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Synthesis of the zeolites on the lightweight aluminosilicate fillers

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ABSTRACT

This work presents the results of synthesis of zeolites from perlite and fly ash microspheres via treatment with sodium hydroxide solution, at low temperatures of 30–90 °C under atmospheric pressure. Obtained products could be active as low-cost agents for the removal of heavy metals from wastewater.

The influences of reaction temperature and time as well as NaOH concentration, on the type of the solid products were investigated. The results showed that mixture of zeolite Y, A and Na-P_1 could be synthesized at temperatures varying in the range of 60–90 °C with NaOH concentration of 3–4 M. Regardless of the type of substrate used, it is possible to obtain the product in a similar way. The synthesized products are characterized by low bulk density, 0.16 and 0.95 g/cm^3 for perlite and microspheres respectively.

1. Introduction

Natural zeolites are a group of hydrated tectoaluminosilicates with a specific and highly differentiated structure containing voids filled with ions and water molecules having a high freedom of movement [1]. Due to this construction, zeolites have many of varied and extremely valuable physicochemical properties and practical applications. The high cation exchange capacity, as well as the possibility of sorption of molecules or ions, decides on the use of zeolites among others in the process of heavy metal cations immobilization [2,3], removal of ammonium ions [4] or radionuclides [5] as well in carbon dioxide capture [6] etc.

Zeolites may be obtained by heating some aluminosilicate materials in the presence of alkaline solutions. Various media of silica are used for synthesis of zeolites, inter alia natural minerals such as: kaolinite [7], volcanic glaze (perlite [8,9], pumice [10]), rice shells [11], diatomite, as well as coal fly ash [12,13] or synthetic silicates [14]. Depending on the type of raw materials and process conditions (temperature, pressure), final product can be obtained in a few hours or days. A type of zeolite structure, which is formed at given temperature, depends to a large extent on the composition of the starting mixture. However, process conditions influence the course of crystallization in systems having the same chemical composition. These include: pH of reaction solution, temperature, pressure and treatment time as well as degree of fineness of reagents or mixing [15]. Zeolites are also the main component of geopolymers as well as slag alkaline binders [16–19].

The aim of this work is to obtain of zeolitic products characterized by low bulk density (<1 g/cm^3) from light aluminosilicate fillers. The synthesis should be carried out in a simple way, at low temperatures and/or with short reaction times. The results of syntheses carried out on a laboratory scale will allow to determine the impact of analyzed factors on the amount and nature of the obtained reaction products. The results will be useful in the selection of parameters for synthesis of a material with potential applications such as floating on water sorbents of heavy metal cations.

Among several possible light aluminosilicate materials such as vermiculite, glass granules, expanded perlite or microspheres, only two latter were selected for synthesis in this work. Others were considered unsuitable for zeolitization process due to insufficient reactivity at low temperatures (crystalline vermiculite) or too small amount of aluminum in the structure (glass granules). Both the perlite and the microspheres are aluminosilicate materials characterized by the similar chemical composition (Table 1). The main difference is in the type of porosity–the perlite has a lamellar structure and open porosity, and porosity of the microspheres can be described as a closed. It was examined whether synthesis may be carried out in the same manner, regardless of the type of the starting material.

2. Experimental

The expanded perlite (*PEX100*, Piotrowice II) and the fly ash microspheres (*EKO EXPORT*) were used as the starting materials. The grain fractions, 0.125–2.0 mm and 0.125–0.5 mm respectively,

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Table 1
Chemical compositions of expanded perlite and fly ash microspheres.

Chemical composition	Expanded perlite	Microspheres
SiO_2	68–75%	45–60%
Al_2O_3	10–13%	20–30%
SiO_2/Al_2O_3	4.5–7.5	1.5–3.0
MgO + CaO	1–4%	1–4%
$Na_2O + K_2O$	6–9%	0.5–2%

were separated. The bulk densities were about 0.11 and 0.83 g/cm^3, respectively. (Pycnometer was used to determine the density of microspheres. In the case of perlite, because of the open porosity, the value is the apparent density.) Perlite was X-ray amorphous and microspheres beyond the aluminosilicate glassy phase contained mullite and small amount of quartz. The chemical compositions (a wavelength dispersive X-ray fluorescence spectrometer (WD-XRF) (Axios mAX 4 kW, PANalytical, Netherland) equipped with Rh source) are collected in the Table 1.

The synthesis was carried out by mixing the perlite or the microspheres with aqueous solution of sodium hydroxide (*POCH*) in the concentration range 0.5–5.0 mol/dm^3. The solid-to-solution ratio was maintained at 1:15 (g/ml). The reactions were performed under atmospheric pressure. Three different temperatures (30, 60 and 90 °C) and various durations (24, 48 and 72 h) were used. The final solid products were recovered by filtration and washing with distilled water until the pH of the filtrate was below 10. The samples were dried at temperature not exceeding 80 °C.

The alteration products were identified by means of Philips X-ray powder diffraction X'Pert system (CuKα radiation). The morphology and the crystal size were studied by scanning electron microscope FEI Nova NanoSEM 200. The existence of zeolite frameworks was confirmed by measured on Bruker VERTEX 70 v vacuum FT-IR spectrometer using the standard KBr (*Merck*) pellets methods.

