

Synthesis and Characterization of High-Quality Zeolite LTA and FAU Single Nanocrystals

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Since Milton synthesized zeolites by means of hydrothermal treatment of alkaline aluminosilicate gels in the 1940s,¹ more than a hundred different kinds of zeolites have been synthesized by optimizing synthesis conditions, such as choosing the suitable reactants, gel composition, temperature, etc., and adding suitable organic structure directing agents.^{2–6} However, zeolites are mostly formed as a fine powder of one to several microns in size, and they contain different kind of faults with high density. The final crystallites are usually aggregated or intergrown within the same families or the same structure as twins.^{7–12} In those cases, they will show chemical and physical properties different from those expected from perfect periodic structures.^{13,14}

Single nanocrystals with high crystallinity are very important for a variety of studies, such as (i) a fundamental understanding of the crystal growth process at the zeolite external surface, especially nucleation and growth processes without any postsynthesis treatment, by high-resolution electron microscopy (HREM);¹⁵ (ii)

applications based on short diffusion times of molecules in their spaces (channels or cages) and their large external surface relative to internal surface area;^{16,17} and (iii) surface reactivity for retreatment such as regrowth/sintering to make larger crystals or thin films.¹⁸ Therefore, to synthesize high-quality zeolite single nanocrystals is of great interest.

FAU and LTA are two most important zeolites which have been extensively used in ion exchange, adsorption, catalysis, and other aspects. It has been reported that in the synthesis of FAU and LTA zeolites, crystal size was obviously decreased with the addition of tetramethylammonium hydroxide (TMAOH).² Recently, Schoeman et al.¹⁹ reported the synthesis of zeolites LTA and FAU with a crystal size of 100 nm in the system of $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-(TMA)}_2\text{O-Na}_2\text{O-H}_2\text{O}$ using silica sol, $\text{Al}_2\text{(SO}_4)_3\cdot 16\text{H}_2\text{O}$, TMAOH, and NaOH as the reactant sources. The synthesis procedure involved several steps including removal of the ammonia and sulfate ions and removal of sodium from the silica sol to control the amount of Na^+ . In addition, the crystal morphologies were not characterized in detail; in particular, the issue of whether the as-synthesized nano crystals were single crystals or not was not discussed.

In our studies, the interest is focused on developing a well-controlled way to synthesize high-quality LTA and FAU single nanocrystals by (i) using pure reactant sources, including tetraethyl orthosilicate (TEOS), Al powder, NaCl, and TMAOH, and (ii) optimizing the synthesis conditions to obtain much smaller nano-LTA (as small as 50 nm) and FAU (80 nm). The as-synthesized crystals are characterized by powder X-ray diffraction (XRD) with Cu K α radiation (Philips PW3050), transmission electron microscopy (TEM by JEOL-3010, Cs = 0.6 mm, at 300 keV), and dynamic light scattering (DLS) with an ELS-800 spectrometer (Otsuka Electronics).

Typically, aluminum powder (99.5%) and sodium chloride were dissolved in an appropriate amount of TMAOH solution. This solution was then filtered through 0.2- μm membrane filter to remove impurities. TEOS was added dropwise to the above clear solution with vigorous stirring, resulting in a homogeneous solution. After 2 days of aging, a gel was formed, and the reaction mixture was transferred into a 250-mL polypropylene bottle and placed in an oven at 100 °C for 11–18 days.

