

## TEMPLATE-FREE SYNTHESIS OF NANOCRYSTALLINE ZSM-5

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### Abstract

Zeolites are crystalline molecular sieves with pores of molecular dimensions, They have a high total surface area that makes them effective in a wide range of applications including catalysis, ion exchange, and selective adsorption. Commercially available zeolites are produced with crystal dimensions of a few micrometers, many times larger than the nanometer sized crystals synthesized in laboratories. The literature notes significant improvements in performance for all applications as the crystal sizes of zeolites are reduced but laboratory synthesis methods are not practical for large-scale production because of the necessity of organic template molecules. ZSM-5 is known for its interconnecting pore channels and its role in petroleum cracking. In this study, a seeded, template free synthesis method for producing nanocrystalline ZSM-5 with a crystal size of approximately 50 nm was developed and optimized. Nanocrystalline ZSM-5 was synthesized without organic templates by using approximately 30 nm long silicalite-1 zeolites as seeds for ZSM-5 crystal growth. The concentration of seed crystals in the synthesis gel and the duration of hydrothermal treatment were varied to optimize yield and quality. ZSM-5 crystals and silicalite-1 seeds were characterized by X-ray diffraction, scanning electron microscopy, nitrogen adsorption isotherms, and laser light scattering particle sizing. SEM images showed that the ZSM-5 crystals from the seeded, template-free synthesis are approximately 50 nm long.

## **Research Topic Selection**

Nanocrystalline zeolites (zeolites with crystal sizes of less than 100 nm) are promising materials for a variety of applications. Several practical barriers exist between the current small-scale laboratory synthesis of nanozeolites and the large-scale efficiency necessary for commercial production. Through a comprehensive literature review and discussions with my mentor, I determined that the use of organic template molecules for synthesis is one of the most substantial issues facing the science because it requires resource-intensive calcination. This study works towards developing synthesis parameters without the use of a template.

## **Introduction**

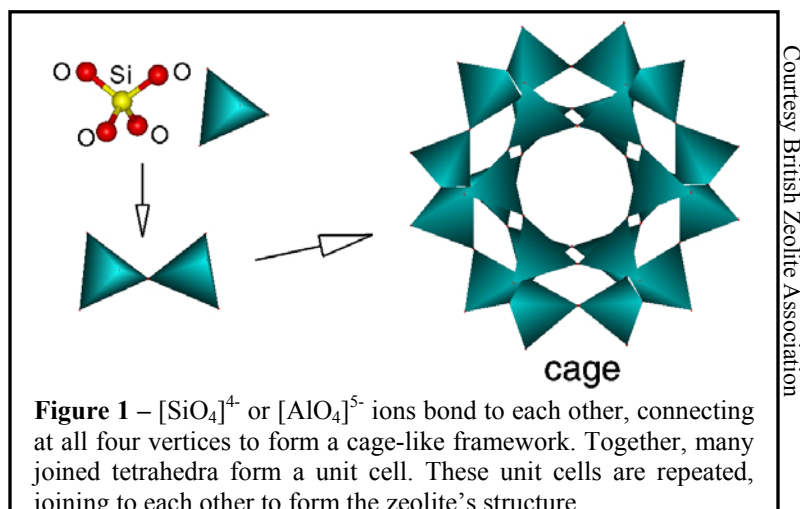
Zeolites are aluminosilicate molecular sieves with properties that continue to intrigue scientists after more than half a century of commercial study and application. The high overall surface area of the crystals makes zeolites particularly effective for use in ion exchange, catalysis, adsorption, and molecular packaging. Today, zeolites are used in a wide range of commercial, military, and industrial applications, from water-softening in laundry detergents to chemical weapons protection. ZSM-5 is widely used as a catalyst in the petroleum refining process to cracking the raw hydrocarbons.

Natural mineral deposits of zeolites are exploited throughout the world, where commercial mining operations extract and refine the crystals for international consumption. However, most zeolites are synthesized with various methods that were

pioneered in the laboratory. Many synthetic zeolites were invented by chemical and oil companies, specifically Union Carbide and Exxon Mobil, during the middle of the twentieth century. Researchers at Union Carbide, led by R.M. Milton, developed the first reliable synthesis of zeolites in 1949 by using a low-temperature hydrothermal method.<sup>1</sup> Today, these same companies continue to lead research and development efforts and the sale of the crystals is worth several billion dollars per year. Zeolite science remains a dynamic and developing field.

Two factors – the structural framework and the chemical composition of the crystals – control the majority of zeolites' properties. The International Zeolite Association (IZA) is the *de facto* authority on zeolite structures. To date, there are more than 160 unique structures registered with the Structure Commission of the IZA.<sup>2</sup> At their most basic, zeolites have a three-dimensional structure of a repeating framework of  $[\text{SiO}_4]^{4-}$  tetrahedra. These tetrahedra join by sharing oxygen atoms at all four vertices to form a cage-like structure, as seen in Figure 1.<sup>1</sup> This sharing creates an infinite lattice of individual building blocks, called unit cells, that permits a great deal of scalability in particle size.

