

PRF # 55690

Project Title: Understanding the Behavior of Guest Molecules Within Zeolite Materials
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The work in my lab at Valparaiso University has focused on the study of the interactions between a dye molecule, known as Brooker's merocyanine (4-[2-(1-methylpyridin-4-ylidene)ethylidene]cyclohexa-2,5-dien-1-one), and Zeolite L in order to generate a new host-guest material and better understand the adsorption process of organic molecules within zeolites that are used extensively in the petroleum industry. Brooker's merocyanine is a unique dye molecule that can be used to probe the effects of protonation, isomerization and solvent effects on dye adsorption to the zeolite using a single molecule. Zeolite L was chosen because it has a straight one-dimensional channel, and it has been used to adsorb other dye molecules for a variety of applications. Our work during this grant period focused on characterizing and optimizing the dye loading of the zeolite by varying dye solution conditions, such as pH or light exposure, or by varying the morphology of the zeolite crystals. We also began a collaboration to see if these materials would exhibit second-harmonic generation (SHG, a nonlinear optical property) in order to understand if there is molecular organization within the channels. Although we have made progress in each of these directions, new questions have developed that require further exploration in the upcoming year.

Research during this funding period initially focused on understanding how the dye molecule was adsorbed by Zeolite L under different conditions. Using primarily UV-Vis spectroscopy, the degree of dye adsorption to "normal" Zeolite L was characterized. "Normal" Zeolite L was synthesized following the International Zeolite Association method¹ to generate microcrystals that were approximately 1 micron in size. A comparison of cationic versus neutral dye adsorption indicated no significant difference in dye adsorption over extended periods of time (a week). Over shorter periods of time, there was a more significant difference between the behavior of the protonated and neutral dye molecule, which we are currently investigating. When Brooker's merocyanine is protonated, it will isomerize from the trans to cis form when exposed to UV light, and a photostationary state that contains both isomers develops. We began studies to determine whether the trans or cis form was preferentially adsorbed to Zeolite L, but further work is necessary to fully characterize these isomers adsorbed to the zeolite.

Another direction of study this past year was to vary the structure of the zeolite host material. Zeolite L was synthesized to create microcrystals of varying aspect ratios by simply altering the ratio of starting materials and the hydrothermal synthesis conditions. The variations selected were hockey pucks, short cylinder and long cylinders following published naming schemes for specific synthesis methods², as shown in Figure 1. In order to achieve SHG, a molecule with a large hyperpolarizability, such as Brooker's merocyanine, must be aligned over a distance similar to the wavelength of the laser used to measure the SHG response. Therefore, it is more likely to occur in larger crystallites, but achieving organization within the channels of large crystallites may be difficult. This led to the interest in exploring the optimal size and shape of crystallites to observe any possible nonlinear optical response. We did not observe significant differences in dye loading among these different morphologies. Initial SHG measurements were made by a collaborator on a dye-loaded short cylinder sample. There was a possible SHG signal detected, but it was similar to the reference sample. This lack of a strong SHG response may be due to re-adsorption of the SHG by the dye molecules at the wavelength of the laser system, indicating a different system may be necessary to make these measurements. It is also possible that the zeolites were not quite large enough to impart the necessary organization, and further studies are underway to generate larger Zeolite L crystallites. It could also be due to random surface adsorption of the dye rather than insertion into the zeolite channels. This will be explored using BET analysis to determine if the channels are filled during dye loading.

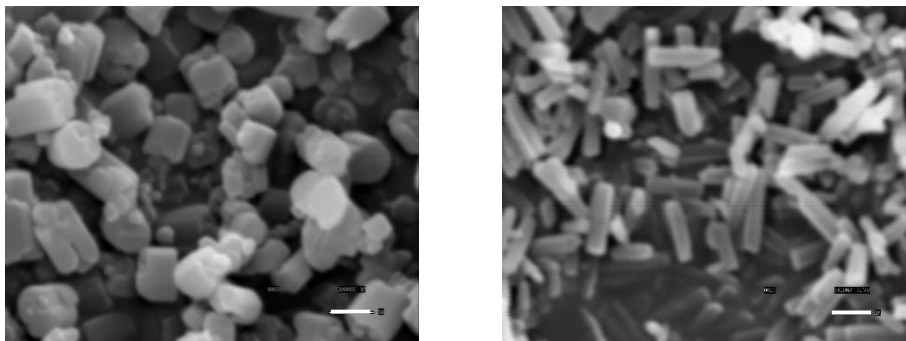


Figure 1: SEM images of hockey puck (left) and short cylinder (right) Zeolite L morphologies. Scale bar is 1 μm .

This funding has been critical to support my research program and train several undergraduates who have been invaluable to completing these studies. During the academic year, Thomas Dabertin extended the research that he began through summer support during the first year of the grant by working on the zeolite morphology studies. Shyann Mattis spent the academic year focused on the pH studies. They were able to use the travel funds from this grant to present their work at the Indiana Academy of Science meeting. I also incorporated their work into my talk at the National American Chemical Society Spring meeting, which I could not have attended without this grant. They both indicated that this research opportunity made them even more interested in pursuing a career in R&D.

This grant also provided a summer stipend for two undergraduate research students. Nicholas Cesario and Maia Wygle were able to confirm and refine the results found during the academic year, as well as further explore the morphology effects. Beyond the lab, they were able to take part in the Valparaiso University summer research program to develop their presentation skills through oral and poster presentations on campus. At the end of the summer, they both expressed interest in continuing discussions of future results from this project as they move forward with their studies and future science careers. I believe this research experience and training will have a lasting impact on their lives, and it has been critical to support my research program over the past year.

¹ IZA Synthesis Commission. Linde Type L. [http://www.iza-online.org/synthesis/Recipes/ Linde Type L.html](http://www.iza-online.org/synthesis/Recipes/Linde%20Type%20L.html) (accessed May 28, 2018).

² Insuwn, W.I; Rangriwatananon, K.R. Morphology-Controlled Synthesis of Zeolite L and Physicochemical Properties. *Eng. J.* **2012**, 1-11.