The resulting solids were collected by centrifugation with a relative centrifugal force (RCF) of 35 kg for 40 min. The products were repeatedly dispersed in distilled water using ultrasonication and centrifugation as above to remove the remaining mother liquid until the

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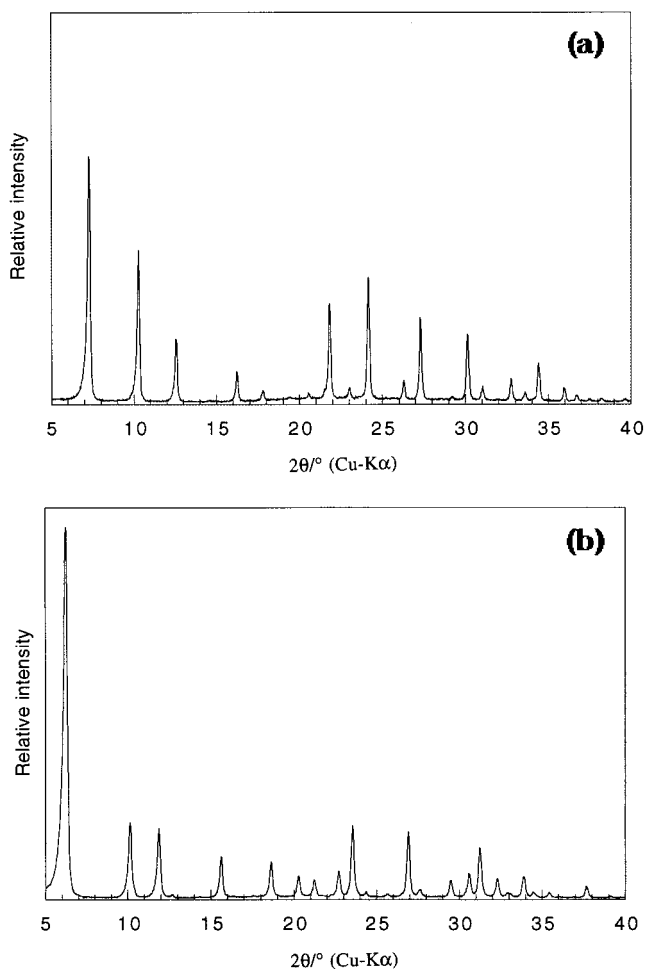
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Table 1. Synthesis Results for nano-LTA and -FAU under Different Conditions^a

