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INSIGHTS INTO NANOCATALYSIS THROUGH ABERRATION-CORRECTED STEM AND DFT CALCULATIONS

A. R. Lupini^{*}, A. G. Franceschetti^{+*}, S. T. Pantelides^{+*}, S. H. Overbury[#], B. Chen[#],
W. Yan[#], S. Dai[#], and S. J. Pennycook^{*+}

^{*}Condensed Matter Sciences Division, Oak Ridge National Lab, Oak Ridge, TN 37831

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

[#]Chemical Sciences Division, Oak Ridge National Lab, Oak Ridge, TN 37831

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^{*}Condensed Matter Sciences Division, Oak Ridge National Lab, Oak Ridge, TN 37831

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

[#]Chemical Sciences Division, Oak Ridge National Lab, Oak Ridge, TN 37831

Abstract:

Oral Presentation

Poster Session Only

The catalytic activity of nano-sized gold particles on suitable substrates offers considerable opportunities for exciting new applications and raises many scientific questions as to how this activity arises. Gold catalysts on a variety of supports were prepared and studied. The catalytic activity was measured and attempts were made to correlate this activity with the substrate and size of particle.

Aberration corrected STEM (Scanning Transmission Electron Microscopy) offers several advantages over conventional TEM for analysis of these catalysts. The higher resolution and sensitivity obtained through aberration correction allows detection of catalyst particles down in size to single atoms. This is an advantage because sub-nm sized particles, consisting of only a handful of atoms, are extremely difficult to directly observe through any other technique. As all of the catalysts prepared had a range of size distributions, using a technique that did not allow the detection of single gold atoms could produce an incorrect correlation of size with activity.

Initial experimental results suggest that it is particles of around 1 nm and even sub-nm that are catalytically active for CO oxidation on substrates composed of three different titania substrates. There is a suggestion that even clusters of as few as 5 or 6 atoms could be active. However single gold atoms did not appear to be active. The catalysts could be deactivated by heating, which resulted in the loss of the smallest gold nanoparticles and the formation of larger nanoparticles (of the order of 10 nm).

Combining the high-resolution STEM images with first-principles density-functional calculations allows considerable insight into the mechanisms for the catalytic activity. Calculations of gold adsorption on the TiO₂ anatase (001) surface show that gold clusters are anchored to oxygen vacancies in the titania substrate, the adhesion energy being almost independent of the number of Au atoms in the cluster. This suggests that small clusters are prevented from moving on the substrate and coalescing to form larger particles (at low temperatures) by the presence of O vacancies. Catalytic oxidation of CO requires co-adsorption of CO and O₂ molecules. We find that single Au atoms bound to O vacancies do not adsorb O₂ molecules (and bind CO only weakly), thus explaining the observation that single atoms are not catalytically active. Larger clusters bind both CO and O₂ molecules, preferentially along the perimeter. We speculate that the observed decrease in the catalytic activity for large particles is a geometric effect, due to the smaller ratio of surface gold atoms located along the perimeter of a nanoparticle or at surface steps.

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