

Chemistry 146B, Spring 2009

Experiment 3. Synthesis, Characterization and Application of a Porous Inorganic Material

Overview

This experiment involves the synthesis and characterization of a porous inorganic material. Both the lab and report will be conducted in pairs. Groups will be studying one of the three classes of porous materials: (i) the synthetic nanoporous zeolite known as ZSM-5; (ii) mesoporous silica, also known in the hexagonal form as MCM-41; (iii) macroporous xerogels. Metal substituted versions of any of these three cases (nanoporous, mesoporous or macroporous) may also be investigated. All groups will characterize their compound by a number of materials characterization techniques available at UCSC. You will also propose a study of the properties and applications of the material, such as catalysis or ion-exchange. The literature will first be searched for possible studies. Students will select the material they wish to study based on their interest in its synthesis, properties and applications. Specific proposed designs will be discussed closely with the instructor and TA during a devoted lab period for this part of the lab. The choice by each group will be determined early in the quarter so that the required chemicals can be ordered.

Introduction

Zeolites are crystalline, microporous three-dimensional aluminosilicates, comprised of corner-sharing TO_4 tetrahedra ($\text{T} = \text{Si}, \text{Al}$).¹⁻⁴ The general formula is $\text{M}_{x/n}[(\text{AlO}_2)_x(\text{SiO}_2)_y] \cdot z\text{H}_2\text{O}$, where M is an extra-framework cation that balances the anionic charge of the framework. The oxygen atoms are doubly-bridging and connect two metal centers; the tetrahedra are arranged into n -membered rings, where $n = 4$ or larger. A six-membered ring, for example, contains six "T-atoms" (Si or Al) and six oxygen atoms. For simplification, the latter are ignored in this nomenclature as well structural representations of zeolites, where metal centers are joined by a straight line (Figure 1).

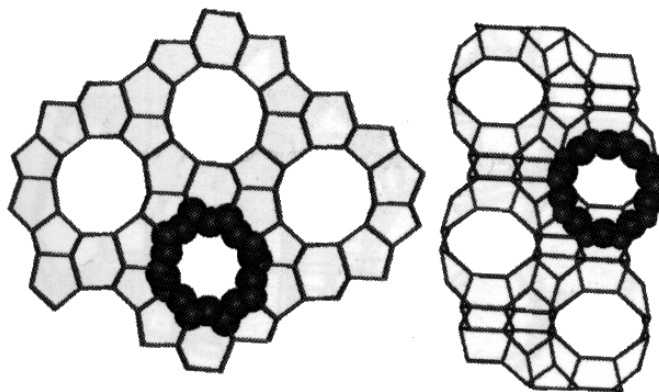


Figure 1. The MFI topology is one example of a zeolite. The dark atoms show the space-filling view.

ZSM-5 contains two intersecting channel systems of specific size and shape that restrict molecular diffusion into and through the framework. The ZSM-5 structure is a commonly occurring framework topology, where the chemical composition of the metal centers can be varied. As a result, there are now over 21 different names for this structure and the material is commonly referred to by its assigned three-letter zeolite structure code, MFI.⁴ The porous material is therefore selective to both size and shape of reactant, intermediate and product since the catalytic reactions occur inside the nanopores of the material. In addition, the high degree of thermal and hydrolytic stability render them useful for catalysis at elevated conditions. For example, when the material is calcined to give porosity and converted to its acid form, strong Brønsted acid sites allow catalysis of hydrocarbon isomerizations inside the nanopores of the material.²⁻⁵

The synthesis of ZSM-5 typically involves a hydrothermal reaction where an aqueous mixture of sodium silicate, sodium aluminate and sodium hydroxide is heated for extended periods of time. Subsequent labs will involve characterization and calcination of the material, conversion to the active acid form if catalysis is going to be studied, followed by study of its properties and applications.

Preparation of ZSM-5, Lab #1

Safety Precaution: The following preparation must be conducted in a fumehood. Solid silicic acid is a light inorganic material and is easily airborne, not unlike asbestos fibers. You must avoid breathing any small, air-suspended particles. In addition, n-propylamine is volatile, easily adsorbed through the skin and toxic.

