

The Electron Economy: Oxidation Catalysis for Energy Management

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Abstract

The energy-efficient removal of electrons is a key chemical step in an efficient electron economy. The objective of this project is to develop efficient electrocatalysts for two important classes of oxidative 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 that is critical to any energy system that uses electrochemistry as an intermediary between electricity and stored fuels.

Introduction

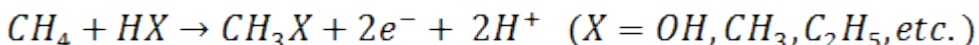
The objective of this project is to develop new classes of supported molecular electrocatalysts for the oxidative conversion of alkanes and the electrooxidation of water. A specific objective is to develop electrocatalysts for the selective conversion of methane to value-added feedstocks and to illuminate the fundamental chemical and electrochemical steps required for the selective and energy-efficient oxidative conversion of hydrocarbons. Our objectives for the electrocatalytic oxidation of water are to develop efficient catalysts and new mechanistic insights that would enable the efficient extraction and harvesting of electrons from water.

Background

Our current electron economy is fueled in large part by the free energy available at high densities in hydrocarbon fuels.^{1,2} Photosynthesis has been the source of electrons to fuel this economy; these electrons have been stored over millennia as hydrocarbon deposits (oil, natural gas and coal) which provide both the bulk of the world's energy needs as well as chemical feedstocks that drive our modern economy. Combustion has served as the primary means of converting the stored chemical energy of hydrocarbons into work; when fuels are combusted, much of the free energy is lost and CO₂ is released into the environment. 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.¹⁻⁴

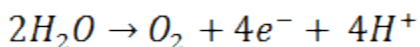
Methane has a high free energy per carbon atom. However, unlike higher hydrocarbons, methane is difficult to ship unless nearby to markets serviced by pipeline and is a relatively inefficient chemical feedstock.^{1,4,5} Absent an economical pipeline, methane is cryogenically liquefied at great energetic expense for shipment in insulated tanker ships to distant markets. Where it is used as a feedstock, it is partially combusted to syngas from which more valuable products are generated by energetically wasteful processes. Thus, it would be highly desirable to find routes to efficiently convert methane by partial oxidation to higher hydrocarbons and alcohols, which are more readily transported and are better chemical feedstocks than methane itself.

The partial oxidation of methane by two electrons proceeds by the general reaction:



The reaction products (CH₃OH, C₂H₆, etc) contain the majority of the high free-energy electrons of the initial methane. Considerable effort has been devoted to the development of new catalyst systems that can effect these selective oxidative conversions of methane to more readily utilized energy or chemical feedstocks.^{4,6-8} A general consensus has evolved that the basic steps of the catalytic cycle would entail: (1) binding and C-H activation of CH₄ by a metal complex to generate the critical M-CH₃ intermediate, (2) oxidation of the M-CH₃ intermediate and (3) elimination of CH₃-X to regenerate the active metal species. Of the small number of systems that achieve a complete catalytic cycle for the partial oxidation of methane,⁸⁻¹¹ one of the most successful is the "Catalytica" system developed by Periana and coworkers in which homogeneous mononuclear (bipym)PtCl₂ complexes (bipym = bipyrimidine) catalyze the oxidative conversion of methane to methane bisulfate in fuming sulfuric acid at 220°C.^{8,9} Some of the limitations of the mononuclear (bipym)PtCl₂ system were proposed to be the slow oxidation of the Pt(II) complex to the critical Pt(IV) intermediate and the inhibition of the catalytic system by water.¹⁰ These advances highlight the critical challenge in developing catalytic systems that can couple hydrocarbon activation with the removal of electrons.

Water is the most abundant source of electrons. However, these electrons have low free energy and, after extracting them from water by the reaction:



they must be electrically pumped into other species. Photosynthesis accomplishes the reaction at a polynuclear manganese cluster, from which the electrons are photochemically pumped into higher free-energy species culminating in the synthesis of carbohydrates. If chemical storage of significant amounts of solar energy is to be realized, energy efficient, scalable water oxidation catalysts will be required.^{2,12,13} The oxidation of water to dioxygen is an exceedingly difficult, multielectron reaction with a standard thermodynamic potential of 1.23 V vs NHE. While precious metal electrodes are able to perform this reaction, significant overpotentials are necessary with the

attendant energy loss. By contrast, the oxygen evolving complex (OEC) of photosystem II (PSII) of photosynthetic organisms is far more energy efficient.^{12,14,15}

Results

In the first three months, we have focused on three primary, complementary objectives: (1) the development of methods to generate molecular catalysts supported on electrode surfaces, (2) the development of supported complexes that can extract electrons from water, and (3) the development of new catalyst systems that can activate and oxidize hydrocarbons. We have extended our previously developed protocols¹⁶ to attach molecular electrocatalysts to indium-tin-oxide (ITO) electrodes^{17,18} utilizing catalytic 5+2 cycloaddition reactions of surface-bonded azides and alkyne-functionalized ligands ("click" chemistry). The higher oxidative resistance of the ITO electrodes relative to the graphite electrodes we have previously used is critical to our efforts to develop electrocatalysts for water oxidation. We have developed new synthetic methods utilizing either azide-functionalized trialkoxysilanes or azide-functionalized phosphates to anchor catalysts to indium-tin oxide (ITO). These studies, in combination with our previous studies on graphite electrodes, have enabled us to anchor and characterize several representative molecular catalysts of Cu, Fe, and Ru to graphite and ITO electrodes (Figure 1). Current studies are focused on the ability of these supported catalysts to extract electrons from water to generate reactive metal oxo complexes.

