

Chemistry in the Center for Catalytic Hydrocarbon Functionalization: An Energy Frontier Research Center

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Abstract Selective catalysts that activate small molecules such as hydrocarbons, dioxygen, water, carbon dioxide and dihydrogen are central to new technologies for the use of alternative energy sources. For example, controlled hydrocarbon functionalization can lead to high impact technologies, but such catalysts require a level of molecular control beyond current means. The Center for Catalytic Hydrocarbon Functionalization facilitates collaborations among research groups in catalysis, materials, electrochemistry, bioinorganic chemistry and quantum mechanics to develop, validate and optimize new methods to rearrange the bonds of hydrocarbons, activate and transform water and carbon dioxide, implement enzymatic

strategies into synthetic systems and design optimal environments for catalysis.

Keywords Carbon dioxide · Catalysis · Energy · Fuel cell · Functionalization · Hydrocarbon · Methane · Methanol

1 Introduction

Widespread access to clean, sustainable energy is arguably society's most important and substantial challenge. Over millions of years, nature stored large amounts of solar energy in the form of coal, petroleum and natural gas. Within the last century, an enormous infrastructure has been built to exploit these fossil resources. For example, in the United States, 84% of energy is derived from fossil resources (petroleum, 37%; coal, 23%; natural gas, 24%) [1]. While the discovery and development of fossil resources has provided the foundation for modern society, concerns regarding the potential negative environmental impact are increasingly relevant. Technologies and processes for efficient, inexpensive and scalable energy that minimize negative environmental impact while decreasing dependence on coal and petroleum are urgently needed. New catalysis technologies are central to achieving this goal. The purpose of the Center for Catalytic Hydrocarbon Functionalization (CCHF), an Energy Frontier Research Center that is funded by the United States Department of Energy, is to pursue fundamental research in the development of next-generation catalysts for energy conversion.

There is a need to develop alternative energy sources that meet the requirements of reduced CO₂ output, abundance and compatibility with current infrastructure. We contend that scaled-up utilization of natural gas, of which

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methane is the primary component, is a viable possibility. Global reserves of methane are enormous. Conservative estimates place the proven United States methane reserves at 192 exajoules (EJ) with an additional 351,230 EJ possible [2]. To place these numbers in context, the total per annum energy consumption of the United States was 107.2 EJ in 2007 [3]. The C:H ratio of methane (CH₄) is favorable when compared to petroleum (–CH₂–) or coal (–CH–), which leads to a decreased amount of CO₂ released per EJ of energy consumed; methane represents a 27% reduction when compared to petroleum and a 47% reduction when compared to coal [4]. Methane is also cleaner when compared to coal in terms of nitrogenous, sulfurous and mercurial impurities. Given the availability of methane and the potential environmental benefits, it is surprising that methane accounts for only 26% of all fossil fuels consumed in the United States [2, 3, 5].

The primary reasons that prevent methane from accounting for a larger portion of the energy economy are location and transportation. Most methane reserves are located in sparsely populated areas that are relatively inaccessible by pipelines or traditional transport vehicles. Inexpensive and safe transportation of large quantities of methane will require either energy intensive liquefaction processes or the construction of expensive pipelines.

Because the existing transportation infrastructure is designed for liquid fuels, one promising solution is to convert gaseous methane to liquid methanol by a highly efficient, low-cost, catalytic process. The production of methanol from methane is attractive because methanol can be used directly as a fuel additive for combustion engines or in a fuel cell application. Methanol can be readily utilized as a feedstock for synthesizing valuable chemicals such as olefins, formaldehyde, gasoline or dimethyl ether. In addition, methanol can be converted to biodiesel via transesterification with triglycerides.

While use of methanol as a transportation fuel does not offset CO₂ output compared with gasoline (65.8 vs. 70.9 kg CO₂ per million Btu), methane (or methanol) has the ability to offset the use of coal for electricity [4]. Furthermore, low temperature methane or methanol fuel cells offer the potential to increase the efficiency of electricity generation and reduce the amount of CO₂ released into the atmosphere.

To further reduce the amount of CO₂ in the atmosphere, processes that convert CO₂ into liquid fuels will be necessary. Achieving this transformation without generating additional CO₂ will require a carbon-neutral, non-fossil energy source. A process for the reduction of CO₂ into a liquid fuel will involve scalable alternative energy, an efficient method to capture CO₂ and a catalytic route to convert CO₂ into a high-energy molecule.

