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Inverse Design, Development and Characterization of Catalytic Adsorbates at Semiconductor/Liquid Interfaces

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14. ABSTRACT
The collaborative team of Batista (Yale University), Kubiak (University of California, San Diego) and Lian (Emory University), including collaborations with Mauricio Cattaneo, Lisa Pfefferle, James Durrant, Eszter Barath, Gary Haller and Michael Grätzel over the past two years, made significant progress towards understanding fundamental aspects of catalytic systems at interfaces, including Re(I) and Mn(I) bipyridyl and Ni complexes for CO2 reduction and development of machine learning methods and in situ spectroelectrochemical sum frequency generation (SFG) techniques for studying catalytic materials. Each project involved an intimate combination of synthetic, electrochemical, computational, and spectroscopic techniques applied to gain mechanistic understanding of catalytic interfaces at the molecular level.

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Is this a Collaboration: Yes.

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Proposed Resources and Project Performance Site: All of the proposed research will be performed in the laboratories of the co-PIs at Yale University, Emory University, and the University of California, San Diego.

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Technical highlight:

- Integration of novel computational and experimental methods to investigate electrochemical and photoelectrochemical CO₂ reduction intermediates *in situ*, identify reaction pathways, and advance the development of electrocatalysts for CO₂-to-fuel conversion.
- Studies of the influence of the electrode-catalyst-electrolyte interface on the hydricity of reaction intermediates, essential for selective CO₂ reduction.
- Spectro-electrochemistry and theoretical characterization of interfacial electron transfer (IET), proton-coupled electron transfer (PCET) and proton-coupled hydride transfer (PCHT), including QM/MM and inverse design methods to elucidate the nature of low free energy pathways for CO₂ reduction.

Executive Summary.

The collaborative team of **Batista** (Yale University), **Kubiak** (University of California, San Diego) and **Lian** (Emory University), including collaborations with Mauricio Cattaneo, Lisa Pfefferle, James Durrant, Eszter Barath, Gary Haller and Michael Grätzel over the past two years, made significant progress towards understanding fundamental aspects of catalytic systems at interfaces, including Re(I) and Mn(I) bipyridyl and Ni complexes for CO₂ reduction and development of machine learning methods and *in situ* spectroelectrochemical sum frequency generation (SFG) techniques for studying catalytic materials. Each project involved an intimate combination of synthetic, electrochemical, computational, and spectroscopic techniques applied to gain mechanistic understanding of catalytic interfaces at the molecular level.¹⁻²⁶

1. Robust Binding of Disulfide-Substituted Rhenium Bipyridyl Complexes for CO₂ Reduction on Gold Electrodes

We have introduced new [Re(L)(CO)₃Cl] catalysts for CO₂ reduction (Figure 1) with sulfur-based anchoring groups on a bipyridyl ligand, where L = 3,3'-disulfide-2,2'-bipyridine (SSbpy) and 3,3'-thio-2,2'-bipyridine (Sbpy).¹ Heterogenization of

homogenous catalysts on electrode surfaces provides a valuable approach for characterization of catalytic processes in operando conditions using surface selective spectroelectrochemistry methods. Ligand design plays a central role in the attachment mode and the resulting functionality of

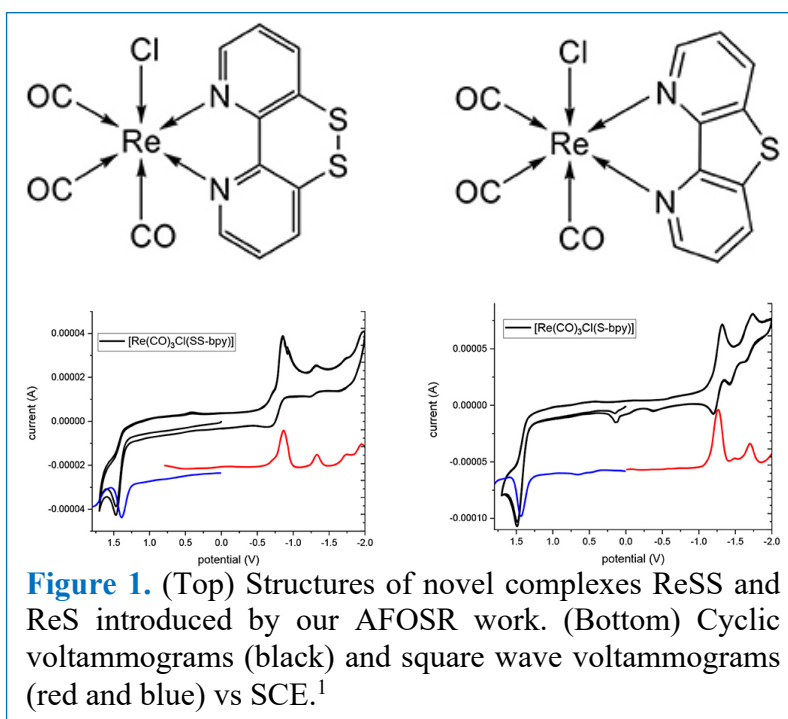
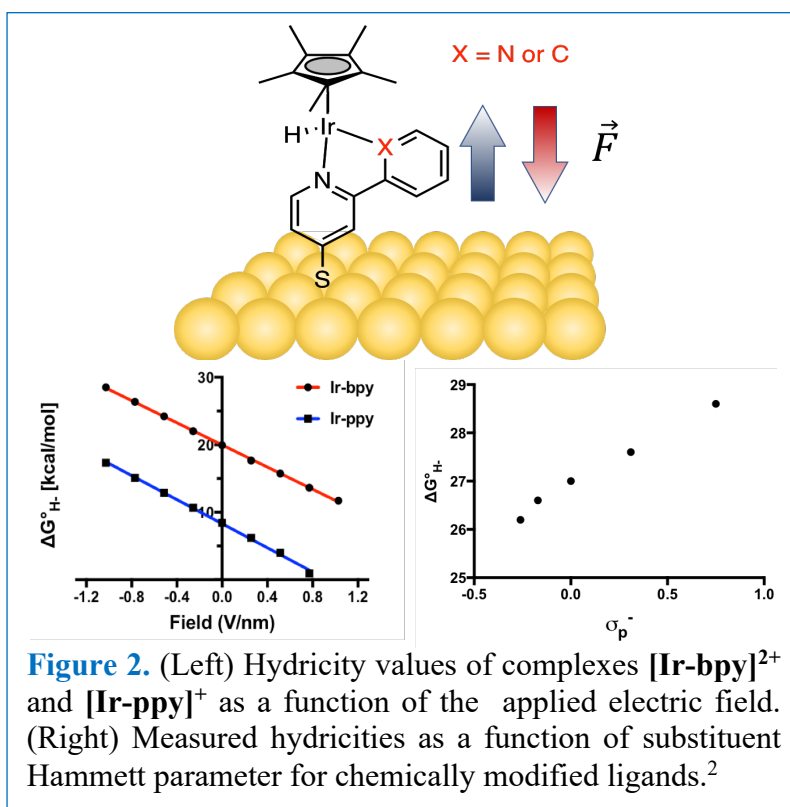


