

Monitoring the electronic structure and charge carrier dynamics of clusters supported on surfaces with femtosecond XUV laser pulses

Mihai E. Vaida, Brett M. Marsh, Bethany Lamoureux, Erica Zhang, and Stephen R. Leone

Departments of Physics and Chemistry, University of California, Berkeley, California 94720, USA and Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA

Surface photoemission spectroscopy (PES) utilizing femtosecond extreme-ultraviolet (XUV) laser pulses is used to investigate the electronic structure and ultrafast charge carrier dynamics in photovoltaic and photocatalytic materials. The laser-based XUV-PES technique can monitor charge carrier dynamics with femtosecond time resolution, surface sensitivity, and element and oxidation state specificity. In a recent published example, n-TiO₂ ultrathin films grown on a p-Si(100) substrate form a heterostructure with a staggered type II band alignment which can be varied by the degree of oxidation of the titanium. Results for the electronic structure of n-TiO₂/p-Si(100) as well as ultrafast photoinduced electron migration across the TiO₂-Si heterojunction are considered.¹

Gold clusters grown on 10 ML MgO(100)/Mo(100) are investigated as a model system for using static XUV PES as a probe of electronic character versus cluster size. Over a range of deposition amounts the electronic character is altered, assumedly as a function of cluster size. As the size of the Au clusters is increased, there is a shift in the photoemission onset, indicating a change in character from non-metallic to metallic gold. The results are compared with theoretical work and previous investigations to validate the PES method. Static photoemission is further utilized to monitor the electronic structure of Zn clusters on p-Si(100) versus deposition. The transition from non-metallic to metallic Zn character is observed at about 0.16 ML of Zn coverage.

Employing the pump-probe PES method, the transfer of electrons to Zn particles and a 3.5 ML metallic Zn film² from Si is investigated. Using IR-pump laser pulses with powers sufficient to cause multiphoton excitation, large surface photovoltage shifts of 1-3 eV are observed for coverages of 0.3 ML and 3.5 ML, while a 0.15 ML coverage results in a 0.1 eV shift. Additionally, the surface photovoltage decay behavior is shown to be size dependent with smaller coverages displaying faster carrier recombination. Power dependence studies show that the observed surface photovoltage shifts are well described by thermionic emission theory.

Finally, XUV transient absorption spectroscopy is used to observe charge transfer dynamics in a Ni/TiO₂/Si photocatalyst junction structure. The element specificity of XUV transient absorption monitors charge injection from the photoexcited Si through the TiO₂ insulator layer and into the Ni overlayer, as well as the subsequent relaxation and equilibration dynamics.

1. Vaida, M. E.; Leone, S. R., Femtosecond Extreme Ultraviolet Photoemission Spectroscopy: Observation of Ultrafast Charge Transfer at the N-TiO₂/P-Si(100) Interface with Controlled TiO₂ Oxygen Vacancies. *The Journal of Physical Chemistry C* **2016**, *120*, 2769-2776.
2. Marsh, B. M.; Vaida, M. E.; Lamoureux, B. L.; Leone, S. R., Measuring the Surface Photovoltage of a Schottky Barrier in Real Time Under Intense Light Conditions: Zn/p-Si(100) by Laser Time-Resolved Extreme Ultraviolet Photoelectron Spectroscopy (in preparation)

AFRL Plasma Chemistry Laboratory: Mechanisms of metal-catalyzed reactions

Nicholas Shuman

Space Vehicles Directorate, Air Force Research Laboratory, Kirtland AFB, NM 87117

An overview of work ongoing in the AFRL Plasma Chemistry Laboratory with a focus on work to decipher the mechanisms of reactions of small metal cations through a combination of experiment, quantum calculation, and statistical modeling. Previous work on ionospheric modification through chemi-ionization of lanthanide metals is summarized and updated, along with further AF needs. Metal ion reactions in the gas phase are in some cases analogous to those occurring at catalytically active sites on surfaces or nanoparticles, but can be studied in isolation from confounding environmental effects allowing for more detailed insight. Mechanisms can be further investigated by varying, for instance, the electronic state of the reactant or through ligation of the bare metal. Two examples are detailed. First, in the reaction of Ti^+ + methanol, previous calculations of the reaction coordinate have suggested diabatic formation of excited state $^4\text{TiO}^+$. Here, experimental kinetics suggest instead adiabatic formation of ground state $^2\text{TiO}^+$. The conclusion is strengthened by statistical modeling of the reaction pathway to reproduce experimental results, and the system is shown to be a failure of a simple model based on the Landau-Zener framework to predict surface-hopping probability. Second, the reaction $\text{Fe}^+(\text{CO})_n + \text{O}_2$ is shown to only proceed at thermal energies in the case of $n = 1$, and example of oxidation of CO by ambient O_2 at a single non-noble metal-atom site. Reactivity in the systems is shown to be promoted by more strongly binding O_2 to Fe^+ in the entrance complex. The thermal kinetics are compared to guided ion beam data. Additionally, the kinetics of metal ions with ozone, relevant to mesospheric chemistry, are shown to proceed through a complicated equilibrium involving M^+ , M^+O , .. $\text{M}^+\text{O}_{n>4}$ species, and studies of the chemistry of cations with unstable radicals and of kinetic modeling of electron attachment processes are summarized.

Monolayer Dynamics at the Air/Water Interface

Michael D. Fayer

Department of Chemistry, Stanford University, Stanford, CA 94305

fayer@stanford.edu Grant # FA9550-16-1-0104

Monolayers, interfaces, and very thin films are fundamentally interesting, and they play important roles in many naturally occurring phenomena and technological processes. In general, molecular structural dynamics at an interface will be very different from those in a bulk material. In bulk materials, from liquids to proteins, ultrafast two dimensional infrared (2D IR) spectroscopy has developed into a powerful method for studying structural dynamics and molecular interactions. The advent of acousto-optic pulse shaping methods has greatly expanded the applicability of 2D IR spectroscopy to an increasing range of important materials. However, it has still been very difficult to study a monolayer or a very thin film because of the small number of molecules that comprise the sample, resulting in very weak signals. We have recently developed a new method for performing 2D IR experiments on monolayers and thin films.¹ The method is briefly described. The near-Brewster's angle reflection geometry enhances the 2D IR signal by as much as a factor of 50 and can reduce data acquisition times by a factor of 100. The new method makes experiments that took weeks now take a few hours to a day. For certain monolayer experiments, we are able to obtain useful data in 5 seconds.

