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

Eng-Poh Ng, Dr.
K-F zeolite nanocrystals synthesized from organic-template-free precursor mixture

Siew-Fang Wong a, Hussein Awalab, Aurélie Vincenteb, Richard Retoux c, Tau Chuan Ling d, Svetlana Mintovab, Rino R. Muktie, Eng-Poh Ng a, *

a School of Chemical Sciences, Universiti Sains Malaysia, 11800, USM, Penang, Malaysia
b Laboratoire Catalyse & Spectrochimie, ENSICAEN, Université de Caen, 14000, Caen, France
c CRISMAT, University of Caen, 6, Boulevard du Maréchal Juin, 14050, Caen Cedex, France
d Institute of Biological Sciences, Faculty of Science, University of Malaya, 50603, Kuala Lumpur, Malaysia
e Division of Inorganic and Physical Chemistry, Institut Teknologi Bandung, Indonesia
f Research Center for Nanosciences and Nanotechnology, Institut Teknologi Bandung, Jl. Ganesha No. 10, Bandung, 40132, Indonesia

Article info
Article history:
Received 28 November 2016
Received in revised form
31 March 2017
Accepted 26 April 2017
Available online 27 April 2017

Keywords:
K-F, EDI
Zeolite
Nanocrystals
Template-free synthesis
Hydrothermal synthesis

Abstract

K-F zeolite nanocrystals (structure code EDI) are synthesized from a template-free Al2O3–SiO2–K2O–H2O precursor system. The use of a very reactive organic-template-free gel system (4SiO2: 1Al2O3: 16K2O: 160H2O) 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.

© 2017 Elsevier Inc. All rights reserved.

1. Introduction

Zeolites are hydrated microporous aluminosilicates made from interlinked [AlO4]3− and [SiO4]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, AEL, APO, 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+, Ba2+,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
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 Å² and 2.0 × 3.1 Å²) [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 micromoned crystals using various precursor suspensions such as Li₂O-Al₂O₃-SiO₂-H₂O [34], Li₂O-BaO-Al₂O₃-SiO₂-H₂O [35], Li₂O-Rb₂O-Al₂O₃-SiO₂-H₂O [36], Li₂O-Cs₂O-Al₂O₃-SiO₂-H₂O [36,37] and (TMA)₂O-Li₂O-Al₂O₃-SiO₂-H₂O [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 K₂O-Al₂O₃-SiO₂-H₂O precursor system. The process of crystallization of the K-F nanocrystals is monitored by microscopic 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%, QR/C), 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%, QR/C), 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 4SiO₂:1Al₂O₃:16K₂O:160H₂O. 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 liquor 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-Kα 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 crystal 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). 29Si and 27Al MAS NMR spectroscopy analyses were performed on a Bruker Avance 400 (9.4 T) spectrometer (TMS as a reference). For 29Si 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 27Al 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.
was amorphous and not even a broad line was discernible in the XRD pattern (Fig. 2a). The XRD result was consistent with the TEM observation where small particles with irregular shape with an approx. size 7.8 nm were formed. The solid yield slowly increased to 30.9% after 1.5 h of hydrothermal heating (Fig. 1). As shown, a broad amorphous band at \(2\theta = 25-35^\circ\) emerged in the XRD pattern indicating that structure re-arrangement of the solid had been occurred. In addition, the TEM image of this sample revealed that the morphology of the initial amorphous particles with irregular shape had transformed to worm-like feature and the particle size had increased to approx. 28 nm as a result of the polymerization of the inorganic oligomers.

The solid yield continuously increased with heating time and an abrupt increment of approx. 32.4% of solid product to 63.3% was observed at 2.3 h (Fig. 1). At this point, the precursor solution became less viscous. The XRD pattern of this solid sample revealed the appearance of several reflection peaks at \(2\theta = 12.74^\circ, 29.01^\circ, 30.17^\circ\) and \(31.81^\circ\), which were attributed to the [110], [221], [112] and [311] planes of the K-F nanocrystals, respectively [32]. The broadening of the Bragg peak was significant, thus revealing the small size of crystalline zeolite domains [39]. Furthermore, TEM analysis also evidenced the transformation of amorphous phase

---

**Fig. 2.** XRD patterns of solid samples extracted after (a) 10 min, (b) 1.5 h, (c) 2.3 h, (d) 2.5 h, (e) 3 h, and (f) 16 h of hydrothermal treatment at 100 °C. * indicates the presence of LTJ crystalline phase.

