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:CeO2-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 5d 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 (CeO2-x) with 8% oxygen atoms removed from the surface and subsurface layers was constructed to simulate a defective CeO2(111) surface containing both surface and subsurface oxygen vacancy defects.

Electronic properties

Surface partial density of states (PDOS) for the 6s, 6p and 5d orbitals of Au in (top) a 19-atom-thick Au(111) slab, (middle) isolated Au19 and (bottom) Au19:CeO2-x. The 6s orbital of Ce and 2p orbital of O in Au19:CeO2-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 5d and 6s band in our computed Au19:CeO2-x models verify the presence of strong hybridization of the Au 5d and 6s 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:CeO2-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.

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