Density Functional Theory of Free and Oxide Supported Metal Nanoclusters and Nanoalloys: A Heterogeneous Catalysis

A

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Name of the Student : **Baraiya Bhumi Arunkumar**

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Name of Supervisor : **Prof. Prafulla Kumar Jha**
Department of Physics, Faculty of Science,
The M. S. University of Baroda,
Vadodara - 390 002, Gujarat, India

Registration No. : **FOS/1987**

Date of Registration : **21/03/2016**

Place of the work : **Department of Physics, Faculty of Science,**
The M. S. University of Baroda,
Vadodara - 390 002, Gujarat, India

Introduction

Metal nanoclusters and nanoalloys i.e., pure or mixed metallic aggregates of dimensions ranging between 1 and 100 nanometers are the subject of great interest in basic science as well as in current technology where they find many applications for their unique properties starting from chemical sensing to heterogeneous catalysis, from magnetic recording to opto-electronic devices. Much emphasis on structure-activity relationships is made in experimental and theoretical research, with the aim of fabricating new materials with well-defined and controllable properties. Synergistic effects are dependent on many factors, e.g., size and structure [1-2]. For catalysis, improvement in activity, selectivity and stability (resistance to poisoning) [3] is achievable with nanoalloys. Intermetallic interactions produce different neighboring atoms [4] and new activated sites (e.g., point defects, interfaces, edges) [5]. Furthermore, electronic, geometric, ligand and ensemble effects [6] affect the *d-band center* position which is crucial for catalytic activity [7].

Nanoclusters offer distinctive physical and chemical properties, with the possibility of fine-tuning size and structures. Clusters of transition metals from group 10 (Ni, Pd, Pt) and group 11 (Cu, Ag and Au), and also their crossover mixtures (nanoalloys) between the two groups are of special interest attributed to their excellent physical, catalytic, optical, electronic and magnetic properties. From alloying, activity, selectivity and stability enhancement is conceivable and another dimension arises – chemical ordering (*i.e.,* mixed *vs.* segregated phases). Detailed theoretical investigation can extend our fundamental understanding of these complicated systems, giving a better understanding of experimental observations and allowing prediction of chemical and physical properties. Although many theoretical calculations have focused on the free clusters [8], it is difficult to get interaction-free clusters. This adds extra complexity when determining the geometric structures and stabilities of the clusters. However, the inclusion of a support is very interesting from a catalysis point of view, as distinct behavior from a variation of support is expected. As an alternative, many supports have been included, either reactive or non-reactive for instance oxide materials at the nanometre scale have tremendous potential in fundamental research for the modern nanotechnologies.

Oxide materials at the nanometer scale (typically up to 10 nm in thickness) have tremendous potential in fundamental research and for the modern nanotechnologies. Due to finite size effects and the dominance of surface and interface phenomena, oxide nanostructures possess novel physical and chemical properties that distinguish them from their respective bulk counterparts. To obtain a fundamental understanding of the physicochemical properties of oxide nanostructures structurally well-defined model systems have been utilized, typically in the form of ultrathin oxide films epitaxially grown on single crystal metal surfaces, with a thickness of 1-3 monolayers (so-called oxide nanolayers). Novel phenomena in their geometric architecture, electronic structure, chemical nature and magnetic behavior have been recognized [9-16], rendering oxide nanolayers vast and unforeseen opportunities in science and technology. A new generation of devices for energy production and communication technologies, such as solid oxide fuel cells, solar energy materials, and tunnelling magnetoresistance sensors, have been designed to exploit the unusual properties afforded by the reduced oxide dimensions. Systems composed of metal particles or metal films supported on an oxide are of immediate relevance for many applications e.g., heterogeneous catalysis, electronic devices, chemical sensors, and biocompatible materials. However, the inclusion of a support is very interesting from a catalysis point of view, as distinct behaviour from a variation of support is expected. Depending on the metal systems being studied, a support can be chosen based on reaction needs.

Depending on the metal systems being studied, a support can be chosen based on reaction needs. For example, in the gold catalyzed oxidation of CO, enhanced reactivity is achieved with Al_2O_3 support, due to the presence of Au-O back-bonding. However, a similar observation is not detected for Au/SiO_2 and Au/TiO_2 catalytic systems, in which gold structures remain unchanged [17]. Metal-support interactions have a targeted and very specific function in catalytic reactions. In the conversion of methanol to CO_2, the Pt nanocluster performance order is $Pt/MgO \geq Pt/TiO_2 >> Pt/Al_2O_3$. Combustion in NH_3 atmosphere still favors the MgO support. Analysis of the X-ray Absorption Spectroscopy reveals the metallic state of Pt but a strong interaction with the TiO_2 and Al_2O_3 resulted in a weaker catalytic behavior. In contrast, there is no evidence for interaction between Pt and MgO [18]. First-principles theoretical approaches able to describe the complexities of the chemical bond in such systems with higher accuracy, but their application is limited by the involved computational effort, rapidly increasing as a function of the size of the system. Among first-principles approaches, density-functional theory (DFT) is most often employed, as it currently represents the best compromise between accuracy and computational effort. Despite the inherent demands of DFT calculations, contemporary advances both in methods and hardware are continuously extending the range of systems to which these approaches can be successfully applied using available computational resources, and nowadays electronic structure simulations are routinely conducted using one of the several black-box packages available [19-20].

