

Microwave Synthesis of Nanostructured Catalysts (1)

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Overview

Studies in the last decade suggest that microwave energy may have a unique ability to influence chemical processes. These include chemical and materials syntheses as well as separations. Specifically, recent studies have documented significantly reduced time for fabrication of Zeolites, mixed-metal oxide and mesoporous molecular sieves employing microwave energy. In many cases microwave syntheses have proved to synthesize new nanoporous structures. By reducing the times by up to over an order of magnitude, continuous production would be possible to replace batch synthesis. This lowering of the cost would make more nanoporous materials readily available for many chemical, environmental and biological applications. Further microwave syntheses have proved to create more uniform systems (defect free) than conventional hydrothermal synthesis procedures. These nanoporous systems of uniform dimension and topology could provide the templates for the assembly of a myriad of nanostructured systems. However, the mechanism and engineering for the enhanced rates of syntheses are unknown. Our focus is in three areas:

1. To control defects, phases, and/or properties of nanomaterials via microwaves.
2. To develop *in situ* characterization methods to monitor nucleation and growth in microwave fields.
3. To study the reactor design on microwave synthesis including varying the microwave frequency

Our collaborative studies focus on understanding the method by which microwave energy can influence the synthesis of nanoporous molecular sieves. We employ a variety of *in situ* techniques (such as Infrared, Raman, UV-vis, and X-ray spectroscopies) to develop and test theories to explain the mechanism(s) and rate enhancement. We are developing the reactors and reactor engineering to use microwaves for these synthesis and other applications. Conner (Chemical Engineering) and Yngvesson (Microwave/Electrical Engineering) are developing the *in situ* and reactor studies. Auerbach (Chemistry) is developing the theory. Hsu (Polymer Science and Engineering) is employing *in situ* vibrational spectroscopy to study the mechanism. And Suib (Chemistry-Univ. Connecticut) is working on synthesis of other nanoporous oxides. Keith Jones from BNL is coordinating the *in situ* X-ray and scattering studies.

The groups have met individually on a weekly basis and collectively four times during the year. We have developed a website where most of the talks presented by the individual PI's and their workers are available: <http://www.ecs.umass.edu/che/micro-synth>. This has been a very exciting and fruitful first year. Some of the highlights are briefly summarized below.

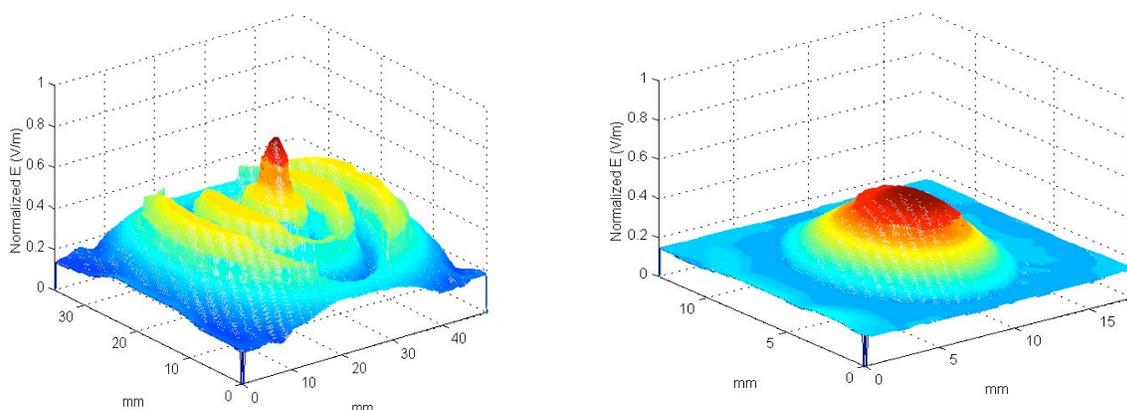
Progress in the First Year's Collaboration

Microwave Synthesis Engineering: There have been over two hundred publications that document the enhanced rate of synthesis of high surface area oxides by microwave power. However, there has been no consistency in the results from different laboratories and few experimental details have been provided. We first studied any differences between different reactor configurations and the various approaches to deliver microwave power to the synthesis

mixtures[2]. We employed four different microwave reactor configurations (ovens such as the CEM MSD and Mars-5®; uniform-field ovens such as the CEM Discover®; waveguide reactors) for different sizes and shapes of the reactors. We found significant differences in the rates and morphology of the products produced in different combinations, varying by orders of magnitude. Yet, the results in each combination were totally reproducible. Crucial variables include:

- Reactor geometry, including total reactor & solution volume
- Applicator (Oven) configuration
- Power delivery (continuous, CW, versus pulsed or high->low...)
- Rate of temperature ramp and hold time.
- The actual (measured) permittivity of the synthesis solution.
- The frequency of the microwave power (!)