2 The Center for Catalytic Hydrocarbon Functionalization

The CCHF is comprised of twelve principal investigators from eleven institutions (Table 1). The researchers in the CCHF have expertise in bioinorganic chemistry, catalysis, electrochemistry, inorganic chemistry, materials chemistry, organic chemistry, quantum mechanics and large scale atomistic simulation. The center is organized into five research thrusts:

1. Development of homogeneous transition metal catalysts for activation and functionalization of small alkanes and other hydrocarbons
2. Development of homogeneous metal oxo catalysts for selective oxidation of small alkanes and other hydrocarbons
3. New materials for selective functionalization of small alkanes and other hydrocarbons
4. Development of low temperature direct methane fuel cells
5. Electrocatalytic reduction of carbon dioxide to produce liquid fuels

2.1 Homogeneous Transition Metal Catalysts for Hydrocarbon Functionalization

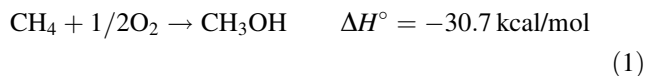
In this research area we are focused on developing new science related to conversion of methane to liquid fuels, especially methanol. The conversion of methane to methanol appears simple; an oxygen atom is inserted into a C–H bond (Eq. 1). Although enthalpically favorable

Table 1 The principal investigators in the Center for Catalytic Hydrocarbon Functionalization and their affiliations

Principal investigator	Institution
Robert C. Bergman	University of California, Berkeley
Robert H. Crabtree	Yale University
Thomas R. Cundari	University of North Texas
Daniel H. Ess	Brigham Young University
William A. Goddard, III	California Institute of Technology
John T. Groves	Princeton University
T. Brent Gunnoe ^a	University of Virginia
Victor S.-Y. Lin ^b	Iowa State University
Thomas J. Meyer	University of North Carolina, Chapel Hill
Roy A. Periana	Scripps Research Institute, Florida
F. Dean Toste	University of California, Berkeley
Andrei N. Vedernikov	University of Maryland

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($\Delta H = -30.7$ kcal/mol), the covalent nature of the C–H bond in methane (105 kcal/mol) necessitates the use of a catalyst for the reaction to proceed at a reasonable rate.



Herein we consider four general mechanisms for homogeneous transition metal catalyzed partial oxidation of hydrocarbons. Shilov-type chemistry with late transition metals proceeds via initial C–H activation followed by oxidation and release of functionalized product (Fig. 1a) [6]. The salient features of Shilov-type catalysts include C–H activation that occurs via an electrophilic substitution, oxidation by an inner-sphere two-electron process accompanied by transfer of chloride, and a carbon functionalization step that is a nucleophilic substitution [7]. An alternative mechanism involving O-atom insertion is shown in Fig. 1b. The oxy-insertion mechanism involves the insertion of an oxygen-atom into a M-alkyl bond to form a M-alkoxide bond. Reaction of the alkoxide complex with a hydrocarbon, via metal-mediated C–H activation, releases the functionalized product and regenerates the M-alkyl. The third pathway is related to enzymatic systems, which generally contain high valent metals (Fig. 1c). Through a net H-atom abstraction step, the metal oxo reacts with a hydrocarbon to form a M–OH and alkyl radical with concomitant decrease in the oxidation state of the metal. The alkyl radical can then combine with the hydroxide ligand to form an alcohol. [8–10] The resulting metal complex can be reoxidized to $\text{M}\equiv\text{O}$. An alternative mechanism with low valent metal oxo complexes involves non-radical, even electron chemistry and avoids H-atom abstraction (Fig. 1d). A net 1,2-addition of the hydrocarbon across the $\text{M}=\text{O}$ bond forms a M-alkyl(hydroxo) complex. Reductive elimination produces an alcohol. Several of these catalytic cycles have already been demonstrated in whole or part thus showing promise toward the goal of developing an economical catalyst for the transformation of methane into liquid fuels. However, certain aspects of each catalytic cycle, such as using molecular oxygen in the Shilov-type cycle or catalytically generating metal oxo systems, remain key challenges to successfully implementing efficient catalytic systems. These advantages and challenges are summarized in Table 2.

