

Selective Anisotropic Growth of Zeolite Crystals

A Senior Honors Thesis

by

TASHA APRIL DESAI

Submitted to the Office of Honors Programs
& Academic Scholarships
Texas A&M University
in partial fulfillment of the requirements of the

UNIVERSITY UNDERGRADUATE
RESEARCH FELLOWS

April 2003

Group: Engineering & Physics 3

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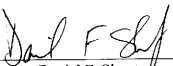
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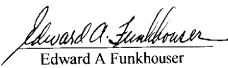
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ABSTRACT

Selective Anisotropic Growth of Zeolite Crystals. (April 2003)

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Precise control over particle size and morphology is emerging as a critical issue in the design of nanostructured materials. The explosive growth of nanoparticle synthesis is a good example of this. As material chemists have developed the ability to synthesize discretely sized and shaped semiconducting and metal/metal oxide nanoparticles, new applications for these materials have emerged including catalysis, sensing, tags for biomolecules such as DNA, and components of colloidal arrays. While numerous advances have been made in nanoparticle synthesis, these have been generally restricted to materials possessing relatively simple structures (fcc, bcc, hcp) with small unit cells. To date, the ability to modulate particle size and shape of more complex oxides such as zeolites has not been demonstrated. That is the goal of this work, to develop the ability to synthesize one- and two-dimensional particles of complex materials, which could be integrated into micro devices such as sensors and electronics. To achieve this end we are attempting to grow zeolite particles in the confined water spaces formed in water/surfactant systems, using these "nanoreactors" to modulate zeolite growth.

Our work to date has focused on the synthesis of two dimensional ($5 \times 100 \times 100$ nm³) particles of ZSM-5 in the presence of sodium-AOT, an anionic surfactant that has a high propensity for forming lamellar bilayer (L_{α}) phases in solution. Our results from this system indicate that while we are forming high aspect ratio particles, they are in fact a sodium silicate phase, not the target phase ZSM-5. Current work is elucidating whether replacing the sodium with other cations such as tetrapropylammonium will give the desired ZSM-5 phase. Also, we are exploring the use of cationic surfactants that seem more promising for this application. If this approach is successful it opens new avenues to crystallizing complex solids with specific shape, size, or morphological properties, opening new applications for zeolite materials.

Dedicated to my parents for their
support as I find my path through life

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I would like to thank Dr. Daniel Shantz for allowing me the opportunity to be an undergraduate researcher and for having the patience to help me in this journey. I would like to thank two of his graduate students, Charles S. Carr and Henry Cheng, for their assistance with experimental equipment and characterization methods.

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INTRODUCTION

Zeolites are a unique, technologically important class of materials related to the natural feldspars and feldsparoids minerals [1, 22, 3]. Zeolites are microporous crystalline tectoaluminosilicates comprised of tetrahedral building units (TO_4 , $\text{T} = \text{Al}$, Si) linked through bridging oxygen atoms. A rich diversity of three-dimensional structures exist in zeolitic materials because of the numerous ways to link these tetrahedra [37]. Zeolites, because they are crystalline, have well defined structures with uniform pore sizes between three to ten angstroms in diameter and can be made with a wide variety of framework compositions, ranging from a $\text{Si}/\text{Al} = 1$ to infinity. Zeolites containing aluminum (Al^{+3}) possess anionic frameworks, resulting in the need for charge-compensating extra-framework cations. A wide range of cations including alkali metal and ammonium cations as well as transition metals can be utilized as extra-framework species. It is also possible to substitute other elements for framework aluminum and silicon atoms including titanium, iron, and gallium.

All of these factors give considerable flexibility for tuning the chemical properties of zeolites and explain why zeolites have found widespread use in heterogeneous catalysis, adsorption and separation of gases, and ion-exchange operations [1,3, 18, 22, 37]. Along these lines the first commercial application of zeolites was in 1954 by Union Carbide for use as drying agents. Zeolites were first

This thesis follows the style and format of MLA Handbook for Writers of Research Papers. (Gibaldi, Joseph. MLA Handbook for Writers of Research Papers. 4th ed. New York: The Modern Language Association of America, 1995.)

introduced commercially in industrial separations and catalytic applications in the late 1950s and early 1960s. Currently, zeolites are used commercially in the separation of gases (e.g. pressure swing adsorption [32]), heterogeneous catalysis (e.g. FCC unit [28]), and in ion-exchange operations, replacing phosphate-based detergents.

