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SYNTHESIS OF SILICALITE-1 AGGREGATES

A Major Qualifying Project Report

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by

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Abstract

The main objective of this project was to synthesize and aggregate larger Silicalite-1 crystals in one step that can eliminate the use of binders. A series of experiments was performed. First, the importance of silica in the synthesizing solution was investigated. Next, the time allowed for the bead to soak in the solution was increased. Then a different type of silica bead was tested. Lastly, the silica to structure directing agent ratio was decreased. The main findings of these experiments were: the presence of silica in the solution provided more evenly dispersed growth of crystals on the bead; the soaking time had little effect on the outcome of the synthesis; and an increase in structure directing agent led to more nucleation sites which covered the bead more uniformly with crystals.

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Acknowledgments

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Introduction

In this project, techniques for synthesizing Silicalite-1 aggregates, a type of zeolite, were investigated. Zeolites are crystalline molecular sieves composed mainly of silica and alumina. Silicalite-1 is a type of zeolite made entirely of silica.[1] The most useful application of Silicalite-1 is to filter harmful organic compounds, such as Methyl tert-butyl ether (MTBE), out of water. Its structure is able to trap the organic molecules within its channels and pores, and since Silicalite-1 is hydrophobic, the water doesn't penetrate the pores. Silicalite-1 crystals would, therefore, serve great purpose in a packed bed tower used to filter water.[2]

Silicalite-1 can be easily synthesized as a powder consisting of small crystals. When crystals are used for packing in a packed bed reactor, a smaller the crystal size creates less void space for fluid to move through. This can lead to a pressure build up at the top of the tower. Therefore, the inherent problem with this application is that the synthesized crystals would create a large pressure drop in such a tower. Current processes take advantage of Silicalite-1 by mixing it with an amorphous binding agent, such as clay, to make larger particles, which are typically 40 percent Silicalite-1.[3] This greatly decreases the efficiency of the filtration because the binder occupies volume and can block the pores and channels of the crystals. ExxonMobil has patented a process without a binder that synthesizes aggregates of Silicalite-1 crystals.[2] Unfortunately, this process requires three separate steps.

Previous projects at Worcester Polytechnic Institute (WPI) have explored different synthesis techniques to address these issues. One WPI student, Bradford Carleen, varied the solution compositions, reagents, and synthesis methods. Carleen was successful in synthesizing Silicalite-1 crystals on a silica bead however the beads did not have the desired properties for application in a packed bed reactor.[4] Another student, Sylvie Gonthier, focused more specifically on seeded crystal growth. Gonthier's solution was successful in creating Silicalite-1 crystals; however she produced crystals in a powder form which is also undesirable for application in a packed bed reactor.[5]

The main objective of this project was to synthesize and aggregate larger Silicalite-1 crystals in one step that would also eliminate the need for amorphous binders. This new, cost effective method would be useful at the industrial level and could decrease the amount of time and energy needed to synthesize the proper sized Silicalite-1 aggregates for use in a packed bed reactor.

Background

This section will outline a brief history of zeolites, and describe their general properties.

Brief History

The distinctive properties of zeolites were first characterized by the famous Swedish mineralogist Axel Fredrik Cronstedt, who discovered them in Svappavaara in North Sweden in 1753.[6] The term "zeolite" meaning "boiling stone," was used to describe the substance because it appeared to bubble when heated in his blow-pipe flame.

The bubbling seen by Cronstedt was caused by water escaping through the pores of the crystals. Each crystal contains many pores and channels that characterize zeolites as molecular sieves. The atomic structures of zeolites are based on three-dimensional frameworks of silica and alumina tetrahedra, meaning that each silicon or aluminum ion is surrounded by four oxygen ions in a tetrahedral configuration. Clusters of these tetrahedra form boxlike polyhedral units that are further linked to build up the entire framework. The formation of these polyhedral units varies with different zeolites, as some may be equidimensional, sheet-like, or chainlike. The framework of a zeolite has a negative charge, which is balanced by the cations housed in the cavities of their structures. Zeolites are low-density structures where between 20 and 50 percent of the volume is voids.[7] So, even though zeolites belong to the molecular sieve class of materials, and the specific composition of the zeolite framework must be restricted to alumina and silica tetrahedral connected at the vertices, this actually defines a very broad spectrum of materials, both manmade and natural, that are useful in many different applications ranging from adsorption to catalysis to ion exchange.[8]

According the International Zeolite Association's Structure Commission, there are 194 different framework types that zeolites can form.[9] The association also has datasheets for 38 naturally-occurring zeolites, which includes stilbite – the type of zeolite that was discovered by Cronstedt. This study will only involve one type of zeolite, however, called Silicalite-1.

Structure and Properties of Silicalite-1

Silicalite-1 is a type of zeolite known as ZSM-5. ZSM-5 is a synthetic aluminosilicate zeolite patented by Mobil in 1975.[3] Silicalite-1 is ZSM-5 without the aluminum. Silicalite-1 has an MFI framework, which is pictured below in Figure 1:

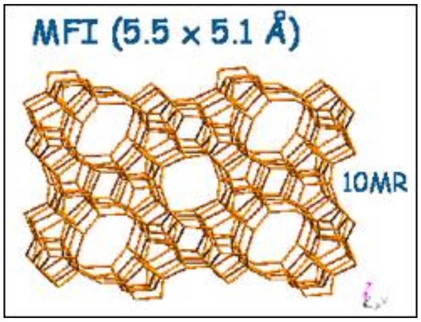


Figure 1: The MFI Structure.[1]

Figure 1 shows that there are many channels, pores, and cavities present in this structure. “10MR, or 10-membered-ring, means that the window is formed by 10 tetrahedra which are connected by shared oxygen atoms.[1] Pores and cavities can be used to capture certain particles while allowing smaller ones of appropriate shape to filter throw the channels. A typical X-ray diffraction pattern that can be used to identify Silicalite-1 is pictured below in Figure 2:

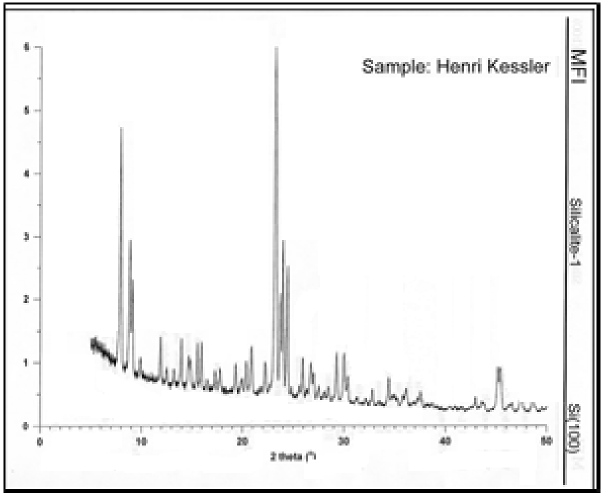


Figure 2: Typical XRD Pattern for Silicalite-1.[10]

The structure of Silicalite-1 gives it unique properties that make it valuable for certain industries.

Applications of Silicalite-1

Zeolites have many daily and industrial applications. Zeolites are used in animal litter, bedding, and additives in feed. Additionally, they are used in odor and moisture control. They are widely used for catalytic cracking in the petroleum industry.[11] The application of zeolite depends largely on its structure, selectivity, and composition. One main use of Silicalite-1 is in packed bed reactors to remove Methyl tert-butyl ether (MTBE) from groundwater because of its selectivity.[4]

Water Purification in Packed Beds

Methyl tert-butyl ether (MTBE) is used as a fuel oxygenate added to gasoline. This volatile organic chemical collects in groundwater, and is harmful to drink. The Environmental Protection Agency (EPA) regulates the levels of MTBE in potable water. If the level exceeds the EPA limit, the water must be purified.[12]

MTBE can be removed from groundwater using a packed, moving or fixed bed reactors using Silicalite-1 as the packing material. Silicalite-1 is used to convert hydrocarbon feeds in a packed bed. The ground water stream comes in contact with the Silicalite-1 in the packed bed, and after a period of time, the unwanted compound is absorbed by the zeolite within its pores. The unwanted compound is then carried off with the zeolite. The water stream leaving the reactor is then cleaned of hydrocarbons. This separation is possible because the hydrocarbons have a similar critical dimension to the pore size of the zeolite. The hydrocarbon will be trapped in the pore of the zeolite, but the water molecules will bypass the crystals.[2]

When Silicalite-1 is used in a packed bed reactor, the pressure drop through the reactor is a concern because of the size of the particles. The largest crystal size of Silicalite-1 used in a reactor is 120 µm. When the water is purified in the reactor, there can be a pressure drop as large as 2000 psi over the reactor. If the size of the particle is increased, the pressure drop over the packed reactor would decrease. Therefore, the aggregation of larger Silicalite-1 crystals is needed.[4]

Binders are used to increase the size of the zeolite particles, but then the particle is therefore not entirely zeolite. In a packed bed reactor, the binder would occupy additional space in the reactor, which in turn would become unused space because the binder cannot sieve the entering stream. The reactor would need to be larger to accommodate the amount of packing, to include both the zeolite and binder. ExxonMobil has addressed this problem by aggregating larger Silicalite-1 crystals for packed bed reactors. Their particles are zeolite-bound-zeolite.[2] This zeolite-bound-zeolite is a larger particle than the zeolite alone, but does not use an unwanted binder. This would lead to a smaller pressure drop in a packed bed reactor, and no unused space in the column.

Synthesis

Robert Milton, a chemist at Union Carbide, began researching the synthesis of zeolites in 1949 in Buffalo, New York. He first started using the chabasite synthesis technique which includes the use of high temperatures and insoluble forms of silica and alumina in weakly basic reaction mixtures. He soon found that he could synthesize zeolites at lower temperatures using soluble forms of silica and alumina in a strongly basic reaction gel. Through his work, Milton was able to synthesize zeolites A and X which led to more research on synthesis techniques for other zeolites.[11] There are a wide variety of techniques that exist for synthesizing ZSM-5. In particular, this investigation uses a hydrothermal method of growing ZSM-5 crystals. There are several factors that affect the size and number of aggregates produced by a synthesis. These factors are discussed in the following sections.

Fundamentals of Crystallization

Crystals are known for their highly ordered structure which includes atoms, ions, or molecules that are arranged in three-dimensional arrays called space lattices. There are several ways that crystallization can occur: the formation of solid particles in a vapor, solidification from a liquid melt, and crystallization from a liquid solution. In this process as well as in industry, the latter method is used in which nucleation (the formation of new particles) occurs in a supersaturated liquid solution. There are two types of primary nucleation: homogeneous and heterogeneous. In homogeneous nucleation, particles are formed without the influence of external walls or particles. This instance is rare because there are almost always external factors affecting the rate of nucleation. For heterogeneous nucleation, solid particles of foreign substances catalyze nucleation which increases the rate of nucleation.[13]

Once nucleation occurs and particles have been formed, the next step is crystal growth. Crystals grow through the diffusion of solute molecules or ions through the liquid to the growing faces of the crystal. Then the solute is accepted and incorporated into the space lattice of the crystal at a finite rate.[13]

Aggregation

There are synthesis techniques that use a binder to mold zeolite powder into aggregates that can be used in fixed beds. Typical binders are alumina, silica, titania, and other clays.[2] However, the use of a binder blocks pores of the zeolites and decreases the active area that can be used for catalysis. Binders can also react with chemicals to form unwanted products in the bed. A better synthesis technique for achieving higher zeolite content in the aggregate was desired.

In 2002, Mobil was the first company to patent a synthesis process for synthesizing a zeolite-bound ZSM-5 structure which was based on the following chemical reaction:

$$SiO_2 + NaAlO_2 + NaOH + N(CH_2CH_2CH_3)_4Br + H_2O \rightarrow \text{ZSM-5} + \text{analcime} + \text{alpha-quartz}$$

This equation is comprised of the five types of ingredients necessary for ZSM-5 synthesis, including a silica source, an alumina source, a mineralizer, a structure directing agent and water, respectively. The process converts a silica binder to a zeolite binder by using the previously mentioned reactants.[2]

Previous students at Worcester Polytechnic Institute (WPI) have conducted multiple experiments to create zeolite aggregates of Silicalite-1. In these studies, silica beads were converted into spherical aggregates of Silicalite-1. For this method, a nutrient solution was placed into a stainless steel autoclave that was lined with Teflon. A mineralizer was added to the solution to increase the solubility of the compound, in these cases sodium hydroxide was used. Mesh wire was then placed in the top of the Teflon liner to suspend silica beads over the nutrient solution. The autoclave was placed into an oven at a predetermined temperature. At the raised temperature, the amorphous silica in the bead was converted to Silicalite-1. One WPI graduate student, Bradford Carleen, found that the conversion started at the edge of the beads and drew silica and structure directing agent from the core. This trend leads to a hollow shell of Silicalite-1 with poor mechanical properties.[4]

Structure Directing Agent

A structure directing agent is typically used as a template for the formation of Silicalite-1. These templates are typically stable under hydrothermal conditions, are relatively hydrophobic to silicate species, are able to dissolve solvent molecules, and are comparable in pore size and shape to the desired zeolite. In 2005, Cheng and Shantz studied the effect of replacing the alkyl group of the tetrapropyl ammonium (TPA) cation used for synthesizing Silicalite-1. They found that the TPA cation leads to the shortest reaction time and largest particle growth rate. The use of a different alkyl group such as methyl or ethyl would hinder the growth of the Silicalite-1 crystals.[14]

Structure directing agents are typically non-recyclable since they are burned off in the calcining process. Thus, an expensive material would have a serious impact on the economic feasibility of the synthesis method.[8] Narayanan et al. conducted syntheses with and without the structure directing agent, TPABr. They found that they were capable of producing ZSM-5 zeolites without the use of TPABr.[15] However, the consequences of neglecting to use a structure directing agent need to be studied more in depth. Despite these findings, this project used TPABr to synthesize Silicalite-1 crystals because there were more successful syntheses documented using TPABr than not.

Temperature

Bradford Carleen, preformed experiments aimed to demonstrate the effects of temperature on crystal growth and time. Carleen made a mixture of 5.505 grams tetrapropyl ammonium bromide, 0.492 grams sodium hydroxide, and 50 grams of water. He placed this solution in autoclaves with 2 grams of silica beads. These autoclaves were placed in the oven at different temperatures: 137 °C, 150 °C, and 180 °C. Samples made at the different temperatures were analyzed to correlate the temperature to the crystal growth and time, and the results are shown below in Figure 3 and Figure 4:[9]

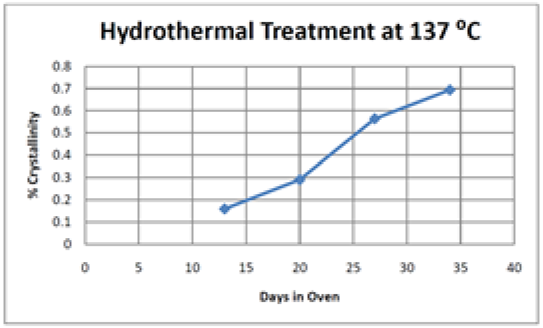


Figure 3: Percent Crystallinity vs. Days in Oven at 137˚C

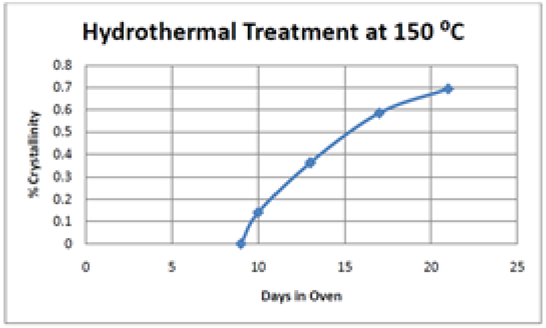


Figure 4: Percent Crystallinity vs. Days in Oven at 150˚C

The crystallization process that took the longest was at 137 °C. When the temperature was 137 °C, the zeolite reached 70 percent crystallinity after 34 days in the oven. The zeolite reached 70 percent crystallinity after 21 days in the oven at 150 °C. The crystals grew fastest at 180 °C. At too-high temperatures, crystal growth will be inconsistent. The crystals formed at 137 °C and 150 °C were coffin-like structures, but crystals formed at 180 °C had a rounded leaf-like morphology. Carleen explained that at higher temperatures, the structure directing agent influences the nucleation of the crystal, which then influences the growth of the crystal.[9]

Time of Aging

Aging time is the time a nutrient solution is allowed to sit before being put into an autoclave and raised to a temperature high enough for crystal growth. As aging time increases, nucleation increases, which ultimately leads to smaller crystals. Crystal size decreases since more nucleation sites will disperse the nutrient amongst a larger quantity of crystals. Thus to prepare a Silicalite-1 aggregate, a minimal aging period was used.

Silica Source

A group of aggregators from Sweden and Bulgaria, Qinghua Li, Boriana Mihailova, Derek Creaser, and Johan Sterte studied the effect of two different silica sources, colloidal silica sols and Tetraethyl Orthosilicate (TEOS). The two types of colloidal silica sols were Ludox TM and Ludox LS. Ludox TM is 39.8 wt. % SiO_2, 0.11 wt. % Na_2O, and the particle size is 22 to 24 nm. Ludox LS is 30.8 wt. % SiO_2, 0.108 wt. % Na_2O, and particle size 11 to 13 nm. Each silica source was used in a solution, and a one-step synthesis was performed. For each solution, small colloidal silica particles were present before heating. The experiment was performed at 60 °C and 100 °C, but the experiment at 100 °C is more relevant.

After heating, the TEOS crystals contained very small sub-colloidal amorphous silica particles that were present throughout the crystallization. The Ludox TM and LS solutions showed no small sub-colloidal silica particles, but these could have been undetected because the smaller particles were hidden by larger sub-colloidal particles present in the Ludox systems.

It was calculated that at 100 °C, the crystal concentration nucleated from TEOS was seventeen times more than the Ludox systems. The average crystal size, zeolite yield, and growth rate of the crystals formed were also compared, and can be seen in Table 1 below:

Table 1: Average Crystal Size, Zeolite Yield, and Growth Rate for TEOS, Ludox TM and LS.[16]

Silica Source	Average Crystal Size (nm)	Zeolite Yield (%)	Growth Rate (nm/hr)
TEOS	101	60.60	3.76
Ludox TM	286	62.00	5.76
Ludox LS	297	61.45	5.61

Although the different silica sources had similar zeolite yields, the average crystal size was larger for the Ludox systems and had a faster growth rate as well. Out of these two options, the Ludox silica sources would more likely be used a packed bed because of their larger crystal sizes.[16]

Aerogel Silica Beads

Aerogels were first synthesized by Steven Kistler in Stockton, California in 1931. Kistler created a solid Aerogel bead from removing the liquid from a wet gel. Kistler's process was a two-step process. The first step of the process was to wash the silica gel with water to remove the salts from the gel. The second step was to exchange the water in the gel for alcohol. To synthesize Aerogel beads, a wet gel is formed and the gel is dried to form a solid. Stanislaus Teichner from Lyon, France synthesized Aerogels from a one-step method. This one step method eliminated the need for the water-to-alcohol exchange as well as the impurities of salts in the gel. When Teichner's method is used, the chemical reaction that takes place is[17]:

$$Si(OCH_2CH_3)_{4\ (liq.)} + 2H_2O_{\ (liq.)} \rightarrow SiO_{2\ (solid)} + 4HOCH_2CH_3\ (liq.)$$

This reaction is usually completed with excess water.

