Rapid Hydrothermal Synthesis of Faujasitic Zeolites

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Abstract: In this paper, we propose modifications to a typical hydrothermal synthesis of zeolite which leads to very rapid crystallization. Water is gradually removed from the reaction mixture leading to a highly concentrated, extensively nucleated supersaturated gel, with the water added back slowly to this gel, crystallization of high-quality zeolite takes place rapidly.
**Introduction**

Zeolites are microporous, crystalline aluminosilicates with the framework made up of T-O-T (T=Si, Al) bonds and enclose cages and channels of molecular dimensions.\(^1\),\(^2\) There are over 150 zeolite frameworks that have been synthesized, and in principle, many more are possible.\(^3\) Zeolites are typically, crystallized by a hydrothermal process, in which the reactants are heated to 50-200\(^\circ\)C for periods of time extending from hours to days. Zeolite crystallization has a slow induction period, followed by a more rapid crystallization process.\(^4\) Decreasing the crystallization time for zeolite synthesis is motivated by cost savings, morphology control, primarily decreasing size of crystals, and increase in purity of the crystalline phase.

Many strategies are reported to speed up zeolite crystallization, and usually shortens the induction time. These include seeding, including tribochemical activation, altered heating profile (higher temperatures typically), multiple heating stages, and microwave radiation.\(^5\)-\(^8\) Zeolite X/Y (FAU) is one of the industrially most important zeolite frameworks, since it finds use in ion-exchange, adsorption and catalysis applications, and is the focus of the present study. The choice of this framework was also motivated by the fact that numerous studies have been carried out on crystallization of FAU zeolites, including its mechanism of formation.\(^9\)-\(^12\) In this study, we report a novel modification of the typical hydrothermal synthesis process, which leads to extensive nucleation and therefore rapid crystallization. Structural and mechanistic information about nuclei formation and crystallization is also reported.

**Experimental Section**

**Materials**
All chemicals were purchased and used as received. Sodium hydroxide pellets (99.4%) were purchased from Fisher chemical. Aluminum hydroxide (76.5%) was purchased from Alfa Aesar. Ludox SM-30 colloidal silica was purchased from Aldrich chemical company. Deionized water (17.5MΩ) was produced from a Nanopure Infinity ultrapure water system from Barnstead.

**Synthesis**

FAU type zeolite was synthesized from an opaque gel with the following composition: 17Na2O:1Al2O3:21.80SiO2:975H2O. The gel was prepared by combining a basic clear solution of NaOH, Al(OH)3 and H2O with colloidal silica Ludox SM-30 while stirring in a polypropylene bottle. The resulting gel was aged while stirring for 4hrs at room temperature. There were six different synthesis protocols that were developed, four of them using this aged gel. Synthesis I involved reaction in Teflon lined stainless steel Parr digestion vessels (bombs), placed within an oven at 100°C. To measure the progress of synthesis, bombs were removed periodically, and analyzed as detailed below. In Synthesis II, the aged gel was transferred to a round bottom flask (PTFE, glass) connected to a graduated pressure equalizing addition funnel with a PTFE stopcock topped with a condenser, as shown in Figure 1. For Synthesis II, only the reflux part of the apparatus was used (temperature of reflux was 100-103°C). For Synthesis III, while under reflux, 40mL of H2O from the reaction was removed by condensation in the addition funnel (about half the volume of water in the flask) over a period of one hour, and the reflux continued. For Synthesis IV, the collected water was then re-added back dropwise to the concentrated gel over a period of another hour, after which the gel was allowed to react under reflux without any further change. Synthesis V used the same apparatus as Figure 1, but the gel composition was twice as concentrated to be 17Na2O:1Al2O3:12.80SiO2:564H2O (also aged for 4 hour), and done under reflux. Synthesis VI used the same composition as Synthesis V and aging conditions, but
40 ml water was added back dropwise after one hour of reflux to achieve the final composition of 17Na₂O:1Al₂O₃:21.80SiO₂:975H₂O, and the reaction was continued under reflux.