Grind up approximately 0.55 g of NaOH pellets with a mortar and pestle. Place 0.50 g of the pre-ground NaOH in a 250 mL beaker. Then add 2.01 g of silicic acid ($\text{SiO}_2 \cdot \text{H}_2\text{O}$) followed by 1.01 g of tetrapropylammonium bromide $[(\text{C}_3\text{H}_7)_4\text{NBr}]$. Add 5.0 mL distilled H_2O and mix as thoroughly as possible with a spatula. Add 1.0 mL n-propylamine ($\text{n-C}_3\text{H}_7\text{NH}_2$) with a pipet and mix thoroughly.

In a separate 50 mL beaker, prepare a solution of 0.25 g of aluminum sulfate $[\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}]$ dissolved in 5.0 mL distilled H_2O . Then add to this solution 0.05 mL of concentrated sulfuric acid via a micro-syringe or pipet. Carefully transfer the contents of the first beaker to the second and mix thoroughly. Slowly add distilled H_2O to give a total volume of approximately 25 mL, using a portion of this distilled water to rinse the solid that remains in the 250 mL beaker into the 50 mL beaker. Finally, mix the contents of the 50 mL beaker thoroughly until the solution is homogeneous, then allow to stir on a magnetic stir plate for approximately ten minutes.

Transfer the majority of this mixture to a 19, 23 or 45 mL capacity Parr Stainless Steel Autoclave. Seal the autoclave by first hand-tightening the top until it can turn no further. Then use the hook spanner wrench to seal the chamber by turning the top by ~ 90 degrees. Place in a pre-heated oven at 160°C for 44 hours.

Filtration of the Product

Remove the autoclave from the oven and place in a stream of cold water from a tap (preferably in a fumehood) to quickly bring the synthesis mixture to room temperature. Cool under running cold water for at least five minutes. When cooled, open the autoclave and vacuum filter the white solid on a Buchner funnel. Wash the solid on the filter paper with copious amounts of distilled water and suction dry the solid for at least 20 minutes. The dried powder should be a very fine, colorless powder. Weigh the solid, and place a small amount of sample in a vial for powder X-ray diffraction analysis.

Calcination of Zeolite ZSM-5

Set up the tube furnace assembly for the calcination step by placing the zeolite in an alundum or quartz boat. Spread the white powder out to maximize the surface area. The alundum boat is placed in the middle of the quartz alumina tube. Attach one end to an N₂ cylinder and the other to a bubbler to monitor the N₂ flow rate. If the tube furnace is not programmable: Slowly heat the tube and its contents to 500°C; water vapor will be released from the solid around 100°C. It is therefore best to heat slowly at this point. Heat in increments of 20°C until 100°C is attained, maintaining each temperature for 5 minutes. Then increase the temperature to 500°C in 100°C increments, holding 10 minutes at each temperature. If the tube furnace is programmable: heat from 20°C to 100°C over 20 minutes at a rate of 4°C/min; then 100°C to 500°C over 40 minutes at a rate of 10°C/min. When the assembly has finally reached 500°C, continue heating for 2 hours. Allow the material to cool and weigh the resulting solid. Another sample is placed in a vial for powder X-ray analysis.

Conversion of ZSM-5

The sodium form of the zeolite is converted to the acid form using the following procedure: the calcined zeolite is placed in a 100 mL beaker and stirred with a 1.0 M (NH₄)₂SO_{4(aq)} solution (10 mL/g zeolite) for 10 to 15 minutes at ambient temperature. The zeolite is collected by vacuum filtration. It is also advantageous to rinse the zeolite with small amounts of acetone to dry the solid and partially remove the brown/black color. Repeat this process twice, following the final treatment by a thorough rinsing with distilled water until the filtrate is free of sulfate anions: periodically test the filtrate by allowing one drop to fall into an aqueous solution of BaCl₂ in a test tube or Erlenmeyer flask. The presence of a BaSO₄ precipitate will indicate that the zeolite still contains adsorbed sulfate ions; if the solution is clear, you may proceed to the next step.

