Graduate Student Projects with Prof. Stephanie MacQuarrie (CBU/MUN)

Please e-mail Stephanie directly if you are interested: Stephanie_MacQuarrie@cbu.ca

PROJECT 1: Controlled Grafting of *Organic Catalyst* Monomers within the Pore Walls of Large Pore Silica-Based Materials.

N-heterocyclic carbenes have been used in organocatalytic reactions, however they cannot be adopted for industrial purposes yet as unacceptably high catalyst loadings are required for reasonable reaction rates. These high catalyst loadings lead ultimately to more expensive, environmentally harmful processes that require large amounts of solvents for purification and separation of the final products. There is extensive need for heterogeneous, large pore (2-50 nm) materials composed of organic catalysts for use as greener alternative organocatalysts. Our research program is directed towards the synthesis of these materials specifically through the preparation and comprehensive characterization of highly organized functionalized mesoporous (2-50nm) materials composed of *N*-heterocyclic carbene (NHC) skeletons. This approach is unique since it combines two important fields of chemistry: **materials** and **catalysis**. The advantages of such functionalized materials are their reusability as heterogeneous catalysts, thermal and chemical stability and simple synthesis by a modular approach. The mesoporous organic-inorganic hybrid materials (PMOs) that are prepared result in improved diffusion and enantioselectivity during catalysis. By controlling the placement of the functional catalysts, to be mainly on the surfaces and not buried inside the walls of the materials we should see very high catalytic activity. In addition to testing these novel materials for catalytic activity, recent literature suggests that they may also be ***useful materials for carbon dioxide capture, therefore we are also investigating their absorption properties (see inset Figure)***. This research program has potential applications in the pharmaceutical and chemical industries. While metal catalyzed reactions are commonly used in pharmaceutical processes, the demand for precious metals is high and there is a limited supply available. Metals will eventually become difficult to obtain, however the proposed organic-based catalysts will not run out in the next century. The reusable, recoverable heterogeneous organic catalysts that we prepare will facilitate the use of organic catalysis by the chemical and pharmaceutical industry.

PROJECT 2: Entrapment of an Oligomeric Enzyme in Ultra Large Pore SBA-15 Generates Highly Stable Reusable Biocatalyst

The use of enzymes as biocatalysts in industrial and pharmaceutical processes is generating vast interest for a variety of reasons including the appeal of utilizing these catalysts in green solvents like water and their ability to perform asymmetric catalysis. Yet several challenges must be addressed before these catalytic processes are economically feasible. In order for enzymes to be effectively used as catalysts in industry ideally they must be i) stabilized under a variety of conditions (varied pH and temperatures) and ii) easily recoverable and reusable. Phenylalanine ammonia lyase transforms L-phenylalanine (L-Phe) into trans-cinnamic acid (t-CA). One of the major clinical applications of PAL is its use in the treatment of phenylketonuria (PKU), a genetic disorder in which there is a deficiency or absence of the enzyme Phenylalanine hydroxylase responsible for the conversion of L-Phe to L-tyrosine (L-Tyr) in the body. The absence of phenylalanine hydroxylase results in an increase of L-Phe in bodily fluids (phenylalaninemia).

In large concentrations L-Phe is a neurotoxin and therefore if not detected and treated with an extremely strict diet PKU results in severe neurological disorders before the age of one. Although the direct administration of PAL may appear to be a suitable treatment for PKU, PAL is very unstable and denatures at room temperature. There is a critical need for the development of a simple method of PAL stabilization. PAL also catalyzes the reverse transformation converting t-CA to optically pure L-Phe, a reaction with considerable industrial significance. This is an economically favorable reaction as t-CA is considerably less expensive than L-Phe. In addition L-Phe is an important precursor to the dipeptide, Aspartame (L-aspartyl-L-phenylalanine methyl ester) which is a common diet sweetener used worldwide in over 6000 commercial products, especially by the diabetic and obese population. Enzyme stabilization and recycling could drastically reduce the cost associated with the use of PAL in both industrial and healthcare settings. We are the first researchers to successfully immobilize PAL in a variety of periodic mesoporous materials. So far our studies show immobilization appears to prevent the enzyme from denaturing greatly maintaining the activated catalytic site. Our approach is simple and capitalizes on the facile synthesis and easy recoverability of periodic mesoporous silicas to generate a *stable, reusable PAL based biocatalyst (*see inset Figure*)*. Although other approaches have reported the stabilization of PAL, this study demonstrates the first immobilization and stabilization resulting in the enzyme being recycled and reused 8 times!

PROJECT 3: Dipyrromethene Functionalized Mesoporous Silicas as Heavy Metal Sensors

The ability to discover and quantify analytes in any chemical or biological environment is a very important area of research, particularly in Cape Breton. Despite many efforts, there is still a large number of interesting analytes that cannot be easily detected. Thus, new methods for **rapid and low-cost testing** must be designed for applications in **industrial manufacturing, waste water cleanup, environmental impact studies and even national security**. Among the different types of chemical sensors, optical sensors utilizing fluorescence appear to be the most sensitive and powerful sensors. In the last two decades a large number of new fluorescent sensing probes have been synthesized, typically by the immobilization of those sensing probes in polymeric matrices. These materials are often costly to develop, break down under harsh conditions and it is often quite difficult to recover the analytes from the polymer matrix. Mesoporous silica's however, are much more resistant to degradation under harsh conditions, easily functionalized and generally cheaper to synthesize making them ideal candidates for sensor supports. We are attaching **dipyrromethene receptors to the surface of ultra large pore silica, for use in sensing a variety of heavy metals (copper, lead, mercury, etc.) in aqueous and organic solutions**. We have chosen the dipyrromethene receptor because it is a highly fluorescent molecule and the excitation wavelengths shift significantly depending on which metal the dipyrromethene group makes a complex with. The immobilized highly fluorescent dipyrromethene receptors on the surface of mesoporous silica will lead to the development of easily reusable, stable heavy metal sensors that will easily be developed into onsite chemical sensors.