Samples were removed at various times during the synthesis process for all of the protocols, and these times varied and are described below. Once removed, samples were immediately cooled in an ice bath for 1hr followed by 30min of centrifugation at 2500rpm. The pellets were lyophilized and stored under vacuum (50mTorr) until analyzed. Before analysis the lyophilized samples were pulverized, washed with ~1.5 liters of water by filtration, and vacuum dried at 60°C. For the Raman spectroscopy experiments, both washed and unwashed samples were investigated.

**Characterization**

XRD patterns were collected using a Bruker Dmax diffractometer using nickel filtered Cu-Kα radiation. Scans were collected from 3-50° 2θ with a step size of 0.02° and a dwell time of 1s. Crystallization curves were constructed from XRD patterns. The crystallinity for a sample from a given reaction was defined by summing the areas of the first 5 Bragg reflections of FAU for that sample at a specified time and normalizing it to the sum of these same peaks from a sample from the same batch after 8hrs.

Crystal morphology was investigated with electron microscopy. Scanning electron micrographs were collected from gold coated samples on a Phillips XL-30 ESEM-FEG. High resolution transmission electron micrographs were collected with a Tecnai F20 system from well dispersed zeolite samples deposited on a lacy carbon film supported on a copper grid.
The development of the zeolite porosity was followed using nitrogen physisorption measurements. Nitrogen sorption experiments were conducted with a Quantachrome NOVA. The surface area was determined according to the Brunauer-Emmett-Teller (BET) calculation procedure. The mesopore size distributions were determined using the Barrett-Jayner-Halenda (BJH) calculation procedure.

Raman spectra of the solid samples were collected with a Renishaw invia microprobe spectrometer equipped with a 633nm laser. The laser power at the sample was 1mW focused from a 5X microscope objective. Spectra were collected with a 1600mm⁻¹ grating giving ~3cm⁻¹ resolution.

Nuclear magnetic resonance spectroscopy was used to estimate the Si / Al ratio of zeolite products. A Bruker DSX 300 MHz superconducting magnet equipped with a dual channel (H-X) MAS probe was used to collect high resolution 29Si (59.6 MHz) and 27Al (78.2 MHz) spectra. Approximately 100mg of sample was packed into a 4 mm zirconium rotor with a Kel-F cap. The 29Si NMR spectra were acquired using a standard CPMAS pulse program with acquisition parameters as follows: spinning rate of 5 kHz, CP contact time of 5ms, 10s recycle delay, 6k-16k scans per sample, and line broadening of 20Hz. The 27Al NMR spectra were collected using Bloch decay with acquisition parameters as follows: a 4μs 90° pulse, spinning rate of 5kHz, 0.5s recycle delay, 128-1024 scans per sample, and line broadening of 20Hz.

Results

Hydrothermal Synthesis

Using the composition 17Na2O:1Al2O3:21.80SiO2:975H2O, several different synthesis protocols were developed. In four of these attempts, first the above composition was aged for 4 hours at room temperature. Synthesis I involved a regular hydrothermal synthesis and was
carried out in Teflon bombs at 100°C. This composition was chosen based on our earlier work that demonstrated FAU formation over a period of 8 hours, with the first crystals appearing in the X-ray diffraction after 4 hours of heat treatment. Figure 2a shows the XRD pattern after two hours of heating and no FAU crystals are apparent.

Synthesis II was carried out with the same aged composition but under reflux conditions in a round bottomed flask with stirring, using the apparatus shown in Figure 1. Figure 2b shows that no FAU crystals are observed in the diffraction pattern, the crystallization process took 6 hours for completion. Synthesis III was done similar to Synthesis II, but during reflux, about half of the water (40 ml) from the reaction mixture was removed by condensation over a period of an hour, and the reflux continued. Figure 2c shows the diffraction pattern after two hours using Synthesis III, the broad reflection peaks characteristic of FAU are observed, but with continued reflux, there is no improvement in the crystallization up to a period of 6 hours. In synthesis IV, the water that was collected over one hour was gradually dripped back into the refluxing reaction mixture over the period of 50 minutes, and then the reaction was allowed to proceed under reflux conditions. Figure 2d shows the diffraction pattern as soon as the water addition is complete (total of ~ two hours, just as in Synthesis II and III). If the water is added all at once in a few minutes, crystallization process is significantly slower (6 hours), and the crystals remain small, as evidenced by the broadness in the diffraction patterns (data now shown). Synthesis V was carried out with the composition that was about twice as concentrated 17Na₂O:1Al₂O₃:21.80SiO₂:564 H₂O (essentially the composition that is in the reactor after the water is removed in Synthesis III and IV), aged for 4 hours and the reaction carried out under reflux. Figure 2e shows the powder pattern after two hours, indicating that some crystallization has taken place, and required 6 hours for complete crystallization, but the diffraction peaks were
not sharp. For Synthesis VI, the same composition as Synthesis V was used, but after one hour of reflux, 40 ml of water was dripped back into the flask over an hour. Figure 2f shows the powder diffraction pattern after two hours (time at which water addition is complete), and shows that the crystallization is accelerated as compared to Synthesis V, but over six hours crystallization, the diffraction bands remained broad.