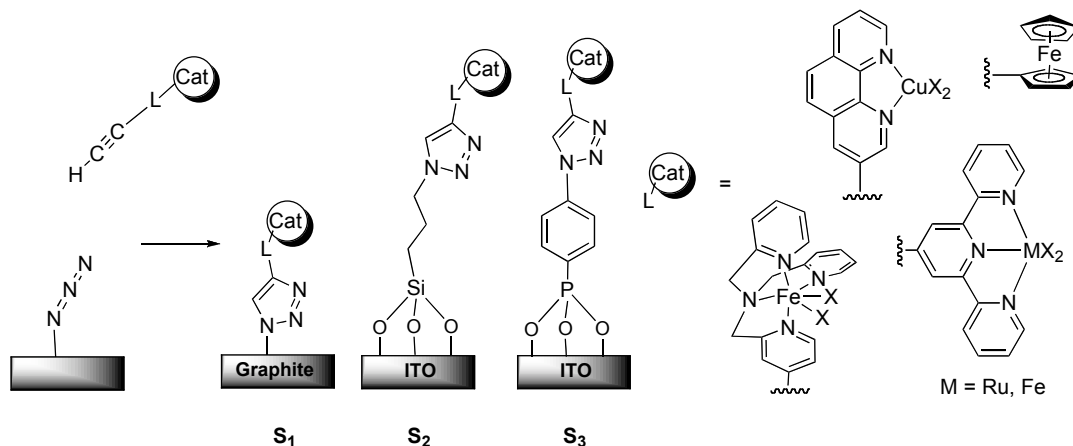


Figure 1. Covalently attached complexes to graphite and ITO electrodes

For hydrocarbon oxidation, previous studies^{8-11,19} have illuminated that removal of electrons from the key metal-alkyl intermediates is the critical step that has limited the efficiency of hydrocarbon oxidation catalysts. We have targeted new classes of bimetallic stacked Pt catalysts that undergo reversible oxidation and reduction between the Pt(II)/Pt(II) and Pt(III)/Pt(III) redox states. The reversible electrochemistry is an attractive and unusual feature of these binuclear Pt(II) complexes relative to mononuclear Pt(II) complexes. To assess the ability of these complexes to activate and functionalize alkanes, we have begun to develop the organometallic chemistry of these complexes.²⁰ We have prepared the novel trimethyl Pt(III)/Pt(III) complex **2A** and have demonstrated that this complex eliminates methane and ethane at elevated temperature. Preliminary results reveal that the Pt(III)/Pt(III) dimers **2B** activate hydrocarbons to generate

Pt(III)/Pt(III) – alkyl complexes, a promising pattern of reactivity for hydrocarbon activation and functionalization. In parallel studies, we have developed modified amide ligands that will enable these dimeric Pt complexes to be tethered to graphite or ITO electrodes. We are currently developing methods to generate supported versions of these binuclear Pt complexes.

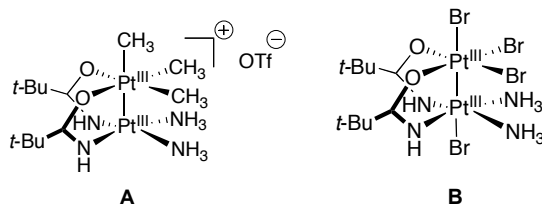


Figure 2: Bi-metallic platinum (III) complexes.

Progress

Progress in the first three months has centered on expanding technology options for generating conductive metal-oxide electrodes functionalized with molecular electrocatalysts. These new capabilities will enable investigations of supported catalysts for water oxidation. In hydrocarbon oxidation, the generation of new families of dimeric platinum complexes that exhibit both reversible electrochemical behavior and C-H activation chemistry provide promising opportunities for the development of new hydrocarbon oxidation catalysts.

Future Plans

Future plans are focused on the investigation Fe, Ru and Mn complexes supported on ITO electrodes as candidate electrocatalysts for water oxidation. A major focus of these efforts will be to illuminate the key steps involved in the removal of electrons from water. For hydrocarbon activation, we plan to investigate the hydrocarbon activation chemistry of the Pt(III)/Pt(III) dimers and the chemical and electrochemical behavior of the alkyl Pt(III) complexes to assess their ability to carry out the electrocatalytic partial oxidation of hydrocarbons. These studies will be coupled to efforts to tether these complexes to either graphite or ITO electrodes.

Publications

No publications have been published in the first three months of this project.

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