2.1.1 Studies Relevant to Shilov-Type and Oxy-Insertion Catalytic Cycles

The goal is to use molecular oxygen as the oxidant, either directly or indirectly, for the low temperature (200–250 °C), selective partial oxidation of hydrocarbons. For several years, research efforts have focused on

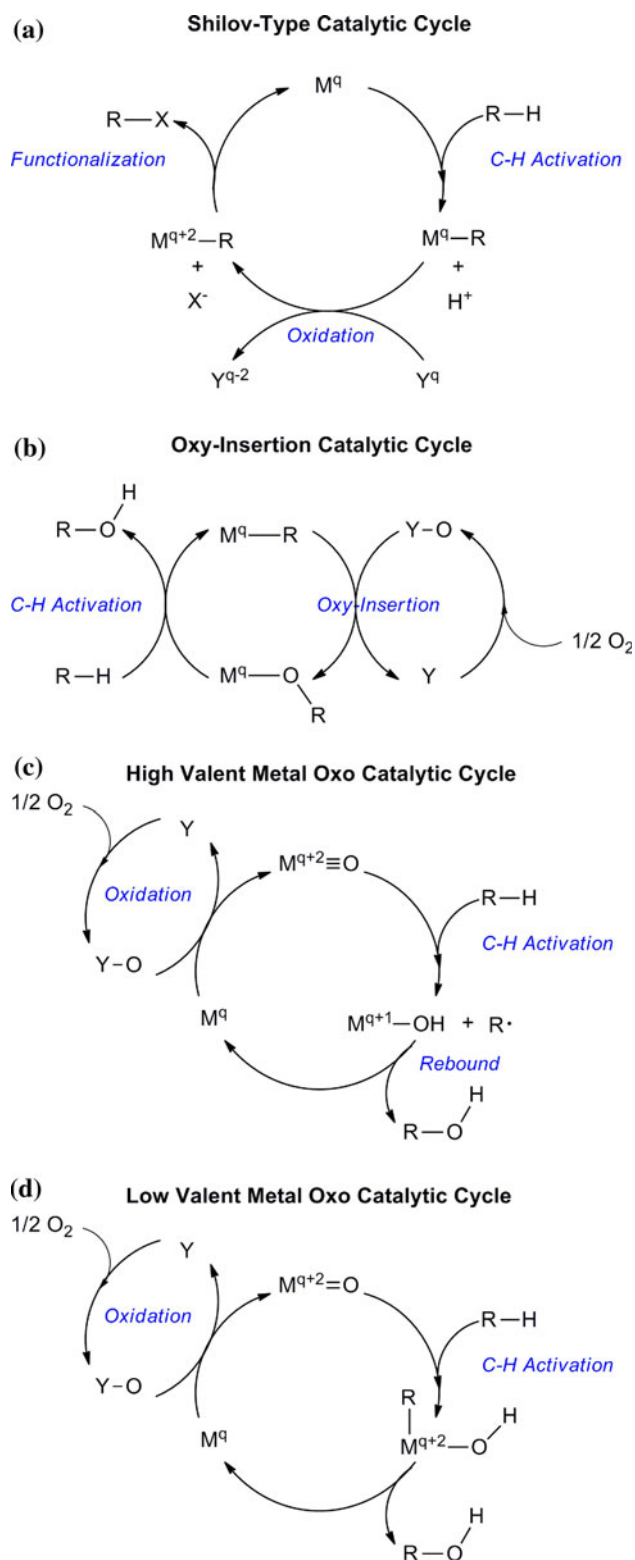


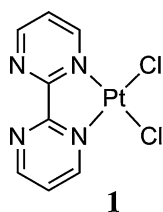
Fig. 1 Four approaches to catalytic C–H functionalization using homogeneous transition metal catalysts

improving catalyst activity and selectivity of the Shilov system. A seminal discovery by Periana et al. was the catalyst (bipyrimidine) PtCl_2 (**1**) [11]. Although a marked

Table 2 The advantages and challenges of each of the four catalytic cycles

Catalytic cycle	Known advantages	Potential Challenges
Shilov-type	Successful catalysts known In some cases, CH ₄ is more reactive than CH ₃ OH	The catalyst must oscillate between two oxidation states To be economical, O ₂ must be incorporated either directly or indirectly
Oxy-insertion	1,2-addition of a C–H bond across a M–OR bond has been demonstrated Oxy-insertion into a M–R bond has been demonstrated The cycle can operate without a formal change in the oxidation state of the catalyst	The oxy-insertion has only been observed with high valent, d ⁰ metals that are incapable of C–H activation 1,2-addition of a C–H bond across a M–OR bond is not well understood Oxy-insertion into the M–R bond is rare and not well understood
High valent metal oxo	C–H activation has been demonstrated The structure and reactivity of high valent metal oxo complexes has been thoroughly investigated	C–H activation where the BDE exceeds 95 kcal/mol has not been reported Catalytic generation of high energy M≡O could be challenging The generation of radicals is potentially concerning The rate of catalysis likely depends on the BDE of the hydrocarbon
Low valent metal oxo	The activation of O ₂ to form a M=O is known The addition of a C–H bond across a metal-imido bond (isoelectronic with an oxo) has been demonstrated	The 1,2-addition of a C–H bond across a metal-oxo bond has not been reported Catalytic generation of M=O could be challenging as few low valent metal oxo complexes are known