As described above, zeolites have found widespread industrial application and have substantially impact society. As one example, consider that the zeolite catalysts used today in fluidized catalytic cracking to produce gasoline are a factor of 3-4 times more efficient in terms of feedstock utilization as compared to the amorphous silica/aluminas used prior to zeolites. However, given the relatively mature nature of zeolite science, researchers are looking to expand the use of zeolites beyond the well-established areas of ion exchange, separations, and catalysis [7].

In the current work we are try to synthesize zeolite particles that possess extremely high aspect ratios, essentially two-dimensional particles. Our initial target is the synthesis of $100 \times 100 \times 5 \text{ nm}^3$ zeolite slabs. This would be substantial, as precise control over particle size and morphology is emerging as a critical issue in the design of nanostructured materials. The explosive growth of nanoparticle synthesis is a good example of this [11, 13]. As materials chemists have developed the ability to synthesize discretely sized and shaped semiconducting and metal/metal oxide nanoparticles new applications for these materials have emerged including catalysis, sensing, tags for biomolecules such as DNA, and components of colloidal arrays [21, 25, 27, 28]. While numerous advances have been made in nanoparticle synthesis, these have been generally

restricted to materials possessing relatively simple structures (fcc, bcc, hcp) with small unit cells. With the exception of a recent report on the synthesis of ALPO_4 -5 fibers [40], the ability to exert precise control over the particle shape and size of materials with larger/more complex unit cells (e.g. zeolites) has not been demonstrated. The ability to synthesize monodisperse two-dimensional particles of zeolites where the direction of crystal growth can be deliberately manipulated would be of great fundamental and practical interest to the materials chemistry and zeolite science communities. From a fundamental viewpoint, the molecular insights needed to make such advanced materials rationally would open new directions in materials research. Moreover, zeolite particles with high surface/volume ratios where discrete crystallographic faces are exposed would be model catalysts for zeolite scientists probing surface-mediated chemical reaction mechanisms proposed in the literature, such as pore-mouth selectivity [36]. The practical impact would lie not only in new materials for existing applications (i.e. catalysis, separations), but also for emerging areas such as microdevices, molecular electronics, and nanostructured materials [6, 35]. Here we propose to achieve this end by coupling surfactant science with inorganic materials synthesis by using the well-defined aqueous domains that can be formed using water/oil/surfactant systems as confined spaces to assemble inorganic materials possessing complex structures.

An example of one such application for the materials we plan to make in this work would be their integration into, microelectronics, or “lab-on-a-chip” devices. For instance, the zeolite particles made in this work could be patterned into the channels of a

microreactor, shown in Figure 1, and used as catalysts, sensors, or absorbents in a “lab-on-a-chip” device. By aligning the pores of the zeolites in an axial orientation, a metal could be passed over the surface to form metal plates or wires.

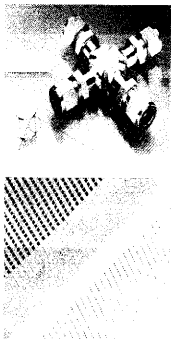


Figure 1 : Microreactor
From Janicke, et al *J. Catal.*
2000, 191, 282

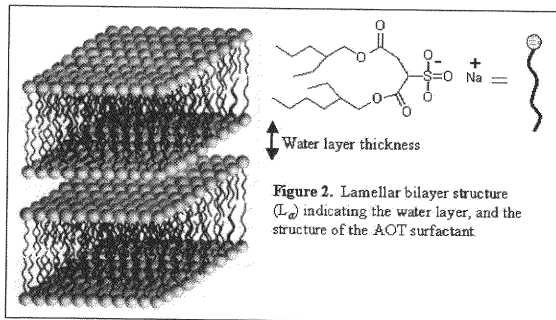
To achieve selective growth in one- or two- dimensions, the particles will be assembled in the presence of amphiphilic molecules such as surfactants. Nonionic alkyl poly (oxyethylene) surfactants and poly (oxyethylene) block copolymers are important families of surfactants and are widely used in “emulsifying, defoaming and antifoaming, coating, thickening, solubilizing, cleaning, lubricating, wetting, pharmaceutical, coal and petrochemical industries, and household applications” [41].