The new method has been applied to study the dynamics and structure of a monolayer at the air/water interface. The surface pressure-area isotherm of tricarbonylchloro-9-octadecylamino-4,5-diazafluorenerhenium(I) monolayer at the air/water interface was reported in the literature. This molecule contains a very useful vibrational probe, the head group $\text{ReCl}(\text{CO})_3$ fluorene, which is located at the interface. Thus, this is an excellent monolayer for the first studies. The experiments discussed here occur in the liquid expanded portion of the phase diagram. 2D IR data that measures spectral diffusion and chemical exchange were conducted at several surface densities. Data at two surface densities, low (area 90 \AA^2) and high (area 60 \AA^2), are discussed. In addition, a water soluble version of the vibrational probe head group, $\text{ReCl}(\text{CO})_3$ bipydicarboxylate, was studied in bulk water for comparison. Electronic structure calculations and preliminary MD simulations show that water is hydrogen bonded to the carbonyls, which are the vibrational probes. In bulk water, the water soluble probe yields a fast spectral diffusion component of 1.5 ps, identical to the previously measured time for water hydrogen bond rearrangement. At the interface, the value is 2.9 ps, suggesting a substantial slowing of hydrogen bond rearrangement in the interfacial water layer. In addition, the bulk water probe and interfacial probe the have a slower spectral diffusion component, which is much slower at the interface. This component may be caused by fluctuations in the number of water molecules hydrogen bonded to the three carbonyls.

At low density, there is a single band in the 2D spectrum. At high density, three bands are observed, two "dimer" bands in addition to the main monomer band. Each dimer band has chemical exchange peaks with the monomer in the 2D spectrum, showing that the monomer and dimers are in equilibrium with a chemical exchange monomer-dimer interconversion time of 40 ps. However, the dimer bands are not always present. Structural fluctuations in the monolayer give rise to configurations that permit the dimer formation. By taking five thousand 5 second data sets, the appearance and disappearance of the dimers were tracked. After several hours one of the dimers no longer occurs, which shows that the structure of the monolayer is evolving over the first few hours after it is formed. Measurements of the spectral diffusion as a function of time after formation of the monolayer display changes for approximately the first 5 hours even in the low density monomer only sample. These results demonstrate that the monolayers in the expanded liquid phase, independent of the density, undergo very slow structural evolution for many hours after they are formed.

1. "Enhanced Nonlinear Spectroscopy for Monolayers and Thin Films in Near-Brewster's Angle Reflection Pump-probe Geometry," Jun Nishida, Chang Yan, and Michael D. Fayer *J. Chem. Phys.* **146**, 094201 (2017).

Grain Boundary Effects in Electrocatalysis

Matthew W. Kanan
Department of Chemistry
Stanford University

We are examining the use of grain boundaries to create highly active surfaces on heterogeneous electrocatalysts. Grain boundaries are the interfaces between mis-oriented crystallites in a polycrystalline material. Using electrochemical measurements and extensive ex situ TEM, we have shown that catalytic activity is directly proportional to grain boundary density for both CO₂ reduction on Au nanoparticles and CO reduction on Cu nanoparticles. This talk will describe our efforts to elucidate the physical origin of grain boundary effects. One model is that grain boundaries create strained regions at their surface terminations and that the strain lowers the barriers for CO₂/CO reduction. We have developed a scanning electrochemical method to directly probe CO₂ reduction activity at terraces and grain boundary surface terminations on flat Au electrodes. By combining scanning electrochemistry with grain orientation mapping and strain mapping, we are correlating activity at grain boundary surface terminations to the degree of grain mis-orientation and the associated strain field. I will also describe our efforts to assess the effects of grain boundaries on the selectivity of CO reduction catalyzed by Cu nanostructures. For these studies, we have developed a gas diffusion cell that enables high CO reduction current densities and high CO conversions under single-pass conditions. Our results provide a basis for utilizing grain boundaries to improve catalysis for CO₂ and CO reduction and tools to explore grain boundary effects in other electrochemical and non-electrochemical reactions.

Achieving Surface Sensitivity in Ultrafast XUV Spectroscopy: Investigating Surface Carrier Dynamics in Catalysts Showing High Selectivity for CO₂ Reduction

L. Robert Baker, Assistant Professor
Department of Chemistry & Biochemistry
The Ohio State University

The ability to probe electron dynamics with surface sensitivity is critical for understanding processes that mediate efficiency and selectivity during catalytic energy conversion and storage. Toward this goal, we have developed a high harmonic generation (HHG) light source for femtosecond extreme ultraviolet (XUV) spectroscopy. Using this light source we investigate the ultrafast carrier dynamics at the surface of single crystalline α -Fe₂O₃, polycrystalline α -Fe₂O₃, and the mixed metal oxide, CuFeO₂. We have recently shown that CuFeO₂ is a selective catalyst for photo-electrochemical CO₂ reduction to acetate, showing 80% Faradaic efficiency at -0.4 V bias vs. Ag/AgCl during visible light illumination. Analysis shows that the selective catalyst is a mixed phase material consisting of CuFeO₂ and CuO. By varying the Fe:Cu atomic fraction from 1.3 to 0.1, it is possible to tune the selectivity for CO₂ reduction from primarily acetate to primarily formate. Here we demonstrate that XUV reflection-absorption spectroscopy of these materials provides element, oxidation, and spin state specific dynamics with femtosecond time resolution. These measurements are also surface sensitive, and by measuring both the real and imaginary components of the complex refractive index, we can differentiate between surface and sub-surface contributions to the excited state spectrum. This work demonstrates the ability to probe ultrafast carrier dynamics with chemical state specificity and surface sensitivity, and the results provide important insights on the mechanism of charge transfer and energy conversion at the surface of photo-excited metal oxide catalysts.

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3. J. Husek, A. Cirri, S. Biswas, and L. R. Baker, "Direct Observation of Small Surface Polaron Formation in Hematite Using Ultrafast XUV Reflection-Absorption Spectroscopy" In preparation.

Balancing near-field enhancement, absorption, and scattering for effective antenna-reactor plasmonic photocatalysis

Kun Li¹, Nathaniel J. Hogan^{2,3}, Matthew J. Kale^{1,4}, Naomi J. Halas^{2,3,5,6}, Peter Nordlander^{2,3,6}, Phillip Christopher^{,1,7,8}*

1. Department of Chemical and Environmental Engineering, University of California, Riverside, Riverside, CA 92521, USA; 2. Department of Physics and Astronomy, Rice University, Houston, TX 77005, USA; 3. Laboratory for Nanophotonics, Rice University Houston, TX 77005, USA; 4. Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA 91125, USA; 5. Department of Chemistry, Rice University, Houston, TX 77005, USA; 6. Department of Electrical and Computer Engineering, Rice University, Houston, TX 77005, USA; 7. Program in Materials Science, University of California, Riverside, Riverside, CA 92521, USA; 8. UCR Center for Catalysis, University of California, Riverside, Riverside, CA 92521, USA

