We are happy to announce that Prof. Mary Watson, from the Department of Chemistry and Biochemistry, has joined the Center for Catalytic Science and Technology. Dr. Watson obtained a Bachelor degree in Chemistry from Harvard, and her Ph.D. in Organic Chemistry at the University of California, Irvine, with Prof. Larry Overman, in 2006, for her studies of the palladium(II)-catalyzed asymmetric allylic imidate rearrangement. She joined the University of Delaware in 2009 after a National Institutes of Health NRSA postdoctoral fellowship at Harvard with Prof. Eric Jacobsen, where she discovered an enantioselective, nickel-catalyzed alkene arylcyanation reaction. At Delaware, Dr. Watson has continued to follow her passion for the use of homogeneous, transition metal-based catalysts to provoke organic molecules to undergo otherwise impossible transformations.

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Upcoming

George C. A. Schuit Lecture
Hubert A. Gasteiger
Technische Universität München
Friday, May 29th at 10 AM
102 Colburn Lab

2015 CCST Research Review
Oct. 7th (3-6 PM)
Oct. 8th (8 AM-3:30 PM)
Clayton Hall Conference Center
Synthesis of covalent organic frameworks (COFs)

Yushan Yan
Chemical & Biomolecular Engineering

Covalent organic frameworks are an emerging class of porous crystalline polymers with a wide variety of applications. Covalent organic frameworks are currently synthesized through relatively few chemical reactions, limiting the exploration of new structures and properties. We have recently discovered that the imidization reaction can be used to prepare a series of large-pore crystalline polyimide covalent organic frameworks. The channel size of PI-COF-3 (42 \times 53 \text{ Å}^2) is among the largest reported for covalent organic frameworks. The PI-COFs show high thermal stability and surface area; in particular, the surface area of PI-COF-3 (S_{\text{BET}} = 2346 \text{ m}^2 \text{ g}^{-1}) exceeds that of amorphous porous polyimides and is among the highest reported for two-dimensional covalent organic frameworks. We also assemble a large dye molecule into a covalent organic framework that shows favorable temperature-dependent luminescent properties.

Catalytic Cross Couplings of Alkyl Electrophiles

Mary Watson
Chemistry & Biochemistry

As recognized by the 2010 Nobel Prize in Chemistry, awarded to UD Professor Emeritus Richard Heck, Ei-Ichi Negishi, and Akira Suzuki, palladium-catalyzed cross coupling reactions have revolutionized the way that carbon–carbon (C–C) bonds are made, and have had far-reaching impact in organic synthesis, materials science, and pharmaceutical development. Historically, these C–C cross couplings have been limited to the use of aryl or vinyl halides as substrates. More recently, alkyl electrophiles have been targeted, allowing the opportunity to deliver enantiomerically enriched chiral products via cross-coupling reactions.

The M. Watson lab is focused on stereospecific cross couplings of alkyl electrophiles to deliver highly enantioenriched, aryl-substituted products. Before their work, two problems plagued stereospecific cross-couplings: some alkyl electrophiles could not be prepared in high enantiopurity and the coupling partners were limited to air-sensitive and often functional group-intolerant reagents. Working towards overcoming these challenges, the Watson lab has developed nickel-based catalyst systems that enable the coupling of both alcohol- and amine-derived electrophiles with aryl boronic partners. Both alcohols and amines can be readily prepared in exceptional enantiopurity, and the aryl boronic partners are both air-stable and functional group tolerant, enabling greater breadth in the molecules that can be prepared via this strategy. Both benzylic and allylic electrophiles have been targeted, delivering a range of product scaffolds important in biologically active molecules. The Watson group is now demonstrating this strategy for a range of related substrates and coupling partners.


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Highly porous non-precious bimetallic electrocatalysts for efficient hydrogen evolution

- Feng Jiao
Chemical & Biomolecular Engineering

Rising concerns about carbon dioxide emissions have led to a growing realization that it is not possible to sustain the world’s current development based on fossil fuels and that a substitution to clean and renewable energy is necessary. Hydrogen, other than being an important chemical feedstock in global industry, is now firmly considered as one of the most likely future global fuels. However, current hydrogen production primarily relies on the steam methane reforming process which is neither sustainable nor favored because the process requires high energy (heat) input and produces carbon dioxide as a by-product. It is widely believed that room temperature electrochemical reduction of water to molecular hydrogen offers a significant promise for supplying carbon dioxide free hydrogen, which can be used directly as a fuel or as reactant to convert carbon dioxide and to upgrade petroleum and biomass feedstocks to value-added chemicals and fuels through hydrotreating processes. However, all these applications require breakthrough discoveries in low-cost electrocatalysts to replace precious metals (i.e. platinum) that are currently the state-of-the-art catalysts.

Prof. Jiao and co-workers recently reported a hierarchical nanoporous copper-titanium bimetallic electrocatalyst that is able to produce hydrogen from water with a rate more than two times higher than that of the current state-of-the-art carbon-supported platinum catalyst. Such high performance origins from the combination of copper and titanium creating unique reaction sites similar to those of platinum. The hierarchical porosity of the catalytic material also contributed to its high activity by simultaneously enhancing the electrode surface area and the mass transport properties. Moreover, the catalyst is self-supported, which further eliminates the overpotential (i.e. energy penalty) associated with the catalyst/support interface. The results have been published in a recent issue of Nature Communications.

The group of Prof. Raul Lobo recently reported the discovery of four new zeolitic materials that can react with methane to form methanol. These materials include the small-pore zeolites Cu-SSZ-13, Cu-SSZ-16, Cu-SAPO-34 and Cu-SSZ-39 (AEI). These copper-containing small-pore zeolites produce methanol with high selectivity after contacting methane with a preoxidized zeolite sample (see figure below). The process is cyclic and repeatable; these zeolites produce more methanol per Cu atom than previously observed for other zeolites like Cu-ZSM-5 and Cu-mordenite and values as high as 0.1 mol MeOH/Cu were observed. Very little carbon dioxide was formed during the reaction. The group carried out spectroscopic investigations of the structure and oxidation state of the copper species as a function of temperature and determined that the active site in these small-pore zeolites is different from the site in the better-known Cu-ZSM-5. The research was recently reported in the journal Chemical Communications (Chem. Commun., 2015, 51, 4447) and was conducted by postdoctoral fellows Matthew Wulfers, Shewangizaw Teketel and graduate student Bahar Ipek.

![Time evolution of the concentration of methanol evolving from copper-containing small-pore zeolites eluted using steam.](image_url)

**Selected Recent Publications:**