Figure 3 compares the SEM of the crystals formed via Synthesis II (6 hours) and IV (2 hours). Synthesis IV appears to be an aggregate of smaller crystals (500 nm-1 µm), whereas the conventional synthesis result is larger, single crystal (2-3 µm) like morphology.

Figure 4 compares the Si NMR of Synthesis I (8 hours) and IV (2 hours), with both methods giving Si/Al ratio of 1.5.

**Characterization of material during the water addition stages of Synthesis IV**

Several experiments were done focusing on Synthesis IV, in the 0-50 min time frame, with a 0 min being the time at which the water is being added back (after 1 hour of reflux) and 50 min being the time at which the water addition is essentially complete.

Figure 5 shows that diffraction pattern of the recovered solid with time. Just before the water is added back (0 min), only amorphous materials are observed. The peaks observed at high 2theta are due to soluble salts precipitated out during the drying process. With the dropwise addition of H₂O back to the concentrated gel, a diffraction pattern consistent with FAU type zeolite is first observed after 20 min. This pattern continues to develop with time as water is added back, and the peaks increase in intensity. There is only a minor increase in the intensity of FAU reflections after water addition is complete at 50 min, with the reaction reaching completion at 3 hours (total time from initiation of reflux).
The evolution of the surface area of the material after water is added back in is presented in Figure 6 and follows a similar trend as the XRD. During the early times of the reaction the surface area is 20-50 m²/g and begins to increase exponentially after water addition begins. This increase is almost complete one hour after water addition (600 m²/g) and saturates at a value of ~660 m²/g.

Figure 7 shows the SEM during the water addition period of 0-50 min time frame, at 0, 20 and 40 min. At the end of the water removal, and before any water is added back (0 min), the SEM indicates the presence of 10 µm aggregates of small particles (100 nm). At 20 min, the small particles are still evident, but underneath them, small (500 nm) well-formed zeolite crystallites are evident. These crystals appear to be growing into each other. At 40 min, there is less of the small particles, and the intergrown FAU crystals of 500 nm primary sizes are clearly visible.

Transmission electron micrographs (TEM) of the material of the sample recovered after water is removed and before water addition shows only amorphous material, but within 10 min of addition of H₂O crystalline regions are evident, as shown in Figure 8a. The corresponding Fourier transforms of the images are seen in Figure 8b. The crystalline material appears to be present uniformly over the sample.

Figure 9 compares the Raman spectrum of the solid samples recovered immediately after water removal during Synthesis IV (one hour after reflux). One of these samples was washed with water, and the other was not. It is clear that washing changes the Raman spectrum. Thus, all of the Raman spectra shown were done on unwashed samples. Our primary focus was in the prominent T-O-T bending region (300 - 700 cm⁻¹). Figure 10 compares the Raman spectra of the gel from the composition 17Na₂O:1Al₂O₃:21.80SiO₂:975H₂O, after aging for 4 hours and after one hour of reflux during which 40 ml of water was removed. The starting amorphous material
is characterized by broad bands at 500 and 600 cm\(^{-1}\). Right after the water removal, the bands are shifted to 470 and 570 cm\(^{-1}\). Figure 11 shows the evolution of the Raman spectra during the water addition. After 10 min, the Raman spectrum shows the appearance of the FAU band at 500 cm\(^{-1}\), and decreasing intensity for the 470 and 570 cm\(^{-1}\) bands. With time, over the next 50 min, the Raman features characteristics of zeolite Y grow in at 350 and 500 cm\(^{-1}\). There is also a band at 700 cm\(^{-1}\), assigned to soluble aluminate species.\(^{14}\)