A defining characteristic of zeolite structure is the intricate pore network found in all zeolites. While each zeolite framework has a unique pore structure, the dimensions of the pores are at the nanometer and subnanometer level, small enough to control shape selectivity on a molecular level.



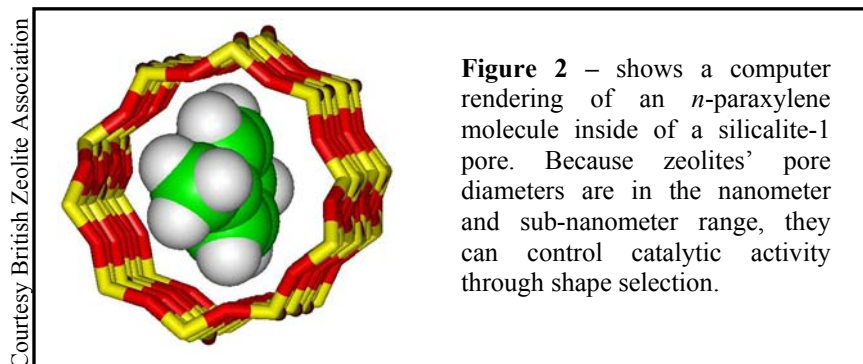
However, in some zeolite species a certain number of the silicon atoms are replaced by aluminum atoms. Because of the difference in valence electrons, the portion of the framework with an  $[\text{AlO}_4]^{5-}$  tetrahedron has a net negative charge, which is locally neutralized by the presence of cations (usually an alkali metal  $[\text{R}^+]$  or an alkaline earth metal  $[\text{R}^{2+}]$ ) on the surface or in the voids of the crystal. These ions are used in reversible exchange reactions on the crystal. Other ions may substitute inside the tetrahedra, increasing the variability of zeolite species.<sup>1-3</sup>

In this study, nanocrystalline ZSM-5 was synthesized using silicalite-1 seed crystals and in the absence of organic template molecules. Because ZSM-5 and silicalite-1 share the MFI framework structure, with ZSM-5 containing some  $[\text{AlO}_4]^{5-}$  tetrahedra that replace the standard silicon-based structures, this combination of synthetic methods should allow ZSM-5 crystal growth to continue from the lattice of the silicalite-1. Also, the templated synthesis methods for nanocrystalline forms of both zeolite species are well established in our lab.<sup>8,9</sup>

Recent studies have shown nanocrystalline zeolites (crystals with particle sizes <100 nm) to have enhanced properties compared to conventional microscale zeolites.<sup>4-10</sup>

Currently, silicalite-1 crystals can be reliably synthesized as small as 20 nm and ZSM-5 as small as 15 nm using high-temperature and high-pressure syntheses.

Several reliable methods for nanozeolite synthesis have been reported in the literature, yet problems with these syntheses prevent nanozeolites from being viable for commercial applications.<sup>11-21</sup> First, synthesis of the smallest crystals takes too long – up to 10 days for 20 nm silicalite-1 crystals.<sup>8</sup> Second, typical product yields of nanozeolite syntheses reported in the literature can be as low as 10%, while yields of up to 100% have been reported for micron-sized zeolites.<sup>22</sup> Finally, organic template molecules appear to be necessary for the pore structure to form correctly. Thus, after hydrothermal treatment the zeolites' pores are filled with the template molecule. To remove the template, the zeolites must be calcined at 600°C for several hours.<sup>8</sup> Not only does this require that another chemical be added to the synthesis gel, increasing the cost and waste of the process, but also the calcinations process is energy- and time-intensive. Synthesizing template-free nanozeolites would avoid these problems, making them more attractive for commercial development.



Several methods of template-free synthesis have been reported for micron-sized zeolites. Successful seeded syntheses are widely reported for micron-sized crystals.<sup>23-25</sup> These methods result in zeolite crystals with a narrow size distribution. The template-free

seeded synthesis for micron-sized ZSM-5 was adapted here to produce nanoscale ZSM-5 crystals.