---

**Fig. 3.** TEM images of samples extracted after (a) 10 min, (b) 1.5 h, (c) 2.3 h, (d) 2.5 h, (e) 3 h, and (f) 16 h of hydrothermal synthesis at 100 °C. Insert of (e) and (f): enlarged area of TEM picture representing the size and morphology of the K-F individual particles.
into the K-F zeolite nanocrystals where the shape of the crystalline particles became more pronounced. The parent zeolite aggregates were sized from 180 to 254 nm, and were constructed of primary nanosized crystals with a flattened cuboid shape (approx. 15 nm) (Fig. 3c). The crystal size measured in TEM result was in line with the crystallite size estimated from the Scherrer equation (17.75 nm). Nevertheless, the amorphous entities were still dominated in the solid materials; only 11.3% of crystallinity was achieved. (Fig. 4).

Upon prolonging the crystallization time to 2.5 h, the solid yield increased to 71.9% and an abrupt increase in the degree of crystallinity from 11.1% to 90.6% was observed (Fig. 4). All the diffraction peaks corresponding to EDI crystalline phase appeared and became more intense [13] (Fig. 5b). Hence, it revealed that polymerization between silicate and aluminate species had taken place. Another IR band due to similar stretching vibration mode also started to form and detected at 1029 cm$^{-1}$, and the intensity of these bands kept increasing upon crystallization time. However, no significant change in the region of 800–400 cm$^{-1}$ was observed indicating that the zeolite crystalline phase had not yet been formed. With heating time prolonged to 2.3 h, the two bands corresponding to the zigzag 8-membered ring subunits appeared at 601 and 569 cm$^{-1}$. This indicated the beginning of the formation of EDI-type zeolite structure in line with the XRD and TEM observations. In addition, two weak signals attributed to the bending vibration of TO$_4$ and symmetric stretching of T–O–T were also detected at 430 and 653 cm$^{-1}$ [13] (Fig. 5c). These bands became more pronounced after 3 h of crystallization (Fig. 5e).

The $^{29}$Si and $^{27}$Al solid-state NMR spectra for samples extracted at different crystallization times were also recorded. The $^{29}$Si NMR spectrum of the sample after 10 min of heating is shown (Fig. 6a). A broad asymmetric signal at ~66.4 ppm was detected; two deconvoluted peaks were used to fit this peak where these two peaks were attributed to the amorphous phase composed of Si(OAl)$_n$Si$_{1-n}$ (n ≤ 4) [42]. In addition, the resonance at ~112.5 ppm was due to the pure amorphous silicate species such as silicon oxides [43]. The Si/Al ratio of this solid sample as revealed by XRF spectroscopy analysis was 1.37. Hence, the NMR and XRF spectroscopy data revealed that at 10 min of heating, all silica species were existed in monomeric and oligomeric silicate anionic forms (SiO$_2$ and AlO$_2$ tetrahedral linked through shared bridging oxygen atoms). These silicate species are the primary building units (PBUs) for the formation of the secondary building units (SBUs) prior to the development of EDI-type zeolite framework structure. In addition, only one single broad but symmetrical band at 58.2 ppm in the $^{27}$Al MAS NMR spectrum was measured, and this band was due to

The crystallographic evolution of nanosized K-F zeolite from the colloidal gel suspension not only can be explained by the change of morphology, but also by the change of their microscopic properties. The IR spectra of the samples taken at different time intervals are shown in Fig. 5. For the sample heated for 10 min, four main IR bands were detected at 1105, 988, 859 and 717 cm$^{-1}$ which were ascribed to typical amorphous aluminosilicate solid [41] (Fig. 5a). When the heating time was further extended to 1.5 h, the IR bands at 1105 and 988 cm$^{-1}$, which were assigned to internal vibration of Si–O–T (T = Si, Al) asymmetric stretching modes, became more intense [13] (Fig. 5b). Hence, it revealed that polymerization between silicate and aluminate species had taken place. Another IR band due to similar stretching vibration mode also started to form and detected at 1029 cm$^{-1}$, and the intensity of these bands kept increasing upon crystallization time. However, no significant change in the region of 800–400 cm$^{-1}$ was observed indicating that the zeolite crystalline phase had not yet been formed. With heating time prolonged to 2.3 h, the two bands corresponding to the zigzag 8-membered ring subunits appeared at 601 and 569 cm$^{-1}$. This indicated the beginning of the formation of EDI-type zeolite structure in line with the XRD and TEM observations. In addition, two weak signals attributed to the bending vibration of TO$_4$ and symmetric stretching of T–O–T were also detected at 430 and 653 cm$^{-1}$ [13] (Fig. 5c). These bands became more pronounced after 3 h of crystallization (Fig. 5e).
tetrahedral Al (Aloct) sites from the amorphous aluminosilicate gel [44] (Fig. 7a).

