

What Good Is Wood?

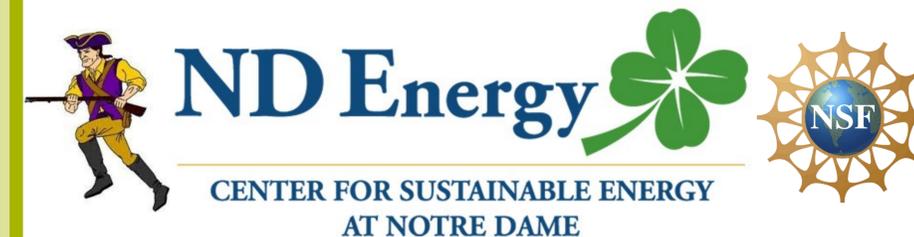
Research Experience for Teachers

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Introduction

Currently, about 95% of transportation in the United States is fueled by non-renewable energy sources. Many people are worried about the cost and availability of fossil fuels. Others are worried that burning fossil fuels is adding too much carbon dioxide to our atmosphere, contributing to global climate change. Due to these concerns scientists and engineers are working to improve existing alternative energy sources, such as bio-fuels. One such effort is the synthesis of catalysts that are able to convert bio-fuels into fossil fuel substitutes.

Zeolites are attractive candidates for catalysts in the production of bio-oils because of their physical and chemical properties. Zeolites are well-defined crystal structures that can be altered to increase their functionality. Currently, they can catalyze the production of long carbon chains from smaller organic molecules. They are also used in a variety of household products, like pet litter and laundry detergent, and industrial processes, like wastewater treatment and refining oil. The base zeolite is usually made up of silicon and oxygen, but other atoms can be added.

In this work a MFI (zeolite) containing 1800 ppm cerium was synthesized and characterized. Catalytic fast pyrolysis of acetic acid, propionic acid, cellulose and the soft hardwood, silver maple (*Acer saccharinum*), at 600°C was performed using the Ce-MFI, HZSM5-23, and a silica gel blank as catalysts. In these experiments the plain SiO₂ was not catalytic. When the acidic HZSM5-23 was used, benzene, toluene, and xylene were formed as well as a substantial amount of coke. However the Ce-MFI catalyst converted acetic acid to acetone as well as propionic acid to 3-pentanone without any color change associated with coke formation. Other studies were performed with cellulose and silver maple however the complex nature of these materials prevented any real evaluation of the benefits of adding Ce to MFI.

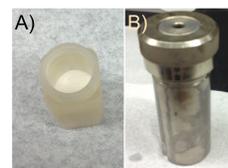


Silver Maple on the University of Notre Dame's campus.

Zeolite Synthesis

A MFI zeolite containing 1800 ppm (0.18 wt%) cerium was produced using the following method:

- 36.0 g of water was stirred at 40°C in white polypropylene vessels with lid.
- 0.0188 g cerium nitrate hexahydrate (Ce(NO₃)₆·6H₂O) and 10.406 g tetraethylorthosilicate (TEOS) were added and allowed to stir for 1 h at 40°C.
- 4.189 g of tetrapropylammonium hydroxide (TPAOH) was added one drop at a time to the stirring solution and allowed to stir at 40°C for 24 h.
- Stir plates were removed from the oven. The solution remained capped and aged at 60°C for 16 h.
- The caps were removed and the solution was allowed to dry at 90°C overnight.
- Steam-assisted crystallization, SAC, was used to crystallize the gel at 175°C for 18 h.
- The resulting material was washed, filtered, and dried in a vacuum oven.
- The product was calcined at 550°C for 5 h.



(a) Gel before SAC (b) Parr acid digestion bomb reactor used for SAC

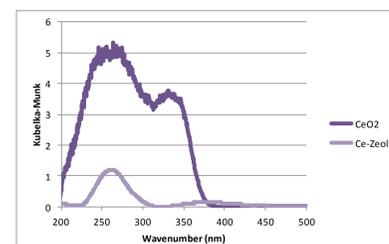


(c) Centrifuge used for washing (d) vacuum filtration of product

Results

Characterization

- N₂ physisorption (NLDFT) showed that the surface area of the Ce MFI was 465 m²/g and the pore volume was 0.201 cc/g.
- Diffuse reflectance UV-Visible spectroscopy data showed that Ce³⁺ was present in the catalyst, see right.



Ce in CeO₂ has two peaks corresponding to Ce³⁺ (left peak) and Ce⁴⁺ (right peak). Ce MFI has only one peak, showing the presence of Ce³⁺ in the catalyst.



