Electronic structure of catalytically active gold clusters supported on cerium oxide

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Introduction

Low concentration gold clusters supported on ceria nanorods (0.01 at.% Au:CeO_{2-x}) exhibit excellent catalytic activity for CO oxidation. And the *s-d* band hybridization was observed in resonant photoemission spectroscopic. We performed density functional theory (DFT) calculation to study ceria supported Au cluster systems. The valence hybridized states in gold clusters and the upshift of Au 5*d* band determined in our modeling results are reciprocally essential to explain the enhanced catalytic activity of supported gold cluster catalysts.

Motivation

Gold catalysts have attracted rapidly growing interests due to the renewal understanding of their catalytic activities towards chemicals reactions of both industrial and environmental importance. Unraveling the unusual valence electronic structure features of gold clusters can open up possibilities in predicting molecular adsorption mechanisms for different gold-cluster-based catalyst designs. And elucidating the electronic structures of supported gold clusters can provide critical clues to the mechanisms for their catalytic activity.

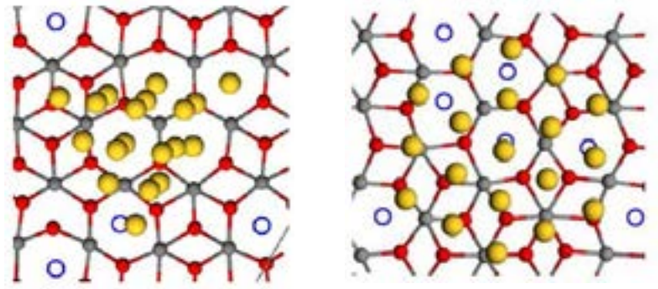
Methods

- Density functional theory (DFT) implemented in VASP code
- Projector augmented-wave (PAW) method
- Plane wave basis set, with energy cutoff around 400 eV
- Generalized gradient approximation (GGA) in Perdew-Burke-Ernzerhof form (PBE)
- DFT+*U* method with $U = 6$ eV for Ce
- Max force is lower than 0.02 eV/Å in optimizations.

Models

1. A 9-atom-layered CeO2 slab model (CeO_{2-x}) with 8% oxygen atoms removed from the surface and subsurface layers was constructed to simulate a defective CeO_2(111) surface containing both surface and subsurface oxygen vacancy defects.
2. Two different structures of gold clusters composed of 19 gold atoms, tetrahedral Au_{19} (t-Au_{19}) and planar Au19 (p-Au_{19}), were considered to represent two extreme cases in the construction of models of a gold cluster on the ceria slab (Au_{19}:CeO_{2-x}).
3. A tetrahedral gold cluster (t-Au_{19}) or a planar gold cluster (p-Au_{19}) was placed on the top of the ceria slab surface and optimized.

Structures

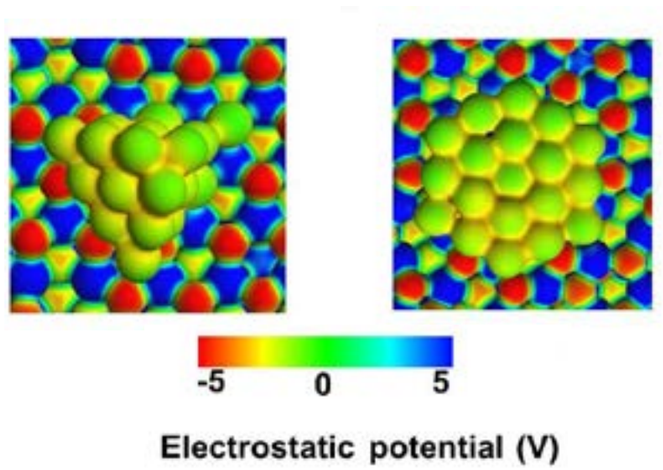


t-Au_{19}:CeO_{2-x} p-Au_{19}:CeO_{2-x}

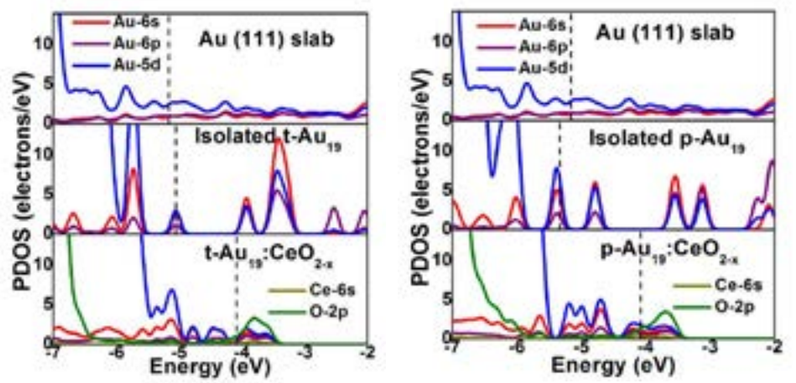
Optimized structures of Au_{19} clusters adsorbed on the top of the ceria slab.

Charge Transfer

The Au_{19} clusters were found to be slightly negatively charged (0.17 or 0.23 electron charge per gold atom for t-Au_{19} or p-Au_{19})



Electronic properties



Surface partial density of states (PDOS) for the 6*s*, 6*p* and 5*d* orbitals of Au in (top) a 19-atom-thick Au (111) slab, (middle) isolated Au_{19} and (bottom) Au_{19}:CeO_{2-x}. The 6*s* orbital of Ce and 2*p* orbital of O in Au_{19}:CeO_{2-x} are also illustrated in the bottom figure. Black dash lines indicate the locations of the Fermi levels with respect to vacuum.

Summary

1. The similarities in the shapes and overlaps of the 5*d* and 6*s* band in our computed Au_{19}:CeO_{2-x} models verify the presence of strong hybridization of the Au 5*d* and 6*s* states in the supported gold clusters.
2. The d-band centre up-shifts determined in the computed PDOS data in these models possibly facilitate the chemisorption of oxygen on low gold concentration Au:CeO_{2-x} catalysts.
3. The disclosure of the electronic structures of the metal clusters will achieve further insights into their structure-reactivity relationship and developing new strategies in catalyst design.

Acknowledgments

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