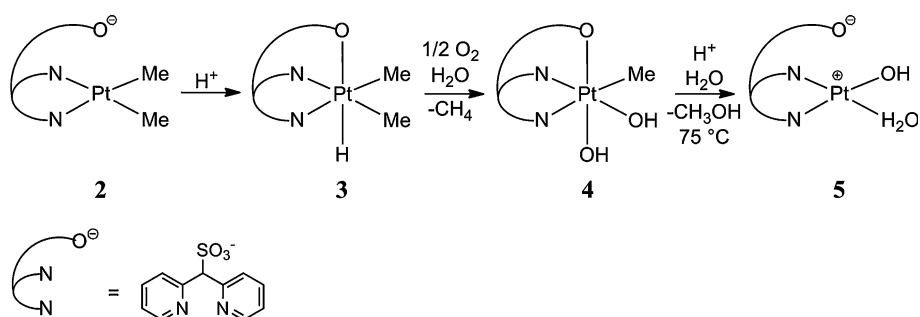
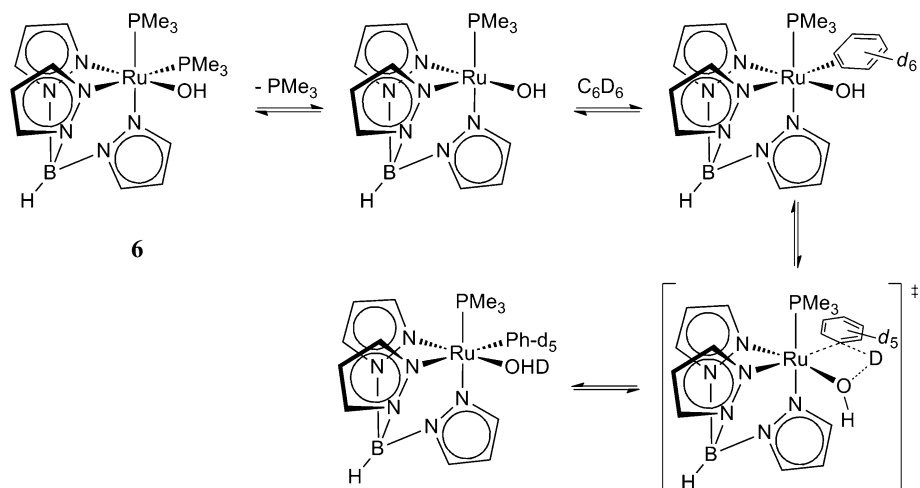
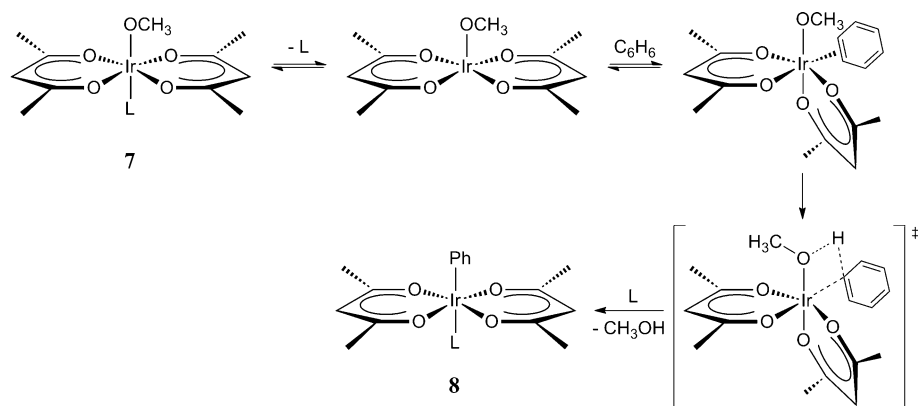
improvement from the Shilov system, the major drawbacks of **1** are (a) turnover frequencies are two orders of magnitude too low and (b) methanol recovery from concentrated sulfuric acid is too costly [12]. Metal-mediated C–H activation has been thoroughly studied, and greater effort must be directed toward understanding metal-mediated C–O bond formation. The Cundari, Goddard, Groves, Gunnoe, Periana and Vedernikov groups are working collaboratively on these efforts.



