

NIRT: Design of Nanoporous Materials for Enantioselective Single-Site Catalysis

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Catalysis plays a key role in emerging “green” manufacturing processes for chemicals, pharmaceuticals, and other materials that improve the quality of life for billions of people. A good catalyst will direct reactant molecules to form desired products rapidly and with little input of energy, while eliminating the production of side products. Nanoporous zeolites are highly attractive for green manufacturing because of their extraordinary selectivity. However, zeolites cannot be used for many important catalytic processes because of limitations in the types of active sites that can be incorporated into them. One particularly compelling feature that has yet to be effectively incorporated into a functional catalytic zeolite framework is chirality (the quality that a right hand is not superimposable on a left hand). Chirality is ubiquitous in biology, and the sale of chirally pure drugs is growing enormously, topping \$100 billion in 2000. In the past, both enantiomers (hands) of a drug might be sold, but it is known that the two enantiomers can have different pharmacologic and toxicologic impacts. This has created the urgent need for better enantioselective catalysts. *The central focus of this project is the design, synthesis, and functional demonstration of new materials that meet this need.*

The past five years have seen an explosion of new open-framework materials based on supramolecular coordination chemistry. Many of these materials are nanoporous solids known as metal-organic frameworks (MOFs). MOFs are a new class of materials synthesized in a building-block fashion from metal-ion vertices that are interconnected by organic linker molecules in a self-assembly process to create highly tailorable crystalline materials with pores of nanometer dimensions. Many MOFs exhibit permanent micro- or mesoporosity and many are stable up to several hundred degrees Celsius, thus mimicking some of the prime features of zeolites. Since MOFs take advantage of the chemical diversity of carbon compounds for the linkers, one can imagine an almost unlimited variety of framework structures and functionalities that could be accessed, including chirality.

We recently reported a new microporous MOF featuring chiral (salen)Mn linkers (See Figure 1.) and showed that it is highly effective as an asymmetric catalyst for olefin epoxidation, yielding enantiomeric excesses that rival those of the free molecular salen compound [2]. The material was characterized by a variety of methods, including thermogravimetric analysis, powder x-ray diffraction, BET surface area analysis, and catalytic testing. The framework confinement of the salen catalytic enhances catalyst stability, imparts reactant size selectivity, and permits catalyst separation and reuse. This approach combines the best features of homogeneous catalysis and heterogeneous catalysis and opens the way for future work, such as the incorporation of other catalytic linkers that catalyze other reactions or that can use molecular oxygen as the oxidant. Another possibility is the fabrication of catalytic membrane reactors.

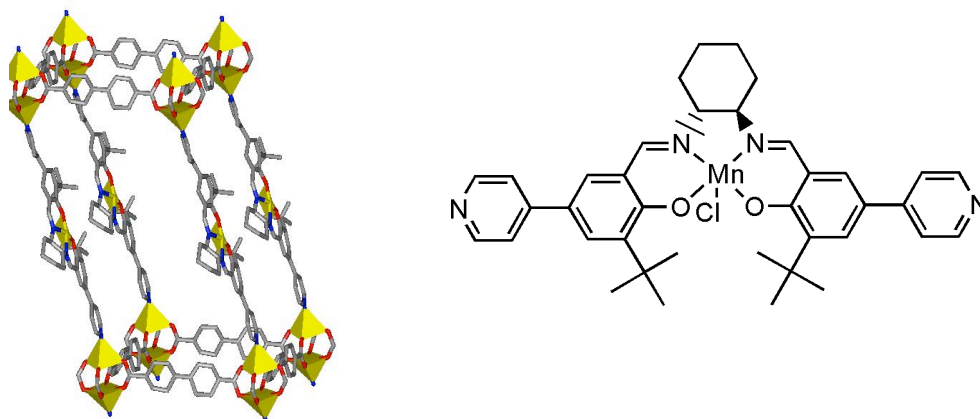


Figure 1. Left: one cavity of the (salen)Mn MOF. Yellow polyhedra represent Zn ions, carbon: grey; oxygen: red; nitrogen: blue; chloride: green; manganese: brown. Right: the (salen)Mn linker molecule incorporated into the MOF.

Because of the predictability of the synthetic routes to MOFs and the nearly infinite number of variations possible, molecular modeling is a particularly attractive tool for screening new structures before they are synthesized [3]. Modeling can, as in other systems, also provide insight into molecular-level details that lead to observed macroscopic properties. We are using a variety of modeling methods. For example, details of chemisorption and catalytic reaction steps at the active site are analyzed using quantum chemical methods. We have made a detailed study of olefin epoxidation on Mn porphyrin compounds (related to salen complexes above), which could be incorporated into future MOFs. Modeling an entire unit cell (or more) using quantum chemical methods is much too expensive computationally. Instead, we use classical force field methods to predict adsorption, diffusion [4], and binding of reactant and product molecules in candidate MOFs. We have recently developed a force field that models the flexibility of the MOF framework. This has led to the interesting observation that some MOFs studied have a negative thermal expansion coefficient (i.e. the unit cell gets smaller when it is heated). This observation is supported by disparate literature observations but has not been noticed previously. Our model matches experimental unit cell parameters very well, and it offers an explanation for this interesting behavior. The flexible lattice model is also a necessary step for future hybrid calculations where the atoms near the active site are treated quantum mechanically and the surrounding atoms are treated with a classical force field (QM/MM).

Green chemistry is an integral part of sustainable development, which is rapidly entering undergraduate science and engineering curricula and the consciousness of the general public. As part of this project, the PI has become the faculty advisor to the Northwestern University chapter of Engineers for a Sustainable World (ESW). This is a national organization that focuses on the challenges of long-term, sustainable development by using engineering to find lasting solutions to reduce poverty and to improve environmental, social, and economic sustainability worldwide. The Northwestern chapter is very active in sponsoring educational activities on campus and in the community. It is also working on 2 projects in Panama, involving solar cells for a remote ranching community and waste-water treatment for a coastal town.

References

- [1] For further information about this project link to <<http://zeolites.cqe.northwestern.edu/NIRT>> or email <snurr@northwestern.edu>
- [2] S.-H. Cho, B. Ma, S.T. Nguyen, J.T. Hupp, T.E. Albrecht-Schmitt, "A metal-organic framework material that functions as an enantioselective catalyst for olefin epoxidation," *Chem. Commun.* 2563-2565 (2006). Highlighted in *Chemical & Engineering News*, June 26, 2006, pp. 38-39.
- [3] R.Q. Snurr, J.T. Hupp, S.T. Nguyen, "Prospects for nanoporous metal-organic materials in advanced separations processes," *AIChE J.* **50**, 1090-1905 (2004).
- [4] D. Dubbeldam, R.Q. Snurr, "Recent developments in the molecular modeling of diffusion in nanoporous materials," *Molecular Simulation*, in press.