CCHF
Center for Catalytic
Hydrocarbon Functionalization

Final Technical Report

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3. Executive Summary

Greater than 95% of all materials produced by the chemical industry are derived from a small slate of simple hydrocarbons that are derived primarily from natural gas and petroleum, predominantly through oxygenation, C–C bond formation, halogenation or amination. Yet, current technologies for hydrocarbon conversion are typically high temperature, multi-step processes that are energy and capital intensive and result in excessive emissions (including carbon dioxide). The *Center for Catalytic Hydrocarbon Functionalization* (*CCHF*) brought together research teams with the broad coalition of skills and knowledge needed to make the fundamental advances in catalysis required for next-generation technologies to convert hydrocarbons (particularly light alkanes and methane) at high efficiency and low cost. Our new catalyst technologies offer the many opportunities including enhanced utilization of natural gas in the transportation sector (via conversion to liquid fuels), more efficient generation of electricity from natural gas using direct methane fuel cells, reduced energy consumption and waste production for large petrochemical processes, and the preparation of high value molecules for use in biological/medical applications or the agricultural sector. The five year collaborative project accelerated fundamental understanding of catalyst design for the conversion of C–H bonds to functionalized products, essential to achieve the goals listed above, as evidenced by the publication of 134 manuscripts. Many of these fundamental advancements provide a foundation for potential commercialization, as evidenced by the submission of 11 patents from research support by the *CCHF*. Particular highlights of possible translation from fundamental advancement to application include: 1) Discovery of new main group catalysts for the conversion of light alkanes to alcohols, which serve as liquid fuels or precursors to higher value chemicals. This effort has led to the formation and funding of a start-up company. 2) Discovery of a new catalytic process for the conversion of arenes and olefins to alkenyl arenes, which are valuable commodity chemicals produced on a scale of hundreds of millions of pounds per year and used as precursors to plastics, soaps and detergents. This led to submission of a patent and ongoing discussions with three large chemical companies about possible development. 3) Development of novel catalysts for the halogenation of C–H bonds. This led to submission of a series of patents and establishment of a collaboration covering radio-labeling for PET imaging with Harvard Medical School/Mass General Hospital. Also, A new spin-off company, *Fluoromic Technologies*, LLC, was founded with the goal of commercially develop these techniques and discoveries. Research development collaboration contracts have been signed by Princeton University to develop aspects of these technologies both with Merck, Inc. and BMS, Inc. Those activities are actively under way. 4) Discovery of a new process, based on simple iodine oxides and chloride (i.e., table salt) for the conversion of light alkanes to alcohols, which serve as liquid fuels or precursors to higher value chemicals. A patent has been submitted for this process and funding to overcome obstacles for scale-up has been secured. (5) Discovery of a new fundamental mechanism underlying the highly selective oxidation of butane to maleic anhydride by the vanadium pyrophosphate heterogeneous catalyst. This new reductive-coupled oxo activation (ROA) mechanism was later (after the EFRC) shown to underlie the promising propane ammoxidation catalyst based on MoVNbTeOx, which led to a predicted new catalyst that would be highly selective. A patent on the development of new generation selective oxidation and ammoxidation catalysts has been filed.

4. Comparison of Research Goals and Accomplishments

Research in the CCHF was directed toward the development of new catalysts for the selective low temperature (generally ≤ 250 °C) conversion of hydrocarbons to higher value materials and related functionalization reactions of C–H bonds. A primary focus was on the conversion of alkanes from natural gas (methane, ethane and propane) to functionalized compounds such as esters, alcohols, diols, etc. Other hydrocarbon and C–H functionalization reactions were part of the CCHF portfolio, including applications in the energy sector, petrochemical industry and fine chemical sector. In addition to the selective functionalization of hydrocarbons, the CCHF supported a thrust targeted toward new catalysts for direct low temperature methane fuel cells. *All of these efforts are unified by the central theme of metal-mediated functionalization of C–H bonds.*

Research in the CCHF was organized into three major approaches, which were labeled as subgroups:

1) The C–H Activation Subgroup employed a strategy for hydrocarbon functionalization that involves initial metal-mediated C–H activation to generate an activated M–C species. Regardless of specific mechanistic details, the C–H activation occurs by an inner sphere pathway (i.e., direct coordination of the C–H bond to the metal center) without a change in oxidation state of the carbon (e.g., $CH_4 + M\text{–}X \rightarrow M\text{–}CH_3 + HX$).

2) The Oxygen Activation Subgroup focused on catalysts that initially form a reactive metal oxo complex, which is then responsible for the C–H functionalization.

3) The Fuel Cell subgroup applied both strategies for C–H functionalization (i.e., CH activation and oxygen activation) for the goal of complete oxidation of methane to CO_2.

I. Goals and Accomplishments for the C–H Activation Subgroup

Efforts in the C–H Activation Subgroup can be sub-categorized into pursuits involving electrophilic late transition metal catalysts and nucleophilic middle transition metal catalysts.

I.A. Electrophilic Late Transition Metal Complexes

I.A1) Goal: Develop a better understanding of catalytic methane functionalization using (bpym)$PtCl_2$ as catalyst (Project 1, p. 11, from 2012 EFRC Review document)

Status: The mechanistic studies of methane and ethane functionalization by (bpym)$PtCl_2$ are complete. Accomplishments include:

- Completed mechanistic study of methane functionalization by (bpym)$PtCl_2$ including elucidation of a key redox step which rapidly regenerates Pt(II) from Pt(IV) complexes.

- Ethane oxyfunctionalization by (bpym)$PtCl_2$ (bpym = 2,2'-bipyrimidine) occurs at rates 100x faster than methane and occurs by a *fundamentally different* catalytic cycle than methane oxyfunctionalization. Ethane oxyfunctionalization was determined to proceed through (now rate limiting) C–H activation, β-hydride elimination, ethylene functionalization, and Pt-hydride oxidation. This catalytic cycle is the first example of alkane oxyfunctionalization by linking classic C–H activation and β-hydride elimination steps and opens a new route for catalytic functionalization of C2 and higher alkanes.

I.A2) Goal: Develop electrophilic Rh catalysts for alkane functionalization (Project 2, p. 12, from 2012 EFRC Review document)

Status: There are three key steps in the desired overall catalytic cycle: 1) C–H activation, 2) oxidation of Rh(I) to Rh(III), and 3) reductive functionalization of Rh(III)-hydrocarbyl bonds. We have employed joint computational and experimental efforts to understand the features required for each step. Substantial progress was made understanding individual steps. Accomplishments include:

- Completed studies of (PNP)Rh complexes as potential catalysts for hydrocarbon functionalization. Here, it was demonstrated that the steric bulk of substituents on the phosphine ligands control the thermodynamics of Rh(III/I) redox reactions, and, hence, the kinetics of important Rh-alkyl functionalization reactions.

- Demonstration that Rh(I) complexes with weakly donating diimine ligands are very effective for catalytic C–H activation. To our knowledge, these catalysts are among the most rapid Rh catalysts for C–H activation of arenes in acidic media.

- Discovery that incorporation of electron withdrawing nitro groups on terpyridyl ligands of Rh(III) methyl complexes allow reductive functionalization of Rh–Me bonds to give MeX in both nonacidic and acidic media.

- We applied *ab initio* thermochemical calculations to intermediates and transition states responsible for the desired $H–CH_3$ cleavage and C–O bond-forming reactions to identify correlations between features of the free energy surfaces and the composition of the synthesized compounds. This approach has identified two new classes of complexes to prepare and test for catalysis: Rh complexes with 8,8'-(xylene)diquinoline ligand platforms and amidinate ligands.

