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ACETONE ADSORPTION ON SYNTHESIZED ZEOLITE FROM NATURAL CLAY MATERIAL

Polish clay material was used as an initial material for synthesis of the FAU type zeolite Y. For clay pre-synthesis preparation was adopted technique of its thermal activation in the temperature range 600-800°C. The temperature of clay material activation and the crystallization time of reaction mixtures on its basis were selected as the most important factors which strongly determined zeolite-formation process and their influence on zeolite Y synthesis was primary investigated. Performed complex investigations for establishment of qualitative and quantitative parameters of zeolitical probes synthesized in the reaction mixture of molar composition $\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:\text{SiO}_2:\text{H}_2\text{O}=5:1:10:200$ and additional amount of NaCl ($\text{NaCl}/\text{Al}_2\text{O}_3=2$). Powder XRD analysis applied for phase identification and quantitative analysis, confirm increasing of zeolite Y amount up to 53 and 58% for materials synthesized during 48 hours from reaction systems on basis of clay material burned at 600 and 700°C, respectively. Results of XRD analysis correspond with experimental data of gravimetric analysis on solid part of reaction mixture (losses of ignition and relative mass grow) and determination of residual Na_2O in liquid phase. With help of home-made installation confirmed fine adsorptive properties of obtained zeolite powders for dynamic removal of acetone from air. Established, that adsorption effectivity of tested materials is strongly related with amount of zeolite phase in the investigated powders and reaches maximal values in the range of 100-105 mg/g for probes after 48 hours of crystallization in cases of clay material activation 600 and 700°C.

Keywords: adsorption capacity, Faujasite, Philipsite, VOC

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1. Introduction

A number of materials with developed internal structure is quite broad. However, large-scale usage in industry finds relatively small group of solids. Among them are the main representatives of the class of amorphous porous (silica gel, porous glass) and highly dispersive (aerosil) silicas, carbon sorbents, active alumina, zeolites and natural mineral sorbents NMS (bentonite, palygorskite, sepiolite, etc.) [1, 2].

When comparing the aggregate properties of each of them, namely the total volume of pores, sorption capacity, the value of specific surface area, average pore size and ability for cation exchange, special attention attracted to representatives of the class of zeolites. This group of minerals is characterized by regular microporous structure and localized in the cavities where cations can be replaced by ions of many elements of the periodic system. The average pore size of zeolite minerals is small and usually does not exceed 1-2 nm, which is close to the size of many organic molecules.

However, only a small group of minerals is widely used [3]. The main among them is natural clinoptilolite, chabazite, erionite, mordenite and synthetic samples of types LTA, FAU, ZSM (5, 12, 22, 48) and some others. Common and cheap natural zeolites are minerals that are widely used in technology. Their total production in the world is about 3-4 millions of tons per year [3]. However, widespread in nature representatives of the class of zeolites are characterized by lower adsorption capacity in comparison to the synthetic ones.

Moreover, they are often presented in the form of polyphasic conglomerates, which complicates their use. Therefore, in numerous selective adsorption and catalytic processes, synthetic analogues such as zeolite A (LTA), X and Y (FAU) are preferred [4]. They are the most open-frame structures and are characterized by high sorption ability for certain VOC characteristics.

These kinds of impurities are emitted into gaseous environment mainly due to production and usage of different resins, adhesives, paints and washing mixtures [5]. One from the common VOCs, the contents of which in air requires stable monitoring is acetone, which in the form of individual substances or in mixtures with other organic substances finds wide human use [6]. Acetone is a polar compound with kinetic diameter of molecule $\approx 4.5 \text{ \AA}$ [7], which provides the possibility for its effective adsorption on zeolite materials.

This assumption is based on the chemical nature filiation of adsorptive and adsorbent and structural features of zeolite structure type FAU, which can ensure the smooth penetration of molecules of acetone in their intracrystalline pore space.

Therefore, a study of the synthesis of zeolite Y on basis of natural raw clay material and determination of its activity due adsorption of acetone vapors has been the subject of this paper.

