

# Studies of Surface Chemistry in the Mullins Lab at UT-Austin

Professor C. B. Mullins  
University of Texas at Austin  
(2/08)

## *GAS-SURFACE CHEMISTRY*

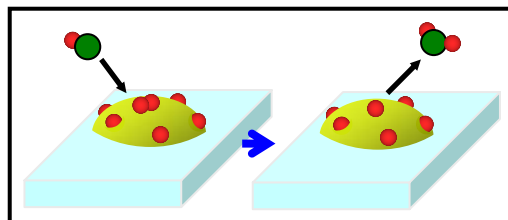
Much of my research expertise regards the interactions of molecules with solid surfaces and in particular the chemical reactions between gas phase molecules and solid surfaces. Gas-surface chemistry is important in several important processes regarding heterogeneous catalysis. For example, the reactors in chemical plants have solid catalysts to promote selective chemical reactions of gaseous reactants. Additionally, the catalytic converter on an automobile uses supported solid catalysts to decompose pollutants from the combustion process to more environmentally benign species. A better understanding of gas-surface chemistry will lead to improved catalytic materials and processes, thus, we have developed a laboratory for the study of such problems. The remainder of this document describes some of my research interests in more detail.

### *Chemistry of Supported Metal Nanoclusters: Studies of Model Catalysts*

The chemical industry is one of the largest in the United States, with sales of over \$300 billion per year and employment of over a million people. It is one of the few industries that produces a favorable trade balance. Catalysis is critical to several of the largest industries in the U.S. and is also vital to several emerging critical technologies.

Catalysts for selective gas-surface chemical reactions are of many varied forms but nearly all are composed of several materials; supports, promoters, and inhibitors. The interaction of these various components and their cumulative catalytic effect are not well understood and, in fact, the interaction of a single molecule with a simple, single-component surface is a difficult problem from first-principles. Thus, catalysts are currently "designed" employing more art (and experience) than scientific guidance. The work in catalytic materials and mechanisms in my laboratories represents our effort in rectifying this situation.

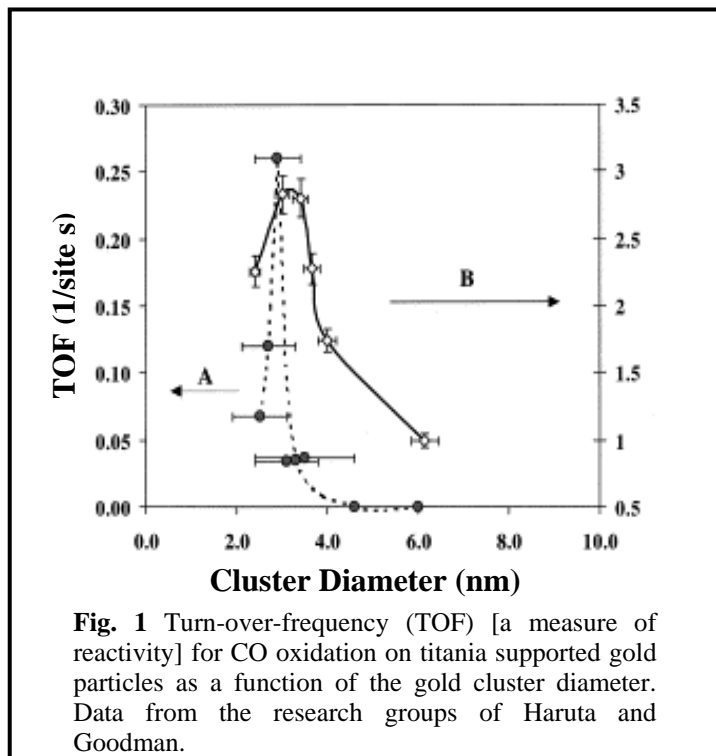
Our research in catalysis focuses on several topics including: (1) The quantum size effects of metal nanoclusters on the catalytic activity and selectivity of particular gas-surface chemical reactions, (2) the controlling mechanisms in heterogeneous catalysis and especially on metal nanoclusters, (3) the effect of promoters, inhibitors, and support on the surface reactivity of metal nanoclusters, (4) the role and identification of intermediate states in surface chemical reactions, (5) the effect of composition of metal nanoclusters (i.e., bimetallic clusters) on catalytic activity, and (6) the synthesis and deposition of size-selected metal nanoclusters on well-characterized metal oxide surfaces.



