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

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Executive Summary

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Definition of the Problem

The proposed thesis work was initiated with the aim 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 vibrational properties with the specific objective to explore the catalytic activity of these systems towards reducing the environmental pollution/production of value aided chemicals by oxidizing/reducing the CO and CO_2 by using first-principles based on density functional theory calculations.

Computational Methodology

The presented structural, electronic, vibrational, and catalytic properties in this thesis were computed using the Quantum Espresso (PWSCF) package [1-2]. Quantum Espresso (QE) is a full ab-initio package implementing both ground-state and linear-response methods. Electronic exchange-correlation interactions were evaluated by the local density approximation (LDA) proposed by Perdew-Zunger [3] and/or generalized gradient approximation (GGA) formulated by Perdew-Burke-Ernzerhof (PBE) [4]. Electron−ion interactions were described using all-electron projector-augmented wave (PAW) pseudopotentials [5]. For geometry optimization, the kinetic energy cut-off for wavefunctions and charge density was chosen higher than the values suggested in the specific pseudopotential files. To improve the convergence of states near the Fermi level, the smearing methods were adopted as per the requirement of the systems with a specific value of finite temperature width [6-7]. The position of all atoms residing in systems was fully optimized until the Hellmann–Feynman force on each atom is less than 10^{-3} to 10^{-4} eV/Å (using the Broyden−Fletcher−Goldfarb−Shanno (BFGS) algorithm) [8]. To avoid the interaction between periodic images of isolated clusters, a large cubic cell with sufficient vacuum region was considered in all three directions throughout the calculations. For the oxide-supported nanoclusters/nanoalloys, a vacuum region was set to 15 Å to avoid the interactions in the z-direction between periodic images of the systems. The first Brillouin zone (BZ) sampling was restricted to the gamma (Γ) point for the isolated clusters and 5 ×5 × 1 Monkhorst-Pack [9] **k**-point sampling grid was used for the Brillouin zone sampling of Cu_2O/Pt_4 and Cu_2O/Pt_3X systems. The XANES spectra presented in **Chapter 3** for Ni_{n+1} and Ni_nCu clusters were calculated using the finite difference method (FDM) and Hedin-Lundqvist exchange-correlation potential implemented in the FDM near-edge structure (FDMNES) ab initio package [10-11]. For the treatment of the long-range dispersion forces, the semi-empirical van der Waals corrections D2 and D3 proposed by S. Grimme [12-13] were employed for the accurate prediction of adsorption properties (more information is provided in chapter 2). The *d-band* model introduced by Bhattacharjee and co-workers (modification of Nørskov and Hammer *d-band* model) [14-15] for the spin-polarized DFT calculations have been adopted to determine the electronic descriptors i.e., *d-band* center (ε_d), *d-band* width (W_d) and fractional filling of *d-band* (f_l) (for both spin-up and spin-down states). The examination of Raman spectra of I_h $\mathrm{Pd_mCu_n}$ clusters have been carried out using the GAUSSIAN09 [16] package by employing the hybrid exchange-correlation functional B3LYP/LanL2MB in **Chapter 4**. In **Chapter 5**, the spin-polarized PBE-D3+U (Perdew–Burke–Ernzerhof functional combined with Grimme's D3 and Hubbard (U) corrections) scheme with a value of U_{eff} = 6 eV for the Cu d-states corrections was used [5,17-18]. The 3 × 3 supercell for Cu_2O (111) surface was modeled as periodic slabs consisting of three Cu_2O layers in which three bottom layers were fixed and other layers were allowed to relax in all three directions. The climbing image nudged elastic band (CI-NEB) method proposed by Henkelman et al. [19-20] (implemented in the Quantum ESPRESSO) was adopted to sketch out the minimum energy path (MEP) and transition state for CO oxidation and CO_2 hydrogenation. In this thesis work, all the pictorial representations of structures, HOMO-LUMO, and charge density differences were prepared by the XCrySDen [21] and Vesta [22] visualization packages.

