

# NANOSTRUCTURED MATERIALS

## Synthesis of Zeolites

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**Z**eolites are crystalline aluminosilicates whose principal constituents are aluminum, silicon, and oxygen.<sup>[1]</sup> They were discovered by Baron Axel F. Cronstedt, who coined their name using the Greek words *zeo* (to boil) and *lithos* (stone) because they bubbled under heating.<sup>[2-4]</sup> The fundamental building blocks of the zeolite framework are the tetrahedral units:  $[\text{SiO}_4]$  and  $[\text{AlO}_4]$ . The silicate  $[\text{SiO}_4]$  unit, shown in Figure 1a, consists of a silicon atom surrounded by four oxygen atoms;  $[\text{AlO}_4]$ , in which Al replaces silicon at the center of the tetrahedron, bears a negative charge. This charge is balanced by that of positive metal ions, mostly alkali cations, sitting in the gaps of the framework.

During zeolite synthesis, the tetrahedral units are joined together via a common oxygen atom to form rings or cage structures, referred to as secondary building units (SBU). The SBUs can be assembled in many ways to produce various types of zeolites. For example, the so-called 5-1 ring SBU (see Figure 1b) generates either ZSM-5 or ZSM-11. Figure 1c illustrates the construction of a continuous framework of ZSM-5 using 5-1 SBUs. This zeolite (Figure 1d) exhibits two intersecting channels: one straight and the other zig-zag.

The extensive research in zeolites was initiated after recognition of the similarity in the composition of zeolites and silica-alumina.<sup>[5]</sup> The latter was used as a cracking catalyst in refineries in the 1950s. At present, zeolites, including ZSM-5, are used to process over 7 billion barrels of petroleum and other chemicals annually, producing tens of billions of dollars per year in revenues.<sup>[6]</sup> ZSM-5, one of the most widely studied zeolites, has dominated the patent literature in applications of nanostructured materials. In addition, the well-defined pores or cavities in nanometer range give rise to unique molecular sieving capabilities and high internal surface areas suitable for a wide range of applications in fields other than industrial catalysis, *e.g.*, ceramics, electronic materials, drug release media, sorbents, and ion exchangers.

The syntheses of zeolites often require the use of small organic species such as quaternary ammonium ions (*e.g.*,  $\text{R}_4\text{N}^+$ ) as templates or structure-directing agents. Detailed mechanistic studies of ZSM-5 synthesis suggest that the hydrophobic hydration sphere formed around TPA (*i.e.*, tetrapropyl ammonium ion) is replaced by inorganic species forming an organic-inorganic nanocomposite. Aggregation of these species results in nucleation and eventually crystal growth in a layer-by-layer fashion.<sup>[7,8]</sup> In 1992, Kresge, *et al.*, had the clever idea of using supramolecular assemblies such as surfactants or polymer liquid crystals as templates, instead of the individual molecules or cations currently used as structure-directing agents for the synthesis of zeolites.<sup>[5,9,10]</sup> The ordered materials were obtained and referred to as mesoporous molecular sieves (MMS). These materials are similar to zeolites, with the notable difference being that their pore sizes are much larger (*i.e.*, from 2 to over 30 nm).

The evolution from the concept of structure-directing to

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that of supramolecular assemblies has led to rapid development in the synthesis of nanostructured materials. These novel nanomaterials opened new opportunities in many areas, such as biosensing, drug delivery, bioseparation, and heterogeneous catalysis.<sup>[11-20]</sup> The simplicity in the concepts of template synthesis, along with the complexity of interrelated factors in zeolite synthesis, make ZSM-5 synthesis an excellent project that allows students to integrate basic principles of nanomaterials synthesis into reaction engineering.

This paper describes an experiment on ZSM-5 synthesis that was performed in our juniors' chemical engineering laboratory at the University of Akron. The objective of this experiment is to provide hands-on experience for the students that includes formation of working teams, performing literature searches, grasping basic concepts of nanostructured material synthesis, experimental design, reactor operation, infrared spectroscopic analysis, troubleshooting, and learning assessment.