Dry the solid in a small dry beaker or the alundum boat in an oven set to 100 to 120°C for 30 minutes. Transfer the dried solid to the tube furnace by spreading over a large surface area in the alundum boat. Heat the materials in air at 500°C for a period of at least 3 hours. Do not pass N₂ gas over the solid since the presence of O₂ is essential

for the conversion. At the end of this time period, you will notice that the zeolite has lost its brownish tinge and should appear white. Cool the material under a stream of nitrogen and store in a sealed vessel in a desiccator to preserve the acid hydrogen form of the zeolite.

Materials Characterization

Analyze your product before and after conversion by powder X-ray diffraction to confirm its structure, purity and crystallinity. The instrument is in the Oliver lab in PSB 253 (the TA or a graduate student in the group will help with sample preparation and show you the data collection process). Print out the diffraction patterns and compare with known data for ZSM-5 (visit <http://www.iza-structure.org/databases>, go to powder patterns and then MFI). Your material should display a pattern similar to the characteristic X-ray diffraction pattern of ZSM-5. A comparison includes the relative intensity of the peaks, peak width and the 2θ values. Using Bragg's Law ($n\lambda = 2d\sin\theta$, where $n = 1$ and $\lambda = 1.5418\text{\AA}$ for $\text{CuK}\alpha$ radiation),⁶ calculate the value of d for the most intense (“100%”) peak for both your experimental and the reference diffraction patterns. How do the d -spacings compare?

Also run the physisorption isotherm for the as-synthesized and hydrogen form of your zeolite on the Micromeritics ASAP 2020 Analyzer in the Oliver group in PSB 253 with your TA or a graduate student of the Oliver group (instrument not available as of 2009).

Investigation of Properties and Applications

The remainder of experiment 3 will be designed by each group member. The following is provided as an example of the investigation of ZSM-5 that has been studied previously in previous offerings of this course. Simpler reactions exist and can be found by searching the literature. Ion-exchange could be studied. In all cases, you must consider the complexity of the reaction and the method(s) by which you will characterize the catalytic products. Examples include NMR, GC, IR and UV-Vis.

Example of the Catalytic Testing of ZSM-5

Note: this reaction has been problematic in previous years for a number of reasons and will not be investigated this year. The information is provided only as an example.

The catalytic properties of ZSM-5 towards xylene isomerization can be investigated. The reaction is carried out in a fumehood, using a simplified catalytic reactor (Figure 2). Place a known mass of ZSM-5 catalyst in the fritted adapter, followed by glass wool. Do not use too much glass wool, or sample, or the xylene will be unable to flow! Using vacuum grease, connect this central piece to glass tubes with ground joints such that glass

tubes are protruding from each end of the tube furnace. Be careful not to over-extend on the heating mantle side or the xylene will recondense before reaching the tube furnace. Heat the tube furnace to 425°C. Connect the rest of the pieces shown in Figure 2 and fill the reagent flask with 8 mL of o-xylene.

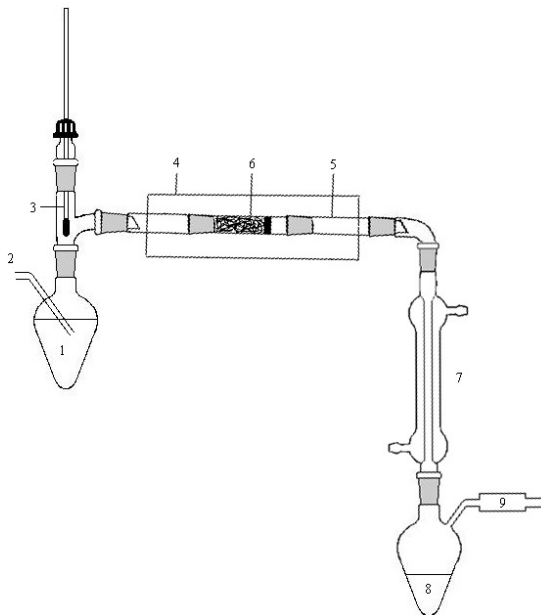


Figure 2. A catalytic reactor used for the isomerization reaction. (1) Heated reagent flask; (2) nitrogen inlet; (3) thermometer; (4) tube furnace; (5) catalyst reactor tube; (6) sintered glass frits to retain catalyst; (7) condenser; (8) product collection flask; (9) bubbler or flow meter.