I.A3) Goal: Study the reactivity of new Pd(II) and Pt(II) complexes with dioxygen with the ultimate goal of extending reactivity to aerobic catalytic reactions (Project 3, p. 13, from 2012 EFRC Review document)

Status: Mechanistic studies of aerobic oxidation using Pt(II) complexes were completed. Accomplishments include:

- The mechanism of the $(dpms)Pt^{II}Me(OH_n)^{(2-n)-}$ (dpms = 2-pyridyl-6-2-pyridylmethanesulfonate) oxidation in water to form $(dpms)Pt^{IV}Me(OH)_2$ and $(dpms)Pt^{IV}Me_2(OH)$ complexes was analyzed by means of kinetics and DFT calculations. At *pH* < 10, $(dpms)Pt^{II}Me(OH_n)^{(2-n)-}$ reacts with O_2 to form a methyl Pt^{IV}–OOH species with the methyl group *trans* to the pyridine nitrogen, which then reacts with $(dpms)Pt^{II}Me(OH_n)^{(2-n)-}$ to form two equivalents of $(dpms)Pt^{IV}Me(OH)_2$. At higher *pH*, the O–O cleavage is inhibited whereas the Pt-to-Pt methyl transfer is not slowed down so making the latter reaction predominant at *pH* > 12. It was concluded that the dpms ligand facilitates Pt(II) oxidation both enthalpically and entropically.

I.A4) Goal: Develop single-site Pt(II) catalysts using mesoporous silica nanoparticles (MSNs) (Project 4, p. 13, from 2012 EFRC Review document)

Status: We prepared and characterized a new single-site Pt material through covalent attachment of a molecular Pt complex to mesoporous silica nanoparticles (MSNs). This complex was demonstrate the be high efficient for aerobic oxidation of olefins. Accomplishments include:

- Pt(II) catalysts with dpms ligands on MSNs are highly effective catalysts for *aerobic* oxidation of olefins. To our knowledge, this is a unique example of Pt-mediated aerobic oxidation of olefin. Importantly, corresponding molecular complexes either do not produce oxidized product or are very inefficient, which demonstrates the importance of the dual approach incorporating both molecular catalysts and advanced nanomaterials.

I.B. Nucleophilic Middle Transition Metal Complexes

I.B1) Goal: Develop catalytic C–H functionalization using Ir catalysts with an emphasis on routes for functionalization of Ir–R bonds (Project 1, p. 14, from 2012 EFRC Review document)

Status: Progress was made on this goal (accomplishments are listed below), but emphasis on this project was reduced to focus on new results with main group catalysts (see Section I.B4 below).

- Developed new Ir catalysts supported by NNC ligands that catalyze C–H activation of benzene in trifluoroacetic acid at higher rates than the previous system.

- Ir-phenyl complexes were synthesized to test the stoichiometric functionalization of Ir-Ph to yield phenyl trifluoroacetate.

- Developed new Ir and Rh catalysts that catalyze C–H activation of CH_4 and benzene in strongly basic media.

I.B2) Goal: Study and develop O atom insertion into M–R bonds of middle transition metals (Project 2, p. 15, from 2012 EFRC Review document)

Status: Substantial progress was made understanding oxygen atom insertion into metal hydrocarbyl bonds. Accomplishments include:

- A joint theoretical/experimental study of O atom insertion into Fe^{II}-hydrocarbyl bonds validated the viability of O atom insertion using a metal and ligand set that is capable of C–H activation. Hence, we demonstrated, for the first time, that a complete catalytic cycle is viable by this new mechanism for hydrocarbon functionalization.

- Determined that flaviniums are effective catalysts for conversion of $MeReO_3$ and H_2O_2 to MeOH (in water) and established mechanism and rate enhancements.

- Combined computational and experimental studies demonstrated that O atom insertion into Rh(III) and Pt(II) hydrocarbyl bonds by Baeyer-Villiger type pathways have prohibitively large activation barriers. Also, using a systematic theoretical study, we predicted that activation barriers for O atom insertion into metal-hydrocarbyl bonds by Baeyer-Villiger type pathways are systematically lower for earlier metals and for first row transition metals. These results point toward design of catalysts that are likely to be viable for the O atom insertion pathways.

- Completed detailed experimental and computational mechanistic study of O atom insertion into W(VI) hydrocarbyl bonds that delineated three different mechanisms, and predicted relative rates under various conditions.

- Used quantum mechanics to identify V^{V}, Mn^{IV} and Cr^{V} as targets for methyl transfer from an organometallic $M–CH_3$ intermediate. This new mechanism involved successive one-electron reductions.

I.B3) Goal: Develop a better understanding of C–H activation using electron-rich M–OR complexes (Project 3, p. 16, from 2012 EFRC Review document)

Status: Project is complete:

- Completed a computational study that provide a basis to understand the ramifications of using electron-rich d^6 metal hydroxide and amides for C–H activation.

I.B4) Goal: Develop alkane and arene functionalization using main group elements (Note: this was a new goal implemented after the 2012 EFRC Review document)

Status: Made substantial novel advancements using main group elements to mediate light alkane and arene functionalization. These efforts have resulted in new intellectual property as well as high impact publications are emerging. Accomplishments include:

- Showed that main group oxidants based on thallium or lead are capable of selective and rapid functionalization of methane, ethane and propane. Reactions performed in acid produce esters of methanol, ethanol, ethylene glycol, isopropanol and 1,2-propylene glycol.

- Discovered that iodate or periodate with catalytic quantities of chloride are effective in nonsuperacidic media (e.g., trifluoroacetic acid, acetic acid) to convert methane, ethane and propane to corresponding mono-functionalized esters with high selectivity and conversion.

II. Goals and Accomplishments for the Oxygen Activation Subgroup

II.A1) Goal: Develop C–H functionalization catalysts based on oxometalloporphyrin complexes (Project 1, p. 17, from 2012 EFRC Review document)

Status: Developed manganese catalysts for C–H halogenation, including challenging fluorination reactions. Extended efforts to new catalysts based on Cr, Fe and Ni. Accomplishments include:

- Discovered and extended a novel and highly practical manganese-catalyzed method to fluorinate strong C–H bonds using fluoride. The efforts were expanded to include radioactive, positron emitting ^{18}F for PET imaging.

- Water-soluble cationic cobalt porphyrins were found to be effective catalysts for the four-electron oxidation of water to oxygen at neutral pH and moderate overpotentials. The ability to oxidize water suggests that these catalysts are likely viable for hydrocarbon oxidation.

- Discovered that water oxidation can be catalyzed by homogeneous, single-site manganese porphyrins at neutral pH in competition with C–H activation.

- Water-soluble cationic cobalt porphyrins were found to be effective H_2O oxidation catalysts at neutral pH and moderate over potentials. These complexes will be tested for catalytic C–H functionalization.

- Used quantum mechanics to predict that a novel *trans*-dioxo vanadium(V) porphyrin would be highly active for hydrogen abstraction from alkanes, due to the high bond energy of the incipient V=O···H bond. Experimental efforts have confirmed computationally predicted V–O–H bond dissociation energies for *cis* complex, but the desired *trans*-dioxo complex has not yet been accessed.

II.A2) Goal: Use electrocatalysis to study metal oxo catalysts for C–H functionalization (Project 2, p. 19, from 2012 EFRC Review document)

Status: Progress was made understanding mechanisms of Ru electrocatalysts for hydrocarbon oxidation, development of new Fe catalysts as well as new materials synthesis techniques to improve catalyst function and longevity. Accomplishments include:

- In non-aqueous propylene carbonate solvent (with just 1 % added water) $[Ru(Mebimpy)(4\text{-}4'\text{-}((HO)_2OPCH_2)_2bpy(OH_2)]^{2+}$, where Mebimpy is 2,6-bis(1-methylbenzimidazol-2-yl)pyridine and $4\text{-}4'\text{-}((HO)_2OPCH_2)_2bpy$ is 4,4'-bis-methlylenephosphonato-2,2'-bipyridine is capable of oxidizing alkylaromatics (toluene, ethylbenzene, and cumene) at room temperature. Oxidation occurs by mechanistically well-defined steps with product control and Faradaic yields up to 95%.