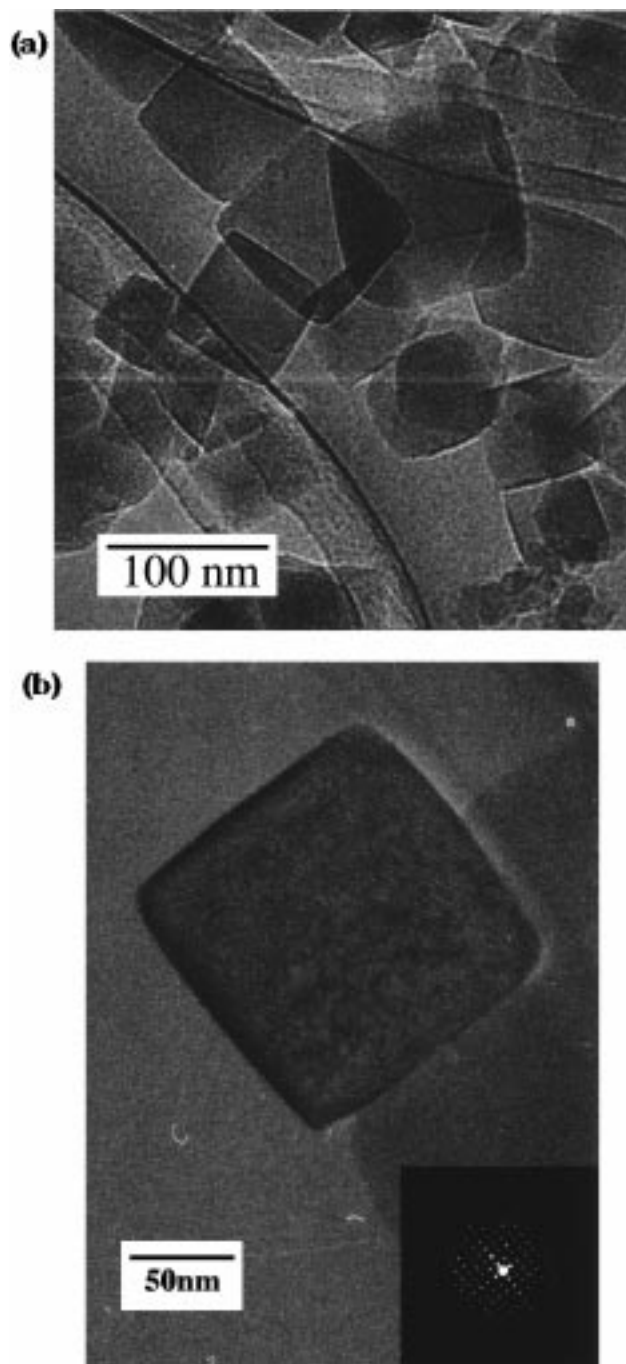
run	reaction mixture molar composition					time (d) ^b	product	
	SiO ₂	Al ₂ O ₃	(TMA) ₂ O	NaCl	H ₂ O		product	size ^c (nm)
1	3.0	1.0	2.4	0.1	276	11	LTA	300–500
2	3.0	1.0	5.0	0.1	276	11	LTA	200–500
3	3.0	1.0	6.0	0.1	276	13	LTA	100–300
4	3.0	1.0	7.0	0.1	276	13	LTA	100–200
5	3.6	1.0	1.5	0.1	276	18	LTA	100–500
6	2.2	1.0	5.5	0.16	500	13	LTA	400–600
7	1.12	1.0	5.5	0.08	276	13	LTA	300–500
8	2.0	1.0	1.5	0.04	276	15	LTA	200–300
9	3.0	1.0	1.5	0.28	276	11	LTA	500–900
10	3.0	1.0	1.5	0.14	276	12	LTA	300–600
11	3.0	1.0	1.5	0.057	276	13	LTA	100–200
12	3.0	1.0	1.5	0.028	276	14	LTA	50+130
13	3.0	1.0	1.5	0.007	276	16	LTA	50+130
14	3.4	0.83	2.3	0.1	300	14	FAU	80
15	3.4	1.0	2.3	0.1	300	14	FAU	80
16	3.4	1.35	2.3	0.1	300	14	FAU	80
17	3.4	1.7	2.3	0.1	300	14	FAU	80

^a T: 100 °C. ^b The crystallization time was taken as the shortest crystallization time to obtain crystals with high crystallinity. ^c The size of the crystallites was evaluated from TEM observation and/or DLS determination.

**Figure 1.** XRD patterns of (a) nano-LTA (run 12) and (b) nano-FAU (run 14).

pH of the dispersion was near 7. The solid samples were obtained by drying at 80 °C for 4 h.

Pure and highly crystalline nano-LTA and -FAU are synthesized in the system Al₂O₃-SiO₂-(TMA)₂O-NaCl-H₂O at 100 °C. Table 1 gives the synthesis results

**Figure 2.** (a) An HREM image of zeolite LTA nanocrystals (run 12) and (b) an image of higher magnification with an electron diffraction pattern (inset).

under different conditions. It is well-known that for zeolite synthesis the choice of reactant sources, such as silica and aluminum sources, and an alkali metal source, as well as the addition of salts, strongly affects the crystallization time, the final crystal size, and crystal morphology.^{20–23} Moreover, the use of pure reactant sources can reduce the number of heteronuclei and favor the formation of single crystals.²⁴ Differing

