On April 27, 2009, the White House announced that the U.S. Department of Energy, Office of Basic Energy Science will invest $777 million in Energy Frontier Research Centers over the next five years. This represents a major effort to accelerate the scientific breakthroughs needed to build a new 21st century energy economy. One of the 46 new EFRC awards was granted to Prof. T. Brent Gunnoe at the University of Virginia (UVA) for the formation of the Center for Catalytic Hydrocarbon Functionalization (CCHF). In addition to UVA, researchers from nine other institutions across the country will “Develop novel catalysts and manipulate their reactivity for the efficient conversion of hydrocarbon gases into liquid fuels.” To achieve this goal, five research thrust areas have been created: 1) study of non-oxo transition metal catalysts for the activation of hydrocarbons, 2) ...
Meet the Principal Investigators

Robert C. Bergman  
University of California, Berkeley  
*Low valent metal oxo catalysts for C-H activation*

Robert H. Crabtree  
Yale University  
*Transition metal catalysts for C-H activation and CO₂ reduction*

Thomas R. Cundari  
University of North Texas  
*Computational studies of new catalysts for C-H activation and functionalization*

Daniel H. Ess  
Brigham Young University  
*Computational studies of transition metal catalysts for C-H functionalization*

William A. Goddard  
California Institute of Technology  
*Computational studies of transition metal catalysts for C-H functionalization*

John T. Groves  
Princeton University  
*Transition metal oxo catalysts for C-H activation*

T. Brent Gunnoe  
University of Virginia  
*Homogeneous and supported transition metal catalysts for C-H activation*

Thomas J. Meyer  
University of North Carolina, Chapel Hill  
*Methane fuel cells and electrochemical reduction of CO₂*

Roy A. Periana  
Scripps Research Institute, Florida  
*Molecular catalysts for C-H activation, methane fuel cells and CO₂ reduction*

F. Dean Toste  
University of California, Berkeley  
*Low valent metal oxo catalysts for C-H activation*

Brian G. Trewyn  
Iowa State University, Ames Laboratory  
*Mesoporous silica nanoparticles as supports for C-H activation and functionalization catalysts*

Andrei N. Vedernikov  
University of Maryland  
*Transition metal catalysts for C-H activation and oxidation*
Members of The Center for Catalytic Hydrocarbon Functionalization participated in the 240th National ACS meeting in Boston, MA held on August 22-26. While the theme of the meeting was “Chemistry for Preventing and Combating Disease,” special sessions were held addressing the future of global healthcare, the consequences of climate change, and the aftermath of the recent Gulf of Mexico oil spill. In the organometallic division, many of the talks focused on new catalysts for the synthesis of organic molecules as well as energy and fuel production.

Amongst the more than 14,000 attendees, CCHF funded talks and posters were presented by Amit Paul and Jonathan Hull (UNC), on the extension of Ru water oxidation catalysts to C-H activation in solution as well as on nanoparticle electrode surfaces; Anna Sberegaeva and Shrinwantu Pal (UMD), on their work with novel Pt(II) complexes and their reactivity toward O$_2$; Joanna Webb (UVA), Bruce Prince (UNT), and Travis Figg (UNT), on experimental and computational efforts to develop new C-O bond forming reactions with late transition metal systems.

The CCHF, represented by T. Brent Gunnoe (UVA), Jonathan Hull (UNC), and Joanna Webb (UVA), was invited to participate in the filming of an ACS video focused on the importance of federal funding. The video, which will be presented to the general public and policymakers, will address the CCHF scientific goals, the difference the Department of Energy, Energy Frontier Research Center funding has made in our research, as well as the societal good that could come from our progress.

A special session, the Commemoration of the Founding of the ACS Journal *Organometallics*, was held over three days honoring the Founding Editor-in-Chief Dietmar Seyferth, professor emeritus at Massachusetts Institute of Technology. Nearly 30 talks summarized old and new research results published in *Organometallics*, placing these results in the context of the future of the field. Speakers included John Bercaw, Maurice Brookhart, Charles Casey, John Hartwig, William Jones, Daniel Mindiola and Richard Schrock. All speakers acknowledged Dr. Seyferth’s commitment to publishing a high-impact journal and provided an anecdote based on their interaction with him while serving as editor. Although, Dr. Casey, a member of the CCHF Scientific Advisory Board, jokingly questioned his steadfast position on the importance of good elemental analysis results.