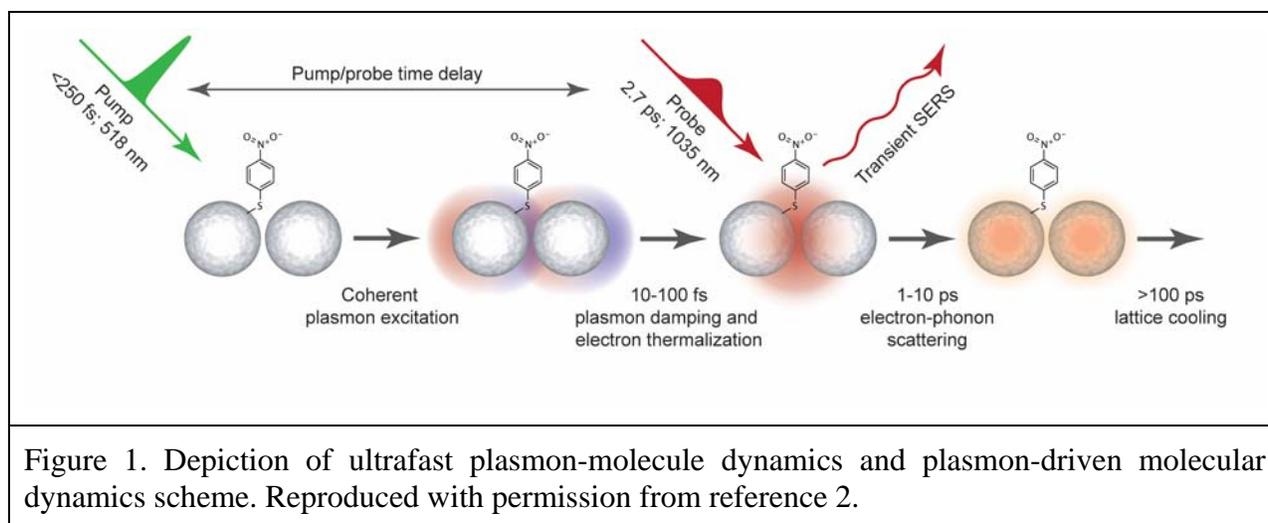
Efficient photocatalysis requires multifunctional materials that absorb photons and generate energetic charge carriers at catalytic active sites to facilitate a desired chemical reaction. Antenna-reactor complexes are an emerging multifunctional photocatalytic structure where the strong, localized near field of the plasmonic metal nanoparticle (e.g. Ag) is coupled to the catalytic properties of the non-plasmonic metal nanoparticle (e.g. Pt) to enable chemical transformations. With an eye towards sustainable solar driven photocatalysis we investigate how the structure of antenna-reactor complexes governs their photocatalytic activity in the light-limited regime, where all photons need to be effectively utilized. By synthesizing core@shell/satellite (Ag@SiO₂/Pt) antenna-reactor complexes with varying Ag nanoparticle diameters and performing photocatalytic CO oxidation, we observed plasmon-enhanced photocatalysis only for antenna-reactor complexes with antenna components of intermediate size (25 and 50 nm). Optimal photocatalytic performance was shown to be determined by a balance between maximized local field enhancements at the catalytically active Pt surface, minimized collective scattering of photons out of the catalyst bed by the complexes, and minimal light absorption in the Ag nanoparticle antenna. These results elucidate the critical aspects of local field enhancement, light scattering, and absorption in plasmonic photocatalyst design, especially under light-limited illumination conditions.

Probing plasmon-driven processes with ultrafast surface-enhanced Raman spectroscopy

Renee R. Frontiera,

Department of Chemistry and Chemical Physics Program, University of Minnesota

Plasmonic nanomaterials are promising candidates for solar-driven catalytic devices, as they interact strongly with light and are known to be capable of driving energetically unfavorable chemical reactions. Their ability to concentrate light to subwavelength volumes leads to the formation of hot spots and hot electrons, which can drive energy flow, modify potential energy surfaces, and enable new photochemical and photophysical processes. However, significant questions remain as to the mechanism of action of a plasmonic photocatalytic system, in part because of difficulties in characterizing the rapid photo-induced dynamics and interactions between the nanoparticle surfaces and proximal molecular species. In particular, the impact of hot carriers on driving photochemistry, including fundamental properties such as their yield and lifetime, is currently poorly defined.



Here we use ultrafast surface-enhanced Raman spectroscopy, a pump-probe technique designed to follow the molecular response of molecules adsorbed on plasmonic nanomaterials, to investigate the response of the coupled molecule-plasmon system to light.¹ By tracking the transient Raman frequency evolution, we can determine the degree of charge transfer and molecular structural change following plasmon excitation. For silver colloidal samples, we find a strong correlation between spatial sites on the nanoparticle surface which generate hot electrons and those which drive photochemistry.² For gold colloidal samples, we have shown that plasmon excitation results in a transient delocalization of electron density, we which estimate results in displacements on the order of 10^9 electrons per multiparticle aggregate.³ In conjunction with the Halas and Nordlander groups, we are investigating the role of transient molecular intermediates in promoting selectivity in photocatalysis with bimetallic antenna-reactor complexes. Our work on the fundamental mechanism of how plasmonic nanomaterials interact with nearby molecular species on the ultrafast timescale should ultimately lead to rational design of plasmon-driven photocatalytic systems. This material is based on work supported by the Air Force Office of Scientific Research under AFOSR Award No. FA9550-15-1-0022.

1. Keller, E. L., Brandt, N. C., Cassabaum, A. A., Frontiera, R. R. *Analyst*, **2015**, *140*, 4922–4931.

2. Brandt, N. C., Keller, E. L., Frontiera, R. R. *The Journal of Physical Chemistry Letters*, **2016**, *7*, 3179–3185.

3. Keller, E. L., Frontiera, R. R., in review.

Enhanced Photocatalysis on TiO₂-Passivated III-V Compounds for Water Splitting and CO₂ Reduction

Profs. Steve Cronin and Alex Benderskii (USC)

We report enhanced photocatalysis for H₂ evolution and CO₂ reduction using TiO₂-passivated InP and GaAs photocathodes.¹⁻³ The TiO₂ layer makes the InP semiconductor photochemically stable. This represents a major step forward in photocatalysis, which has typically been limited to metal oxide materials. In addition to making these surfaces stable, the TiO₂ film, deposited by atomic layer deposition (ALD), also provides a substantial enhancement in the efficiency of H₂ evolution. We find that passivating GaAs with just a few nm of TiO₂ produces a shift in the onset potential of H₂ evolution by +0.35 V at 1 mA/cm₂ and enhances the photocurrent by 32-fold over bare GaAs (at 0 V vs. RHE). Here, thinner TiO₂ films produce a larger enhancement than thicker films, which correlates with the higher density of O-vacancies (i.e., Ti³⁺ surface states) observed in these thinner films using X-ray photoemission spectroscopy (XPS). While TiO₂ films 1-5nm thick produce large enhancements, no enhancement is observed for TiO₂ thicknesses above 10 nm, which are crystalline and, therefore, considerably more insulating than thinner amorphous TiO₂ films.

