

[Note: This is a reprint of an abstract. Contents of this document should not be quoted or referred to without permission of the author(s).]

To be presented at Microscopy and Microanalysis 2004, the annual meeting of the Microscopy Society of America, be held in Savannah, Georgia, August 1-5, 2004.

**Aberration Corrected STEM Analysis of Gold Nanoparticle
Catalytic Activity**

A. R. Lupini, A. G. Franceschetti*, S. T. Pantelides*, S. Dai, B. Chen, W. Yan,
S. H. Overbury, S. J. Pennycook

Oak Ridge National Lab, Oak Ridge, TN 37831

*Department of Physics, Vanderbilt University, Nashville, TN, USA

"The submitted manuscript has been authored by a contractor of the U.S. Government under contract No. DE-AC05-00OR22725. Accordingly, the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U.S. Government purposes."

Prepared by the

CONDENSED MATTER SCIENCES DIVISION
OAK RIDGE NATIONAL LABORATORY

Managed by
UT-BATTELLE, LLC, for the
U.S. DEPARTMENT OF ENERGY
Under Contract DE-AC05-00OR22725

March 2004

Aberration Corrected STEM Analysis of Gold Nanoparticle Catalytic Activity

A.R. Lupini, A.G. Franceschetti*, S.T. Pantelides*, S. Dai, B. Chen, W. Yan, S.H. Overbury, S.J. Pennycook

Oak Ridge National Lab, Oak Ridge, TN 37831

*Department of Physics, Vanderbilt University, Nashville, TN, USA

The oxidation of CO is a very important reaction that could lead to safer, cleaner cars and homes for us all [1]. It is therefore exciting technologically, as well as remarkable scientifically that the catalytic activity of gold for CO oxidation can be changed from extremely inactive in the bulk to extremely active in nanometer sized clusters [2]. Although several mechanisms have been proposed, the exact route and details of this catalytic activity are still unknown.

High angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) provides some advantages over other microscopy techniques for analysis of heavy metal catalysts. HAADF STEM, also known as Z-contrast imaging, provides the ability to examine such catalysts in their active form, and achieve extremely high spatial resolution (better than 1 Angstrom) combined with single atom sensitivity [3]. The recent advent of aberration correction is providing exciting advances in the resolution and sensitivity of such instruments [4]. At ORNL, we are in the process of installing an aberration corrected electron spectrometer (a Gatan Enfina) on the aberration corrected 100 kV electron microscope. Here the spectrometer aberrations are corrected by a quadrupole coupling module (supplied by Nion Co.) in a similar manner to the objective lens C_s -correction. This allows spectra to be obtained with a resolution that approaches the fundamental energy spread of electrons from the field-emission tip (<0.3 eV). One of the first applications has been to examine these nanocatalysts in more detail, and some of the first results will be presented.

We have produced nanoparticle catalysts on a variety of titania (anatase, rutile, brookite, and mesoporous) supports with different Au particle size distributions. These have been examined and seem to show similar trends in activity: Samples containing the very smallest gold particles – single atoms [Fig. 1] – are relatively inactive, while larger particles – tens of nanometers [Fig. 2] – again have reduced activity. Nanoparticles in the intermediate size range – around a nanometer [Fig. 3] – are associated with the most active samples. Z-contrast images suggest that many of the active particles are only a single monolayer thick, giving them a raft-like appearance. These smallest nanoparticles are much more visible than in the equivalent TEM (or bright field STEM) image [Fig. 4]. Heat deactivated samples were found to have fewer of the small active rafts, which appear to agglomerate into larger particles.

Density functional theory calculations show that gold nanoparticles bond only weakly to the surface of titania, but more strongly at oxygen vacancy sites. The gold atom that bonds to the O vacancy will provide an anchor for a gold nanoparticle. It further transpires that a single gold atom (on an oxygen vacancy) does not bond O molecules. However for larger clusters of several atoms, it is energetically favorable for O_2 and CO to bond. As the clusters get larger, it is still possible for the oxygen to bond, but there will be fewer sites available per gold atom. Large gold particles are unable to bond oxygen, and so have the least activity.

The combination of aberration corrected STEM and density functional theory has therefore revealed some of the details of nanoparticle gold catalyzed CO oxidation and thus been shown to be an incredibly useful tool in unraveling real catalysis problems [5].

