



A simple synthesis procedure to prepare nanosized faujasite crystals

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ABSTRACT

The interest in synthesizing zeolites with crystals in the nanometric size range has increased greatly in recent years; however most of the works depend on using organic structure directing agents. In this work nanosized crystals of zeolite faujasite were successfully synthesized without the use of organics. Among the synthesis parameters studied, the increased alkalinity of the synthesis gel was found to be the one that caused a decrease in the final particle size. The high alkalinity coupled with an aging step proved to be very effective in affording faujasite nanocrystals with high microporosity and external area. Thus it is possible to obtain nanocrystals of this zeolite using environmentally more friendly procedures, since they avoid the use of organic structure directing agents and their subsequent calcination.

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1. Introduction

Synthetic zeolites are widely used as catalysts or adsorbents in petroleum refining, petrochemicals production, and fine chemistry. For example, FAU (Y), MFI (ZSM-5), and LTA (A) zeolites are used in fluid catalytic cracking (FCC), aromatic alkylation and adsorbents, respectively. The ultrastable zeolite Y, USY, is the principal component of FCC catalysts [1–3].

This zeolite has a three-dimensional pore structure with a window diameter of approximately 0.74 nm, inherent surface acidity, and high structural resistance to withstand severe hydrothermal conditions during regeneration in the FCC process [1]. Studies using nanosized zeolite crystals for polyolefin cracking showed for instance that the catalytic activity depends directly on the external surface area present in the nanocrystalline HZSM-5 samples [4].

Particle size reduction from the micrometer to the nanometer scale leads to substantial changes in the properties of the materials. The use of zeolites formed by nanosized crystals, for example, had an important impact in traditional application areas such as catalysis [5–7] and separation [8]. The ratio of external to internal number of atoms increases rapidly as the particle size decreases, therefore, zeolite nanoparticles present large external surface areas and higher activity [6]. The external acidity is important when the zeolite is meant to be used as a catalyst in reactions involving bulky molecules, such as 1,3,5-tri-isopropylbenzene [9]. In addition,

smaller zeolite crystals will have more pore mouths exposed in the external surface. Consequently, this material presents less diffusion limitations when compared to micrometer-sized zeolite crystals [5,11].

Zeolite nanocrystals can also be used in other catalysis and adsorption systems, such as thin films, fibers, and self-standing zeolite membranes while offer advantages in photochemistry, electrochemistry and optoelectronics [5,12–15].

Synthesis of nanocrystals of A, Y, silicalite, sodalite, ZSM-5 and Beta zeolites have been previously reported [16–24]. Colloidal zeolite suspensions of LTA- and FAU-type zeolites have been prepared from diluted clear solutions containing a large amount of tetramethylammonium cations at temperatures ranging from room temperature to 100 °C [18,23–25]. The synthesis of FAU nanocrystals in the absence of organic template is less common. Zhan et al. studied the influence of temperature and stirring on the synthesis of FAU nanocrystals from systems using tetraethyl orthosilicate as the Si source. The authors observed that the best conditions to obtain faujasite nanosized crystals were by stirring the reaction mixture at 250 rpm for 2 days at 60 °C [26]. More recently, Huang et al. synthesized FAU nanocrystals from gel systems containing aluminum isopropoxide by using a “three-stage” heating scheme with temperatures between 25 and 60 °C. The first stage at 25 °C was performed under agitation at 650 rpm. Secondly, the precursor was moved into a pre-heated oven set at 38 °C and aged for 24 h. At the final-stage, the precursor gel was hydrothermally treated at 60 °C for 48 h. This system yielded 100–300 nm crystal aggregates built of 10–20 nm nanocrystals [27].

Considering the increasing importance of nanosized zeolite in catalysis [6,7,9], in this work the synthesis conditions for obtaining zeolite FAU nanocrystals using a static system without organic

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directing agent and organic precursors of Si and Al were investigated. The influence of hydrothermal treatment time, aging time and the alkalinity of the synthesis gel on the crystal size was investigated.

2. Experimental

2.1. Zeolite synthesis

The reactants used were sodium hydroxide pellets (Quimis, 99%), fumed silica (Aerosil 380, Evonik/Degussa), sodium aluminate (Riedel de Haën, 54% Al_2O_3 :41% Na_2O :5% H_2O), sodium chloride (Merck, 99%) and deionized water.

The zeolite was initially prepared according to the traditional composition, similar to that previously reported by Hu et al. [28]. Appropriate amounts of sodium hydroxide and water were mixed under stirring until the solution became clear. The aluminum source (sodium aluminate) was added to the aqueous solution of sodium hydroxide and stirred until completely dissolved. The silica source (Aerosil 380) was added under manual stirring until a homogeneous gel was obtained. Typically, the final molar composition of aluminosilicate gel obtained was: 5.5 Na_2O : Al_2O_3 :10 SiO_2 :180 H_2O : x NaCl. The mixture was transferred to Teflon-lined stainless steel autoclaves and maintained at 100 °C for different crystallization times. The solid product was separated by centrifugation, washed several times with distilled water and dried at 60 °C. Table 1 shows the conditions and composition of the samples that were synthesized in this work.

