



Global Climate & Energy Project
STANFORD UNIVERSITY

The Electron Economy: Oxidation Catalysis for Energy Management

Investigators

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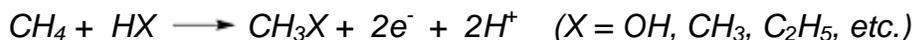
Objective

This research seeks to develop efficient electrocatalysts for two important classes of chemical transformations. The first transformation is the oxidative conversion of methane to alcohols or higher hydrocarbons that would convert natural gas into valuable liquid fuels without the release of any carbon dioxide. The second transformation is the oxidation of water which is critical to any energy system that uses electrochemistry as an intermediary between electricity and stored fuels.

Background

Our modern economy is fueled in large part by the free energy available at high densities in liquid hydrocarbon fuels. When liquid fuels are combusted in today's engines, much of the free energy is lost and the fuel carbon is introduced into the environment as CO₂. Chemists describe these combustion reactions as the transfer of electrons from carbon to oxygen atoms with a concomitant harvesting of the free-energy of the electrons. In the near future, the free energy of the electrons in fossil carbon sources must be harvested much more efficiently. Further out, entirely carbon-neutral sources of high free-energy electrons will be required.

For methane oxidative conversion:



the reaction products (CH₃OH, C₂H₆, etc) contain the majority of the high free-energy electrons of the initial methane. Current options for bringing these electrons to market include gasification and liquefaction, both of which lead to loss of free energy and carbon.

For water oxidation:



the electrons must be pumped out of the water via electrical input. This can be accomplished with standard precious metal catalysts, but at efficiencies which are unacceptably low. Photosynthesis accomplishes the same objective (thereby giving plants the electrons they need to thrive), but in a system whose efficiency is even lower.

Approach

This project will search for organometallic catalysts with multiple metal atoms to accomplish oxidative methane conversion and water oxidation. For oxidative conversion of methane, di-platinum catalysts (molecules with two platinum atoms at their centers) will be examined. The organometallic reaction chemistry and catalytic properties of the platinum "blues" (see Figure 1) has only recently been described [1] and provides a unique opportunity for methane conversion. To date no catalytic cycles are known which couple methane activation chemistry with the facile oxidation and functionalization chemistry of the Pt(III)/Pt(III) dimers.

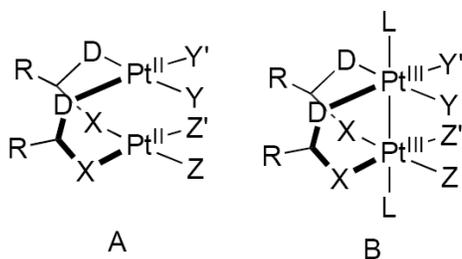


Figure 1: Bi-metallic platinum complexes. Platinum can exist in the (II) or (III) oxidation state.

Polynuclear manganese complexes will be the focus of the search for water oxidation catalysts, although cobalt, iron and ruthenium will also be considered. Rapid screening of a large number of discrete polynuclear metal-oxide/hydroxide compounds will be performed. Ethynylated organic ligands will be used in assembling the catalysts and will allow for exquisite electronic and ligation variations via synthetic modifications at the atomic level.

Both types of catalysts must be immobilized on an electrode surface if they are to be effective in an electrochemical energy conversion system. The investigators' previous GCEP effort developed "click" chemistry for the immobilization of organometallic catalysts on graphitic surfaces via azide linkages. Similar immobilization chemistry will be pursued during this project, and it is expected that methane conversion catalysts will work well on graphite electrodes. Water oxidation catalysts, however, will have to operate in more challenging environments. Click chemistry for catalyst attachment to conductive metal oxides will therefore be developed. Different conductors such as indium tin oxide and aluminum-doped zinc oxide will be tested with multiple azide-based attachment strategies (see figure 2).

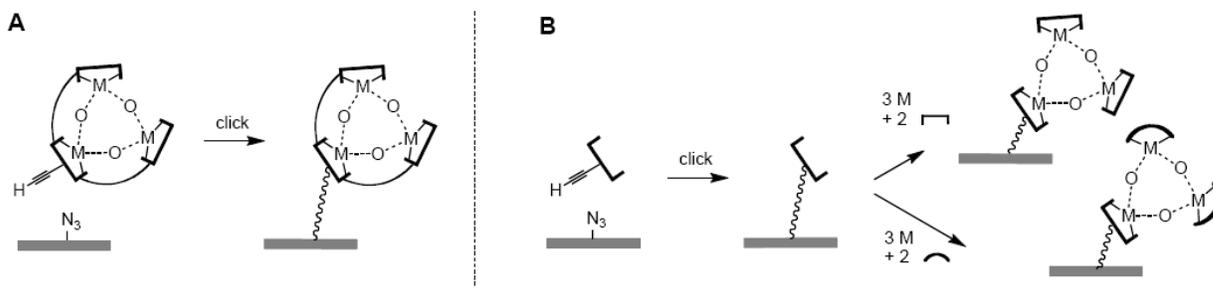


Figure 2: Different attachment strategies for polynuclear metal-oxide clusters on a surface: **(A)** a preformed trinuclear oxide cluster is clicked directly to the surface; **(B)** an immobilized ligand seeds the self assembly of a trinuclear oxide cluster.

The mechanism and kinetics of specific electrocatalytic oxidation reactions with site-isolated catalysts will be determined using the electrochemical techniques of potentiodynamic (cyclic) voltammetry and hydrodynamic (rotating disk) voltammetry. Mechanistic studies using isotope and hydrocarbon exchange will also be used to identify the most active complexes for reaction steps such as C-H activation

References

[1] K. Matsumoto and M. Ochiai, "Organometallic chemistry of platinum-blue derived platinum (III) dinuclear complexes," *Coordination Chemistry Reviews* 231, 229-238 (2002).