## EXPERIMENTAL

**Materials and Equipment** • Sodium hydroxide (certified A.C.S. grade), tetrapropyl ammonium bromide (*i.e.*, TPA) (98+%), and sulfuric acid (0.1 M standardized solution) were obtained through Alfa Aesar; sodium aluminate (~8% H<sub>2</sub>O, 99.9% Al) was purchased from Strem Chemicals; and Aerosil silica was generously donated by Cabot Corporation. All chemicals were used without further purification. The hy-

drothermal synthesis of zeolite was conducted in a 300 cm<sup>3</sup> stainless steel autoclave (Pressure Products Inc). The samples were analyzed by X-ray diffraction (XRD) [Phillips APD3700 X-ray diffractometer (Cu-K<sub>α</sub> radiation)] and infrared spectroscopy (IR) [Nicolet Magna 550 Series II infrared spectrometer equipped with a DTGS (deuterated tri-glycine sulfate) detector].

**Synthesis** • The key steps involved in the hydrothermal synthesis of ZSM-5 can be seen in Figure 2 (next page): preparation of solutions containing the Si and Al precursors along with the structure-directing agent, mixing, aging, hydrothermal treatment, filtration, drying, and calcination. Solution A, containing the Si precursor and the structure-directing agent (TPA), was prepared by dissolving 11.1 g of Aerosil silica in 32 ml of 1.25 M NaOH solution and then adding 81 ml of 3.2 wt% TPA aqueous solution. Solution B was obtained by dissolving 0.6 g of sodium aluminate (NaAlO<sub>2</sub>) in 10 ml of H<sub>2</sub>O.

Mixing Solutions A and B under vigorous stirring resulted in a homogeneous gel at pH 13. The pH of the gel was then adjusted to 11 by addition of 0.1 M H<sub>2</sub>SO<sub>4</sub>. The resulting gel was aged for 2 h prior to hydrothermal treatment. Aging is crucial to obtain the desired crystalline phase and to accelerate crystallization. The aged gel was finally loaded in a stainless steel autoclave and heated at 150°C for 4 h. The hydrothermal treatment is a thermally activated process. Increasing the temperature of the reactant solution above the boiling point facilitates the crystallization process, *i.e.*, supersatura-