References:

- [1] A. T. Bell, *Science* **299**, 1688 (2003)
- [2] M. Haruta, M. Date, *Applied Catalysis A* **222**, 427 (2001)
- [3] A. Y. Borisevich, *These proceeding* (2004)
- [4] O. L. Krivanek, et al, *Ultramicroscopy* **96**, 229 (2003)
- [5] This work was supported by the USDOE under contract DE-AC05-00OR22725 managed by UT-Battelle, LLC.

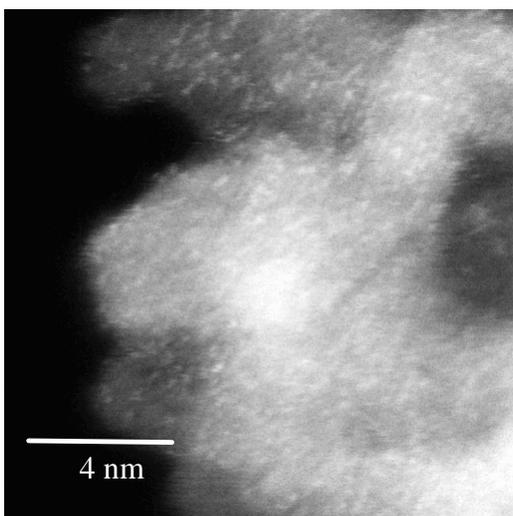


Fig. 1 HAADF image of Au on titania (low activity sample). The small spots are single gold atoms.

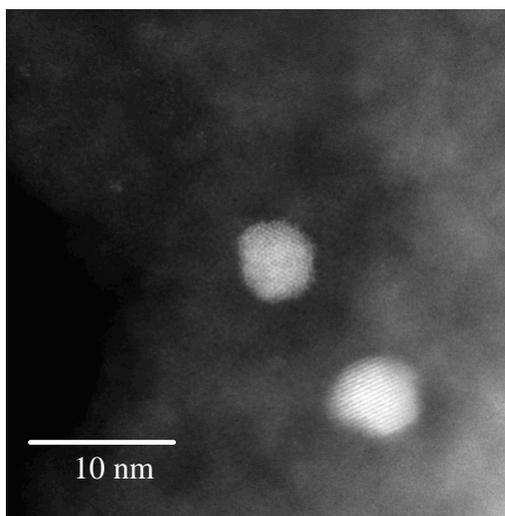


Fig. 2 HAADF image of Au on titania (low activity sample). Larger gold particles are visible.

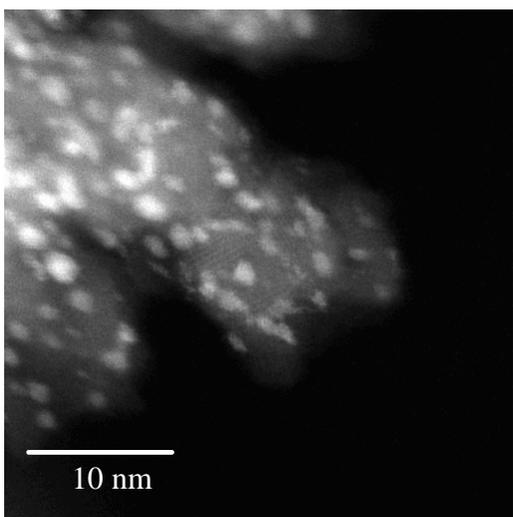


Fig. 3 HAADF image of Au on titania (highly active sample). Nanometer sized rafts are visible. Image acquired simultaneously with fig 4.

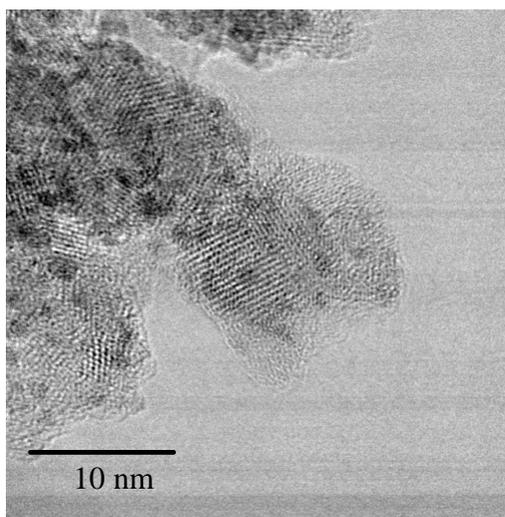


Fig. 4 Bright field image (equivalent to TEM image) acquired simultaneously with fig 3. Gold rafts are less visible, but the crystalline structure of the titania is clearer.