Numerous graduate students attended the talk by Jorge Cham, founder of PhD Comics. Cham’s talk focused on the power of procrastination and its role in maintaining sanity during graduate school, concluding that procrastination is essential to mental health.

The only thing missing from the meeting was industrial-sized dryers. Due to a relentless Nor’easter, attendees spent all four days of the meeting soaking wet and wrestling with inverted hotel umbrellas. However, some of the famous sights of Boston including the Freedom Trail, the site of the Boston Tea Party, Paul Revere’s home, the home of John and Abigail Adams, and Fenway Park made for a memorable trip.
Efficiency of electrocatalytic water oxidation is limited by the amount of catalyst which covers the electrode. Nanostructured oxide surfaces offer the potential to increase current density due to the increase in surface area. Researchers at UNC have demonstrated this concept with derivatized nanoITO (Sn(IV)-doped In$_2$O$_3$). In a recent communication (Dalton Trans. 2010, 39, 6950), Meyer et al. reported a 12-fold increase in current density using the same ruthenium (II) catalyst on nanoITO versus traditional electrodes. This corresponds to a turnover rate of 0.027 s$^{-1}$ and an O$_2$ yield of 95%. This nanoITO offers additional advantages because it is optically transparent thus allowing real-time, spectrophotometric monitoring of voltammograms. This new technology can also be applied to electrocatalytic hydrocarbon oxidation.

Oxidation of the metal-carbon bond in (HBpz$_3$)ReO(R)(OTf) [HBpz$_3$ = hydrotris(1-pyrazolyl)borate] by dimethyl sulfoxide (DMSO) or pyridine N-oxide was studied by the Mayer group in the mid 1990s. When R= phenyl (Ph), the Re-phenoxide was formed. Changing the R group to ethyl (Et) results in the exclusive formation of (HBpz$_3$)ReO$_3$ and acetaldehyde. In a recent publication (Organometallics 2010, 29, 2026), Goddard et al. used computation to examine the difference in mechanism. The reaction with (HBpz$_3$)ReO(Ph)(OTf) proceeds via 1,2-migration with a barrier of 17.9 kcal/mol. The barrier for 1,2-migration in (HBpz$_3$)ReO(Et)(OTf) is only slightly higher at 22.1 kcal/mol. However, a lower energy pathway (12.0 kcal/mol) exists which involves $\alpha$-hydrogen abstraction by OTf to give a Re-ethylidene. At this point, the oxidant transfers an O atom to form acetaldehyde. These results suggest that the identity of the R group greatly influences the reaction mechanism.

Partial and selective oxidation of hydrocarbons is the foremost goal of the CCHF. Recently, the Crabtree group described the partial oxidation of a variety of hydrocarbons using Cp* iridium catalysts (JACS 2010, 132, 12550). Using ceric ammonium nitrate as the terminal oxidant and water as the O-atom source, hydrocarbons are transformed to the corresponding alcohols in 10-72% yield. A labeling experiment where H$_2^{18}$O was used as the solvent showed that the labeled O was selectively incorporated into the product. Furthermore, these reactions show remarkable selectivity such that oxidation of cis-decalin gives 23% 9-decalol with a cis:trans ratio of 300:1.

Examples of iridium catalysts for the partial oxidation of hydrocarbons.
It is generally accepted that C-H activation is a fundamental step in the functionalization of hydrocarbons. To date, the best examples of catalytic hydrocarbon functionalization operate via electrophilic activation of the C-H bond in strongly acidic solvents. The Periana group recently published an extended communication which described complexes that achieve nucleophilic C-H activation in the presence of bases (JACS, 2010, 132, 12542). The complex (IPI)RuCl$_3$ where IPI = 2,6-diimidizolylpyridine undergoes in situ reduction with Zn to give the catalytically active $[(IPI)Ru^I(OH)(H_2O)]^+$. In the presence of KOD/D$_2$O and the ruthenium complex, water-soluble hydrocarbons such as isophthalic acid undergo H/D exchange. The most interesting aspect of this system is that the rate of H/D exchange is accelerated with increasing base concentration. This is the first example base promoted C-H activation.

