

CENTER FOR CATALYTIC SCIENCE & TECHNOLOGY

Departments of Chemical & Biomolecular Engineering and Chemistry & Biochemistry

Spring 2015 Highlights

Professor Mary P. Watson joins CCST



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 arylation 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

(Mary Watson continue)

Intrigued by the ability of transition metal-based compounds to catalyze reactions with exceptional efficiency and selectivity, her group is focused on harnessing their power in new transformations. In particular, they develop catalytic systems based on non-precious metals, such as copper and nickel, to enable the synthesis of highly enantioenriched chiral products. They prioritize the use of inexpensive and widely available reagents to maximize the convenience and impact of their reactions. This research will lead to the development of new methods for the synthesis of biologically active molecules and other important materials. These methods will allow greater efficiency and novel bond constructions in the synthesis of stereochemically complex molecules, with applications that extend to natural products synthesis, drug discovery and process chemistry. The development of these methods will also provide a platform for mechanistic investigations, which will provide a better understanding of how these catalysts interact with substrates and enable the design of future catalysts. Her research has received generously support from the University of Delaware Research Foundation, the American Chemical Society Petroleum Research Fund, the National Institutes of Health (R01 and COBRE programs), and the National Science Foundation (Early Career Award). The impact of her research program has also been recognized with a Rising Star award from the Women Chemists' Committee of the American Chemical Society. We are very pleased to have her join our center.

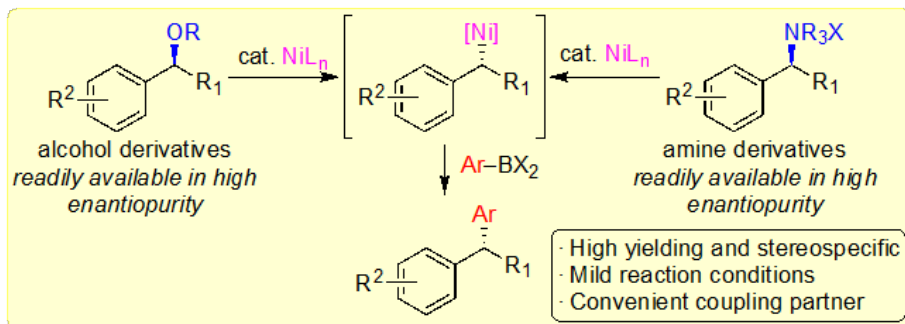


Catalytic Cross Couplings of Alkyl Electrophiles

• 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 enantioenriched 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.

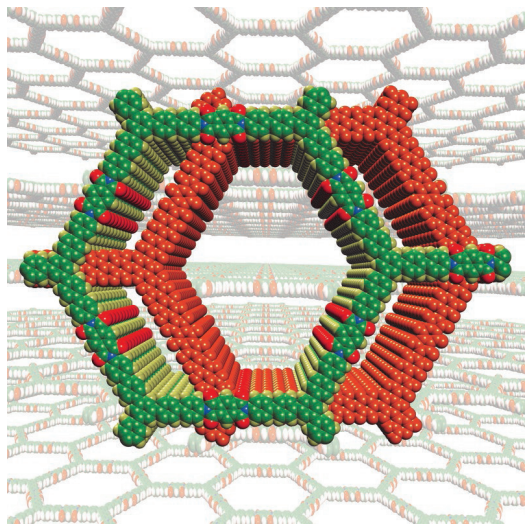
1. Maity, P; Shacklady-McAtee, D. M.; Yap, G. P. A.; Sirianni, E. R.; Watson, M. P. Nickel-Catalyzed Cross Couplings of Benzylic Ammonium Salts and Boronic Acids: Stereospecific Formation of Diarylethanes via C-N Bond Activation *J. Am. Chem. Soc.* 2013, 135, 280. doi: 10.1021/ja3089422
2. Zhou, Q.; Srinivas, H. D.; Dasgupta, S.; Watson, M. P. Nickel-Catalyzed Cross-Couplings of Benzylic Pivalates with Arylboroxines: Stereospecific Formation of Diarylalkanes and Triarylmethanes *J. Am. Chem. Soc.* 2013, 135, 3307. doi: 10.1021/ja312087x



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 × 53 Å²) 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_{BET} = 2346 m² 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.



