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Synthesis and structure of analcime and analcime-zirconia composite derived from coal fly ash cenospheres

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ABSTRACT

Cubic analcime and analcime-zirconia composite with the Si/Al ratio of 2.04 and 2.16, respectively, was synthesized by hydrothermal treatment of coal fly ash cenospheres (Si/Al = 2.7) at 150 °C. The scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS), powder X-ray diffraction (PXRD), X-ray photoelectron spectroscopy (XPS), synchronous thermal analysis (STA) methods were used to study the morphology, composition and structure of the products. Two main types of analcime bearing particles were obtained, such as hollow microspheres with attached analcime icositetrahedra of 5–50 μm in size and individual analcime crystals of a narrow particle size distribution ($D_m = 41$ μm) with incorporated zirconia (4.8 wt% Zr). The high quality of the crystalline fractions allowed an accurate full-profile PXRD analysis of complete analcime crystal structure and composition including anisotropic displacement parameters of all atoms and H-positions of water molecules.

1. Introduction

Analcime (ANA) is a natural occurring zeolite with a tetragon-trioctahedron habit which has a typical unit cell composition of $Na_{16}[(AlO_2)_{16}(SiO_2)_{32}]\cdot 16H_2O$ with a Si/Al molar ratio of 1.8–2.8 [1,2]. For its synthetic analogs the Si/Al ratio varies in a more wide range (1.5–3.0) depending on the cation nature, Si and Al sources, and conditions of synthesis [3]. Analcime has a 3-dimensional system of non-intersecting channels with the pore openings of 2.6 Å composed of four-, six- and eight-membered oxygen rings. High symmetry icositetrahedral morphology of analcime crystals is attractive for designing novel materials of a regular polyhedron form [4–6].

Due to minimal pore entrances compared to other zeolites, analcime is useful in separation of light gas/hydrocarbon mixtures, e.g. H_2/C_3H_8, based on the molecular sieving effect [7]. Synthetic analcimes, pure and metal (Mn, Ti, V) modified in T-positions, are efficient in a heterogeneous catalysis, e. g. cyclohexene oxidation in a liquid phase [8], and an ion exchange for removal of heavy metals from wastewater [9]. Analcime is the object of some studies in relation to the problem of nuclear waste disposal [10–14]. This narrow-pore zeolite can be used in nuclear waste burial as a sorptive barrier for radioactive elements because of its ability to bind actinide cations (U^{4+}, Th^{4+}) by sorption irreversibly providing the reliable immobilization of toxic metals [10]. The similarity of framework topology of analcime and pollucite, $(Cs_{1-n},Na_n)(H_2O)_n[AlSi_2O_6]$ [2], is the basis of methods for incorporation of radioactive ^{137}Cs in ANA phases resulting in pollucite or pollucite-analcime solid solutions [11–14].

Numerous studies are concerned with transition metal modified (exchanged/impregnated) zeolites as precursors of aluminosilicate-based ceramics including electronic ceramics [15] and ceramic bodies for electromagnetic shielding [16]. Zr bearing zeolites are of particular interest because they can be converted to refractory zirconia-aluminosilicate ceramic materials [17] having a potential as a chemically stable radioactive waste form [18]. Two kinds of Zr bearing zeolite precursors can be considered, such as zeolites modified at an atomic level by Zr^{4+} incorporation in T-sites or

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cation positions, and zeolite based composites with Zr bearing matter embedded in the zeolite body. As for the analcime based precursor, the incorporation of large Zr atoms (R = 0,72 Å) in the dense analcime lattice and extra-framework positions is hardly probable due to the restrictions of bond lengths [1]. The Zr incorporation in the analcime body as a Zr bearing matter has not been reported yet.

Traditionally hydrothermal methods are applied to synthesize zeolites of different topologies starting from alkaline solution of pure chemicals (e.g. sodium silicate, sodium aluminate) [19]. As it was reported by Fang et al. [5], the lower rate of glass dissolution compared to that of gel or fine chemicals provides large analcime crystallites of up to 600 μm by hydrothermal treatment of sodium aluminosilicate glass at 150–210 °C.

The cost-effective synthetic routes to analcime are based on conversion of available natural and technogenic raw materials, such as clay minerals (Si/Al = 1.4) [8], coal fly ash (Si/Al = 1.6) [20], natural clinker (Si/Al = 2.5–3.0) [21], quartz syenite (Si/Al = 3.7) [22], and volcanic glass perlite (Si/Al = 4.6) [23]. However, most of the sources didn't provide a high purity of the analcime product containing the additional zeolite phases (GIS, CAN, FAU, etc.).

Recently, coal fly ash cenospheres (CFAC) were considered for synthesis of low-siliceous zeolites without seeding and templating as an alternative aluminosilicate source of the sphere shaped morphology and glassy structure with the appropriate silica-alumina composition (Si/Al = 1.1–2.9) [24–26]. The CFAC properties have been found to be suitable for their use as a template core and a Si and Al source in the zeolite synthesis. The advantage of this approach is possibility to use CFAC of required chemical and phase composition provided by separation of a CFAC concentrate on the basis of differences of individual globules in size, density, and magnetic properties [27–29]. In most cases the direct transformation of the CFAC material, in dependence on reaction parameters (temperature, duration, alkaline concentration, solid-to-liquid ratio), results in zeolitic phases of different structural types, such as NaX (FAU, JCPDS 12–0228), NaA (LTA, JCPDS 43–0142), NaP1 (GIS, JCPDS 40–1464), chabazite (CHA, JCPDS 12–0194), analcime (ANA, JCPDS 19–1180), and/or hydroxysodalite (JCPDS 11–401) [25]. Among them, only zeolite NaP1 was shown to crystallize as an individual phase under certain conditions (T = 100–120 °C, 1.5–2.5 M NaOH) [25,26]. As it has been noted by Vereshchagin et al. [25], analcime crystallized at elevated temperatures (T > 150 °C) but detailed results on zeolite formation from CFAC under temperatures higher than 120 °C were not reported anywhere.