We also report photocatalytic CO₂ reduction with water to produce methanol using TiO₂-passivated InP nanopillar photocathodes under visible wavelength illumination.² Again, the TiO₂ passivation layer provides a stable photocatalytic surface and substantial enhancement in the photoconversion efficiency and selectivity through the introduction of O-vacancies associated with the nonstoichiometric growth of TiO₂ by ALD. Plane wave-density functional theory (PW-DFT) calculations confirm the role of oxygen vacancies in the TiO₂ surface, which serve as catalytically active sites in the CO₂ reduction process. PW-DFT shows that CO₂ binds stably to these oxygen vacancies and CO₂ gains an electron (-0.897e) spontaneously from the TiO₂ support. The TiO₂ film increases the Faraday efficiency of methanol production by a factor 5.7X under an applied potential of -0.6 V vs NHE, which is 1.3 V below the E⁰ (CO₂/CO₂⁻) = -1.9 eV standard redox potential.

In order to further understand the strong dependence of these photocatalysts on TiO₂ thickness over the range of 0–15 nm, we performed cross-sectional high resolution transmission electron microscopy (HRTEM) of GaAs/TiO₂ heterojunctions.³ Thinner films (1–10 nm) are amorphous and show enhanced catalytic performance with respect to bare GaAs. HRTEM images and electron energy loss spectroscopy (EELS) maps show that the native oxide of GaAs is removed by the TiCl₄ ALD precursor, which is corrosive. Thicker TiO₂ films (15 nm) are crystalline and have poor charge transfer due to their insulating nature, while thinner amorphous TiO₂ films are conducting.

We report measurements of photocatalytic water splitting using Au films with and without TiO₂ coatings.⁴ In these structures, a thin (3-10nm) film of TiO₂ is deposited using atomic layer deposition (ALD) on top of a 100nm thick Au film. We utilize an AC lock-in technique, which enables us to detect the relatively small photocurrents (~μA) produced by the short-lived hot electrons that are photoexcited in the metal. Under illumination, the bare Au film produces a small AC photocurrent (<1 μA) for both the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER) due to hot electrons and hot holes, respectively, that are photoexcited in the Au film.

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Structure and Optical Spectra of Magic-Size Nanoclusters

Kiet Nguyen, Paul Day, Ruth Pachter

Air Force Research Laboratory, Materials & Manufacturing Directorate
Wright-Patterson Air Force Base, Ohio 45433-7702

Colloidal cadmium chalcogenide magic-size nanoclusters have drawn much attention for optical application, and moreover in providing an atomically precise system to probe structural changes, as well as the effects of ligands and solvent on one-photon absorption (OPA) spectra by using density functional theory (DFT) and linear and quadratic response time-dependent DFT (TDDFT). At the same time, prediction of these effects is complicated by the accuracy of calculation. Here, we present structure and spectra for stoichiometric and nonstoichiometric cadmium sulfide and cadmium selenide nanoclusters in comparison to experimental data, varying the size, ligands and solvent, which will overall enable a unified understanding of the response and enable design for improved functionality. In this context, effects of phenyl, para-nitrophenyl, and para-cyanophenyl substitutions on the two-photon absorption (TPA) cross-section will be described.

In addition, we report on the structure and optical properties of a silver sulfide cluster that demonstrated dual emission, which was observed when the nanocluster is in crystalline form. A supposition on stabilization of a higher energy excited state by an excimer-like complex was analyzed by calculations for a cluster dimer, formed through π -stacking of aromatic groups bonded to the sulfur atoms. Due to the complexity of the system, we applied a one-dimensional method for dimer optimization, which predicts only partially the red-shift of the emission energy. Interestingly, calculations of the TPA cross-sections for the isolated cluster, as well as the crystal structure geometry, indicate significant off-resonance TPA enhancement.

Spectroscopic Measurements for Next-Generation Space Technologies

Christopher Annesley and Jaime Stearns
Air Force Research Laboratory, Space Vehicles Directorate
Kirtland AFB, NM

The LaSR (Laser Spectroscopy and Reactivity) Lab studies plume species spectroscopically to better understand chemical transformations that occur in the space environment. In one project, we are studying VUV induced UV fluorescence of chemical thruster plume species. To date, we have examined water photodissociation by 121.6 nm radiation (Lyman- α) to determine the rovibrational population distribution of OH(A) product. This allows assessment of different measures from the literature of the fluorescent quantum yield taken directly and indirectly. The other major project in the lab is studying ionic liquids that are being adopted as propellants in satellite thrusters. Specifically, our research program utilizes gas-phase spectroscopy and mass spectrometry to explore the fundamental optical and structural properties of ionic liquid neutral pairs and ionic clusters. Using infrared spectroscopy, we have made several findings concerning the ion pair [EMIM][TF2N]. First, we identified the existence of multiple low energy conformers within [EMIM][TF2N] with the use of selective deuteration along with infrared spectroscopy. Additionally, important anharmonic effects in the spectra of imidazolium-based cations were identified. We are now expanding our studies to larger, charged clusters. We have made the first experimental threshold CID measurements of charged clusters, where we have identified dissociation pathways and determined binding energies. These values are important inputs for modeling electrospray thrusters. We have also undertaken a theoretical investigation on the hypergolic reaction of dicyanamide-based IL clusters with nitric acid. These theoretical results provide new insight into the reaction and provide the basis for future experimental work to be carried out in the laboratory and together will provide guidance to the next generation of ionic liquid based bipropellants.

AFOSR Project:

Atomically Precise Metal Nanoclusters: Structure, Dynamics and Catalysis

Rongchao Jin (Carnegie Mellon Univ.)

In this talk I will present our recent advances in metal nanocluster research (e.g. gold and Au/Ag bimetal). A series of atomically precise $Au_n(SR)_m$ nanoclusters (where, SR = thiolate ligand) have been achieved in the size range of 1–3 nm. More importantly, their atomic structures (metal core plus surface ligands) have been successfully determined, for example, ranging from the subnanometer $Au_{18}(SR)_{14}$ to the 2.2 nm $Au_{246}(SR)_{80}$ structure. These structurally characterized nanoclusters provide the basis for understanding the evolution behavior of electronic and optical properties, structural pattern formation, and nanoparticle assembly mechanism. Studies on the electron dynamics have clearly mapped out the transition from the excitonic to plasmonic state, which occurs around the size of Au_{333} . The well defined nanoclusters have also been explored for catalytic applications in CO_2 reduction/water splitting processes and some mechanistic insights are obtained.