This thesis work is based on such first-principles theory and simulations, and is about the utility of various tools for the investigation of free and oxide-supported metal nanoclusters and nanoalloys as heterogeneous catalysts in prototypical and industrially relevant oxidation (CO) and reduction (CO_2) reactions.

Objectives

The aim of this proposed work is to study the atomic and electronic structure of free and oxide supported nanoclusters and nanoalloys, to understand their morphology and bonding configurations, behavior at the molecular level, modified electronic and dynamical properties, and optical transitions in adsorbed systems using Density Functional Theory (DFT) and cluster embedding method.

a. Determination of equilibrium ground state (energetic) and geometrical structures or active surfaces (atomic configurations) of the Au and Pt nanoparticles or its clusters deposited on oxide supports (TiO_2, vanadium pentoxide, SnO_2, Al_2O_3 etc) under investigation.

b. The analysis of formation enthalpy to find the thermodynamically diameter (shape) dependent (and shape) most stable structure. Further also calculate potential energy diagram for adsorption when induced and intrinsic surface energy excess for nanoclusters.

c. To compute electronic band structure, electronic density of states and charge density contour.

d. To perform subsequent calculations to examine the effect of various kinds of defects such as vacancies and impurity atoms, and the interactions between them. These calculations will be important as defects are known to have a significant effect on the bonding and electronic properties of heterogeneous ultra nanocatalysts.

e. To calculate phonon dispersion curve, phonon density of states, and allied properties for of Free and Oxide Supported Metal Nanoclusters and Nanoalloys using first principles calculation.

f. To calculate magnetic moments for values of the bond length at equilibrium using full-potential, spin-polarized, all-electron density-functional calculations for heterogeneous ultra nanocatalysts as well as surface of heterogeneous ultra nanocatalysts in different site growth direction.

g. To calculate optical properties of metal nanoparticles and their clusters on oxide supports.

Thesis organization

The present thesis is organized in the following manner.

Chapter 1 is describing the background and motivation of this thesis work. This chapter is all about the brief review on the recent development occur in the field of heterogeneous catalyst for CO oxidation and CO_2 reduction into value added-chemicals along with other important catalytic activities as well. The latest progress of free and oxide supported metal nanoclusters and nanoalloys, their potential applications, challenges appeared during the catalytic activity and improved strategies are also presented in detail.

The **chapter 2** present the background and principles of the electronic structure calculations (*ab initio* – especially the **Density Functional Theory (DFT)** along with the Grimme's dispersion corrections (D2 and quite recently improved D3) and the research methodology for structural optimization in detail.

Additionally, the methodologies to determine the reaction barriers during catalytic reactions were also briefly discussed.

In **Chapter 3,** we address the structural stability, electronic properties and effect of metal-metal interaction on Raman spectra of icosahedral (I_h) Pd_mCu_n (m + n = 13) clusters (presented in Figure. 1) using first-principles calculations based on dispersion-corrected density functional theory (DFT-D2). This chapter also encompasses the investigation of CO_2 adsorption and hydrogenation (to value added chemicals) over I_h clusters (made up of 13-atom and 55-atom). The effect of the Cu-doping (percentage in the parent cluster ranging from 50-65%) on heterogeneous catalytic activity also discussed in detail.

The **Chapter 4** presents the first-principles based on spin-polarized density functional theory (DFT) calculations to unveil the role of Cu atom on degrading CO poisoning mechanism over Ni_nCu clusters. This chapter initial addresses systematic investigation of structural, magnetic and electronic properties of Ni_{n+1} and Ni_nCu clusters ($1 \leq n \leq 12$). X-ray absorption near-edge structure (XANES) spectra of Ni K-edge extract the information of the oxidation states and coordination environment of metal sites of clusters. In addition, the quantum chemical descriptors for Ni_{n+1} and Ni_nCu clusters are also analysed in detail. As proceed further, this study operated with the two forms of dispersion corrections i.e., D2 and D3 to DFT (with LDA and GGA functionals) for the consideration of vdW interactions during CO adsorption. The PBE-D3 approach found capable in yielding the experimentally observed preferential site for CO adsorption. The effect of spin polarization on reactivity of transition metals (TMs) towards CO adsorption, critical assessment of electronic reactivity descriptors such as d-band center, d-band width and fractional filling of d-band examined using spin-polarized d-band center model also explored. The effective Löwdin charge analysis confirms the occurrence of donation-back-donation process in between adsorbate-adsorbent. Lastly, this chapter contains the CO oxidation reaction pathway within the Langmuir−Hinshelwood (L−H) mechanism and $Ni_{12}Cu$ cluster inspected as potential candidate for CO oxidation with the lowest activation barrier and negligible possibility of Ni poisoning. This chapter provide valuable strategy for rational design of catalyst in essence to CO oxidation with no Ni-poisoning.