- Developed a spectroelectrochemical technique where the catalyst, $[Ru(Mebimpy)(4\text{-}4'\text{-}((HO)_2OPCH_2)_2bpy(OH_2)]^{2+}$ can be attached to the surface of optically transparent metal oxide electrodes, such as planar ITO (Sn(IV)-doped In_2O_3) and FTO (fluorine-doped SnO_2) electrodes and nanostructured ITO (*nano*ITO) and the spectral changes of the catalyst can be monitored real-time during electrochemical experiments to give insight into reactive intermediates.

- Four distinct intermediates, $Ru^{IV}{=}O^{2+}$, $Ru^{IV}(OH)^{3+}$, $Ru^{V}{=}O^{3+}$, and $Ru^{V}(OO)^{3+}$, formed by oxidation of $[Ru(Mebimpy)(4,4'\text{-}((HO)_2OPCH_2)_2bpy)(OH_2)]^{2+}$ on *nano*ITO have been identified and separately utilized for selective electrocatalytic benzyl alcohol oxidation to benzaldehyde in aqueous solution with rates ranging over four orders of magnitude.

- Successfully synthesized a new Ru dimer containing a water oxidation catalyst and light-absorbing chromophore, $[(bpy)_2Ru(4\text{-}Mebpy\text{-}4'\text{-}bimpy)Ru(tpy)(OH_2)]^{4+}$, that demonstrates electrocatalytic reactivity towards aliphatic hydrocarbon C–H bonds.

- During photocatalytic hydrocarbon oxidation studies, confirmed the transient and steady production of key intermediates, $-Ru^{III}OH_2^{3+}$, $-Ru^{III}OH^{2+}$ and $-Ru^{IV}O^{2+}$ - on surfaces co-loaded with $-Ru^{II}P^{2+}$ and $-Ru^{IV}O^{2+}$ by excitation of $-Ru^{II}P^{2+}$ to $-Ru^{II}P^{2+*}$, injection, and cross-surface electron transfer.

- Distinguished rapid ($>10^8$ s^{-1}) nearest neighbor electron transfer from slow (micro to millisecond) long-range electron transfer that occurs by multiple step and self-exchange electron transfer across the surface.

- Demonstrated that a monomeric Fe(III) complex, $[Fe(dpaq)(OH_2)]^{2+}$, where dpaq is 2-[bis(pyridine-2-ylmethyl)]amino-*N*-quinolin-8-yl-acetamido), promotes olefin epoxidation in organic media with H_2O as a co-substrate.

- Developed a new procedure for the fabrication of high-surface area metal oxide electrodes on reticulated vitreous carbon (RVC) supports.

- Applied atomic layer deposition (ALD) for the stabilization of a single-site hydrocarbon oxidation catalyst on metal-oxide electrode surfaces, including demonstration of unprecedented electrocatalytic oxidation reactivity under basic conditions.

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- Distinguished rapid ($>10^8$ s^{-1}) nearest neighbor electron transfer from slow (micro to millisecond) long-range electron transfer that occurs by multiple step and self-exchange electron transfer across the surface.

II.A3) Goal: Develop and study mechanism of C–H functionalization by Ir oxo complexes (Project 4 (Note: should have been labeled Project 3), p. 21, from 2012 EFRC Review document)

Status: Developed novel Ir oxo mediated C–H functionalization reactions and developed understanding of the mechanism of reaction of these unique complexes. Accomplishments include:

- Although metal oxo complexes are common intermediates in C–H functionalization chemistry, both biological and synthetic, examples of late transition metal oxo complexes (here, defined as Group 9 or later) functioning in this capacity are relatively rare. Work in the CCHF identified a novel series of Ir catalysts that oxidize C–H bonds, and mechanistic studies were used to delineate the reaction pathways. Computational studies implicated a formally Ir(VI) intermediate that functionalizes C–H bonds. This intermediate is best considered as an Ir(V) oxyl complex. Also, combined experimental and computational studies indicate that Cp*Ir precursors likely form a bis-*μ*-oxo iridium dimer as the active catalyst for hydrocarbon oxidation.

II.A4) Goal: Understand the mechanism of butane oxidation to form maleic anhydride using vanadium-based catalysts (note: this was a new goal added to the CCHF based on synergy with other metal-oxo based C–H functionalization catalysis).

Status: Discovered of a new fundamental mechanism underlying the highly selective oxidation of butane to maleic anhydride by the vanadium pyrophosphate heterogeneous catalyst. All experimental attempts at determining the mechanism had failed.

- We carried out the first full periodic boundary conditions DFT calculations (unit cells of 200 atoms) on this system. The newly proposed reductive-coupled oxo activation (ROA) mechanism explained the selectivity for all 14 steps connecting butane to maleic anhydride, with every activation barrier lower than 22 kcal/mol. The major surprise was that the P=O bond could activate the strong C–H bond of butane because it was coupled through a bridging oxygen to a reducible V=O center with oxidation state +5. This led then to activation barriers for all C–H activation steps less than 20kcal/mol.

- We examined the promising propane ammoxidation catalyst based on MoVNbTeOx for which the structure was too complicated for experimental mechanistic studies. Again, research in the CCHF carried out the first full periodic boundary conditions DFT calculations (unit cells of 200 atoms). Armed with the insight of the ROA mechanism (see above), the various steps responsible for the activation of propane to propene, which occurs on a site involving two Te=O sites (oxidation state +4) and one V=O site (oxidation state +5) connected by bridging oxygens, were disentangled. This site is connected to other V=O sites (oxidation state +5) through additional bridging oxygens. We used these insights to design new highly selective oxidative dehydrogenation catalysts for propane and ethane and more selective propane ammoxidation catalysts.

III. Goals and Accomplishments for the Fuel Cell Subgroup

III.A1) Goal: Develop electrochemistry of surface-attached complexes with hydrocarbons (Project 1, p. 23, from 2012 EFRC Review document)

III.A2) Goal: Synthesis of derivatives of known molecular CH catalysts that react with methane for attachment to electrodes (Project 2, p. 24, from 2012 EFRC Review document)

III.A3) Goal: Study the electrochemistry of known molecular CH activation catalysts in solution or surface-attached in the presence and absence of hydrocarbons (Project 3, p. 24, from 2012 EFRC Review document)

Status: The addition of Professor Andy Herring to the CCHF and Fuel Cell Subgroup had a positive impact on progress in the Fuel Cell Subgroup as efforts transitioned to the development new direct methane fuel cells. This project leveraged combined expertise in fuel cells, materials synthesis and molecular catalysts. Exciting progress was made, but substantial opportunities for fundamental advancement and development of new fuel cells remain. Accomplishments include:

- Demonstrated, for the first time, covalent attachment of molecular ligands for tethering single-site molecular catalysts to the surface of ordered mesoporous carbon. This novel synthetic approach allowed us to develop first generation anode catalysts for direct methane fuel cells that operate at low temperatures (< 100 °C) and are not poisoned by carbon monoxide. These catalysts achieve 250 μW $mgPt^{-1}$, which provides a *three order of magnitude improvement* over the performance reported by General Electric in the 1960s and *an order of magnitude better* than a commercial ELAT electrode with methane. This is notable since these Pt catalysts do not represent optimized materials but rather are the initial entry point. We have shown that the activities of our first generation Pt catalysts are dependent on the ligands of the active Pt site, and the observed structure/activity relationship as a function of ligand identity lends confidence that the catalysts can be tuned to enhance performance.

- Coated reticulated vitreous carbon electrodes with *nano*ITO demonstrated enhanced surface area for surface attached electrocatalysts. The resulting hybrid electrodes are highly stabilized toward elevated temperatures and under strongly oxidative conditions.

