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Preparation of small analcime particles with narrow size distributions from acid-treated larger analcime particles

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ABSTRACT

Narrowly size distributed analcime particles of 0.38–3.7 μm were hydrothermally synthesized from alkaline synthesis mixtures containing seeds of acid-treated larger analcime particles (25 ± 4.2 μm). Treatment of the larger particles with dilute HCl (~0.5 N) led to fine cracking as aluminium dissolved; more concentrated HCl (>3.0 N) led to larger cracks and particles' breaking. The acid-treated analcime particles dissociated into small zeolite domains in the alkaline synthesis mixture and acted as seeds to grow analcime particles. Seeds prepared with 1.0 N HCl grew into analcime particles of 0.38 ± 0.03 μm; the use of 4.0 N HCl resulted in analcime particles of 2.7 ± 0.07 μm. The analcime particles' sizes could be controlled through the concentration of HCl used in the preparation of the seeds. Narrow particle size distributions arose due to the seeds in the synthesis mixtures and the rapid hydrothermal growth of analcime particles.

1. Introduction

Zeolites are widely used as catalysts, adsorbents and detergent builders [1–4]. Their frameworks determine the size and shape of their pores and their Si/Al molar ratios determine their acidity and hydrothermal stability. While both properties fundamentally affect their applicability, the size and shape of zeolite particles also strongly influence their performance. Small particles reduce the diffusion length of materials in catalytic reactions and adsorption, resulting in better performance. However they are difficult to recover from slurry and suffer from high pressure drops in packed beds, limiting their applicability. Therefore for optimized performance, zeolites require finely controlled particle sizes.

Zeolite particles are grown from nuclei by crystallization and the concentration of nuclei in synthesis mixtures usually governs the particle size distributions of the resulting zeolites [5–7]. Since ageing synthesis mixtures at ambient temperature allows many nuclei to form but suppresses crystals' growth, it can result in high concentrations of nuclei that produce small particles with narrow size distributions [8,9]. Small zeolite particles can be added to synthesis mixtures to act as seeds to facilitate the rapid production of uniformly size distributed zeolite particles [10–14]. A synthesis mixture's composition and crystallization conditions influence the size distribution of the resulting zeolites by controlling the rates of nuclei formation and crystal growth [15,16]. The control of zeolite particles' size distributions by ageing, seeding and adjusting reaction conditions is largely based on experimental investigation rather than theoretical calculation and therefore requires much work to achieve suitable particle sizes. The effect of seeding for an synthesis mixture of analcime on the size distribution of its particles may be very definite when a pure analcime cannot be obtained from the synthesis mixture without seeding.

Analcime is a natural zeolite of ANA topology with a Si/Al molar ratio of *ca.* 2.0 [17]. Its small pore entrances comprise bent eight membered rings (8MR) of oxygen atoms that suppress even the adsorption of small, straight hydrocarbons, making its only reported industrial application as the adsorbent in the separation of hydrogen/propane mixtures [18]. Hydrothermal reactions of alkaline aluminate-silicate mixtures can easily produce polyhedral analcime particles. Large, heterogeneous particles of 60–600 μm can result from hydrothermal reactions of dissolved glass at 150–210 °C [19]. The transformation of zeolite Y in aqueous media at low temperature and without organic template provides ANA crystals with regular icositetrahedron of 3–7 μm [20]. The transformation of perlite to analcime particles by treatment with NaOH solution was also reported [21]. Although small analcime particles with narrow size distributions can enhance adsorbents' separation ability, the synthesis of small, uniformly sized analcime particles are not well reported. However, the seeding of efficient amounts of analcime into the synthesis mixtures may result in producing small particles with a narrow size distribution. The nuclei concentrations of the synthesis mixtures actually correspond to the sizes of produced analcime particles.

The selective removal of aluminium from zeolite frameworks by acids divides the particles into small zeolite domains separated by silica-rich regions, while maintaining the zeolite framework. When acid-treated zeolites are added to synthesis mixtures, alkaline

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species dissolve the silica-rich regions and disperse the zeolite domains. Treating zeolites with dilute acid produces many fine cracks in the particles and treatment with concentrated acid results in larger cracks. The acid treatment of analcime particles can therefore provide a facile preparation method of uniformly sized analcime particles. The number of seeds in a synthesis mixture can be controlled by varying the concentration of acid.

This work reports the preparation of seeds for the synthesis of small and uniformly sized analcime particles by the acid treatment of 25 μm analcime particles. The concentration of acid determined the number of seeds resulting from the large analcime particles. The acid-treated analcime particles were added to synthesis mixtures and subsequently crystallized rapidly at elevated temperatures to suppress further nucleation and allow precise engineering of the analcime particles' size. Particles were reliably produced with specific size distributions, demonstrating the utility of acid-treated analcime seeds.

2. Experimental

2.1. Synthesis of large analcime particles and acid treatment

Analcime particles were synthesized from sodium silicate solution (Daejung, 30 wt.% SiO_2), sodium aluminate (Junsei, 56 wt.% Al_2O_3), and sodium hydroxide (Daejung, 98%). Large analcime particles (ANA_parent; average diameter, 25 μm) were hydrothermally synthesized from a synthesis mixture comprising $8.0Na_2O{:}1.0Al_2O_3{:}11.5SiO_2{:}900H_2O$. The synthesis mixture was crystallized in a Teflon-lined stainless steel autoclave at 150 °C for 2 days under static conditions. The solid phase was then washed several times with deionized water and dried at 100 °C for 12 h.