Pyrolysis tubes containing catalyst and acetic acid after pyrolysis. From left to right the catalysts were Ce MFI, Silica, and HZSM5-23. The formation of coke is most evident in the tube containing HZSM5-23.



Pyrolysis tubes containing silver maple sawdust and catalyst (from left to right) before pyrolysis, after pyrolysis with Ce MFI, after pyrolysis with SiO₂, and after pyrolysis with HZSM5-23. The creation of coke is most evident in the tubes containing silica gel and HZSM5-23.

Catalyst Tests with Pyroprobe and GC/MS

- The Ce MFI showed much better conversion of acetic acid to acetone than the model system, and converted less of the acetic acid to coke than the HZSM5-23, see left.
- The Ce MFI was able to convert propionic acid to 3-pentanone without any visible production of coke.
- The Ce MFI was able to convert cellulose to much more furfural and propane than the model system was, but did not produce any acetone. The HZSM5-23 performed much better than the Ce MFI in terms of valuable products produced (i.e., hexane, benzene, toluene, naphthalene, and xylene), but the Ce MFI produced less coke than either of the other catalysts, see left.
- The silver maple (*Acer saccharinum*) sawdust poses the most complicated system for decomposition via pyrolysis and in this complicated system Ce MFI did not perform any better than the SiO₂. Again, the HZSM5-23 converted the sawdust to more valuable products, but the Ce MFI produced less coke than either of the other catalysts, see left.

Connection to the Classroom

My biology classes cover enzymes, which are catalysts, but I wasn't inspired to change my curriculum in regards to catalysts. Instead, I decided to create a theme for my biology classes this year, "The Power of Plants," because the Hicks Lab makes catalysts for bio-fuel applications, my classes will learn more about how bio-fuels demonstrate just how powerful plants are. To those ends, my students will construct photobioreactors, where microalgae produce lipids that can be burned as a bio-fuel, debate which energy crop would be best, investigate how plant architecture relates to growth rate, and explore photosynthesis, cellular respiration and fermentation.



Biology Curriculum Highlights

IDOE Biology Standards: 9-10.RS.3, 9-10.WS.7, B.1.2, B.3.1, B.3.2, B.3.3, B.4.1, B.4.2, B.4.4
NGSS: HS-LS1-3, HS-LS1-5, HS-LS1-6, HS-LS1-7, HS-LS2-3, HS-LS2-5, HS-LS2-7

Ecology Unit Student Activities

- Read about biomass and its potential to replace fossil fuels.
- Design an experiment that determines the optimal growing conditions for the green alga, *Chlorella protothecoides*, which is regarded as one of the best candidates for commercial manufacture of microalgae-derived biofuel.
 - Construct microalgae photobioreactors from plastic water bottles.
 - Measure the concentration of algal cells using a hemocytometer and compare those results to growing conditions.
 - Possibly visit Dr. Hicks' lab at Notre Dame, where they will do catalytic fast pyrolysis on the samples to see exactly which fuel was produced by the algae and hopefully relate the amount of fuel produced to the concentration of cells within the photobioreactors.
- Debate about which type of plant would be the best energy crop for large-scale biofuel production.



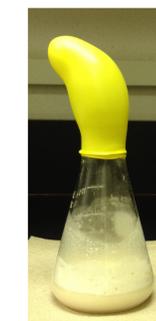
Student photobioreactor set-up

Chemistry Unit Student Activity

- Use knowledge of biofuels and learn about catalysts while doing a macromolecule 'scavenger hunt'.

Cellular Energy Unit Student Activities

- Check the amount of sugar in foods using refractometers and determine the source of that sugar.
- Grow three types of potential energy crop plants.
 - Calculate their growth rates.
 - Relate their ability to photosynthesize to their architecture.
- Measure how much energy (for organisms or bio-fuels) is in several foods.
- Determine whether plants do cellular respiration by placing aquatic plants in dark and light conditions and comparing pH.
- Investigate ideal conditions for fermentation in yeast, which can be used as a CO₂ source for microalgae in photobioreactors.



Set-up for yeast fermentation

Acknowledgements

Thank you to everyone in Dr. Hicks' group, especially Dallas and Ryan, for helping me this summer! You have all been so patient, welcoming and taught me so many things that I can take back to my classroom this fall. I have enjoyed spending my summer in your lab very much and look forward to coming back to see our results this fall!

Also, I would like to thank the NSF and the Center for Sustainable Energy at Notre Dame for making this experience possible.