1. Fang Q., Zhuang Z., Gu S., Kaspar R.B., Zheng J., Wang J., Qiu S., Yan Y., Designed synthesis of large-pore crystalline polyimide covalent organic frameworks. *Nature Communications* 2014, 5:doi:10.1038/ncomms5503



Understanding the hydrogen oxidation mechanisms

• Yushan Yan
Chemical & Biomolecular Engineering

The hydrogen oxidation/evolution reactions are two of the most fundamental reactions in distributed renewable electrochemical energy conversion and storage systems. The identification of the reaction descriptor is of critical importance for rational catalyst design and development. We recently reported correlation between hydrogen oxidation/evolution activity and experimentally measured hydrogen binding energy for polycrystalline platinum examined in several buffer solutions in a wide range of electrolyte pH from 0 to 13. Correlating the hydrogen oxidation/evolution activity to the hydrogen binding energy renders a monotonic decreasing hydrogen oxidation/evolution activity with the hydrogen binding energy, strongly supporting the hypothesis that hydrogen binding energy is the sole reaction descriptor for the hydrogen oxidation/evolution activity on monometallic platinum.

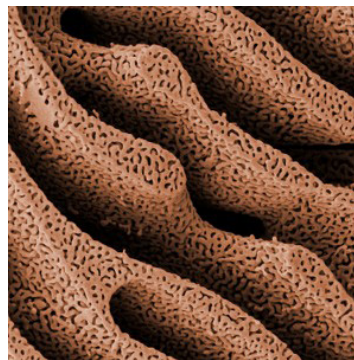
1. Sheng W., Zhuang Z., Gao M., Zheng J., Chen J.G., Yan Y., Correlating hydrogen oxidation and evolution activity on platinum at different pH with measured hydrogen binding energy. *Nature Communications* 2015, 6: doi:10.1038/ncomms6848.



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.



SEM image of np-CuTi after selective dealloying.

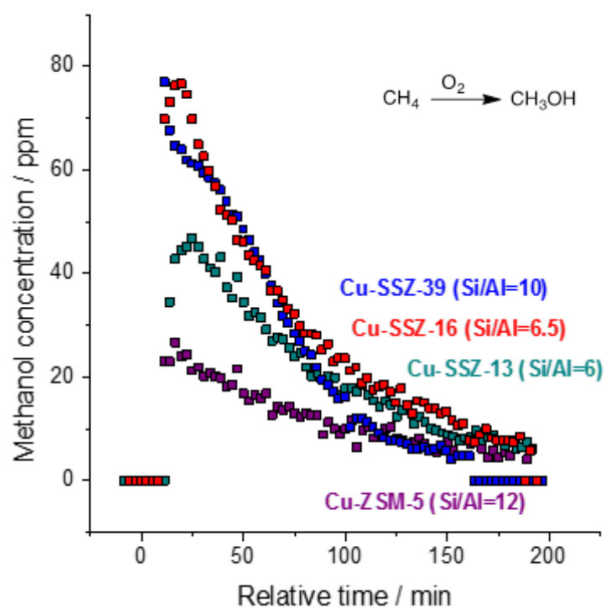
Prof. Jiao and co-workers recently reported a hierarchical nanoporous copper-titanium bimetallic electrocatalyst that is able to produce hydrogen from water with a rate more than two times higher than that of the current state-of-the-art carbon-supported platinum catalyst. Such high performance originates 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*.

1. Q. Lu, G. Hutchings, W. Yu, Y. Zhou, R. Forest, R. Tao, J. Rosen, B. Yonemoto, Z. Cao, H. Zheng, J. Xiao, F. Jiao & J. Chen. *Nat. Commun.* 6:6567, doi:10.1038/ncomms7567 (2015)

Methane to Methanol Conversion on Cu-Zeolites

• Raul Lobo
Chemical & Biomolecular Engineering

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 pre-oxidized 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.