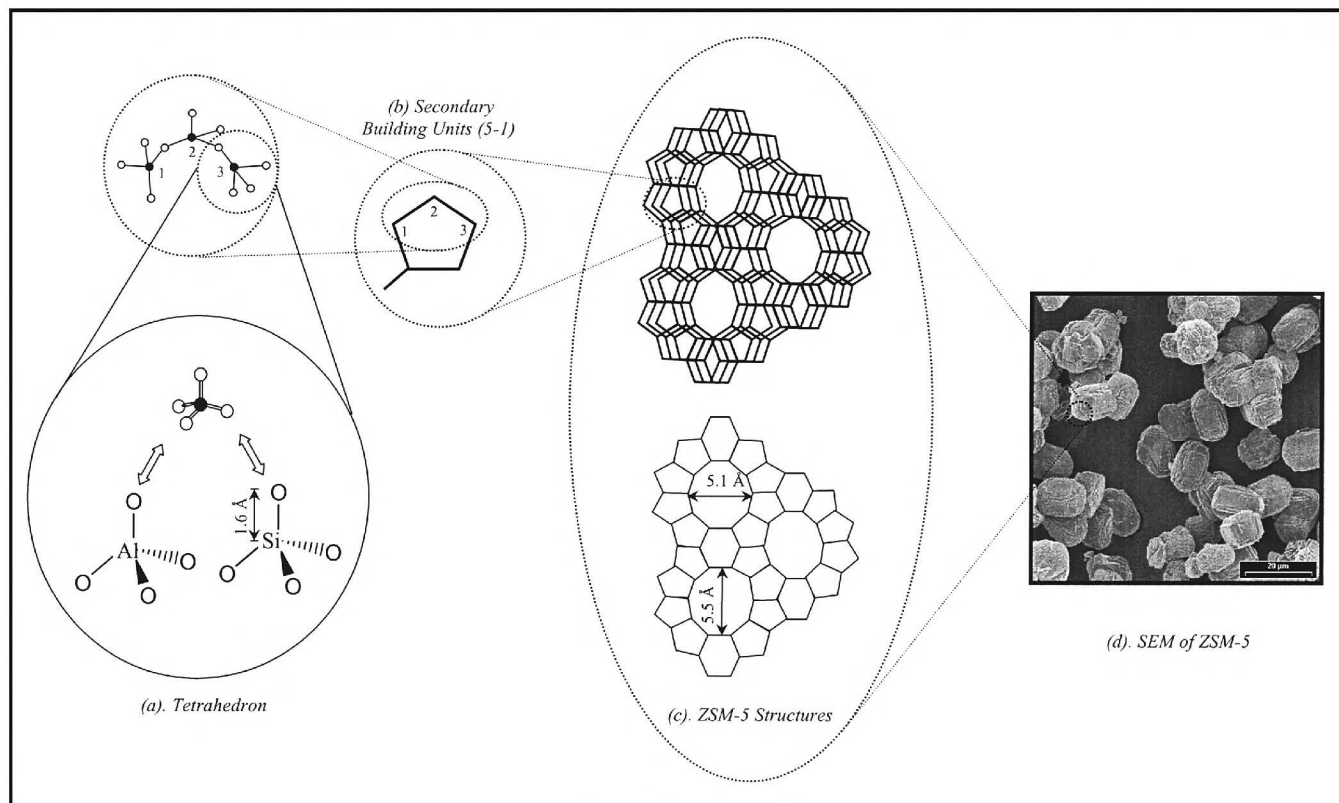


Figure 1. Structure of ZSM-5.

tion, nucleation, and crystal growth. To monitor the crystallization process, 8 ml of gel reactant/ZSM-5 product mixture was sampled via a sampling valve every 30 min for analysis. The samples were filtered, dried, and then pressed in the form of thin disks for XFD and IR analyses.

## RESULTS AND ANALYSIS

The appearance and evolution of an XRD pattern characteristic of ZSM-5 zeolite is shown in Figure 3. The well-defined X-ray diffraction pattern manifests the crystalline microstructure of XSM-5.<sup>[21]</sup> The IR spectra of ZSM-5 samples, which exhibit two key bands at  $450\text{ cm}^{-1}$  and  $548\text{ cm}^{-1}$ , are shown in Figure 4. The former is due to the Si-O stretching of the tetrahedral unit, whereas the latter is due to the double 5-1 ring (SBU) vibration.<sup>[22]</sup> The peak intensity in the XRD pattern and the IR intensity of the  $548\text{ cm}^{-1}$  band reflect the extent of the crystallization process.

The crystallinity of the samples was determined by comparing the XRD peak intensity and the intensity ratio of the  $548$  to  $458\text{ cm}^{-1}$  IR bands with those of calibrated samples. Crystallinity calibration was carried out by measuring the intensity of a number of standard samples (*i.e.*, mixtures of pure ZSM-5 from Zeolyst and Aerosil silica) of known ZSM-5 concentrations. The crystallinity determined here corresponds to the zeolite yield, which is defined as the ratio of the amount of zeolite to the initial amount of  $\text{SiO}_2$  and  $\text{NaAlO}_2$ .