Figure 1. (Top) Structures of novel complexes ReSS and ReS introduced by our AFOSR work. (Bottom) Cyclic voltammograms (black) and square wave voltammograms (red and blue) vs SCE.¹

the heterogenized catalyst as determined by the orientation of the catalyst relative to the surface and the nature of specific interactions that modulate the redox properties under the heterogeneous electrode conditions. Our spectroscopic and electrochemical analysis combined with computational modeling at the density functional theory level identified the complex $[\text{Re}(\text{SSbpy})(\text{CO})_3\text{Cl}]$ as a multi-electron acceptor that combines the redox properties of both the rhenium tricarbonyl core and the disulfide functional group on the bipyridyl ligand. The first reduction at -0.85 V (vs. SCE) involves a two-electron process that breaks the disulfide bond, activating it for surface attachment. The heterogenized complex exhibits robust anchoring on gold surfaces, as probed by vibrational sum-frequency generation (SFG) spectroscopy. The binding configuration is normal to the surface, exposing the active site to the CO_2 substrate in solution. The attachment mode is thus particularly suitable for electrocatalytic CO_2 reduction.

2. Controlling Hydricity of Catalytic Adsorbates with Applied Electric Fields

We found that applied electric fields can precisely control the hydricity of catalysts at electrode interfaces. Hydricities of Ir half-sandwich complexes, including Ir-bipyridine $[\text{Ir-bpy-H}]^+$ and Ir-phenypyridine $[\text{Ir-ppy-H}]^+$, are shifted by >17 kcal mol $^{-1}$ across the typical range of applied voltages, exceeding the reported range of hydricity changes accessible by chemical modification of the complexes with a wide range of substituents (Figure 2).² The catalysts were selected because they are catalytically

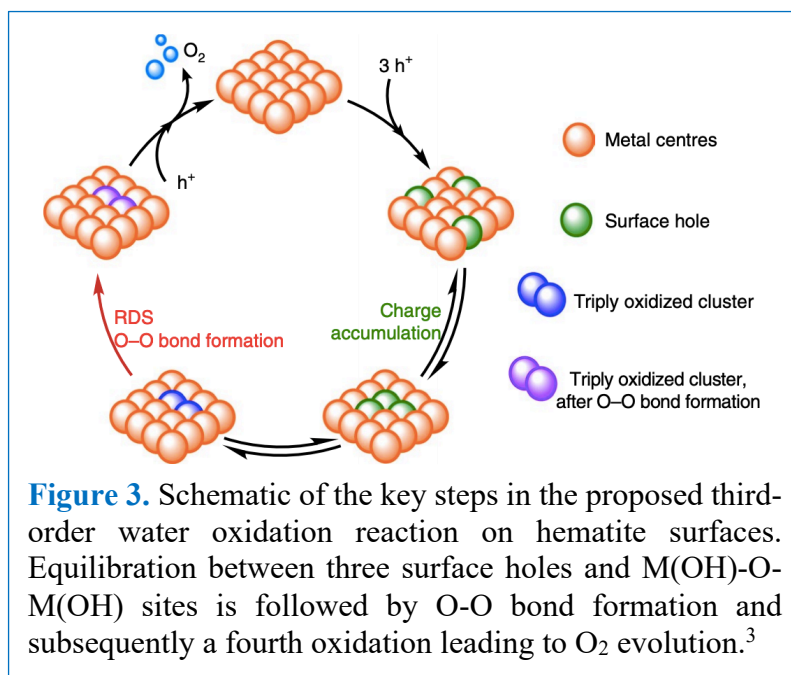


active while remain redox inactive over a large potential range, allowing for the isolation of electric field effects on reactivity. Importantly, we found that the Stark tuning rates of Ir-H stretching modes are directly correlated with hydricity changes induced by the applied electric field, providing valuable spectroscopic probes of the actual electric field at the catalytic site and potential reactivity of the hydride. We anticipate the reported findings should be particularly valuable for studies of non-Faradaic electrochemical control of catalytic activity and selectivity of catalysts at interfaces by applied external fields. Ongoing work involves experimental confirmation of the computationally predicted changes in hydricity as well as studies of field effects on transfer hydrogenation activity.

3. Multi-hole water oxidation catalysis on hematite photoanodes revealed by operando spectro-electrochemistry and DFT

We have studied water oxidation kinetics on four metal oxides, focusing particularly on hematite which remains a significant experimental and theoretical challenge, in an effort to elucidate the catalytic mechanism of this multi-redox reaction on metal–oxide photoanodes (Figure 3).³ Water oxidation is the ideal ultimate source of electron for fuel forming reactions and often the key thermodynamic bottleneck of photoelectrochemical devices for fuel synthesis.

We observed that hematite is able to access a reaction mechanism that is third order in surface-hole density, assigned to equilibration between three surface holes and $M(OH)-O-M(OH)$ sites, with low activation energy ($E_a \approx 60$ meV). Density functional theory was used to determine the

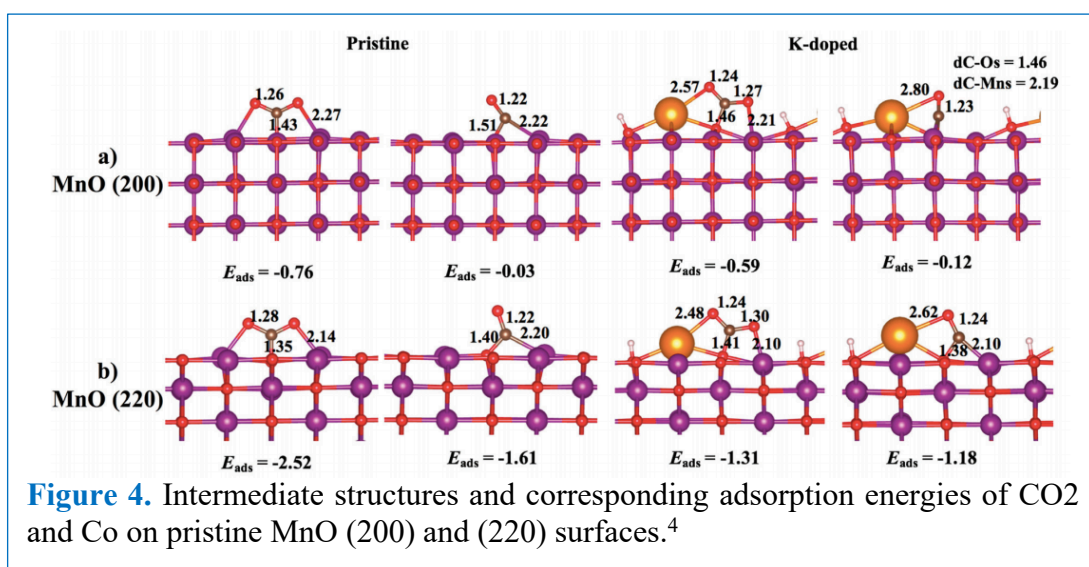


energetics of charge accumulation and O–O bond formation on hematite (110) surface,

finding a mechanism that shows parallels with the function of the oxygen evolving complex of photosystem II.