Selected Recent Publications:

- "Non-precious metal electrocatalysts with high activity for hydrogen oxidation reaction in alkaline electrolytes", Sheng W., Bivens A.P., Myint M., Zhuang Z., Forest R.V., Fang Q., Chen J.G., Yan Y., Energy & Environmental Science 2014, 7(5): 1719-1724.
- "Electrochemical Energy Engineering: A New Frontier of Chemical Engineering Innovation", Gu S., Xu B., Yan Y., Annual Review of Chemical and Biomolecular Engineering, Vol 5 2014, 5: 429-454.
- "Efficient Water Oxidation Using Nanostructured alpha-Nickel-Hydroxide as an Electrocatalyst", Gao M., Sheng W., Zhuang Z., Fang Q., Gu S., Jiang J., Yan Y., Journal of the American Chemical Society 2014, 136(19): 7077-7084.
- "The Effect of Adsorbed Molecule Gas-Phase Deprotonation Enthalpy on Ion Exchange in Sodium Exchanged Zeolites: an in-situ FTIR Investigation", B. Murphy, M. Davis, B. Xu, Top. Catal. 2015, DOI: 10.1007/s11244-015-0383-z.
- "Ring Activation of Furanic Compounds on Ruthenium-Based Catalysts", Mironenko, A. V., Gilkey, M. J., Panagiotopoulou, P., Facas, G., Vlachos, D. G., and Xu, B.* J. Phys. Chem. C, 2015, 119 (11), pp 6075–6085.
- "Radical Cation Intermediates in Propane Dehydrogenation and Propene Hydrogenation over H- Fe Zeolites", Yun, J. H.; Lobo, R. F., Journal of Physical Chemistry C 2014, 118, 27292, DOI: 10.1021/jp504453n.
- "Effects of temperature pretreatment on propane cracking over H-SSZ-13 zeolites", Yun, J. H.; Lobo, R. F., Catalysis Science & Technology 2015, 5, 264, DOI: 10.1039/c4cy00731j.
- "A DFT study of furan hydrogenation and ring opening on Pd(111)", Wang, S., Vorotnikov, V. & Vlachos, D.G., Green Chem. 16, 736-747 (2014).
- ***ACS Editors' Choice***: "Kinetic Regime Change in the Tandem Dehydrative Aromatization of Furan Diels-Alder Products", Patet, R. E., Nikbin, N., Williams, C. L., Green, S. K., Chang, C., Fan, W., Caratzoulas, S., Dauenhauer, P. J., and Vlachos, D. G., 2015, DOI: 10.1021/cs5020783.
- "Chromium Mediated Reductive Coupling of Isonitrile Forms Unusual Heterocycles", J. Shen, G. P. A. Yap and K. H. Theopold, J. Am. Chem. Soc. 2014, 136, 3382. DOI: 10.1021/ja501291p.
- "Ferrocenyl-Substituted Tris(pyrazolyl)borates - A New Ligand Type Combining Redox Activity with Resistance to Hydrogen Atom Abstraction", E. R. Sirianni, G. P. A. Yap and K. H. Theopold, Inorg. Chem., 2014, 53. DOI: 10.1021/ic5015658.
- "Reaction and Catalyst Families in the Modeling of Coal and Biomass Liquefaction Kinetics", Horton, S.; Klein, M. T., Energy Fuels 2014, 28, 37–40.
- "Molecular-Level Kinetic Modeling of Resid Pyrolysis", Horton, S., Zhang, L., Hou, Z., Bennett, C. A., Klein, M. T., and Zhao, S., Ind. Eng. Chem. Res. ASAP, DOI: 10.1021/ie504157.

Save the Date
2015 CCST Research Review

10/07/2015 (3:00 pm - 6:00 pm)

10/08/2015 (8:00 am - 3:30 pm)