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Spectroscopic investigation of hydrothermally synthesized zeolites from expanded perlite

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ABSTRACT

The results of vibrational spectroscopy studies of zeolites synthesized from expanded perlite using hydrothermal method were presented. The starting material used was a waste obtained during the production of expanded perlite. The effects of synthesis temperature and time, as well as NaOH concentration and solid to liquid ratio on the obtained products were determined. The resulting materials were analyzed regarding phase composition. In particular, the structures of materials were examined using FT-IR spectroscopy in the middle and far infrared ranges as well as Raman spectroscopy. The results were compared to the XRD and XRF measurements, as well as SEM observations.

It has been found that by using a sufficiently high concentration of NaOH, it is possible to efficiently synthesize zeolite at temperatures above 50 °C. The presence of zeolite phase was confirmed by the measurement of spectra. Pseudolattice range, i.e. 800–400 cm^{-1}, was analyzed in detail. In this range, bands associated with the ring vibrations occur. They are characteristic for secondary building units (SBU) existing in zeolite structure. Depending on time, temperature and NaOH concentration, zeolite X, A, Na-P1 and hydroxysodalite have been identified as synthesis products in autogenous pressure.

1. Introduction

Zeolites are aluminosilicates characterized by unique physical and chemical properties, which show a very wide range of applications. In view of the high demand for commercial use, zeolites are produced on a large scale. By heating aluminosilicate materials in presence of alkaline solutions it is possible to obtain a final product in a few hours or days, depending on the type of raw materials and process conditions (temperature, pressure). The crucial factor for the formation of different types of zeolites is undoubtedly the chemical composition of the starting material, in particular, the presence of silica and alumina. However, the process conditions such as: pH of the reaction solution, the temperature, pressure and treatment time, as well as the degree of fineness or mixing, and other factors influence the course of crystallization in systems having the same chemical composition [1]. Some properties of the zeolites may be controlled during synthesis, including a type of obtained structure, SiO_2/Al_2O_3 molar ratio, pore size or density of the structure.

Various aluminosilicate materials can be used in the synthesis of zeolites; among other natural materials such as: kaolinite [2], perlite [3–6], pumice [7,8], rice hulls, diatomite, fly ashes [9–11], etc. The current trends in research on the synthesis of zeolites are shaped by environmental aspect [12–14] – it is assumed that waste materials can be used for this purpose. Inter alia, the waste (subgrain) obtained in the production of expanded perlite can be applied here, particularly due to their aluminosilicate composition as well as expected high reactivity in an alkaline environment. However, due to the variable composition of raw materials, and thus formed products, the syntheses of zeolites from waste materials are difficult to control and describe.

Infrared spectroscopy is a method widely used in the investigation of aluminosilicates and can be successfully used for the analysis of the zeolites [15,16]. Both IR and Raman spectroscopy are very helpful methods for determining of zeolite structure types and studying the structural details. Analyzing the pseudolattice region of the spectra, it is possible to identify secondary buildings units (SBU) of zeolite framework, which comprise rings and double rings of tetrahedra [17]. Other structural information obtainable from the infrared spectrum is the Si/Al ratio. Additionally, infrared spectroscopic studies provide information about short and medium-range order of the structure, which makes them one of the most important tools used for this type of description, especially if the presence of an amorphous phase can be expected [18–20]. Among other things, vibrational spectroscopy studies

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are particularly useful in the analysis of synthesis products – a perfect example would be the synthesis of zeolite materials from fly ash, e.g. [21–23].

The aim of this work is to examine usefulness of IR and Raman spectroscopy in the description of the synthesis of zeolites from waste materials, for example, expanded perlite. An attempt to determine the correlation between the obtained vibrational spectra and the hydrothermal synthesis product formed under different conditions was taken.

2. Experimental

By-product derived from an expanded perlite production process (particle size < 0.4 mm) was used as the starting material. XRD analysis confirmed that the phase compositions are mainly amorphous aluminosilicate phase. The results of quantification of starting material normalized to 100% (X-ray fluorescence spectrometer (WD-XRF) Axios mAX 4 kW, PANalytical) were as follows (in wt.%): SiO_2 – 75.39%, Al_2O_3 – 13.36%, Na_2O – 4.61%, K_2O – 4.11%, Fe_2O_3 – 1.22%, CaO – 0.97%, MgO – 0.11%, and others – 0.23%.

The synthesis was carried out by mixing the perlite with aqueous solution of sodium hydroxide in the concentration range 0.5–5.0 mol/dm^3. The solid-to-solution ratio was maintained at 1:15 (g/ml). Crystallization was conducted in closed vessels (the water content was maintained unchanged upon the process). The amount of sodium in the ration system calculated on SiO2/Na2O was 2.79–0.33. The reactions were performed under atmospheric pressure. Different temperatures in the range: 30–90 °C, for 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 measuring time was 4 h per sample, in the range of 10–90 (2θ) and step over was 0.008°. Morphology and crystal size were studied by scanning electron microscope FEI Nova NanoSEM 200 (Samples were sputtered with graphite).