The Aerogels, like other porous materials can be classified by their pore size. Micropores are pores of diameter 2 nm or smaller. Pores with diameters between 2 and 50 nm are mesopores, and macropores have pore diameters greater than 50 nm. Aerogel beads have micropores, mesopores, and macropores, but most of the pores are mesopores. The size of pores in the Aerogel is important because the mesopores allow liquid to penetrate the Aerogel bead. A downfall to the Aerogel beads is when handled roughly, the Aerogel beads break like glass. Additionally, silica Aerogel beads are destroyed when contacted with liquid.[17]

Silica to TPA Ratio

In one Silicalite-1 unit cell, there are 9 6 silica atoms for every 4 TPA molecules. The ratio of silica to TPA in the Silicalite-1 unit cell is 24. As the amount of template, TPA, increases, the nucleation rate increases. Increasing the TPA increases the number of nucleation sites and smaller crystals are formed. Therefore, the amount of TPA used must be increased for more nucleation to occur. Smaller crystals are formed from solutions with lower silica to TPA ratios. The ratio must be less than 24 so that there is enough template to synthesize Silicalite-1 crystals.[18]

Experimental Procedure and Results

General Procedures

Safety Precautions

Safety was always the number one priority throughout this project. Safety eye goggles were worn at all times and hair was tied back when in the lab. Heat resistant gloves were used whenever hot items needed to be removed from the oven.

Preparing the Standard Solution

It was decided that a "standard" batch composition would be used throughout the experiments. Then certain parameters such at the Si: TPA ratio were varied based on the "standard" composition. However, it is important to note that all of the reactants remained the same, only their molar ratios were varied. This "standard" batch composition was taken from "Investigation of the Formation of Silicalite Crystallites on Silicalite Crystals used as Seeds" by Sylvie Gonthier because of Gonthier's success in repetitively synthesizing Silicalite-1 crystals in her work.[5] This solution was referred to as "standard" solution in all of the experiments performed. The batch composition used was as follows in Table 2:

Table 2: Batch Composition for the "Standard" Solution

Substance	Brand	Amount (g)
Tetrapropyl Ammonium Bromide	Aldrich	6.44
Triple exchanged and triple filtered purified water	Barnstead Nanopure II	10.8
Ludox AS40 Colloidal Silica	Aldrich	27.2
Ammonium Hydroxide	Aldrich	28.2

Autoclaves

Small Autoclaves

Autoclaves from the lab were collected and Mr. Ferraro made brand new Teflon liners for them. Figure 5 below is an example drawing of the liner (in white) inside an autoclave (in gray):

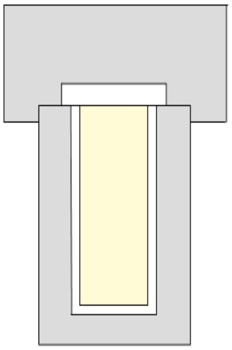


Figure 5: Small autoclave system; Teflon liners shown in white

Before the liners could be used in an experiment, they had to be cured. To cure the liners, they were filled up ¾ full with distilled water. They were then closed and placed into their respective autoclaves. The autoclaves were placed into the oven at 150°C for approximately 24 hours. No air leaks were observed during the curing of the liners. They were then removed from the autoclaves and cleaned using dish detergent and water. Then they were ready for use.

Using the Small Autoclaves

This procedure was used for creating Silicalite-1 powder only. Larger autoclaves were used for experiments involving silica beads. After a solution was made and placed into a clean liner for a small autoclave, the liner was placed into the autoclave. Next, the autoclave was tightened using a vice grip and wrench and then placed into an oven at 150°C. After a predetermined amount of time, the autoclave was taken out of the oven and placed into a bowl of ice to cool. The autoclave was then opened and the liner removed. Next, the liner was opened and its contents were poured onto filter paper that was placed over a vacuum pump to remove any excess water. The filter paper, along with the prospective Silicalite-1 crystals, were then placed back into the oven at 150°C for approximately ten minutes to further dry the sample. The sample was then taken out of the oven and collected in a vial for analysis. The liner and autoclave were then cleaned with dish detergent and water prior to its next use.

Large Autoclaves

To allow the crystals to grow on silica beads undisturbed in a controlled setting, Mr. Ferraro created two Teflon trays designed specifically for two large autoclaves, illustrated below in Figure 6:

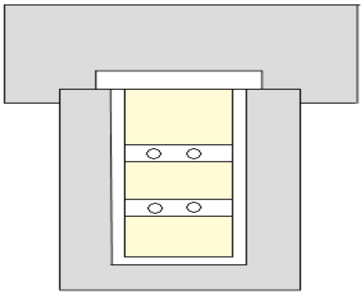


Figure 6: Large autoclave system

Each tray had a diameter of 4cm and a height of 1cm. The trays featured twelve holes with a 3mm diameter, slightly smaller than the average silica bead size in order to prevent the bead from falling through. The trays stacked directly on top of each other and had a 4mm wide hole through the center where a nylon screw was used to move each tray individually. There were also eight holes through the sides of the trays with a diameter of 5mm to allow vapor to move through the system, as pictured in Figures 7 and 8:

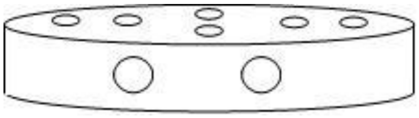


Figure 7: Side View of a Teflon Tray

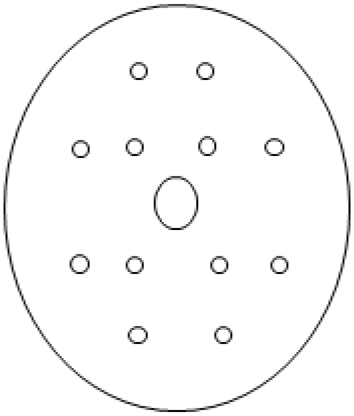


Figure 8: Top View of a Teflon Tray

These liners and trays were cured just like those made for the small autoclaves and then cleaned before use in experiments. Figures 9 and 10 show actual images of the liners and trays created:

Figure 9: Teflon Lid, Liner, and Trays

Figure 10: The Assembled Liner and Trays

Using the Large Autoclaves

When the large autoclaves were used in an experiment, multiple beads were placed in the holes on the trays suspended above solution. For all tray tests, liquid was poured into the bottom of the liner until the level reached just below the height of the bottom tray. One tray was placed into the autoclave using the Nylon screw then beads were placed in the holes on the trays. These beads were treated before being placed on the trays. The second tray was placed on top of the first tray, and again beads were placed in the holes of the tray. The autoclave was securely fastened with vice grips and a wrench.

Scanning Electron Microscope

In order to analyze the samples, it was necessary to use a Scanning Electron Microscope (SEM). This was chosen because it was difficult to inspect the surface of a silica bead using an optical microscope. SEM analysis made distinguishing between a silica bead and Silicalite-1 crystals possible. An Amray Model 1610 Turbo Scanning Electron Microscope was used for all images captured. In the last experiment, where the ratio of Si: TPA was 3, a JEOL 840 SEM was used while the other was under repair.

Preparing a Sample for SEM Analysis

For Powder

Double-sided carbon tape was placed onto the pin mount. Then a small amount of powder was sprinkled onto the carbon tape with a spatula.

For Beads

To prepare the beads for SEM analysis, two beads from each experiment were selected. One bead was covered in either carbon paint or tape with the exception of a small portion for examination. The bead was placed directly onto the mounting plate using the carbon paint or tape for adhesion, leaving the exposed section facing up.

To look at the cross section of a bead, the second bead was cleaved in half using a sharp knife and tweezers that held the bead in place. Extreme caution was used in the process so as not to damage the bead nor cause any physical harm. The round side of the cleaved bead was surrounded in carbon tape and stuck to the mounting plate so that the cross section faced up.

Sputtering

The machine used to sputter the samples was the Denton Desk II. The samples were sputtered with palladium for 15 seconds. The pin mount with sample was placed into the sputtering machine and the system was turned on. Once the pressure in the chamber was pumped down below 30 millitorr, the “sputter” button was pushed. Using the gas control knob, the pressure was set to approximately 75 millitorr. The time was set for 15 seconds. After pushing the “start” button, the current was set to 45 milliamps using the control knob. The machine sputtered the samples for 15 seconds, and then the samples were ready for SEM imaging.

X-Ray Diffraction

In order to complete X-Ray Diffraction (XRD) analysis, the sample had to be calcined. The sample was calcined by placing it in a crucible and putting it into an oven while it was slowly heated to and held at 500°C for approximately 24 hours. The calcining process removed any leftover template (TPA) from the crystals so that a more accurate XRD pattern could be generated. Mr. Alex Augustine then performed the XRD analysis with the Rigaku X-Ray Diffraction machine, and the results were compared to those published on the International Zeolite Association’s (IZA) website.

Validation of Methods

It was necessary to develop proper laboratory techniques for synthesizing Silicalite-1 crystals before performing various experiments. A validated process was followed to ensure that Silicalite-1 crystals could be synthesized with comparable results.

Experimental Procedure

The validated process used was published by Sylvie Gonthier. A standard solution was placed into the oven at 150°C for 13 days. The sample was then filtered, dried, and collected in a vial for analysis.

Results

The sample was analyzed with an optical microscope where coffin-like shapes could be seen, which is characteristic of Silicalite-1 crystals. The type of crystals that were made was confirmed using SEM and XRD.

SEM pictures were used to better look at the structure of the crystals. Figure 11 below shows an image of the crystals synthesized:

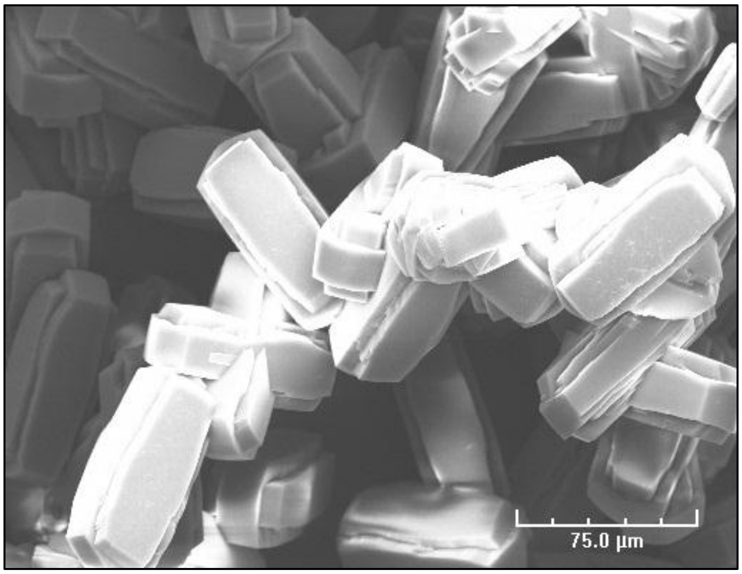


Figure 11: Silicalite-1 Crystals Made Using Sylvie Gonthier's Batch Composition, Image at 500X

Figure 11 shows the coffin-shaped crystals that were seen in the optical microscope, which suggested that Silicalite-1 crystals were successfully synthesized.

On the following page, Figure 12 shows the results that the team got from performing XRD analysis on the sample. Figure 13 shows a standard XRD of Silicalite-1 from the IZA website.

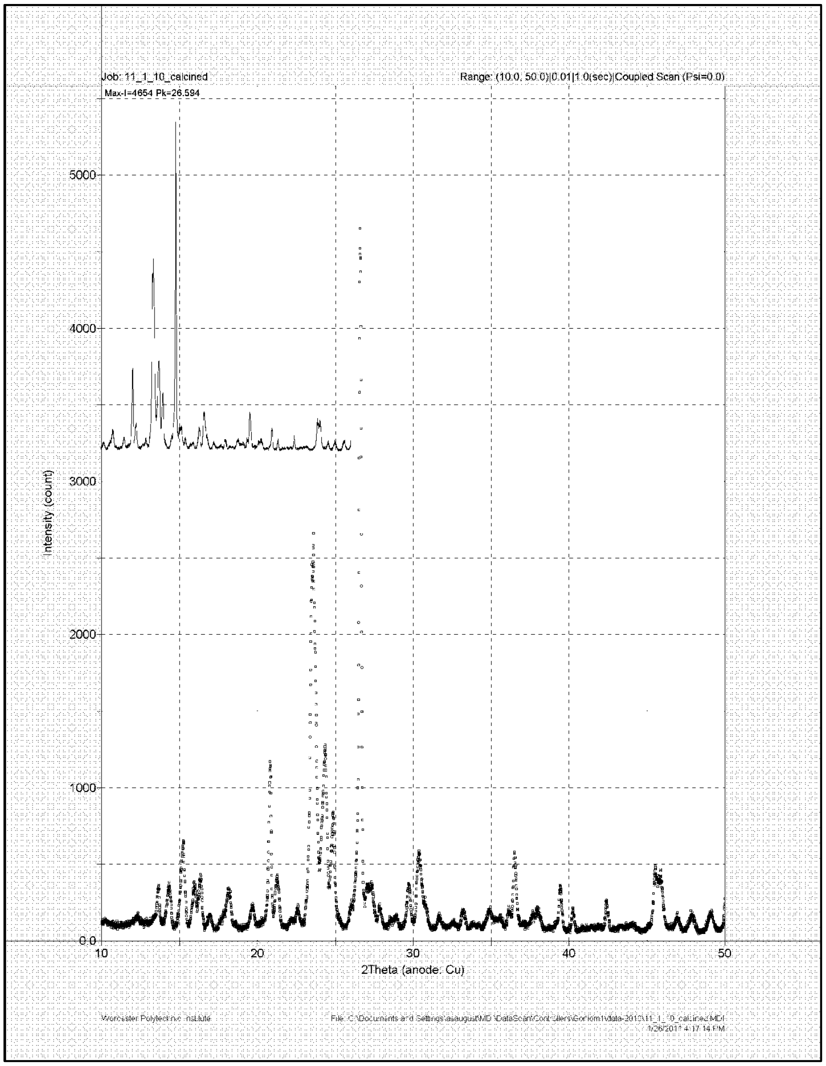


Figure 12: XRD Analysis of the Sample

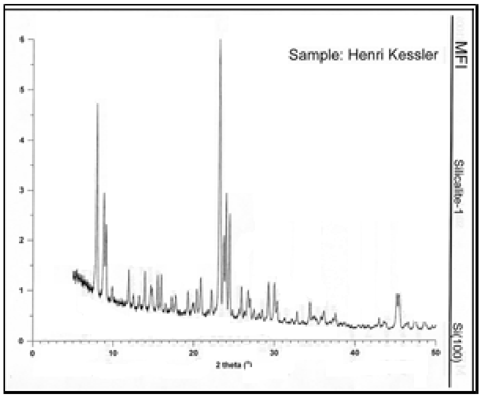


Figure 13: XRD of Silicalite-1 Crystals from the IZA Website

One can see based on Figure 13 that there should be significant peaks below 2-theta equal to 10, which the XRD that was used at WPI was not capable of measuring. Both images have significant peaks around 2-theta equal to 24 however. This confirmed that Silicalite-1 crystals were successfully synthesized.

Silica Beads

After successfully synthesizing Silicalite-1 crystals using a validated method, the next step was to perform basic experiments using amorphous silica beads. The silica beads absorb water quickly and crack into pieces. Because of this, the beads had to be pre-hydrated in order to remain intact when they came in contact with the solutions that were made. The beads were "hydrated" by placing them in a desiccator over water at room temperature so that they would adsorb water vapor.

Water Content of Hydrated Beads

Ms. Pranoti Navare used the Thermogravimetric Analysis (TGA) machine to help determine the water content of a hydrated bead that had been in a desiccator for a month. The TGA has a small balance surrounded by a furnace where a sample is heated at a certain rate and the change in weight percent is graphed. The results of the TGA are shown below in Figure 14:

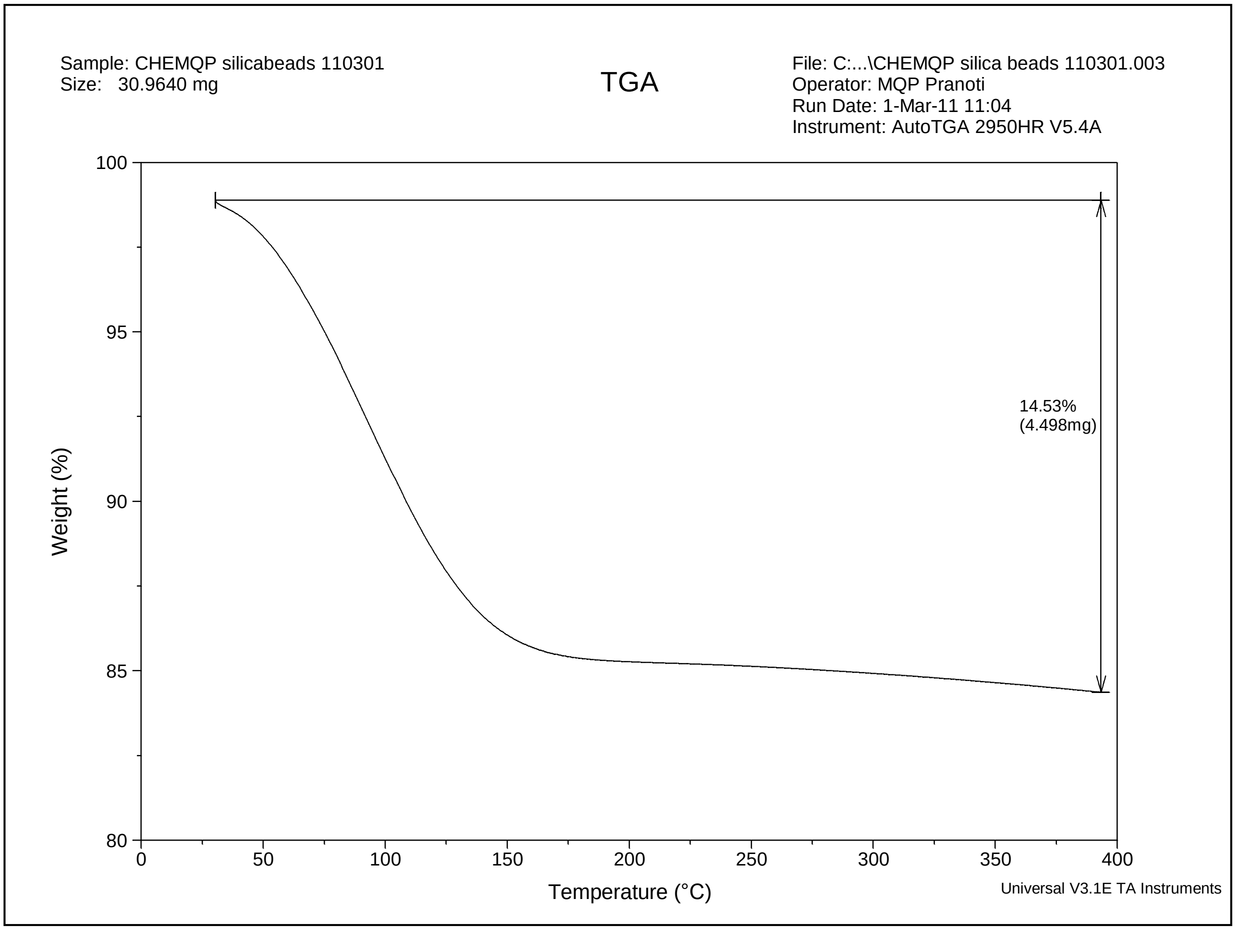


Figure 14: Results from TGA Analysis of a Silica Bead

From the TGA results in Figure 14, it can be seen that as the temperature was raised from 35°C to 400°C, the silica bead lost a total of 14.5 percent of its weight. Since the largest change in weight occurred around 100°C, it was determined that the change in weight was a result of water evaporating out of the bead. Therefore, the hydrated beads were assumed to contain approximately 15 weight percent water.