Within the CCHF, the Vedernikov and Goddard groups are working to develop a fundamental knowledge base for reactions that transform Pt-alkyl and O₂ to Pt-alkoxide. Vedernikov et al. have demonstrated that oxidation by O₂ and functionalization to form methanol occurs from a ligated Pt(II) dimethyl complex (Scheme 1) [13, 14]. The anionic bi- or tridentate ligand di(2-pyridyl)methanesulfonate (dpms) allows for a multistep process where [(κ²-dpms)Pt^{II}Me₂][−] (**2**) can be protonated to give (κ³-dpms)Pt^{IV}(H)Me₂ (**3**). Complex **3** is oxidized by

molecular oxygen in aqueous solution to (κ³-dpms)Pt^{IV}(OH)₂Me (**4**) and methane. Heating complex **4** in the presence of acid allows for reductive elimination of methanol to give (κ²-dpms)Pt^{II}(OH)(H₂O) (**5**). Work in the CCHF is building on these preliminary results to optimize the oxidation process and couple this reaction with systems that can achieve C–H activation.

The platinum complexes described above achieve C–H activation by electrophilic substitution (Fig. 1a), an alternative mechanism could involve 1,2-addition of C–H bonds across nucleophilic M–OR bonds, possibly in the absence of a formal change in the metal oxidation state (Fig. 1b). Gunnoe et al. have reported reversible C–H activation of benzene with TpRu(PMe₃)₂(OH) (**6**) when heated in the presence of C₆D₆ to give TpRu(PMe₃)₂(OD) and C₆D₅H [15, 16]. The mechanism of this exchange likely involves phosphine dissociation followed by coordination and activation of benzene (Scheme 2). Likewise, Periana, Goddard et al. have reported C–H activation with favorable thermodynamics using (acac)₂Ir(OCH₃)(L) (**7**) where L = pyridine or MeOH, an air, protic and thermally stable complex [17]. Heating complex **7** in benzene results in the formation of (acac)₂Ir(Ph)(L) (**8**) and methanol (Scheme 3). Aromatic C–H activation was also observed by Bercaw et al. with [(COD)Rh(μ₂-OH)]₂ [18]. Similar reactions were discovered by Goldberg et al. with [2,6-bis(di-*tert*-butylphosphinomethyl)pyridine]Rh–X

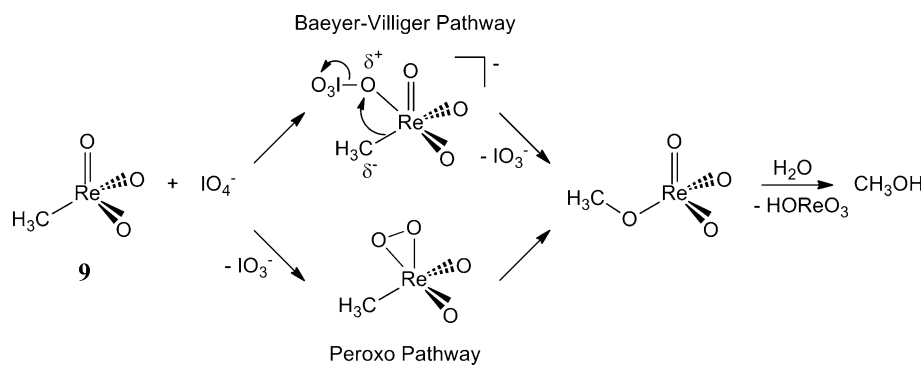
Scheme 1 Reaction of a platinum complex with molecular oxygen**Scheme 2** Reversible reaction of a ruthenium complex with benzene**Scheme 3** Irreversible reaction of an iridium complex with benzene

complexes where X is an oxygen ligand such as acetate or hydroxide [19, 20].

The observation of net 1,2-C–H addition across M–OR bonds of Ru, Ir and Rh complexes demonstrates the feasibility of a key step in the catalytic cycle shown in Fig. 1b. Although much remains to be learned about this transformation, to date, all examples are based on d^6 or d^8 transition metal complexes. At this point, the critical limitation to the development of the catalytic cycle shown in Fig. 1b is the oxy-insertion step. Substantial effort in the CCHF is being directed toward understanding metal-mediated C–O bond

formation via the oxy-insertion route and targeting new methods to achieve such reactions. Oxy-insertion into a M–alkyl bond has been observed by Periana, Goddard et al. with methyltrioxorhenium (MTO, **9**) and oxygen-atom donors such as IO_4^- [21–23]. Computation showed that the activation barrier for a pathway that is analogous to the Baeyer–Villiger reaction is 17 kcal/mol while a peroxo pathway has an activation barrier of 25 kcal/mol (Scheme 4). Researchers in the CCHF are engaged in a broad effort to understand the metal-mediated oxy-insertion reaction and to extend this transformation to systems capable of catalytic turnover.

