

Understanding the relationship between Surface Structure and Catalytic Properties in Heterogeneous Catalysts.



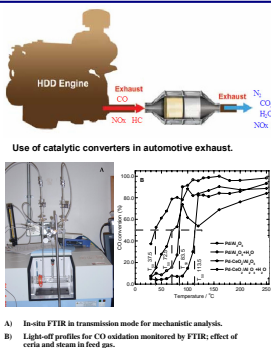
Mechanistic Analysis of Pd-based Auto exhaust Catalysts

85% of cars sold worldwide are fitted with catalytic converters. Without them, the average family car in the US would emit 15 tons of pollutants (carbon monoxide, hydrocarbons and nitrogen oxides), over a 10-year lifespan. Catalytic converters removes up to 98% of these pollutants.

Precious group metals (Pd, Pt and Rh) are widely used as catalyst in catalytic converters. Addition of ceria shifts the light-off to lower temperature and reduces cold-start emissions. It also helps to prevent sintering of palladium nanomaterials at high temperatures.

Similar projects sponsored by NSF involves doping of Pd in perovskite structure. This enhances the mobility of Pd in-and-out of its perovskite lattice, which increases activity for CO oxidation and reduces sintering.

Sponsored by Catalytic Solutions, Inc. and National Science Foundation



A) In-situ FTIR in transmission mode for mechanistic analysis. B) Light-off profiles for CO oxidation monitored by FTIR; effect of ceria and steam in feed gas.



Back Row (Left to Right) : Eric Deguns, Dr.Juergen Eckert, Professor Susannah Scott, Dr. Udayshanker Singh, Sam Fleischman, Robert Savinelli, Dr. Tony Moses, Dr. Ziyad Taha*, Dr. Naveen Ramsayb*, Cathleen Yang, Heather Leffesser* (alumni status indicated by *). Not shown are: Brian Vicente, Andrew Seaward, and Justin Butler

Our group conducts both fundamental and applied research in surface chemistry and catalysis. The lab members are a combination of post doctoral researchers, engineering students, and chemistry students who work closely together to solve problems at the interface of chemistry and reaction engineering. Collaborations with researchers in the chemistry, chemical engineering, and materials department are ongoing. We frequently use: XRD, XPS, NMR, SEM, operando FTIR, BET, GC, GPC, GC-MS, UV-VIS, and DFT. XAS experiments are completed at the Stanford Synchrotron Research Laboratory, and operando quick-EXAFS spectra are collected at Argonne National Laboratory.

<http://www.chemengr.ucsb.edu/~cweb/faculty/scott/>



X-ray Absorption Studies of Model Catalysts

Heterogeneous catalysts can be formed by supporting (or grafting) a molecular species onto an oxide support. Silica is a widely used support for supported transition metal catalysts. We use compounds which give well-defined surface reactions leading to uniform materials. For example, grafting GaMe₂ onto silica results in a 1:1 ratio of Ga per silanol

$nSiOH + GaMe_2 \rightarrow nSiOGaMe_2 + nH_2$
 Samples are taken to XRD, where intense X-rays are used to bombard samples. The element specific absorption of the X-rays produces a spectrum which can be modelled to gain information on the chemical environment and surrounding atoms of the absorber. The EXAFS of SiO₂/GaMe₂ material showed that the material is always dinuclear in gallium, previously established in for literature. Table 2, et al. Organometallics, 2006 in press.

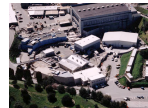


Figure: (left) Stanford Synchrotron Radiation Laboratory; (right) schematic of XAS setup

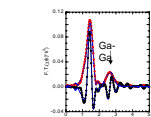


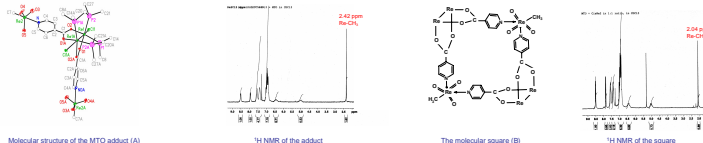
Figure: (left) Ga K-edge EXAFS of silica-supported GaMe₂. Each grafting site is dinuclear in Ga; (right) A DFT model of dinuclear Ga site



Molecular Architecture using CH₃ReO₃ (MTO)

MTO behaves as a strong Lewis acid towards pyridine type bases and forms trigonal bipyramidal or octahedral Lewis base adduct depending on the type of donor bases. A metal complex can behave as a base towards MTO if it has dangling pyridine groups available for further coordination. The reaction of MTO with the dirhenium complex (Re₂(μ-dppm)₂Cl₂(μ-C₆H₄NCOO)₂) in CH₂Cl₂ forms either the adduct A or the molecular square B depending on the reaction stoichiometry. In the NMR of the adduct A the Re-methyl signal shifts high field (2.42 ppm) compare to the Re-methyl signal (2.65 ppm) of free MTO due to the binding of MTO-rhenium with nitrogen. The binding of two nitrogen atoms to the MTO-rhenium in the molecular square shifts the Re-methyl signal more high field (2.04 ppm).