### Experimental Section

**Materials.** Tetraethylorthosilicate (TEOS), Sodium Hydroxide (NaOH), tetrapropylammonium hydroxide 40% wt aqueous solution (TPAOH), ultrapurified water, and sodium aluminate ( $\text{NaAlO}_2$ )

**Silicalite-1 seed crystal synthesis.** Silicalite-1 seed crystals were synthesized using clear-gel solutions according to the established methods in our lab.<sup>8</sup> To start a synthesis, measured amounts of  $\text{H}_2\text{O}$ , TEOS, NaOH, and TPAOH solution were covered and stirred together overnight to ensure complete TEOS hydrolysis. When the mixture was uniform and clear, the gel was transferred into covered, glass vials for hydrothermal treatment at  $60^\circ\text{C}$  for 240 hours. Silicalite-1 crystals were recovered by centrifugation at 14000 RPM, washed using ultrapurified water, centrifuged again, and dried overnight at  $80^\circ\text{C}$ . X-Ray Diffraction (XRD), 7-Point BET Nitrogen Adsorption Isotherms (BET), Dynamic Laser Back-scattering (light scattering), and Scanning Electron Microscopy (SEM) were used to characterize the crystals and verify their size. To increase the product yield, unused synthesis gels were recycled and reused according to the procedures of Song *et al.*<sup>22</sup>

**Seeded ZSM-5 Synthesis.** ZSM-5 crystals were synthesized using a new method developed for this study. Measured amounts of TEOS, NaOH,  $\text{H}_2\text{O}$ , and  $\text{NaAlO}_2$  were mixed, covered and stirred overnight over low heat to ensure complete TEOS and  $\text{NaAlO}_2$  hydrolysis. After the gel was uniform and clear,  $\text{H}_2\text{O}$  was added to compensate

for mass lost to evaporation. Measured amounts of the prepared gel and seed crystals were mixed and sonicated until a colloidal suspension was achieved. The seven variable groups were prepared according to the specifications of Table-1. The mixture was then transferred to stainless steel autoclaves equipped with Teflon liners and heated as specified in Table 1.

**TABLE 1**

Sample	Temp (°C)	% Seeds (% wt)	Time (h)	Other Changes
Z-1	165	1	48	
Z-2	165	1	24	
Z-3	165	1	12	
Z-4	165	1	24	Use seeds from recycled synthesis
Z-5	165	1	24	2x H <sub>2</sub> O
Z-6	165	5	24	
Z-7	165	1	24	No H <sub>2</sub> O added after stirring

The synthesis conditions for nanocrystalline ZSM-5 synthesis seeded with nanocrystalline silicalite-1

**X-ray Diffraction.** A Siemens D5000 X-ray diffractometer with a Cu K $\alpha$  target and a nickel filter was used to collect XRD powder patterns for the samples. XRD patterns were collected between  $2\theta$  angles of 5 and 55°. To determine particle size, Scherrer's Equation was used. The full-width-at-half-maximum (fwhm) was obtained for each ZSM-5 sample from a common peak. Scherrer's Equation is given below:<sup>26</sup>

$$T = \frac{K\lambda}{\beta \cos\theta}$$

T = crystal size (nm)

K = crystal shape factor (2.76)<sup>8</sup>

$\lambda$  = the wavelength of the X-ray for the Cu target (1.542 Å)

$\beta$  = fwhm

$\theta$  = Bragg's angle

**Scanning Electron Microscopy.** SEM images of the ZSM-5 crystals were acquired using a Hitachi S-4000 scanning electron microscope. To prepare the sample for

SEM, a drop of dilute colloidal solution of the sample was placed onto the SEM sample stud surface and the sample was sputter-coated with gold.

**Nitrogen Adsorption Isotherms.** Nitrogen adsorption isotherms were obtained on a Quantachrome Nova 1200 multipoint BET apparatus using approximately 0.2 g of sample for each measurement. Immediately prior to the N<sub>2</sub> adsorption, each sample was vacuum degassed at 120 °C for 1 hour. The specific surface area was measured by the BET method, which was performed automatically by the instrument.

**Laser Light Scattering.** A Malvern High Performance Particle Sizer was used to obtain size distribution data. A small volume of very dilute colloidal suspension was sonicated and placed into a low-volume cuvette. The instrument software determined all correlation equations automatically.

## **Results**

**Silicalite-1 seed crystals.** Silicalite-1 seed crystals were successfully synthesized from clear nutrient gels, the most reliable methodology in our lab. Synthesis conditions were manipulated with the goal of attaining the smallest possible particles for use as seed crystals. After a 240-hour hydrothermal treatment at 60°C, the crystals were extracted in powder form and characterized to verify that the product was in fact silicalite. To increase the product yield of the synthesis, the unused synthesis gels were recycled and subjected to another hydrothermal treatment at 60°C but for only 48 hours. This recycling process was repeated successfully twice, yielding about 50% more zeolite powder than the original synthesis batch alone. The third recycled batch did not yield any new particles, indicating that the nutrients were either too dilute to react or had been used up.