4. Catalytic manganese oxide nanostructures for the reverse water gas shift reaction

We have investigated the catalytic performance of MnO₂ nanostructures as applied to the reverse Water Gas Shift (rWGS) reaction in an effort to elucidate fundamental structure–property relationships of nanomaterials that are critical for many catalytic applications (Figure 4).⁴ We have shown that the support-free MnO derived from MnO₂ 1D, 2D and 3D nanostructures are highly selective (100% CO₂ to CO), thermally stable catalysts (850 °C) and differently effective in the rWGS. Up to 50% conversion is observed, with a H₂/CO₂ feed-in ratio of 1 : 1. From both experiments and DFT calculations, we find the MnO₂ morphology plays a critical role in governing the catalytic behaviors since it affects the



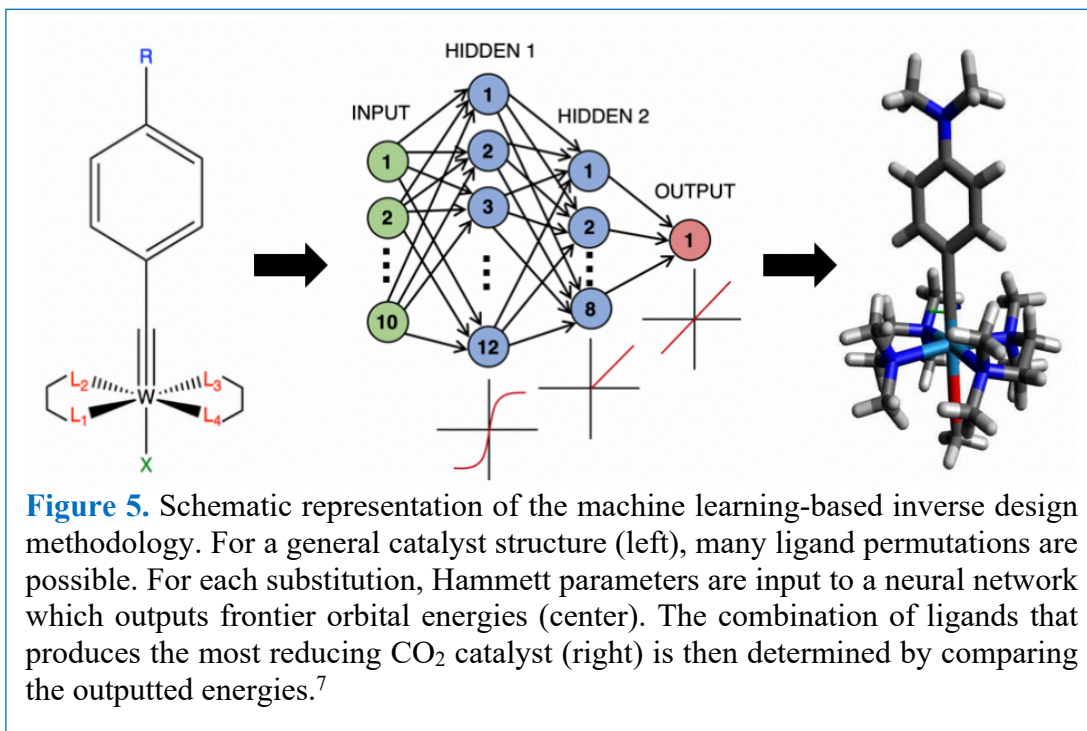
predominant facets exposed under reaction conditions as well as the intercalation of K⁺ as a structural building block, substantially affecting the gas-solid interactions. The relative adsorption energy of reactant (CO₂) and product (CO), $\Delta E = E_{\text{ads}}(\text{CO}_2) - E_{\text{ads}}(\text{CO})$, is found to correlate linearly with the catalytic activity, implying a structure–function relationship. The strong correlation found between $E_{\text{ads}}(\text{CO}_2) - E_{\text{ads}}(\text{CO})$, or more generally, $E_{\text{ads}}(\text{R}) - E_{\text{ads}}(\text{P})$, and catalytic activity makes ΔE a useful descriptor for characterization of efficient catalysts involving gas-solid interactions beyond the rWGS.

5. Multi-time Formulation of Matsubara Dynamics

The computation and interpretation of nonlinear vibrational spectroscopy is of vital importance for understanding a wide range of dynamical processes in molecular systems. To address that challenge, we have developed a generalization of Matsubara dynamics for the evaluation of multi-time correlation functions.⁵ We showed that the Matsubara approximation can be used to approximate the two-time symmetrized double Kubo transformed correlation function. By a straightforward extension of these ideas to the multi-time realm, a multi-time Matsubara dynamics approximation can be obtained for the multi-time response functions in terms of multi-time double symmetrized Kubo transformed thermal correlation functions.⁶ Although not a practical method, due to the presence of a phase-term, this multi-time formulation of Matsubara dynamics represents a benchmark theory for future development of Boltzmann preserving semiclassical approximations to general higher order multitime correlation functions. It also reveals a connection between imaginary time-ordering in the path integral and the classical dynamics of multi-time correlation functions.

6. Hammett neural networks: prediction of frontier orbital energies

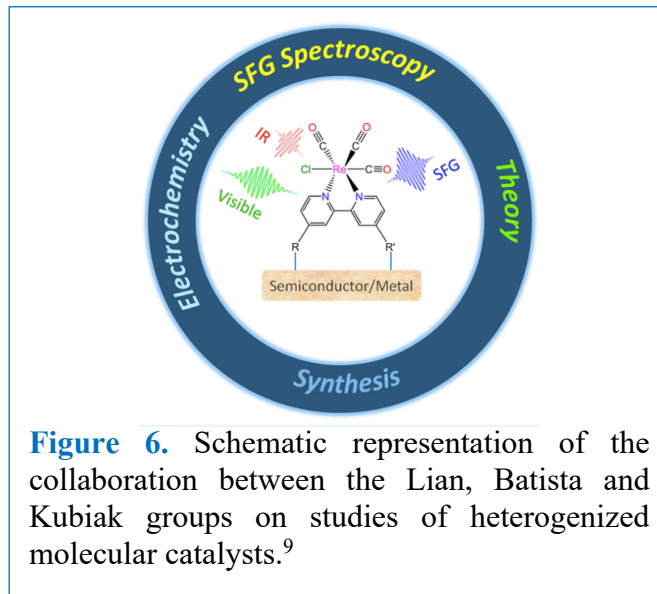
The rational design and development of catalysts presents a problem of large chemical space. We have developed an inverse design method utilizing machine learning's



