

SYNTHESIS AND SPECTROSCOPIC STUDY OF ZEOLITE A TYPE AND X TYPE

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ABSTRACT

The synthesis of zeolites Type NaA and NaX from kolinite by conventional alkaline activation was investigated. In this research, NaA and NaX zeolites was synthesized via hydrothermal method. The final products were characterized by X-ray diffraction, FT IR spectroscopy, DTA – TGA thermal techniques and scanning electron microscopy (SEM). It is found that the reaction time has a great effect on the crystalline of the synthesized zeolites.

Keywords: *synthesis; Zeolites A and X TYPE, X-ray, DTA-TGA and FT-IR spectroscopy.*

INTRODUCTION

The studies on synthetic zeolites with low content of SiO₂ like NaA, NaX and NaY, rock Чуйтеmaterials, clays, kaolin and waste materials like ash cinder are mainly used [1-4]. The studies in this direction are focused on the use on the use of cheap and easily available natural materials or waste products.

Kaolinite [Al₂Si₂O₅(OH)₄] is well known and widely spread mineral of the kaolin group. It is dioctahedral 1:1 layered aluminosilicate with two kinds of surface interim layers. One of them is composed of structures of quartz type where each silicon atom resides in the center of a octahedron with oxygen atoms and hydroxyl groups at the vertices. Besides, the hydroxyl groups remain on one side of gibbsite-type layer the oxygen atoms are on the other side (quartz side). The structure of kaolinite stipulates its plastic properties [5-7].

The use kaolin to synthesize zeolites type A I X is based on the fact that this mineral can be preliminarily activated. As it has been reported earlier, the kaolin properties can hardly be improved by chemical methods since its reactivity is very low. The changes observed after alkali or acidic treatment are scarce, even under extreme conditions. Therefore, kaolin is usually used after isothermal activation (calcination) at temperatures from 600 to 900°C to obtain meta-kaolin which is active reaction phase. This is accompanied by loss of the crystallization water and significant structural changes – the major part of AlO₆ octahedrons is transformed into tetra- and penta-coordinated units. The best conditions for preparation of meta-kaolin have been reported by many authors, all of them showing optimal temperature in the range 600 - 800°C.

MATERIALS AND METHODS

The following initial materials were used for the preparation of zeolites type A and X: kaolin from “Kaolin” Company (Bulgaria), NaOH, LiOH, SiO₂ and Al₂O₃, NaOH, LiOH, SiO₂ and Al₂O₃, used were of Laboratory Reagent (LR) grade. Kaolin (grade “BoExtra”) has the following chemical composition, according producer. (Tabl.1)

Table 1 Chemical analysis of kaolinite minelar

| Component | Mass. % |
|--------------------------------|----------------|
| SiO ₂ | 49.0 ± 2.00 |
| Al ₂ O ₃ | 36.50 ± 0.50 |
| TiO ₂ | 0.30 ± 0.05 |
| Fe ₂ O ₃ | 0.75 ± 0.05 |
| CaO | 0.15 ± 0.05 |
| MgO | 0.25 ± 0.05 |
| Na ₂ O | 0.15 ± 0.05 |
| K ₂ O | 0.60 ± 0.05 |
| LOI* | 12.00 ± 0.60 |
| * Loss of ignition | |

Particle size distribution in % (SediGraph 5100)

| | |
|---------|-------|
| > 10 µm | 2.00 |
| < 5 µm | 87.00 |
| < 2 µm | 67.30 |

Synthesis of zeolite NaA

Zeolite type A was synthesized in two main stages:

- Thermal activation of kaolin to obtain meta-kaolin.
- Hydrothermal treatment of meta-kaolin in different alkali media.

The meta-kaolinization of initial material was carried out (after drying at 110°C for 1 h) at 600, 650 and 700°C in a muffle oven with isothermal period of 2 h.

The hydrothermal alkali treatment of meta-kaolin was performed using a series of sample mixtures as shown in Tabl.2 in the following sequence. Different amounts of meta-kaolin and aqueous alkali solutions of different contents of NaOH are intensely homogenized at 60°C for 30 min. The homogenized past-like mixture is the placed in an autoclave reactor and treated at 140°C and 6-8 atm pressure for 3 h.

Table 2 Compositions of experimental products

| Product | Quantity of mixture at correlation/alkaline solution (g/100 ml) | Concentration of NaOH, (N) |
|----------------------|---|-------------------------------------|
| Z₁ | 10:00 | 6 |
| Z₂ | 20:00 | 6 |
| Z₃ | 10:00 | 8 |
| Z₄ | 20:00 | 8 |
| Z₅ | 30:00 | 8 |

The product (zeolite type A) obtained is washed several times with water and ethyl alcohol (to pH 7-8) and then dried at 110°C for 1 h and activated at 620°C for 2 h. The products synthesized were analyzed by XRD, FT IR spectroscopy and DTA-TGA techniques.

Synthesis of zeolite NaX

The activated (metakaolinated) natural product was dry mixed with amorphous SiO₂ to prepare homogeneous mixture. The sodium-alumosilicate solution (SAS) was added to obtain gel-like product. The SAS was prepared from fresh solutions of sodium silicate (SS) and sodium aluminate (SA).

SS was prepared so as the SiO₂ concentration in the solution was 160-170 g/l, while that of Na₂O - 60-65 g/l. In the SA solution, the Al₂O₃ concentration was 210-220 g/l, while that of Na₂O - 300-320 g/l.

