Three regimes of catalyst characterization

- Gas phase kinetics (GC, mass spec., etc.)
- Operando observation of reaction intermediates (IR, Raman, etc.)
- Catalyst characterization:
  - Surface (XPS, ISS, BET, Chemisorp., etc.)
  - Bulk (XRD, XAS, etc.)

Structure-Function relationships derived through:
- qualitative correlations
- computational catalysis
Work at Tufts University under the NIRT program aims at identifying and understanding potential differences in reactivity between oxidized clusters of \( \text{Au}_n^+ \) or \( \text{Pt}_n^+ \) stabilized in various supports and \( \text{Au}^0 \) or \( \text{Pt}^0 \) nanoparticles for low-temperature catalytic oxidation reactions.

We have earlier shown the importance of oxidized gold and platinum clusters in ceria for the water-gas shift reaction (\textit{Science} 301 (2003) 935).

In recent work we have found that the dry CO oxidation reaction is much more facile on \( \text{Au}^0 \) than on oxidized gold clusters, as shown here for \( \text{Au-CeO}_2 \) catalysts. The difference is due to a much stronger CO-Au bond on the oxidized clusters than on metallic gold nanoparticles. (\textit{J. Catalysis}, accepted).

\textbf{Senior team members:} T. Haas (co-PI, Tufts) H. Saltsburg (co-PI, Tufts); J. Rodriguez (collaborator, Brookhaven National Lab); A. Frenkel (collaborator, Yeshiva U.) \textit{Other collaborators:} F. Boccuzzi (U.Torino); F. Meunier (Queens U. Belfast)
Biocatalysis

Vadim Guliants, U. Cincinnati (UC), CTS - 0403897

Effects of surface curvature and confined nanoscale environment on biocatalytic activity.
Francisco Zaera
University of California, Riverside
Award # CTS-0423859

This collaborative project, involving the groups of Professors Francisco Zaera (University of California, Riverside), Sergio Fuentes (UNAM, Ensenada), and Giorgio Zgrablich (University of San Luis, Argentina), aims to develop a better molecular-level understanding of the nature of catalysts for NO\textsubscript{x} reduction.

The project has two components: one where the fundamental chemistry of NO\textsubscript{x} on Rh single crystals is studied by molecular beams and Monte Carlo simulations, and another where novel sol-gel synthetic methods are used to prepare palladium catalysts supported on zirconia and lanthana oxide mixed with alumina.

The data on the right corresponds to recent work on the first. The kinetics of N\textsubscript{2}O decomposition on Rh(111) single-crystal surfaces were investigated to understand two unusual observations derived from our previous work on this system, namely: (1) the lower rates for N\textsubscript{2}O decomposition seen at higher reaction temperatures; and (2) the lower total nitrogen yields and final oxygen surface coverages that accompany that behavior. Experimentally, it was determined that after the rhodium surface is rendered inactive by N\textsubscript{2}O decomposition at high (520 K) temperatures, significant activity is still possible at lower (350 K) temperatures. The Monte Carlo simulations explain these observations by assuming that the surface sites required for the activation of adsorbed N\textsubscript{2}O increase in size with increasing reaction temperature [R. O. Uñac et al., J. Chem. Phys. 125 (2006) ASAP].

In the second, ceria-zirconia-alumina supports with different Ce/Zr ratio were prepared by a sol-gel technique. FTIR characterization of CO adsorbed on oxidized and reduced samples revealed that the Ce/Zr ratio modifies both the surface properties of the support and the oxidation state of the palladium. The catalyst with a 50:50 Ce/Zr molar ratio displays the highest ability to stabilize palladium in an oxide state and the highest activity to oxidize CO [G. Perez-Osorio et al., Appl. Catal. A (2006) in press].

Time evolution of isothermal rates of N\textsubscript{2} production from N\textsubscript{2}O decomposition on clean Rh(111). Data from Monte Carlo simulations (solid lines) are contrasted with results from molecular beam experiments for different temperatures. Good agreement is seen in all cases.
Catalytic kinetics and mechanisms

Susannah Scott
UC Santa Barbara  CTS-0500489
Redesigning Cr/SiO₂ polymerization catalysts

Wenbin Lin
UNC at Chapel Hill  CHE-0512495
Engineerable, uniform asymmetric catalysts based on metal-organic frameworks

Ar
O
H + ZnEt₂ \( \text{Ti(O')Pr}_4 \) \( (R)-1 \) Ar
OH
H
up to 93% ee
**Computation/Fuel Cells**

M. Mavrikakis group  
U. Wisconsin at Madison  
CTS-0134561

Volcano-type behavior exhibited by ORR on Pt monolayers supported on various metals