pattern-finding capabilities (Figure 5).⁷ In this way, the property spaces for frontier orbital energies and energy gaps for a tungsten-benzylidene CO₂ reduction catalyst were formed. Using Hammett parameters as input for the supervised machine learning model, and outputting frontier orbital energies, we were able to demonstrate the power of this feature set via achieving mean squared errors of less than 1% for all models tried. Furthermore, these models were demonstrated to be generalizable beyond the ligand set used for training, and found to correctly predict the ligand combinations for the largest and smallest frontier orbital energy gaps. This demonstrates the use of Hammett parameters beyond ligands on phenyl rings in organic complexes, thus offering the possibility to explore chemical space quickly for a variety of catalyst structures. On this topic, we have also recently written a review article focused on the grand challenge of *in silico* catalyst design using inverse design and machine learning methods.⁸

7. Accounts of Chemical Research Review on Heterogenized Molecular Catalysts

We have reviewed our close collaboration between the Lian, Batista, and Kubiak groups that resulted in an integrated approach to investigate how the semiconductor and metal surfaces affect the properties of the attached catalyst (Figure 6).⁹ Understanding the fundamental physicochemical properties of such heterogeneous systems, includes a molecular level characterization of reactivity of surface-bound Re/Mn catalysts, substrate–adsorbate interactions, and photoinduced or electric-field-induced effects on Re/Mn catalysts. For example, the surface may act to (un)block



substrates, (un)trap charges, (de)stabilize particular intermediates (and thus affect scaling relations), and shift potentials in different directions, just as protein environments do. The Account also summarizes recent studies in quantifying the electric field strength experienced by the catalytically active site of the Re/Mn catalyst bound on a Au electrode

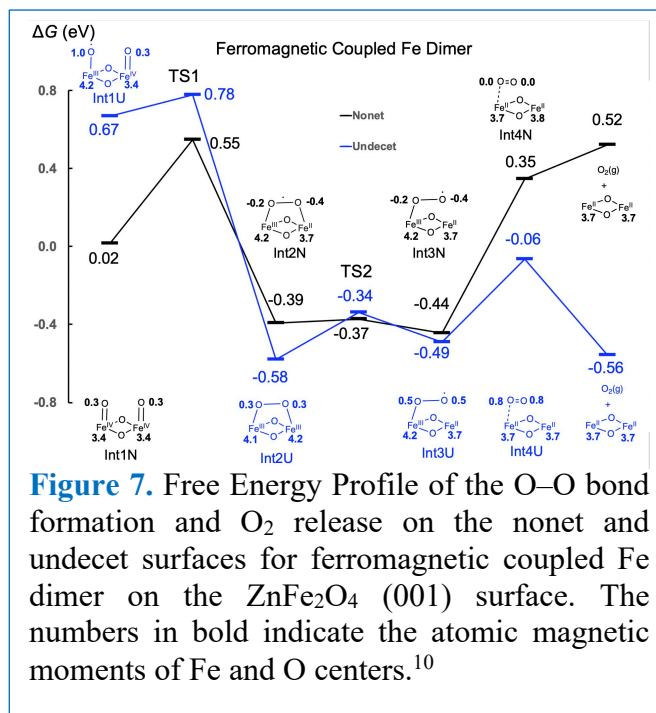
based on a combined electrochemical SFG and DFT study of the Stark tuning of the CO stretching modes of these catalysts. Finally, future research directions on surface immobilized molecular catalyst systems are discussed.

8. Magnetic Field Effect on Catalytic Water Oxidation

Magnetic spinel ferrites such as ZnFe_2O_x and NiFe_4O_x have recently been shown to display significant magnetic field rate enhancements in water oxidation, but little is known regarding the underlying molecular mechanism (Figure 7). Therefore, we

have studied the mechanism of water oxidation on a ZnFe_2O_4 (001) surface to provide understanding about the possible origins of the observed magnetic field effect on the catalytic rate.¹⁰

Our results indicate that spin state crossing plays an important role in O–O bond formation and O_2 release. In addition, the local

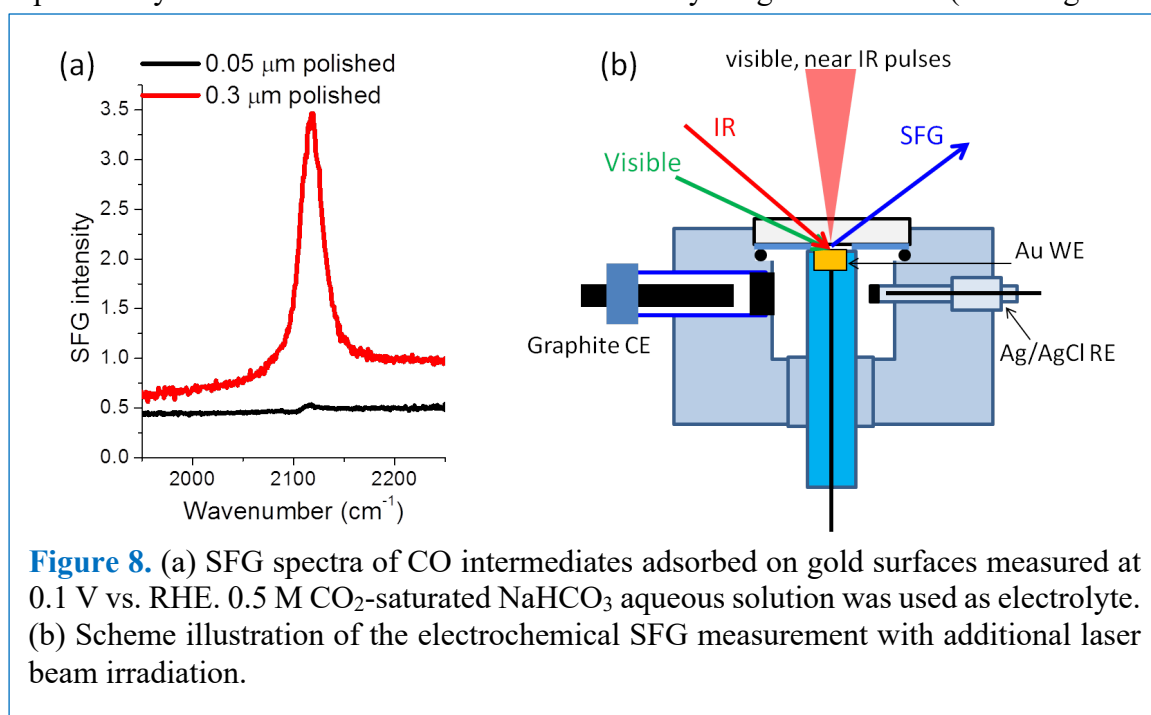


magnetic field and its gradient can be greatly amplified near the surface of magnetic particles. Besides the preference for ferromagnetically metal dimers in an external magnetic field, we suggest that the observed magnetic field effect can also be attributed to the inhomogeneous Zeeman interaction which increases the coupling between different spin states on top of the standard spin-orbit coupling to promote intersystem spin-state crossing. Our study highlights the importance of including several spin states in modeling catalytic water oxidation, which is an intrinsically

spin-forbidden reaction going from singlet H₂O to triplet O₂. Given the ubiquity of intersystem-crossing and spin-forbidden reactions in renewable energy technologies, photochemistry, and organometallic chemistry, we anticipate similar effects based on surface enhanced magnetic field may find applications in fields beyond water oxidation.