Quantum Dots as Sensitizers and Photocatalysts for Organic Transformations and Reduction of CO₂ to Fuel-forming Molecules

Emily A. Weiss, Dept. of Chemistry, Northwestern University

This talk describes some strategies for and demonstrations of the use of colloidal semiconductor nanocrystals (quantum dots, QDs) as photosensitizers (light harvesters) and catalysts for photo-redox reactions, including carbon-carbon coupling reactions, H-atom abstraction, and CO₂ reduction to CO. In some cases, the visible-light absorbing QDs are complexed with coordination compounds to drive the reaction (Figure 1). In other cases, the QDs perform the functions of both sensitizer and catalyst; here, we demonstrate the dependence of photocatalytic efficiency on the surface chemistry of the particles.

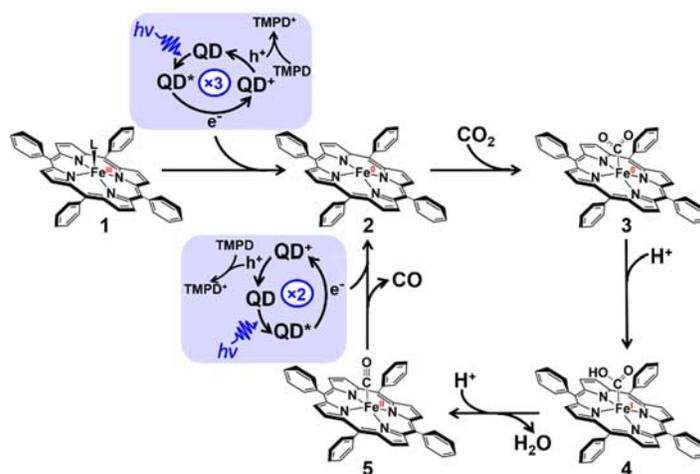


Figure 1. Scheme for reduction of CO₂ to CO using a combination of CuInS₂ QDs and an iron tetraphenyl porphyrin (FeTPP), via three electron transfers from the QD to FeTPP to form the catalytically active Fe(0) state.

Studies of Dynamic Material Interfaces in Extreme Environments

Steven J. Sibener, The James Franck Institute and Department of Chemistry, The University of Chicago

The scattering of atomic and molecular beams from well-characterized surfaces is an incisive method for studying the dynamics of gas-surface interactions, providing precise information on energy and momentum transfer as well as complex reaction mechanisms. Scanning probe measurements provide a powerful complement to scattering data as SPM measurements give a direct route to the visualization and spectroscopic characterization of interfacial atomic and nanosystems. This AFOSR program is examining critical aspects of the chemical and physical behavior of dynamic material interfaces operating in extreme environments. Extreme conditions encompass high and low temperature regimes, high velocity gas flows, optical and charged particle illumination, and severe oxidative environments where interfacial aerodynamic performance (energy and momentum transfer characteristics), morphological change, and chemical stability need to be assessed and quantified.

We will report at this year's meeting on several achievements: (i) Our newest scattering instrument is now fully operational, combining in one facility both reactive scattering and time-sequenced STM/AFM visualization of reacting surfaces. This was initially used to examine the site-specific oxidation of Si(1x1)-(7x7) [1]. (ii) In a major new effort, we are studying the erosion and ablation of graphite when exposed to energy selected beams of molecular oxygen. We are observing reaction probabilities and the morphological evolution of the reacting HOPG (basal plane), with the observation of faceted, direction independent, and channel formation depending of substrate temperature, defect density, incident beam energy and angle of incidence [2]. Moreover, in support of aerothermodynamic calculations, we are initiating scattering experiments where we monitor velocity and angle distributions for energy transfer and oxidative reaction products, these studies for both basal and prismatic HOPG interfaces. (iii) We will also report on the dynamical interactions of molecular hydrogen with a new, relatively redox-stable methylated interface that is of importance to next-gen electrochemical energy systems, (1x1) methyl-terminated Si(111) [3], as well as dynamical studies of few-layer graphene sheets [4]. (iv) We have extended our studies of energetic embedding of neutral species into ice to include molecular species, for example, CO₂ [5], demonstrating that this is a general mechanism for gas-surface interactions, and that it is a significant new channel by which incident species can be trapped under conditions where they would otherwise not be bound stably as surface adsorbates. This is an important new mechanism for understanding gas-surface energy & momentum exchange in high velocity gas flows, and for trace gas collection and concentration. Our newest focus is on clathrates, systems of interest for hydrocarbon energy recovery.

Selected Recent Publications

1. Temporally and Spatially Resolved Oxidation of Si(111)-(7x7) using Kinetic Energy Controlled Supersonic Beams in Combination with Scanning Tunneling Microscopy, Bryan Wiggins, L. Gaby Avila-Bront, Ross Edel, and S. J. Sibener, *J. Phys. Chem. C* **120**, 8191-8197 (2016).
2. Atomically-resolved Oxidative Erosion of HOPG Basal Plane Graphite Using Supersonic Beams of Molecular Oxygen in Conjunction with STM/AFM Visualization, Ross Edel, Tim Grabnic, and S. J. Sibener, in preparation (2017).
3. Experimental and Theoretical Study of Rotationally Inelastic Diffraction of H₂(D₂) from Methyl-Terminated Si(111), Kevin J. Nihill, Zachary M. Hund, Alberto Muzas, Cristina Diaz, Marcos del Ceuto, Terry Frankcombe, Noah T. Plymale, Nathan S. Lewis, Fernando Martin, and S. J. Sibener, *J. Chem. Phys.* **145**, 084705/1-12 (2016). [Journal of Chemical Physics Editor's Choice Article for 2016.]
4. Growth, Structure, and Vibrational Properties of Few Layer Graphene Grown on Rh(111), K. D. Gibson and S. J. Sibener, *J. Phys. Chem. C* **120**, 24158-24164 (2016).
5. Capture of Hyperthermal CO₂ by Amorphous Water Ice via Molecular Embedding, Grant G. Langlois, Wenxin Li, K. D. Gibson, and S. J. Sibener, Invited Feature Article for the Special Issue: "Dynamics of Molecular Collisions XXV – Fifty Years of Chemical Reaction Dynamics", *J. Phys. Chem. A*, **119**, 12238-12244 (2015).

Simulations of Dynamics Associated with Ablation and Gas-Phase Collisional Energy Transfer

William L. Hase

Department of Chemistry and Biochemistry

Texas Tech University

Lubbock, TX 79409

Chemical dynamics simulation software and models were developed to study dynamics of gas-surface collisions associated with ablation. Collisions of N₂ with a graphite surface were simulated to study attributes of energy transfer in ablation. The simulations were performed versus collision energy, incident polar angle, and surface temperature and the properties analyzed include: (1) the translational and rotational energy distributions of the scattered N₂ molecules; (2) the distribution of the final polar angle for the scattered N₂ molecules; and (3) the number of bounces of the N₂ molecules on the surface before scattering. Direct scattering with only a single bounce is dominant for collisions nearly perpendicular to the surface. Scattering with multiple bounces becomes important for incident angles far from the surface normal; e.g. 70°.