In **Chapter 5,** we thoroughly investigate, the role of support effects (TiO_2 and Cu_2O oxide surfaces) on the kinetics of catalytic activity (reduction and oxidation of CO_2 and CO, respectively) of pure and bimetallic clusters (crossover using DFT calculations. The comparative relevant kinetic mechanisms are explored at various surface sites on free and supported clusters as well as clusters bound at support point defects (vacancies/ divacancies). This chapter establish the superior role of support in stabilization of free cluster and reduction of the reaction barrier compared to unsupported ones.

Chapter 6 concludes and summarizes the most important findings and potential applications of this thesis work. This chapter also includes the future research directions and scope in the field of rational design of novel free and oxide supported heterogeneous catalysts (nanoclusters and nanoalloys) with improved strategy and testimonials.

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List of Publications Related to Thesis

1. **Bhumi A. Baraiya**, Venu Mankad, Prafulla K. Jha, *Uncovering the structural, electronic and vibrational properties of atomically precise* Pd_mCu_n *clusters and their interaction with* CO_2 *molecule*, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy (Spectrochim. Acta A), **229**, 117912, (2020). **DOI:** 10.1016/j.saa.2019.117912.

2. **Bhumi A. Baraiya**, Venu Mankad and Prafulla K. Jha, *Interaction Mechanism of CO with Pd-Rich Copper Clusters*, AIP Conference Proceedings, **2115**, 030543 (2019). **DOI:** 10.1063/1.5113382.

3. **Bhumi A. Baraiya**, Venu Mankad, Prafulla K Jha, Degrading CO poisoning over foreign atom seized $Ag_{12}M$ icosahedral bimetallic clusters, AIP Conference Proceedings, **2265**, 030612, (2020).

4. **Bhumi A. Baraiya**, Hemang Tanna, Venu Mankad, Prafulla K. Jha, Dressing of Cu Atom Stimulating the Poisoning Free CO Oxidation over $Ni_{12}Cu$ Cluster (submitted to ACS Catalysis).

List of Publications Non-related to Thesis

1. Aditya Dey, **Bhumi A. Baraiya**, Souren Adhikary, Prafulla K. Jha, First-Principles Calculations of the Effects of Edge Functionalization and Size on the Band Gap of Be_3N_2 Nanoribbons: Implications for Nanoelectronic Devices, ACS Applied Nano Materials (ACS Appl. Nano Mater.) 2020. DOI: 10.1021/acsanm.0c02809.

3. **Bhumi A. Baraiya**, Narayan N Som, Venu Mankad, Guangfen Wu, Jinlan Wang and Prafulla K. Jha, *Nitrogen-Decorated Borophene: An Empowering Contestant for Hydrogen Storage*, Appl. Surf. Sci. (Applied Surface Science), 527, 146852, (2020). **DOI:** 10.1016/j.apsusc.2020.146852.

4. Sharad Babu Pillai, **Bhumi A. Baraiya**, Deepak Upadhyay, Venu Mankad, Prafulla K. Jha, *Catalytic activity and underlying atomic rearrangement in monolayer CoOOH towards HER and OER*, International Journal of Hydrogen Energy (Int. J. Hydrog. Energy), 2019. **DOI:** 10.1016/j.ijhydene.2020.03.075

5. **Bhumi A. Baraiya**, Venu Mankad and Prafulla K. Jha, *Incisive study on stability and vibrational properties of NO_x ($x = 1$ to 3) over Pt surfaces: A comparative analysis*, Surface Science (Surf. Sci), **690**, 121467, (2019). **DOI:** 10.1016/j.susc.2019.121467.

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10. **Bhumi A. Baraiya**, Venu Mankad and Prafulla K. Jha, *Adsorption Energetics of Atoms and Diatomic Gases with Electrocatalysis Approach towards Hydrogen and Oxygen Evolution Reaction on Pt Surfaces*, ChemistrySelect, **3**, 10515–1052 (2018). **DOI:** 10.1002/slct.201802072.