The blend obtained was mixed for 1 h in a special mixer at temperature of 50-70°C. The next stage was granulation of the amorphous blend and thermal treatment of the granules [8].

The granulation was carried out in a specially designed and manufactured fluidized-bed installation for granulation of clayish products [9]. It allows simultaneous mixing and drying (up to 60-80 °C of ceramic blends, preparation and separation of granules sized from 0.5 to 4 mm. For the purpose of the present work, the sizes of the granules obtained were 1-3 mm.

Tabl.3 shows the exemplary compositions of the initial amorphous blends from which granules were obtained.

Table 3. Compositions of initial amorphous blends

| Zeolite, index | MK (650) g | Amorphous SiO₂, g | SS, ml | SA, ml |
|-----------------------|-------------------|-------------------------------------|---------------|---------------|
| Z ₁ | 100 | 18 | 90 | 42 |
| Z ₂ | 100 | 17 | 85 | 45 |
| Z ₃ | 110 | 19 | 95 | 43 |
| Z ₄ | 110 | 18 | 80 | 45 |
| Z ₅ | 110 | 20 | 95 | 40 |

The next very important stage is the crystallization (zeolitization) of formed and granulated amorphous blend. It was carried out using crystallization solutions containing: aqueous solutions of NaOH and LiOH solutions were 260 g/l with respect to Na₂O and 200 g/l with respect to LiO. Exemplary compositions of crystallization solution are presented in Tabl.4.

Table 4. Compositions of the crystallization solutions

| Solution index | Aqueous Solution of NaOH, ml | Aqueous Solution of LiOH, ml | SS, ml |
|-----------------------|-------------------------------------|-------------------------------------|---------------|
| R ₁ | 100 | 4 | 25 |
| R ₂ | 100 | 6 | 30 |
| R ₃ | 110 | 4 | 30 |
| R ₄ | 120 | 6 | 30 |
| R ₅ | 130 | 6 | 35 |

RESULTS AND DISCUSSION

For comparison, the FT IR vibrational frequencies observed and the values reported in the literature are presented in Tabl. 3.

Table 5. IR vibrational frequencies of the experimental and literature data of kaolinite

| Vibrations | Wave number (cm ⁻¹) (experimental) | Literature wave number according [15,16] |
|-----------------------|--|---|
| $\nu(\text{OH})$ | 3696 | 3695 |
| $\nu(\text{OH})$ | 3620 | 3620 |
| ΔOH | 913 | 912 |
| Al-O | - | 1116,1010 |
| Si-O | 538 | 552 |
| $\nu(\text{Si-O-Si})$ | 469, 430 | 469, 428 |
| AlO-H | 790,755 | 794,754 |
| | 756, 697 | 756, 694 |

The FT IR spectra of the initial kaolin clearly shows the presence of bonded hydroxyl groups at 3696 and 3620 cm⁻¹, the peaks for Si-O at 469 and 430 cm⁻¹ as well as the peaks for the Si-O-Si groups at 790 and 755 cm⁻¹.

Tabl.6 presents comparative data on FT IR vibrational frequencies of meta-kaolon observed and these reported in the literature. A wide peak for the vibrational frequencies of SiO groups udn be seen at 1087 cm⁻¹ and another one for Al-O at 800 cm⁻¹.

Table 6. FT IR vibrational frequencies of the experimental and literature data of metakaolinite

| Vibrations | Wave number (cm ⁻¹) (experimental) | Literature wave number according [15,16] |
|------------|--|---|
| Al-O | 800 | 800 |
| Si-O | 1087 | 1090 |
| Si-O-Si | 466 | 467 |

After the hydrothermal syntheses, the best results were obtained for the zeolite type A. It was studied further and compared to the commersal product Zeolite Type NaA.

The FT Ir spectra of Zeolite type A, further the frequencies observed at about 1000 cm⁻¹ indicate for the Si-O-Al bonds in TO₄ tetrahedrons (T is Si or Al). On the left-hand side of the FT IR spectra, several well shaped peaks at about 3450 cm⁻¹ and 1650 cm⁻¹ can observed, which indicate for the zeolite water. The experimentally obtained FT IR spectra prove the formation of zeolite NaA due to the coincidere of the IR waves at 1004, 670, 554 and 464 cm⁻¹ with these of the IR spectrum of the commercial zeolite NaA (336-8 Aldrich).

FT IR spectrum and SEM micrograph of zeolite type X with zeolitization parameters – R₂ (Table 4) , 95 °C, 36 h can be see that product obtained had structure of Zeolite Type NaX.

CONCLUSIONS

The possibility to prepare synthetic zeolites Type A and X from Bulgarian kaolin as the basic raw materials studies. The synthesis of zeolites NaA and NaX involves preliminary formation of granules by the method of “fluidized bed”, followed by crystallization (zeolitization). This, the following experimental results were obtained:

- The conditions of kaolin thermal treatment (650°C, 2 h) were studied and the transformation into meta-kaolin phase and suitability for synthesis of Zeolite Type

NaA were investigated by the method of FT IR spectroscopy and DTA/TGA analysis.

- The conditions for thermal treatment of the initial material of Bulgarian origin (kaolin “BoExtra”) were studied and it was found to be suitable for synthesis of Zeolite Type NaX.
- Using the method of “fluidized bed”, the conditions for preparation of suitable granules (“Blackberry” Type) with preferred size (1-2 mm) were studied with amorphous ceramic blends containing kaolin, amorphous SiO₂, sodium silicate and sodium aluminate at proper quantitative ratios.

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