The experimental ZSM-5 crystallization curve, which plots the crystallinity of the zeolite versus the hydrothermal treatment time, is shown in Figure 5. The parallel between the crystallinity as measured by XRD and by IR indicates that the relative intensity of the  $458\text{ cm}^{-1}$  band can serve as a reliable index of the ZSM-5 crystallinity and yield during its synthesis, allowing the use of a low-cost infrared spectrometer to determine the ZSM-5 structure. The zeolite crystallization curve usually exhibits an S-shaped profile with an inflection point, which separates the induction period and the autocatalytic growth period. ZSM-5 synthesis at  $150^\circ\text{C}$  can be completed in 5.5 h with a final crystallinity near 100%. The key parameters governing the zeolite crystallization include hydrogel molar concentration, alkalinity (*i.e.*, pH), temperature, template, pressure, and seeding. The complexity of the interactions of these factors makes zeolite synthesis an interesting laboratory project that allows each team of students to design their own experimental parameters and carry out the experiment at a specific set of conditions.

## DISCUSSION

In a two-hour lecture, the instructor covered nanomaterial synthesis and applications, the basic principles of zeolite synthesis, and typical characterization techniques such as X-ray diffraction and infrared spectroscopy as well as safety issues. A graduate assistant demonstrated the operation procedure of the autoclave and the infrared spectrometer. A list of the tasks and time needed to complete them can be found in Table 1.

A typical experiment team consists of four students, and a typical synthesis procedure for ZSM-5, as shown in Figure 2, is given to them. The first homework assignment is to use SciFinder Scholar to search for a ZSM-5 synthesis recipe from journal articles or patents and to compare the literature recipe with the given one. Experience with literature searches allows students to gain a better understanding of the process of translating scien-

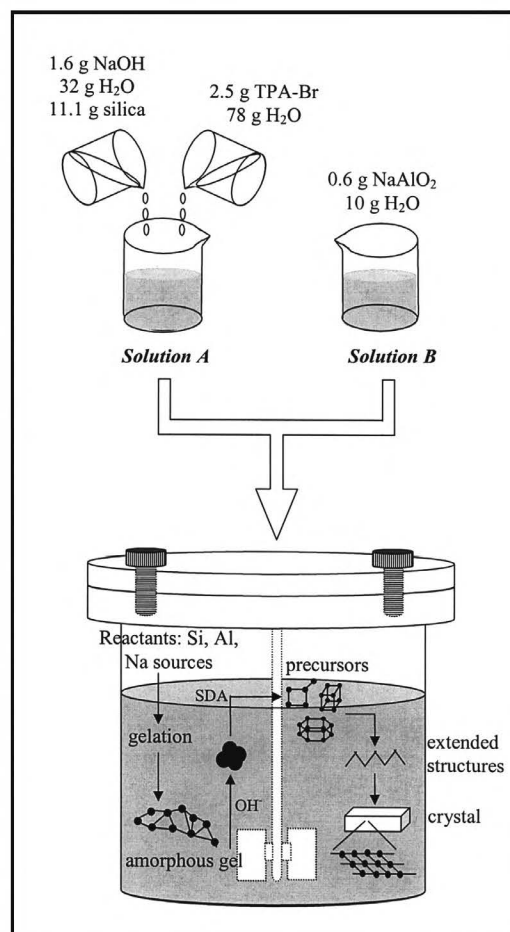


Figure 2. Hydrothermal synthesis of ZSM-5.