These surfactants have good interfacial stabilization properties and the advantages of being low-cost, nontoxic, and biodegradable. Low molecular weight surfactants

such as block polymers also have the advantage of permitting solution organization of larger structural features [41]. This characteristic was applied to zeolites in the hope of organizing the particles and growing the zeolites with the desired morphology. To facilitate this anisotropic crystal growth, we use water domains between surfactant bilayers, the size of which can hopefully be varied by adjusting the surfactant/water ratio. By using these “nanoreactors” to enhance the growth rate of zeolite particles in

specific directions, we hope to grow particles with the desired morphology.

Surfactants are a class of organic molecules with a hydrophobic (water fearing) tail group and a hydrophilic (water loving) head group. The amphiphilic nature of these molecules allows their aggregation state to be adjusted based on the amount of surfactant present, the surfactant/solvent ratio, and temperature. The surfactant used during this research was bis (2-ethylehexyl) sulfosuccinate sodium salt, or AOT (Figure 2) because of its ability to generate a lamellar structure in solution over a wide range of AOT/water ratios. By varying the amount of water in the system we can systematically vary the thickness of the water layer between the AOT layers. This should facilitate making particles of varying thickness in the short dimension. Based on studies in the literature varying the surfactant between 10-40% weight should enable us to vary the water layer thickness between 20 and 5 nm [2].



In this work, we have focused on the growth of ZSM-5 (Figure 3) in these confined aqueous spaces. This material was chosen as its synthesis has been extensively studied (4,14,16,29-31,33,34,38) and it is well known that it can be nucleated and crystallized from bulk solutions under very mild conditions. During this research, zeolites with the MFI framework were synthesized by mixing tetrapropylammonium hydroxide (TPAOH), which acts as the structure-directing agent, a silicon source, and water. ZSM-5 is a member of the pentasil family, so named as their framework structures are built from five-membered rings [15].

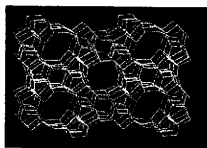


Figure 3 -- MFI framework – from the International Zeolite Association [12]

Throughout the course of this research, I became familiar with different methods of synthesis as we attempted to make the thin plates of zeolite crystals. Using several methods of characterization, we have qualitative evidence that we are making high-aspect ratio particles. Moreover, we have some tentative evidence (by infrared spectroscopy) that these materials possess the same structural subunits as ZSM-5. However, characterizing these materials has proved much more difficult than initially anticipated. In addition, the use of this surfactant, AOT, has also hindered our progress, as it was difficult to remove it from the sample. To circumvent this problem, other methods of collection were used to facilitate the removal; however, the use of certain methods introduced other factors to the experimental setup, such as the problem of aggregation of the particles when using a centrifuge to collect the sample. Overall, I was able gain experience with several characterization methods and experimental setups as we found alternatives to problematic procedures.

EXPERIMENTAL METHODS

Experimental Procedure

To synthesize the zeolite nanoslabs, nine grams of tetraethyl orthosilicate is added to 7.9 grams of a forty percent aqueous solution of tetrapropylammonium hydroxide in a teflon container. This solution undergoes vigorous stirring for thirty minutes at which time nine grams of water is added. Previous work [29] has shown that the resulting clear solutions contain uniform particles 2.8 nm in size. Once the nanoslab mixture has been allowed to age for an hour at room temperature the appropriate amount of AOT is added under vigorous mixing. After a homogeneous mixture is obtained, the container is put in a constant temperature bath or oven for the heating period. Initial attempts to recover the zeolite product will utilize filtration after diluting the solutions with excess water so the surfactant content is less than one weight percent.

The three synthesis parameters we varied are the surfactant/water ratio, temperature, and reaction period (vary between 1-3 days). Increasing the temperature should increase the rate at which the zeolite particles grow in size from the initial precursors. An added benefit of choosing AOT as our surfactant is that the lamellar microstructure is retained over a wide range of temperatures at the AOT/water ratios we are employing [2]. The water/AOT ratio is varied to determine if we can utilize varying the water layer thickness to control the thickness of the final material obtained. Overall, by analyzing these parameters, we hoped to assess how the synthesis temperature,

synthesis duration, and AOT content influenced the assembly of the zeolite nanoparticles.

