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K-F zeolite nanocrystals synthesized from organic-template-free precursor mixture

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ABSTRACT

K-F zeolite nanocrystals (structure code EDI) are synthesized from a template-free Al_2O_3–SiO_2–K_2O–H_2O precursor system. The use of a very reactive organic-template-free gel system ($4SiO_2$: $1Al_2O_3$: $16K_2O$: $160H_2O$) enables the crystallization of EDI-type nanosized zeolite to accomplish within 3 h at 100 °C. The K-F zeolite crystals have flattened cuboid shape morphology (ca. 27 nm) and they tend to agglomerate and form secondary spherical particles (ca. 310 nm). The K-F zeolite nanocrystals have high alumina content (Si/Al ratio = 1.10) and high crystalline solid yield (79%) offering a promising route for large-scale production of hydrophilic zeolite nanoparticles.

1. Introduction

Zeolites are hydrated microporous aluminosilicates made from interlinked $[AlO_4]^{3-}$ and $[SiO_4]^{4-}$ tetrahedral units. Zeolites are widely used as catalysts, ion exchangers, adsorbents and molecular sieves due to their high surface area, acidity/basicity, molecular sieving and ion-exchange properties [1–3]. Particularly, nanosized zeolite crystals with crystallite size below 100 nm in at least one dimension have receiving tremendous scientific interest owing to their reducing diffusion path length and large external surface area, which affects their magnetic, optical, electrical and catalytic properties [4,5]. As a result, it expands the application of zeolites towards sensors [6], catalysis [7], lubricants [8], optical layers [9], drug delivery [10], medicine [11], etc. [4].

So far, a number of zeolite (LTA, MFI, MEL, LTJ, LTL, FAU, BEA, GIS, EMT, MOR, SOD) and zeotype (AFI, AEI, AFO, CHA, AEL) nanocrystals has been successfully synthesized [4,12–14]. In most cases, organic templates are introduced into the synthesis precursor to selectively direct the formation of zeolite structure and to control the size of zeolite crystals. The prepared precursors are then treated under supersaturation condition to enable nucleation to take place more readily than crystal growth [15]. This synthesis approach, which uses large amount of expensive organic templates, however, is a major source of waste and it has been found to pose hazards to human health and environmental safety. In respect to this, several strategies such as recycling of the non-reacted chemicals [16], ionothermal [14], seed-induced [17], post-milling recrystallization [18] and confined space synthesis [19,20] approaches have been used to overcome this challenge.

Recently, significant efforts have been devoted to the synthesis of zeolite and zeotype nanocrystals free of organic template [21–27]. Unlike conventional organo-templating method, the metal cations (e.g. Li^+, Na^+, K^+, Ba^{2+}, Cs^+, etc.) are added to the synthesis mixture as a structural directing agent (SDA) for controlling the phase and size of the final crystalline product. To date, there are 8 types of nanosized zeolites (EMT [21], FAU [22–24], GIS [28], LTA [29], LTJ [13], LTL [30], MOR [31], SOD [25]) that have been prepared free of organic templates. The use of this approach for

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synthesizing the zeolite nanocrystals is highly desired as it is cheap, non-toxic, environment-friendly and the crystals can be dispersed (stabilized) in colloidal suspensions. Hence, it is expected that the template free zeolites would be attractive for applications without the need of high temperature treatment (calcination).

Linde type F (structure code EDI) is a small-pore zeolite. This type of zeolite is interesting because it has three-dimensional pores interconnected by the apertures of two different types of 8-membered ring channel systems (diameter of 2.8 × 3.8 $Å^2$ and 2.0 × 3.1 $Å^2$) [32]. The naturally occurring Edingtonite and the synthetic Linde F zeolite have the EDI-type framework structure [33]. Several papers reported on the synthesis of EDI zeolites with micronsized crystals using various precursor suspensions such as $Li_2O–Al_2O_3–SiO_2–H_2O$ [34], $Li_2O–BaO–Al_2O_3–SiO_2–H_2O$ [35], $Li_2O–Rb_2O–Al_2O_3–SiO_2–H_2O$ [36], $Li_2O–Cs_2O–Al_2O_3–SiO_2–H_2O$ [36,37] and $(TMA)_2O–Li_2O–Al_2O_3–SiO_2–H_2O$ [37]. The synthesis of nanosized EDI-type zeolite, however, is still not yet reported and it is the basis of this study.

In this work, nanosized K-F zeolite with EDI-type framework topology is synthesized in organotemplate-free $K_2O–Al_2O_3–SiO_2–H_2O$ precursor system. The process of crystallization of the K-F nanocrystals is monitored by micropscopic and spectroscopic methods.