Heat the o-xylene to its boiling temperature (140°C). Flow N₂ gas through the hot o-xylene at a low to moderate flow rate (indicated by the bubbler) to act as a carrier gas. Place the collection flask in an ice bath to ensure condensation of the xylenes, which should occur within 10 minutes. Cool the product mixture to ambient temperature and collect a ¹H NMR spectrum of both o-xylene and the product. Integrate the two peaks to determine the extent of conversion to p-xylene (Figure 3).

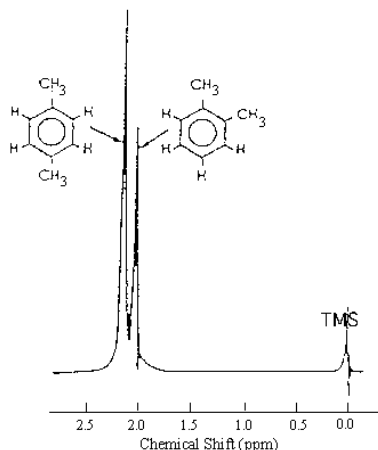


Figure 3. ^1H NMR of the xylene mixture allows the identification of the different isomers produced from the catalyst H-ZSM-5 (measured on a Bruker 360 MHz Spectrometer).

Also analyze the product by gas chromatography (GC). The mobile phase, or carrier gas, is an inert gas (helium). The xylene sample is volatilized at the injector and moves through the column [8' by 1/8", 10% OV101 as the liquid phase, Chrom-P-AW-DMGS (80/100 mesh) as the solid support]. The separation process occurs as a result of repeated sorption-desorption acts. These arise from the differences in the distribution coefficients of the individual sample components during the movement of the sample components across the stationary phase. At the end of the column, the components should emerge at different times. They are then detected and the resulting signal is displayed on a recorder or printer. The peak area is used to determine the relative amounts of the individual components present in the sample.

The optimum conditions for the GOW MAC 550P are as follows: injector temperature: 140°C; column temperature: 135°C; detector temperature: 157°C; bridge current: 150 mA; gas flow: ~ 4 cc/min; attenuation: 8; sample size: 1 mL; chart speed: 10 mm/min. Also collect GC traces of 1.0 mL of pure samples of o-xylene, m-xylene, p-xylene and mixtures such as 1:1:1 volumes of o-,m-, and p-xylenes. The retention times of these components are calculated and the peak area is determined by cutting out (estimate the baseline) and weighing them. Is the column capable of separating o-,m-, and p-xylenes? Keeping in mind that gas chromatography separates components on the basis of their boiling points and polarity, are your experimental results supported by theory?

For Your Report

This experiment was a small-scale version of a major industrial process, as the size- and shape-selective zeolite ZSM-5 is an industrially important catalyst. Ion-exchange has been performed to render the sodium form of ZSM-5 (Na-ZSM-5) and subsequently the hydrogen form, H-ZSM-5. Powder X-ray diffraction spectra have been

obtained on the initially synthesized zeolite and the sodium form. Compare the experimental spectra to literature spectra. Use the Bragg equation to calculate the d-spacing of the most intense (100%) peak in the Na-ZSM-5 spectrum. Isomerization of o-xylene to p-xylene was performed and analyzed by a ^1H NMR assay and gas chromatography. In your report, propose a possible mechanism for the catalysis of o-xylene to p-xylene and support this mechanism with literature references.

References

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Additional Reading

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