The Effect of a Solution on Silica Beads

Next, it had to be ensured that the silica beads would remain intact even in the standard solution at high temperatures. The beads were placed into a liner filled ¾ full of the standard solution into a small autoclave at 150°C. The beads did not dissolve after 24 hours in contact with the solution, but after three weeks in the oven, the beads had dissolved and the solution had fully converted into Silicalite-1 crystals.

Minimum Day Test

The next step was to complete a test to determine an appropriate amount of time to leave the autoclaves in the oven and also to observe the effect that time had on crystal size.

Experimental Procedure

In this experiment, the excess standard solution from previous experiments was poured into three different liners. The liners were then placed into their respective small autoclaves, tightened, and then placed in an oven at 150°C. The autoclaves were removed from the oven at different times: one after one day, one after three days, one after five days, and one after seven days. Afterwards, all of the Silicalite-1 crystals were examined in an optical microscope and by SEM imaging as well to confirm the results and better determine crystal size.

Results

Samples examined after one day in the oven were found to have barely converted into Silicalite-1 crystals using an optical microscope, thus no further analysis was performed.

The sample taken out of the oven after three days was examined under an optical microscope, where it was determined that a significant amount of crystallization had occurred. The sample was placed in an SEM and Figures 15 and 16 show the results:

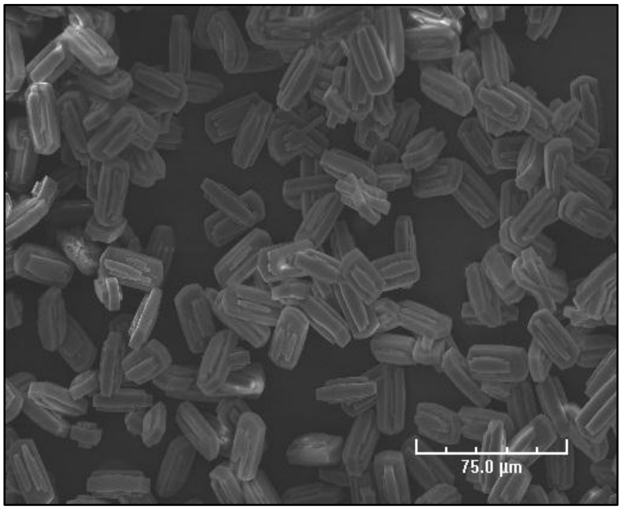


Figure 15: After three days, at 500X

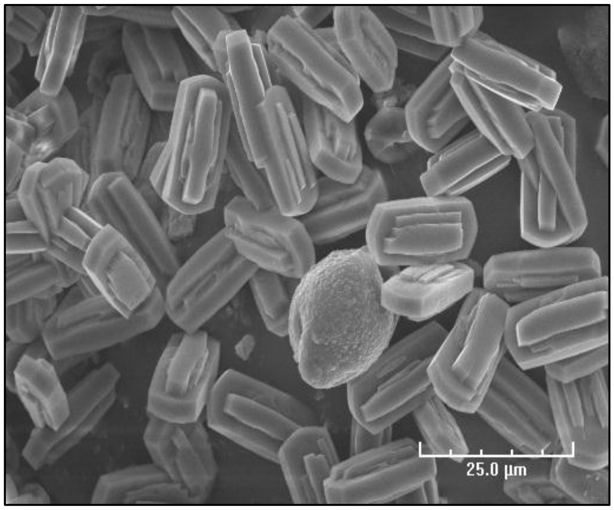


Figure 16: After three days, at 1000X

Figure 15 shows that many Silicalite-1 crystals were synthesized. There was not a lot of intergrowth between the crystals, which had an average length of about 20µm, although most crystals appeared as twins as evidenced by the growth out of the planar faces. Figure 16 shows that although crystals were formed, unconverted silica was still present after three days, so three days is not enough time for future samples to be in the oven.

The sample removed from the oven after five days is shown in Figures 17 and 18:

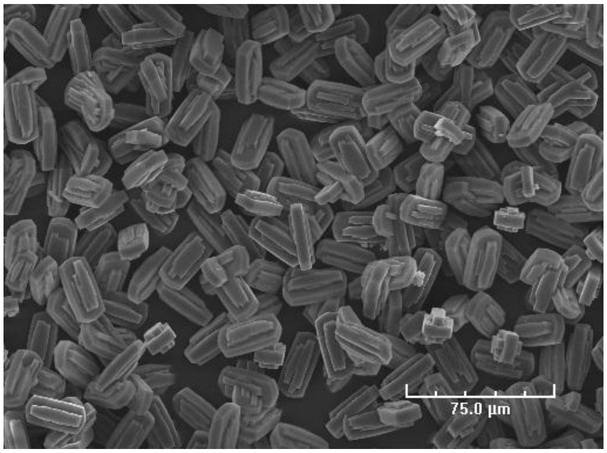


Figure 17: After five days, at 500X

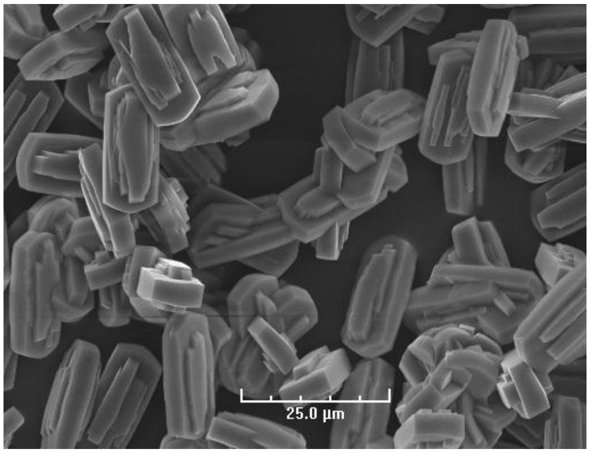


Figure 18: After five days, at 1000X

Figure 17 shows that there was more intergrowth between crystals after five days than three days. The average length of the Silicalite-1 crystals that were synthesized in five days is about 22µm, which is slightly larger than those synthesized in only three days. The larger crystal size indicates that crystallization was still occurring beyond three days.

The samples shown after seven days are shown in Figures 19 and 20:

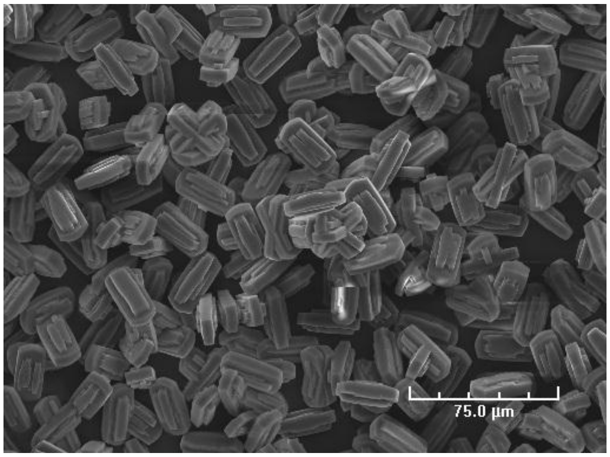


Figure 19: After seven days, at 500X

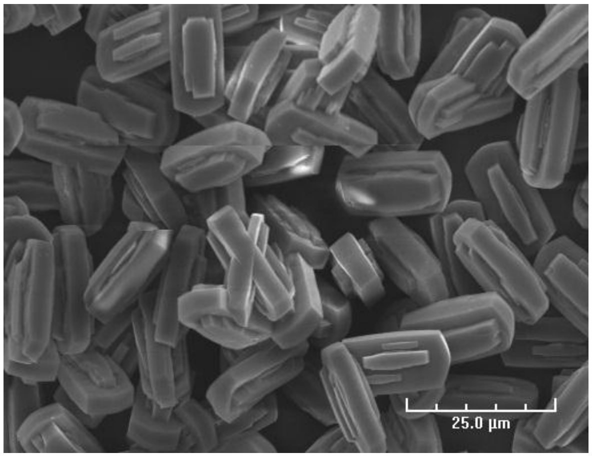


Figure 20: After seven days, at 1000X

Figure 19 shows that there was even more intergrowth between the crystals after seven days. It was also noted that crystals grew at ninety degree angles to each other. All of the solution had been converted into Silicalite-1 crystals. The average length of the Silicalite-1 crystals that were synthesized in seven days was about 22µm, which was the same as after five days.

Although there was not a large change in crystal size between five and seven days, it was decided that seven days in the oven was an appropriate amount of time to fully convert any future samples.

Aging of Solution

Experimental Procedure

To determine how the solution aged with time, the leftover solution from a previous experiment was placed in a 120 mL enclosed plastic container and left to sit at room temperature for a week. Another solution, also enclosed in a 120 mL plastic container, was left in the refrigerator at approximately 0^{o}C for a week.

Results

After one week, observations were recorded for the two solutions, one kept at room temperature and the other at 0^{o}C. Both solutions formed highly viscous gels. The color changed from a translucent milky color to a more opaque white. It was also noted that when the containers were turned upside down, the gel did not move as seen in Figure 21:

Figure 21: Solution Aged One Week at Room Temperature Turned Upside Down

It was also observed that when the solution was aged, there were many instances where two crystals grew perpendicular to each other. This can be seen in Figure 22. As the solution aged, nucleation occurred at both room temperature as well as freezing temperatures. This nucleation caused the crystals to grow perpendicular to each other, causing the phenomenon called twinning. This happened throughout the crystals synthesized from aged solutions. To minimize twinning in the crystal samples, a new solution was made for each following experiment and any excess solution was discarded.

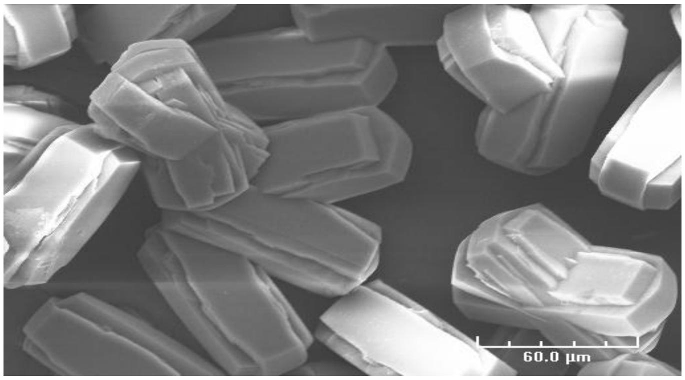


Figure 22: Twinning and intergrowths from aged solutions; heated 7 days at 150 °C

First Tray Test

Experimental Procedure

In the first experiment completed with the new autoclave setup involving the two Teflon trays, three setups were tested. The standard solution for this experiment was taken from the remains of solution from a previous experiment. The first set of beads was a set of four hydrated beads that were submerged in a small amount of the standard solution at the bottom of the autoclave. The second set of beads was a set of four hydrated beads that were soaked in standard solution and then placed on the bottom Teflon tray. The third set of beads was a set of four hydrated beads placed directly onto the top Teflon tray without any treatment.

Results

The first set of beads that were submerged in standard solution at the bottom of the autoclave at 150°C for seven days fully converted to Silicalite-1. However, the beads shrank in size and were difficult to separate from the solution which had also converted to Silicalite-1 crystals. Thus the beads crumbled easily. The second set of beads which were first submerged in the standard solution and then placed onto the bottom tray had an outer crust of crystals where the gel was. However, underneath the loosely attached crust was amorphous silica. The third set of beads which were not treated showed no crystals, only amorphous silica.

From this test we concluded that the beads should not be left submerged in solution as they will be difficult to remove and will not maintain the necessary shape for application in a packed bed reactor. Also, a new solution should be made each time so that the solution placed on the beads is a liquid rather than a gel so that the liquid will penetrate into the bead rather than remain on the outside. It was also concluded that the beads must be treated before placing them into the autoclave rather than relying on the vapor form of the solution.

Silica versus No Silica in the Solution

Experimental Procedure

In this experiment, the difference between including silica in the solution and removing the silica from the solution was investigated. Two different solutions were made, one with the standard composition and the other without using the Ludox colloidal silica source (see Table 3). Four beads per solution were soaked for a minute and then placed onto separate trays. 3mL of 30 percent ammonium hydroxide solution was placed at the bottom of the Teflon liner of the large autoclave before the two trays were stacked on top of each other and placed into the liner. The large autoclave was closed and placed into the oven at 150°C for seven days.

Table 3: Batch Composition for Solution without Silica

Substance	Brand	Amount (g)
Tetrapropyl Ammonium Bromide	Aldrich	6.44
Triple exchanged and triple filtered purified water	Barnstead Nanopure II	10.8
Ammonium Hydroxide	Aldrich	28.2

Results

The beads soaked in the solution containing silica showed crystal growth on the exterior of the beads. There was no significant crystal growth beyond the exterior of the bead.

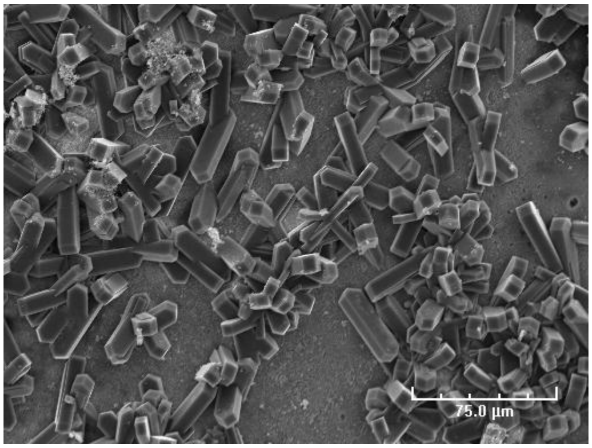


Figure 23: The outer surface of the bead with silica in the solution at 500X

From Figure 23 it is clear that Silicalite-1 crystals grew on the outer surface of the beads. There was also a significant amount of crystals that grew into each other. The crystals are 45µm on their longest side. Interestingly, there were intergrowths, but almost no twinning. This is because a new solution was prepared in order to avoid twinning.

The beads that were soaked in solution that did not contain silica had sporadic crevices where crystals grew. These areas appeared like craters filled with highly inter-grown Silicalite-1 crystals. Below, Figures 24, 25, and 26 are images taken from the SEM of the entire bead and then closer views of each section of crystal growth:

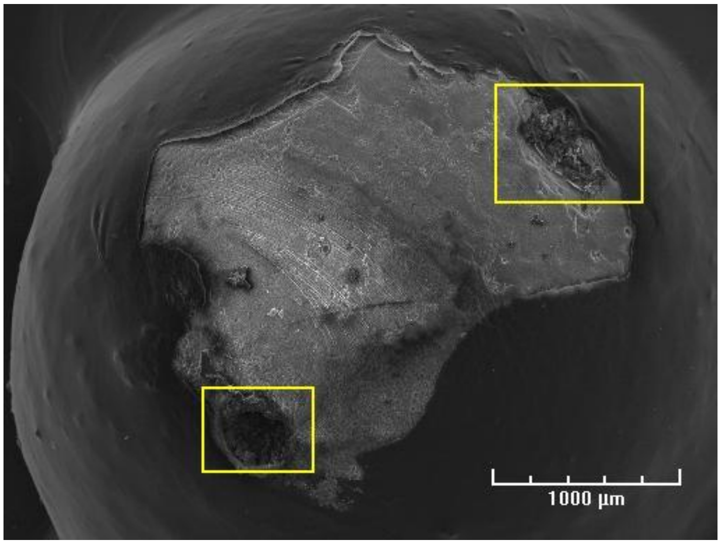


Figure 24: Two sections of crystal growth on the bead without silica solution at 40X

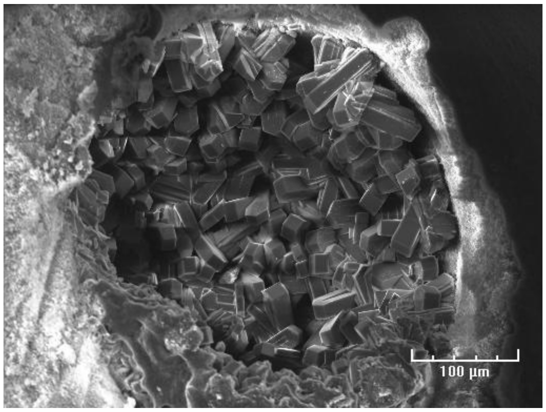


Figure 25: Top right corner of Figure 25 at 300X

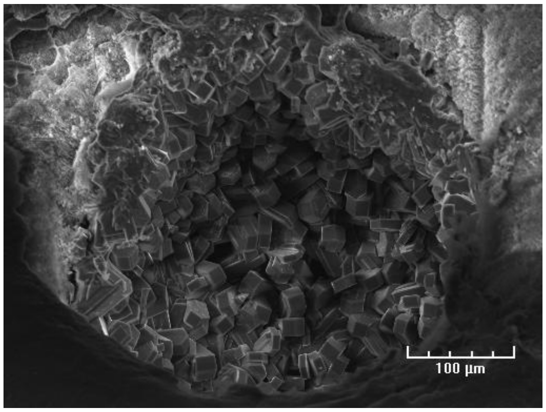


Figure 26: Bottom left corner of Figure 25 at 300X

The crystals in the crevices are 60µm in length, which was longer than the crystals that grew on the beads with silica in the solution. The beads soaked in silica-less solution showed more sporadic and dense crystal growth whereas the beads soaked in the standard solution containing silica showed more evenly dispersed crystal growth on the surface of the bead.