We have recently been researching supported gold nanoclusters and the next several paragraphs summarize some of our thoughts regarding the surface chemistry of gold nanoparticles.

Gold has long been regarded as catalytically "inert" and, indeed, bulk gold surfaces do not readily facilitate either dissociative or molecular chemisorption. However, in the last 15 years, initially through the efforts of Haruta and coworkers and more recently via studies by Goodman, *et al.*, supported gold nanoclusters, particularly those between ~1-5 nm in size, have attracted attention due to their unique catalytic properties [see Fig. 1]. Additionally, studies of

adsorption and reaction on relatively small *gas-phase* gold clusters (2-27 atoms) have shown striking size dependent behavior. In recent years, supported gold nanoparticles have been shown to be particularly effective as catalysts for low temperature CO oxidation, selective oxidation of



propene to propylene oxide, the water gas shift reaction, and several other chemical conversions. Low temperature CO oxidation has been of particular interest since this is a reaction that has been investigated on numerous model catalysts and the chemistry finds applications in indoor air quality, production of high quality CO<sub>2</sub> lasers and as a guard bed catalyst to prevent CO poisoning of proton exchange membrane (PEM) fuel cells.

Microscopic details of the chemistry of small metal clusters placed on planar supports can be effectively explored employing surface science techniques. However, only a few investigations of this type regarding gold clusters have been conducted, in part, because of the difficulty of chemisorbing reactants on the gold nanoparticles. Although some

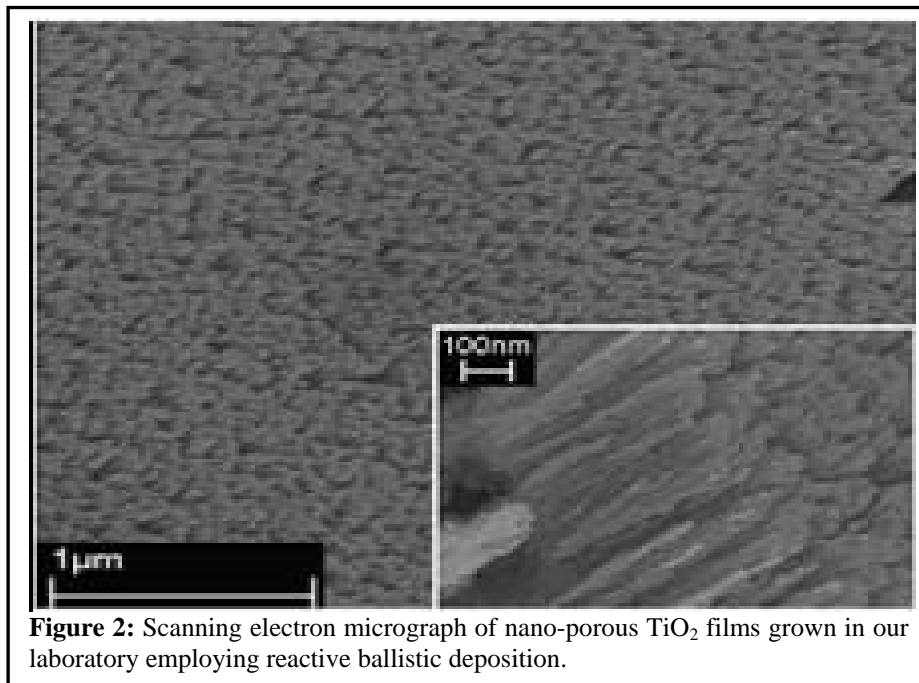
notable progress has been made via these studies, many questions remain: What is the origin of the gold particle size effect? What is the nature and structure of the active site? What is the mechanism of the reaction? In oxidation reactions is *molecularly* adsorbed oxygen or *atomically* chemisorbed oxygen the necessary or rate-limiting surface reactant? What is the role of the metal oxide support? How can sintering (and subsequent catalyst deactivation) be avoided? Our goal has been to contribute to the understanding of some of these issues through the study of specific surface chemical reactions on size-selected, well-characterized, titania supported gold nanoparticles in the 1-5 nm range.