These findings were supported by monitoring the temperatures and pressure within the reactor and measurements of the permittivity of the reactor solution before and after reaction. These variables were then employed to simulate the actual distribution of the microwave field within the reactor. Examples of the distribution of energy through the center of different reactors are shown below.



We further found that different syntheses responded to different reactor variations in different ways, i.e., the progress and optimum for silicalite syntheses was different that that for Y-zeolite. Not all zeolite syntheses were significantly enhanced in the presence of microwaves. It is apparent that the microwave engineering needs to be considered and the experimental details be provided for any studies involving the use of microwave energy in chemistry.

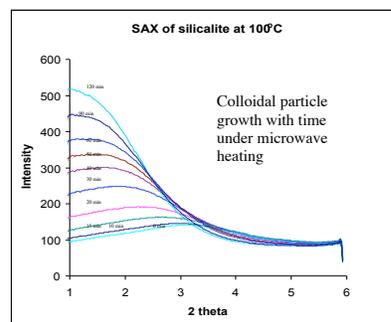
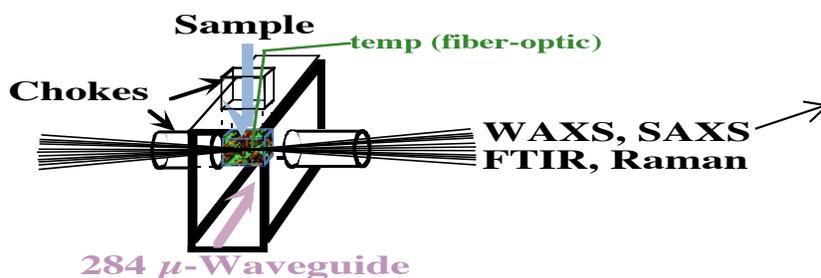
Synthesis Chemistry: We have already studied the synthesis of over a half a dozen different zeolites and found that most, but not all, were over an order of magnitude faster with the use of microwaves. We also found that many other metal oxide syntheses were dramatically enhanced in microwaves. These include todorokite and mixed metal oxide catalysts.

Synthetic todorokite, OMS-1 is a multivalent manganese oxide with an average oxidation number (AON) of manganese from 3.4 to 3.7. Mixed-valent manganese oxides often crystallize as porous tunnel structures built of MnO_6 octahedras. They are used in oxidation catalysis, environmental catalysis, batteries, as adsorbents and chemical sensors. BET surface area of variable frequency microwave-made materials is ~3 times higher than constant frequency mw

and conventionally made OMS-1. Differences in todorokite morphology can be due to selective heating that is a result of microwave interaction with the material[3]. Constant frequency microwave-made OMS-1 is more effective in catalytic oxidation than the corresponding conventionally synthesized OMS-1.

Mixed Oxide Catalysts: Mixed metal oxide $\text{Ni/TiO}_2\text{-SiO}_2$ has been synthesized using sol-gel method and microwave heating. The synthesis procedure included pre-hydrolysis, incorporation of nickel precursor, hydrolysis, gelation, and drying followed by calcinations. There is significant reduction in the synthesis time of mixed oxides and a “sponge-like” morphology that can have an effect on the surface area and catalytic activity. We have also synthesized a variety of mixed metal oxide, MMO, partial oxidation catalysts and find more rapid formation of a single-phase system of uniform morphology which preliminarily results in a higher selectivity catalysts.

In Situ Spectroscopy: Systems have been developed to study the samples under microwave synthesis conditions. A diagram of one of these systems is shown below. A 300 watt, 2.45 GHz Sairem microwave source was coupled to one end of the waveguide with a water load at the other end. This system was employed at the X10A beam-line at Brookhaven National Laboratory for the wide angle X-ray, WAXS and small angle X-ray, SAXS studies. A fiber optic system will be employed for the RAMAN or FTIR studies. Preliminary studies show changes in the SAXS (below right) which reflects changes in the colloidal suspension from whence silicalite is formed; although, similar changes are not evident for Y-zeolite syntheses, possibly giving insight into differences in their microwave enhancement mechanisms, rates and chemistries.



Summary

This NIRT team has made considerable progress in their ongoing collaboration on this project. Each of the above studies represents contributions from at least two of the research groups involved. The next several years will build on these collaborations and the tools we are developing to understand Microwave Synthesis of Nanostructured Catalysts.

References

- [1] For further information about this project link to < <http://www.ecs.umass.edu/che/micro-synth/> > or email <wconner@ecs.umass.edu>
- [2] Conner, W. C., Tompsett, G., Lee, K-H and Yngvesson, K.S. J. Physical Chemistry B, 108,37, 13913-20 (9/16/2004) Cover Article
- [3] Malinger, K. A., Laubernds, K., Son, Y.-C., Suib, S. L. Chem. Mater. 2004