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Influence of the reaction time on the crystal structure of Na-P1 zeolite obtained from coal fly ash microspheres

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ABSTRACT

This paper presents a study of the influence of time on the mineral structure formation of GIS Na-P1 zeolite. Lightweight microspheres were used as a source of silica and aluminium. Material subjected to this study was synthesized on a quarter-technical scale using a prototype installation. Chemical, mineralogical, and textural properties of the material were determined by means of X-Ray diffraction (XRD), X-Ray fluorescence (XRF), scanning electron microscopy equipped with a system of chemical composition analysis based on energy dispersive X-ray (SEM–EDS), volumetric adsorption analyzer (ASAP 2020), Fourier transform infrared spectroscopy (FTIR) and particle size analyzer (PSA). Experimental calculations based on Miller indices show the interesting and indeed astonishing phenomenon of the lattice parameters ripening as a function of time. Both unit cell parameters (a, b, c and volume) and the amount of zeolite present increase with synthesis time. This process is clearly observed using the XRD and FTIR method. Structural, morphological and textural properties of the final product indicate that it could potentially be useful as an adsorbent for various types of environment pollution.

1. Introduction

The energy industry is one of the major sources of environment pollutants. The branch of this sector that deals with coal combustion generates significant amounts of waste, referred to as coal combustion by-products (CCPs). CCPs include slugs, slug–ash mixtures, ashes and microspheres, which are all very harmful to earth ecosystems [1]. A microsphere (MIC) is a post combustion by-product that occurs mainly in fly ash (FA) and less often in slug mixtures. MIC is produced during coal combustion processes in pulverized-fuel boilers. The strongly-dispersed mineral substance melts with increasing temperature. After reaching a temperature of about 1200 °C, the mineral particles adopt a spherical shape under the influence of surface tension forces. These particles are capable of forming glassy phases and eutectic mixtures (aluminosilicates, clays, quartz, feldspar). Simultaneously, cavities are formed within the newly formed spherical particles, due to the release of the combustion gases. The structure of the MIC particles then stabilizes [2]. The MIC is composed of both crystalline and amorphous aluminosilicate and mullite phases, the contribution of which depends on the conditions of the combustion process. Morphologically, MIC occurs as the smallest, hollow, spherical particles within the fly ashes. The MIC wall thickness usually oscillates from 2 to 30 μm, which is 5–10% of the sphere diameter [3,4]. Its mineral and chemical composition is very similar to F-type fly ashes. Both are aluminium and silicon carriers [5], which allows MIC and FA to be classified as potential substrates for zeolite synthesis [6].

Synthetic zeolites are defined as crystalline, porous, aluminosilicate, inorganic polymers consisting of a three-dimensional system [7]. In general, they are made from interlinked tetrahedrons of alumina (AlO_4) and silica (SiO_4) with alkali or alkaline–Earth metals such as sodium, potassium and magnesium [8,9], acting as charge balancing cations. Atoms of Al^{3+} and Si^{4+} may be substituted by other tetrahedral elements (T). When some Si^{4+} atoms are substituted heterovalently, the whole frame achieves a net negative charge. This charge is compensated for by cations present in the structure channels. The specific zeolite crystal structure is a result of the spatial bonding of primary building units (PBUs), which are SiO_4 and AlO_4 tetrahedrons. These tetrahedrons, through bonding with oxygen bridges to form larger systems, are defined as secondary building units (SBUs). Within SBUs, various kinds of structural rings occur. The connection of SBUs with free corners results in characteristic channels and chambers, called cavities, which create zeolites porosity [7, 10]. The general crystallochemical formula for minerals from aluminosilicate zeolite group has the form: $Me_{x/n} = [Al_xSi_yO_{2(x+y)}]\cdot zH_2O$; Me – exchangeable metal

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cations with n valence (generally they are alkali or alkaline-Earth metals e.g.: Na^+, K^+, Ca^{2+}, Mg^{2+}, Sr^{2+}, Ba^{2+}), y:x – Si:Al ratio. It is between 1 and 5. x:z – number of water molecules.

The specific structure of zeolites carries a number of important features, including ion exchange, adsorption, molecular sieves or catalytic properties [6]. This makes zeolites useful in wide range of applications, such as environmental protection [11,12], catalysis [13], the aquaculture industry [14] and building materials [15,16]. Due to the ion-exchange and sorption properties of zeolites, they are also used in water purification [9, 17, 18], clean-up of petroleum spills [19], water vapour adsorption processes [20] and gas sorption [21–23]. The commercial application is still limited because of the powdered form of synthetic zeolites derived from fly ash. Efforts focused on suitable binder assortment and the development of an effective and efficient granulation process are currently in progress.

Synthetic zeolites may be obtained from numerous types of materials. Potential substrates must be rich in aluminium, silica or aluminosilicate phase. The aluminium and silica carriers for zeolite synthesis are natural minerals such as kaolinite [24,25], pumice [26], obsidian [27], diatomite [28], diatomaceous earth [29], and some waste materials including coal fly ashes [30,31], perlite [32], rice husk fly ash [33,34] and discarded electronics devices [35]. These substrates are conventionally converted into zeolites through thermal or hydrothermal treatment in an alkaline medium.