2. Materials and methods

2.1. Materials

Among the raw materials, which are often used for the synthesis of zeolite phases, traditionally considered pure reagents that allow for the introduction into the composition of the reaction mixture, alumina and siliceous components. These include silica sol, amorphous silica, silica gel, liquid glass, sodium aluminate [8]. Clay minerals are valuable mineral raw materials for fine inorganic synthesis.

The clay mineral from Poland was used as silica and aluminium source for zeolite synthesis. The raw material was in the form of powder with the following characteristics: moisture – 0,8%, loss of ignition – 11,9%. Composition of this material is shown in Table 1. The sodium chloride and silica gel was produced by Chempur, sodium hydroxide (CZDA) was produced by POCH.

Table 1. Chemical composition of clay mineral

Tabela 1. Skład chemiczny materiału ilastego

| Component | SiO ₂ | Al ₂ O ₃ | Fe ₂ O ₃ | TiO ₂ | CaO | MgO | K ₂ O |
|-----------|------------------|--------------------------------|--------------------------------|------------------|-----|-----|------------------|
| Content | 52,5 | 34,5 | 0,8 | 0,5 | 0,1 | 0,1 | 0,6 |

2.2. Synthesis process

The material was thermally activated at different temperatures: 600, 700 and 800°C. The calcination temperature affects the surface properties of clay material.

Based on chemical composition the molar ratio of used raw clay material was calculated as Al₂O₃ : 2,3 SiO₂. For synthesis process the following molar ratio of Na₂O : Al₂O₃ : SiO₂ : H₂O - 5 : 1 : 10: 200 [9, 10, 11] was used. In order to make the process faster, in the first step, 5,9 cm³ NaOH solution was mixed with 1,8 cm³ NaCl solution. Next, additional deionized water, SiO₂ and 0,8 g of clay was added to the mixture and left for 42 hours at ambient temperature. After that it was heated to 99°C for different length of time (1, 8, 24 i 48h). Finally the samples were separated from the liquids and washed several times with deionized water until a neutral pH was reached. Sodium content in liquid solutions was determined by Flame Photometry (BWB Technologies Flame Photometer). Separated material was dried at 110°C and crushed.

Synthesized material characterization

The loss of ignition (*LOI*) was measured by weighting the mass of samples before (*m*₁) and after (*m*₂) heating (SNOL 8.2/1100):

$$LOI (\%) = \frac{m_2 - m_1}{m_2} \cdot 100\% . \quad (1)$$

The phase characterization was carried out by X-ray diffraction (XRD) (PANalytical Empyrean diffractometer with Cu K α radiation, operated at 40 mA and 25 kV). The diffraction data was analyzed using PDF4+ database and the Rietveld method.

2.3. Acetone adsorption

The adsorption of acetone vapours was examined in a self-made system consisting of a flow control valve, fixed-bed column, flowmeter and concentration analyzer [12]. Briefly, stream of the mixture of nitrogen and methane at a pressure 0,4 bar was directed to a sorption column with the test sample. The concentration of acetone at the column outlet was monitored on-line with gas chromatograph (Thermo Scientific 1300 TRACE GC with column TR-5).

3. Results and discussion

3.1. X-ray diffraction analysis

The XRD analysis was primarily conducted for a definition of qualitative and quantitative characteristics of products after hydrothermal synthesis. As it shows on Figure 1. the crystallization process of reactive mixtures on basis of thermoactivated clay material leads to formation of zeolitical phases with Faujasite (FAU) structure type with characteristic diffraction peaks (d, nm): 1,43; 8,75; 7,46; 5,68; 4,76 etc. It was found that the clay material activation temperature and time of crystallization significantly influenced the amounts of faujasite in the obtained products and their qualitative composition. In initial stages of synthesis the crystalline part of probes are mainly represented by faujasite type zeolite Y and residual phases of β -Quartz and Muskovite-2M1, originated as impurities of initial clay rock. Through the crystallization process, the relation between zeolite and impurities increases, which means that its amounts grows, reaching a maximum of 53-58 wt% into crystalline part of obtained powders until 48 hours of reaction. It should be noted that after 24 hours of synthesis the phase of Muskovite-2M1 disappears and instead of this some amounts of newly originated zeolite phase, identified as philipsite, was reported. Adjunction results were obtained from the XRD analysis data by investigated peculiarities of zeolite synthesis on basis of clay materials using some additional physical-chemical analytical techniques.