9. Plasmon-assisted CO₂ Reduction on Rough Gold Electrodes

Work in progress involves studies of plasmonic hot electrons on the CO₂ electrochemical reduction on gold electrodes in aqueous electrolyte solution. We use gold electrodes with two different roughness, which were polished by 0.05 μm (smooth) and 0.3 μm (rough) alumina powders. Preliminary SFG results show that the roughened gold electrode exhibits much higher CO₂ reduction activity than the smooth one. As shown in Figure 8a, the surface population of CO intermediates on the rough gold is significantly larger than that on the smooth gold. It is noted that such difference in activity cannot be explained by the difference in surface areas caused by roughness factors (smooth gold: ~



1.0; rough gold: ~ 1.6). The illumination of the visible beam (800 nm) used for SFG probe is found to play a crucial role in promotion of CO_2 reduction activity on roughened gold electrodes. To further distinguish the plasmonic and thermal effects of the laser illumination, systematic studies including SFG measurement with additional laser beam irradiation and photocurrent measurement are ongoing (Figure 8b).

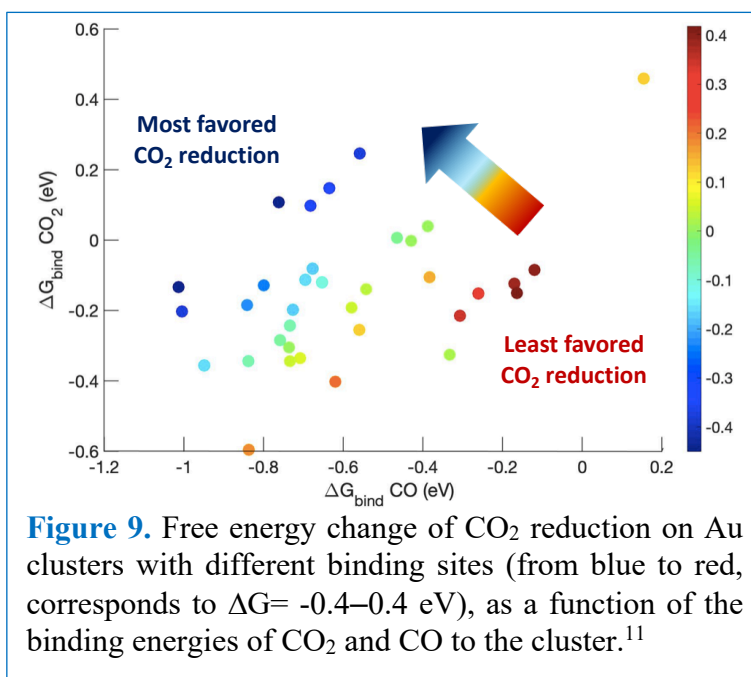
10. Discovery of Gold Morphologies with atypical CO_2 Reduction

The thermodynamics of CO_2 reduction on defects systematically cut from a Au (111) surface was explored and found many sites with spontaneous reactivity for the overall reaction. Analysis of the favorable structures for a structure-function relationship is still underway. Initial results demonstrate the canonical inverse relationship between the strength of CO_2 and CO binding to Au and show that as CO binding becomes more favorable, so does the overall

reduction reaction. Our clusters do however show a uniform spread around this trend, suggesting area for tunability (Figure 9).

Additional tests are examining if these favorable sites are selective for CO_2 reduction, or if they may also

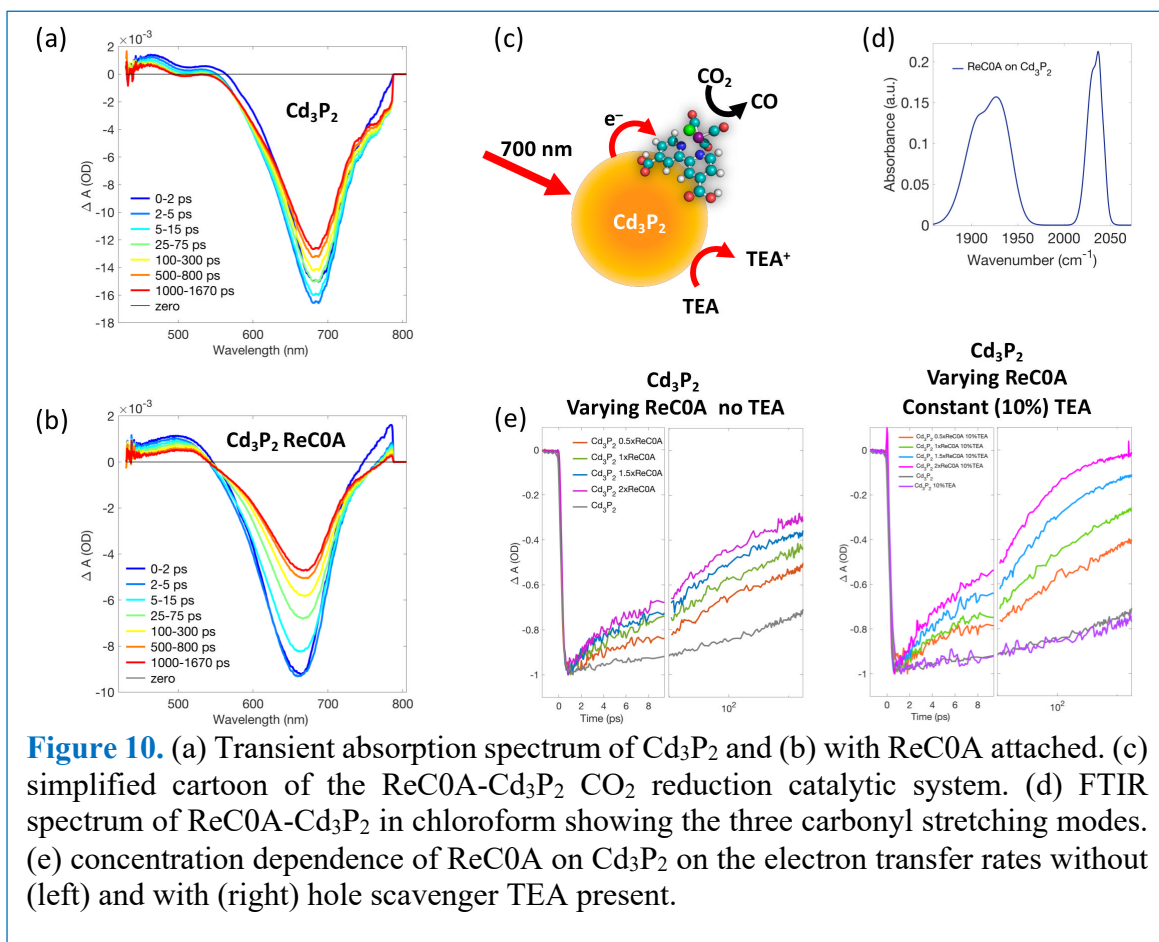
favorably perform hydrogen evolution or oxygen reduction. Finally, options for