5. Project Activities

***Mission Statement*:** The Center for Catalytic Hydrocarbon Functionalization fostered collaborations among groups with expertise in catalysis, inorganic chemistry, electrochemistry, bioinorganic chemistry, materials chemistry, organic chemistry and computational chemistry to enable fundamental advancements leading to next generation catalysts for selective, low temperature, hydrocarbon functionalization.

The CCHF aimed to develop improved hydrocarbon functionalization catalysis by developing new highly efficient molecular catalysts or supported molecular catalysts for direct oxidation/functionalization of hydrocarbons to valuable materials and fuels. Although light alkane conversion was a focus, we also sought catalysts for conversion of more complex hydrocarbons.

One of the foremost challenges for the development of catalysts for the selective functionalization of hydrocarbons (especially the conversion alkanes to alcohols) is achieving high selectivity at high product concentrations. Despite advances in techniques to characterize surfaces and to study reactivity of solid-state systems, the complexity of heterogeneous catalysis and surface reactivity makes it difficult to elucidate novel and well-defined mechanisms. Furthermore, rational tuning of solid catalysts remains difficult. Highly selective catalysts for hydrocarbon functionalization would benefit from rational catalyst design based on thorough mechanistic understanding and controlled synthesis. As a result, catalyst design in the CCHF incorporated homogeneous and supported catalysts based on molecular complexes. Although the majority of large-scale industrial processes use heterogeneous catalysts, examples of homogeneous catalysts for large-scale processes are known, and thus there are no inherent features that would prevent use of a homogeneous catalyst system for scaled hydrocarbon functionalization reactions.

The generation of reactive free radicals has been used to functionalize hydrocarbons including light alkanes. But, the homolytic C–H bond dissociation enthalpy (BDE) of CH_3X products [X = Cl (BDE = 100 kcal/mol), Br (BDE = 101 kcal/mol), or OH (BDE = 96 kcal/mol)] are lower than the C–H BDE of methane (105 kcal/mol). Thus, a common disadvantage of processes that exploit reactive radical intermediates is greatly reduced selectivity at higher conversions. As a result, the CCHF emphasized non-radical processes or processes in which radical products are protected from rapid reaction. This allowed us to build in selectivity that opposes trends in C–H BDEs.

The unifying element to all research thrusts in the CCHF was the development of molecular or single-site supported catalysts for the selective conversion of C–H bonds of hydrocarbons, especially methane, to C–X bonds (where X is not H). This fundamental link between the different pursuits in the CCHF provided intellectual overlap and synergy among the center's research thrusts. We pursued two main strategies for C–H functionalization:

- The C–H Activation Subgroup used metal-mediated C–H activation to generate an activated M–R species that is functionalized in subsequent steps. The C–H activation step occurs by direct coordination of the C–H bond to a metal center without a change in oxidation state of the carbon.

- The Oxygen Activation Subgroup used reactive metal oxo complexes (or related, such as metal imido) to functionalize the C–H bond. There is no direct interaction between the metal and the C–H bond, and the cleavage of the C–H bond increases the carbon oxidation state.
- Our pursuit of catalysts for direct methane fuel cells (Methane Fuel Cell Subgroup) incorporated both C–H functionalization strategies for complete oxidation of methane to CO_2.

I. Activities for the C–H activation subgroup

Substantial fundamental advancements were achieved by the efforts in the C–H activation subgroup of the CCHF. For example, we: A) developed a deeper understanding of the catalysis using electrophilic Pd and Pt catalysts in acidic media, including a novel extension to efficient functionalization of ethane, a major component of natural gas, to high value partially oxidized products and a detailed understanding of aerobic oxidation transformations; B) demonstrated that with rational design of ancillary ligands metal-alkyl bonds of "earlier" transition metals (i.e., earlier than Group 10) can undergo reductive nucleophilic functionalization, which opens the possibility of catalytic alkane partial oxidation in non-super acidic media; C) using the strategy described in "B," new catalysts for the single step production of alkenyl arenes were developed, which has attracted considerable industrial attention; D) designed and demonstrated that covalent attachment of molecular catalysts onto mesoporous silica nanoparticles enables efficient and stable aerobic oxidation of olefins (these materials represent a novel approach for hydrocarbon oxidation processes); E) demonstrated and developed unprecedented and impactful alkane partial oxidation using simple main group elements (importantly, these processes are efficient for methane, ethane *and* propane); F) discovered a novel iodate and periodate mediated light alkane partial oxidation using inexpensive chloride salts (importantly, these processes are efficient for methane, ethane *and* propane); G) advanced fundamental understanding focused on the design of transition metal complexes that mediate C–O bond formation, which is a key step in hydrocarbon partial oxidation chemistry. A few illustrative and more specific examples of activities and outcomes of the C–H activation subgroup are given below:

→ A detailed mechanistic and theoretical analysis of ethane functionalization by (bpym)$PtCl_2$ in sulfuric acid revealed significant details about this surprising process, including: a) Ethylbisulfate is the kinetic product of the reaction, which is then converted into isethionic acid under the reaction conditions. b) Efficient catalysis for ethane oxyfunctionalization occurs at rates 100x faster compared to methane and is the result of a *fundamentally different* catalytic cycle. Ethane oxyfunctionalization proceeds through rate limiting C–H activation, β-hydride elimination, ethylene functionalization, and Pt-hydride oxidation. c) This catalytic cycle is the first example of alkane oxyfunctionalization by linking classic C–H activation and β-hydride elimination steps.

→ We completed an effort to quantify and compare rates of C–H activation using new rhodium complexes supported by diimine ligands, (BO)Rh(coe)(TFA) (BO = 2,2'-bisoxazoline); coe = cyclooctene; TFA = trifluoroacetate) and (DAB^F)Rh(coe)(TFA) (DAB^F = *N*,*N*-bis-(pentafluorophenyl)-2,3-dimethyl-1,4-diaza-1,3-butadiene). These complexes are among the most activate catalysts for arene C–H activation that function in acidic media and demonstrated that will careful ligand design, informed by understanding of reaction mechanisms, middle transition metal catalysts can activated C–H bonds in the presence of protic solvents. We reported that the electron-deficient nature of ancillary ligands is important to prevent highly exothermic and irreversible oxidation to form Rh(III) in acidic media.

→ Experimental realization of computational predictions regarding the increased efficacy of electron-withdrawing functionalities on poly-pyridyl supporting ligands for C–X bond formation by Rh(III)-methyl complexes. We demonstrated that $[(NO_2)_3\text{terpy}]RhMeX_2$ undergoes reductive elimination of MeCl and MeTFA (TFA = trifluoroacetate), whereas $[(^t\text{Bu})_3\text{terpy}]RhMeX_2$ does not eliminate MeX. *These reactions are central and critical for overall catalytic conversion of light alkanes to oxyfunctionalized products, which are important for new routes to upgrade natural gas.* Importantly, $[(NO_2)_3\text{terpy}]RhMeX_2$ undergoes reductive functionalization in HTFA, acetic acid, and water to yield 25% MeTFA, 40% MeOAc, and 70% MeOH, respectively. These are, to our knowledge, the only examples of oxyfunctionalization of Rh–R bonds in acidic media. In contrast, $(^t\text{Bu})_3\text{terpy}]RhMeX_2$ gives only protonation to form CH_4, which is the expected and more commonly observed reaction of Rh–Me bonds. These results demonstrate that ligand donor ability can be used to tune Rh^{III} methyl complexes toward formation of MeX over methane in acidic media.