In a seminal study, Heiz and co-workers investigated the capability of MgO supported size-selected gold clusters composed of 1 to 20 atoms to oxidize carbon monoxide. The small gold clusters were soft-landed from the gas-phase after size-selection by a quadrupole filter. They found that the number of atoms in these small clusters profoundly affected the catalytic chemistry and that Au<sub>8</sub> was the smallest cluster to oxidize CO. More recently, Anderson and co-workers have conducted investigations on titania with similarly generated, size-selected gold clusters composed of 1-7 atoms and found cluster-size dependent oxidation chemistry. We have conducted chemical investigations of *larger* size-selected gold clusters than those mentioned above. In particular, we have studied Au clusters in the 1-5 nm size range as identified by Haruta and Goodman as highly active for oxidation catalysis [Fig. 1]. Surface chemical studies of titania supported Au clusters in the 1-5 nm range employing ultra-high vacuum surface science techniques have previously been performed, however, for these investigations, samples were prepared by evaporating gold onto the TiO<sub>2</sub>(110) substrate and this leads to a relatively broad particle size distribution. We will soon begin fabricating samples with gold particle sizes in the 1-5 nm range employing a new cluster generating device recently purchased. Cluster size dispersions of  $\sim \pm 10\%$  are achievable and this is a large improvement over evaporative techniques. Regarding surface chemical reactivity studies, we will employ molecular beam

reactive scattering methods as well as temperature programmed desorption, and higher pressure measurements of surface reactions. We will also conduct complementary investigations on Au(111) for comparison with the nanocluster results. Studies of oxidation and hydrogenation reactions will be performed; in the recent past, we have studied oxidation of carbon monoxide and the oxidation of methanol.

### ***Growth of Nanostructured Films via Reactive Ballistic Deposition***

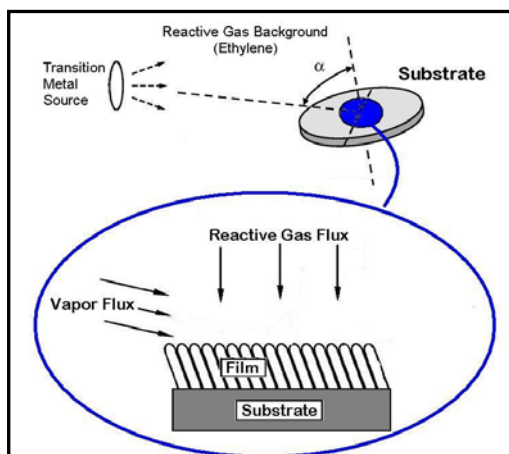
Recently, the reactive ballistic deposition (RBD) technique has been used to create thin films consisting of highly porous arrays of nano-whiskers of several different materials (e.g., see Figure 2). The technique consists of evaporation of a metal onto a cold substrate at oblique angles in a background of reactive gas (Figure 3). The resulting high surface area, reduced dimensionality nano-



**Figure 2:** Scanning electron micrograph of nano-porous TiO<sub>2</sub> films grown in our laboratory employing reactive ballistic deposition.

whisker arrays have high concentrations of surface defect sites. These sites will likely facilitate dissociative and recombinative reactions, while a large and readily accessible surface area will provide enough sites for chemistry to proceed at a sufficiently high rate. Because of these properties, RBD films have great potential for heterogeneous catalysis applications.

Brett and coworkers have been pioneers regarding the growth and physical characterization (SEM, TEM, X-ray diffraction, spectrophotometry) of such films employing a wide variety of materials deposited by a related technique which they refer to as glancing angle deposition (GLAD). Electron microscopy reveals that films deposited in this manner consist of large arrays of highly porous, whisker-like structures (e.g., Fig. 2). Brett et al. have also demonstrated how various deposition parameters allow control over the shape and dimensions of the structures. Additionally, these investigators have studied the structural and optical effects of annealing, and also constructed a dye-sensitized solar cell (DSSC) using a TiO<sub>2</sub> film grown by RBD.