**Discussion**

Six different synthesis protocols were investigated, and the XRD patterns are shown in Figure 2. Synthesis I and II with identical compositions 17Na\(_2\)O:1Al\(_2\)O\(_3\):12.80SiO\(_2\):975H\(_2\)O were carried out in Teflon bomb or by reflux, respectively. Both the reflux method (Synthesis II) and bomb method (Synthesis I) did not result in crystal formation within two hours. Synthesis III, in which 40 ml of the water was removed from the flask during the first hour of reflux (17Na\(_2\)O:1Al\(_2\)O\(_3\):12.80SiO\(_2\):975H\(_2\)O to 17Na\(_2\)O:1Al\(_2\)O\(_3\):12.80SiO\(_2\):564H\(_2\)O) by slow, gradual removal while under reflux conditions resulted in crystals appearing after 2 hours, but the quality of the crystals were poor. In Synthesis IV, water was similarly removed over 60 min (40 ml) and the water added back gradually dropwise (50 min) to reach the initial concentration again accelerated the growth of FAU. The intensity and sharpness of the powder pattern indicates that high quality FAU crystals are being formed within two hours, and with continued heating, there is minor improvement in crystal quality. Synthesis V, with the composition 17Na\(_2\)O:1Al\(_2\)O\(_3\):12.80SiO\(_2\):564H\(_2\)O from the start formed FAU crystals within 2 hours, but the quality of the crystals are poor. Synthesis VI, with a similar starting composition as Synthesis V, but with water added back during the second hour of reflux, formed crystals within two hours,
was faster than Synthesis V, but the quality of crystals did not approach that of Synthesis IV, even after 6 hours of heating. A comparison of the crystallization behavior of Synthesis IV with the results of the all of the other synthesis protocols and compositions indicate that the water cycling method is leading to fastest crystallization kinetics, and is the focus of this discussion. The elemental analysis of the framework indicates that Synthesis I and Synthesis IV result in similar Si/Al ratios (Figure 4), so the acceleration effect during the cycling reflux is not due to framework Si/Al changes.

During Synthesis IV, the reaction proceeds under reflux as water is removed from the reaction and re-condenses in the addition funnel (Figure 1). As a result, the concentration of hydroxide ions increases within the gel. It is well known that increasing the hydroxide ion concentration increases the solubility of species, and possible leads to supersaturation of species responsible for nucleation.\textsuperscript{15} No zeolite crystals are present at the conclusion of the water removal (45 ml in ~50 min from a total of 90 ml). However, addition of 15-20 ml of water (over 20 mins) to the concentrated reactant solution lead to well crystallized zeolite whose amount grows as water is added back with time. The SEM of the gel immediately after removal of the water shows that the amorphous aggregates are made up of small particles (Figure 7). Upon addition of water within the first 20 min, there are multiple crystals present within each gel particle, which intergrow with time. The HRTEM does not show any evidence of crystallinity upon immediate removal of the water, but within 10 min of water addition, there are crystalline regions throughout the sample (Figure 8). These crystalline regions are not large enough to provide reflections in the XRD pattern. These nanosized regions of ordered material serve as the sites for crystallization as the gel matures in the next steps of the reaction. From the morphological studies, we propose that there is extensive nucleation throughout individual gel particles during the \textit{in situ} concentration
of the gel by evaporation, but without proceeding to crystallization. High supersaturation within the gel particle via interaction with the entrapped solution is proposed to drive the nucleation. Previous studies, such as in case of zeolite A, the gel was found to have a porous structure and liquid filled vacuoles were found within the gel particle, and protozeolitic nuclei were proposed to nucleate at the gel-vacuole liquid interface. The optimum size of the pores in which nucleation occurs is determined both by accommodation of nuclei of certain size, as well as having high supersaturation conditions for species responsible for nucleation.

