Modelling the Properties of Gold Nanoparticles

A Thesis presented for the degree of
Doctor of Philosophy
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Certificate of Originality

I certify that the work in this thesis has not previously been submitted for a degree nor has it been submitted as part of requirements for a degree except as fully acknowledged within the text.

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Benjamin J.-S. Soulé de Bas

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Glossary of Acronyms

AE	All-Electron
BSSE	Basis Set Superposition Error
CC	Coupled Cluster
CCSD	Coupled Cluster with Singles and Doubles
CG	Conjugate Gradient
CI	Configuration Interaction with Singles and Doubles
CISD	Configuration Interaction
CM	Centre of Mass
CP	Counterpoise Correction
DFT	Density Functional Theory
DZP	Double-ζ plus Polarisation
EAM	Embedded Atom Model
FC	Force Constant
$\mathrm{F_S}$	Surface F-centre
GGA	Generalised Gradient Approximation
HOMO	Highest Occupied Molecular Orbital
LAPW	Linear Augmented Plane Wave
LCAO	Linear Combination of Atomic Orbitals
LDA	Local Density Approximation
LJ	Lennard-Jones
LMTO	Linear Muffin-Tin Orbitals
LSDA	Local Spin Density Approximation

LUMO	Lowest Unoccupied Molecular Orbital
MD	Molecular Dynamics
MP2	Second-Order Møller-Plesset
PES	Potential Energy Surface
PS	Pseudopotential
PW	Plane Wave
SA	Simulated Anneal
TB-SMA	Tight-Binding Second Moment Approximation
TPR	Temperature Programmed Reaction

Abstract

The physical and chemical properties of gold nanoparticles were investigated using first-principles density-functional theory in the local density approximation. The low-energy structures of gold nanoparticles containing from 3 to 38 atoms were determined using a combination of semi-empirical potential and DFT calculations. At the DFT-LSDA level, planar structures persist up to Au_6 and lie close in energy to the 3D ground-state structures for $7 \leq n \leq 10$ atoms. Ordered structures are predicted as being stable for $n \leq 9$. Beyond this size, disordered structures dominate with the notable exception of the tetrahedral Au_{20}. The present DFT calculations predict numerous structural isomers being energetically equivalent or lying close in energy to the ground-state structures. The HOMO-LUMO energy gap is found to decrease as the cluster size increases, which indicates a transition towards a metallic behaviour at larger sizes. The thermal behaviour of gold clusters containing 7, 13 and 20 atoms was investigated using isothermal density-functional molecular-dynamics simulations. At each size, the global minimum energy structure and a low lying isomer are used as the starting structures. In most cases, the clusters exhibit high-temperature melting without showing any sharp transition from a solid-like to a liquid-like phase, but rather pass through a region of transformation between structural isomers. The starting structure used in the simulation is shown to have a considerable effect upon the subsequent thermal behaviour. The Au_{20} ground-state structure contrasts with the other clusters and remains tetrahedral up to its melting at about 1200 K. The adsorption of Au_{20} on a regular and defective (100) MgO surface was investigated using a combination of DFT MD simulations, single-point calculations and structure optimisations. Au_{20} is found to bind quite weakly to the regular (100) MgO surface, favouring Au-O interactions. The Mulliken population analysis used in conjunction with charge density maps reveals that the resulting bond mainly arises from an electrostatic polarisation of the cluster by the substrate. When adsorbed on a surface F-centre defect, Au_{20} binds to the oxide surface with a significantly enhanced strength. The analysis of the resulting interaction indicates that, in addition to being polarised, Au_{20} is charged by the defective surface. Based upon the results of the present investigation, different reaction mechanisms for the oxidation of CO by Au_{20} supported on MgO are proposed.