→ Kinetics and mechanistic study of the previously discovered photo-initiated aerobic oxidation of $(\text{dpms})Pd^{II}Me(OH)^-$ (dpms = 2-pyridyl-6-2-pyridylmethanesulfonate) leading to methanol and ethane in water were performed. The Pd^{IV} dimethyl complex $(\text{dpms})Pd^{IV}Me_2(OH)$, an intermediate in the aerobic oxidation of $(\text{dpms})Pd^{II}Me(OH)^-$, was shown to be inert in C–O bond forming reactions. But, $(\text{dpms})Pd^{IV}Me_2(OH)$ undergoes facile and clean elimination of ethane at 21 °C ($t_{1/2}$ = 6 min). The analogous monomethyl complex, $(\text{dpms})Pd^{IV}Me(OH)_2$, a presumed intermediate responsible for methanol formation, could not be observed even when oxidation was performed at -60 °C using $NaIO_4$ in aqueous methanol. Instead, $(\text{dpms})Pd^{IV}Me_2(OH)$ formed. These results highlight facile Me group transfer between Pd metals, which suggest Pd catalysts are likely more viable for methane to ethane conversion rather than methane oxyfunctionalization. These results were extended to the Pt complex $(\text{dpes})Pt^{II}Me(OH_2)$ (dpes = 2-pyridyl-6-2-pyridylethanesulfonate). A theoretical analysis of the oxidation reactivity of $(\text{dpes})Pt^{II}Me(OH_2)$ showed that the steric congestion created by the extra methyl group at the bridging carbon lowers the barrier for the oxidation step and enhances thermodynamic stability of the Pt^{IV} product.

→ The mechanism of aerobic oxidation of $(\text{dpms})Pt^{II}Me(OH_n)^{(2-n)-}$ was determined by a joint experimental/computational effort. It is concluded that the dpms ligand facilitates oxidation of Pt(II) to Pt(IV) both enthalpically and entropically.

→ Demonstrated epoxidation of norbornene with molecular oxygen by $C\text{-}^{\text{alkyl-1}}$DPMS-TMOS-MSN *with dramatically improved activity and stability over molecular catalyst*. For the MSN supported catalysts, deactivated, insoluble dimer was not observed, unlike the molecular species. These experiments validate the strategy of tuning molecular catalysts for selectivity and reactivity then supporting on nanoparticles to enhance catalyst stability.

→ A substantial effort was to develop alkane functionalization using main group elements, and much progress was made. For example, telluric acid ($Te(OH)_6$) was determined to react with methane, ethane and propane to generate Te–alkyl products in TFA_2O/HTFA solvent. While *in-situ* ^{1}H NMR studies suggest that complex mixtures of products are obtained with ethane and propane, only a singular product is observed for methane. In an effort to move from stoichiometric to a catalytic system for main group elements, we began to examine Bi^V as a potential catalyst. $Bi(TFA)_3$ in HTFA was demonstrated to activate alkanes with high yield and selectivity. Many other examples of main group mediated alkane functionalization were developed, and this chemistry forms the foundation of an entirely new approach for the conversion of natural gas to liquid fuels and high value chemicals.

→ The study of iodine-based alkane partial oxidation was pursued. For example, a new process using iodate or periodate in combination with catalytic amounts of chloride for hydrocarbon functionalization was developed. Also, the direct partial oxidation of methane, ethane, propane to their respective trifluoroacetate esters by the ligated I^{III} reagents C_6H_5-I(OAc)$_2$ and C_6F_5-I(TFA)$_2$ was achieved. Mechanistic studies support a non-free-radical electrophilic C–H activation and an alkyl-iodonium salt reductive functionalization mechanism.

→ Broad understanding of metal-mediated C–O bond formation was achieved. This effort involved a collaborative team consisting of the Gunnoe, Goddard, Groves, Periana and Cundari groups. A primary conclusion is that a highly nucleophilic alkyl group is required to achieve O atom insertion from single O atom donor reagents.

II. Activities for the oxygen activation subgroup

Fundamental goals of the oxygen activation subgroup were to access novel types of catalysts that involve metal oxo intermediates, develop new electrocatalytic approaches (which have not been applied to hydrocarbon functionalization), understand ligand design to control selectivity and to access impactful halogenation reactions. Major advancements were achieved, including: A) discovery of unique Ir oxo catalysts for hydrocarbon oxidation; B) novel Mn based catalysts where use of axial ligand to control rates of rebound are critical to product selectivity and catalytic efficiency for C–H halogenation reactions; C) elucidation of substantial details of electrocatalytic hydrocarbon oxidation using Ru based catalysts, where it has been demonstrated that many catalysts for water oxidation are substantial potential also for hydrocarbon functionalization chemistry; D) discovery of a new mechanism for butane oxidation using V based catalysts. A few illustrative and more specific examples of activities and outcomes of the oxygen activation subgroup are given below:

→ Novel C–H halogenation reactions (chlorination, bromination and fluorination) using non-heme manganese catalysts were achieved. For example, work in the CCHF elucidated and extended a practical manganese-catalyzed method to fluorinate strong C–H bonds using fluoride. The effort has expanded to include radioactive, positron emitting ^{18}F for PET imaging. For example, CCHF funded work has resulted in the first aliphatic C-H ^{18}F-fluorination reaction for PET imaging:

- For developing ^{18}F labeling reactions, the first challenge is the low concentration of [^{18}F]fluoride (~10^{-4} M). The manganese salen fluorination catalyst with a weak coordinating axial ligand, *p*-toluenesulfonate (OTs), can effectively trap the low-concentration [^{18}F]fluoride with over 90% efficiency.
- Another challenge for ^{18}F labeling is the short half-life of ^{18}F (110 min). Catalysts developed in the CCHF can efficiently label various molecules *within 10 minutes* with remarkable radiochemical yield (RCY) up to 74%.
- In sharp contrast with most other ^{18}F labeling methods, methods developed in the CCHF showed good water tolerance. Even with 3% water in the reaction solution, we can still observe a moderate RCY. This is a significant advantage. Utilizing this feature and the high affinity between Mn(salen)OTs and [^{18}F]fluoride, we can circumvent the conventional and laborious [^{18}F]fluoride "dry-down" process that is usually required prior to the labeling step, dramatically shortening the time for automated synthesis and preserving high levels of the imaging label.

→ We found that the method is applicable to late-stage ^{18}F-labeling of a variety of small molecule probes, building blocks and bioactive molecules. Without the need for target pre-activation, the method leads to fast access to labeling molecules that are hard to make or inaccessible by previous methods and high-throughput radiolabeling is enabled.

→ Water-soluble cationic cobalt and manganese porphyrins were found to be effective water oxidation catalysts at neutral pH and moderate overpotentials. These catalysts were extended to hydrocarbon oxidation in aqueous solutions. Scant attention has been given to using catalysts for water oxidation for hydrocarbon oxidation, and we believe that work in the CCHF effectively highlights synergistic opportunities.

→ While heme thiolate proteins have been shown to have basic ferryl oxygen, the same has not been shown for synthetic model systems that are used in oxyfunctionalization reactions. We measured such a pKa for the first time. Ferryl heme oxo moieties of model systems were found to be basic with an observable pK_a. This suggests that the ability of Fe porphyrin model systems to hydroxylate C-H bonds derives from both the oxidizing power of the complex and the pK_a of the corresponding ferryl complex. The discovery that ferryl oxygen can be basic will influence how chemists consider development of first-row transition metal oxo catalysts for hydrocarbon oxidation.