Ions are important in the Earth's atmosphere and for plasmas around fast moving vehicles in the lower atmosphere. To assist in studies by the Viggiano and Troe research groups of ion-molecule kinetics, energy transfer dynamics was simulated for collisions of He and N₂ with the propylbenzene cation. This required calculating accurate intermolecular potentials for He and N₂ interacting with the cation. The unified model for simulating liquid and gas phase intermolecular energy transfer was used for these studies. The simulation results are compared with experiment.

If time permits, a model for constraining zero point energy (ZPE) flow in unimolecular and bimolecular reactions with reaction intermediates will be discussed.

Multiconfigurational Pair-Density Functional Theory for Charge Transfer Processes

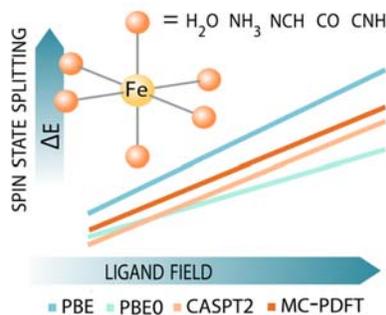
Laura Gagliardi and Donald G. Truhlar

Department of Chemistry, Supercomputing Institute, and Chemical Theory Center,
University of Minnesota, Minneapolis, Minnesota, 55455, USA

We have recently proposed and tested a new formulation of density functional theory called multi-configuration pair-density functional theory (MC-PDFT), which is based on a combination of multi-configuration wave function theory with a new kind of density functional called an on-top density functional.[1] The application of MC-PDFT to accurately describe charge-transfer phenomena for both ground and electronically excited states will be discussed. We will also present our recent study of spin-state orderings in nine Fe(II) and Fe(III) complexes with ligands of diverse ligand-field strength using MC-PDFT.[2] The performance of this method was compared to that of complete active space second-order perturbation theory, CASPT2, and Kohn-Sham density functional theory, KS-DFT. We also investigated the dependence of CASPT2 and MC-PDFT results on the size of the active-space. MC-PDFT reproduces the CASPT2 spin-state ordering, the dependence on the ligand field strength, and the dependence on active space at a computational cost significantly reduced as compared to CASPT2.

[1] L. Gagliardi, D. G. Truhlar, G. Li Manni, R. K. Carlson, C. E. Hoyer, and J. Lucas Bao, Multiconfiguration Pair-Density Functional Theory: A New Way To Treat Strongly Correlated Systems, *Acc. Chem. Res.*, 50, pp 66–73 (2017)

[2] L. Wilbraham, D. G. Truhlar, L. Gagliardi, and I. Ciofini Multiconfiguration Pair-Density Functional Theory Predicts Spin-State Ordering in Iron Complexes with the Same Accuracy as Complete Active Space Second-Order Perturbation Theory at a Significantly Reduced Computational Cost *J. Phys. Chem. Lett.* accepted (2017)



Surface Chemistry and Microplasma Studies of Reactive Processes at Plasma-Surface Interfaces

Yuxin Yang¹, Michelle Hofman², Dwayne Yang¹, Laura Kraya¹, Xiaofang Yang¹, Luxherta Buzi¹, Marlene Patino³, Sophia Gershman³, Igor Kaganovich³, Kevin Pardinias⁴, Nan Yao⁵, Yao-Wen Yeh^{5,6}, Yevgeny Raitses³, and Bruce E. Koel¹

¹Department of Chemical and Biological Engineering, Princeton University, Princeton, NJ 08544

²Department of Chemistry, Princeton University, Princeton, NJ 08544

³Princeton Plasma Physics Laboratory Princeton, NJ 08543

⁴Dept. of Mechanical and Aerospace Engineering, Princeton University, Princeton, NJ 08544

⁵Princeton Inst. for Sci. and Technol. of Mater. (PRISM), Princeton Univ., Princeton, NJ 08544

⁶Department of Electrical Engineering, Princeton University, Princeton, NJ 08544

Microplasma discharges have emerged as an important direction for plasma development, providing atmospheric pressure discharges at modest power input, and offering promising applications in environmental remediation and energy. Plasma-materials interactions in these plasmas are key, but improved understanding of the surface chemistry and processes at these interfaces is needed to increase efficiency and selectivity in reactive catalytic plasmas such as those for methane conversion or dry reforming. Hydrogen atoms and ions are important reactive species in these plasmas, and we have carried out experiments on the interactions of these species with clean and adsorbate-covered Ni(110) surfaces used as a model catalyst. A focus of our work has been to investigate the formation and reactivity of bulk (subsurface, absorbed) hydrogen that can be formed from incident hydrogen ions on Ni(110). The H⁺ ion energy affects the distribution and desorption temperature of bulk hydrogen, as revealed by temperature programmed desorption (TPD). Subsurface hydrogen is much more reactive than surface-bound adsorbed hydrogen, and we have explored the chemistry of bulk hydrogen with adsorbed CO, CO₂, and C₂H₄ (ethylene) on Ni. Reactions of H⁺ ions incident on these adsorbed layers were investigated. Finally, the secondary electron emission (SEE) yield from Ni(110) was examined for 50 eV to 3 keV electrons for a range of temperatures, impact angles, and adsorbates. These experimental measurements are closely aligned with theory/modeling research by the group of George Schatz at Northwestern University.

A focus of the plasma physics and modeling component has been on the design and characterization of a microdischarge cell that can be used inside an environmental scanning electron microscope (ESEM) for in-situ characterization of reactive plasma-surface interactions. The discharge was characterized in two configurations: micro hollow cathode (MHC) and micro hollow anode (MHA). The electrical and optical emission spectroscopy (OES) data demonstrated that MHC and MHA plasmas are non-equilibrium: $T_e > T_{\text{gas}}$. The MHA can potentially offer a better controllability of the electron energy distribution function, which could be an advantage for fuel reforming and other microplasma applications.

Understanding plasma enhanced dry reforming on nickel catalysts; Photocatalysis for converting N₂ to NH₃

George C. Schatz

Northwestern University, Evanston IL 60208

Dry reforming is a process wherein CH₄ and CO₂ react to give synthesis gas and/or liquid fuels. Dry reforming is normally done under high temperature and pressure conditions, with a Ni catalyst, however it has recently been discovered that if a plasma is also present near the catalyst, then it is possible to get this reaction to go under modest conditions close to room temperature and atmospheric pressure. The role of the plasma in this process is poorly understood. In this talk I will describe several electronic structure studies that my group has done to describe the processes involved in plasma enhanced dry reforming, including both the role of the plasma, and the gas-surface chemistry that occurs in the presence of plasma species. The plasma is known to fragment the reacting gases, especially CH₄ into CH₃ + H and other species, so we will study the interaction of methane and fragments with various Ni surfaces, to show how this enhances chemisorption, surface dissociation, and subsequent reaction with species already on the surface. A highlight of this work involves the reaction of hydrogen with adsorbed CO₂ and CO to give CO, water and other products. The results include comparisons with experiments from the Koel group at Princeton, and with other groups. We have also studied the influence and ions and electrons on surface chemistry, including secondary electron excitation.