N-containing nanofibers for ORR

\[ O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \]
Nano Scale Characterization

Renu Sharma
Arizona State University
CTS-0508434 and 0625340

Controlled growth of catalyst particles for CNT synthesis

Peter A. Crozier, Renu Sharma and Jim Adams
Arizona State University
CTS-0306688

Activity variations in individual nanoparticles
Novel nanostructures and their atomic-scale probing before and after high-temperature processing within an electron microscope

*Award Title: GOALI: Atomic-scale investigation of high dielectric constant thin films using in situ and other techniques*” (Academic Liaison with American Air Liquide)

Micro-image and chemical depth profiling (resolution of ~ 0.2 nm) of an alumina/interface layer/silicon stack of alumina deposited on silicon from the novel tris(diethylamino)aluminum precursor [as-deposited (left), annealed at 800 °C inside an electron microscope (right)].
Novel Materials/Syntheses

C. Buddie Mullins  
University of Texas at Austin  
CBET-0553243

Structured Pt/SWNT catalyst  
electrically connected to a Si wafer

Daniel E. Resascco  
University of Oklahoma  
CTS-0308619

Thin films of porous titania nanocolumns

TEM of single column from film  
showing porosity
Catalytic oxidation using ozone is a promising technology for the low-temperature destruction of volatile organic compounds, such as acetone. A silica-supported manganese oxide (MnO$_2$/SiO$_2$) was used because of its strong oxidizing ability. EXAFS showed that a 3 wt % sample had isolated octahedral Mn atoms while a 10 wt % sample had clusters resembling fragments of Mn$_3$O$_4$. The rate was higher on the clusters, indicating that multiple adjacent Mn centers facilitated the reaction.

\[
\text{CH}_3\text{COCH}_3 + 8 \text{O}_3 \rightarrow 3 \text{CO}_2 + 3 \text{H}_2\text{O} + 8 \text{O}_2
\]

Raman spectroscopy at reaction conditions showed the presence of two surface intermediates, a peroxide species derived from ozone, with a band at 890 cm$^{-1}$, and an adsorbed species with intact C-H bonds derived from acetone, with a band at 2930 cm$^{-1}$. Simultaneous measurements of rate and coverage showed that the adsorbed acetone intermediate reacted with atomically adsorbed oxygen species to form complete oxidation products.
One of our overarching goals has been to investigate how photo-reversible control of protein structure with light-responsive surfactants could be used to control enzyme activity. We soon realized that while in vitro conformations from small-angle neutron scattering (SANS) provide unique insight into catalytic processes, enzyme dynamics can have considerable influence on activity. Both native and partially-folded lysozyme display similar active sites, however, neutron spin echo (NSE) detects nanosecond/nanometer domain motions in the partially-folded form. This increased molecular flexibility leads to 5× superactivity relative to the native state.

Five students (two graduate, two undergraduate, and one high-school), all of whom are young female scientists, have been involved in this NSF-sponsored work.

**Photo-control of lysozyme form, dynamics, and function**

- **Native state:**
  - rigid, no detectible ns/nm motions
- **Partially-folded state:**
  - flexible, ns/nm domain motions
  - 5× superactivity vs. the native state

**SANS**

**X-ray cryst.**

**UV**

**Visible**

**Active site**
W.C. Conner, S. M. Auerbach, S.L. Hsu, S. L. Suib, and S.K. Yngvesson

NIRT: Microwave Synthesis of Nanostructured Catalysts
CBET - 0304217

In situ measurement of SAXS/WAXS of microwave synthesis of zeolites

MFI

SAXS

WAXS
Conventional vs Microwave Synthesis of NaA - in situ WAXS

Figure 1 (a) WAXS spectra of zeolite formation at 80°C from a precursor with a composition of 44 SiO$_2$ : Al$_2$O$_3$ : 5 Na$_2$O : 800 H$_2$O using conventional heating.  (b) intensity of NaY, NaA and Sodalite peaks (111), (200), and (110) respectively, with time.

Microwave synthesis of NaA is faster and produces a purer product
To better understand the chemistry of metal-semiconductor and metal-insulator interfaces important for improved design of catalysts and devices, the **adsorption and reaction of silicon-containing compounds on single-crystal metal surfaces** is being studied. Model compounds are employed as adsorbates to identify the detailed bonding interactions between metals and silicon or oxidized silicon.

**Top:** Adsorbing $\text{Si}_n\text{O}_{1.5n}\text{H}_n$ clusters on single crystal surfaces creates a well-defined interface that can be studied at the molecular level.

**Bottom:** Surface silicides have been observed to react with surface oxygen atoms on multiple metal surfaces to form submonolayer $\text{SiO}_x$ films, creating model interface systems for controlled study.