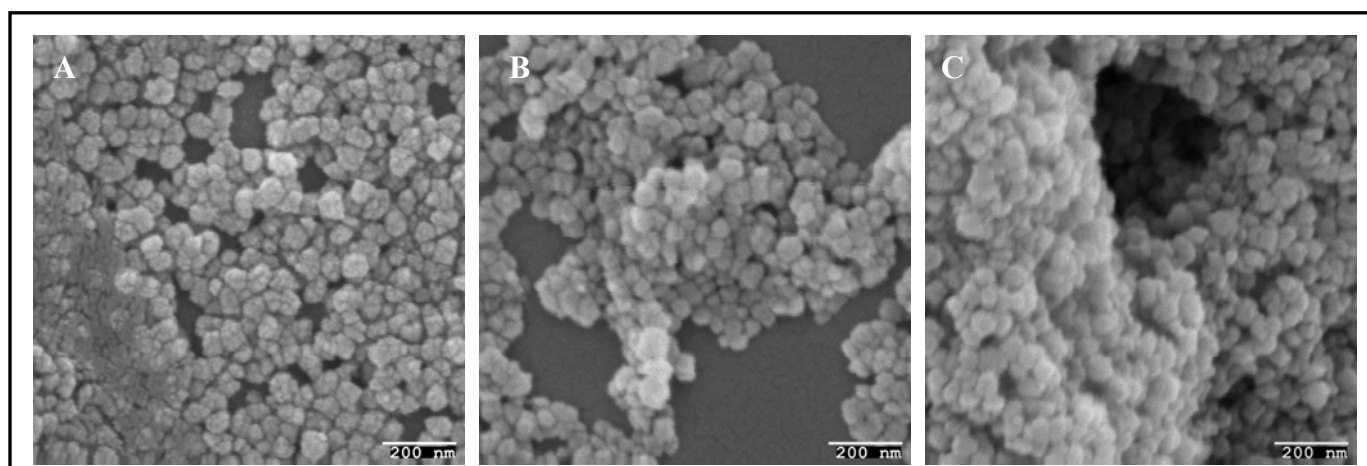
XRD patterns showed that the product was crystalline. The pattern was matched against a standard for silicalite and agreed very well. The as-synthesized particles were analyzed using a 7-point BET surface-area test. An external surface area of  $103 \text{ m}^2/\text{g}$  was measured for the uncalcined sample, which still had organic template blocking the internal surface. Using the model developed by Song *et al.* and reported in the literature, this external surface area was converted to a particle size.<sup>8</sup> The model is shown below:

$$S_{\text{ext}} = 3214/x$$

Where  $S_{\text{ext}}$  is the external surface area in  $\text{m}^2/\text{g}$  and  $x$  is the silicalite-1 crystal size in nm assuming a cubic crystal.

Using Song's model and the surface area measured from the BET analysis, the silicalite-1 seed particles were calculated to be approximately 31 nm on a side, assuming a cube.

The relative size distribution of the silicalite-1 seeds was measured using light scattering. This method consistently reported sizes in the 70 nm range, far larger than the sizes reported by the BET and SEM methods.



**Figure 3** – Three SEM images with scale bars showing silicalite-1 seed crystals. The image (A) of the original batch of silicalite-1 seeds shows the aggregation of the particles. Single particles of about 30 nm can be identified within mini-aggregates, which are about 60 nm across. Image B shows aggregation in a sample of the first recycled batch of silicalite-1 seeds, made from the left-over synthesis gels of the original batch. This image shows the larger aggregates that stretch several microns across. A close-up micrograph of that same sample (C) shows the difficulty of picking out primary particles for measurement even at a high magnification.

Finally, images of the silicalite-1 crystals were obtained using a scanning electron microscope. From these micrographs, visible in figure 3, average particle size was calculated for each sample by measuring about 50 primary particles. It is obvious from the images that the samples were significantly aggregated, even after extensive sonication. This aggregation made the measurement of the primary particles more difficult because some aggregates were as small as two or three particles. Others were so large that they extended over several microns, as visible in image C of figure 3. Nevertheless, particle-size measurements from these images determined that the silicalite-1 crystals were about 30 nm and that they had a cubic shape, validating the use of Song's model for converting BET surface area measurements to particle size.

**Seeded Template-free ZSM-5 synthesis.** The powdered silicalite-1 seeds produced in the first part of this study were used as seed crystals for ZSM-5 template-free synthesis. This synthesis procedure was developed by combining ideas from our lab's current methods for producing nanocrystalline ZSM-5 with recipes for seeded syntheses that produce micron-sized zeolites.<sup>9,27</sup> Batches of seeded ZSM-5 were synthesized according to the specifications in Table 1. Duration of hydrothermal treatment, gel composition, and seed source were all varied in independent batches.

Once the zeolites were extracted from the synthesis broth, they were characterized using XRD, light scattering, and SEM. Powder XRD patterns were acquired for each sample. These scans became the source for line-width measurements and particle-size calculations using Scherrer's Equation. They also confirmed or rejected the crystallinity of each sample. The results of this analysis can be found in Table 2.

