, next, we have a vibration at 555 cm^{-1} which is result from the double four-member rings (D4R) and there is a deformational vibration of the bond Si(Al)-O at 464 cm^{-1}.

Introduction

The zeolites are natural minerals discovered in the middle of XVIII century by the Swedish geo-chemist Gronsted. The zeolites in nature are wide spread, but there is no interest of working with them in technological processes because it is complex and expensive. As a result of that emerged need to obtain synthetic zeolites. First laboratory synthesis of molecular sieves-zeolite is conducted in 1939-1940. The interest for these materials rise especially at the end of 50's years of XX century, when the scientists started to obtain synthetic zeolites in relatively simple conditions, and at the same time they used them in many practical processes (catalysis, drying of gaseous, adsorption, chromatography etc).

As consequence of that, the field of scientific research, despite low-temperature synthesis and synthesis with hydrothermal method, spread to structural testing, process modeling, catalysis, ionic exchange, adsorption and separation, membrane processes and application research. These researches are still up to date and each day the number of zeolites enlarges. The result from that is growth of industrial production of zeolites and spreading of their application in industrial processes.

Structure and composition

The zeolites are crystal alumosilicates of alkali and alkaline earth metals with three-dimensional structural lattice formed of the tetrahedars of SiO_2 and Al_2O_3. The tetrahedars are constructed from four oxygen atoms surrounded with Si and Al atoms. Because Al is 3 valent the tetrahedars of AlO_2 are negatively charged so in the structure of the zeolite emerges extra negative electricity that must be in balance with the needed number of cations (Na^+, K^+, Ca^{2+}, Mg^{2+}, Sr^{2+}, Ba^{2+}, Ag^+, Cu^{2+}, Zn^{2+}) according to the need in the process in which the zeolite is used.

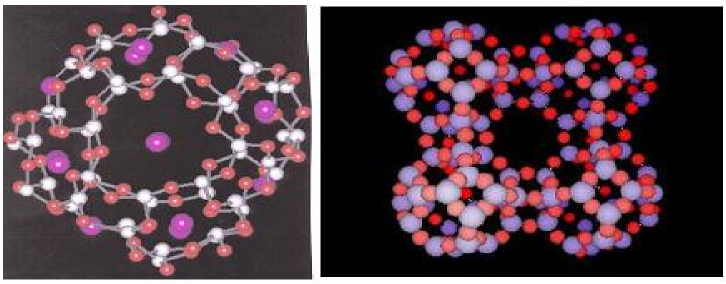

Figure 1. Zeolite structures

Experimental

The floating ashes are obtained as a waste material from thermal power plant in Bitola, Macedonia. In our case, we used it as a raw material for synthesis of zeolite because caries great amount of SiO_2 and Al_2O_3 which are necessary for synthesizing the zeolite. Very characteristic for these ashes is that in their composition has certain amount of Fe oxides. The chemical composition of the floating ashes is given in Table1.

Table 1. Chemical composition of floating ashes

Substances	Percent (%)
SiO_2	52.36
Al_2O_3	23.92
Fe_2O_3	7.91
CaO	7.52
MgO	2.32
Na_2O	0.90
K_2O	1.80
SO_3	1.20
Loss due to heating	1.90
Summed	99.88

Raw materials for synthesis of zeolite

The composition of the zeolites can be given with the formula:

$$\mathbf{M_{2/n} \cdot Al_2O_3 \cdot xSiO_2 \cdot yH_2O}$$

For the synthesis of zeolite we need four components:

1) Component of silicon acid
   - Solution of alkali silicate (water glass)
   - Colloid salt of silicon acid
   - Silicon acid
   - Floating ashes
2) Component of aluminum oxide
   - Solution of alkali aluminate
   - Fresh aluminum oxide
   - Aluminum salts

- Alumina, boxite and other minerals

3) Component of metal oxide
    - Alkali and alkaline earth metals
4) Water

From these four components, for the synthesis, reaction mixtures are prepared and it is possible to synthesize different types of synthetic zeolites with changing the ratio of quantities and crystallization conditions. Basic task and difficulty when synthesizing zeolite is to obtain zeolites that are with homogenous composition, structure and size of crystals. The success of solving this problem depends mostly from the course and strict compliance with the conditions of synthesis. Basic factors from which the composition, the size of crystals and the structure are depending are: the composition of raw material, the composition of hydrogel and conditions of crystallization (temperature, time of crystallization, concentration and alkalinity of the environment etc).