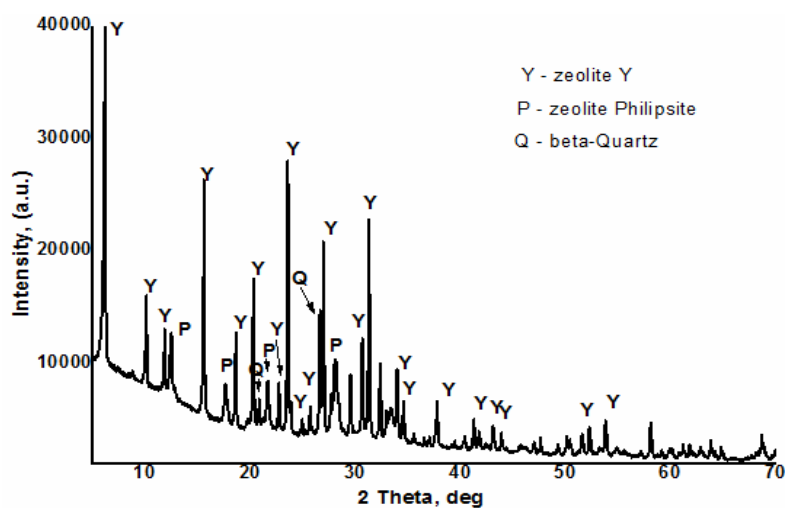


Fig. 1. XRD pattern of zeolite powder synthesized at 48h from thermoactivated clay material (600°C, 5h)

Rys. 1. Obraz XRD zeolitu syntezowanego przez 48h z aktywowanego termicznie materiału ilastego (600°C, 5h)

3.2. Effect of calcination temperature

The comparison of different activation temperature of the starting material was based on the mass growth of product during the synthesis (Fig. 2).

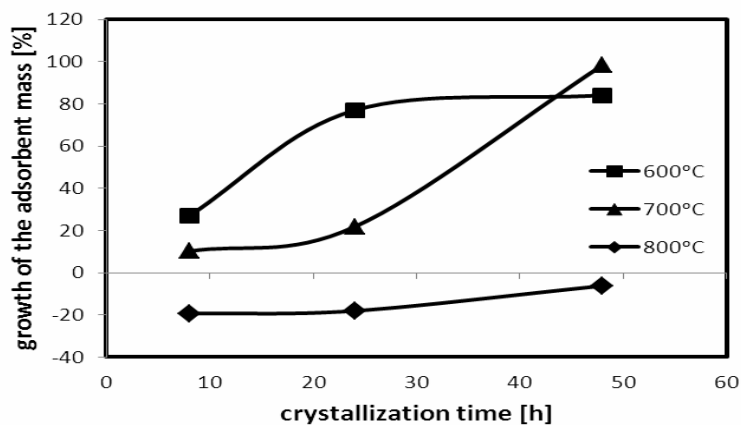


Fig. 2. The mass growth [%] of the zeolitical materials synthesised from clay material activated at different temperatures

Rys. 2. Wzrost masy [%] materiałów zeolitowych syntezowanych z materiału ilastego aktywowanego w różnych temperaturach

The comparison of obtained data identified that in case of temperature 800°C, the contact time does not influence the growth of the adsorbent mass. Instead the evident growth of the product mass was observed for temperatures 600°C (approx. 85%) and 700°C (approx. 100%). The difference between the sample mass obtained for both temperatures is major after 24 hours of reaction and minor after 48 hours. The biggest increase in mass in the case of the activation temperature of 600°C was achieved at 24 h (approx. 50%) and for the activation temperature of 700°C at 48h (approx. 76%).