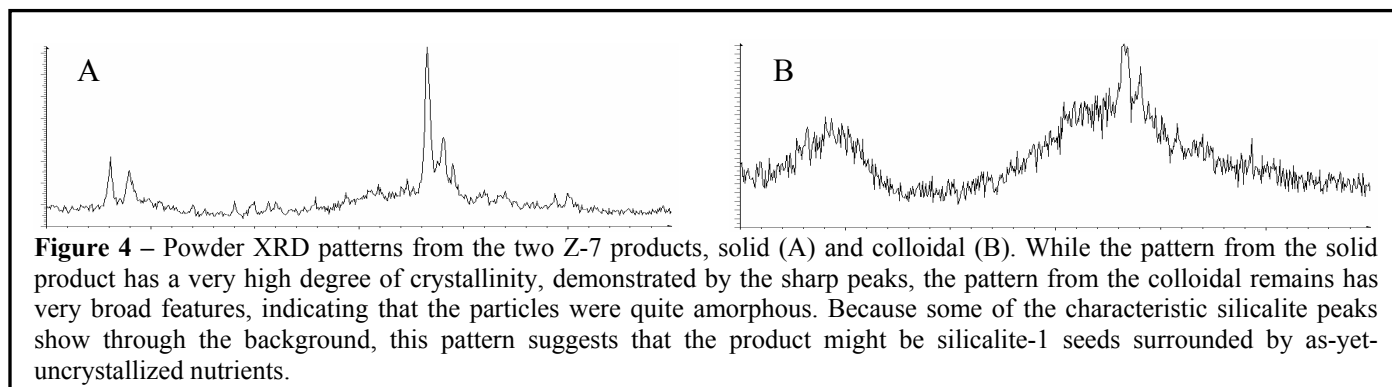
TABLE 2

Sample	Synthesis Time (h)	Product Components	Crystalline Nature <sup>a</sup>	Percent of Product Colloidal <sup>b</sup> (%)	XRD Scherrer's Crystal Size <sup>c</sup> (nm)	SEM Measured Size <sup>d</sup> (nm)
Z-1	48	Solid Colloidal	Yes Yes**	0.1	30.46 33.21	48 (17)
Z-2	24	Solid Colloidal	Yes Yes**	83.5	18.27 34.8	52 (13)
Z-3	12	Colloidal	No	100.0	N/A	57 (11)
Z-4	24	Solid Colloidal	Yes Yes*	77.0	18.27 18.28	
Z-5	24	Colloidal	Yes**	100.0	18.27	
Z-6	24	Solid Colloidal	Yes Yes	77.1	40.59 19.23	
Z-7	24	Solid Colloidal	Yes No	85.1	24.35 N/A	

ZSM-5 crystals, synthesized using silicalite-1 seeds about 30 nm across, were measured using different methods. <sup>a</sup> This is a qualitative measure of crystallinity derived from XRD patterns. Stars denote the relative amount of amorphous material represented on the XRD pattern. <sup>b</sup> Colloidal percentages were found by dividing the mass of the colloidal product by the sum of the colloidal and solid products. <sup>c</sup> XRD patterns were used to determine crystal size according to Scherrer's Equation ( $K=2.76$ ) using a common peak at approximately  $2\theta=8^\circ$ . Although these data consistently underestimate crystal size compared to SEM verification, sizes determined from Scherrer's are useful for observing trends in crystal size. <sup>d</sup> An average of about 50 particles from each representative image. The numbers in parentheses are the standard deviations.

Interestingly, the products of these ZSM-5 syntheses were not uniform. All but two of the syntheses contained two distinct types of zeolite product inside the autoclave's Teflon liner: a colloidal suspension and a solid substance with varied consistency. These two distinct products were separated by filtering and characterized independently. Some batches had solids that had the look and consistency of jelly, while other solids were manifest in solid, brittle sheets. These solid remains always displayed a very crystalline nature on XRD patterns as seen in Figure 4-A, which shows the XRD pattern for Z-7 solid. This pattern is representative of all the solid remains of the seeded syntheses in its distinctly crystalline peaks. These patterns were always consistent with standards for ZSM-5. In contrast, colloidal remains indicate the presence of both crystalline and