From this experiment we concluded that it was necessary to continue including silica in the solution to get a more uniform growth of Silicalite-1 crystals around the bead.

Beads Soaked in Standard Solution for 24 Hours

SEM images of silica beads treated momentarily with solution showed little crystal growth in the center of the bead after seven days. The beads in previous experiments may not have been soaked long enough for the solution to fully penetrate it. Therefore, hydrated silica beads were soaked in the standard solution for a full 24 hours before being placed in the large autoclaves and into the oven.

Experimental Procedure

The beads were soaked for 24 hours at room temperature to increase the amount of solution that penetrated the beads. Eight beads were placed on the two trays in the larger autoclaves and were suspended above ammonium hydroxide. The autoclaves were left in the oven at 150°C for seven days.

Results

Using SEM imaging, it was determined that crystals grew both in and on the surface of the silica bead. Figures 27 and 28 show the results of this experiment:

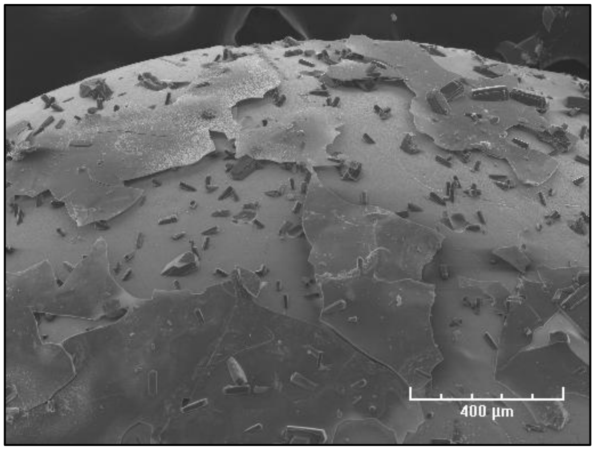


Figure 27: Bead soaked for 24 hours, at 100X

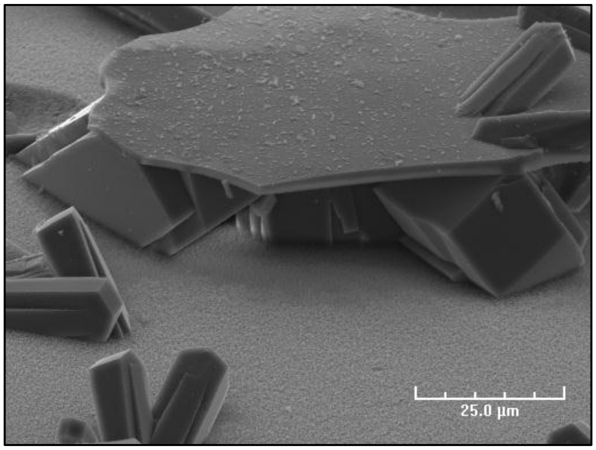


Figure 28: Bead soaked for 24 hours, at 1000X

Figure 27 shows that the surface of the bead had flakes with crystals growing under and around them. More of the surface could have been covered with these flakes, but they may have been disturbed during their removal from the liners as well as during the preparation of the SEM sample. Figure 28 shows a close-up of the Silicalite-1 crystals growing underneath the flakes. Both Figures show that there were also crystals growing on the surface of the bead away from flakes. There were two different sized crystals, some approximately 80µm and some 25µm long. These crystals, however, did not cover the entirety of the bead's surface.

A bead from this experiment was cleaved in half so that an image of its cross section could be taken. This picture is shown below in Figure 29:

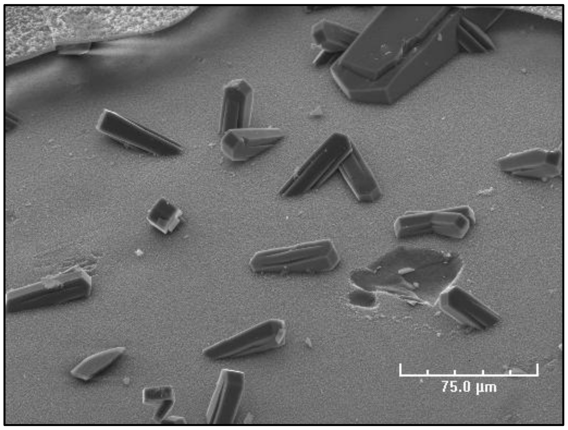


Figure 29: Cross Section of a Bead Soaked 24 Hours, at 500X

Figure 29 shows that the cross section had very few crystals in the center, most likely because the solution still did not penetrate the bead fully. There was no significant difference between soaking a bead for a minute or for 24 hours. It was concluded that in following experiments, the beads would be soaked for a minute.

Aerogels

Aerogel beads were softer, more porous beads that were used in the following experiment to allow the solution to better penetrate through the center of the bead.

Experimental Procedure

The Aerogel beads were soaked with the standard solution for a minute. Eight beads were placed on the two trays in the larger autoclaves and suspended above ammonium hydroxide. The large autoclave was placed in the oven at 150°C for seven days. One observation before even placing the beads in autoclaves was that that the Aerogel beads weakened in the solution during RT soaking.

Results

The Aerogel beads were very weak and crumbled easily. It was therefore very difficult to remove t hem from the autoclave, and the structural integrity of the bead was compromised. SEM images of the powder were taken and it was found that the powder did contain Silicalite-1 crystals. The crystals from the Aerogels were approximately 32µm long. These crystals can be seen in Figures 30 and 31. There was also a lot of leftover material from the Aerogels that surrounded all of the crystals, which can be seen in both figures as the amorphous shapes. If it was just amorphous silica, the amount of the unused substance could be decreased by adding more template (TPABr).

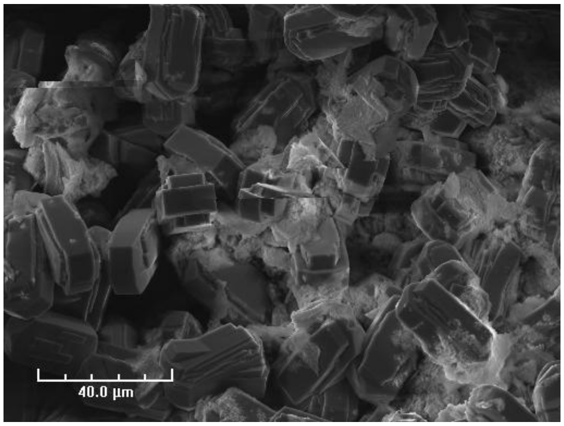


Figure 30: Aerogel Bead Powder at 700X

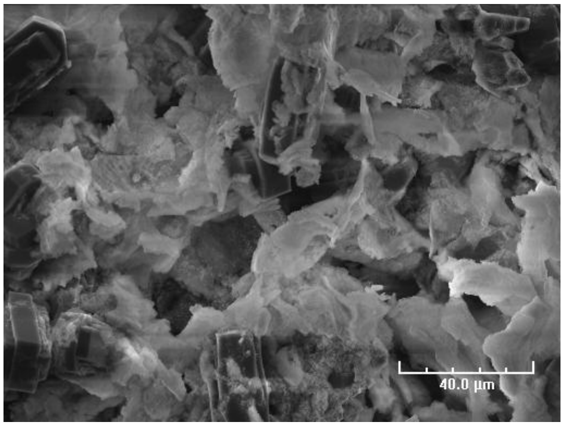


Figure 31: Aerogel Bead Powder at 700X

These beads were too porous and fragile, so the Aerogel beads would not be suitable for their intended application in a packed bed reactor. A semi-porous bead with a good balance between hardness and porosity would be the best option to consider in future experiments.

Changing the Si: TPA Ratio to 5.6

Another reason there were not be crystals growing in the center of the beads was because there was not enough template to convert all of the silica into Silicalite-1 crystals. The standard solution previously used had a ratio of 7.47, which means it had excess template. The high concentration of TPA outside of the bead, partnered with no TPA in the center of the bead, created a concentration gradient to draw template into the bead to convert silica past the bead's surface. It was believed that there was still not enough template in the solution to convert the bead, thus more was added.

Experimental Procedure

For this experiment, excess template was used (see Table 4). The desired ratio of silica to TPA was approximately 5.6. The beads were soaked in the solution for a minute and then placed in a large autoclave in the oven at 150°C for seven days.

Table 4: Batch Composition for Si: TPA Ratio of 5.6

Substance	Brand	Amount (g)
Tetrapropyl Ammonium Bromide	Aldrich	8.57
Triple exchanged and triple filtered purified water	Barnstead Nanopure II	10.8
Ludox AS40 Colloidal Silica	Aldrich	27.2
Ammonium Hydroxide	Aldrich	28.2

Results

SEM images of the beads were taken to see if crystals were growing in the center of the silica bead. Contrary to what was expected, there were actually fewer crystals growing on and in the silica beads with a higher amount of template, TPABr. The Silicalite-1 crystals seen in Figure 32 and Figure 33 below were thinner and longer than crystals grown in previous experiments. The average length of the crystals was 20µm. In experiments with the “standard solution”, the average length of the crystals was 45µm. In the cross section of the bead, no crystals were found, which meant that the solution still did not penetrate into the interior of the bead.

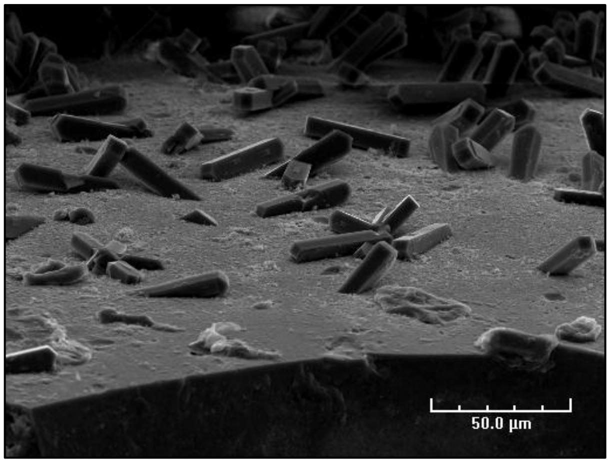


Figure 32: Increased TPA Solution, at 600X

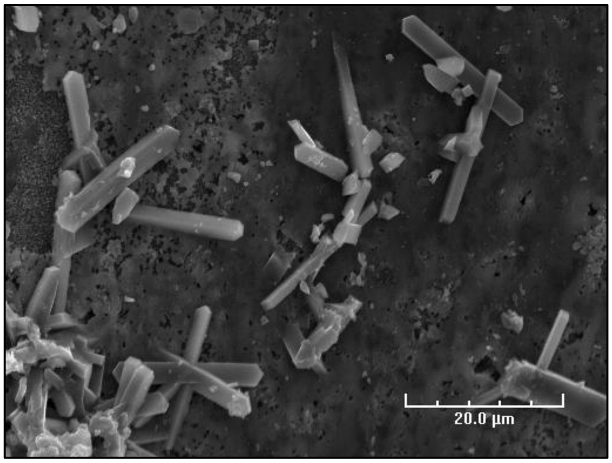


Figure 33: Increased TPA Solution, at 2,000X

Increasing the amount template therefore did not increase the amount of crystals growing on the outside of the bead or increase the amount of crystals growing in the center of the beads. As expected, the size of the crystals decreased as the amount of template decreases.

Changing the Si: TPA Ratio to 3

Although crystals grew on the outside of the beads, the crystals did not cover the entire surface for a Si: TPA ratio of 5.6. The number of nucleation sites on the bead must be increased for the bead to be covered in crystals. Therefore, the amount of TPA in the solution must be increased.

Experimental Procedure

The ratio of silica to TPA was decreased for this experiment to a ratio of 3. The beads were soaked in the solution for a minute and then placed in a large autoclave in the oven at 150°C for seven days. The following composition in Table 5 for the solution was used:

Table 5: Batch Composition for Si: TPA Ratio of 3

Substance	Brand	Amount (g)
Tetrapropyl Ammonium Bromide	Aldrich	16.09
Triple exchanged and triple filtered purified water	Barnstead Nanopure II	10.8
Ludox AS40 Colloidal Silica	Aldrich	27.2
Ammonium Hydroxide	Aldrich	28.2

Results

Images of the surface and cross section of a bead were inspected using SEM imaging. These images showed that decreasing the ratio of silica to TPA from 5.6 to 3 increased the crystal growth on the surface of the bead. These crystals more uniformly covered the bead which is a positive quality for aggregates used in water purification. Figures 34 and 35 show the crystals forming a thick layer on the surface of the bead.

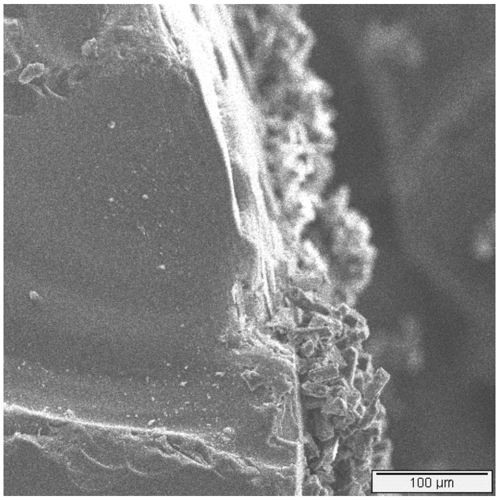


Figure 34: Edge of the Bead at 200X

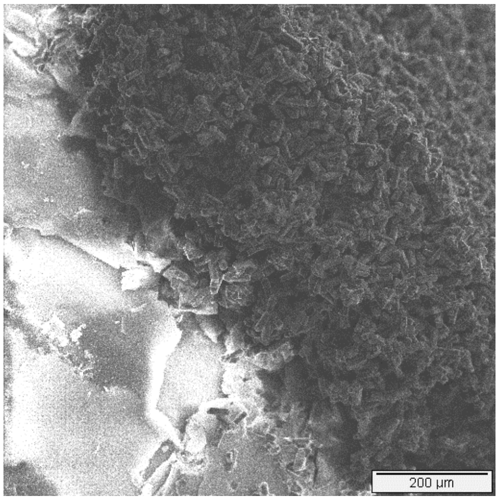


Figure 35: Crystals on the Outer Surface at 100X

With the decreased ratio, more crystals formed a shell around the bead. It was evident in Figure 34 that this growth was not completely uniform on the surface as there were several patches of amorphous silica. Although crystal growth on the surface was much more significant with more TPA, there was no crystal growth on the inside of the bead. Figure 36 is an SEM image of the cross section of a bead.

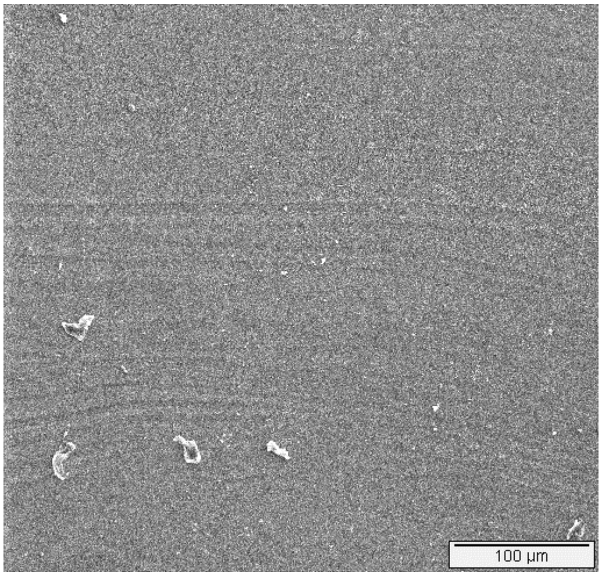


Figure 36: Cross Section of Bead at 200X

Because there was negligible growth on the inside of the bead, thus a new method to grow crystals throughout the beads, rather than only on the surface, must be explored.

Sources of Error

When SEM images of the cross section were taken, the beads were cut with a sharp knife to expose the center of the bead. The bead was cut several times to get the desired piece of bead for SEM imaging. Although the knife was used to cut away at the bead, many crystals were compromised in the process. This could have led to distorted images.

Holes to cradle the beads were machined into the trays for the larger autoclaves. The sizes of these holes were slightly smaller than the average size silica bead. Once theses autoclaves were placed in the oven, some beads on the trays fell through either to the tray below or into the solution at the bottom. This could be due to the size of the beads that were used. The average size silica bead was used to determine the size of the holes so some of the beads used in experiments were smaller than the holes. Additionally, when treated with solution and placed in the oven, the beads may have slightly decreased in size. This was because as the crystals formed, the density increased, which caused the volume to decrease. The heating effects caused the beads to decrease in size and fall through the holes in the trays in the autoclaves. Another possible reason for the shifting of beads could have been due to the handling of the autoclaves. The beads could have easily rolled out of the holes if the autoclave was not level.

Finally, during the mixing of the solution, the ammonium hydroxide vaporized at room temperature. This could have affected the composition of the solution. The vaporization of the ammonium hydroxide probably did not affect the outcome of the experiment; however the solution should be made and used in a timely fashion to minimize the loss of ammonium hydroxide to vaporization.

Conclusions

The main objective of this project was to synthesize and aggregate Silicalite-1 crystals. Even though the Silicalite-1 crystals never fully penetrated the bead, significant crystal growth occurred on the surface. Whether or not there was a substantial amount of crystal growth to effectively purify organic compounds from water would need to be determined. It is likely that more crystal growth is needed around the bead as well as within it. Further testing would be needed in order to determine if the beads are suitable for application in a packed bed reactor.

Several conclusions were drawn based on this series of experiments. The first conclusion that was made was that there was a strong correlation between using aged solutions and the twinning of Silicalite-1 crystals because nucleation occurs in the solution while aging at room temperature. Additionally, one week was a suitable amount of time to synthesize crystals in an oven at 150°C. It was also concluded that the beads must be treated with a new liquid solution before placing them into the autoclave rather than relying on a vapor form of the solution in the autoclave. As for the batch composition of the solution itself, it was necessary to include silica to have evenly dispersed crystal growth on the surface of a bead. Another thing to note was that when the amount of template in the recipe was increased, the density of nucleation sites increased. This caused more crystals to form which were consequently smaller in size. These findings will be helpful for further development in this area.

The largest challenge in this study was to achieve crystal growth beyond the surface of the bead. Throughout the various experiments performed, it was evident that crystal growth was restricted to the exterior of the bead. This could have been due to the difficulty of impregnating the bead with solution. Also, the path of least resistance was for growth to occur at the surface of the bead and extend outward rather than into the bead. Because there was still amorphous silica present, more TPABr might be necessary to fully convert the silica bead.

Recommendations for Future Work

The main area for improvement in aggregating Silicalite-1 crystals is increasing crystal growth throughout the bead. There are several ways this could be achieved through making modifications to the process used in this project. One way is to find a more porous silica bead. Another solution could be to further study different impregnation techniques.