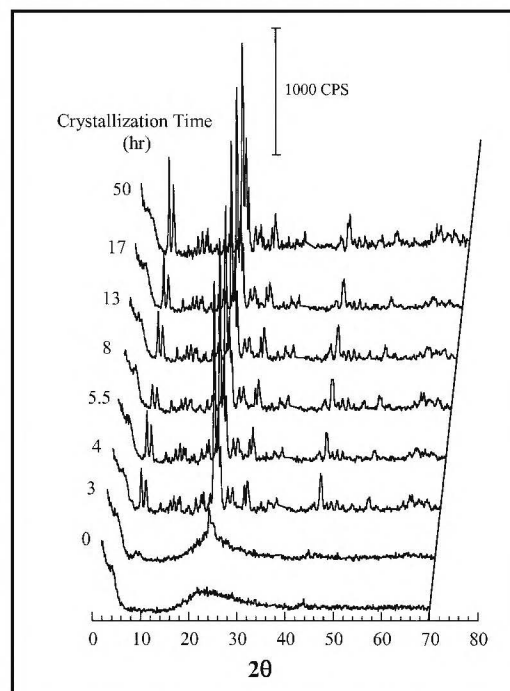
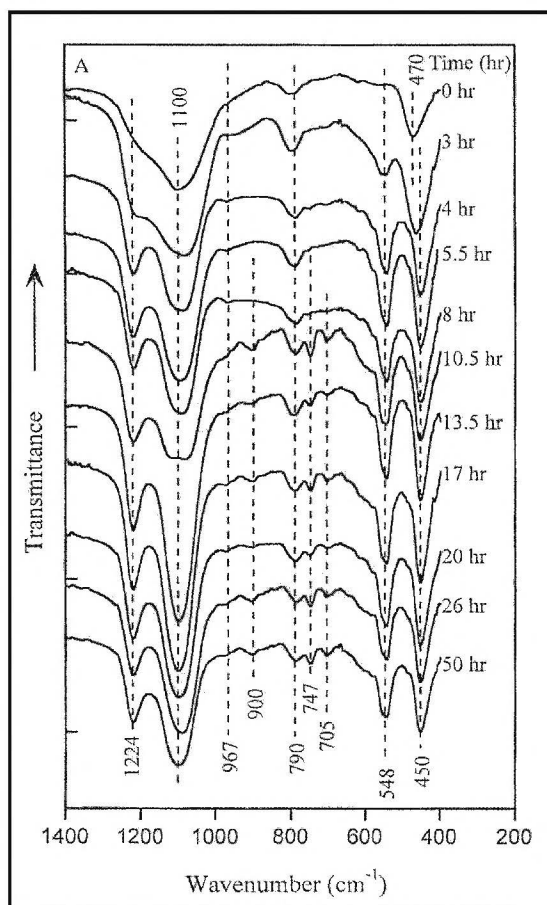
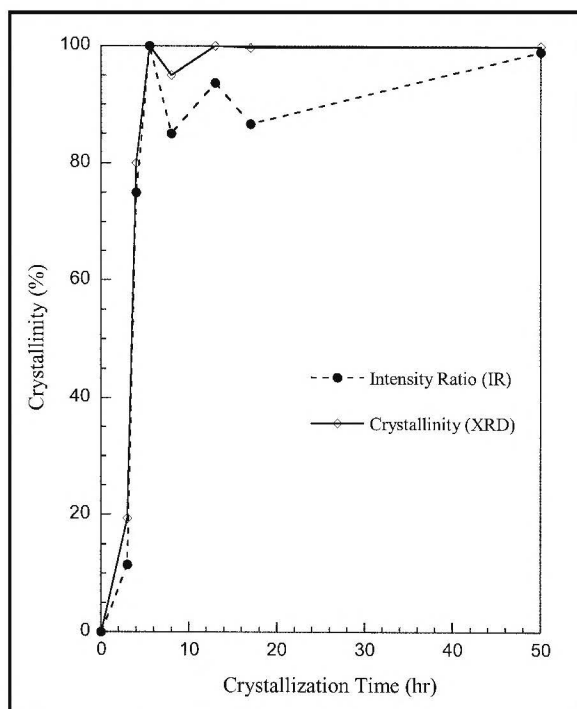


Figure 3. XRD pattern of as-synthesized XSM-5 samples vs. crystallization time at  $150^\circ\text{C}$ .