The existence of zeolite frameworks was confirmed by analysis of the spectra in the middle and far infrared. For comparison, the spectra of pure minerals (zeolite Y and sodalite) have been measured. Spectra were measured on Bruker VERTEX 70v vacuum FT-IR spectrometer using the standard KBr or polyethylene pellets methods for MIR and FIR spectra, respectively. They were collected in the region of 4000–100 cm^{-1} after 128 scans at 4 cm^{-1} resolution. Precise estimation of the number of bands and their intensity changes is possible after decomposition of the spectra into component bands. Spectra decomposition has been carried out using Spectra-Calc (Galactic Industries Corp.) program. For all the spectra, the baseline correction has been carried out before the decomposition process.

Raman spectra were collected in the region 1400–100 cm^{-1} through a confocal Raman microscope coupled to a single grating LabRAM HR800 spectrometer equipped with a notch filter and a CCD camera detector. Measurements were performed in backscattering geometry with the 532 nm green line, diode laser (laser power at the sample ~8 mW), as excitation, a laser spot size of ~1 μm in diameter and a resolution of <1 cm^{-1} (grating 1800 gr/mm).

3. Results and discussion

Influence of NaOH concentration and temperature on the amount and type of zeolitization products was analyzed. Examples

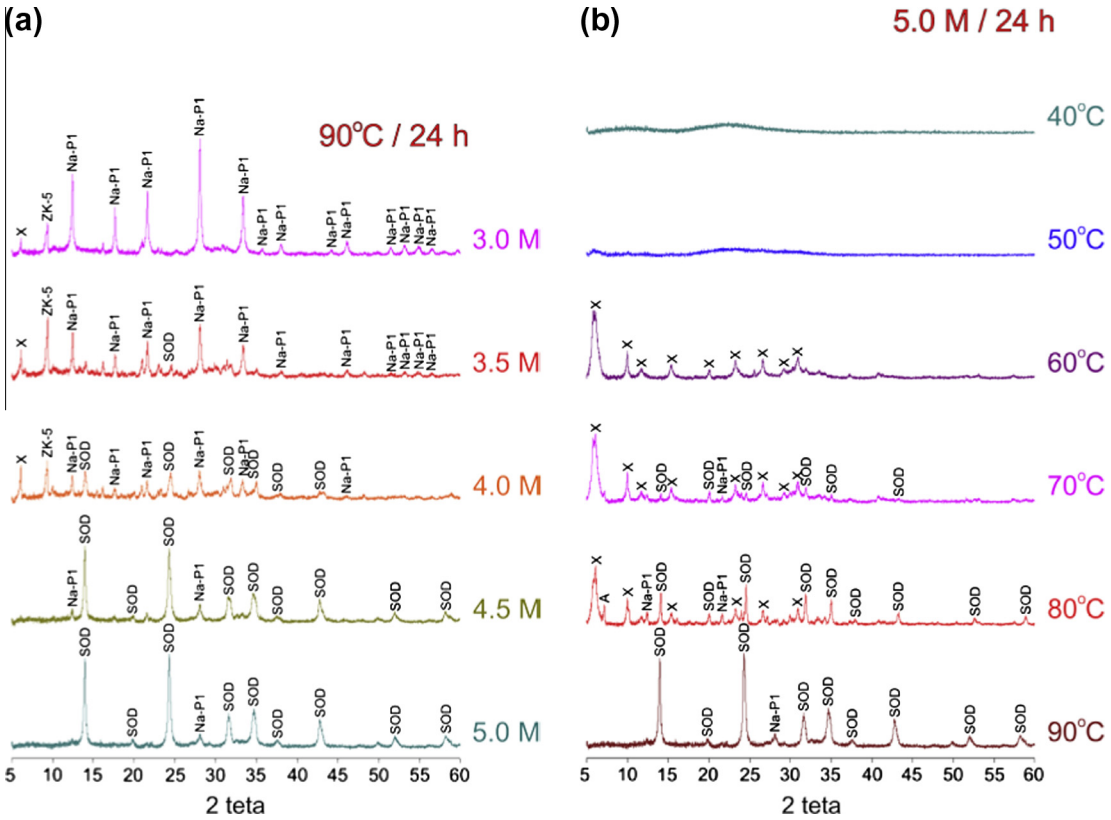

Fig. 1. XRD patterns of the obtained samples: (a) depending on NaOH concentration (90 °C, 24 h); (b) depending on temperature (5.0 M NaOH, 24 h). The abbreviations: X – zeolite X, A – zeolite A, ZK-5 – zeolite ZK-5, Na-P1 – zeolite Na-P1, SOD – sodalite.