**Figure 3:** Schematic of RBD growth of a transition metal carbide film. The film is formed on the substrate by reaction of a directionally deposited transition metal with ambient hydrocarbon gas.

While morphological effects related to the deposition conditions of these films have been studied, as well as some optical and other physical properties, *characterization of the chemical/catalytic properties of RBD films is quite limited.* Indeed, Dohnalek and Kay and Taga and coworkers were the first to recognize that

nano-structured surfaces like those deposited by Brett *et al.* might have unique catalytic properties and that such chemistry had not been previously studied.

Using the RBD method to create films has several significant advantages over traditional methods of preparation. As Kay and coworkers have demonstrated using MgO, by deposition at various angles of incidence and substrate temperatures, both highly porous and well-ordered dense films can be fabricated. The MgO RBD films are highly porous (~90%), high-surface area (~1000 m<sup>2</sup>/g), and thermally stable (1200 K) crystalline films. The films consist of a tilted array of porous nano-scale crystalline whiskers as shown by SEM and TEM images at the top of Figure 4.

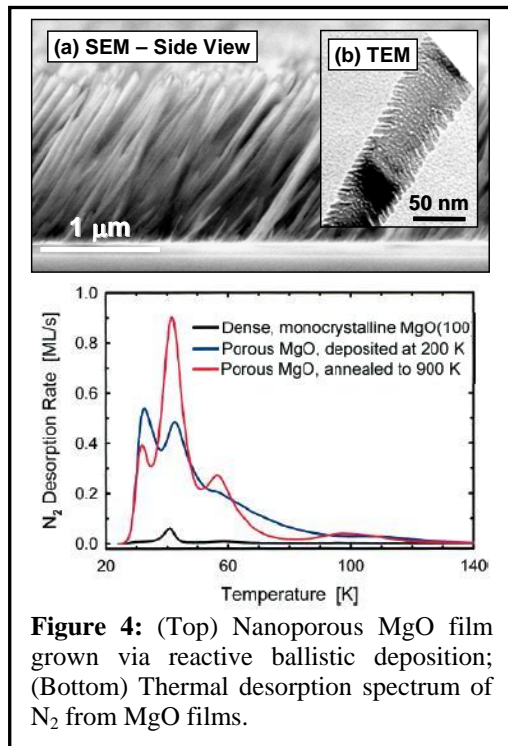
Surprisingly, individual whiskers exhibit a high degree of crystallographic order with respect to each other. Physisorption of N<sub>2</sub> allowed measurement of the adsorption capacity and the energy distribution of binding sites on the surface of the porous films. These films have chemical binding sites analogous to those on MgO(100), as seen via a temperature programmed desorption measurement in Figure 4. However the fraction of high-energy defect binding sites is greatly enhanced on the RBD films. Such defect sites are generally believed to exhibit enhanced chemical activity thereby making these materials potentially attractive candidates for applications such as sensors and heterogeneous catalysts.

Recently, in collaboration with investigators at Pacific Northwest National Laboratory, we have completed an investigation of the nature of TiO<sub>2</sub> RBD films grown at glancing angles and an account of this research has been published. In this investigation nano-porous, high-surface area films of TiO<sub>2</sub> (see Fig. 2) were synthesized by reactive ballistic deposition of titanium metal in an oxygen ambient. Auger electron spectroscopy (AES) was used to investigate the stoichiometric dependence of the films on growth conditions (surface temperature and partial pressure of oxygen). Scanning and transmission electron microscopy confirmed that the films consist of arrays of separated filaments. The surface area and the distribution of binding site energies of the films were measured as functions of growth temperature, deposition angle, and annealing conditions using temperature programmed desorption (TPD) of N<sub>2</sub>.