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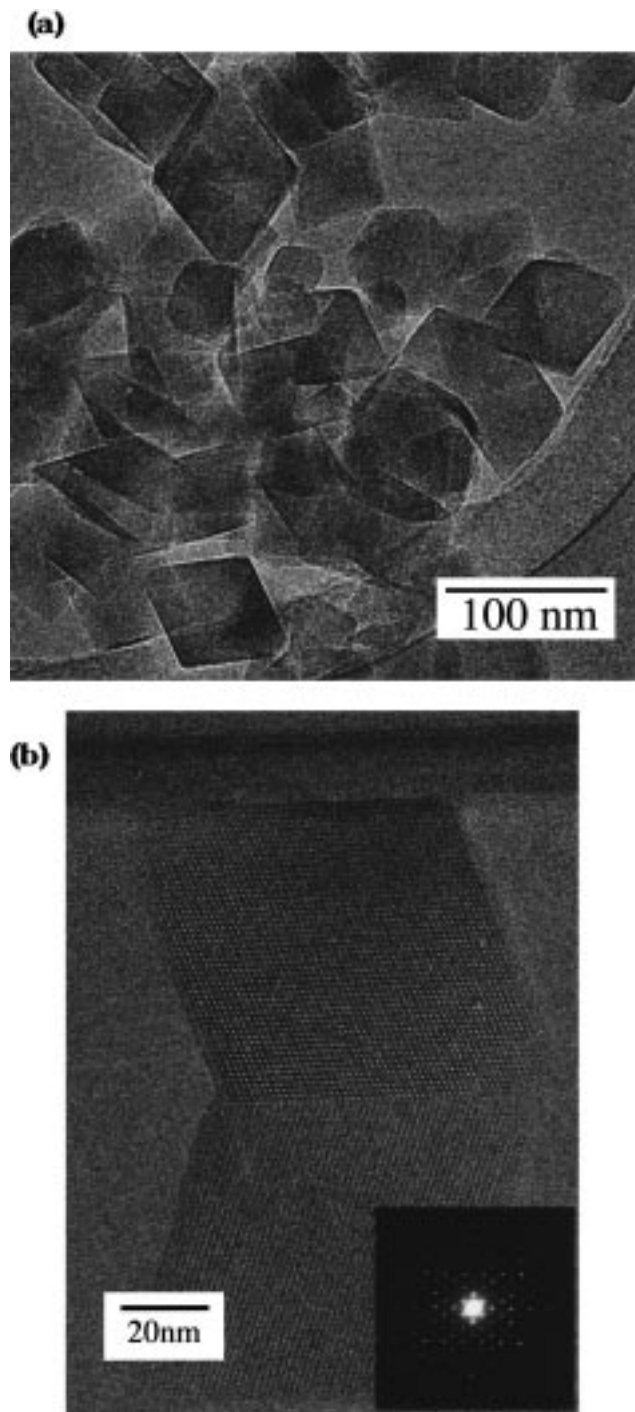


Figure 3. (a) An HREM image of zeolite FAU nanocrystals (run 14) and (b) an image of higher magnification with an electron diffraction pattern (inset).

with the previous report by Shoeman et al.,¹⁹ not only do we use pure sources, but we also use NaCl instead of NaOH. In this case, the alkalinity of the reaction mixture is only controlled by the amount of TMAOH. NaCl plays the role of supplying the Na⁺ cations, as well as acting as a salt affecting the crystallization and crystal morphology through its effect on the dielectric constant of the solution.^{21,23}

The ratios of (TMA)₂O/Al₂O₃, SiO₂/Al₂O₃, and NaCl/Al₂O₃ all have essential influence on the final crystal

