

# Fundamental Reaction Processes for CO Oxidation at Gold Nanoparticles Studied Using Density-Functional Theory

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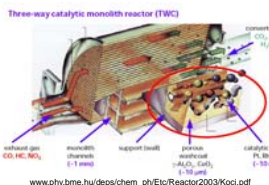
## Introduction

Small Au clusters supported on oxide substrates exhibit strong catalytic activity for oxidation of CO molecules. The exact reasons for this are not entirely understood. One possible mechanism for catalysis at Au clusters is related to electron-confinement effects which lead to electronic properties favorable for reaction. Other possible mechanisms involve interactions of the Au cluster or reactants with the substrate

We explore using density-functional theory (DFT) a new reaction pathway for the dissociation of O<sub>2</sub> molecules at a neutral Au<sub>6</sub> cluster. Our preliminary results suggest that strong catalytic properties might be possible even without interactions with a substrate.

## Applications

- Au nanoshells and Infrared Lasers for cancer treatment<sup>1</sup>
- Biohazard detection
- Manufacturing of emulsion-based paints, wall-paper, paste and wood glue
- Production of cheaper solar cells
- Catalysis
  - CO oxidation (As seen in catalytic converter diagram to right)
  - NO<sub>x</sub> reduction



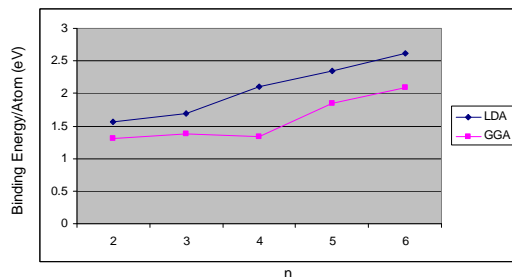
## Theoretical Approach

•We performed spin-polarized DFT calculations using the generalized-gradient approximation due to Wang and Perdew<sup>2</sup>. We used the VASP electronic-structure code to perform all of our calculations<sup>3</sup>.

•Compared to prior DFT calculations on small Au clusters, we applied the projector-augmented wave (PAW) method<sup>4</sup>. This is an all-electron method which is expected to be more accurate than standard pseudopotential calculations yet still computationally very efficient.

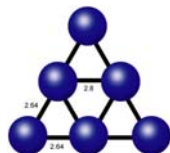
•One important effect that has not been included in these calculations is spin-orbit coupling. This may be an important factor for catalysis at noble-metal nanoparticles.

## Binding Energy/Atom for Au<sub>n</sub> Clusters with n = 2 - 6



• Comparable to results obtained by other methods<sup>5</sup>.

## Au<sub>6</sub> Ground State Structure



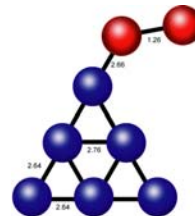
- Several different possible structures considered.
- Clusters relaxed to ground state.
- Best Au<sub>6</sub> cluster has a planar structure.
- Bond lengths in good agreement with previous results<sup>5</sup>.

## Molecular Adsorption of O<sub>2</sub>

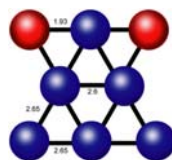
• Various possible adsorption sites were considered.

• Lowest-energy adsorption site in good agreement with other GGA calculations.

• O<sub>2</sub> binding energy of 0.5 eV comparable to results for smaller clusters<sup>5</sup>



## Dissociated O<sub>2</sub> on Au<sub>6</sub>



• Binding energy of 0.7 eV.

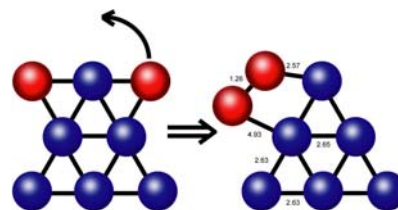
• Stronger binding indicates possibility of dissociation.

• Reaction pathway and energy barrier for dissociation needed.

## Energy Barrier for O<sub>2</sub> Dissociation

• Energy barrier of 0.006eV computed.

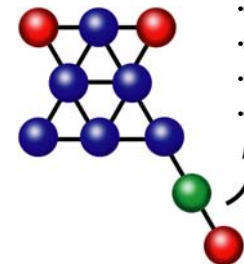
• Need to continue to lowest molecular-adsorbed state.



• Estimate of net reaction barrier for dissociation is 0.51eV.

• Earlier DFT calculations found ~3eV for a different path<sup>7</sup>.

## Reaction Barrier for CO Oxidation



- CO bonded to cluster.
- Binding energy and reaction pathway being computed.
- Not clear yet what energy barrier dominates reaction.
- CO binding energy is 1.18eV.

## Conclusions and Future Work

• Low energy barrier (0.51eV) for O<sub>2</sub> dissociation.

• Energy barrier lower than previous calculations (~3eV)<sup>7</sup>.

• Reaction pathway appears better than previous calculation<sup>6</sup>.

• Binding energy for CO stronger with dissociated oxygen than without<sup>5</sup>.

• Indication that the resulting reaction barrier is potentially important in catalysis.

• Energy barrier for CO oxidation being computed.

• Charged clusters may have lower energy barriers.

• Full study of Au clusters on oxide surfaces for future work.

## References

1. L.R. Hirsh, et al., PNAS **100** (2003) 13549
2. Y.Wang and J.P. Perdew, Phys. Rev. **B44**, 13298 (1991)
3. G. Kresse and J. Hafner, Phys. Rev. **B47**, 558 (1993); Phys. Rev. **B49**, 14251 (1994); G. Kresse and J. Furthmuller, Phys. Rev. **B54**, 11169 (1996); Comput. Mater. Sci. **6**, 15 (1996)
4. P.E. Bloechl, Phys. Rev. **B50**, 17953 (1994); G. Kresse and D. Joubert, Phys. Rev. **B59**, 1758 (1999)
5. X. Wu et al., J. Chem. Phys. **117**, 4010 (2002)
6. G. Mills, M.S. Gordon, and H. Metiu, Chem. Phys. Lett. **359**, 493 (2002)
7. B. Yoon, H. Hakkinen, and U. Landman, J. Chem. Phys. **A107**, 4066 (2003)

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