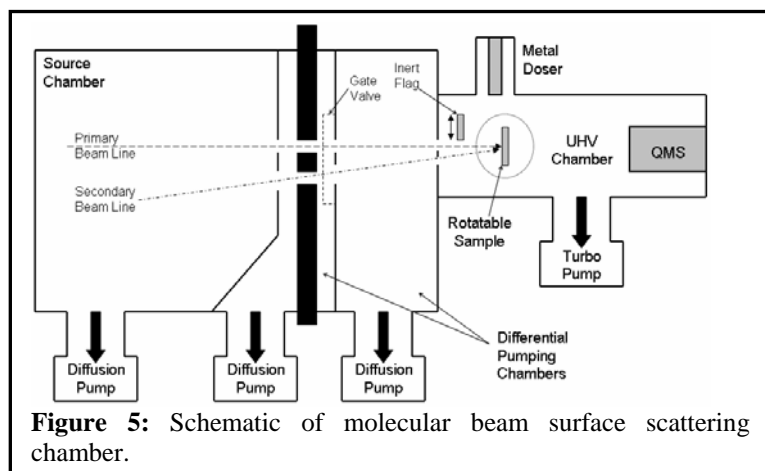
There are very few fundamental studies of surface chemistry on surfaces as complex as those discussed here. Reactive ballistic deposition at glancing angles is a versatile and controllable method for creating interesting surfaces, from simple, epitaxial, dense films to complex, high surface area films. We are particularly interested in increasing the fundamental understanding of surface chemical reactions on complex surfaces. Specifically, how do surface defects affect the chemistry of a surface? How can we relate the knowledge we currently have of single crystalline well-characterized surfaces to the more complex surfaces found in industrial catalysts?

### *Facilities and Personnel*

My research group currently employs three complementary experimental devices to acquire basic data regarding the reactivity of relevant molecules on crystalline substrates of technological and scientific importance. All of the apparatus have been designed for accurately measuring various aspects of surface chemical reactions and all have the basic structure depicted



in Fig. 5. We also collaborate with other scientists on campus as well as in other parts of the country [Professor Greg Sitz (Physics), Prof. Tom Truskett (Chem. Engr.), Prof. Gyeong Hwang



(Chem. Engr.), Prof. Graeme Henkelman (Chemistry), Dr. Bruce Kay (Pacific Northwest National Laboratories)]. In addition to the apparatus described immediately above, we also have affiliations with the Texas Materials Institute (TMI) and the Center for Nano and Molecular Science (CNM) at the University of Texas at Austin. These two interdisciplinary organizations provide access for UT-Austin researchers to a variety of experimental equipment which

are helpful in materials research including scanning and transmission electron microscopes. Currently, scanning electron microscopy images are obtained using a LEO 1530 scanning electron microscope (SEM), and transmission electron microscopy (TEM) images are gathered using a JEOL 2010F. These tools, coupled with x-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) (available in the Surface Analysis Laboratory of TMI), x-ray diffraction (XRD), and energy dispersive spectroscopy (EDS) (which is coupled with the LEO 1530) provide valuable information about morphology, crystal structure, and elemental composition of deposited films. Finally, we sometimes use computational tools (molecular dynamics simulators) to aid in the understanding of our experimental measurements.

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My group is a good match for hard-working students primarily interested in experiment (and possibly some theory) regarding fundamental issues related to gas-surface interactions. Interest in chemistry and the development of mechanical skills is important for success in my group. Our research activities are funded by the Department of Energy, the National Science Foundation, the Defense Threat Reduction Agency, the Welch Foundation, and the American Chemical Society Petroleum Research Fund.