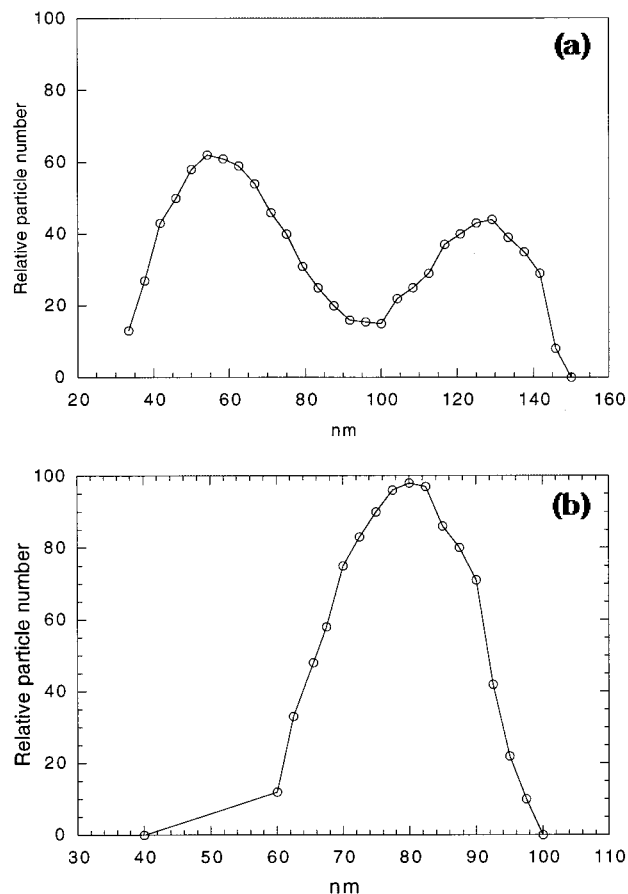


Figure 4. Particle size distribution for (a) nano-LTA (run 12) and (b) nano-FAU (run 14).

size of LTA. It can be seen from Table 1 that increasing the (TMA)₂O/Al₂O₃ ratio results in the reduction of the crystal size of LTA (runs 1–4). But further increasing the (TMA)₂O/Al₂O₃ ratio over 7 does not favor the formation of a pure phase of LTA. Changing the SiO₂/Al₂O₃ ratio also causes a change of the final crystal size of LTA. The crystallization rate, yield, and size of the crystals strongly depend on the addition of sodium chloride. It is noted that decreasing the NaCl/Al₂O₃ ratio results in a decrease of the crystal size and a longer crystallization time (runs 9–13). The existence of a trace amount of NaCl in the reaction mixture is essential for the formation of LTA since, without addition of NaCl, LTA could not be crystallized. The reason might be that Na⁺ plays the role of stabilizing the D4R of the LTA structure. Under well-optimized conditions, LTA nanocrystals as small as 50 nm can be obtained (runs 12 and 13). Figure 1a shows the powder XRD pattern of LTA (synthesized by run 12), indicating high crystallinity. Energy-dispersive X-ray analysis gives an Si/Al ratio of examined crystallites of 1.3. The features of the crystals are characterized by TEM. Figure 2 show HREM images of nano-LTA crystals. The images show both high crystallinity and perfect crystal morphology. It is clear from the low-magnification image that the crystal has typical cubic morphology with different sizes of ca. 50 or 130 nm in-edge. The particle size distribution can be estimated from the low-magnification image and is further characterized by DLS (Figure 4a). DLS measurement of zeolite LTA shows two maxima at 50 and 130 nm in the size distribution, which is in agreement with the TEM observation. This bimodal

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size distribution potentially reflects different nucleation process.^{25–27} Further crystallization kinetics studies on the nucleation of nano-LTA are going on.

Single nanocrystal FAU can be obtained by runs 14–17. High-quality FAU single nanocrystals as small as 80 nm are formed over a wide range of Si₂O₃/Al₂O₃ ratios. It is found that decreasing the amount of NaCl results in FAU single nanocrystals with low yield and low crystallinity. The powder XRD pattern of FAU (run 14) with high crystallinity is shown in Figure 1b. Energy-dispersive X-ray analysis gives a Si/Al ratio of examined crystallites (run 14) of 1.8. Figure 3 shows HREM images of nano-FAU crystals. The images

clearly show (i) a complete periodic arrangement of the channels throughout the crystals with very high crystallinity confirmed in higher magnification together with an electron diffraction which is shown in correct orientation to the image, (ii) a regular octahedral crystal morphology with a size of ca. 80 nm in-edge, and (iii) a uniform crystal size distribution. DLS analysis of the FAU samples gives a monodistributed size, as shown in Figure 3b. The average crystal size was determined to be 80 nm, which is in agreement with the TEM observation.

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