The recent literature certainly does not exhaust the issue of using MIC as a substrate in the hydrothermal synthesis of zeolite material [32,36]. Previous studies focused on the synthesis conditions and development, and on their influence on the mineral composition of the final product. However, there are limited studies focused on the impact of the synthesis conditions (time, substrate concentration, mixing rate, etc.) on the unit cell parameters and on the textural parameters. These are important characteristics to assess the efficiency of the zeolite synthesis process.

The aim of this study was to convert a MIC from Stalowa Wola Power Plant (Poland) into Na-P1 zeolite. The synthesis process was implemented on a quarter–technical scale in a prototype installation [30]. The effect of the conversion time on the resultant Na-P1 zeolite material properties has been investigated. Experimental calculations of the unit cell parameters were used in an innovative way to observe the Na-P1 zeolite structure evolution as a function of reaction time. This may allow to use it as an additional factor in the optimization of the process parameters in the quarter-technical installation.

2. Experimental

2.1. Materials

A microsphere fraction (MIC) concentrate was obtained from the combustion of coal at Stalowa Wola Power Plant (Poland). The microsphere used in this research was obtained from fly ash through the wet method separation. The method is based on the sedimentation process, using significant differences in the density of individual fly ash fractions. The microsphere is characterized by a much lower density (about 0.69 g/cm^3) in relation to other fractions in fly ash (about 2.1 g/cm^3), which makes it easy to separate. Sodium hydroxide used in the zeolite synthesis was purchased from STANLAB.

2.2. Experimental method

The Na-P1 synthesis procedure was performed according to a method previously described by Wdowin et al. [30]. 90 dm^3 water solution of 3M sodium hydroxide (NaOH) was heated to 80 °C in a reaction vessel. 15 kg of raw MIC was then added to the heated NaOH solution and the reaction time was set up to 26 h. The synthesis process was performed at atmospheric pressure. During the conversion, samples were collected from the reactor after 2, 4, 6, 10, 14, and 26 h (h) [37]. To investigate the influence of time on zeolitization process efficiency, the sampled materials were analysed in terms of their chemical and mineral composition, as well as their structural and textural properties. The most attention was given to the evolution of the Na-P1 unit cell parameters observed as a function of time.

2.3. Characterization methods

The phase composition was determined with the powder X-ray diffraction method (XRD) using a PANalytical X'pert MPD diffractometer (with a PW 3050/60 goniometer), Cu lamp, and a graphite monochromator. The analysis was performed within the angle range of 5–65 °2Θ. PANalytical X'Pert Highscore software was used to process the diffraction data. The identification of mineral phases was based on the PDF-2 release of the 2010 database formalized by the ICD and on the IZA-SC Database of Zeolite Structures. The experimental calculations of the unit cell parameters were performed using UnitCell software. The spatial model of Na-P1 zeolite cell was prepared using Mercury 3.7 Windows software.

The morphological forms and the chemical composition of the main mineral components were determined by means of a scanning electron microscope (SEM) FEI Quanta 250 FEG equipped with a secondary electron detector and a system of chemical composition analysis based on the energy dispersive X-ray-EDS of the EDAX company.

Chemical analysis was performed with the energy dispersive X-ray fluorescence method (EDXRF), using the Epsilon 3 PANanalytical spectrometer with RTG Rh 9W, 50 kV, and 1 mA lamp. The analysis ranged from Na to Am. The sample was air-dried.

N_2 adsorption–desorption measurements were carried out at 77 K in the range of relative pressure p/p_0 from 0.01 to 0.99, using the ASAP 2020 volumetric adsorption analyzer (Micromeritics). The specific surface areas (S_{BET}) of the samples were evaluated using the standard Brunauer-Emmett-Teller (BET) method for nitrogen adsorption data [38,39]. The method "t" [40,41] was used to calculate the surface and volume of mesopores and micropores. The total pore volumes were estimated from single-point adsorption at a relative pressure p/p_0 of 0.99. The average pore diameters and the average mesopore diameters were calculated as well. Additionally, the micropore volumes were calculated with the Dubinin-Radushkevich theory [42,43].

Fourier transform infrared spectroscopy (FTIR) analysis was done using the DRIFT technique in the 4000-400 cm^{-1} spectral range at 4 cm^{-1} resolution with 64 scans (Thermo Scientific Nicolet 6700 spectrometer).

Particle size analysis was performed using laser diffraction technique on Mastersizer 3000 (Malvern) apparatus.

3. Results

3.1. XRD results

The XRD results indicate that the raw microsphere is composed mainly of amorphous aluminosilicate glass, mullite and quartz. Significant increase of background in the 15–40 °2Θ angular range suggested a substantial amount of the amorphous phase. Quartz and mullite phases are represented by a set of diffraction peaks corresponding to characteristic d_{hkl} values, for quartz (3.34, 4.25, 1.81, 2.45, 2.28, 2.12, 1.54, 1.38) and for mullite (3.37, 3.42, 2.20, 2.54, 5.37, 1.52, 2.68, 1.44, 2.29, 2.89). The peaks at 2.69, 2.51, 1.69, 1.84 and 1.48 also indicate an insignificant amount of iron oxides in the sample (Fig. 1).

XRD patterns indicate that the monomineral zeolitic phase was present in all of the obtained materials. The first weak peaks corresponding to Na-P1 zeolite appeared already after 4 h of the synthesis. This zeolite is represented by the following set of diffraction peaks: 3.17, 7.10, 4.10, 5.02, 2.68, 2.36, 1.96, 2.89 when compared with the Na-P1 zeolite XRD standard pattern, reference no. 00-039-0219 from