As previously mentioned, a new silica source should be examined. The silica beads used were very hard and not porous enough for the solution to fully penetrate the bead. The Aerogel beads used, on the other hand, were too porous so they were incredibly delicate, soft and easily crumbled. Thus, they would not be a viable option for use in a packed bed reactor. The bead must be porous enough to absorb the solution, and also have room for internal crystal growth. The beads must also maintain their structure after crystallization occurs in order to be viable for application in a packed bed reactor. For future experiments, semi-porous silica beads should be explored.

In this study, the only impregnation technique used was soaking the bead in the solution. In the future, other techniques for driving the solution into the bead should be investigated. Such techniques may include using a needle to inject the bead with solution, increasing the soaking time beyond 24 hours, and manipulating the concentration gradient of silica between the solution and the bead.

Based on these recommendations, the best route for future experiments is first to evaluate the importance of pore size in the silica bead. Once the optimal pore size has been determined, different impregnation techniques should be studied.

These recommendations are all future possibilities for Major Qualifying Projects at Worcester Polytechnic Institute.

References

1. Schmidt, W. "Structure of Zeolites "Web. <http://www.mpi-muelheim.mpg.de/kofo/institut/arbeitsbereiche/schmidt/research_e.htm>. Web. 4 Oct. 2010.

2. Verduijin, Johannes Petrus, Masstje van den Berge, Jannetje, and Machteld Mertens. Preparation of Zeolite-Bound FAU Structure Type Zeolite and use Thereof. ExxonMobil Chemical Patents Inc, assignee. Patent US 6,350,428 BI. Feb. 26, 2002.

3. Narita, Eiichi; Sato, Keiichi; Yatabe, Noboru; Okabe, Taijiro. “Synthesis and Crystal Growth of Zeolite ZSM-5 from Sodium Aluminosilicate Systems Free of Organic Templates”. Industrial & Engineering Chemistry Product Research and Development 1985 24 (4), 507-512

4. Carleen, Bradford. "Hydrothermal Synthesis Process for the Production of Silicalite-1 Crystal Aggregate Packing Particles." Master's Thesis Worcester Polytechnic Institute, Print.

5. Sylvie Gonthier. “Investigation of the Formation of Silicalite Crystallites on Silicalite Crystals used as Seeds.” 1993. Master's Thesis Worcester Polytechnic Institute, Print.

6. Colella, C.; Gualtieri, A. F., “Cronstedt's Zeolite”. *Microporous and Mesoporous Materials* 2007, 105, 213-221.

7. Leavens, Peter B. "Zeolites."Web. <http://www.encyclopedia.com/topic/Zeolites.aspx>. Web. 20 Sept. 2010.

8. Barrer, R. M., *Zeolite and Clay Minerals as Sorbents and Molecular Sieves*. Academic Press Inc.: New York, 1978.

9. *Zeolite Framework Types.* Structure Commission of the International Zeolite Association. Web. <http://izasc-mirror.la.asu.edu/fmi/xsl/IZA-SC/ft.xsl> Web. 29 Sept. 2010.

10. *MFI: Silicalite-1.* Synthesis Commission of the International Zeolite Association. Web. <http://www.iza-online.org/synthesis/default.htm> Web. 15 Sept. 2010.

11. Rabo, Jule A., and Michael W. Schoonover. "Early Discoveries in Zeolite Chemistry and Catalysis at Union Carbide, and Follow-Up in Industrial Catalysis." *Applied Catalysis A: General* 222.1-2 (2001): 261-75. Web.

12. Squillace, Paul J., et al. "Preliminary Assessment of the Occurrence and Possible Sources of MTBE in Groundwater in the United States, 1993-1994." *Environmental Science & Technology* (1996): 1721.

13. McCabe, Smith and Harriot, Unit Operations of Chemical Engineering, Seventh Edition, McGraw-Hill, New York, NY (2005), Chapter 27. Print

14. Cheng, Chil-Hung, and Daniel F. Shantz. "Silicalite-1 Growth from a Clear Solution: Effect of Structure-Directing Agent on Growth Kinetics." *The Journal of Physical Chemistry B* 109.29 (205): 13912,13912-13920.

15. Narayanan, S., et al. "Synthesis of ZSM-5 Type Zeolites with and without Template and Evaluation of Physicochemical Properties and Aniline Alkylation Activity." *Catalysis Letters* 34.1 (1995): 129-38.

16. Li, Qinghua, et al. "The Nucleation Period for Crystallization of Colloidal TPA-Silicalite-1 with Varying Silica Source." *Microporous and Mesoporous Materials* 40.1-3 (2000): 53-62.

17. Hunt, Arlon, and Michael Ayers. "Silica Aerogels." *Silica Aerogels*. E.O. Lawrence Berkely Nations Laboratory, 2004. Web. 3 Apr. 2011. <http://eetd.lbl.gov/ecs/aerogels/sa-home.html>. Web. 29 March 2011.

18. Auerbach, Scott M., Kathleen A. Carrado, and Prabir K. Dutta, eds. *Handbook of Zeolite Science and Technology*. Marcel Dekker, 2003.

Appendix

Materials Used

Ludox AS-40 Colloidal Silica, 40 wt% suspension in water
Aldrich
Batch #128238AB

Ammonium Hydroxide, NH_3 content 28-30%
Aldrich
Lot #11526DO

Tetrapropyl Ammonium Bromide, 98%
Aldrich
Lot #05024HT

t.h.e. desiccant, 4 mesh
Lot #23227547

Triple exchanged and triple filtered purified water
Barnstead Nanopure II

Calculating Molar Silica to TPABr Ratio

Molecular Weight of TPABr

Molecular formula: $(CH_3CH_2CH_2)_4N(Br)$ OR $C_{12}H_{28}N^{\cdot}Br$

$$Carbon: 12 * 12\frac{g}{mol} = 144\frac{g}{mol}$$

$$Hydrogen: 28 * 1\frac{g}{mol} = 28\frac{g}{mol}$$

$$Nitrogen: 1 * 14\frac{g}{mol} = 14\frac{g}{mol}$$

$$Bromide: 1 * 80\frac{g}{mol} = 80\frac{g}{mol}$$

$$Molecular\ Weight\ of\ TPABr = 144\frac{g}{mol} + 28\frac{g}{mol} + 14\frac{g}{mol} + 80\frac{g}{mol} = 266\ \frac{g}{mol}$$

Molecular Weight of Silica

Molecular Formula: SiO_2

$$Silicon: 1 * 28\frac{g}{mol} = 28\frac{g}{mol}$$

$$Oxygen: 2 * 16\frac{g}{mol} = 32\frac{g}{mol}$$

$$Molecular\ Weight\ of\ Silica = 32\frac{g}{mol} + 28\frac{g}{mol} = 60\ \frac{g}{mol}$$

"Standard Solution"[5]

Molecules of Silica

$$27.2\ \ grams\ of\ Ludox\ AS - 40\ Colloidal\ Silica$$

$$40\%\ Silica\ Solution \to 10.88\ \ grams\ of\ Silica$$

$$Molecular\ Weight = 60\ grams/mole$$

$$10.88\ \ grams\ of\ Silica * \frac{1\ mole}{60\ grams} * \frac{6.023 * 10^{23}\ molecules1\ mole}{1\ mole} = 1.09 * 10^{23}$$

Molecules of TPABr

$$6.44\ grams\ of\ TPABr$$

$$Molecular\ Weight = 266\ grams/mole$$

$$6.44\ grams\ of\ TPABr * \frac{1\ mole}{266\ grams} * \frac{6.023 * 10^{23}\ molecules}{1\ mole} = 1.46 * 10^{22}$$

Ratio

$$\frac{Molecules\ of\ Silica}{Moelcuels\ of\ TPABr} = \frac{1.09 * 10^{23}\ molecules}{1.46 * 10^{22}\ molecules} = 7.47$$

Brad Carleen's Solution[4]

Molecules of Silica

$$10.88\ \ grams\ of\ Ludox\ AS - 40\ Colloidal\ Silica$$

$$40\%\ Silica\ Solution \rightarrow 4.35\ \ grams\ of\ Silica$$

$$Molecular\ Weight = 60\ grams/mole$$

$$4.35\ \ grams\ of\ Silica * \frac{1\ mole}{60\ grams} * \frac{6.023 * 10^{23}\ molecules}{1\ mole} = 4.36 * 10^{22}$$

Molecules of TPABr

$$6.44\ grams\ of\ TPABr$$

$$Molecular\ Weight = 266\ grams/mole$$

$$6.44\ grams\ of\ TPABr * \frac{1\ mole}{266\ grams} * \frac{6.023 * 10^{23}\ molecules}{1\ mole} = 1.46 * 10^{22}$$

Ratio

$$\frac{Molecules\ of\ Silica}{Moelcuels\ of\ TPABr} = \frac{4.36 * 10^{22}\ molecules}{1.46 * 10^{22}\ molecules} = 3.00$$

"Standard Solution" with Excess TPABr

Silica to TPA of 5.6

Molecules of Silica

$$27.2\ \ grams\ of\ Silica$$

$$40\%\ Silica\ Solution \rightarrow 10.88\ \ grams\ of\ Silica$$

$$Molecular\ Weight = 60\ grams/mole$$

$$10.88\ \ grams\ of\ Silica * \frac{1\ mole}{60\ grams} * \frac{6.023 * 10^{23}\ molecules}{1\ mole} = 1.09 * 10^{23}$$

Molecules of TPABr

$$8.59 \; grams \; of \; TPABr$$

$$Molecular \; Weight = 266 \; grams/mole$$

$$8.59 \; grams \; of \; TPABr * \frac{1 \; mole}{266 \; grams} * \frac{6.023 * 10^{23} \; molecules}{1 \; mole} = 1.95 * 10^{22}$$

Ratio

$$\frac{Molecules \; of \; Silica}{Moelcuels \; of \; TPABr} = \frac{1.09 * 10^{23} \; molecules}{1.95 * 10^{22} \; molecules} = 5.60$$

Silica to TPA of 3

Molecules of Silica

$$27.2 \;\; grams \; of \; Ludox \; AS - 40 \; Colloidal \; Silica$$

$$40\% \; Silica \; Solution \rightarrow 10.88 \;\; grams \; of \; Silica$$

$$Molecular \; Weight = 60 \; grams/mole$$

$$10.88 \;\; grams \; of \; Silica * \frac{1 \; mole}{60 \; grams} * \frac{6.023 * 10^{23} \; molecules}{1 \; mole} = 1.09 * 10^{23}$$

Molecules of TPABr

$$16.09 \; grams \; of \; TPABr$$

$$Molecular \; Weight = 266 \; grams/mole$$

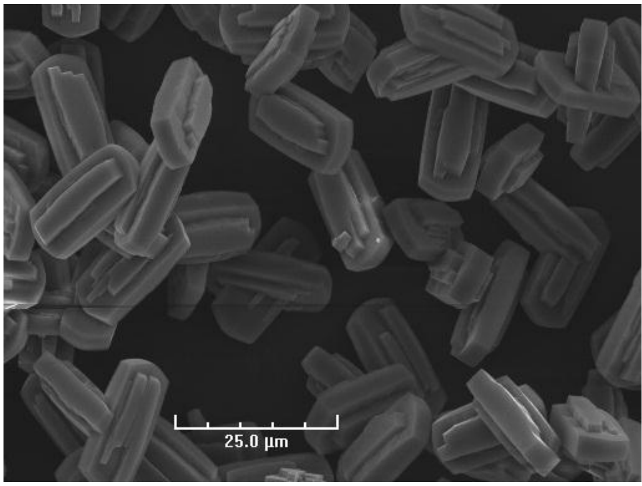
$$16.09 \; grams \; of \; TPABr * \frac{1 \; mole}{266 \; grams} * \frac{6.023 * 10^{23} \; molecules}{1 \; mole} = 3.64 * 10^{22}$$

Ratio

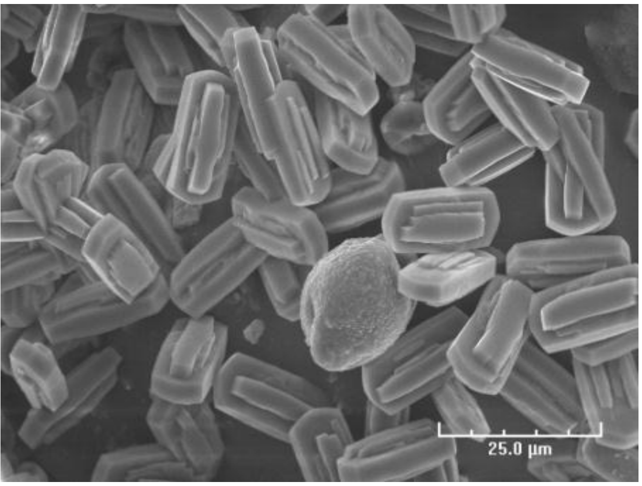
$$\frac{Molecules \; of \; Silica}{Moelcuels \; of \; TPABr} = \frac{1.09 * 10^{23} \; molecules}{3.64 * 10^{22} \; molecules} = 3$$

Other SEM Pictures

Minimum Day Test



3 Days at 1,000X



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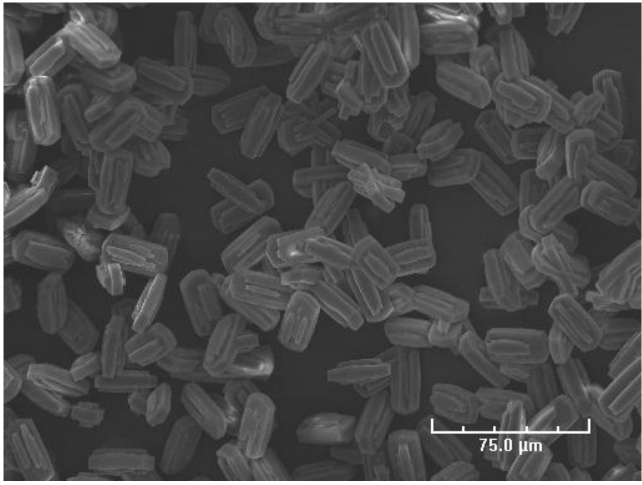

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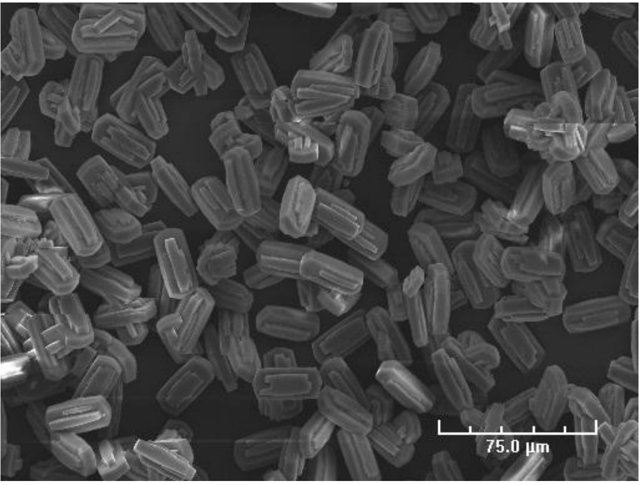
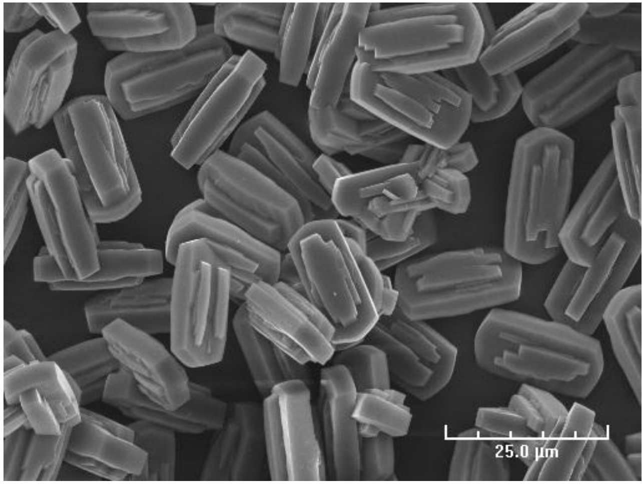
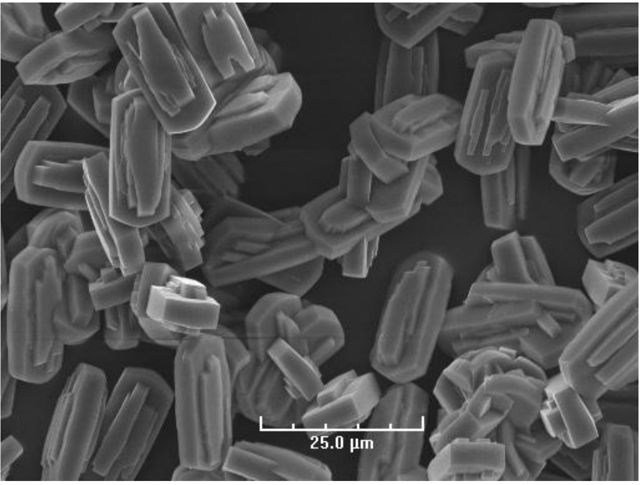


3 Days at 500X



5 Days at 1,000X



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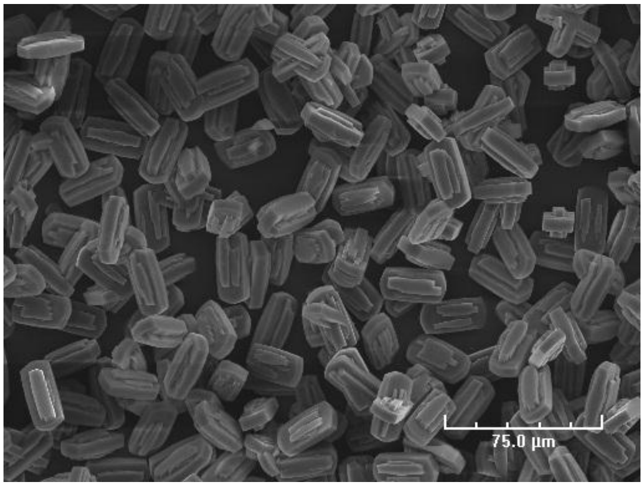

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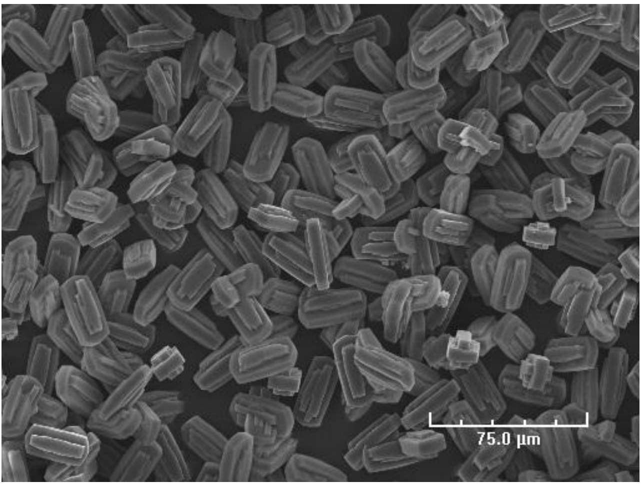