2.2. Characterization

The zeolite samples were characterized by means of conventional techniques: powder X-ray diffraction (XRD), N_2 physisorption isotherm, scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The crystallinity and phase purity of the solids were determined by powder X-ray diffraction (XRD) using a Rigaku diffractometer (Ni-filtered $\text{CuK}\alpha$ radiation, 40 kV, 40 mA) at a scan rate of 2°/min from 5° to 35° with a step size of 0.02°. After background subtraction, the intensity under the peaks in the 23–24.5° 2θ ($hkl = 533$) range was taken as a measure of the crystallinity, by comparison to a highly crystalline sample prepared in

Table 1
Composition of the reaction mixture and synthesis conditions for the different samples synthesized at $\text{H}_2\text{O}/\text{Al}_2\text{O}_3$ molar ratio of 180 and $\text{SiO}_2/\text{Al}_2\text{O}_3$ of 10.

Sample ^a	$\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$	HT ^b (h)	Aging (h)	x NaCl
B5.5-24 h	5.5	24	0	0
B5.5	5.5	6	0	0
B6.5	6.5	6	0	0
B7.5	7.5	6	0	0
B8.5	8.5	6	0	0
B8.5-2 h	8.5	2	0	0
B8.5-4 h	8.5	4	0	0
B8.5-6 h	8.5	6	0	0
B8.5-8 h	8.5	8	0	0
B8.5-10 h	8.5	10	0	0
B8.5-12 h	8.5	12	0	0
B8.5-24 h	8.5	24	0	0
B8.5-48 h	8.5	48	0	0
B8.5-A24	8.5	6	24	0
B8.5-A48	8.5	6	48	0
B8.5-A72	8.5	6	72	0
B5.5-A72	5.5	6	72	0
B7.5NaCl	5.5	6	0	4
B8.5NaCl	5.5	6	0	6

^a The sample code is the following: B = $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$, A = aging time.

^b Hydrothermal treatment time.

this work. Scherrer's equation was used to estimate the primary size of FAU crystals. The full-width at half maximum (FWHM) was determined at the peaks 2θ of 15° (3 3 1), 23° (5 3 3) and 26° (6 4 2), using metallic Si as the reference to correct peak width. The unit cell parameter (a_0) of the faujasites was calculated using an internal silicon standard (10 wt.%); the samples containing the standard were previously humidified for 24 h in a balanced atmosphere chamber with a saturated solution of CaCl_2 . The (3 1 1), (5 3 3) and (6 4 2) peaks were used to determine a_0 . Nitrogen sorption experiments were carried out at -196 °C on a Micrometrics ASAP 2020 after degassing the sample at 200 °C for 2 h. The micropore volume (V_{Micro}) and external area (S_{Ext}) were determined by the t -plot method. The morphology and size of zeolite crystals or particles were examined by scanning electron microscopy (SEM) and transmission electron microscopy (TEM), using a Phillips XL 30 FEG and Philips CM 120, respectively. After sonication to break up large aggregates a droplet of the methanol suspension was deposited onto Cu grids and examined by TEM. The chemical composition of the synthesized zeolites was determined by several methods. To calculate the average composition of the sample through Energy Dispersive X-ray Spectroscopy (EDS), the spectra were measured in different regions of the samples using a Philips microscope XL 30 FEG. ^{27}Al and ^{29}Si Solid-state Nuclear Magnetic Resonance high-power decoupling (HPDEC) and $^1\text{H}/^{29}\text{Si}$ cross-polarization/magic angle spinning (CP/MAS) spectra were obtained on a broad band Bruker 400 Avance + (400 MHz) spectrometer using 4 mm rotors. The spinning frequency used for ^{29}Si was 10 kHz, while the spinning frequency for ^{27}Al NMR was 15 kHz.

3. Results and discussion

3.1. Alkalinity influence

The effect of alkalinity on the properties of the product was verified by changing the number of moles of Na_2O in the gel synthesis. This transformation was achieved by adding sodium hydroxide amounts for $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ molar ratios of 5.5, 6.5, 7.5 and 8.5. The hydrothermal treatment time was of 6 h at 100 °C. Fig. 1 shows the diffraction patterns for different samples. The increased amount of Na_2O in the gel synthesis caused an intensity decrease in the diffraction peaks.

For sample B8.5, synthesized with the highest $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ content, early contamination is indicated by an asterisk in Fig. 1d, which probably belongs to the zeolite phase NaP1 (GIS type). Thus, the limit of the $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ ratio to form the faujasite phase, under these synthesis conditions, is of 8.5. As noted by some authors, the intensity decrease in the diffraction peaks, as well the increase of its width is related to the decrease in the size of crystals in this sample [10].

These samples were characterized by scanning electron microscopy; the micrographs obtained are shown in Fig. 2. Fig. 2 demonstrates that the increase in Na_2O content in the reaction mixture, and consequently in the basicity, caused a decrease in particle size. For samples B5.5 and B6.5 (Fig. 2a and b) well defined particles with octahedral morphology are observed, characteristic of the faujasite phase. However, the crystal dimensions obtained by diffraction (D_{hkl}) and physisorption measures (D_{Ext}) presented in Table 2, suggest that these particles are polycrystalline, composed of nanosized crystals. With increasing basicity of the reaction mixture, the particles become more irregular, and no defined morphology was observed for sample B8.5 (Fig. 2d).

The change in morphology can be best seen in Fig. S1 (Supplementary information), which shows higher magnification of the sample micrographs with the highest and lowest $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ content in the reaction mixture. It can be observed that the increasing

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