Design of Nanoporous Molecular Square Catalysts using Multiscale Modeling

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This project is developing multiscale materials modeling approaches and applying them to novel nanoporous materials for selective oxidation catalysis. The modeling approaches span hierarchically from the atomic level, through mesoscale domains, and up to macroscopic scales. Much progress has already been made over the years in developing modeling techniques appropriate for various time and length scales, e.g. quantum chemistry approaches at the atomic level, molecular dynamics simulations for length scales of hundreds of Angstroms, and engineering models at macroscopic scales. The grand challenge – essential for solving complex, integrated problems – is to effectively *link* these different techniques into a comprehensive hierarchical approach. Another large challenge is to use these methods to truly design *new* nanoscale materials. We present here our efforts toward these challenges.

The target of our modeling efforts is to model, computationally refine, and substantially amplify the performance of novel mesoporous "molecular square" (MS) catalysts that have the potential to function as artificial enzymes. See Figure 1. Using modeling to guide experiment, these materials can be designed at the molecular level, self-organized into channel systems, and further organized into macroscopic structures for use in chemical reactors. This type of chemical design and self assembly is a powerful method for construction of materials of use in nanotechnology.
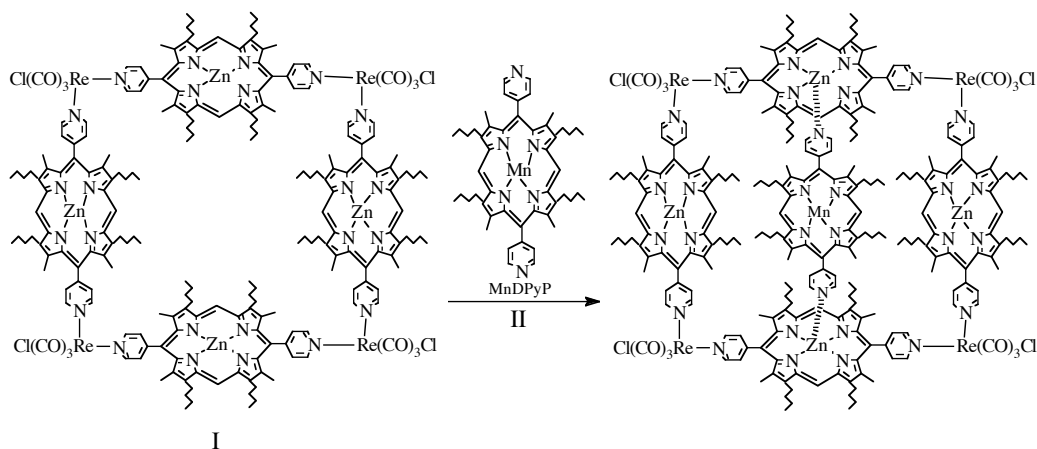
Figure 1: A molecular square based on Zn porphyrin walls and Re corners (I) and a MnDPyP-catalyst (II) combine to create an enzyme catalyst mimic.

Membrane Reactors: Nanoscale Chemical Factories

We have recently developed supported membranes that act as nanoscale filters, allowing small molecules to pass through, but blocking large molecules [2]. The membranes are built from molecular square subunits, each having identically sized 2 nanometer openings. The filters may

have applications in chemical separations and in selective sensing of heavy metals, volatile organic compounds [3], and bio-markers (small proteins, etc.) relevant to human health. We have also recently reported that MSs can be used to encapsulate chemical catalysts to form assemblies that behave in solution as artificial enzymes, rapidly converting cheap chemical feedstocks into valuable precursors for pharmaceutical molecules [4]. We have now successfully combined the two ideas: Catalyst-containing squares have been organized as thin-film arrays of nanoscale reactors or factories. Molecules passing through the factories are not only sorted on the basis of their size, but once sorted are processed chemically to convert them into building blocks for pharmaceuticals, high-performance polymers, and other useful material.

It is useful to assemble the nanoscale factories as extended arrays for several reasons. First, the catalysts are tremendously stabilized by encapsulation within arrays. Rather than processing only 50 or 60 feedstock molecules before degrading, each array-encapsulated catalyst can process around a million molecules. Second, by behaving as nanoscale filters, the MS arrays deliver to the catalysts only those feedstock molecules having the right pre-determined size; those that are larger than desired are completely excluded from the tiny factories. Third, unlike individual catalysts used in solution, the solid arrays can be separated from the reaction products simply by removing the array from the reaction solution.