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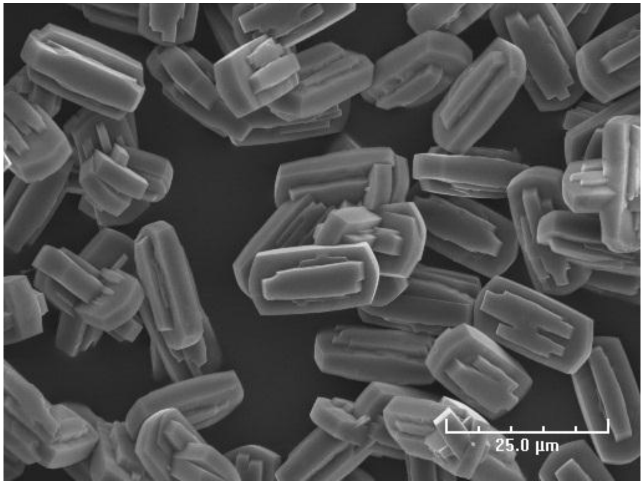
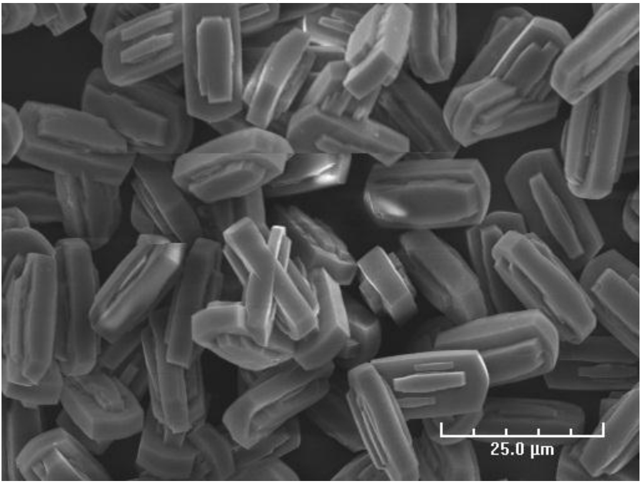


7 Days at 1,000X



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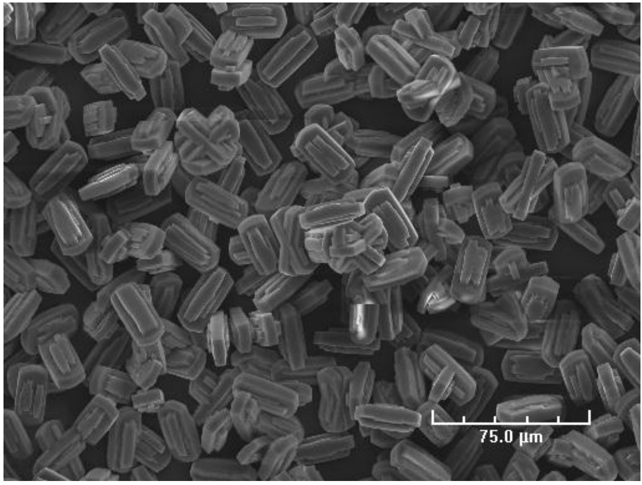

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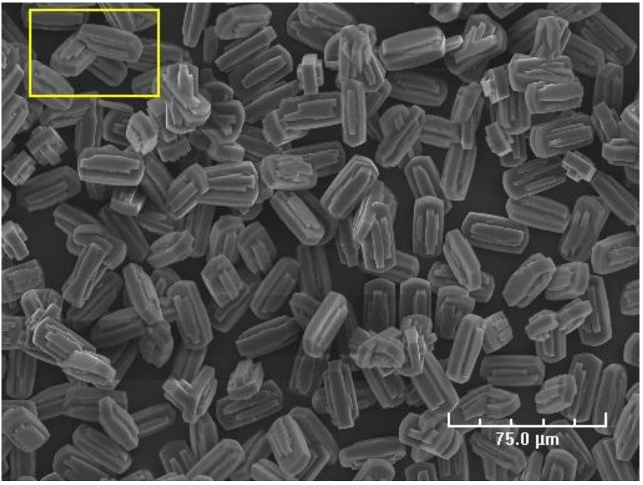
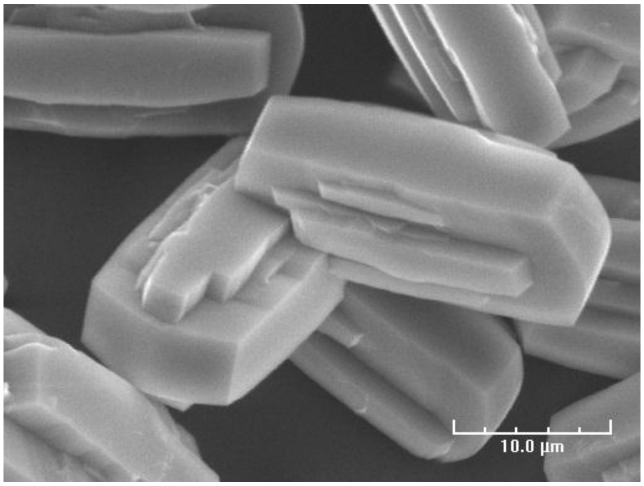
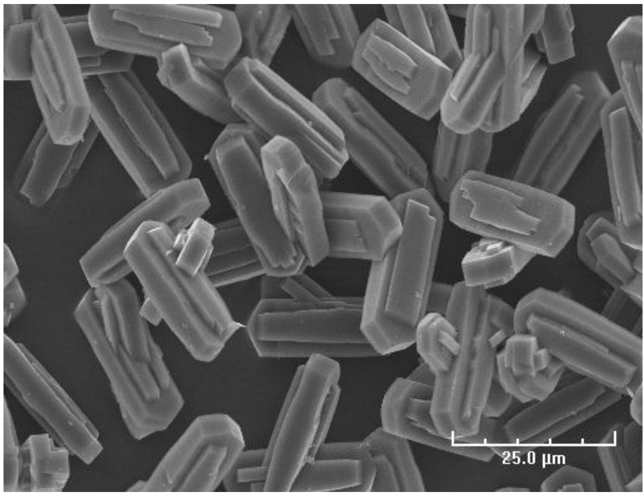


7 Days at 500X

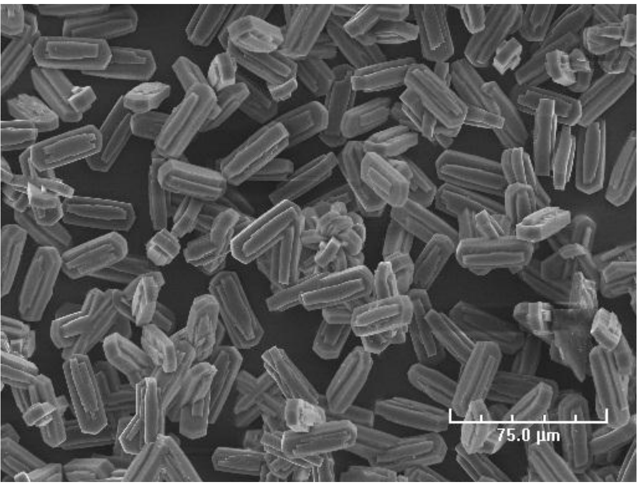


7 Days at 3,000X

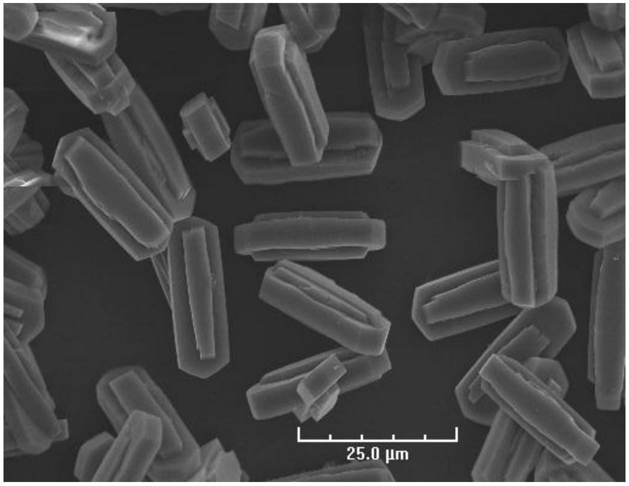
First Tray Test



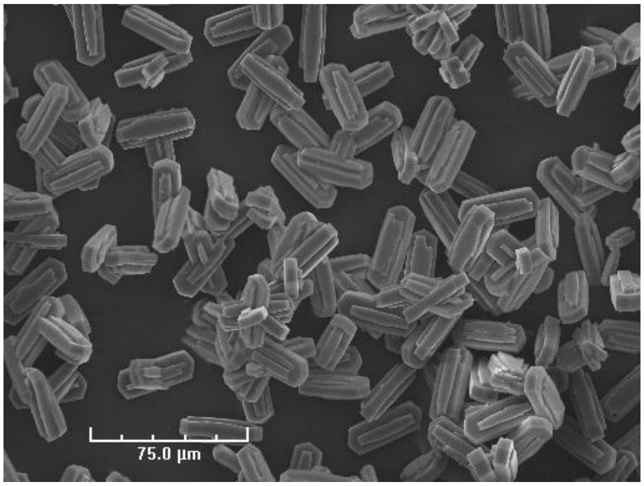
Calcined powder at 1,000X



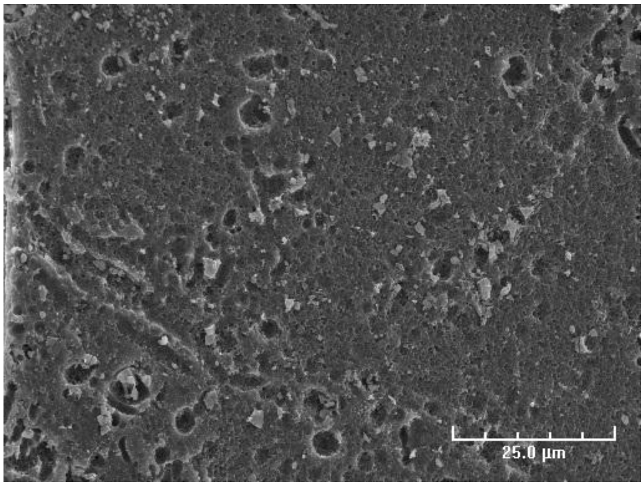
Calcined powder at 500X



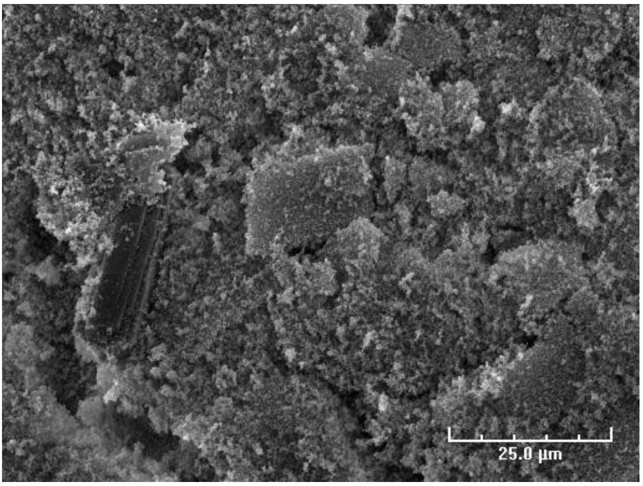
Calcined powder at 1,000X



Calcined powder at 500X

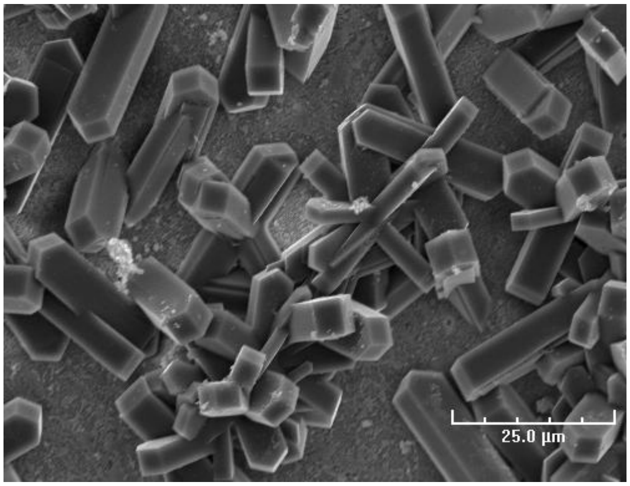


Unsoaked Bead at 1,000X

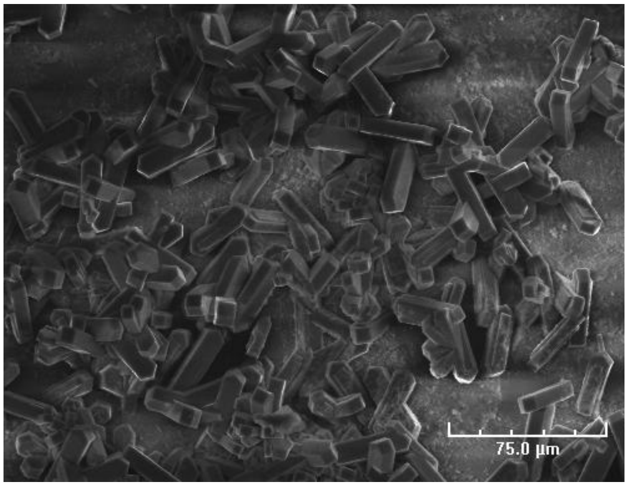


Bead Soaked in Solution at 1,000X

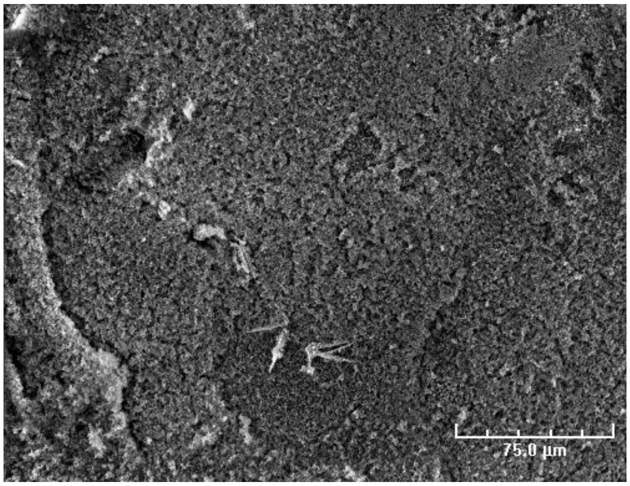
Silica versus No Silica in the Solution



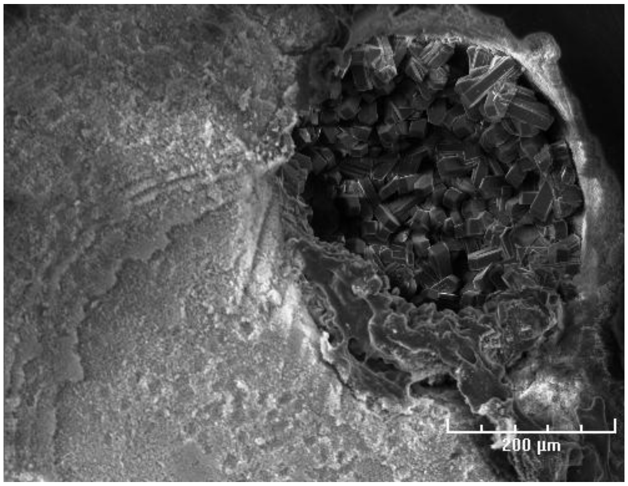
Bottom Tray, soaked with silica at 1000X