experimental identifiers of these favorable sites are being explored to provide easy recognition of what sites are present on an experimental Au surface.¹¹

11. Cd_3P_2 Quantum Dot and Re CO_2 Reduction Catalyst

Experiments have been performed attaching the rhenium CO_2 reduction photocatalyst, $\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}$, with carboxylic acid anchoring groups (ReCOA) or disulfide (ReSS), to Cd_3P_2 quantum dots (QD; 700-900 nm) to extend the absorption required to initiate the reaction into the visible part of the solar spectrum, facilitating the CO_2 reduction reaction (Figure 10). We have characterized the electron transfer process

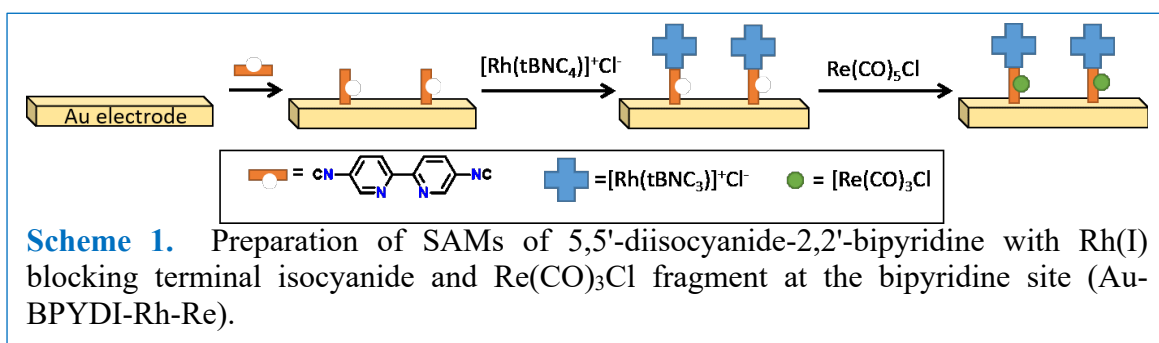


from the QD to the ReCOA catalyst and added a hole scavenger, triethylamine (TEA), to replenish the QD with electrons. This step is necessary because the Re complex requires 2

electrons to reduce CO₂. Our results show that the electron transfer rate increases by a factor of 4 when the TEA is present (Figure 9). Other than the TEA acting as a hole scavenger, the TEA raises the conduction band of the quantum dot by ~300 meV, and possibly also extracts hydrogens from the QD surface, making the surface more negative, and thus have an even higher reduction potential. The preliminary results of the electron transfer from the QD to ReSS show that the rate is slightly faster than that of the electron transfer to ReCOA. Ongoing studies computational studies are investigating how the anchoring group affect the rate of electron transfer from quantum dots to rhenium CO₂ reduction catalysts.

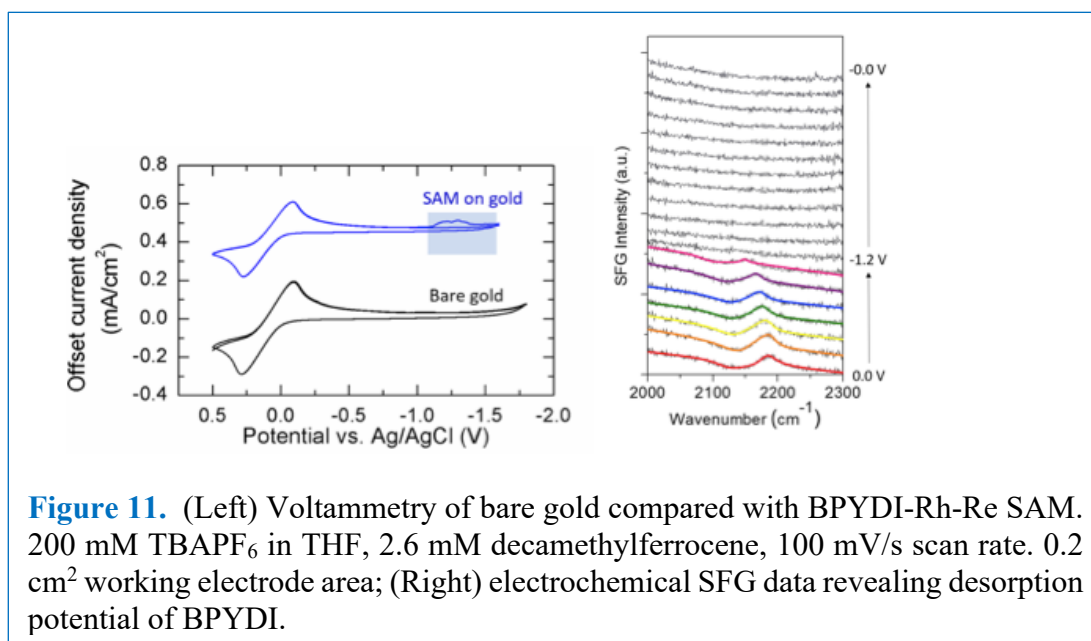
12. Isocyanide Anchoring Groups for Re and Mn CO₂ Reduction Catalysts

Ongoing work with isocyanide self-assembled monolayers (SAMs) on gold entails heterogenizing analogs of known CO₂ reduction catalysts. SAMs of 5,5'-diisocyanide-2,2'-bipyridine were synthesized. This ligand was prepared as a SAM, capped with a rhodium complex to avoid rhenium coordination at both the terminal isocyanide and bipyridine, and subsequently metallated with rhenium at the bipyridine site (Scheme 1), and its voltammetric behavior was analyzed in THF electrolyte with decamethylferrocene as a



potential reference. The data indicates irreversible reductions occurring at approximately -1.2 and -1.3 V vs. Ag/AgCl, which are not repeatable in a subsequent trace (Figure 11,