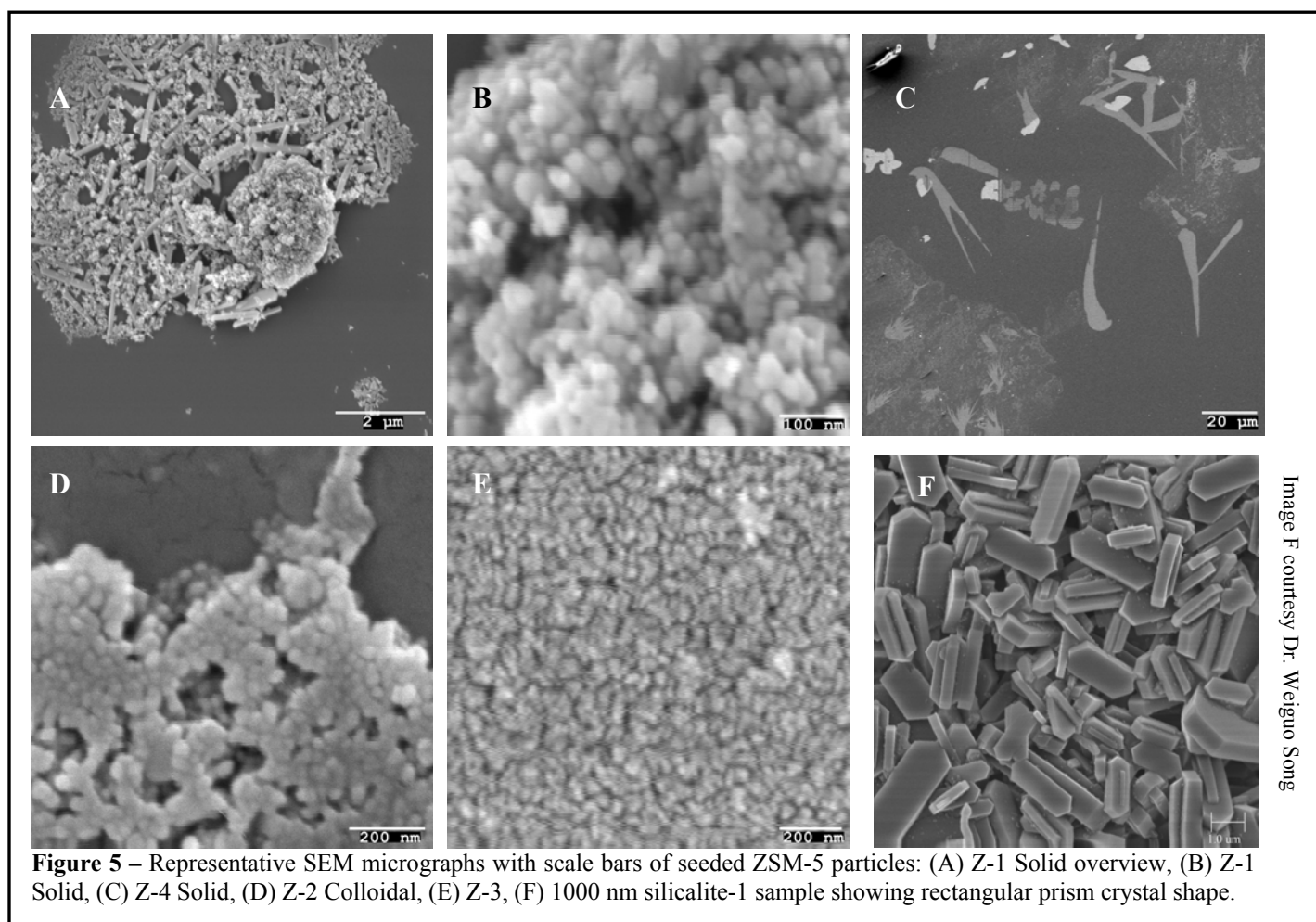
amorphous components with some batches yielding completely amorphous particles in the suspension. Figure 4-B shows how the broad features visible in many XRD patterns of colloidal products has within it some characteristic silicalite-1/ZSM-5 peaks.



Light-scattering data were also collected for the ZSM-5 samples. Just as was the case with the silicalite-1 samples, the ZSM-5 samples produced particle-size readings far above the expected values, around 500 nm. It was again hypothesized that aggregation caused the ineffective readings. This hypothesis was later supported by evidence from SEM micrographs that showed large aggregates of up to several microns across.

SEM images were acquired from several seeded ZSM-5 samples. Technical difficulties prevented clear SEM images from being acquired for many of the samples. Some of these problems were caused by the thick sheets of solid zeolite remains in some samples. These sheets were so thick that they prohibited clear focusing at magnifications large enough to inspect individual zeolites particles. Instead, low-magnification overviews were used to examine aggregate size, as in Figure 5-C. Nevertheless, the SEM images that were acquired contained information crucial for sizing and visual verification of the syntheses.

In sample Z-1, which received a 48-hour hydrothermal treatment, SEM images showed large, rectangular prisms interspersed with the nanocrystalline zeolites. This phenomenon is visible in Figure 5-A. These prisms, which are more than 1 micron in length, were assumed to be larger ZSM-5 crystals because they are identical in appearance to conventionally synthesized micro-scale zeolites as seen in Figure 5-F.<sup>8</sup> While the genesis of these particles is unclear, they severely distort the size distribution of the sample.