Scanning Electron Microscopy (SEM)

One technique used to study the zeolite crystals is scanning electron microscopy. This technique can be used to characterize organic and inorganic materials and surfaces. The area to be examined is irradiated with a finely focused electron beam, which is either static or swept in a raster across the sample's surface. When the electron beam hits the surface, several different types of signals can be produced including secondary electrons and backscattered electrons. These signals can be used to determine many characteristics of the sample such as composition, surface topography, and crystallography [9].

There are several reasons that can explain the usefulness of the SEM including the high resolution that can be obtained. Most commercial instruments have a resolution on the order of ten nanometers with advanced instruments achieving resolutions better than two to five nanometers. In addition to high resolution, the SEM also produces a three-dimensional image of the sample, which is a "direct effect of the larger depth of field, as well as to the shadow-relief effect of the secondary and backscattered electron contrast" [9].

Samples to be analyzed using scanning electron microscopy need not be made thin enough to transmit electrons, as SEM measures the backscatter of electrons and not the absorbance. SEM is also able to help characterize samples with pronounced topography, which makes it a versatile and powerful machine and therefore a major tool in research and technology [9].

To generate an image, the electron gun, at the top of the electron column, produces a source of electrons and accelerates them to an energy between one and forty keV. However, the diameter of the beam produced is too large to generate a sharp image at high magnification. Therefore, electron lenses are used in the microscope to reduce the beam diameter and place a smaller, focused electron beam on the sample [9].

The scanning electron microscope that will be used in the future to analyze the zeolite crystals uses a conventional triode electron gun, which consists of a tungsten wire filament as the cathode, a Wehnelt cylinder or grid cap, and an anode. Before an image can be generated, the filament must be saturated. The filament current is increased until the beam current reaches a point where it no longer increases, a condition that is known as saturation. Then the user can be sure that the electron gun is producing a stable beam current [9].

X-Ray Diffraction

The first step in the characterization of any zeolite is verifying that the material synthesized is crystalline and contains no impurities. Diffraction techniques are the most suitable tool for studying the crystallinity of zeolites as they probe long-range

order. Most zeolite syntheses do not provide crystals of sufficient size and quality for analysis using single-crystal techniques, so usually powder x-ray diffraction (PXRD) methods are employed. Here we use PXRD to identify the phase synthesized and verify it is a pure phase free of amorphous material. This is done by assigning Miller indices to all of the reflections (peaks) in the XRD pattern and comparing the experimentally observed positions of these reflections to those for the known structure. A detailed discussion of the theory of scattering and diffraction is not given here, but can be found elsewhere [8, 10, 17, 19].

In x-ray diffraction, a packed sample is subjected to an x-ray beam, which interacts with the sample to produce a signal. Some of the photons may not appear in the transmitted beam due to transformations within the sample. For instance, some may have undergone scattered radiation by deviating from their course without a loss of energy. Others may have suffered a small loss of energy by a slight change of wavelength, which is called incoherent scattering. In addition, photons may be absorbed by atoms of the sample, which causes the atoms to be excited and eject an electron. Through this photoelectric effect the atoms return to ground state and emit either another electron or X-photons whose wavelength is a characteristic of the sample [10].

X-rays are electromagnetic radiation with a wavelength much shorter than visible light. The x-ray source used in this work is $\text{CuK}\alpha$ which has a wavelength of $\lambda = 1.541 \text{ \AA}$. Crystalline materials possessing periodicity on this length scale will coherently

$$\lambda = 2d_{hkl} \sin \theta$$

scatter x-rays according to Bragg's law

In Equation 1, λ is the x-ray wavelength, d_{hkl} is the distance between planes with Miller indices hkl , and θ is the angle of the incident x-rays. Figures 4 and 5 show a representation of the Bragg reflection process and a typical powder XRD pattern for a zeolite. Experimentally the x-ray wavelength and positions of the reflections are known so here we need to be able to assign all the reflections hkl values (i.e. index the powder pattern). For materials of known structure, this is done by deconvoluting the PXRD peaks and comparing the positions of the observed reflections to the known values based on structures published in the literature [24]. Further, the positions of the reflections can be calculated from Bragg's law using an appropriate expression for d_{hkl} based on the symmetry and parameters of the unit cell. For the case of cubic symmetry with unit cell parameter a , the expression for d_{hkl} can be found from