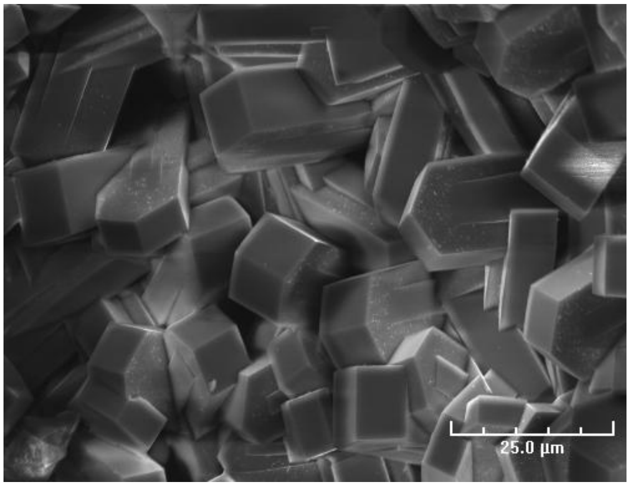
Bottom Tray, soaked with silica at 500X



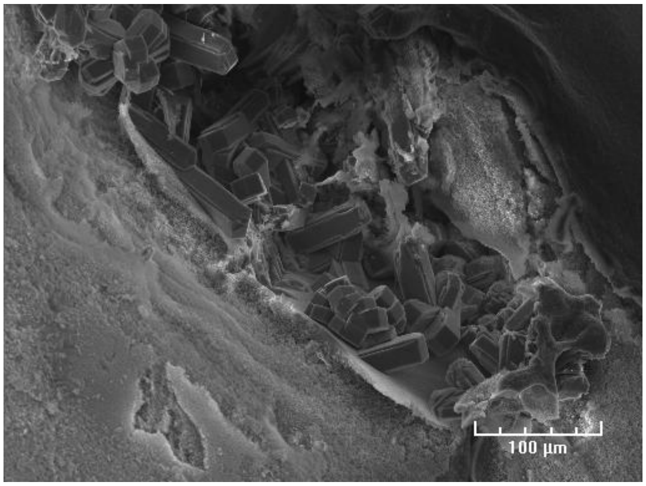
Top tray bead, no silica at 500X



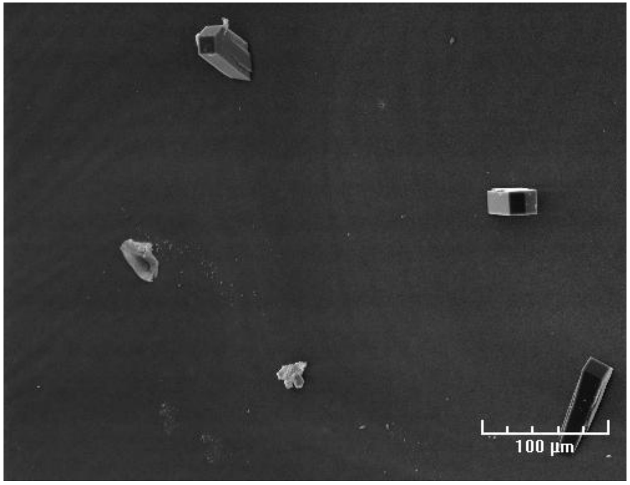
Top tray bead, no silica at 200X



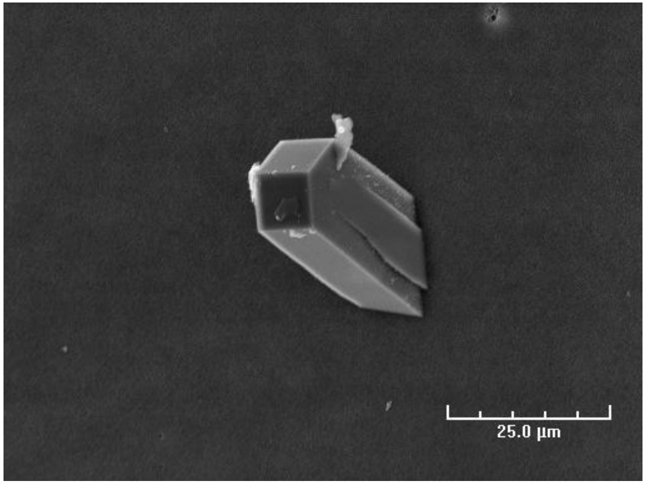
Top tray bead, no silica at 1000X



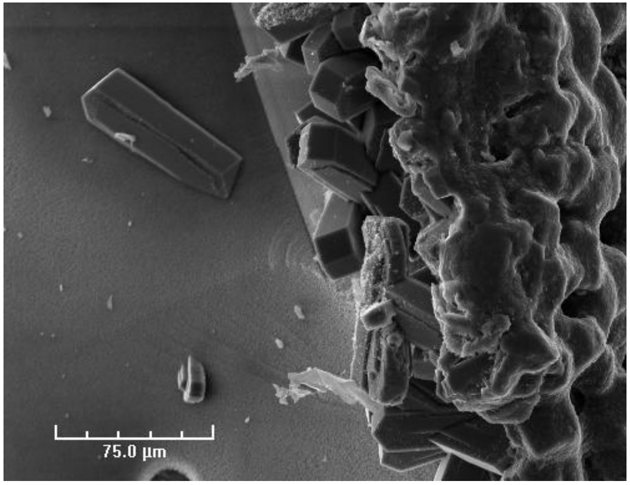
Top tray bead, no silica at 300X



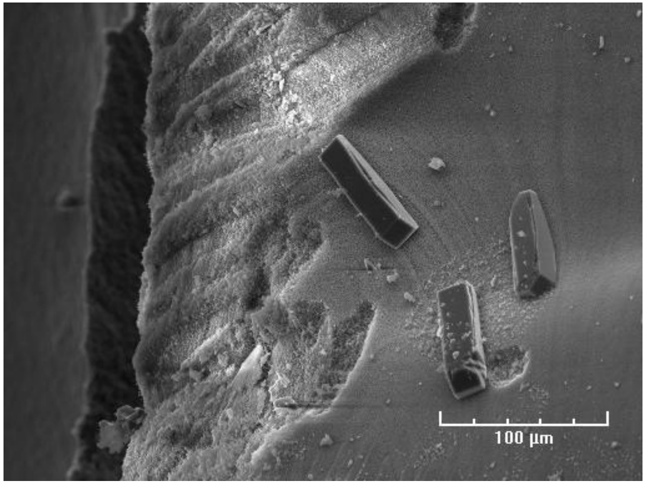
Cross Section of Top Bead at 300X



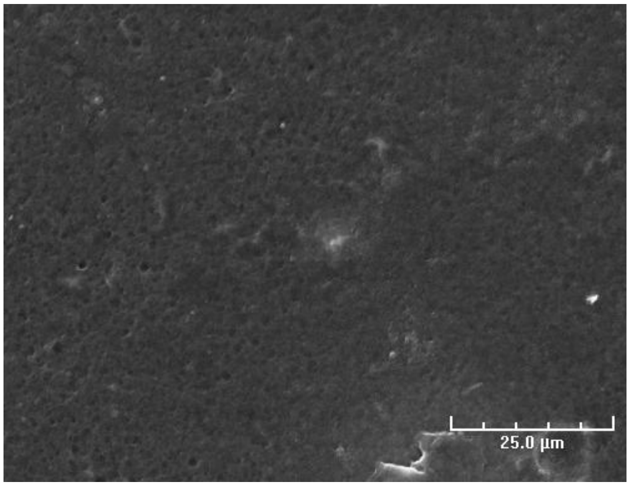
Cross Section of Top Bead at 1,000X



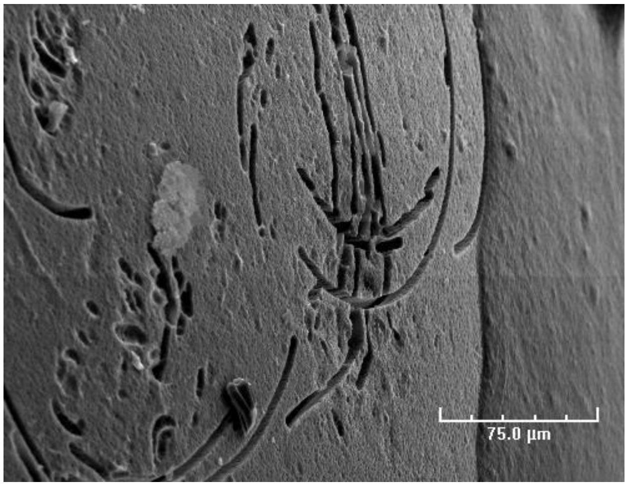
Cross Section of Top Bead at 500X



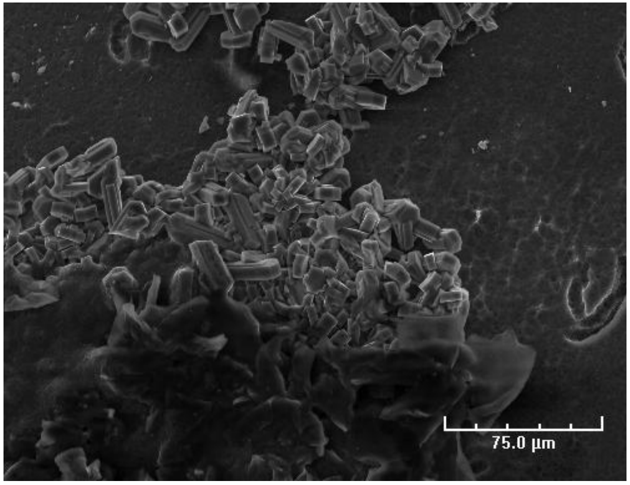
Cross Section of Top Bead at 400X



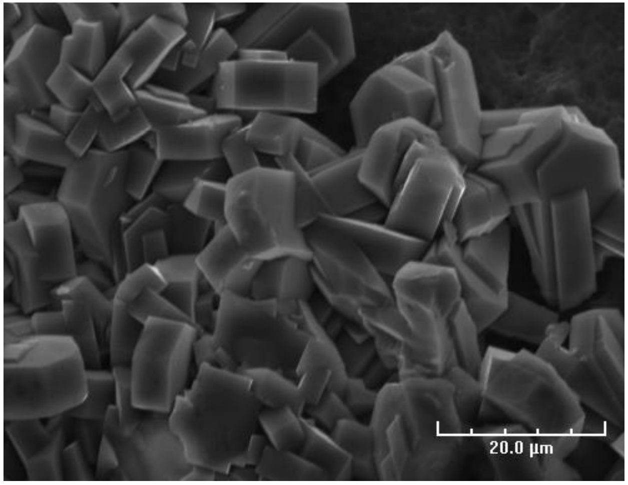
Bead that Fell Through the Tray at 300X



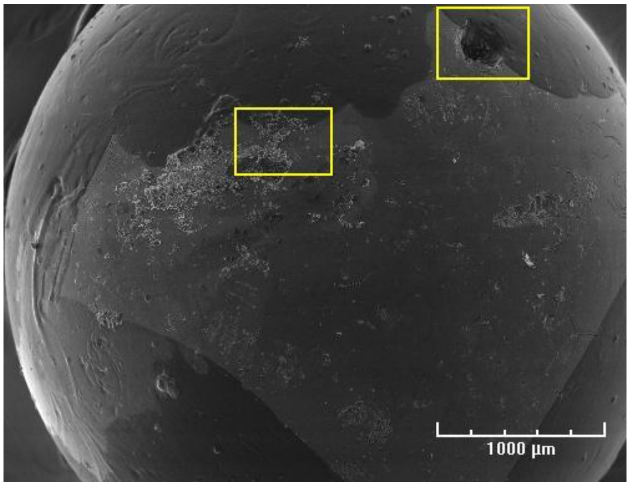
Bead that fell through the tray at 500X



Bead that fell through the tray at 500X

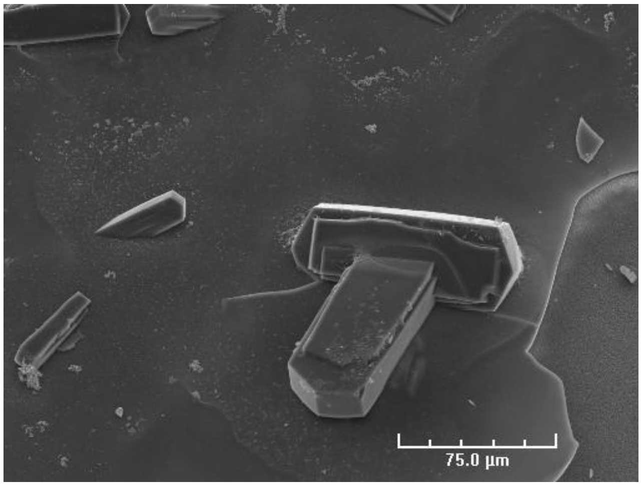


Bead that fell through the tray at 2,000X

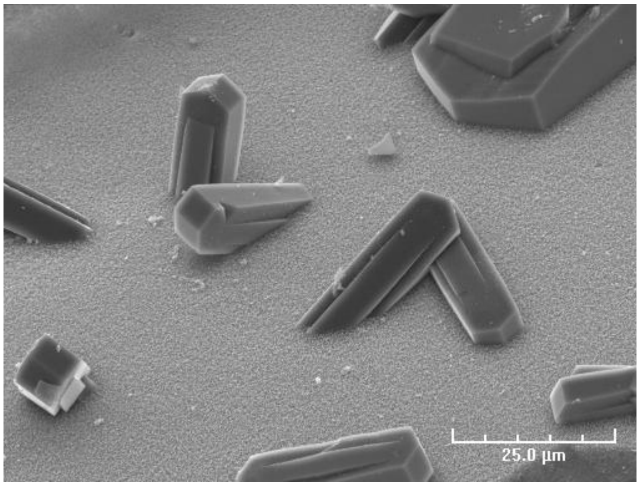


Bead that fell through the tray at 40X

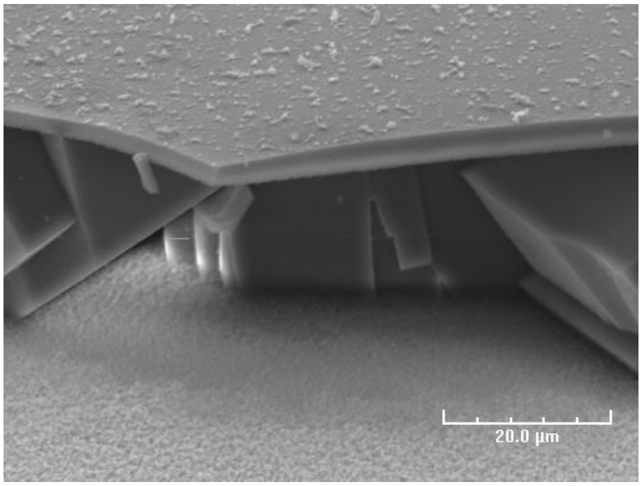
Beads Soaked for 24 Hours



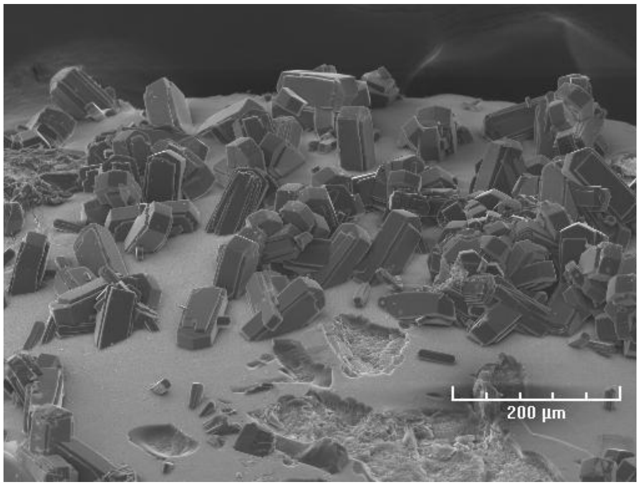
Bead Soaked for 24 Hours, Surface at 500X



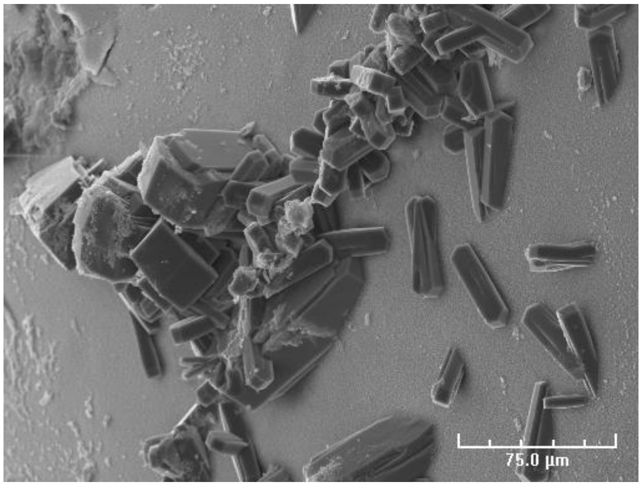
Bead Soaked for 24 Hours, Surface at 1,000X



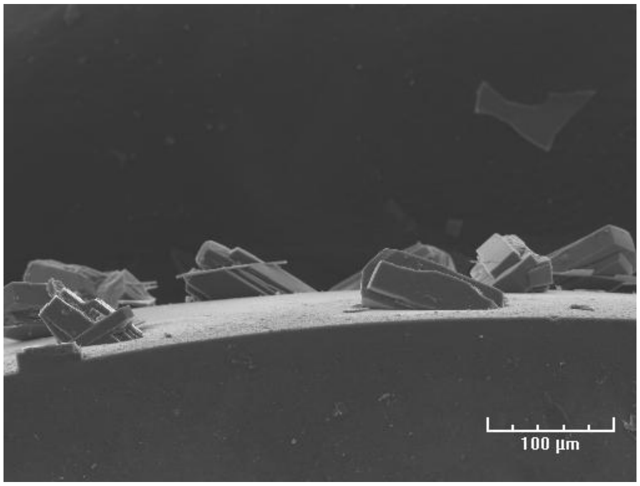
Bead Soaked for 24 Hours, Surface at 2,000X



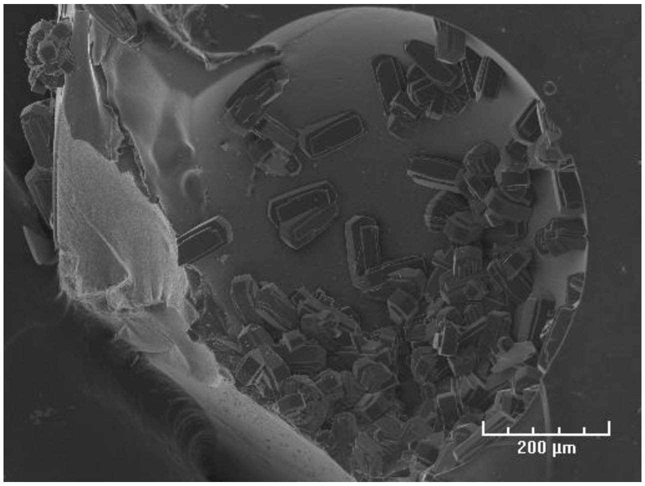
Bead Soaked for 24 Hours, Surface at 200X



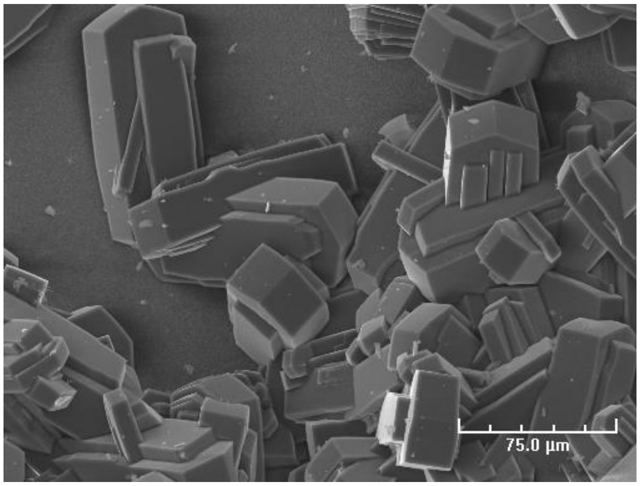
Bead Soaked for 24 Hours, Surface at 500X