## Discussion

**Silicalite-1 synthesis.** Because the left over gels from the silicalite-1 synthesis can be recycled, the process has the potential for a vastly improved yield over conventional nanozeolite syntheses. SEM images confirmed a narrow size-distribution, reaffirming the quality of the synthesis. Because these seeds need not be calcined, their synthesis is relatively simple. Also, the seeds can be sized using the surface-area model from Song *et al.*<sup>8</sup>

**Silicalite-1 gel recycling.** Normal nanozeolite synthesis methods usually yield very little usable product. By recycling the unused synthesis gels after each round of silicalite-1 synthesis, the chemical ingredients normally used for only one synthesis were stretched to three batches. By using this recycling procedure, about 50% more silicalite-1 was produced than would have been produced without recycling. In a commercial setting, this process would be extremely valuable because producers would be able to save money on chemical costs and reduce waste. Further work with recycled syntheses might lead to even higher yields.

The success of synthesis group Z-4 verifies the quality of these recycled syntheses. XRD patterns of Z-4 show no decrease in crystallinity from Z-2, which had the same synthesis parameters except for the source of the seed crystals. The yields of these two groups, Z-4 and Z-2, are also similar. These results show that seeds produced with recycled synthesis gels are usable. Without this finding, the implications of recycled syntheses would be diminished. Moreover, these results confirm the importance of Song *et al.* by determining that his crystals are no different in function than conventional ones.

**Seeded synthesis theory.** The use of seed crystals in zeolite synthesis is well documented for micron-sized particles. Simply put, seed crystals provide a solid surface area on which nutrients in synthesis gels might grow.<sup>23-25</sup> There are several advantages to using seeds. First, the presence of a growth surface in the synthesis gel removes the need for self-nucleation, one of the most time-consuming portions of the synthesis process. In terms of commercial application, this property is appealing. Second, seeded syntheses traditionally have a very narrow size distribution. Finally, seeding can help a synthesis overcome the presence of impurities that would normally prevent nucleation.<sup>28</sup>

There are four main theories for the actions of seed crystals in zeolite synthesis. First, the seeds might remain inert, not affecting the synthesis at all. In this case, the seeds would still be present at the end of the entire process. Second, the seeds might dissolve into synthesis gels, adding nutrients that might later be used for synthesis. Third, nutrients in the synthesis gel might be deposited on the surface of seeds crystals. In this case, there would be a core seed crystal in the middle of any zeolite with the framework of the final zeolite product surrounding it. In general, this growth method would yield a product with a similar size-distribution range to the seed crystals. This idea is considered the most likely situation when the synthesis gel has enough pre-formed surface area to accommodate all of the nutrients awaiting growth.<sup>28</sup>

Finally, the most desirable type of seeded synthesis is largely unexplained on the atomic level. In this scenario, the addition of seed crystals initiates a wave of secondary nucleation throughout the synthesis gel. This secondary nucleation occurs most often when the synthesis gels appear to be near-perfect but still will not nucleate. Researchers hypothesize that active impurities or growth poisons exist in the gel that inhibit

nucleation alone. Because the number of secondary nucleation events is a geometric function of the surface area added, these inhibitors might be overpowered in a seeded synthesis. Because very little is known about the nature of this type of nucleation, it is very difficult to design an experiment to test for it. The literature notes that one method of controlling the balance between secondary nucleation and growth on top of the seed crystals is to manipulate the relative concentrations of nutrients and the surface area of the seed crystals added.<sup>28</sup>

The sizes of the ZSM-5 crystals – only about 20 nm larger than the seeds in some samples – indicate that the third type of crystal growth, deposition and crystallization of nutrients on the surface area of seed crystals, occurred in these syntheses. This is verified by XRD patterns of the colloidal, amorphous synthesis products, which show clear signs of crystallinity underneath the amorphous material. This indicates that the seed crystals are surrounded by amorphous, as-yet-uncrystallized nutrients. Because ZSM-5 and silicalite-1 crystals share the same MFI framework structure, it presumably would be simple for the ZSM-5 framework to grow directly out of the silicalite-1 crystals' surfaces. If this hypothesis is correct, the particles are not uniform throughout. Each crystal would have a core of as-synthesized silicalite-1 surrounded by the template-free ZSM-5 framework.

**Seeded ZSM-5 product yield.** The low yield of nanozeolite syntheses is one of the primary challenges to shrinking commercial zeolites from the microscale to the nanoscale. Analyzing the yields of the different template-free syntheses provides clues to the optimal combination of synthesis parameters to create the highest-quality zeolites as well as the most crystal growth. According to the powder XRD patterns from the seeded

ZSM-5 products, maximizing the production of solid zeolite product is the most desirable synthesis goal because the patterns show that solid products are the most crystalline.

Table 3, below, shows various calculations of product yield for all of the seeded ZSM-5 syntheses.