$$1/d_{hkl}^2 = \frac{h^2 + k^2 + l^2}{a^2} \quad 2$$

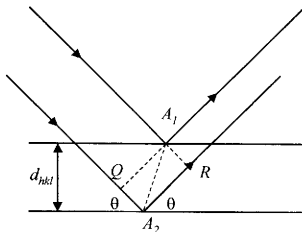


Figure 4: Detailed geometry of Bragg reflection. The path difference between the two rays A_1 and A_2 is $(QA_2 + A_2R)$ which is equal to $2d_{hkl}\sin\theta$. Adapted from reference [19]

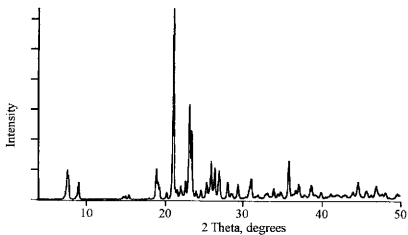


Figure 5: Typical PXRD pattern of an as-synthesized zeolite.

After all of the reflections are assigned hkl values, the unit cell parameters of the synthesized material are determined using a least-squares algorithm and compared to the reported values. If it is not possible to assign hkl values to all the observed reflections in the XRD pattern, then either the phase contains impurities or the symmetry is lower than expected. The structures of most zeolites are solved after the organic structure-directing agent is removed by exposure to air at higher temperatures (calcination), and it has been shown that the symmetry of the as-made material can be different (usually lower) than that of the calcined material. The presence of amorphous impurities is manifested as a broad featureless line in the range of 20-30 degrees 2θ .

Infrared Spectroscopy

Another characterization method employed was infrared spectroscopy. A beam of radiation in the infrared region of the electromagnetic spectrum is allowed to interact with the sample. The sample absorbs some of the wavelengths and allows others to continue through unchanged. All molecules have a certain amount of energy throughout their structure, which causes the bonds to stretch and contract and thus, vibrate. This energy is not continuously variable but is instead quantized; the molecule can stretch or bend only at specific frequencies. Therefore, when a molecule is irradiated with electromagnetic radiation, energy is only absorbed when the frequency of the radiation is the same as the frequency of the vibrational motion.

As a molecule absorbs the radiation, the vibration increases in amplitude. By measuring the infrared spectrum, we are able to see the different motions a molecule has because each absorbed frequency corresponds to a specific molecular motion. Interpreting these motions allows us to see what bonds are present in the molecule.

RESULTS

Each sample was prepared from a standard zeolite mixture. Nine grams of tetraethyl orthosilicate was added to a solution of 7.9 grams of forty percent aqueous solution of tetrapropylammonium hydroxide, nine grams of water, and the appropriate amount of AOT. The solution was then allowed to mix for the necessary period of time before centrifuged at 2000 rpms for five minutes. Afterwards, the solution was filtered, and the solid was collected and allowed to dry before undergoing x-ray diffraction. The parameters varied during the course of this research were the reaction time, surfactant/water ratio, and temperature.

The first set of samples was run at thirty-five weight percent AOT at fifty degrees Celsius. The time that the sample was allowed to mix was varied.

TABLE 1

Varied Reaction Time

Sample	Reaction Time	Final Mass
012	2 hours	2.23 grams
014	4 hours	3.14 grams
013	20 hours	2.54 grams
011	24 hours	3.39 grams

Overall, by examining Table 1, it appears that the longer the solution was allowed to stir, the greater the final mass of the sample. The discrepancy of the 4-hour sample could be due to contamination of the sample or failure to remove all of the surfactant from the sample. A representative x-ray diffraction pattern is shown below for the sample allowed to react for two hours.

