

## **A New Class of Oxidation Catalysts: the role of atomically dispersed metals in nanostructured oxides**

*NSF NIRT Grant 0304515*

**Maria Flytzani-Stephanopoulos, Howard Saltsburg, Terry Haas<sup>1</sup>, Regina Valluzzi,  
Jose Rodriguez<sup>2</sup>**

Tufts University, Department of Chemical and Biological Engineering, and <sup>1</sup>Department of  
Chemistry, Medford, MA

<sup>2</sup>Brookhaven National Laboratory, Chemistry Department, Upton, NY

The need for high purity hydrogen for use in low- temperature fuel cells has led to a resurgence of interest in the purification of hydrogen derived from reforming carbon -based feedstocks. A common process used to reduce the carbon monoxide concentration of the reformat gas to an acceptable level is the water gas shift reaction (WGSR). In the reaction, carbon monoxide is combined with water to form carbon dioxide and hydrogen over an appropriate catalyst. Many studies over the last ten years have shown that gold nanoparticles supported on various oxides are effective catalysts for the WGSR. In order to design and optimize such a catalyst it is important to know the details of the catalytic steps involved in the reaction. A number of proposals have been offered to explain the process but all depend on the properties of the metallic gold nanoparticles. Recent work in this laboratory has demonstrated that for the system of nanoparticles of gold on nanocrystalline cerium oxide, the gold nanoparticles do not participate directly in the WGS reaction, but are merely spectators (2). The active catalytic entity is nonmetallic: either a cluster of a few atoms or more likely gold ions. These entities are formed on nanocrystalline cerium oxide, during the initial preparation but once the particles are removed there is no effect on the process. The removal of 90% of the gold that was initially present in the form of metallic particles suggests that the economics of the catalytic process can be improved substantially. This finding formed the basis for the work carried out under this NIRT grant.

A main goal of the project is to prepare and evaluate gold- and platinum-doped nanostructured cerium oxide catalysts containing only a small fraction of the gold or platinum metals previously used for the WGSR, the preferential CO oxidation (PROX) and other redox reactions. In work carried out during the past year, we have collected new evidence that the active sites in these catalysts are gold or platinum ions strongly associated with the surface oxygen defects of ceria. Thus, preparation of the carrier oxide in the form of nanocrystals with a high density of oxygen defects is crucial for the activity of Au- or Pt-doped oxide catalysts. The extension of these findings to other supported metal-oxide catalyst systems is an overarching goal of this NIRT project.

The specific project objectives are to investigate the metal ion or cluster interaction with ceria and other oxide supports, and to study the metal ion activity in the absence of underlying lattice oxygen, by imbedding metal ions in thermally stable biopolymers [3]. Fabrication of nanotowers of alternating metal and oxide layers with one nanoscale dimension as film edges is another project objective. These will be used to delineate the importance of the metal-oxide interface for catalytic reaction [4] and to make comparisons with traditional nanocatalysts. Theoretical calculations complement and guide the experimental effort.

The project is an interdisciplinary effort involving faculty from Tufts University and researchers from Brookhaven National Laboratory. Dr. Maria Flytzani-Stephanopoulos, professor of Chemical and Biological Engineering(ChBE), is the principal investigator of the project. The co-PIs are: Prof. Howard Saltsburg (ChBE), Dr. Regina Valluzzi (Materials, ChBE) and Prof. Terry Haas (Chemistry). Dr. Jose Rodriguez, a senior chemist at Brookhaven National Laboratory, is a no-cost collaborator responsible for catalyst characterization by synchrotron radiation. The outreach part of the grant involves training of high school teachers in collaboration with the Wright Center of Innovative Higher Education at Tufts, and organizing a series of lectures in nanotechnology for advanced energy materials and catalysts to bring distinguished researchers in the field to campus.

The following are highlights from the first- year activities of the NIRT project:

- Low-content (<0.6 at %) gold-ceria catalysts were prepared by one-pot synthesis via a gelation /coprecipitation method using urea. Gold ion substitution in ceria is inferred by lattice expansion of the latter. Assuming that the active sites are Au-O-Ce structures and that gold is atomically dispersed in the oxide for materials prepared as above, or by cyanide leaching of high-content gold ceria samples, allows calculation of the turnover frequency of the water-gas shift reaction, as shown in Fig.1 [2,5]. A remarkable agreement is seen for very different sample preparation and dopants in ceria (La, Gd).
- The nature of the site for catalytic activity of the ceria-gold system is being addressed using a controlled structure catalyst. We used photolithography to create a resist pattern on a Si wafer that consists of eleven million ten-micron square openings with fourteen micron spacings between the squares. Using an electron beam evaporator, we deposited alternating layers of gold and cerium oxide (both of nanometer thickness) capping the nanotower with inert silica. Thus, only the edges of the stacked layers in each ten-micron tower are active and exposed to reactants. All nanotowers are identical. The total catalytic area exposed is less than one cm<sup>2</sup> and a recycle reactor with an online mass spectrometer is employed for kinetic studies. The catalyst structure is shown in Figure 2. We have carried out the oxidation of CO using nanotowers with the same total exposed cerium oxide area, but varying the number of gold-ceria interfaces. The CO oxidation reaction rate scales with the number of interfaces. The activation energy (~ 48 kJ/mol) is similar to that measured on gold-ceria particle catalysts [6,7].
- We were able to stabilize the WGS activity of gold-ceria in long term operation and in cyclic shutdown-startup operation in the full reformat gas by adding a small amount (< 0.5 %) of oxygen in the gas. Fig. 3 shows the stabilizing effect of oxygen in long term operation at 300 °C. This is a significant milestone for further development of this type catalyst for fuel cell applications [8,9]. A patent application was filed on 11/5/04.
- A Tufts-wide lecture series entitled: “Distinguished Lectures in Nanotechnology for Advanced Energy materials and Catalysts” was inaugurated this year. The 2004-05 lecturers are: Bruce Gates (UC Davis), Christos Flytzanis (Ecole Normal Supérieure, Paris), James Dumesic (U Wisconsin), Gabor Somorjai (UC Berkeley), and Francis DiSalvo (Cornell U.).