→ We developed a detailed understanding focused on utilization of well-defined Ru *electrocatalysts* for hydrocarbon oxidation. For example, $[Ru(Mebimpy)(4\text{-}4'\text{-}((HO)_2OPCH_2)_2bpy(OH_2)]^{2+}$ (Mebimpy = 2,6-bis(1-methylbenzimidazol-2-yl)pyridine; $4\text{-}4'\text{-}((HO)_2OPCH_2)_2bpy$ = 4,4'-bis-methlylenephosphonato-2,2'-bipyridine) is capable of oxidizing alkylaromatics (toluene, ethylbenzene, and cumene) at room temperature. Oxidation occurs by mechanistically well-defined steps with product control and Faradaic yields up to 95%. Four distinct intermediates, $Ru^{IV}{=}O^{2+}$, $Ru^{IV}(OH)^{3+}$, $Ru^{V}{=}O^{3+}$, and $Ru^{V}(OO)^{3+}$, formed by oxidation of $[Ru(Mebimpy)(4,4'\text{-}((HO)_2OPCH_2)_2bpy)(OH_2)]^{2+}$ on *nano*ITO were identified and separately utilized for selective electrocatalytic benzyl alcohol oxidation to benzaldehyde in aqueous solution with rates ranging over four orders of magnitude. Also, these efforts were extended to successfully synthesize a new Ru dimer containing a water oxidation catalyst and light-absorbing chromophore, $[(bpy)_2Ru(4\text{-}Mebpy\text{-}4'\text{-}bimpy)Ru(tpy)(OH_2)]^{4+}$, and demonstrated electrocatalytic reactivity towards aliphatic hydrocarbon C–H bonds. Also, a focus of this project was to attach molecular catalysts to solid supports, and much fundamental advancement in synthetic and characterization was achieved, including the development of a new procedure for the fabrication of high-surface area metal oxide electrodes on reticulated vitreous carbon (RVC) supports and the use of atomic layer deposition (ALD) for the stabilization of a single-site hydrocarbon oxidation catalyst on metal-oxide electrode surfaces.

→ The fundamental mechanism underlying the highly selective oxidation of butane to maleic anhydride by the vanadium pyrophosphate heterogeneous catalyst had remained a mystery since its discovery at Monsanto in ~1980. This catalyst is the basis for industrial production of 500 kilotons of maleic anhydride annually. Everyone "knew" that the V=O bonds must be responsible but there was no hint for why they would be sufficiently active nor any credible sequence for the 14 steps needed to convert butane to maleic All experimental attempts at determining the mechanism had failed. Efforts in the CCHF focused on the first full periodic boundary conditions DFT calculations (unit cells of 200 atoms) on this system. This led to the very surprising result that the P=O bond could activate the strong CH bond of butane with a barrier of only 14 kcal/mol. In analyzing these results we discovered that is because it was coupled through a bridging oxygen to a reducible V=O center with oxidation state +5.

→ $Cp^{*}Ir^{III}(chelate)Cl$ (chelate = multiple bidentate ligands) and related complexes were demonstrated to be precatalysts for stereoretentive hydroxylation using Ce^{IV} salts or $NaIO_4$ as stoichiometric oxidants. Light hydrocarbons such as methane and ethane can be functionalized yielding the overoxidized products of CO_2 and HOAc. Although the oxidation of methane and ethane is not selective, the ability to functionalize these light alkanes with a metal oxo complex is very rare and is a noteworthy advance toward general functionalization of strong C–H bonds. Detailed mechanistic studies reveals that the Cp* ligand is lost under catalytic conditions, but nanoparticle formation is not observed for Cp^*Ir^{III}(chelate)Cl suggesting homogenous catalysis. Ultimately, the active catalyst was identified as a binuclear di-μ-oxo-di-Ir(IV) complex that retains the chelate ligand.

III. Activities for the fuel cell subgroup

The focus on fuel cell developments for transportation has used hydrogen as the fuel. Although this seems to provide power with minimal CO_2 footprint, there remain serious problems, particularly generation of H_2 (without solar or nuclear power H_2 is produced by reforming hydrocarbons leading to CO_2 production) and storage. Development of efficient, direct methane fuel cells that operate at low temperatures (< 250 °C) would constitute a major breakthrough since there are enormous CH_4 reserves. A direct methane fuel cell operating at low or intermediate temperature is highly challenging, with very few literature reports. Activation of the strong C–H bond is the key step in the oxidation. But the advantages of methane such as large gravimetric energy density, 55.6 MJ kg^{-1}, and easy availability have elicited much interest in the direct methane fuel cell. The theoretical overall cell potential for a direct methane fuel cell is 1.084 V.

Current fuel cells for natural gas typically operate either integrated external reforming to generate H_2 or fuel cells based on solid oxides or molten carbonates at high temperatures (>800 ºC). The high temperatures are required since CH_4 shows almost no reactivity at lower temperatures (<200 ºC) with the most active electrodes developed to date. Fuel cells based on the direct use of CH_4 that operate at <200 ºC could increase efficiency, allow broader use and faster implementation and dissemination that could reduce both dependence on petroleum. In addition, given efficiency increases compared to combustion engines, scaled use of low temperature methane fuel cells could dramatically reduce CO_2 emissions. The focus of the research in the fuel cell subgroup was to design of anodic electrocatalysts for the half-cell reaction that could be used to design lower temperature (<200 ºC) direct CH_4 fuel cells. Such a challenge **<u>lies at the interface of organometallic chemistry, electrochemistry, materials science and engineering.</u>** Hence, the CCHF was uniquely positioned to address this challenge. Thus, the CCHF built on its core focus of catalytic C–H conversion to design electrocatalysts for fuel cell applications. This subgroup achieved new fundamental advancements using molecular catalysts supported on various materials for electrocatalytic methane oxidation. <u>Importantly, we developed (to our knowledge) the most active low temperature *direct* methane fuel cell catalyst.</u> A few illustrative and more specific examples of activities and outcomes of the fuel cell subgroup are given below:

→ We developed well-defined platinum organometallic complexes covalently anchored to ordered mesoporous carbon (OMC) for electrochemical oxidation of methane in a proton exchange membrane fuel cell at 80 °C. A maximum normalized power of 403 μW/mg Pt was obtained, which was 5 times higher than a modern commercial catalyst and two orders of magnitude greater than Pt black catalyst. The observed differences in catalytic activities for oxidation of methane were linked to the chemistry of the tethered catalysts, determined by X-ray photoelectron spectroscopy. The chemistry/activity relationships demonstrate a novel and tangible path for the design of electrocatalytic systems for C–H bond activation that afforded superior performance in direct methane fuel cells for potential commercial applications.

→ Successfully demonstrated the synthesis, and verified through considerable material characterization including nitrogen sorption, electron microscopy (TEM & SEM), and X-ray diffraction, of highly uniform ordered mesoporous carbon (OMC) materials with tunable pore sizes and controlled morphology. For example, demonstrated, for the first time, covalent attachment of molecular ligands for tethering single-site molecular catalysts to the OMC surface. Specifically, we demonstrated that a bromo derivative of 2,2'-bipyridine can be covalently tethered to OMC through lithiation of defect sites in the sp^2 carbons on the surface. Following the attachment of the ligand, we coordinated copper and demonstrated selective oxidation of benzyl alcohol. The tethered material was fully characterized by Raman spectroscopy, X-ray photoelectron spectroscopy, thermogravimetric analysis and titration of the bipyridines by HCl to verify that the catalysts were covalently attached to the OMC surface.

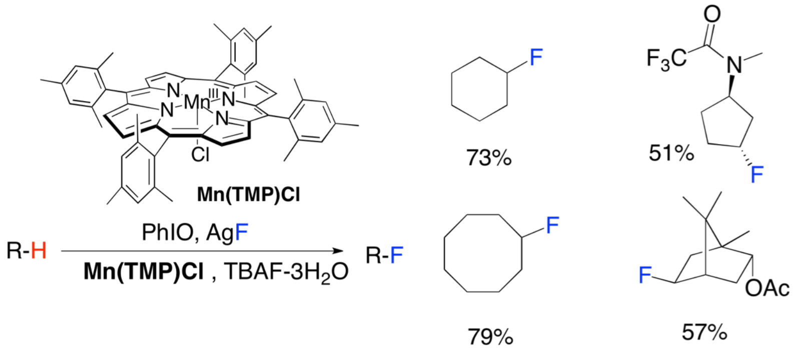
→ We coated reticulated vitreous carbon (RVC) electrodes with *nano*ITO, which enhanced the surface area for surface attached electrocatalysts. At the same time, the resulting hybrid electrodes are highly stabilized towards elevated temperatures and under strongly oxidative conditions.