The second part of this talk will consider the reaction mechanism underlying recent work from the Kanatzides group at Northwestern in which it was discovered the iron-sulfur clusters present in gel materials can participate in the photocatalytic conversion of N₂ to ammonia under ambient conditions. We find that the mechanism is related to what happens with the nitrogenase enzyme, but with important differences that arise from photon-induced delivery of electrons to the iron-sulfur clusters.

From Hybrid Materials to Rocket Propulsion: Air Force Applications Enabled by Basic Research

Joseph M. Mabry

Air Force Research Laboratory
Aerospace Systems Directorate
Edwards Air Force Base, CA 93524

The study of hybrid materials and their impact on composite material properties has led to a better understanding of the design and function of structured material surfaces. While the contributions of surface energy and surface roughness to wetting-resistance and other surface properties have been known for some time, a better understanding of the effects of surface geometry enabled the design and production of unique surfaces with remarkable surface properties, the utility of which is partially realized because of the potential to create desirable surface features during processing and surface preparation. This improved fundamental understanding has also been applied beyond liquids, to icing and other types of surface fouling, where in-depth understanding of these interactions has enabled the creation of functional surfaces useful in a variety of Air Force applications. This presentation will discuss the research and development of such surfaces, from basic research to application. These applications are among the areas of need in Air Force materials that will be discussed.

Surface-Supported Cluster Catalysts: Fluxionality, Statistical Nature, and Design

Anastassia N. Alexandrova

UCLA, CNSI

Sub-nano surface-supported catalytic clusters, especially in the presence of adsorbates, generally have many low-energy isomers accessible at elevated temperatures of catalysis. The most stable isomer may not be the most catalytically active. Additionally, isomers may interconvert with barriers of varying heights, in response to the environment, i.e. exhibit fluxionality, during catalysis. We model such catalysts as statistical ensembles in realistic conditions, using a number of novel methods. We will show how all practically-important properties of cluster catalysts, such as size-dependent activity, selectivity, and stability against deactivation, are in fact ensemble-average. Side-by-side with the experiment, we demonstrate that, and explain why Pt₇ on alumina is much more active toward alkene dehydrogenation than Pt₈ and Pt₄ on this support. We will then present the design nano-alloys of Pt clusters, which are remarkably selective against coke in this reaction, as again confirmed experimentally (coking is one of the main ways in which cluster catalysts deactivate). These findings were possible only within the ensemble representation of the catalyst.

Concepts and Materials for Sub-Nano Chemistry

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Michael A. Duncan

Department of Chemistry, University of Georgia, Athens, Georgia 30602-2556

We have developed new technology to produce and isolate ultra-small sub-nanometer metal or metal compound particles. These systems, which may also be referred to as large "clusters," have been well-studied in the gas phase, but we now isolate them for the first time as materials. The objective of our research is to discover new sub-nanometer clusters and to evaluate their potential for materials with specific catalytic, electronic, magnetic, and optical properties. An additional goal is the functionalization of these particles so that they can be assembled into networks or arrays. We focus on ligand-coated metal and metal compound (oxide, carbide, silicide) particles, usually containing fewer than 30 atoms. These species are produced in the gas phase using the laser ablation method. Fundamental measurements use molecular beams, mass spectrometry, infrared laser spectroscopy, and computational chemistry to investigate structures and surface-ligand interactions. Synthetic measurements use a new flowtube reactor, applying insight gained about surface interactions, to ligand-coat the ultrasmall metal particles and to collect them in solution. These materials are investigated with laser desorption mass spectrometry, optical spectroscopy, and computational chemistry, as well as measurements of electrochemistry, catalysis, or magnetism. The fundamental and synthetic studies complement each other, providing unanticipated discoveries and improved understanding of metal particle chemistry in the sub-nanometer size range.

In recent progress, gas phase experiments have investigated cerium oxide clusters and their photodissociation pathways. The CeO_2 stoichiometry of the bulk is prominent in even the smallest nanoclusters. Synthetic experiments have explored the production of chromium oxide and metal-silicon clusters, as well as pure metal clusters of silver or aluminum. In a study of vanadium carbide systems, known from the gas phase to form "met-cars" cage and nanocrystal structures, an accidental oxygen leak proved fortuitous, leading to the discovery of new vanadium oxy-carbide nanorod and "nanostar" structures, with 30-50 nm dimensions. Characterization of these new systems is in progress.

Studies of bare and complexed metal oxide clusters by slow photoelectron imaging and infrared photodissociation of cryogenically cooled anions

Daniel M. Neumark
Department of Chemistry
University of California
Berkeley, CA 94720

Transition metal oxides play a key role in many catalytic processes. Studies of the chemistry and spectroscopy of size-selected transition metal oxide clusters provides fundamental insights the properties of these compounds. We investigate these clusters by two complementary methods, both of which are performed on cryogenically cooled anions: slow-electron velocity-map imaging (cryo-SEVI) and infrared photodissociation (IRPD) spectroscopy. Recent work has focused on the splitting of water on TiO_2 clusters; the two methods show that splitting indeed occurs and provide unambiguous spectroscopic signatures for water splitting. In addition, results will be presented on the cryo-SEVI spectrum of SmO^- that yield new spectroscopic information on SmO , a molecule of considerable interest to AFOSR. Finally, new transition state spectroscopy results on benchmark bimolecular and unimolecular reactions will be discussed.

Controlling energy transfer through mode-selective plasmonics.

Kenneth L. Knappenberger, Jr.,^{1*} Tian Zhao,¹ Kyoungweon Park,² and Richard A. Vaia²

¹Department of Chemistry and Biochemistry, Florida State University, Tallahassee, FL 32306-4390

² Air Force Research Laboratory, 2941 Hobson Way, Wright Patterson Air Force Base, Dayton, Ohio 45433

klk@chem.fsu.edu

Plasmonic nanoparticle assemblies offer unique opportunities for controlling energy at the nanoscale. Here, we describe experimental outcomes in three key areas critical to understanding plasmon-mode-specific light-matter interactions: 1) selective amplification of specific light polarization states; 2) structure-dependent plasmon coherence times; and 3) plasmon-mode-specific spatial localization of electromagnetic energy to nanoscale volumes. Interferometric single-particle nonlinear optical (NLO) imaging techniques developed in our lab provide high spatial accuracy and precision along with femtosecond time resolution for examining nanoparticle assemblies. Femtosecond time-resolution is achieved by employing a sequence of phase-locked laser pulses to examine the nanostructures. Determination of plasmon coherence times using these methods provides a quantitative measurement of mode-specific quality factors, which are important for assessing the efficiency of nanostructures for using electromagnetic energy. Based on our coherence data, one-dimensional nanorods are promising building blocks of nanoparticle networks for using electromagnetic energy at the nanoscale. The effectiveness of the nanorods results from the inherent length-to-diameter aspect-ratio-dependent tunability of the longitudinal plasmon resonance (LSPR) frequency. The LSPR of high aspect ratio nanorods can be energetically decoupled from interband relaxation channels, which are a major source plasmon decoherence, thus explaining the experimental results. Indeed, studies of nanorod trimers indicate the plasmon coherence time can be increased by approximately 100% for nanoparticle networks of specific symmetries. I will also demonstrate how the combination of polarization- and time-resolved NLO imaging can be used in combination to correlate plasmon coherence times to interference between specific inter-particle resonances.