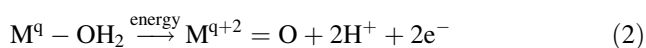
Scheme 4 Two possible pathways in the reaction of MTO with an oxidant



2.1.2 Metal Oxo Catalysts

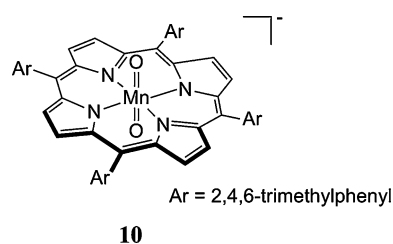
The CCHF will explore C–H functionalization through two distinct classes of metal oxo complexes: high valent and low valent. Divergent reactivity is expected as the high valent oxo will exhibit oxene character while the low valent oxo is expected to exhibit oxide character. For high valent metal oxo complexes, oxidizing power is critical because C–H activation, via net H-atom abstraction by the oxo ligand, formally reduces the metal. In addition, the reduced metal hydroxide must possess sufficient affinity for the alkyl radical in order to achieve a rapid rebound step. For low valent metal oxo complexes, it is likely important for the oxo to be basic in order to activate the C–H bond and form M(alkyl)(OH). The researchers involved in these projects are the Bergman, Crabtree, Cundari, Goddard, Groves, Gunnoe, Meyer and Toste groups.

For high valent metal oxo complexes, research is being directed toward new structural motifs that will enhance metal oxo reactivity and selectivity so that functionalization of more inert substrates such as methane and benzene will be possible. Understanding how to control the rate of the rebound step (i.e., selectivity) and developing methods to access high valent metal oxo complexes without the use of powerful oxidants are necessary for successful catalysis. In general, harsh oxidants are not amenable to large scale reactions. An alternative approach is to electrocatalytically generate the metal oxo in water as shown in Eq. 2. The electrocatalytic generation of a high valent metal oxo from a metal aquo species has been demonstrated by the Meyer group, while the use of water as the O-atom source in the functionalization of hydrocarbons has been shown by the Crabtree group [24–28]. Ultimately, the energy input to drive the electrocatalysis could come from a renewable energy source. This type of reactivity allows for an inexpensive, abundant oxidant to promote catalysis.

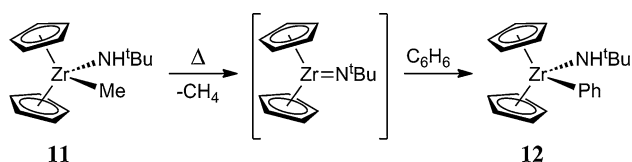


Oxomanganese(V) porphyrin complexes display rich oxo-transfer chemistry as a result of prototropic equilibria

involving the axial ligand. The Groves group has found that the protonated oxoaqua- and oxohydroxo-manganese species are the active O-atom transfer agents, while the resting state is a novel *trans*-dioxomanganese(V) complex (**10**) [29]. This species is the first *trans*-dioxo complex for any first-row transition metal to be isolated and characterized. The recognition that these species exist and that their reactivity toward C–H bond oxygenation can be modulated by acid–base chemistry is central to controlling oxidation chemistry. In particular the manganese system has been shown to be effective even with very strong C–H bonds (~100 kcal/mol). Furthermore, the catalytic conditions can be modified to favor either C–H hydroxylation or halogenation [30]. Studies in collaboration with the Goddard group have indicated that *trans*-dioxovanadium(V), *trans*-dioxochromium(V) and *trans*-dioxoiron(VI) species may be accessible and tunable for reaction with the C–H bonds of methane.



An alternate approach to the use of high valent and oxidizing metal oxo complexes is a low valent metal oxo catalyst. Our interest in low valent metal oxo systems comes from early transition metal imido species that are capable of activating sp^2 and sp^3 C–H bonds [31–41]. For example, Bergman et al. reported that heating $\text{Cp}_2\text{Zr}(\text{Me})(\text{NH}^t\text{Bu})$ (**11**) in benzene releases methane and forms $\text{Cp}_2\text{Zr}(\text{Ph})(\text{NH}^t\text{Bu})$ (**12**) via a transient $[\text{Cp}_2\text{Zr} = \text{N}^t\text{Bu}]$ intermediate (Scheme 5) [32]. In the presence of CH_4 , $(^t\text{Bu}_3\text{SiNH})_3\text{Zr}(\text{CD}_3)$ (**13**) undergoes H/D exchange to give $(^t\text{Bu}_3\text{SiNH})_3\text{Zr}(\text{CH}_3)$ (**14**) and CD_3H at elevated temperature (Scheme 6) [31]. This exchange proceeds