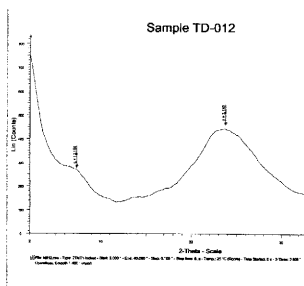


Figure 6: X-ray diffraction for Sample TD012

Through examination of the x-ray diffraction patterns of the samples (Figure 6), one can conclude that the samples produced similar signals with only a slight difference in intensity of the peaks. Interpreting the x-ray diffraction results is not trivial; however, we can conclude that these materials are not amorphous silica. X-ray diffraction ran on amorphous silica does not exhibit the low angle-feature observed at a two theta value of 7 degrees. Our hypothesis is that we have made small (less than twenty nanometers)

particles of ZSM-5, however, additional experiments, such as scanning electron microscopy, are needed to validate this hypothesis.

Upon running scanning electron microscopy on the sample reacted for two hours, we produced an image which allowed us to conclude that we were not making the intended plates we had hope for (Figure 7). We were able to conclude that we were making small particles, but the characteristics of the sample did not match what we had hypothesized. This could be due to several reasons such as the aggregation of the particles, the preparation of the sample before characterizing, or any residual surfactant on the sample. In addition, SEM is generally inconclusive due to our inability to disperse the particles during synthesis, to the side effects of the sputtering process, and to instrumental limitations as a high accelerating voltage can lead to charging of the sample.

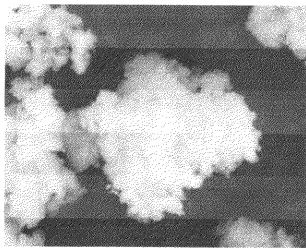


Figure 7: SEM for sample reacted for 2 hours (x2000)

The next set of samples was run at thirty-five degrees Celsius for twenty-four hours with the surfactant/water ratio varied.

TABLE 2

Varied Surfactant/Water Ratio

Sample	Percent AOT	Final Mass
021	15	0 grams
020	20	0.25 grams
018	35	2.41 grams

By comparing the data in Table 2, it can be concluded that the higher the weight percent of the AOT used, the larger the final mass of the sample would be. In addition, the size of the samples seemed to increase with an increase in percent AOT. This conclusion will be validated or invalidated with the results of the scanning electron microscopic image to be developed at a later date.

The x-ray diffraction of these samples is similar to those in Figure 6. Based on the signals produced, one can conclude that the samples are of similar material as the positions of the peaks are relatively similar although the intensities vary (Figure 8).

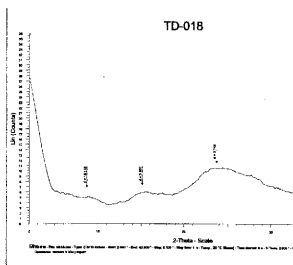


Figure 8: X-ray diffraction for 35 weight% AOT sample

Finally, various collection techniques were tested at two hours.

TABLE 3

Varied Collection Techniques

Sample	Percent AOT	Temperature (C ⁰)	Final Mass
010	35	50	2.39 grams
012	35	50	2.23 grams
015	35	50	1.63 grams

The first sample (010) was only filtered, sample 012 was centrifuged at 2000 rpms for five minutes, and sample 015 was centrifuged at 400 rpms for 30 minutes. It appears that there was little difference in the final mass for the first two samples, but the last sample had a final mass over half a grams less than the other two. This could have been caused by the inability for the particles to settle out of solution at such a low speed.

Temperature was also varied, but the final mass of the samples did not change with temperature. Therefore, we can conclude that there is little correlation between temperature and sample mass.

A colloidal zeolite solution was prepared for a basis for comparison. Dynamic light scattering was performed on the solution to determine the size of the particles. It can be concluded from the data that the particles have an average diameter of fifteen nanometers.

In addition, infrared spectroscopy was performed on the samples. The presence of a peak around 550 cm^{-1} is consistent with silicate building units similar to that of ZSM-5 in the sample.