→ We studied catalysis using both anion exchange and proton exchange membranes. The membrane electrode assembly for the anion exchange direct methanol fuel cells was fabricated using the ruthenium oxo based molecular catalyst and commercial platinum catalysts as the anode and a commercial catalyst based on iron and cobalt (carbon supported) from Acta® as the cathode catalyst with a polyphenylene based anion exchange membrane (supplied from Sandia National Lab). The direct methane fuel cells based on a proton exchange membrane used the Nafion™ 117 membrane and a commercial carbon gas diffusion layer with platinum catalysts as electrodes. Various ratios of ruthenium molecular catalyst to commercial platinum catalyst were studied as anode material for alkaline direct methanol fuel cell (DMAFC) to optimize the best ratio in terms of performance. *Improved methanol fuel cell performance was shown in the presence of the ruthenium based molecular catalysts and platinum as compared to the baseline platinum-only anode catalyst.* Studies were done as a function of anode and cathode temperatures to optimize performance at 30 °C anode temperature and 50 °C cathode temperature. The maximum current density was 11.69 mA cm^{-2} and the peak power density was 2.8 mW cm^{-2} at this experimental condition, this performance is 2 orders of magnitude greater than previously reported.

Summary of Activities and Outcomes

The fundamental advancements outlined above moved the field of catalytic hydrocarbon functionalization into dramatically new and novel directions and opened several new avenues for potential application. These advancements were built on highly collaborative efforts between groups with a wide range of expertise including catalysis, inorganic chemistry, electrochemistry, bioinorganic chemistry, materials chemistry, organic chemistry and computational chemistry. Many of these advances are in various stages of study for potential application. Thus, we believe that the research efforts in the CCHF effectively achieved primary goals of the EFRC program: 1) to advance fundamental science based on collaborative efforts and 2) to focus efforts on "use inspired research" where new advancements present maximum opportunity for potential commercial and societal impact. Below is an outline of fundamental research in the CCHF that led to new intellectual property (note that the details below provide only a brief overview):

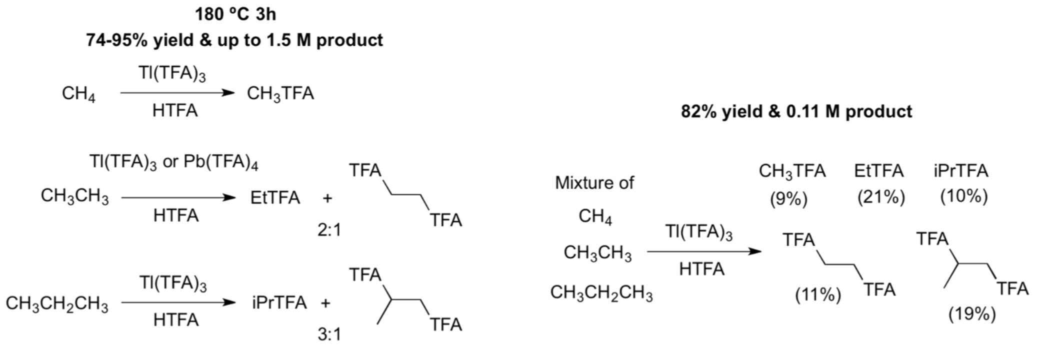
Mn Catalysts for C–H Fluorination: Research in the CCHF resulted in the discovery that Mn porphyrin complexes catalyze alkyl C–H chlorination and bromination using hypohalite under mild conditions. Importantly, substrates with strong C–H BDE, such as neopentane (BDE ~100 kcal/mol), can be selectively halogenated. Mechanistic investigations of the chlorination reaction revealed that certain axial ligands such as fluoride, hydroxide and oxo could dramatically reduce the radical rebound rate, which provides a strategy to control the functionalization step. The chlorination chemistry was extended to Mn porphyrin catalyzed C–H fluorination using fluoride ion under mild conditions (Scheme 1). Simple alkanes and complex molecules are selectively fluorinated at otherwise inaccessible sites. Experiments and DFT calculations published in *Science* show that in the fluorination reaction F atom transfer from Mn(Por)F_2 to alkyl radical has a surprisingly low activation barrier, suggesting the involvement of a trans-difluoro Mn complex in the catalytic cycle.



Scheme 1. Mn-catalyzed fluorination of hydrocarbons.

The discovery of this new reaction to convert simple fluoride ion sources into fluorinating agents has far-reaching practical implications. Many of the small organic molecules that have been prepared in useful quantities are new compositions of matter. Drug companies are interested in these compounds as building blocks for fluorinated versions of known and new drugs. Other molecules will be of use to micro-electronic fabrication technologies. A further advantage of Mn-fluorides over electrophilic fluorinating agents is the very practical application of radioactive PET tracer studies using the short-lived ^{18}F isotope. While technically challenging, this new catalytic fluorination has already cleared formidable hurdles and is in development now.

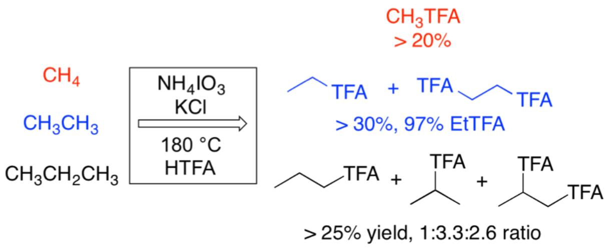
Main Group Catalysts: One important disadvantage is that transition metals with a d electron count < 10 often exhibit prohibitively slow RH coordination that is required for C–H activation due to loss of ligand field stabilization energy (LFSE). This disadvantage can be overcome through the use main group (MG) elements. With completely filled d-orbitals (d^{10}), MG elements are not subject to a loss of LFSE during RH coordination and coordination can be orders of magnitude faster compared to transition metal systems. Additionally, MG elements can form polar-covalent M–C bonds that can facilitate both C–H activation and M-R functionalization. These characteristics coupled with the high electrophilicity and oxidation potential of MG cations such as those based on I^{III}, Se^{VI}, Te^{VI}, Tl^{III} , Pb^{IV}, Bi^{V}, etc., suggest that these could be the basis for effective systems for alkane C–H functionalization. CCHF researchers demonstrated that several of these MG cations, I^{III}, Tl^{III} and Pb^{IV} (MX_n) efficiently react with methane, ethane and propane at 180 ºC to generate molar amounts of alcohols at >95% selectivity and near quantitative yields based MX_n (Scheme 2). Thus, methane can be selectivity converted to methanol, ethane to ethanol (easily converted to ethylene) and ethylene glycol and propane to isopropanol (easily converted to propylene) and propylene glycol with high. These reactions can be carried out with a mixture of methane, ethane and propane to selectively generate the corresponding alcohols in "one pot." This would avoid costs currently associated with separation of the light alkanes from natural gas feedstocks.



Scheme 2. Results for alkane functionalization using main group catalysts.

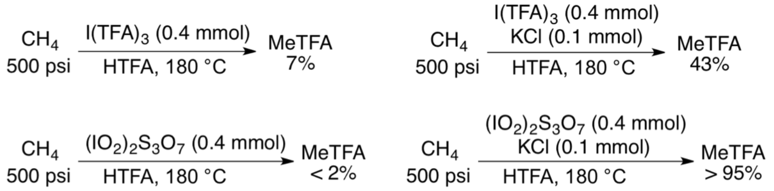
New Iodine-Based Process: Iodine species are capable of functionalizing non-polar C–H bonds through non-radical pathways. But, transitioning these catalysts to weaker acids or more dilute media has been a challenge. Researchers in the CCHF discovered that the combination of iodate or periodate and chloride is efficient for converting light alkanes (methane, ethane and propane) to mono-functionalized products in protic media.