The analcime seeds were prepared by the acid treatment of ANA_parent with 0.5–5.0 N HCl (Daejung, 35%) under reflux at 90 °C for 2 h. The seeds were labelled 'ANA_Ax', with 'x' denoting the concentration of acid used in the acid treatment. For comparison, ANA_mortar was ground in a mortar by hand and ANA_ball was ground in a ball mill.

2.2. Synthesis of variously sized analcime particles

Analcime particles were synthesized by adding ANA_Ax seeds to a synthesis mixture comprising $25.0Na_2O{:}1.0Al_2O_3{:}11.5SiO_2{:}840H_2O$. The amount of seeds added was 1 wt.% of the total amount of the synthesis mixture. Hydrothermal reactions of the synthesis mixtures containing the seeds were at 170 °C for 3 h in a rotating oven at 100 rpm. The oven was ramped at 6 °C/min. The resulting zeolites were centrifuged, washed several times with deionized water and ethanol (Daejung, 99.9%) and sonicated. The synthesized analcime particles were labelled 'ANA_Fx', with 'x' denoting the concentration of HCl used in the preparation of the seeds.

2.3. Characterization of analcime particles

Particles' X-ray diffraction patterns were examined by high-resolution X-ray diffractometry (HR-XRD; PANalytical, X'Pert PRO Multi Purpose). Their crystallinity was determined from the relative ratio of the summed area of the peaks at $2\theta = 15.8°$, 26.0° and 30.5° to that of ANA_parent. Particles' morphologies and sizes were identified by scanning electron microscopy (SEM; JEOL, JSM-7500F) and their Si/Al molar ratio was calculated from the analysis results of acid-filtrates using an inductively coupled plasma mass spectrometer (ICP-MS; PerkinElmer, Nexion 300X). The Si/Al molar ratio of the large analcime was determined using an X-ray fluorescence spectrometer (XRF; PANalytical, Axios Minerals). Surface areas and pore volumes were obtained using an automatic volumetric adsorption measurement system (Mirae SI, NanoPorosity-XQ). The determination methods used for the measurements of micropore and mesopore volumes were Horvath-Kawazoe (HK) and Barrett-Joyner-Halenda (BJH) methods, respectively. Weight losses with increasing temperature were recorded by thermogravimetric analysis (TGA; Mettler Toledo, TGA/SDTA851^e). Temperature-programmed desorption (TPD) profiles of ammonia from the acid-treated ANA zeolites were recorded on laboratory-made TPD apparatus. Acid-treated analcime particles (0.1 g) were charged in the centre of a quartz reactor tube with an O.D. of 1/4 in. and pretreated in a 100 ml/min helium (Shinil, 99.999%) flow at 550 °C for 1 h. After cooling to 150 °C, the acid-treated analcime particles were saturated by adding pulses of ammonia (Korea gas, 99.999%). The physically adsorbed ammonia was removed by purging with a helium flow for 1 h. The temperature of the reactor was then increased to 850 °C at 10 °C/min and the desorbed ammonia was continuously monitored by mass spectrometry (Balzers, QMS 200).

3. Results and discussion

3.1. Acid treatment of ANA zeolite

The XRD pattern of ANA_parent (Fig. 1) was in good agreement with reported pattern [22]. SEM image show spherical particles with facets. The average particle size was 25 ± 4.2 μm and the Si/Al molar ratio was 2.3.

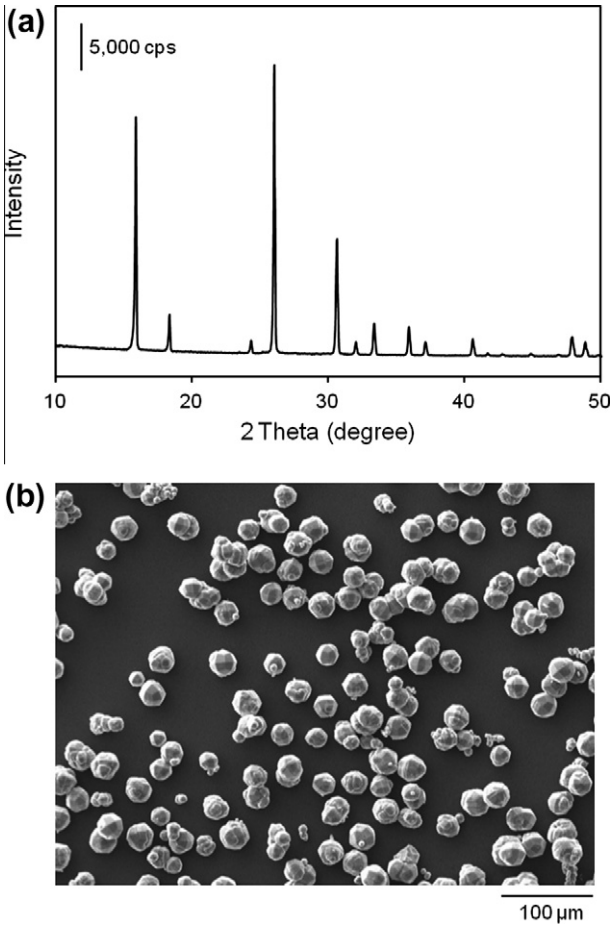

Fig. 1. (a) XRD pattern and (b) SEM image of ANA_parent.