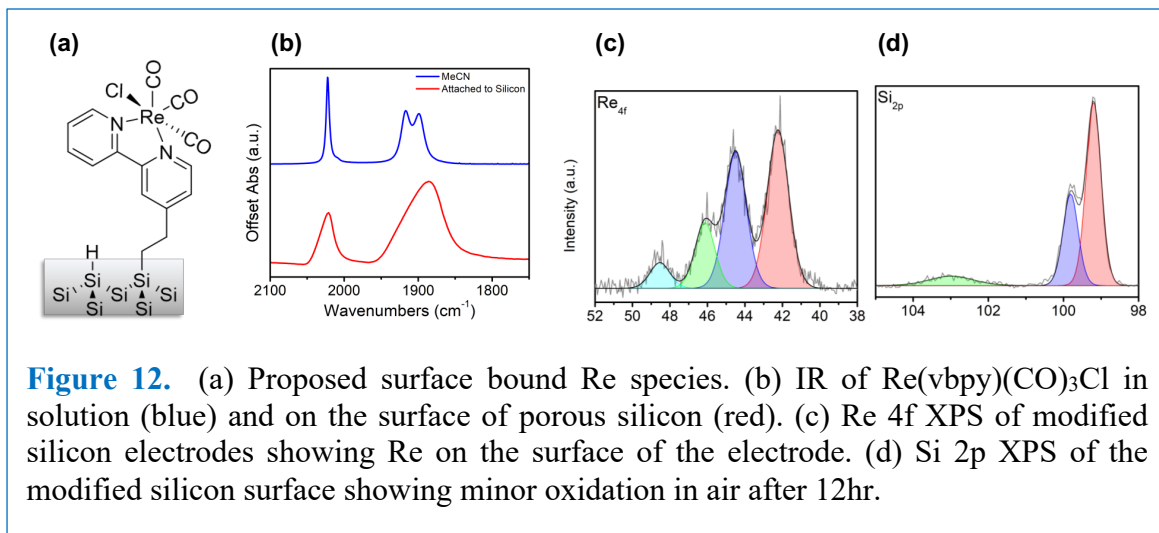
left), suggesting desorption of the SAM. Accordingly, electrochemical SFG of the SAM shows a disappearance of the isocyanide stretch at -1.2 V vs. Ag/AgCl (Figure 10, right). Nevertheless, these isocyanide SAMs may be stable to lower potentials than other similar attachments such as thiol SAMs, and thus ongoing work entails efforts to synthesize Mn(5,5'-diisocyanide-2,2'-bipyridine)(CO)₃Br with isocyanides unmetallated. These catalysts should have more modest reduction and operating potentials than the Re versions of the catalyst.



13. Hydrocarbon Linkers for the Re CO₂ Reduction Catalysts on Silicon

The process of photoelectrochemical reduction of CO₂ to CO using Re(bpy-R)(CO)₃Cl catalysts can be broken down into 3 critical processes: (1) the light absorption and charge carrier generation, (2) heterogeneous charge transfer, and (3) the homogeneous catalytic reduction of CO₂ by the catalyst. Previous work in the lab has shown that the first and third steps are facile, but the second is the limited step in the homogeneous catalysts. In an effort to understand the second step and improve on it, we have begun research into the surface attachment of the Re(bpy)(CO)₃Cl catalyst to the surface of doped silicon. The

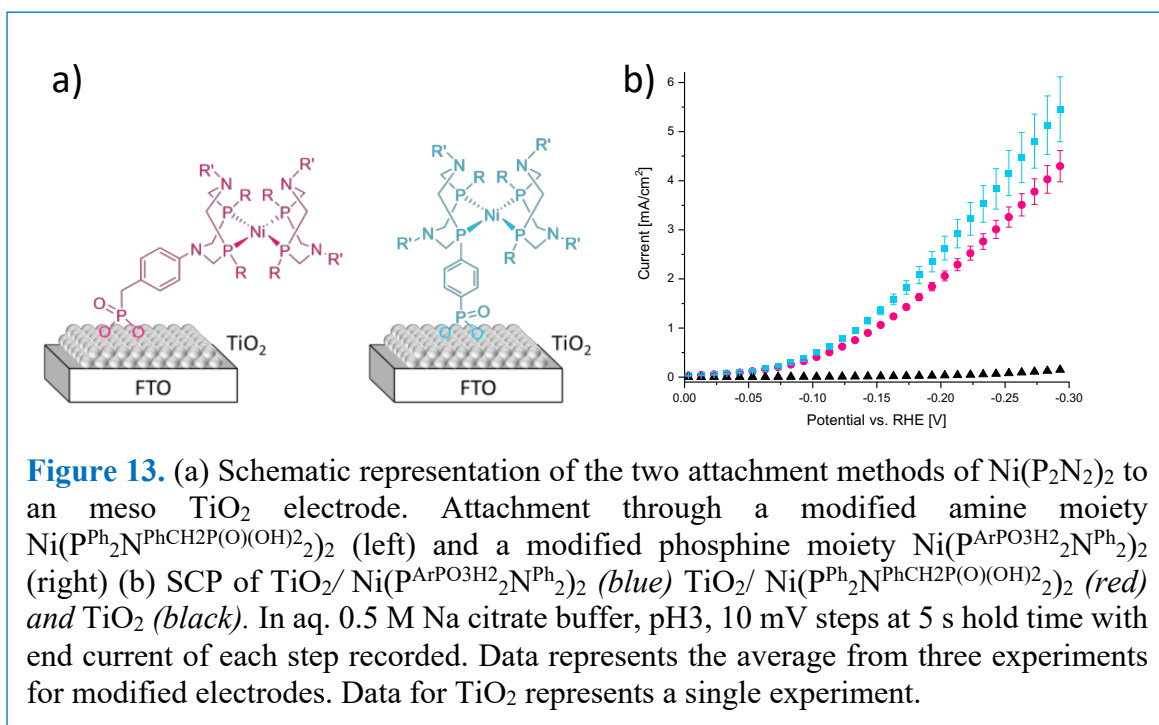
goal of the project is to understand how surface immobilization of the complex to the surface affects charge transfer and catalysis (Figure 12). In addition, these linkers should also be quite stable in very reducing conditions, allowing us to obtain in-situ spectra of surface bound catalyst at different redox states. For this, 4-vinyl-2,2'-bipyridine (vbpy) was synthesized and characterized. Metallation of this ligand to $\text{Re}(\text{CO})_5\text{Cl}$ to create $\text{Re}(\text{vbpy})(\text{CO})_3\text{Cl}$ has been characterized and studied as homogeneous electrocatalysts. Surface attachment of this catalyst shows facile modification of the surface, leaving the catalyst intact. In addition, the modification of the silicon has shown a stability towards oxidation, a common degradation pathway for silicon materials.