In this paper, we report the hydrothermal synthesis of analcime and zirconia bearing analcime at 150 °C starting from CFAC with Si/Al = 2.7, characterization of their structure, composition and morphology by PXRD, SEM-EDS, XPS and STA.

2. Experimental

2.1. Chemicals and materials

Chemicals used in this work were of reagent grade quality obtained from the commercial supplier (OOO "Reactiv", Russia) and used without further purification.

The CFAC material used for the analcime synthesis was fraction −180 + 80 μm having a bulk weight of 0.38 g cm^{-3} and a specific surface area of 0.2 m^2 g^{-1} which was provided by the separation procedure of a CFAC concentrate resulted from combustion of Kuznetsk coal (Russia) at Tom-Usinskaya power plant (Kemerovo region, Russia) as it was reported earlier [27]. Chemical and mineral compositions of the initial CFAC material are summarized in Table 1. A total overview of the CFAC globules is shown in Fig. 1.

2.2. Synthetic procedures

Analcime was synthesized by hydrothermal treatment of a reaction mixture comprising of 10 g CFAC and 133 mL 1.5 M NaOH with 1.0 SiO_2/0.18 Al_2O_3/0.89 Na_2O/65 H_2O molar composition and liquid-to-solid (L/S) ratio of 5/1 (v/v). The reaction mixture was crystallized in a Teflon-lined stainless steel autoclave at 150 °C for 68 h under stirring by rotation of the autoclave (30 rpm). The grey solid phase (GS) was then washed several times with distilled water, filtered and dried at 65 °C for 24 h. The output of the solid calculated relative to the mass of initial CFAC was 81%. The subsequent separation of the GS product by particle sizes was done using sieves with apertures of 36 μm, 71 μm, 100 μm and 224 μm. Samples GS > 224 μm, GS 100–224 μm, GS 71–100 μm, GS 36–71 μm and GS < 36 μm were isolated by sieving the GS product with yields of 1.4, 49.0, 18.9, 28.5 and 2.2%, respectively.

Zirconia bearing analcime was synthesized by hydrothermal treatment of CFAC in sodium alkaline solution in the presence of zirconium (IV) citrate ammonium complex used as a Zr source. In a typical synthesis, 5 g zirconium (IV) citrate ammonium complex was added to 133 mL 1.5 M NaOH solution upon stirring at room temperature followed by addition of 10 g CFAC resulting in the reaction mixture of 1.0 SiO_2/0.18 Al_2O_3/0.89 Na_2O/0.15 ZrO_2/65 H_2O molar composition with L/S ratio of 5/1 (v/v). The mixture was transferred into the Teflon-lined stainless steel autoclave for crystallization by heating the suspension at 150 °C for 48 h under stirring by rotation of the autoclave (30 rpm). The white-and-grey solid (Zr-WGS) product was separated by filtration, washed with distilled water several times until neutral reaction of a supernatant occurred followed by centrifuging the suspension. Two layers were visually identified in centrifuge test tubes as white (Zr-WS) and grey (Zr-GS) solids, each of which was recovered and then dried at 65 °C for 24 h. The outputs of the Zr-WS and Zr-GS solids calculated relatively the mass of initial CFAC was 32 and 10%, accordingly. Each layer was additionally separated into fractions by particle sizes using sieves with apertures of 36 μm and 71 μm resulting in samples Zr-WS <36 μm, Zr-WS 36–71 μm with yields of 29 and 71%, respectively, and Zr-GS >71 μm, Zr-GS <36 μm with yields of 97 and 3%, respectively.

2.3. Characterization techniques

Chemical composition of CFAC fraction was determined according to State Standard (GOST) No. 5382-91 [30].

Powder X-ray diffraction data were collected on a PANalytical X'Pert PRO (Netherlands) diffractometer equipped with a solid state detector PIXcel using Cu Kα radiation over the 2θ range 12–120°. The samples were prepared by grinding with octane in an agate mortar and packed into a flat sample holder for the PXRD measurements in the Bragg-Brentano geometry. The full-profile crystal structure analysis was done using the Rietveld method [31] with the derivative difference minimization (DDM) [32] refinement.

Morphologies of product particles were identified by scanning electron microscopy (SEM) using TM-1000 and TM-3000 (Hitachi, Japan) instruments. To study elemental composition of surfaces and polished sections of analcime particles the SEM-EDS examination was performed using the TM-3000 microscope equipped with the Bruker microanalysis system including an energy-dispersive X-ray spectrometer with a XFlash 430 H detector and QUANTAX 70 software. The polished sections of analcime particles were prepared by fixing in an epoxy resin with successive grinding and polishing with the use of STRUERS materials and equipment