Multiscale Modeling

If the nanoscale factories can be further improved (higher throughput, selective manufacturing of right-handed versus left-handed mirror image molecules, even longer catalyst lifetimes) and if they can be adapted to a wide variety of chemical manufacturing processes, they will lower the costs of a wide range of specialized chemical processes while also greatly decreasing the environmental impact. This development will require a better understanding of their properties on the microscopic level. Multiscale modeling can be of great use for this purpose.

Starting at the most detailed level of description, embedded cluster Density Functional (DF) calculations have been carried out on the "simple" MSs with pyrazine and bipyridine walls. These units are small enough so that "one-shot" calculations can be made with a single embedded cluster. The somewhat more complex zinc porphyrin MS was treated by a half-cluster embedding, which still contains two-fold redundancy useful in verifying precision of the electron density and energy levels. Optical absorption profiles were calculated for the three structures in the dipole approximation, for comparison with experimental absorption in solution. The Divide & Conquer algorithm, which cuts the macromolecular system into atom-centered interacting fragments and allows for much larger system sizes, was applied to the analogous manganese-based systems, building a data-base for better understanding of the role of rhenium in the chemical bonding and electron density critical to corner-post rigidity and its coupling to wall components.

Using force field simulations, we have preformed grand canonical Monte Carlo simulations to predict adsorption uptake (isotherms) for various small molecules within crystalline arrays of small pyrazine and bipyridine squares. Molecular dynamics simulations have also yielded a first look at diffusion rates in these systems. To investigate the role of electronic interactions of adsorbates with the MSs, DF calculations were carried out to simulate the approach and interaction of benzene, fluorobenzene, chlorobenzene, and toluene with a wall of the pyrazine-

and bipyridine-based MS. Since these molecules are too large to fit comfortably within the MS box, a repulsive interaction was found in the interior as expected. For approach (in vacuum) to an exterior wall, a simplified geometry, with the only variable being the ring-ring separation, was initially adopted. The order of binding energy calculated was found to be exactly the reverse of that inferred from experimental adsorption measurements [3]. This implies that either (1) more complex atomic rearrangements, such as H-atom and CO ligand repositioning occur, or (2) theoretical refinements beyond standard DF methodology are needed, or (3) spatial interactions due to MS packing in thin-film geometry play an important role. Both possibilities (1) and (2) are being examined; (3) is considered unlikely at present.

For squares where crystal structure data is not available, we are using a combined force field and DF approach to predict structures of single squares as well as to obtain information about how they may pack in space. Using the porphyrin-specific implementation of the DREIDING force field, we have found minimum-energy structures for the porphyrin square I shown in Figure 1. Contrary to expectations, the porphyrin rings are predicted to lay flat (as shown in Figure 1), rather than creating a "box." Critical features of the structure were then tested using the DF approach by examining the angle-dependent energies depending upon orientation of MS walls, ranging from upright to flat, using output data from the molecular mechanics (MM) simulations. Comparison between DF and Hartree-Fock results suggests that calculated torsional force constants (desired to refine the MM force fields) are sensitive both to the level of theory employed, and to details of atomic rearrangement during the torsional motion. More detailed studies are planned to determine the accuracy which may be obtainable.

In order to characterize the effectiveness and selectivity of the molecular squares as practical catalysts, an understanding of inter- and intra-catalyst transport and reaction at macroscopic scales is required. Continuum models were therefore formulated to account for both reaction and transport effects and to capture the behavior of the molecular squares in different reactor configurations. Inputs to the models include sorption coefficients and diffusion rates calculated from the molecular simulations. Three configurations were examined: flow through a membrane film; flow over a film on an inert, nonporous support; and flow through a packed bed with molecular squares supported on spherical pellets. The resultant sets of non-linear PDEs were solved using a finite difference approach that required the application of a split-step method for some reactor configurations. The effect of different operating conditions and the impact of various reactor configurations was probed for short length scales. However, the disparate orders of magnitude of the parameters in the different regions prohibited the exploration of longer length scales of practical relevance. Currently, a gap-tooth scheme, i.e., a continuum model with both coarse and detailed descriptions, is being explored as a method for accessing longer length scales.

References
[1] For further information about this project link to **<http://zeolites.cqe.northwestern.edu>** or email **<snurr@northwestern.edu)>**
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