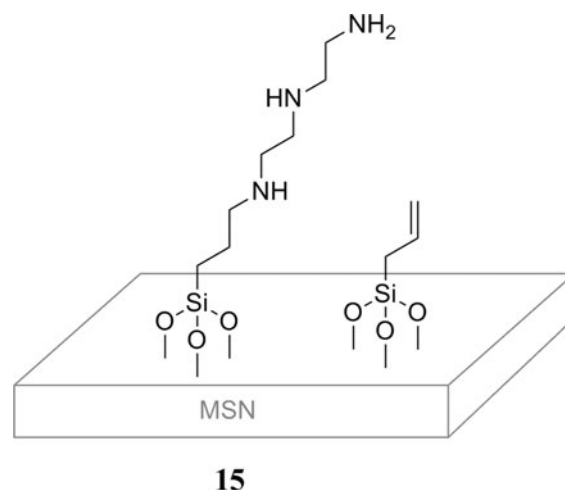


Scheme 5 Benzene activation by a zirconium imido complex

through the transient zirconium imido complex $[(^t\text{Bu}_3\text{SiNH})_2\text{Zr} = \text{NSi}^t\text{Bu}_3]$. Calculations by the Cundari group on a titanium analog show that the energetics of the metal-imido/hydrocarbon adduct dictates the selectivity of the activation [39]. These and related examples are very promising because they demonstrate the addition of a C–H bond across a metal-heteroatom bond. Imido ligands are isoelectronic with oxo ligands, and it is conceivable that reactivity analogous to early transition metal imido systems can be achieved. If extended to metal oxo systems, C–O reductive elimination will provide a route to alcohols as shown in Fig. 1d. The oxophilicity and electrophilicity of early transition metals makes them poor candidates for release of functionalized hydrocarbons and catalysis. In the CCHF, researchers are synthesizing low valent, late transition metal oxo complexes and probing for C–H activation via 1,2-addition of the C–H bond across metal oxide bonds.

2.2 Advanced Materials and Understanding of Heterogeneous Systems

Recent advances in materials synthesis provide new opportunities to tailor catalyst features. Functionalized nanoparticles such as mesoporous silicas, as developed by the Lin group, are competent supports for both organic and inorganic catalysts [42]. Appending multiple groups to the mesoporous silica nanoparticles (MSN) in addition to the catalyst allows for selectivity to be controlled by physicochemical properties such as polarity and hydrophobicity [42]. Rhodium and chromium catalysts have been supported on MSN and are competent for the desired catalytic transformations [43, 44]. For example, bifunctionalized MSN materials with 3-[2-(2-aminoethylamino)ethylamino]propyl and allyl groups attached via siloxy linkages can control the selectivity in competitive nitroaldol condensation reactions (15) [42]. Collaborative work in the CCHF employs increasingly sophisticated synthetic methods for the preparation of mesoporous silicas to rationally design catalysts for hydrocarbon functionalization with the goal of controlled product selectivity. Similar to enzymes with hydrophobic and hydrophilic pockets, the advanced materials will have different regions that can influence the catalysis. The Cundari, Gunnoe and Lin groups are involved in this research effort.



Other types of heterogeneous catalysts, solid multi-metal oxides, are used in a number of industrial processes to oxidize hydrocarbons. Vanadium oxide (V_2O_5) catalyzes the oxidative dehydrogenation of propane. The C–H activation step has been examined computationally by the Goddard group with V_4O_{10} as a model, and the energetically favorable path involves the formation of an isopropyl radical [45]. Oxidation of propene by bismuth molybdates ($\text{Bi}_x\text{Mo}_y\text{O}_z$) accounts for the majority of the eight billion pounds of acrolein produced annually [46, 47]. $\text{Bi}_x\text{Mo}_y\text{O}_z$ operates by a two site mechanism where the Bi(V) site activates the propene and the remainder of the chemistry occurs on the MoO_z [48, 49]. A number of multi-metal oxides that have shown activity for selective oxidation or ammoxidation of propane and selective oxidations of butane are known but the mechanism by which they work is not. Using QM combined with the ReaxFF reactive force field, the Goddard group is determining the structure at the active sites of these materials and the chemical mechanism leading to selective oxidation. In all cases, it is only $\text{V}=\text{O}$ at V^{V} sites that can activate the small alkanes; but oxo groups on a second metal, $\text{Mo}=\text{O}$ (for Mo^{VI} with two $\text{Mo}=\text{O}$) or $\text{Te}=\text{O}$ (for a Te^{IV} site) play an essential role in the selective functionalization [50, 51]. From these studies the Goddard group is designing experimental tests to probe specific mechanistic steps. This information will be used to suggest new anodes for the methane fuel cell and bimetallic homogeneous catalysts for methane functionalization.