Scheme 3 summarizes results in HTFA (TFA = CF_3CO_2), which is the optimal solvent from our preliminary studies. The reactions work over a range of temperatures (100 °C – 235 °C) and pressures (100 – 800 psi). Rates of conversion are excellent. For example, ~25% methane conversion (500 psi) is observed in 20 minutes at 235 ºC, and at ~20% methane conversion < 2% is over-oxidized only to $^{13}CO_2$ with CH_2X_2 and CHX_3 products not observed under most conditions. Ethane conversion and selectivity are excellent at >30% with nearly quantitative selectivity for mono-functionalized EtX (X = TFA or Cl).



Scheme 3. Iodate/chloride mediated conversion of light alkanes gives high yields and selectivity after 1 h at 180

Stoichiometric methane conversion using $I(TFA)_3$ or $[IO_2]^+$ is not efficient in the absence of chloride, but when KCl is added MeTFA production is efficient (Scheme 4). Methane conversion is successful in acetic acid, perfluorobutyric acid, HTFA diluted with water (3:1 mol:mol HTFA:water is efficient medium), $HTFA/C_6F_{12}$ mix and water. The addition of O_2 to methane or ethane reaction does not alter product distribution or the efficiency of the conversion. The oxidation of toluene by KCl/KIO_3 results only in electrophilic aromatic halogenation products.



Scheme 4. Impact of chloride on stoichiometric conversions of methane using $I(TFA)_3$ and $(IO_2)_2S_3O_7$.

Enhanced Surface Area Oxide Electrodes for Electrosynthetic Applications: High surface area electrodes consisting of thin layers of nano-structured ITO (Sn(IV)-doped indium tin oxide, *nano*ITO) on reticulated vitreous carbon (RVC) electrodes were designed and fabricated (Figure 1). Greatly enhanced effective surface areas are achieved by coating the RVC electrodes with *nano*ITO derivatized with surface-bound phosphonated catalysts. The resulting hybrid electrodes are highly stabilized at elevated temperatures and under highly oxidative environments; conditions that would lead to oxidation of the bare RVC electrode. This approach offers a versatile platform for electrocatalysis that can be applied to C–H bond functionalization reactions.

New Catalysts for Single-Step Production of Alkenyl Arenes: Research in the CCHF demonstrated how to stabilize Rh(I) catalysts for C–H activation under oxidizing conditions. This fundamental advancement formed the foundation of new Rh catalysts that convert arenes, olefins and an air recyclable oxidant to alkenyl arenes. These catalysts achieve unique selectivity, producing only or primarily alkenyl arene under most reaction conditions, and they generally achieve quantitative yield based on the limiting reagent, which is generally the *in situ* oxidant.

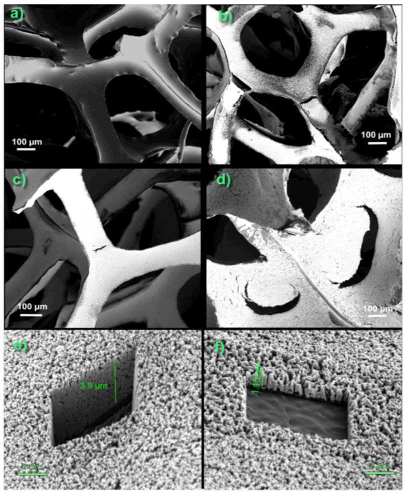


Figure 1. SEM micrographs for a) bare RVC electrode and RVC|*nano*ITO electrodes prepared from ITO suspensions at concentrations of b) 10, c) 100 and d) 200 mg/mL of ITO. Cross-sections for the electrode in (c) are presented in (e) and (f).

6. Products

a. Publications

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133. Vaughan, Benjamin A.; Webster-Gardiner, Michael S.; Cundari, Thomas R.; Gunnoe, T. Brent "A rhodium catalyst for single-step styrene production from benzene and ethylene" *Science*, **2015**, *348*, 421-424. DOI: 10.1126/science.aaa2260.

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b. Web site

The website for the CCHF can be found at: http://artsandsciences.virginia.edu/cchf/

c. Collaborations Fostered

Below is a list of collaborative efforts in the CCHF (PI names are given as initials):

1. Hydrocarbon Oxygenation (RAP/DHE/TRC/JTG/TBG/WAG/JTG/ANV)
    a. Oxygen Atom Insertion into Metal-Hydrocarbyl Bonds (RAP/DHE/TRC/JTG/TBG)
    b. Group 9 Catalysts for Partial Oxidation of Hydrocarbons (TBG/WAG/TRC/JTG)
    c. Pd and Pt Catalysts for Aerobic Hydrocarbon Oxidation (ANV/BGT/TBG/WAG)
    d. Main Group Mediated Hydrocarbon Functionalization (RAP/DHE/WAG/TBG/JTG)
        - d^{10} Main group systems (RAP/DHE)
        - Iodine catalysts (TBG/JTG/WAG/RAP/DHE)
    e. Catalysts Based on Metal Oxo Complexes (JTG/WAG/RHC/TJM)
    f. High-valent iron and manganese in aqueous solution (JTG/WAG)
    g. Catalysts based on Fe, Ru and Cu (TJM/DHE/JTG/WAG)
    h. Metal oxide-modified electrodes for oxidation catalysis (TJM/RHC/JTG/DHE)
    i. Electrocatalytic C–H oxygenation reactions (JTG/TJM/WAG/DHE)
2. Hydrocarbon Halogenation (JTG/WAG)
3. Hydrocarbon Amination (RHC/TRC/TBG)
4. Catalysts for Methane Fuel Cells (RAP/TJM/AMH/WAG/DHE/BGT/TBG/ANV)

d. Technologies/Techniques

N/A

e. Inventions/Patent Disclosures, Patent Applications, Patents Issued and Patents Licensed

Issued Patents

1. US Patent 8,993,793; Multi-Functional Mesoporous Silica Catalyst; Chen, Hung-Ting; Kobayashi, Takeshi; Lin, Victor Shang Yi; Pruski, Marek; Tsai, Chi-Hsiang; March 31, 2015

Published Applications

1. WO 2016/154416 AI, September 29, 2016 and PCT/US2016/023979; Catalysts and Methods for Forming Alkenyl and Alkyl Substituted Arenes; Gunnoe, Thomas B.; Vaughan, Benjamin Austin; Webster-Gardiner, Michael S.

2. WO/2014/210270, Dec.31, 2014 and PCT/US2014/044272, June 26, 2014; Compositions and Methods for Hydrocarbon Functionalization; Gunnoe, Thomas B.; Fortman, George; Boaz, Nicholas; Groves, John T.

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Periana, Roy A.; Konnick, Michael M.; Hashiguchi, Brian G.

4. WO/2016/033061, Mar. 3, 2016 and PCT/US2015/046721; Process for the Functionalization of Heteroalkanes and Arenes; Periana, Roy A; Konnick, Michael; Hashiguchi, Brian

5. 14770039, Feb. 25,2014; Oxidation of Alkanes to Alcohols; Periana, Roy A; Hashiguchi, Brian G.; Konnick, Michael M.; Bischof, Steven M.

6. 14224606, Mar. 25, 2014; High Surface Area Reticulated Vitreous Carbon-Nanoparticle Metal Oxide Electrodes; Mendez Agudelo Manuel; Alibabaei, Leila; Concepcion, Javier J.; Dares, Christopher J.; Meyer, Thomas J.

7. 15028310, Oct. 9, 2014, US20160264512; C-Halogen Bond Formation; Groves, John T.; Liu, Wei; Huang, Xiongyi

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f. Other Products

> 150 invited presentations that acknowledged EFRC support