Conducting the low-temperature synthesis and structural testing

The low-temperature synthesis of zeolite 4A is conducted in water suspension in glass reactor with agitator and feedback cooler with thermostat. The components (floating ashes, Na aluminate, NaOH and water) are taken in such ratio that is calculated according to material balance for securing the molar ratios of zeolite type 4A. These components are stirred (strongly) for about one minute and then the mixture is leaved to “grow old” for 24 hours at room temperature. The process of crystallization of zeolite type 4A, which belongs to the group of natural zeolite NaA (sodalite), lasts 2,4 and 6 hours. After the termination of crystallization, the reaction mixture is filtrated and washed with distilled water until the pH=9 is reached. The obtained zeolite is dried at temperature of 393K. The technological Scheme for production of zeolite 4A is given in Figure 2.

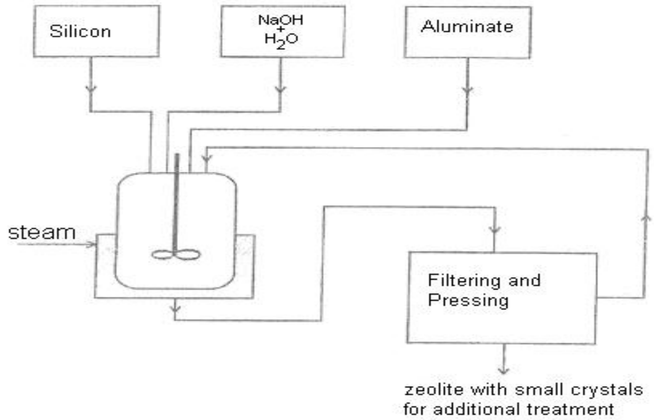

Figure 2. Technological Scheme for production of zeolite 4A

To the obtained zeolite we conducted chemical analysis and structural testing, with IR method. The IR spectrum of the commercial zeolite is given in Figure 3.

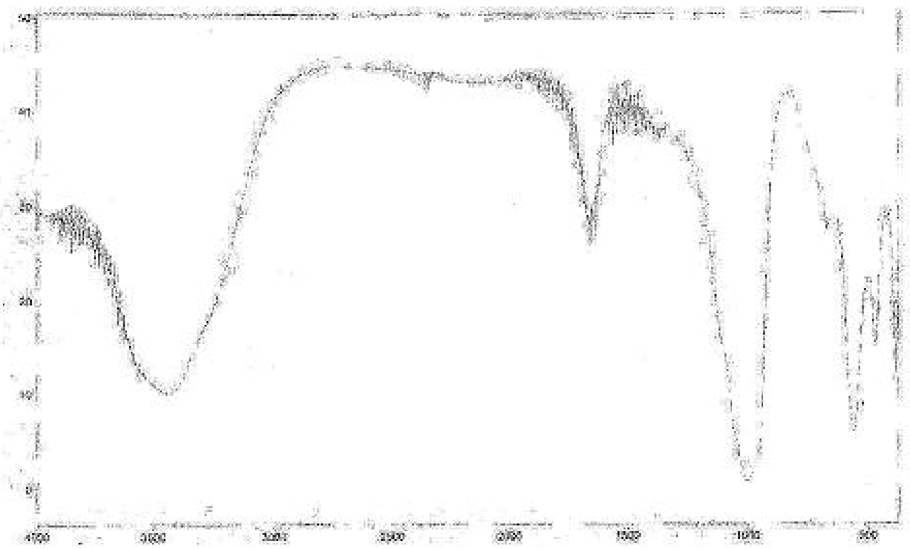

Figure 3. IR spectrum of the commercial zeolite

We conducted structural testing of the floating ashes with IR spectroscopy. The IR spectrum of the floating ashes is given in Figure 4. The IR spectrum is characterized with peak values in the area 1200-1000 cm^{-1} with maximum value at 1000 cm^{-1} which is characteristic for Si(Al)-O connection. There is a peak in the area of 3500-3400 cm^{-1} due to hydroxyl groups from the components from the ashes.