14. Investigation of immobilization effects on $\text{Ni}(\text{P}_2\text{N}_2)_2$ electrocatalysts

$\text{Ni}(\text{P}_2\text{N}_2)_2^{2+}$ complexes have been extensively studied as homogenous and heterogenous molecular electrocatalysts for the hydrogen evolution reaction (HER). Historically, the synthetically most accessible derivatives were utilized to surface immobilize molecular electrocatalysts. However, in recent years it was discovered that a smart attachment can enhance catalysis dramatically. The $\text{Ni}(\text{P}_2\text{N}_2)_2$ family is an interesting example to study

immobilization effects. While the pendent amines play a crucial role in the widely accepted catalytic mechanism for HER, all previous studies unanimously utilized this very same amine as the anchor point to attach the catalyst to electrodes. Precisely how the attachment moiety influences the catalyst attached to the surface has not been investigated previously. A new synthetic route to complexes of the type $\text{Ni}(\text{P}_2\text{N}_2)_2^{2+}$ with highly functionalized, surface attachable phosphine substituents was developed (Figure 13). This enabled us to directly compare the *P*-attached catalyst ($\text{Ni}(\text{P}^{\text{ArPO}_3\text{H}_2}_2\text{N}^{\text{Ph}_2})_2$) to the previously reported *N*-attached catalyst ($\text{Ni}(\text{P}^{\text{Ph}_2}\text{N}^{\text{PhCH}_2\text{P}(\text{O})(\text{OH})_2}_2)_2$) that utilized the pendent amine for attachments. Using HER as the benchmark reaction $\text{Ni}(\text{P}^{\text{ArPO}_3\text{H}_2}_2\text{N}^{\text{Ph}_2})_2$ showed a 15 % higher current density than its *N*-attached counterpart.



15. Methane Combustion via Formate Intermediates Over Hematite

Effective methane utilization for either clean power generation or value-added chemical production has been a subject of growing attention worldwide for decades, yet challenges persist mostly in relation to methane activation under mild conditions. Here we

report hematite, an earth-abundant material, to be a highly effective and thermally stable catalyst for catalytic methane combustion (CMC) at low temperatures ($< 500^{\circ}\text{C}$) with a low light-off temperature of 230°C and 100% selectivity to CO_2 (Figure 14).¹³ The performance is comparable to those precious-metal-based catalysts with an incredibly low apparent activation energy of $17.60 \text{ kcal}\cdot\text{mol}^{-1}$. From our theoretical calculations, the active site is found to be a tetrairon center with an antiferromagnetic diiron couple, which is analogous to that of the methanotroph enzyme methane monooxygenase. Surface studies with in situ (Diffuse Reflectance Infrared Fourier Transform Spectroscopy) DRFITS and first-principles density functional theory (DFT) calculations reveal the evolution of reaction intermediates from a methoxy $\text{CH}_3\text{-O-Fe}$, to a bridging bidentate formate b-HCOO-Fe , to a monodentate formate m-HCOO-Fe before CO_2 is eventually formed as temperature increases. The formation of the stable reaction intermediates also provides future possibilities of upgrading methane to value-added chemicals *via* heterogenous catalysis.

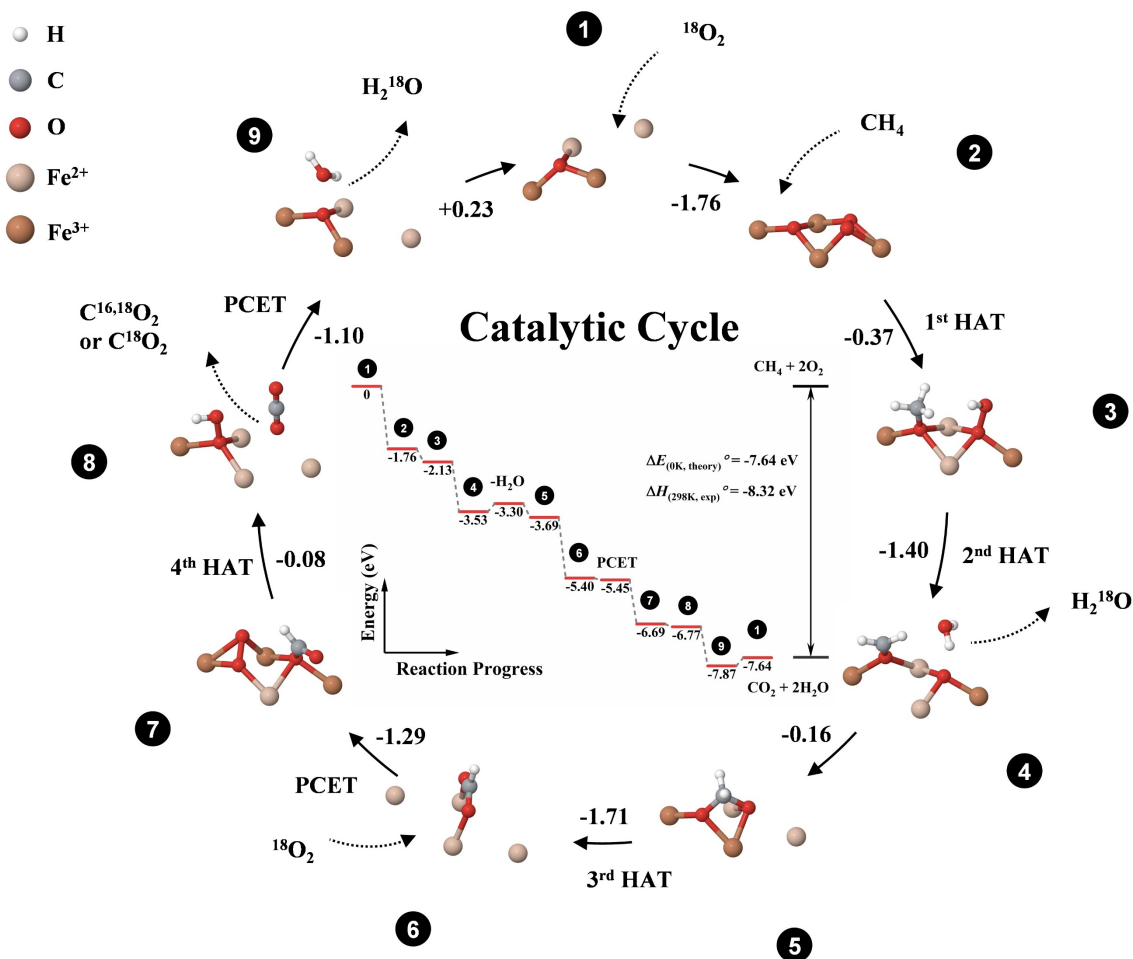


Figure 14. Proposed catalytic cycle for the CMC reaction at high temperatures via molecular-oxygen-assisted pathway with calculated energetic changes. The energy difference for this cycle equals to the theoretical heat released by the CMC reaction at 0K (-7.64 eV), and it's close to the standard heat of the reaction at 298K.¹³

Publications (PI: Batista, AFOSR grant FA9550-17-1-0198)

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