After 1.5 h of hydrothermal treatment, the Si/Al ratio reduced to 1.30 according to XRF analysis. The $^{29}$Si NMR band shifted from $-86.4$ to $-85.1$ ppm and it became narrower. This signal was associated with an amorphous silica phase. While after 1.5 h of hydrothermal treatment, a very small symmetric peak at $-84.5$ ppm attributed to the Si(OAl)$_4$ species originated from EDI-type zeolite appeared.

For $^{27}$Al solid state MAS NMR, the peak due to tetrahedral Al sites was also shifted to 58.9 ppm and a weak broad band was also found at 0.6 ppm (Fig. 7b). The weak broad band was due to the presence of octahedrally coordinated aluminum (Aloct) or extraframework Al (EFAL). Hence, the existence of trace amount of these Aloct species indicated the participation of Al and structure rearrangement of the material via condensation of $\equiv$OH groups; these results were in a good accordance with the TEM and XRD results. After 2.3 h of heating, the $^{27}$Al NMR peaks were shifted again (Aloct: 58.9–59.7 ppm; Aloct: 6.0 to 0.1 ppm) and the Aloct species completely disappeared after 3 h (Fig. 7c and d). Only one strong, narrow and symmetry line appeared at 61.5 ppm indicating ordered framework with single Aloct environment [45].

For $^{29}$Si solid state MAS NMR, the peak at $-85.1$ was also shifted to $-84.4$ ppm and it became even more resolved after 2.3 h (Fig. 6c). Nevertheless, the pure silicate amorphous phase at $-110.3$ ppm still existed; a decrease of the Si/Al ratio from 1.30 to 1.18 was measured too. This weak band disappeared after 3 h of crystallization, and the Si/Al ratio of the material further reduced to 1.10 (Fig. 6d). The $^{29}$Si NMR signal of fully crystalline K-F zeolite was symmetric, sharp and narrow, which implied high homogeneity of the chemical environment, with a defined Si atom coordination in the EDI zeolite lattice tetrahedral sites.

The extraframework Al is observed during the transformation process of amorphous phase to the crystalline EDI zeolite phase. In other words, the presence of extraframework Al species indicates that the synthesis is still not completed. Furthermore, the presence of extraframework Al can also be due to the amorphous edges in not fully crystalline zeolite nanocrystals. Therefore, octahedrally coordinated Al peak was observed at 0.1–0.6 ppm in the $^{27}$Al MAS NMR spectra of partial crystalline samples (Fig. 7b and c). However, when the crystallization process was completed, only one peak at 61.5 ppm was detected by $^{27}$Al MAS NMR spectroscopy (Fig. 7d), which is related to the tetrahedrally coordinated Al (framework Al). This indicates that fully crystalline zeolite particles have formed. These results are in a good agreement with our previous work reporting on the synthesis of template free nanosized FAU zeolite [22].

EDI-type zeolite nanocrystals were studied by N$_2$ adsorption-desorption analysis but without success. Type I adsorption isotherm, which is usually shown by medium and large pore zeolites at low P/P$_0$, was not observed for the EDI type zeolite [46]. Instead, the amorphous solid and nanosized EDI-type zeolite exhibited Type IV adsorption behavior with type H3 hysteresis loop, which indicates the capillary condensation in open slit-shaped mesopores (Fig. 8) [47]. Such phenomenon is due to the smaller pore diameter of EDI zeolite ($2.8 \times 3.8 \, \text{Å}^2$ and $2.0 \times 3.1 \, \text{Å}^2$) than the size of N$_2$ probe molecule ($\sigma = 3.64 \, \text{Å}$) [48]. The nanosized EDI-type zeolite with a high ratio of external to inner surface can be engineered in various forms (colloid, coated layer, free powder, etc.) and used in selective gas separation, separation of linear olefins from paraffin, hydrogen storage, semiconductors and chromophore occlusion.

In summary, the synthesis of nanosized K-F zeolite with EDI topology by using organo-template-free precursor system is
The resulting nanosized zeolite crystals with a size of 27 nm exhibit flattened cuboid shape and they tend to form spherical agglomerates (180–254 nm). The EDI-type nanosized crystals have a Si/Al ratio of 1.10 and the negative charge of extraframework is counterbalanced by basic K⁺ cations. Such zeolite nanocrystals are extremely useful for the industrial chemical processes that involves catalytic and adsorption processes due to their hydrophilic and oleophobic nature.

References