3.3. Effect of crystallization time

Four different contact time (1, 8, 24 and 48h) were applied to evaluate the time of crystallization. It was expected that the increasing of crystallization time decrease mass of sodium in the filtrate while increasing the loss of ignition. As depicted in Figure 3, the concentration of sodium in the filtrate is a function of crystallization time, for materials activated at 600°C. With increasing the time of zeolitization the sodium content decreases. The greatest reduction of sodium in the filtrate was observed in the first hour of crystallization. After 8 and 24 hours of reaction the content of sodium were comparable.

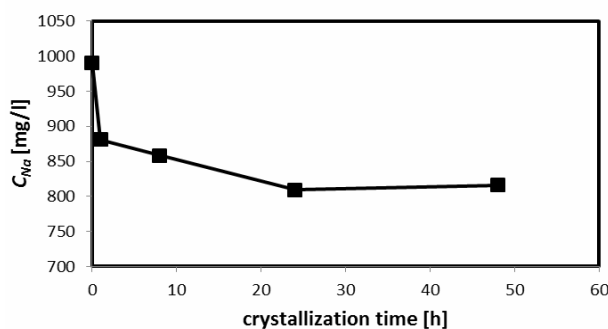


Fig. 3. The concentration of sodium in the filtrate as a function of crystallization time.

Rys. 3. Stężenie sodu w filtratach w funkcji czasu krystalizacji

The loss of ignition as a function of crystallization time for materials activated at 600°C and 700°C is depicted in Fig. 4. As can be seen, the highest loss of ignition after 48 hour of crystallization (18% *LOI*) was obtained for the material activated at 600°C, while for activation at 700°C (48h of reaction) the loss of ignition was 12%. The increase in zeolite content in the reaction product should be associated with an increase in the *LOI* [%]. The comparison of the curves (Fig. 4.), identified that the difference in *LOI* (1-6%) is not dependant on crystallization time.

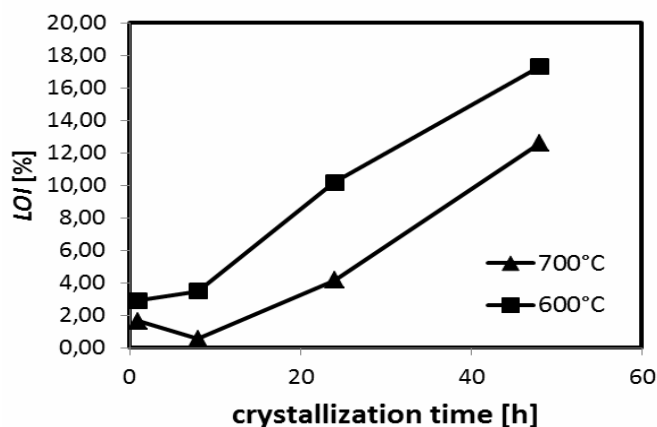


Fig. 4. LOI [%] of synthesised zeolitical materials as a function of crystallization time

Rys. 4. LOI[%] syntezowanych materiałów zeolitowych w funkcji czasu krystalizacji

3.4. Adsorption of acetone

The effect of calcination temperature and crystallization time on adsorption abilities of synthesized materials was compared in Fig. 5. The adsorption capacity (q_e) of acetone increases with increasing the crystallization time. The highest value of acetone adsorption capacity was achieved for the materials (600°C, 48h and 700°C, 48h) synthesized for 48 hours. In the case of the materials calcinated at 700°C there is a stronger effect of the crystallization time on the adsorption capacity.