2. Experimental

2.1. Hydrothermal synthesis of nanosized K-F zeolite

The potassium-form Linde type F (K-F) nanozeolite was prepared as follows: Initially, aluminum hydroxide (5.791 g, 98%, ACROS Organic), potassium hydroxide pellets (19.217 g, 85%, QRëC) and distilled water (47.494 g) were added into a 125 mL polypropylene bottle. The mixture was magnetically stirred (400 rpm) at 105 °C for 16 h in order to obtain a clear aluminate solution. In addition, a clear silicate solution was prepared in another 250 mL polypropylene bottle by mixing potassium hydroxide pellets (39.013 g, 85%, QRëC), LUDOX HS-40 (16.567 g, 40%, Sigma-Aldrich) and distilled water (21.972 g) under continuous stirring (400 rpm). Both aluminate and silicate solutions were cooled down to room temperature. The aluminate solution was then added slowly into the silicate solution under vigorous stirring. The precursor suspension became viscous upon the addition of aluminate solution. Stirring by hand with a spatula was needed at the end of the mixing process in order to obtain a homogeneous gel mixture with a molar composition of $4SiO_2:1Al_2O_3:16K_2O:160H_2O$. The precursor gel was continuously stirred for an additional 10 min prior to subjected to crystallization at 100 °C. The crystallization was interrupted and the samples (15 mL) were taken out at different time intervals (10 min, 1.5, 2.3, 2.5, 3.0 and 16.0 h) throughout the hydrothermal process. The white solid products were isolated from the mother liquors *via* high-speed centrifugation (20,000 rpm, 30 min). The solids were continuously purified with distilled water until the final suspensions reached a pH of 8. The suspensions containing crystalline K-F nanoparticles were then freeze-dried.

2.2. Characterization of solids

The crystallinity and purity of the powder samples were analyzed using a PANalytical X'Pert PRO diffractometer with Cu-K_α monochromatized radiation (λ = 1.5406 Å). The samples were scanned with a step size of 0.02° and a scan speed of 0.2°/min. The degree of crystallinity was determined by evaluating the intensity of the three most intense XRD peaks at 2θ of 12.68° [110], 29.04° [112] and 30.2° [301], in comparison to a reference sample (K-F synthesized for 3 h). In addition, the crystallite size of the K-F zeolites was estimated by the Scherrer equation.

The morphological features and the crystal size of amorphous particles and zeolite nanocrystals were examined using a FEI Titan 80–300 transmission electron microscope (TEM) operating at an acceleration voltage of 200 kV. The size of the amorphous or crystalline single particles was determined by randomly counting of 50 particles through TEM observations obtained in different spot areas. The Si/Al ratio of samples was obtained using a Philips PW2404 XRF instrument. The infrared (IR) spectra of the solids were also recorded with a Perkin Elmer spectrometer (System 2000) within the range of 1400–400 cm^{-1} using KBr pellet technique (KBr: sample weight ratio = 200:1). ^{29}Si and ^{27}Al MAS NMR spectroscopy analyses were performed on a Bruker Avance 400 (9.4 T) spectrometer (TMS as a reference). For ^{29}Si solid state MAS NMR spectroscopy study, the measurements were carried out at 12 kHz and a single pulse excitation was used with a delay of 30 s. The spectra were obtained with a pulse length of 2.7 ms, a repetition time of 6 s and a contact time of 4 ms [38]. Each spectrum was obtained with 20,000 scans. For ^{27}Al solid state MAS NMR investigation, the measurements were performed at 104.2 MHz with a spin-rate of 7 kHz, pulse length of 1.9 μs and a relaxation time delay of 2 s. Each spectrum was obtained with 5000 scans. The porosity of amorphous and crystalline K-F zeolite samples were evaluated using a Micromeritics ASAP 2010 instrument. The powders (ca. 150 mg) were first dehydrated at 300 °C under vacuum overnight prior to sorption measurement at -196 °C.

3. Results and discussion

The synthesis of nanosized K-F zeolite was performed by first mixing of both transparent aluminate and silicate solutions under vigorous stirring. The resulting clear mixture solution slowly turned cloudy and became very viscous during the addition of aluminate solution into the silicate solution. This indicated that polymerization of aluminate and silicate monomers had been taken place. The gel was then subjected to hydrothermal treatment at 100 °C.

At 10 min, the precursor gel became less viscous and started to liquefy. A small portion of sample was withdrawn, centrifuged, washed and dried in order to obtain the solid product; 25.2% of solid yield was collected (Fig. 1). From the XRD analysis, the solid

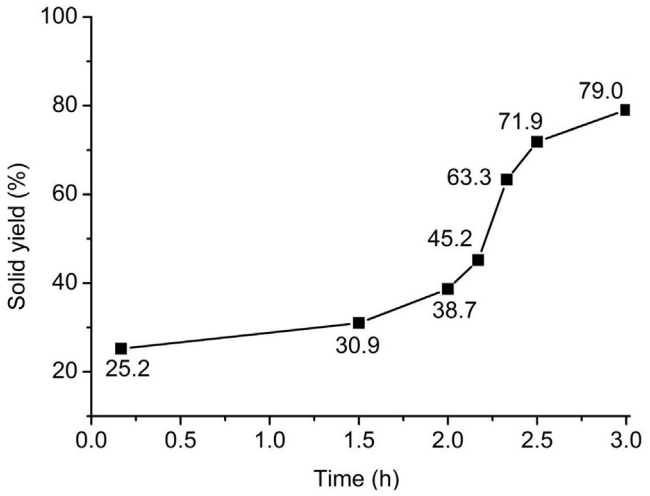

Fig. 1. Yield of solid samples collected after different time intervals of hydrothermal treatment at 100 °C.