Summary and Key Findings

The development of active, selective, and energy-efficient heterogeneous catalysts is key to a sustainable future since heterogeneous catalysis is at the “core” of the chemicals and energy industries. The design, testing, and implementation of robust and selective heterogeneous catalysts based on insights from fundamental studies such as “ab initio calculations” have a tremendous impact in the modern catalysis and energy sectors. The work presented in this thesis was conducted with two principal objectives in mind: (1) to design and study the poisoning-free carbon monoxide (CO) oxidation over free and oxide supported nanoclusters/nanoalloys to avoid the deactivation of the catalyst and (2) to study monometallic and bimetallic nanoclusters/nanoalloys to reduce CO_2 into sustainable carbon-based fuels. The findings presented in this thesis enlighten the origins and limitations of the concept of “Potential Energy Path” for computational catalyst screening and proposes design strategies for new catalytic materials that can be applied to a range of problems in heterogeneous catalysis. The structural, electronic, magnetic, and catalytic properties of free and oxide supported metal nanoclusters and nanoalloys were explored within the framework of density functional theory (DFT), to obtain an atomic-level understanding of the catalytic mechanism. Novel and practical methodologies have been adopted to design novel heterogeneous catalysts and control their catalytic performance [23-24]. The CO oxidation and reduction of CO_2 were studied using spin-polarized DFT calculations in conjunction with the dispersion corrections (D2 and D3), and climbing-image nudged elastic band (CI-NEB) method, to obtain the accurate reaction pathways, transition state structures, and activation barriers associated with the specific reactions. The electronic reactivity descriptors derived from the improved *d-band* model are also explored and discussed in detail. The main contributions and chapter wise (chapter 3 to chapter 5) general conclusions drawn from studies are described below:

The findings presented in **Chapter 3** were performed using first-principles calculations based on spin-polarized density functional theory. The role of the Cu atom in degrading the poisoning of carbon monoxide (CO) over Ni_nCu clusters is unveiled in this study [25]. The search has been initiated with the examination of structural, magnetic, and electronic properties of Ni_{n+1} and Ni_nCu clusters ($1 \le n \le 12$). X-ray absorption near-edge structure (XANES) spectra of Ni K-edge are computed to extract the information on the oxidation states and coordination environment of metal sites of the clusters. This study is operated with the two forms of dispersion corrections, i.e., D2 and D3, with standard DFT (with LDA and GGA functionals) for the consideration of van der Waals interactions during CO adsorption. The PBE and PBE-D3 approaches are found to be capable of yielding the experimentally observed preferential site for CO adsorption. The advantage of PBE-D3 over PBE-D2 scheme is that the C_6^{ab} and R_{ab} were computed specifically for each a/b atomic pair in D3 correction, which represents a substantial improvement over existing damping functions, as it affords significant reductions in errors associated with noncovalent interaction energies and geometries. The effect of spin-polarization on the reactivity of transition metals (TMs) toward CO adsorption is crucially assessed by the electronic reactivity descriptors such as *d-band* center, *d-band* width, and fractional filling of *d-band* using a spin-polarized *d-band* center model. The effective charge transfer from Cu to Ni atoms makes Ni atoms more efficient of charge and is attributed to the degrading adsorption of CO over Ni_nCu clusters. The $Ni_{12}Cu$ cluster stands out with good CO oxidation activity for the Langmuir-Hinshelwood (L-H) reaction pathway.

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 using first-principles calculations based on dispersion-corrected density functional theory (DFT-D2) is presented in **Chapter 4**. The relative stability of I_h Pd_mCu_n clusters over monometallic I_h Pd_{13} and Cu_{13} clusters by calculating the average binding energy per atom, mixing energy, second-order energy difference, and average bond length was investigated. The I_h Pd_5Cu_8 cluster found the most stable bimetallic cluster with the 2.88 eV, -0.218 eV, and 0.678 eV average binding energy per atom, mixing energy and second-order energy difference, respectively. This work figures out the chemical enhancement, modulation in electronic properties, and Pd–Cu bond length in I_h Pd_mCu_n clusters after systematic doping of Cu-atom. The doping effect of the Cu atom in the Pd cluster was also analyzed through the calculation of Raman spectra of I_h Pd_mCu_n clusters. In the case of I_h Cu_{13} cluster, the contraction of Cu–Cu bond length as compared to its bulk form resulted in a significant blue-shift of characteristic Raman peak (212 cm^{-1}) of I_h Pd_{13} cluster. Finally, the interaction mechanism of the CO_2 gas molecule over Pd–Cu alloy clusters provides an in-depth understanding of the effect of composition on the reactivity of the CO_2 gas molecule [26]. The CO_2 hydrogenation over Pd_5Cu_8 cluster, the HCOOH is mainly produced by the reactions steps of $CO_2^* \rightarrow HCOO^* \rightarrow HCOOH^* \rightarrow HCOOH^{(g)}$. The rate-determining step was recognized as $HCOO^* \rightarrow HCOOH^*$, with an activation barrier of 0.78 eV. The CH_3OH and CH_4 were determined to be formed by the reactions of $CO_2^* \rightarrow COOH^* \rightarrow CO^* \rightarrow HCO^* \rightarrow H_2CO^* \rightarrow H_3CO^* \rightarrow CH_3OH^* \rightarrow CH_3OH^{(g)}$ and $CO_2^* \rightarrow COOH^* \rightarrow CO^* \rightarrow HCO^* \rightarrow H_2CO^* \rightarrow H_3CO^* \rightarrow CH_3^* + O^* \rightarrow CH_3 + H^* \rightarrow CH_4^* \rightarrow CH_4^{(g)}$, respectively. These results offer an efficient strategy for precise tailoring of the catalytic behavior of bimetallic Pd-Cu clusters and promote the development of a highly efficient catalyst for CO_2 hydrogenation [27].