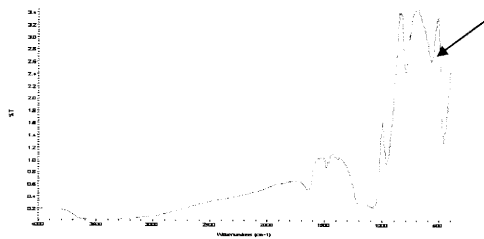


Figure 9: Infrared Spectrum of a colloidal zeolite sample

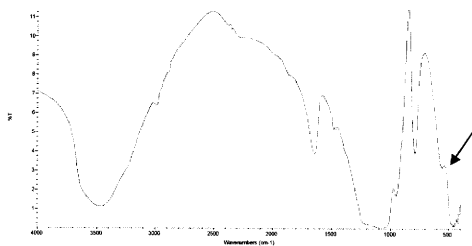


Figure 10: Infrared Spectrum of ZSM-5 made in the presence of AOT

By comparing the above spectrum with that of the colloidal zeolite solution, we have qualitative evidence that the materials we are synthesizing have similar structural units to that of ZSM-5. Therefore, we still retain the properties of a zeolite even with the addition of the surfactant.

Experiments were also performed to examine different synthesis procedures. For instance, a nanoslab solution was made with 9 milliliters of water, 7.9 tetrapropyl ammonium hydroxide, and 9 grams of tetraethyl orthosilicate. Then 5.71 grams of AOT (surfactant) was added to the solution to make a 40 weight percent AOT solution. As a comparison, another solution was made by placing the same amount of AOT in a flask and then adding water, tetrapropyl ammonium hydroxide, and tetraethyl orthosilicate. The previous solution, TD022, was filtered with 4000 milliliters of water, and the solid was recovered. However, the other sample, TD023, did not filter, and the sample collected retained the surfactant on it, which was evident in the infrared spectrum produced by the sample (Figure 11).



Figure 11: Infrared Spectrum of Sample TD023

The sample where I was able to remove all of the surfactant did not produce any peaks signifying the presence of AOT as seen in Figure 12.

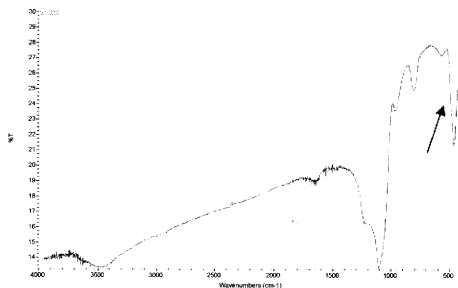


Figure 12: Infrared Spectrum for Sample TD022

In addition, scanning electron microscopy was performed on the samples to produce an image of the particles. The sample made with the premade nanoslab solution appeared to be a cluster of round particles, which was not what we intended to synthesize (Figure 13).

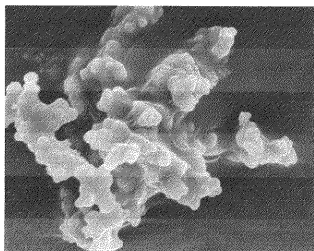


Figure 13: SEM of TD022 (x3000)

However, the other sample was less distinguishable. The image was inconclusive as we are not sure if the particle was zeolite or surfactant. If it was a zeolite particle, it did not form in the intended plate-like structure (Figure 14).

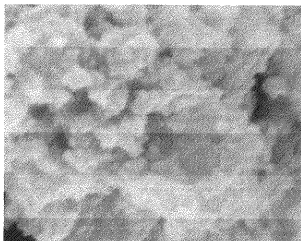


Figure 14: SEM of TD023 (x15000)

The effect of the ratio of tetrapropyl ammonium hydroxide was also examined. A solution with a TEOS:TPAOH:H₂O ratio of 1:0.18:20 was made and added to surfactant to synthesize a 35 weight percent AOT sample (TD024). A similar sample was made with a TEOS:TPAOH:H₂O ratio of 1:0.1:20 (TD026). Both samples were reacted for twenty-four hours at fifty-five degrees Celsius. By studying the infrared spectrums, we can state that qualitatively there is no difference in the composition of the samples (Figure 15 and 16).