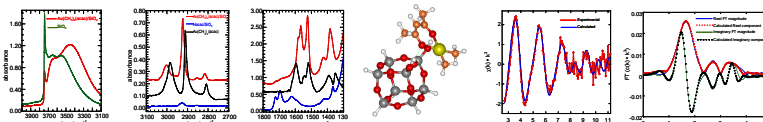
Funded by Department of Energy



Understanding the First Interaction of Au(CH₃)₂(acac) with Silica

Although bulk gold is inactive as a catalyst, nano-sized gold particles and molecular organogold complexes are active, particularly when supported on metal oxides. However, the stability of the active forms of Au relative to bulk Au is often low. Relating the structures of gold catalysts to their activities and understanding their evolution under reaction conditions is key to slowing deactivation. We have studied the interaction of a volatile organogold precursor, Au(CH₃)₂(acac), with SiO₂ by XAS, FTIR, and DFT calculations

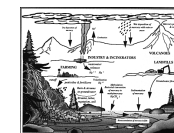
Funding provided by University of California



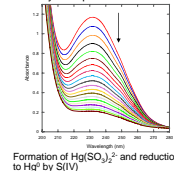
The CH₃ frequencies increase with grafting due to H-bonding. The spectrum more closely resembles that of the molecular complex than that of the AuAcac. These observations imply that the molecular complex stays intact as it is adsorbed on the support. After grafting the organogold complex, the IR intensity of the isolated hydroxyl stretching mode decreases, and a new band at 3447 cm⁻¹ is observed. The peak is displaced from the hydrogen-bonded hydroxyl peak of unmodified silica, and is identified as a new hydrogen-bonding interaction between the organogold complex and the silica surface.

The reconstructed Fourier transform magnitude of the EXAFS shows an intense peak at 1.65 Å corresponding to atoms in the first coordination sphere directly bonded to Au, as well as several weaker peaks at higher R corresponding to non-bonded atoms in the second and higher coordination spheres. The latter are not evidence of Au-Au interactions, but are consistent with the acac ligand remaining coordinated to mononuclear Au.

Mercury Redox Reactions



Mercury transport in the environment



Formation of Hg(SO₄)₂ and reduction of Hg(II) to Hg(0) by Si(IV)

We are studying redox reactions that lead to the reduction of mercury in coal-fired power plants. Most or the air-borne mercury emissions in the United States come from coal-fired power plants. The mechanisms by which mercury is reduced post-combustion in coal-fired power plants are not known. This hinders accurate simulations of mercury transport and deposition. Effects of various emissions reduction strategies are, therefore, difficult to predict. One of the goals of this project is to identify and quantify reactions of mercury in order to aid models in simulating and predicting the redox behavior of mercury.

Funded by Electrical Power Research Institute



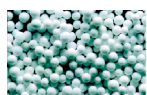
Ziegler-Natta Type Polymerization Catalysts

Ziegler-Natta catalysts are typically prepared by impregnation of a Ti source on a MgCl₂ support.

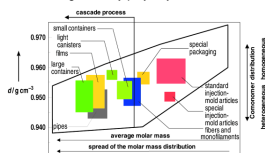
The catalyst requires activation, which is commonly achieved by an organoaluminum complex, such as triethylaluminum or MAO.

The choice of activator effects many properties of the system, including catalyst activity, thermal stability, and polymer properties. The aim of this project is to investigate the role of the activators in the catalyst system.

Funding provided by the Dow Chemical Company.



High-density polyethylene beads



Scope of polyethylene uses.

Bates, L.L. Angew. Chem. Int. Ed. 77, 2002, 5210-5230.



Polyolefin Clay Nanocomposites

The addition of inorganic fillers to polyolefins is well established. Materials such as carbon black, talc, glass and clay are added to enhance the physical properties of the plastics. Further enhancement of the properties is possible if the filler size is decreased and the aspect ratio is increased, this is possible with clays as they have high aspect ratios and small sizes (~100 nm x ~1 nm).

In our lab we study clay/polyolefin composites using a variety of techniques including: GPC, NMR, XAFS, FT-IR, RAMAN, UV-Vis, XPS, TEM, XRD, DRIFTS, GC-MS, DMA, TGA and DSC.

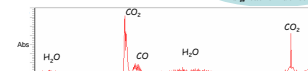
Funding provided by Mitsubishi Chemical



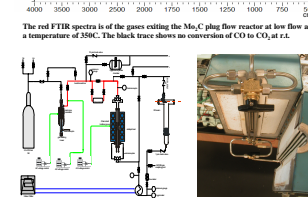
300 ml Parr reactor used in lab to produce polyolefins.

Catalytic properties of transition metal carbides

The water-gas shift reaction makes H₂ and removes CO, which is great for fuel cells.



The red FTIR spectra is of the gases exiting the Mo₂C plug flow reactor at low flow and a temperature of 350C. The black trace shows an conversion of CO to CO₂ at 2.4.



Schematic drawing, (left), of water-gas shift catalyst testing station. (right) Dual plug flow reactor for Mo₂C and WC catalyst beds. Gas comes in from the top and goes out the bottom.

Transition Metal Carbides, such as molybdenum carbide, and tungsten carbide, are known to catalyze a variety of chemical reactions. These reactions include the water-gas shift reaction, methane reforming, and olefin methanation.

We seek to properly characterize and test the catalytic activity of metal carbide nano-particles synthesized by our collaborators in the Materials Research Lab (Seshadri group).

Unsupported metal carbides powders are characterized using: BET, XRD, XPS, XANES, EXAFS, and SEM.

Catalysis is tested at various temperatures and flow rates in a gas flow reactor. Gas composition is exit out of the reactor is monitored using FTIR, GC, and MS.

Funded by Department of Energy