The complete elimination of Pt poisoning during CO oxidation still stands as a big challenge. **Chapter 5** represents a comprehensive theoretical study of Pt_4 and Pt_3X (where X = Co and Au) clusters are deposited on $Cu_2O(111)$ surface and their catalytic activity for CO oxidation has been performed using the spin-polarized density functional theory [28]. Molecular adsorption and reaction path based on the L-H mechanism have been explored. Our results confirm that, at the nanoscale, the catalytic properties of surface-deposited clusters can be majorly impacted by strategic doping and the choice for the supporting surface (strong metal-support interaction) through the inversion of CO adsorption site from Pt to Au and Co for $Pt_3Au/Cu_2O(111)$ and $Pt_3Au/Cu_2O(111)$ systems attributed to the modification in the d-states of the Pt after the substitutional doping of Au and Co atoms. The bimetallic cluster Pt_3Au show enhanced catalytic activity, whereas the monometallic Pt_4 and Pt_3Co clusters get easily poisoned and deactivated in the presence of CO and oxygen. While this resolves the problem of Pt-poisoning, good reaction kinetics are predicted through low barriers for Langmuir-Hinshelwood mechanisms of CO oxidation for $Pt_3Au/Cu_2O(111)$. A novel design strategy of *d-band* center and CO oxidation on supported Pt_4 and Pt_3X clusters is proposed in this study to eliminate Pt-poisoning and excellent CO oxidation activity [29-30].

Future Prospects

Environmental and energy concerns have pushed the necessity to reduce CO_2 emissions caused by the utilization of fossil fuels. For the positive impact on the world, there is an urgent need for the design and real-life implementation of heterogeneous catalysts for CO_2 conversion in value-aided chemicals and renewable fuels with new catalytic processes and more synthetic strategies is a tremendous opportunity. We illustrated in our results that catalyst performance can be affected by metal-support interaction, size, and shape of catalysts and promoters. DFT studies gear up to provide an understanding of the individual steps of the chemical reaction. Various reaction paths and questions can be examined and discussed by theoretical approaches and aid to obtain superior catalysts which would make the entire process more effective and selective towards specific chemicals. To go beyond the knowledge generated from the particular cases, one should focus to establish a universal theory that will envelop and provide an explanation on all of the cases in metal catalysis without the existence of any outliers, regardless of photochemical, electrochemical, or photoelectrochemical catalysts. To make this possible, it requires combine efforts from physicists and chemists on solid-state chemistry, physical chemistry of surface, and chemical reactivity. For this one should combine more “realistic” in situ/-operando characterizations with highly accurate theoretical work.

In general, future research directions are proposed as follows:

1. Develop and formulate novel concepts in catalyst design to increase the adsorption and activation of reactants along with the phase stability and high density of catalytically active sites.
2. Perform microkinetic modeling to provide insights within an extreme peripheral environment like pressure and temperature variations or under defective conditions.
3. To map out catalytic steps at the molecular level and to develop simple paradigms for classes of reactions such as for CO_2 conversion.
4. Focus on theoretical characterization techniques capable of mapping transient chemical changes with improved spatial resolution down to the single site such as STM, XANES, and so on.
5. Design and develop economically affordable, environment-friendly, and scientifically ideal heterogeneous catalysts.

In other words, we should construct a profound molecular mechanistic insight involving dynamic transformations of heterogeneous catalysts and molecular interactions at the gas/solid interface to deal with the complicated chemical reactions when going from molecular catalysis to heterogeneous catalysis.

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