**Figure 4.** IR spectra of as-synthesized XSM-5 samples vs. crystallization time at 150°C.



**Figure 5.** Crystallizations (%) vs. crystallinity time.

tific discovery to practical technology. Students are strongly encouraged to either modify the given recipe or use a literature or patented recipe to design and implement their experiment for zeolite synthesis. Extra bonus points are given to teams that use literature recipes. The team that chooses a literature recipe must submit its recipe to the instructor to ensure the safety and availability of required chemicals. Of the seven teams in the 2000 class, only two opted for a literature recipe.

Experimental planning involves selection of hydrothermal synthesis conditions and assignment of tasks to each student on the team. Each student is responsible for a specific task. Students who are not involved in a specific assignment are required to observe and understand their teammates' tasks. The total time needed for the experiments is 12.5 h.

To help students increase their understanding of the interrelationship between reaction engineering and nanomaterials synthesis, as well as to promote their ability to link experimental observations to fundamental concepts, we posed several questions, which can be found in Table 1. These questions provide a framework for students to prepare their reports and for the instructor to evaluate the students' understanding and creativity.

Our 1999 learning survey revealed that the typical problem encountered in zeolite synthesis was plugging of the sampling valve. Peer review and close supervision of the students' performances revealed that the majority (90%) of the students accomplished the assigned tasks. Peer review also pointed out the problems students encountered in coordinating the experimental work. The final grade of individual students was obtained by adjusting the team report grade based on each student's contribution

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**TABLE 1**  
**Experimental Tasks**

- Formation of the team and distribution of tasks
- Literature search
- Selection of a synthesis process
- Designing and planning the experiment
- Implementation
  1. Preparation of precursor solution (0.5 hr)
  2. Hydrothermal treatment (7 h)
  3. Filtration and drying (3 h)
  4. Infrared analysis (2 h)
- Report preparation
  1. Kinetics of zeolite syntheses. Are you able to derive a meaningful rate expression and obtain reaction order and rate constant for zeolite synthesis?
  2. What are the factors governing the zeolite synthesis? Discuss the phase behavior as well as heat and mass transfer in the autoclave during zeolite synthesis.
  3. Compare the results obtained with those in the literature.
  4. Propose and design a novel nanostructured material based on the concept of templated synthesis and self-assembly.
- Peer review:
  1. Task distribution
  2. Time management
  3. Coordination
  4. Quality of work
  5. Objective accomplishment

R	universal gas constant = 8.31 (J/mol-K)
s	Stoichiometric coefficient of the product (positive value) or reactant (negative value) species
$\Delta S$	entropy change of reaction (J/K)
T	temperature (K)
t	time (s)
U	reactant utilization (moles consumed/moles fed)
V	voltage (V or mV)
w	mass transport parameter used in Eqs. (13) and (14) (mV)
z	mass transport parameter used in Eqs. (13) and (14) (cm <sup>2</sup> /mA)
$\alpha_a$	a lumped kinetic parameter equal to 1 for the oxygen reduction reaction
$\epsilon_e$	overall energy efficiency = current efficiency * voltage efficiency
$\epsilon_f$	current efficiency = theoretical reactant required/ amount of reactant consumed (g/g)
$\epsilon_v$	voltage efficiency = actual cell voltage/reversible potential (V/V)
$\eta_{act,a}, \eta_{act,c}$	activation polarization at the anode and cathode, respectively (mV)
$\eta_{conc,a}, \eta_{conc,c}$	concentration polarization at the anode and cathode, respectively (mV)

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and results of peer evaluation.

## CONCLUSION

ZSM-5 synthesis serves as an excellent example to introduce students to the basic concepts of templated synthesis and self-assembly that govern nanomaterials synthesis. This experiment brings together a number of subjects that students have learned from their previous courses: infrared spectroscopy (from organic chemistry), kinetic analysis and reactor operation (from reaction engineering), heat transfer (from transport phenomena), and phase behavior (from thermodynamics). The project also requires students to demonstrate their creativity and innovation through the experimental design and implementation of a nanostructured material synthesis.

## ACKNOWLEDGMENTS

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