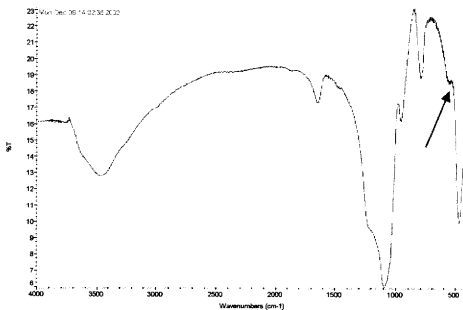


Figure 15: Infrared Spectrum of TD024

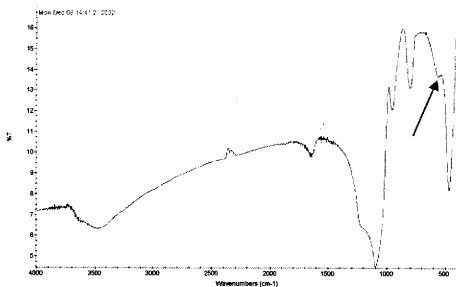


Figure 16: Infrared Spectrum of TD026

Similarities were also apparent in the scanning electron microscopy images produced by both samples (Figure 17 and 18). However, in both cases, round particles were made. We had hoped to make flat plates and can conclude that there is another factor that needs to be changed in the experimental procedure.

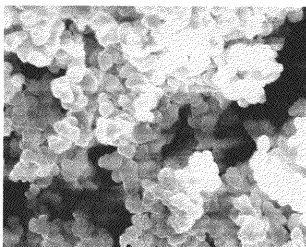


Figure 17: SEM for TD024 (x2500)

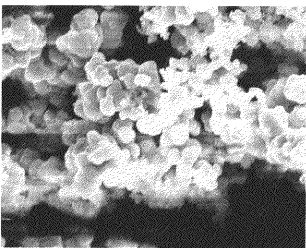


Figure 18: SEM for TD026 (x2300)

SUMMARY

Many problems were encountered throughout the course of this research. In the area of synthesis, we were unable to remove all of the surfactant during the washing of the sample. Therefore, the presence of AOT was evident in all of the characterization methods. In addition, it was much more difficult to characterize the samples than had been expected. The samples charged when subjected to the electron beam with scanning electron microscopy, making it difficult to obtain high quality images. The difficulty with SEM was due to our inability to effectively disperse the particles, which caused us to not get high-resolution images of the individual particles. In order to make good images, we need to use another instrument such as field emission SEM. With this instrument we can get much better images of samples, even when poorly dispersed. As an example, the sample shown in Figure 19 is a FE-SEM of zeolites made in the presence of DODAB. Even though this sample is poorly dispersed, the resolution/image quality is much higher than previous samples. The surfactant led to the presence of sodium in the sample and the formation of sodium silicate phases. This also led to inconclusive infrared spectrums as the peak at 580 wavenumbers could be due to the presence of this silica.

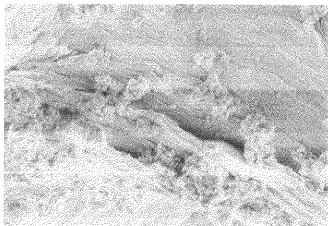
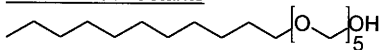


Figure 19: FE-SEM of sample in the presence of DODAB

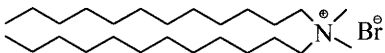
As many of the problems lay with the surfactant, different surfactants will be used in the future. Some of the surfactants we will experiment with are shown in Figure 20. We will also ion exchange the Na-AOT to remove the propensity for sodium silicate formation. To remove the surfactant, we will use Soxhlet extraction.

Nonionic Surfactants



$C_{12}E_5$ (C_{12} hydrophobic tail, 5 ethylene oxide units)

Cationic Surfactants



Didodecyldimethylammonium Bromide: $(C_{12})_2N^+(CH_3)_2Br^-$



Dioctadecyldimethylammonium Bromide: $(C_{18})_2N^+(CH_3)_2Br^-$

Figure 20: Surfactants to be used in the future

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VITA

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For the last three years, I have been a student at Texas A&M University as a chemical engineering major. I plan on graduating in May 2004 with a Bachelor of Science. Since November of 2001, I have been doing research on zeolites under the direction of Dr. Daniel Shantz. Through this venture, I have gained experience with different methods to synthesize zeolites and have also become familiar with several characterization methods as mentioned in my thesis. I have also participated in the Undergraduate Summer Research Grant program and am applying this to the Engineering Scholar's Program. In addition, I participated in the Student Research Week at Texas A&M University in April 2003.