CHAPTER 6

Conclusions and Future Prospects

6.1 Summary

The development of active, selective, and energy-efficient heterogeneous catalysts is key to achieve 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 modern catalysis and energy sectors. The work presented in this thesis were conducted with two principal objectives: (1) to design and study the poisoning-free carbon monoxide (CO) oxidation over free and oxide supported nanoclusters/nanoalloys (NCs/NAs) to avoid the deactivation of the catalyst and (2) to study monometallic and bimetallic NCs/NAs to reduce CO_2 into sustainable carbon-based fuels. The findings presented in this thesis enlighten the origin and limitations of the concept of "Minimum 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. 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 work 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. The search has been initiated with the examination 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 were computed to extract the information on the oxidation states and coordination environment of metal sites of the clusters. This study was operated with two forms of dispersion corrections, i.e., D2 and D3, with standard DFT (with LDA and GGA functionals) in order to include 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 was investigated by calculating the average

binding energy per atom, mixing energy, second-order energy difference, and average bond length. The I_h Pd_5Cu_8 cluster stand out as 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 provide an in-depth understanding of the effect of composition on the reactivity of the CO_2 gas molecule. The CO_2 hydrogenation over Pd_5Cu_8 cluster, the HCOOH is mainly produced by the reaction step: $CO_2^* \rightarrow HCOO^* \rightarrow HCOOH^* \rightarrow HCOOH^{(g)}$. 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 reaction: $CO_2^* \rightarrow COOH^* \rightarrow CO^* \rightarrow HCO^* \rightarrow H_2CO^* \rightarrow H_3CO^* \rightarrow CH_3OH^* \rightarrow CH_3OH^{(g)}$ 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.

The complete elimination of Pt poisoning during CO oxidation still stands as a big challenge. **Chapter 5** presents a comprehensive theoretical study of Pt_4 and Pt_3X (where X = Co and Au) clusters deposited on $Cu_2O(111)$ surface where their catalytic activity for CO oxidation has been performed using the spin-polarized density functional theory. 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). 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.

6.2 Future Scope

Environmental and energy concerns have pushed the necessity to reduce CO_2 emissions caused by the utilization of fossil fuels. For having positive impact on the world, there is an urgent need of 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. 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 to 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 combined 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:

- 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.
- Perform microkinetic modeling to provide insights within an extreme peripheral environment like pressure and temperature variations or under defective conditions.
- To map out catalytic steps at the molecular level and develop simple paradigms for classes of reactions such as for CO_2 conversion.
- 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.
- 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.