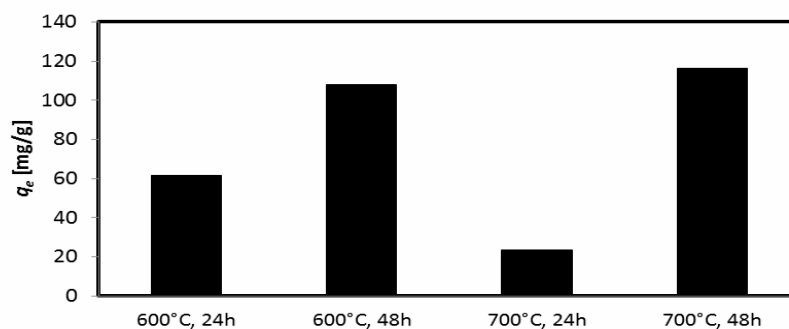


Fig. 5. The adsorption capacity of the zeolitical materials synthesised from clay material calcinated at 600°C and 700°C, after 24 or 48 hours of reaction

Rys. 5. Pojemność adsorpcyjna materiałów zeolitowych syntezowanych z materiału ilastego kalcynowanego w 600°C i 700°C, po 24 i 48 godzinach reakcji

4. Conclusion

Investigated clay material rock activation at temperature ranges of 600-700°C is enough for high values of zeolite Y formation in the considered reaction systems over its hydrothermal synthesis. The selection of crystallization time depends on the activation temperature of the raw material. It was determined that the zeolite amount increased with the increase of crystallization time. Meanwhile after 24 hours of synthesis the formation of new zeolite phase in the form of phillipsite was reported. Obtained synthetic zeolite has a great potential as an effective adsorbent material for acetone uptake.

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ADSORPCJA ACETONU NA ZEOLITACH SYNTEZOWNYCH Z NATURALNYCH MATERIAŁÓW ILASTYCH

Streszczenie

Celem badań była synteza zeolitu typu Y z naturalnego materiału ilastego pochodzącego z Polski. Prawidłowy przebieg procesu krystalizacji wymagał wstępnej aktywacji termicznej surowego materiału ilastego w temperaturach z zakresu 600-800°C. Ustalono że temperatura aktywacji termicznej materiału wyjściowego oraz czas krystalizacji mieszanin reakcyjnych są najważniejszymi parametrami wpływającymi na przebieg procesu syntezy zeolitu, dlatego skupiono się na optymalizacji tych parametrów. Na podstawie badań wstępnych przyjęto następujący skład molowy mieszanin reakcyjnych $\text{Na}_2\text{O} : \text{Al}_2\text{O}_3 : \text{SiO}_2 : \text{H}_2\text{O} = 5 : 1 : 10 : 200$. Wprowadzono dodatkowo NaCl, w takiej ilości że stosunek molowy $\text{NaCl}/\text{Al}_2\text{O}_3$ wynosił 2. Przeprowadzono szereg badań w celu wyznaczenia parametrów ilościowych oraz jakościowych zsyntezowanych próbek. Analiza XRD stosowana do identyfikacji faz oraz ich analizy ilościowej, wykazała zawartość zeolitu typu Y w zsyntezowanych próbkach w ilości 53 i 58% odpowiednio dla materiałów aktywowanych w 600 i 700°C, których czas krystalizacji wynosił 48h. Wyniki analizy XRD pokryły się z innymi wykonanymi analizami, tj.: oznaczeniem straty po prażeniu, względnego wzrostu masy produktu oraz stężenia Na_2O w roztworze poreakcyjnym. Przy wykorzystaniu specjalnie przygotowanej instalacji laboratoryjnej wyznaczono pojemność adsorpcyjną materiałów względem acetonu. Ustalono, że efektywność adsorpcji jest ściśle związana z ilością fazy zeolitowej w próbkach. Najwyższą pojemności adsorpcyjne wynoszące 100 – 105 mg/g uzyskano dla próbek krystalizowanych przez 48h, których temperatura aktywacji wynosiła 600 i 700°C.

Słowa kluczowe: pojemność adsorpcyjna, fujazyt, filipsyt, LZO

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