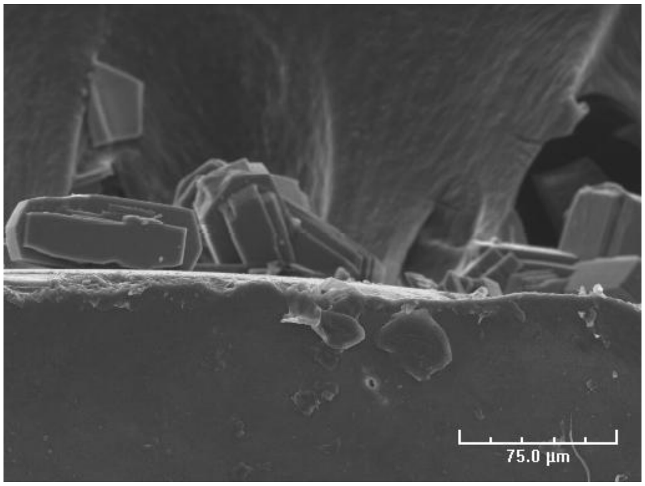
Bead Soaked, Cross Section at 300X



Bead Soaked, Cross Section at 150X

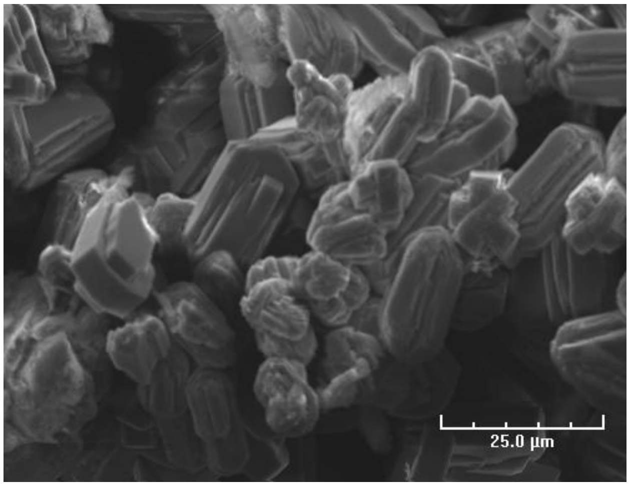


Bead Soaked, Cross Section at 500X

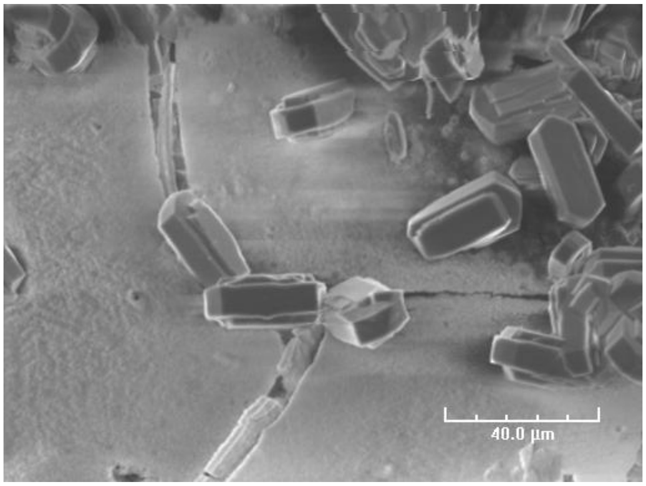


Bead Soaked, Cross Section at 500X

Aerogel Bead



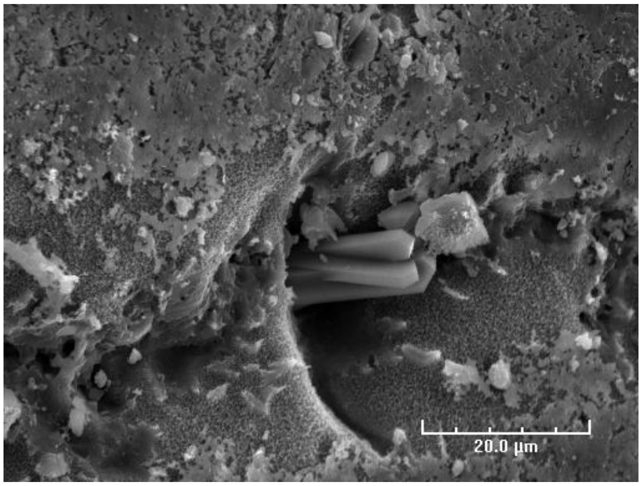
Aerogel Bead at 700X



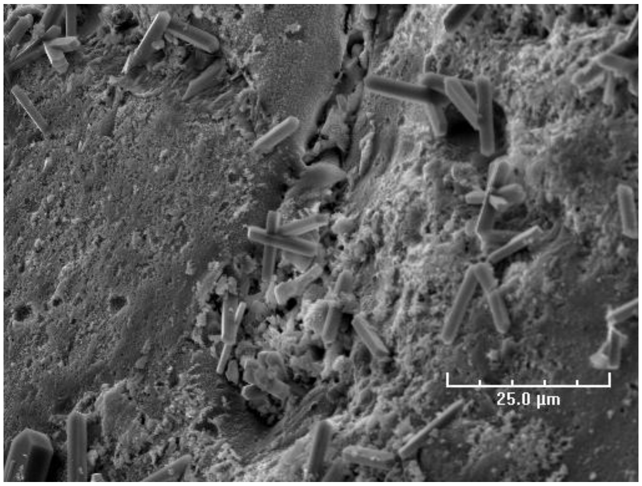
Aerogel Bead at 1,000X

Changing the Silica to TPA ratio

Ratio of 5.6

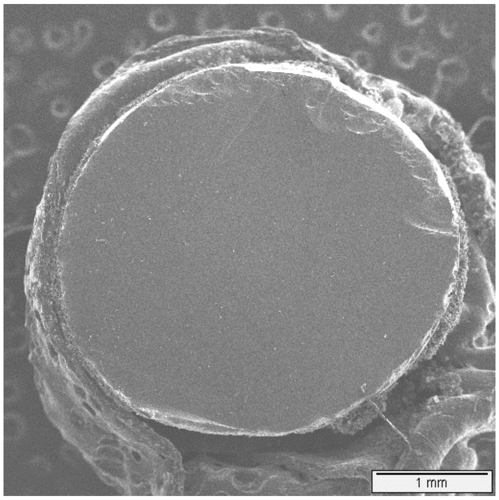


Bead with Silica:TPA ratio of 5.6 at 2,000X

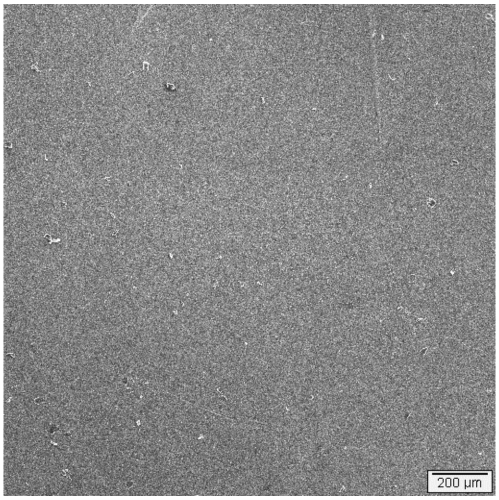


Bead with Silica:TPA ratio of 5.6 at 1,000X

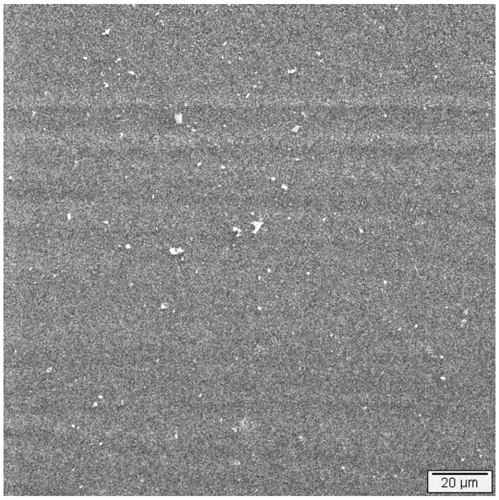
Ratio of 3



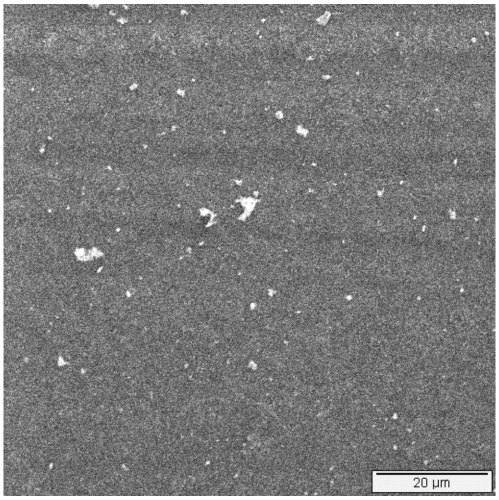
Cross Section of Bead at 20X



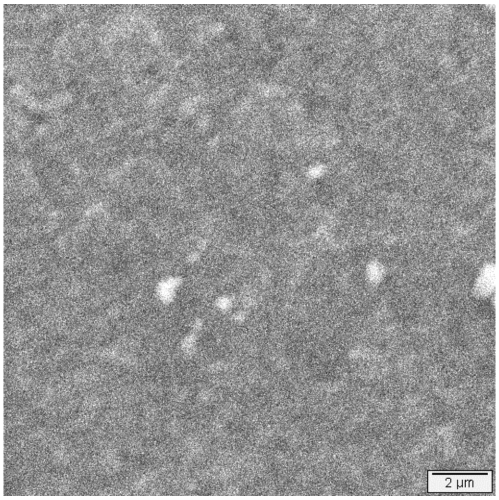
Cross Section of Bead at 50X



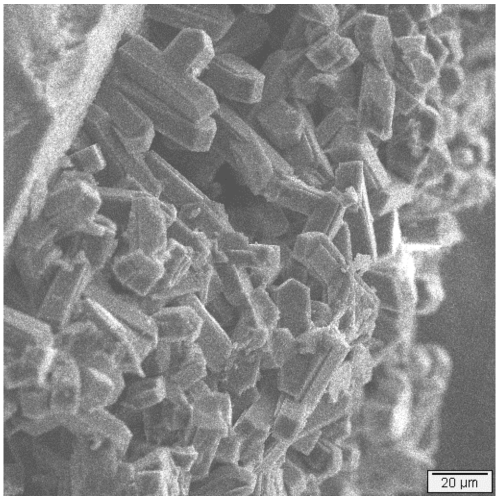
Cross Section of Bead at 500X



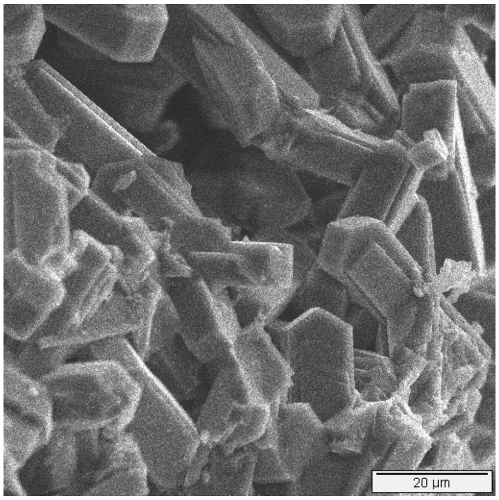
Cross Section of Bead at 1000X



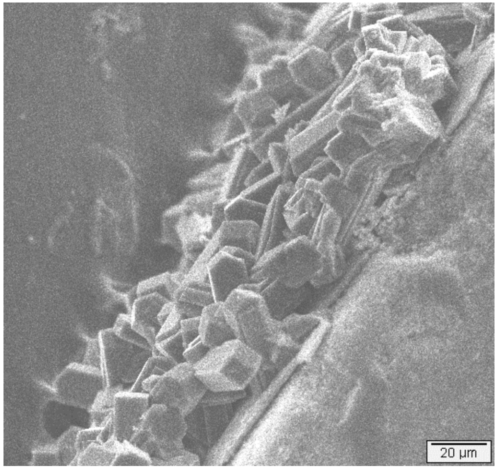
Cross Section of Bead at 5000X



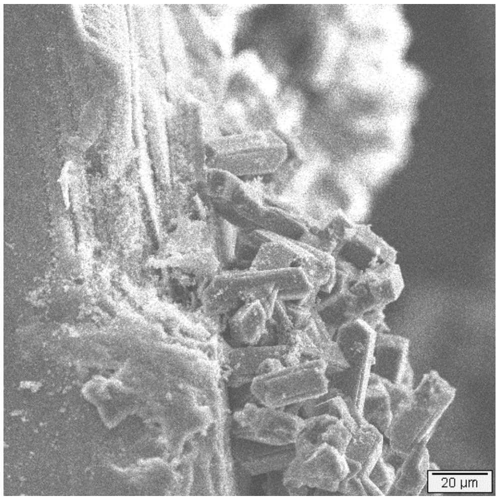
Edge of the Bead at 500X



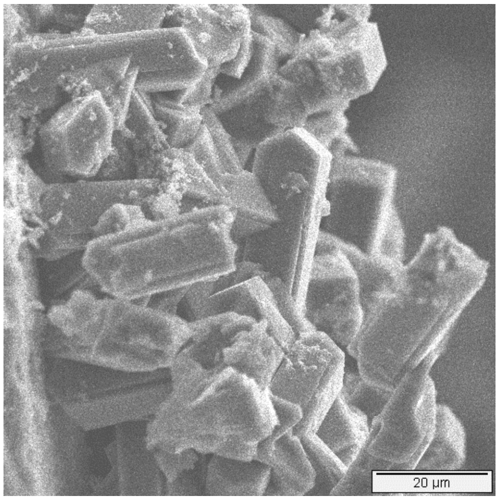
Edge of the Bead at 1,000X



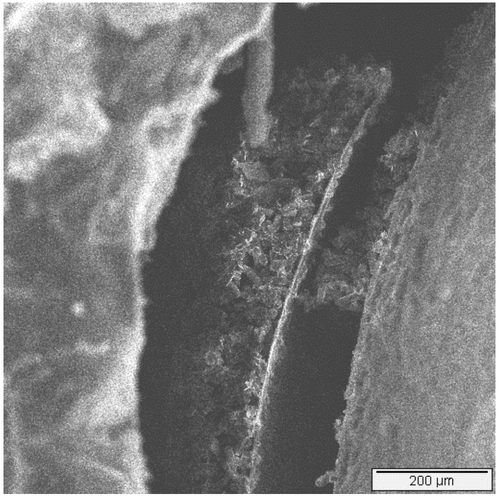
Edge of the Bead at 500X



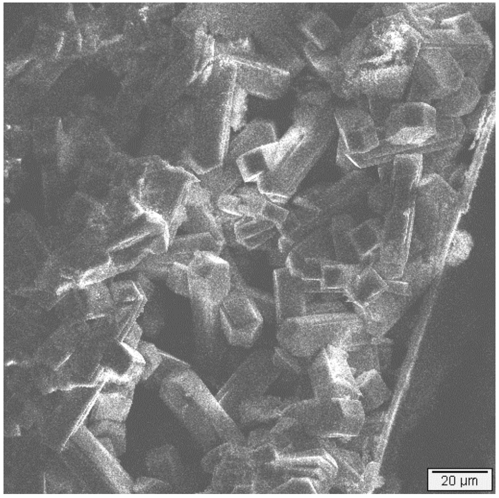
Edge of the Bead at 500X



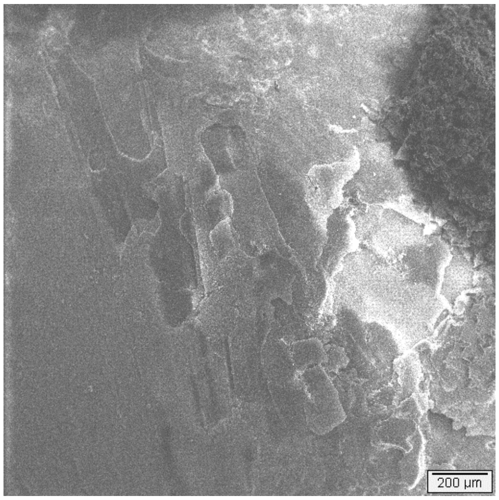
Edge of the Bead at 1000X



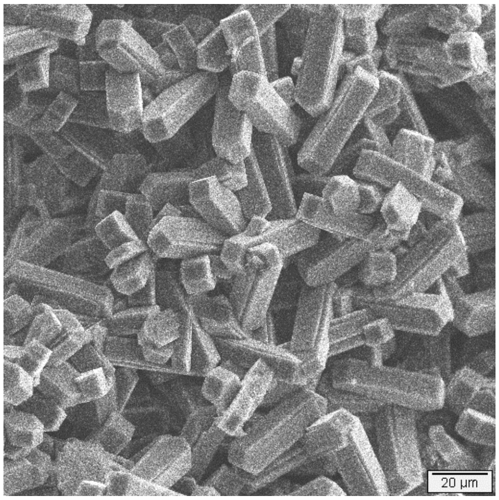
100X



500X



Surface of Bead at 50X



Surface of Bead at 500X

Sputtering Deposition Procedure

For Denton Desk II

1. Let the chamber pump down to 30 millitor or less.
2. Push the Sputter button in. The pressure burst may cause the system to jump out of the sputter mode. If this occurs, push the sputter button again.
3. Let the chamber pump down to below 20 millitorr. Set the gas flow control know for a stable pressure of approximately 75 millitorr. This is the proper sputter deposition pressure.
4. Move the shutter knob, the black knob labeled 1 on the top of the unit, counterclockwise and against the side of the Pyrex liner. This folds the shutter and moves it away from the pedestal.
5. Push the manual start button and set the current to 45 milliamps. Verify that there is a pinkish plasma glow. Hit the stop button. The system is now ready to start a timed deposition.
6. Set the timer to the desired deposition time. (30 seconds will give a coating of approximately 100Ang on a smooth surface. A rough surface can require 60 seconds for a 100Ang coating). Push the timed start button.

Exxon Mobil Patents

Exxon Mobil has other patents for aggregating zeolite bound zeolites than the patent explored in this project.

1. US Patent.6,111,157 (2000) Hendriksen, Dan Eldon, Mohr, Gary David, Verduijn, Johannes Petrus, Smith, and Robert Scott, Assigned to Exxon Chemical Patent Inc. (Houston, TX) “Aromatic conversion processes and zeolite bound zeolite catalyst useful therein,” 2482.

2. US Patent. 20010002426 (2002) Mohr, Gary David and Janssen, Marcel Johannes Gerardus, Filed by Exxon Chemical Co. (Baytown, TX) “Hydrocarbon conversion process using a zeolite bound zeolite catalyst,” 263.

3. US Patent.5,993,642 (1999) Mohr, Gary David, Chen, Tan Jen, Clem, Kenneth Ray, Janssen, Mechilium Johannes Geradus, Ruziska, Phillip Andrew, Verduijn, Johannes Petrus, van den Berge, and Jannetje Maatje, Assigned to Exxon Chemical Patent Inc. (Houston, TX) “Hydrocarbon conversion process using a zeolite bound zeolite catalyst,” 2484.

4. US Patent.6,039,864 (2000) Mohr, Gary David, Verduijn, and Johannes Petrus, Assigned to Exxon Chemical Patent Inc. (Houston, TX) “Hydrocarbon conversion process using a zeolite bound zeolite catalyst,” 2483.

5. US Patent.6,198,013 (2001) Mohr, Gary David, Chen, Tan Jen, Clem, Kenneth Ray, Janssen, Mechilium Johannes Geradus, Ruziska, Philip Andrew, Verduijn, and Johannes Petrus, Assigned to Exxon Chemical Patent Inc. (Houston, TX) “Toluene disproportionation process using a zeolite bound zeolite catalyst,” 2481.

6. US Patent.6,458,736 (2002) Mohr, Gary David, and Janssen, Marcel Johannes Gerardus, Assigned to ExxonMobil Chemical Patent Inc. (Houston, TX) “Hydrocarbon conversion process using a zeolite bound zeolite catalyst,” 1568.

7. US Patent. 20030127360 (2003) van den Berge, Jannetje Maatje and Mohr, Gary David, Assigned to ExxonMobil Chemical Company (Baytown, TX) “Preparation of high silica zeolites bound by zeolite and use thereof,” 2397.