Synthesis VI, which started with the more concentrated composition (17Na₂O:1Al₂O₃:12.80SiO₂:564H₂O), and water was added back just like Synthesis IV after one hour of reflux was also speeded up, but the crystals remained small with broad diffraction peaks even after heating for 6 hours. So, the removal of the water during the reflux step is providing more extensive nucleation than a concentrated composition, though in both Synthesis IV and VI, the composition after two hour of reflux is identical.

The Raman spectra indicate that washing disturbs the structure of the gel. There are metastable structures that disappear upon washing, so the nuclei only exist under the basic supersaturation conditions. After 1hr of heating under reflux, during which water is removed, and the morphological studies indicated extensive nucleation, the Raman spectrum shows bands at 470 and 570 cm⁻¹. The broad bands are indicative of a distribution of T-O-T angles. These bands are at a different frequency than the aged gel sample, indicating that nucleation is altering the structure of the gel. Band at frequencies around 470 cm⁻¹ have been observed, and assigned to 4 MR, the band around 570 cm⁻¹ has been assigned to branch structures.

Water addition was essential to crystal growth in Synthesis IV. There are several studies that suggest that reorganization of the gel structure to form crystals occur by interaction with the
liquid medium. A possible role of water could be to facilitate transport of nutrients from the amorphous gel phase to the growing crystal. Mass transport issues become relevant for crystal growth since species used in growth need to be replenished. Rate of addition of water is also important, if the water is added back fast (45 ml within minutes), the rate is slowed down, and could be due to dilution of the growth species that need to be delivered to the growing crystal. Besides transport, water could also minimize interparticle repulsions via a shielding effect. Use of intergrowth supporting substances that lower the large negative zeta potential has been shown to promote intergrowth of zeolite crystals.

**Conclusion**

The rapid crystallization of FAU from our system is unprecedented. In essence, we have effectively mixed the highly supersaturated, nucleating nature of the concentrated gel with the favorable conditions for crystallization characteristic of the reference gel composition by cycling water through the reaction. The net result is a gel that rapidly supersaturates forming a high concentration of primary nuclei that then rapidly crystallize upon addition of H₂O. As a result, a zeolite product of high quality can be obtained in a fraction of the time of traditional hydrothermal synthetic techniques.

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References


Figure 1: Reaction vessel for Synthesis II-VI.
figure 2: XRD patterns corresponding to the solid products isolated after 2hrs from a traditional hydrothermal synthesis (a, Synthesis 1), a reflux synthesis (b, Synthesis 2), a reflux synthesis with water removal (c, Synthesis III), reflux synthesis that is rehydrated in a drop wise fashion (d, Synthesis IV), a concentrated reflux reaction (e, Synthesis V), and a Synthesis V in which water is readded in a dropwise fashion (f, Synthesis VI)
Figure 3: SEM images of solid products isolated from Syntheis IV after 2hrs (a) and from Syntheis II after 6hrs (b).
Figure 4: NMR spectra of fully crystalline products isolated from Synthesis IV after 2hrs (a) and from Synthesis I after 8hrs (b).
Figure 5: XRD patterns of solid products isolated from Synthesis IV after water is added back at 0min (a), 10min (b), 20min (c), 30min (d), 40min (e), and 50min (f).
Figure 6: Evolution of the BET surface area of products isolated from Synthesis IV.
Figure 7: SEM images of solids isolated from Synthesis IV after water is added back at 0min (a), 20min (b), and 40min (c).
Figure 8: High resolution TEM images (a) and their respective Fourier transforms (b) of washed solids isolated from Synthesis IV after water is added back 0 min (a) and after 10 min at two magnifications (bottom two traces).
Figure 9: Raman spectra of solid obtained from Synthesis IV just before water is added back after 60 min reflux: unwashed (a), and washed (b) samples.

Figure 10: Raman spectra of Synthesis IV gel with after 60min reflux, with water removal (a), and before reaction but after ageing at room temperature for 4hrs (b).
Figure 11: Raman spectra of unwashed solids obtained from Synthesis IV after 0min (a) 10min(b) 20min (c) 30min (d) 40min(e) 50min(f).