**ADDRESS:** Department of Chemical Engineering  
University of Texas at Austin  
1 University Station C0400  
Austin, TX 78712-0231

**email:** [mullins@che.utexas.edu](mailto:mullins@che.utexas.edu)

**web-site:** <http://www.che.utexas.edu/mullins/>

**Phone:** (512) 471-5817

**FAX:** (512) 471-7060

**CHARLES BUDDIE MULLINS**  
Department of Chemical Engineering  
1 University Station C0400  
University of Texas at Austin  
Austin, TX 78712-0231  
(512) 471-5817 office  
[mullins@che.utexas.edu](mailto:mullins@che.utexas.edu)

## EDUCATION

<b>IBM Almaden Research Center</b>	<b>Post-Doc. in Physical Sciences Div.</b>	<b>1989-91</b>
<b>California Institute of Technology</b>	<b>Ph.D. in Chemical Engineering</b>	<b>1990</b>
IBM, Grace, and Link Fellowships – Matriculated 9/83 – Thesis defense 9/89		
<b>University of Tennessee</b>	<b>B.S. in Chemical Engineering</b>	<b>1982</b>
While employed full-time at Oak Ridge National Laboratory (1977-1983)		
<b>University of Texas at Austin</b>	<b>M.S. in Nuclear Engineering</b>	<b>1977</b>
<b>University of Texas at Austin</b>	<b>B.S. in Physics</b>	<b>1975</b>

## PROFESSIONAL APPOINTMENTS

<b>Professor of Chemical Engineering</b> (Z. D. Bonner Professorship) <b>and Graduate Studies Committee, Dept.'s of Chemistry and Materials Science</b> University of Texas at Austin	<b>2001-Pres.</b>
<b>Associate Professor of Chemical Engineering</b> (with Tenure) University of Texas at Austin	<b>1997-2001</b>
<b>Assistant Professor of Chemical Engineering</b> University of Texas at Austin	<b>1991-1997</b>
<b>Research Scientist/Engineer</b> Oak Ridge National Laboratory	<b>1977-1983</b>

## SELECTED RECENT PUBLICATIONS (from a total of ~130 publications)

- D. W. Flaherty, Z. Dohnalek, A. Dohnalkova, B. W. Arey, D. E. McCready, N. Pnnusamy, C. B. Mullins, and B. D. Kay, "Reactive ballistic deposition of porous TiO<sub>2</sub> films: growth and characterization," *J. Phys. Chem. C* **111**, 4765-4773 (2007).  
<http://pubs.acs.org/cgi-bin/article.cgi/jpcck/2007/111/i12/pdf/jp067641m.pdf>
- J. Gong, R. A. Ojifinni, T. S. Kim, J. D. Stiehl, S. M. McClure, J. M. White, and C. B. Mullins, "Low temperature CO oxidation on Au(111) and the role of adsorbed water," *Top. Catal.* **44**, 57-63 (2007).  
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- J.D. Stiehl, T.S. Kim, S.M. McClure, J. Gong, and C. B. Mullins, "Reactivity of Molecularly Chemisorbed Oxygen on a Au/TiO<sub>2</sub> Model Catalyst," *J. Phys. Chem. B* **110**, 20337 (2006).  
<http://pubs.acs.org/cgi-bin/article.cgi/jpcb/2006/110/i41/pdf/jp062766c.pdf>
- J. Gong, R.A. Ojifinni, T.S. Kim, J.M. White, and C.B. Mullins, "Selective catalytic oxidation of ammonia on atomic oxygen precovered Au(111)," *J. Am. Chem. Soc.* **128**, 9012 (2006). <http://pubs.acs.org/cgi-bin/sample.cgi/jacsat/2006/128/i28/pdf/ja062624w.pdf>
- T.S. Kim, J. Gong, R.A. Ojifinni, J.M. White, and C.B. Mullins, "Water Activated by Atomic Oxygen on Au(111) to Oxidize CO at Low Temperatures" *J. Am. Chem. Soc.* **128**, 6282 (2006). <http://pubs.acs.org/cgi-bin/article.cgi/jacsat/2006/128/i19/pdf/ja058263m.pdf>
- J.D. Stiehl, T.S. Kim, S.M. McClure, and C.B. Mullins, "Formation of Molecularly Chemisorbed Oxygen on TiO<sub>2</sub>-Supported Gold Nanoclusters and Au(111) from Exposure to an Oxygen Plasma Jet," *J. Phys. Chem. B* **109**, 6316 (2005).  
<http://pubs.acs.org/cgi-bin/article.cgi/jpcb/2005/109/i13/pdf/jp044553y.pdf>