**TABLE 3**

<u>Sample</u>	<u>Synthesis Time (h)</u>	<u>Colloidal Product</u>	<u>Solid Product</u>	<u>Product Syn Gel</u> <sup>a</sup>	<u>New Crystal Nutrients</u> <sup>a,b</sup>
Z-1	48	0.17%	99.83%	6.94%	6.01%
Z-2	24	83.47%	16.53%	5.74%	4.80%
Z-3	12	100.00%	0.00%	4.35%	3.39%
Z-4	24	77.02%	22.98%	7.88%	6.96%
Z-5	24	100.00%	0.00%	3.71%	2.75%
Z-6	24	77.09%	22.91%	9.54%	5.02%
Z-7	24	85.13%	14.87%	8.75%	7.83%

Table 3 shows different calculations of product yield for the seeded, nanocrystalline ZSM-5 syntheses. The column headings show the formula used to calculate each yield. <sup>a</sup> The mass of the total synthesis gel is denoted by “Syn Gel,” while “Nutrients” denotes the mass of the nutrients in the synthesis gel, ignoring the mass of the seed crystals. <sup>b</sup> “New Crystal” represents the mass of the total synthesis product from which the mass of the seed crystals has been subtracted.

The data clearly show that the ratio of solid product to colloidal product increases dramatically as the duration of hydrothermal treatment is increased. Z-1, which was heated at 165°C for 48 hours, is almost entirely solid, while there was no solid product in Z-3, the 12-hour synthesis. The XRD patterns of the solid, crystalline products of these syntheses are nearly identical, the colloidal, amorphous products also have similar patterns. Together, these data imply that over time, the colloidal, amorphous products are converted to the solid form. In addition, the total yield, shown in column four, increases as the duration of the hydrothermal treatment increases from 12 to 48 hours. All of this information indicates that increasing the synthesis time is a reliable method to increase the overall yield as well as increase the quality of the products.

Syntheses Z-4, Z-5, Z-6, and Z-7 were each heated for 24 hours and should be compared with Z-2 to determine the effect of each variable. Obviously, doubling the H<sub>2</sub>O added after stirring was not helpful, as Z-5 has no solid product and a lower overall yield. In contrast, Z-7, which received no additional H<sub>2</sub>O after stirring, had a significantly higher overall yield as well as more new crystallization, represented in the last column of Table 3. This batch had no significant change in the ratio of solid to colloidal product from Z-2, indicating that heating Z-7 for 24 more hours would have completely changed the colloidal products to solid, following the trend of Z-2 and Z-1.

Increasing the proportion of seed crystals to nutrients, as in Z-6, seems to have a small effect on the yield and the production of new crystalline material. This technique seemed to drastically increase the solid-to-colloidal ratio, compared to the proportion of seed crystals to nutrients in Z-2. Nevertheless, this does not seem to be the optimal variable group because the production of new crystalline material is still less than in Z-7.

**ZSM-5 sizing.** As discussed above, determining the size of ZSM-5 particles proved difficult. Using BET surface area analysis with a mathematical model to determine crystal size would be ineffective because the pores of the new zeolites are not plugged up with TPAOH, the organic template molecule. This is necessary for determining the size through BET. SEM images provide visual clues to the size of the particles, but the method has drawbacks. Intense aggregation in the samples was evident in micrographs, making it difficult to pick out distinct primary particles. Moreover, the solid remains of many syntheses were too thick for the SEM to acquire clear pictures. Light scattering was also impeded by this aggregation. XRD line-width analysis provides a qualitative measure of particle size, useful for filling in gaps in SEM information.

## **Conclusions**

A seeded, template-free synthesis method for producing nanocrystalline ZSM-5 with a crystal size of approximately 50 nm was developed. This method is an improvement over conventional methods of synthesizing nanocrystalline zeolites because the use of organic template was eliminated. This decreases the cost and chemical waste associated with the process. Silicalite-1 seed crystals were synthesized using standard hydrothermal techniques to achieve a small crystal size of 30 nm confirmed by BET nitrogen adsorption analysis, XRD, and SEM. The unused silicalite-1 synthesis gels were recycled to increase the product yield.

These silicalite-1 crystals were used as seeds to synthesize template-free ZSM-5 crystals approximately 50 nm long, which were characterized using SEM and XRD. In each batch, there were two types of synthesis products – solid remains and a colloidal suspension – which were composed of crystals in different stages of development; the solid remains were far more crystalline than the colloidal remains. There is a direct relationship between the duration of the hydrothermal treatment and the crystallinity as well as between the duration and the overall yield. In addition, reducing the amount of H<sub>2</sub>O in the synthesis gel increased crystallization of amorphous nutrients.

Because the use of an organic template molecule is an obstacle to the commercial adoption of nanocrystalline zeolites, this study brings industrial production of nanocrystalline ZSM-5 closer to fruition. Future studies might explore a more efficient method of sizing seeded, template-free particles as well as examine the relative catalytic efficiency of the particles. Finally, these methods might be adapted to producing template-free versions of other nanozeolite species.

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