Manganese porphyrins are active catalysts for the oxidation of hydrocarbons, producing only a small amount of halogenated byproducts. Adding a source of halogen, such as sodium hypochlorite, results in predominantly halogenated hydrocarbons. The Groves group has recently reported a biphasic system using Mn(TPP)Cl or Mn(TMP)Cl as the catalyst and sodium hypochlorite as the halogen source in the presence of tetrabutylammonium chloride as the phase transfer agent to selectively oxidize hydrocarbons to the mono-chloro product (JACS 2010, 132, 12847). A variety of hydrocarbons could be halogenated including neopentane (BDE =~100 kcal/mol). The chlorination of trans-decalin was selective for methylene protons, and when the Mn(TMP)Cl catalyst was employed, 2-chlorodecalin was produced with 76% selectivity. The mechanism is thought to involve radicals as evidenced by the rearrangement of norcarane.

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development of metal oxo complexes for hydrocarbon activation, 3) design of new materials for selective functionalization of hydrocarbons, 4) development of new methane fuel cells and 5) understanding of electrocatalytic reduction of carbon dioxide.

The central tenet of the CCHF is that catalytic conversion of small molecules, including CH$_4$, O$_2$, H$_2$O and CO$_2$, is a critical and key component to a new energy economy. The initial research focus will be on efforts related to the conversion of methane to liquid fuels, development of methane fuel cells and strategies for electrocatalytic reduction of carbon dioxide. In order to develop new fundamental chemistry relevant to solving challenging issues, research in the CCHF combines diverse expertise and multiple approaches. The researchers in the CCHF are experts in bioinorganic chemistry, catalysis, electrochemistry, inorganic chemistry, materials chemistry, organic chemistry and quantum mechanics. The CCHF is designed to support collaboration between multiple research groups such that difficult, high-stakes problems may be addressed.
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functionalization; specifically, metal oxo catalysts for C-H activation, oxygen-insertion chemistry, mixed metal oxides for ammoxidation reactions, mesoporous silica nanoparticles as supports for homogenous catalysts and the exploration of aluminum imido chemistry. The application of ruthenium catalysts for water-splitting (see page 2) to C-H activation was also discussed.

Keynote addresses were presented by Dr. Dan DuBois of the Pacific Northwest National Laboratory, Prof. Alan Goldman of Rutgers University and Prof. W. Dean Harman of the University of Virginia. Dr. DuBois spoke about the formation of transition metal hydrides with phosphino ligands featuring nitrogenous coordination sites. Prof. Goldman discussed C-H activation in the context of alkene isomerization and hydrogenation with iridium complexes. Prof. Harman’s address focused on transition metal activation of arenes for organic transformations. All three talks were well received and provided context for the goals of the CCHF.

A poster session was held on Thursday evening May 27 which featured work from CCHF researchers and UVA chemists. More than 20 posters were presented. The poster session reinforced the topics presented earlier in the day and allowed a forum for discussion of the current and proposed research in the CCHF.

Overall, the meeting was highly successful.

Upcoming Events

NOVEMBER 2010
- Subgroup Meetings

JANUARY 2011
- Subgroup Meetings
- Principal Investigator’s Meeting; January 7, 2011; Pasadena, CA

MARCH 2011
- Subgroup Meetings
- ACS National Meeting; March 27-31, 2011; Anaheim, CA

JULY 2011
- Subgroup Meetings

MAY 2011
- Department of Energy EFRC Meeting; May 24-27, 2011; Washington, DC

JUNE 2011
- CCHF Annual Meeting; June 2-3, 2011; Charlottesville, VA

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