- J.D. Stiehl, T.S. Kim, S.M. McClure, and C.B. Mullins, "Reactivity of molecularly chemisorbed oxygen on TiO<sub>2</sub> supported gold nanoclusters," *J. Am. Chem. Soc.* **126**, 13574 (2004). <http://pubs.acs.org/cgi-bin/article.cgi/jacsat/2004/126/i42/pdf/ja046390x.pdf>
- S.M. McClure, T.S. Kim, J.D. Stiehl, P.L. Tanaka, and C.B. Mullins, "Adsorption and reaction of nitric oxide with atomic oxygen covered Au(111)," *J. Phys. Chem. B* **108**, 17952 (2004). <http://pubs.acs.org/cgi-bin/article.cgi/jpcbfc/2004/108/i46/pdf/jp047335d.pdf>
- J.D. Stiehl, T.S. Kim, S.M. McClure, and C.B. Mullins, "Evidence for molecularly chemisorbed oxygen on TiO<sub>2</sub> supported gold nanoclusters and Au(111)," *J. Am. Chem. Soc.* **126**, 1606 (2004). <http://pubs.acs.org/cgi-bin/article.cgi/jacsat/2004/126/i06/pdf/ja039214h.pdf>
- J.D. Stiehl, T. S. Kim, C.T. Reeves, R.J. Meyer, and C.B. Mullins, "Reactive scattering of CO from an oxygen atom covered Au/TiO<sub>2</sub> model catalyst," *J. Phys. Chem. B* **108**, 7917 (2004). <http://pubs.acs.org/cgi-bin/article.cgi/jpcbfc/2004/108/i23/pdf/jp0496102.pdf>
- T.S. Kim, J.D. Stiehl, C.T. Reeves, R.J. Meyer, and C.B. Mullins, "Cryogenic CO oxidation on TiO<sub>2</sub> supported gold nanoclusters pre-covered with atomic oxygen," *J. Am. Chem. Soc.* **125**, 2018 (2003). <http://pubs.acs.org/cgi-bin/article.cgi/jacsat/2003/125/i08/pdf/ja028719p.pdf>

### **SELECTED AWARDS**

- Lockheed Martin Aeronautics Company Award for Excellence in Engineering Teaching at the University of Texas at Austin, 2004.
- Union Carbide Corporation Research Innovation Recognition Award for Catalysis, 1999.
- Texas Excellence Teaching Award for Most Outstanding Teaching in the UT-Austin College of Engineering, 1999.
- Office of Naval Research Young Investigator Award, 1993-96.
- National Science Foundation Presidential Young Investigator Award, 1991-1996.

**GRADUATE and POSTDOCTORAL ADVISORS:** (Ph.D. Advisor) Professor W. Henry Weinberg; (Postdoctoral Advisors) Dr. C. T. Rettner, Dr. D. J. Auerbach, and Dr. J. Coburn.

**GRADUATE STUDENTS and POSTDOCS ADVISED by CBM:** J. E. Davis (Union Carbide), A. Selidj (deceased), S. G. Karseboom (Albemerle), M. C. Wheeler (Univ. of Maine), D. C. Seets (Seagate), K. A. Pacheco (Motorola), B. A. Ferguson (Cyprus Semiconductor), P. D. Nolan (Exxon-Mobil), C. T. Reeves (Celanese), R. J. Meyer (Univ. of Illinois at Chicago), D. J. Safarik (Los Alamos National Laboratory), P. L. Tanaka (Exxon-Mobil), J.D. Stiehl (Intel), T. S. Kim (Samsung), S. M. McClure (Texas A&M University).

**CURRENT GRADUATE STUDENTS (located in CPE 4.412):** Jinlong Gong (Chemical Engineering), Minta Akin (Chemistry), David Flaherty (Chemical Engineering), Rotimi Ojifinni (Materials Science), Ming Pan (Chemical Engineering), Ting Yan (Chemistry), Nathan Hahn (Chemical Engineering), Son Hoang (Chemical Engineering).