2.3 Methane Fuel Cells

Currently, coal represents 48% and methane represents 21% of source fuel for electricity in the United States [52]. The dominant reason for the discrepancy is the difference in cost of the fossil fuels. Switching to all-methane power

Scheme 6 Methane activation by a zirconium imido complex

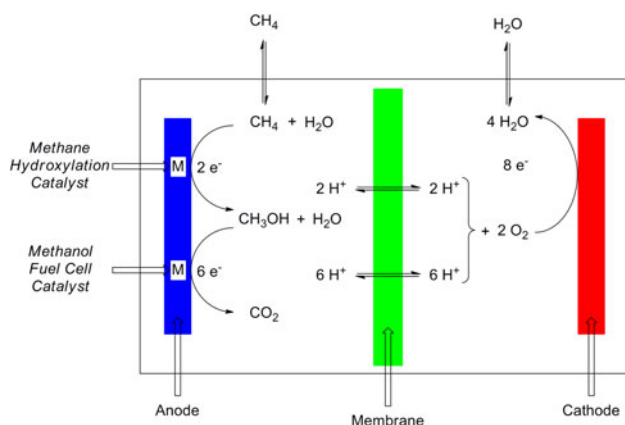
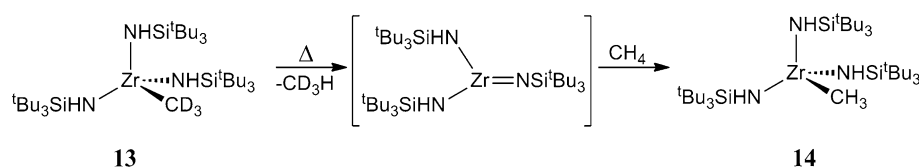
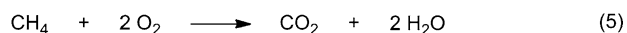
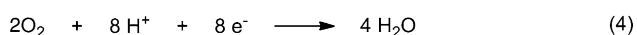
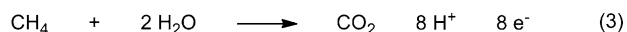


Fig. 2 A schematic of a methane fuel cell

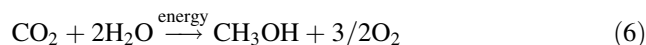
plants could provide substantial environmental benefits in the generation of electricity by relieving dependence on coal. A low temperature methane fuel cell that increases efficiency compared to combustion could render methane economically competitive with coal. A methane fuel cell involves the electrochemical oxidation of CH_4 and reduction of O_2 (Eqs. 3–5). The oxidation of CH_4 will likely require catalysts attached to the anode while the reduction of O_2 will occur at the cathode (Fig. 2). Catalysts at the anode are required to reduce overpotentials as well as to reduce activation barriers and, hence, temperature. The Goddard, Meyer and Periana groups are exploring catalysts for component reactions of a methane fuel cell.



2.4 Reduction of Carbon Dioxide as a Means of Energy Storage

As alternative energies are accessed, an important challenge will be to develop processes that store the energy in chemical bonds via the production of liquids that can be utilized as fuels. A predominant focus in the CCHF is the efficient conversion of C–H to C–O bonds, but in the long term, the conversion of C–O to C–H bonds using renewable energy sources to drive this conversion could be the basis for energy storage. The ultimate goal in this focus area of the CCHF is to use carbon-neutral alternative energy such as solar, wind, nuclear, etc. to convert H_2O

and CO_2 to CH_3OH and O_2 (Eq. 6). The resulting methanol could be used as a fuel directly or converted to other products. For this process to occur, there are two general challenges that need to be considered simultaneously: (1) CO_2 sequestration (how do we efficiently “trap” CO_2 from the atmosphere?), and (2) coupling the alternative energy to the catalytic conversion of CO_2 and H_2O to fuels. Catalysts for the concentration and reduction of CO_2 are being designed by the Crabtree, Goddard and Periana groups.



3 Summary and Outlook

The main research thrusts in the CCHF aim to advance the development of catalysts for conversion of small molecules that are directly related to new energy platforms. By fostering collaborations between several groups with diverse expertise, the CCHF will accelerate fundamental advances in catalysis related to hydrocarbon functionalization.

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