3. Results and discussion

Temperature, reaction time and concentration of sodium hydroxide, as parameters influencing the zeolitization products were investigated. Fig. 1 shows an exemplary series of XRD patterns illustrating the reaction product of perlite in contact with solution of 0.5–5.0 M NaOH at 90 °C for 72 h. Depending on NaOH concentration, identified phases are: zeolite X, zeolite Na-P$_1$, zeolite A and hydroxysodalite. The results show, that at atmospheric pressure and over a range of temperatures and NaOH concentrations, the major product was zeolite Na-P$_1$. This result corresponds to related literature [20]–at a crystallization temperature below 100 °C the most stable structure is gismondine-type zeolite, Na-P$_1$. It is visible, that low sodium hydroxide solution concentrations, 1.0–3.0 mol/dm^3, favored the formation of zeolite Na-P$_1$–in this range the amount of a crystalline phase increases in proportion to the concentration of NaOH. At higher concentrations (>3.5 mol/dm^3) zeolite X as coexisting phase appears, whereas the highest concentration (5.0 mol/dm^3) led to the formation of significant amount of hydroxysodalite. Reduction in synthesis time or temperature results mainly in the quantity of products. Regardless those, the solution of 0.5 mol/dm^3 did not give any crystalline product.

The presence of aluminosilicate framework in the obtained samples was confirmed using IR spectroscopic technique. MIR spectra of the sample obtained at 90 °C for 72 h are presented in Fig. 2. Every zeolitized solids show similar IR spectra, which contain a number of vibration bands of the structural units present in the structure of the material.

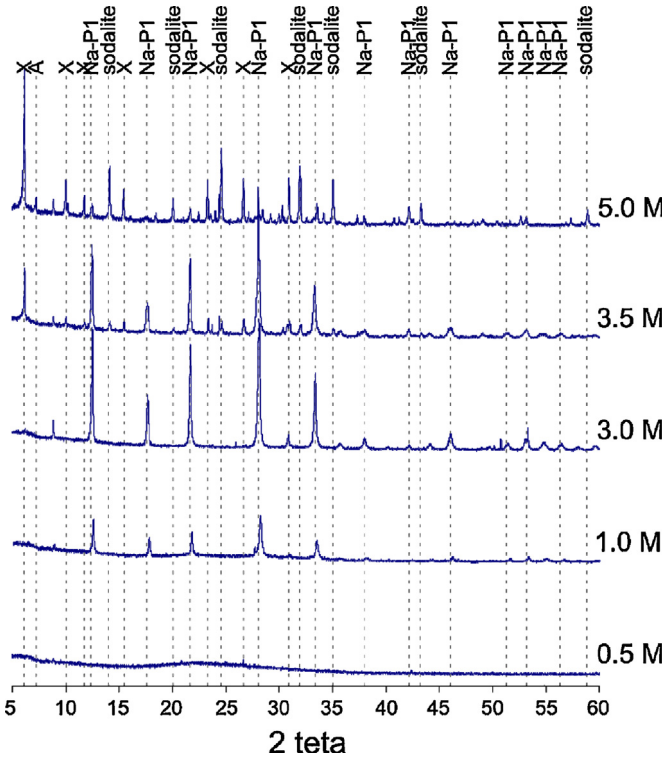

Fig. 1. XRD patterns of products formed by reactions of expanded perlite in 0.5–5.0 M NaOH at 90 °C for 72 h.

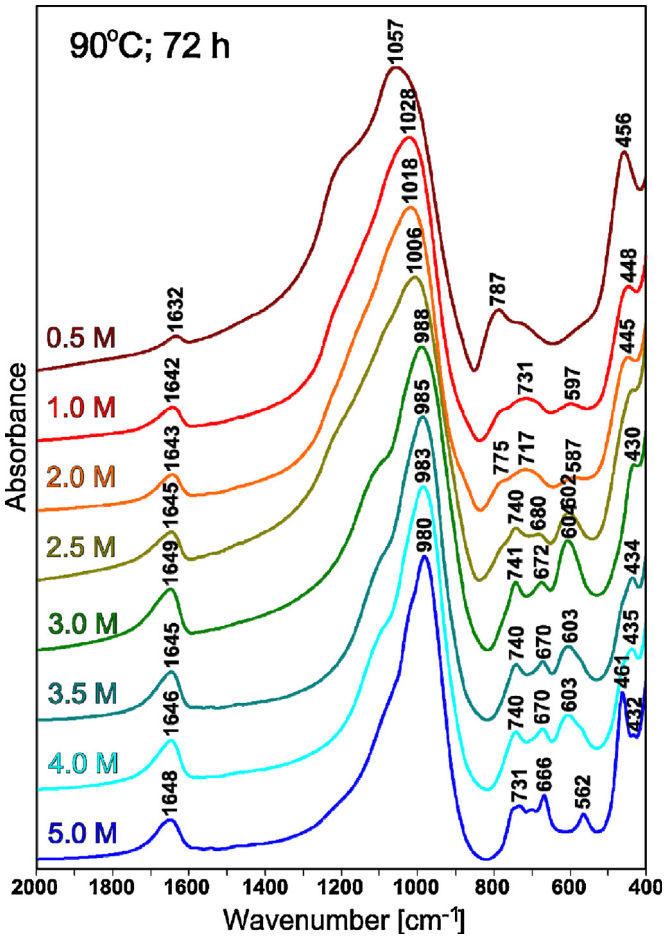

Fig. 2. FT-IR specrta of products formed by reactions of expanded perlite in 0.5–5.0 M NaOH at 90 °C for 72 h.