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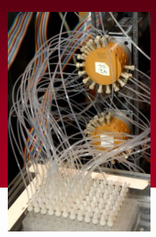
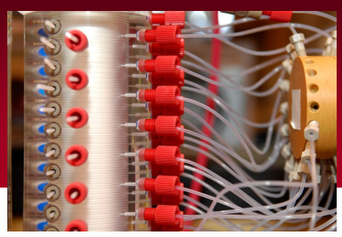


The Gene and Linda Voiland School of
Chemical Engineering and Bioengineering
2015 Seminar Series
Monday, September 14, 2015
12:10 p.m. Todd 311

Wendy Shaw
Physical Sciences Division
Scientist, TL
Pacific Northwest National Laboratory

Wendy Shaw is a Scientist at Pacific Northwest National Laboratory (PNNL) in Richland, WA. She earned her Bachelor of Arts in Chemistry from Seattle of Arts and Whitman College, Walla Walla and her Ph.D. in Physical/ Biophysical Chemistry from University of Washington. Her areas of expertise include: gaining a fundamental, molecular-level understanding of the role of the enzyme scaffold, or outer coordination sphere, on molecular catalysts. Investigating the role of proton channels, the environment around the active site, structural stability and dynamics on catalysts for H2 production and oxidation as well as CO2 hydrogenation, using 1-, 2-, and 3-dimensional NMR and dynamic NMR techniques to characterize novel catalysts and catalytic intermediates for the interconversion of H+ to H2, O2 to H2O and N2 to NH3, respectively.

Mimicking Enzymatic Function in Molecular Catalysts for Energy Transformations

Enzymes are capable of shuttling gases, protons and electrons with great speed and precision. Enzymes are also capable of very specifically controlling the local environment around the catalytic active site. Using the large range of functional groups available with the 20 naturally occurring amino acids, and the structural control of the protein architecture, precise placement of hydrophobic or hydrophilic groups is achieved which control the enzyme active site hydrophobicity, charge, steric accessibility and electronic character. Furthermore, enzymes are dynamic molecules that can control the desired environment by a subtle or significant change in structure. The superior rates and specificity of enzymes as compared to homogeneous catalysts demonstrate that the outer coordination sphere (OCS) is as essential as the active site for efficient function.

Our program focuses on trying to capture these desirable enzymatic traits in homogeneous catalysts. Dynamics, active site environment and proton channels are the features of the OCS that are the focus of these studies. We are developing redox active catalysts which oxidize and produce H2, mimicking the hydrogenase enzyme. Like other enzymes, hydrogenase enzymes use many OCS features to very efficiently convert H+ to H2 and back again. Our initial work in this area has focused on incorporating small peptides around the active site of the Ni(PR2NR'2)2 hydrogen production/oxidation catalysts to explore how the local environment can influence catalytic rates. We have found that the addition of small peptides retains or enhances the activity of the parent catalyst, while demonstrating that regions remote from the active site do modulate this activity. Larger peptides also enhance activity, and importantly, provide a scaffold upon which a more complex outer coordination sphere can be designed and added. We are also combining computational and experimental approaches to add a proton channel to the Ni(P2RN2R')2 catalyst active site. Adding a single amino acid has resulted in a two-relay proton channel, and altering the amino acid has resulted in a reversible catalyst that maintains fast rates, demonstrating the essential contribution of the outer coordination sphere in achieving outstanding performance. The dynamics of the OCS are being investigated by incorporating ligands which change shape as a function of an applied stimulus. Applying a stimulus to these metal-bound ligands can alter the catalytic activity, mimicking in a general way the dynamic and regulatory role that outer coordination spheres of enzymes play. These studies have demonstrated that stimulus sensitive ligands can be used to control catalytic activity during catalytic hydrogenation, and investigating their contribution to hydrogen production catalysts is currently underway. Combining these approaches allows us to explore and develop a mechanistic understanding of the role of the OCS in both enzymes and molecular catalysts, allowing us to capture the essential features into homogeneous catalysts, with the potential of enhancing the rates, selectivity and specificity of the catalyst.