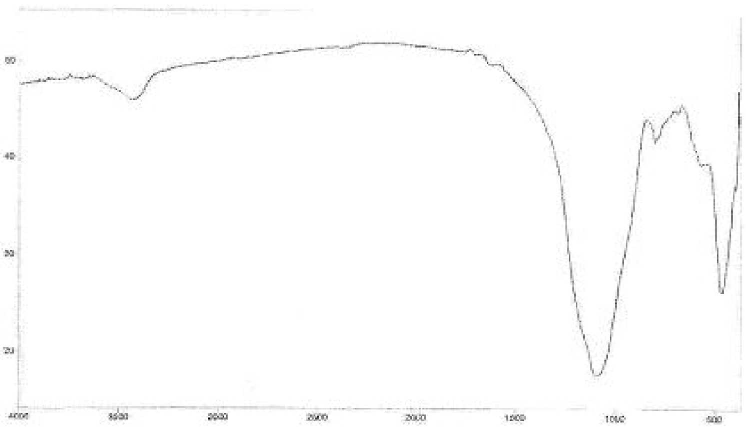

Figure 4. IR spectrum of the floating ashes

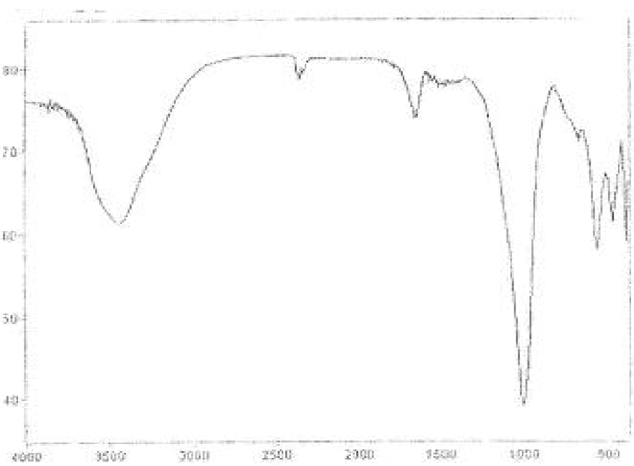

Figure 5. IR spectrum of the obtained zeolite from floating ashes

The IR spectrum of the obtained product (zeolite) is given in Figure 5. The assignation of the spectrum is conducted according to the table for zeolites. The peak values in the area of 3600-3400cm^{-1} with maximum value at 3500 cm^{-1} is a result of the vibrations of the OH^- groups from the water, while the peak at 1665 cm^{-1} is a result of the molecular water. In the area 1300-400 cm^{-1} there are the basic vibrations of the bond of Si(Al)-O zeolites. The peak at 1000 cm^{-1} is antisymmetric and valent vibration, but the peak at 670 cm^{-1} is a valent vibration which is very weak, next, we have a vibration at 555 cm^{-1} which is result from the double four-member rings (D4R) and there is a deformational vibration of the bond Si(Al)-O at 464 cm^{-1}.

Conclusion

From the conducted testing we can conclude that the obtained zeolite from floating ashes has the same characteristic as the commercial zeolite. The product is tested as an adsorbent of heavy metals, loader in rubber industry; further examinations will be directed towards its usage in pharmaceutical industry.

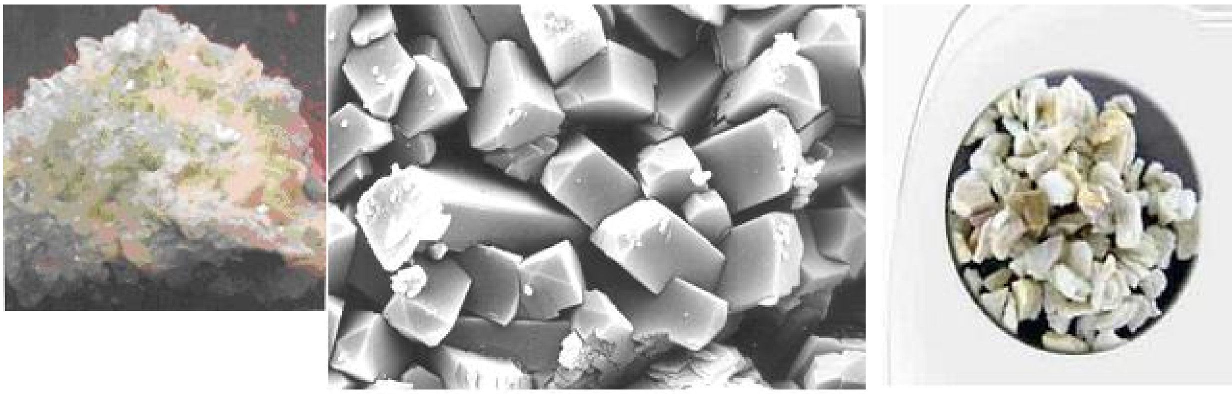

Figure 6. Zeolite crystals

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