Simulating Reactivity in the Condensed Phase: Absorption Behavior and Structure of CO₂-Reactive Ionic Liquids

Edward J. Maginn
Department of Chemical and Biomolecular Engineering
University of Notre Dame
Notre Dame, IN 46556

Ionic liquids have gained considerable interest recently for their ability to dissolve large amounts of gases such as CO₂. In addition to physical solvation, ionic liquids can be made to chemically bind CO₂ by attaching amine functional groups to the ions. Experimentally it is difficult to predict how the solubility of CO₂ and the underlying liquid structure depend upon the nature of the ions and reactive functional groups attached to the ions. In the past we have shown that highly accurate physical solubilities can be obtained from molecular simulations, but these methods fail when chemical reactivity is involved. Here we demonstrate that the solubility of chemically reacting ionic liquids can be computed directly using two different methods. First we describe a thermodynamic cycle that requires as input gas phase quantum chemical calculations of the free energy of reaction along with liquid phase classical molecular dynamics simulations of the enthalpies of vaporization, condensation and mixing. Second, we describe a new reactive Monte Carlo (RxMC) method that enables the direct calculation of the reactive absorption isotherm as a function of pressure. Both methods give near quantitative agreement with experimental isotherms. We then go on to show that the underlying structure of these liquids can be described via simulations. Quantitative agreement with experimental x-ray scattering structure functions is obtained, but the simulations provide three-dimensional information on the organization in the liquid that is not available from the experiments. The RxMC method can be used to predict how the condensed phase or local environment shifts the equilibrium distribution of products for other reactions. We have extended the method to show how nanoconfinement (such as that present in zeolites or other porous catalysts) can shift the equilibrium distribution of reacting xylene isomers.

Metal-Promoted H-ZSM-5 for Endothermic Reforming of Alkanes

Yu-Hao Yeh and Raymond J. Gorte
311 Towne Building, 220 S. 33rd Street
Department of Chemical & Biomolecular Engineering
University of Pennsylvania, Philadelphia, PA 19104 USA

ABSTRACT

A major challenge associated with hypersonic aircraft is thermal protection of the engine, since air cooling is not possible at high velocities. An approach that has been used for controlling the temperatures of critical engine components in the US Air Force X-51A program involves using the fuel itself as a coolant before it enters the combustion chamber. While the amount of heat that can be taken up by the fuel is limited by the maximum temperature to which the fuel can be heated, it is possible to increase the cooling capacity of the fuel by performing endothermic reactions on it. Two possible reactions that have been investigated in this work are the acid-catalyzed cracking reactions that occur in acidic zeolites and the aromatization reactions that occur over Ga- and Zn-exchanged zeolites.

Initial work focused on supercritical, high-pressure reactions of n-hexane over H-ZSM-5, with and without the addition of Pt, Ga, or Zn, and determined reaction endothermicities from the product distributions. For unpromoted H-ZSM-5, the product distribution indicated that the endothermicity is low and decreases with increasing pressure. The addition of Ga or Zn to H-ZSM-5 significantly increased the endothermicity of the reactions by increasing the selectivity to form small aromatics. By contrast, the addition of Pt had a minor effect on both the rate and product distribution. Adsorption studies aimed at understanding the role of Zn in H(Zn)ZSM-5 showed that at low ion-exchange levels, less than 0.5 Zn/Al, each Zn cation displaced one Brønsted-acid site. FTIR of adsorbed acetonitrile-d₃ and calorimetric measurements of adsorbed CO at 195 K indicated that the exchanged Zn cations form Lewis-acid centers. A model in which the Zn cations, acting as Lewis-acid centers, polarize intermediates formed at Brønsted sites provided a way of understanding the observations.

The heat flows associated with conversion of n-hexane on H-ZSM-5 and H(Zn)-ZSM-5 were also measured directly for reaction at 60 bar and both 673 and 773 K. The acid-catalyzed reactions over H-ZSM-5 were found to be only mildly endothermic (<10 kJ/mol) at low conversions and exothermic at all conversions above 50%. The reactions on H(Zn)-ZSM-5 were significantly more endothermic (40 to 50 kJ/mol) for conversions below 70%; however, the reactions also became exothermic at very high conversions. Measurements of the product distributions showed that the reaction endothermicity for H(Zn)-ZSM-5 at lower conversions was likely due to formation of significant amounts of benzene, toluene, and xylene but that these were converted to higher molecular weight products at high conversions.

AFOSR Publications

- 1) "Heat-Flow Measurements for n-Hexane Reactions on H-ZSM-5 and H(Zn)-ZSM-5: Implications for Endothermic Reforming in Hypersonic Aircraft", Y.-H. Yeh, C.-E. Tsai, C. Wang, and R. J. Gorte, submitted.
- 2) "A Study of Zn and Ga Exchange in H-[Fe]ZSM-5 and H-[B]ZSM-5 Zeolites", Y.H. Yeh and R. J. Gorte, *Industrial & Engineering Chemistry Research*, 55 (2016) 12795-805
- 3) "Adsorption of Small Alkanes on ZSM-5 Zeolites: Influence of Brønsted sites", Y.-H. Yeh, R. J. Gorte, S. Rangarajan, and M. Mavrikakis, *Journal of Physical Chemistry C*, 120 (2016) 12132-38.
- 4) "Zn-promoted H-ZSM-5 for Endothermic Reforming of n-Hexane at High Pressures", Y.-H. Yeh, S. Zhu, P. Staiber, R. F. Lobo and R. J. Gorte, *Industrial & Engineering Research*, 55 (2016) 3930-3938.
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- 6) "Endothermic Reforming of n-Hexane on metal (Pt, Ga) containing H-ZSM-5 at High Pressures" Y.-H. Yeh, J. Yu, J. Luo, and R. J. Gorte, *Industrial & Engineering Chemistry Research*, 54 (2015) 10675-83.