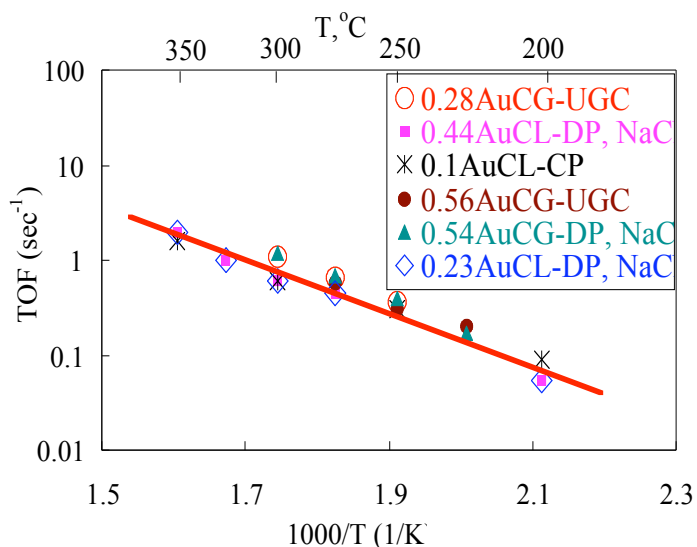


Fig.1. Turnover frequency of WGS over nanostructured gold-ceria catalysts. Gas composition (mol): 11%CO-26%H<sub>2</sub>O-26%H<sub>2</sub>-7%CO<sub>2</sub>/He

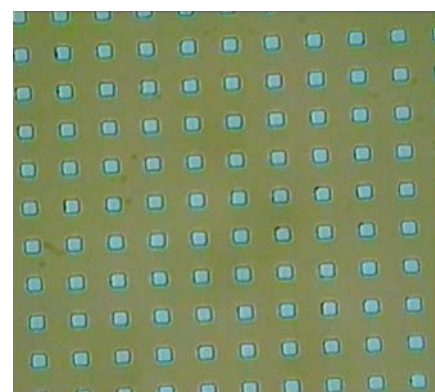


Fig.2. Ceria (6nm)-gold (3 nm) layered nanotowers: 54- nm height; 10 μm squares.

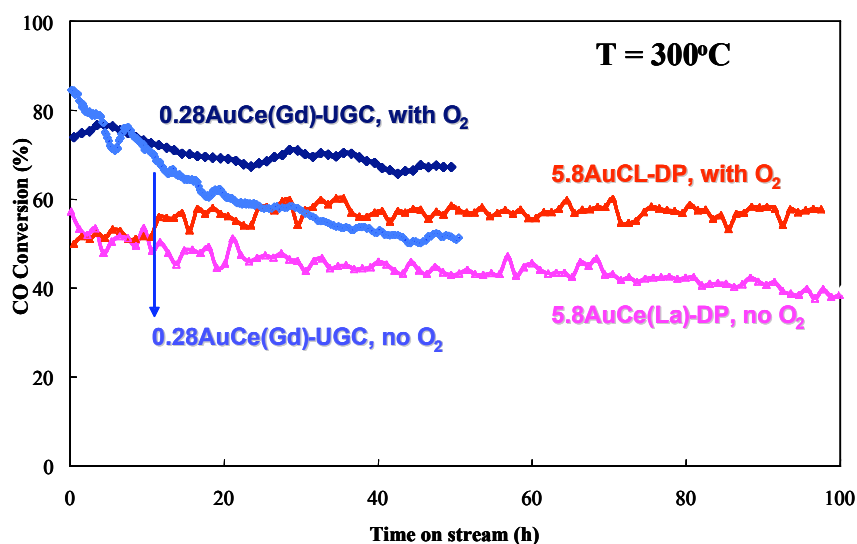


Fig. 3. Addition of 0.5% O<sub>2</sub> in the feed gas mixture stabilizes the WGS activity of gold-ceria catalysts. Gas composition (mol): 11%CO-26%H<sub>2</sub>O-26%H<sub>2</sub>-7%CO<sub>2</sub>/He; Space velocity: 15,000 h<sup>-1</sup>.

## References

- [1] For further information about this project, email: [mflytzan@tufts.edu](mailto:mflytzan@tufts.edu)
- [2] Qi Fu, Howard Saltsburg, Maria Flytzani-Stephanopoulos, *Science* 301 (2003) 935-938; published online 3 July 2003 (10.1126/science.1085721); Qi Fu, Ph.D. thesis, Tufts University, February 2004
- [3] Regina Valluzzi, R. Guertin, Terry Haas MRS (S29.011) March 2003
- [4] Ioannis Zuburtikudis, Howard Saltsburg, *Science* 258 1337 (1992)
- [5] Qi Fu, Weiling Deng, Howard Saltsburg, Maria Flytzani-Stephanopoulos, *APCATB*, invited paper, *in press*
- [6] Janice DeJesus, M.S. thesis, Chemical and Biological Engineering, Tufts University, May 2004; Wei Liu and M. Flytzani-Stephanopoulos, *J. Catal.* 153 (1995) 317
- [7] Zheng Zhou, Ph. D. thesis, Tufts University, in progress.
- [8] Weiling Deng, Ph.D. thesis, Tufts University, in progress.

[9] Weiling Deng et al., paper 13b, presented at AIChE 2004 Annual Meeting, Austin, TX, Nov.7-12, 2004