

6 | Conclusions and Future Prospects

In light of the motivation and objectives that were introduced at the beginning of this thesis in chapter 1, this chapter summarizes the findings and conversations from the preceding chapters. We briefly highlight the most important and remarkable aspects of this thesis, emphasizing and restating the unusual/extraordinary outcomes of our first-principles computations. Together with my aspirations to continue researching and exploring catalytic systems, we also briefly address future prospects and scope for further explorations that may branch out from the results provided and discussed in the thesis.

6.1 Conclusion

Since heterogeneous catalysis is at the “heart” of the chemicals and energy industries, developing active, selective, and energy-efficient heterogeneous catalysts is essential to achieving a sustainable future. The development, examination, and use of resilient and specific heterogeneous catalysts, grounded in fundamental research like “*first-principles calculations*” have a significant influence on contemporary catalysis and energy domains. The work discussed in the thesis was conducted with the main objective of designing an efficient and practicable single-atom catalyst (SAC) for some key chemical reaction like CO oxidation reaction, hydrogen evolution reaction (HER) and water-gas shift (WGS) reaction, as these reactions have great energy and environmental impact on society. The findings presented in the thesis provides a through insights of electro-catalytic properties of transition-metals (TMs) based SACs towards above mentioned reactions. The geometric, electronic and catalytic properties of TM-SACs supported over various substrates are investigated by employing state-of-art density functional theory (DFT) calculations in conjugation with spin-polarization and van der Waals’ dispersion corrections (D3). In the work presented here, we used precise computational concept of minimum energy path (MEP) by employing climbing-image nudged elastic band (CI-NEB) method to investigate and analyze an accurate reaction pathway along with the energy profiles, transition/intermediate state structures and activation energy for specific mechanism of particular reaction and the concept of electronic reactivity descriptors (ERDs) by employing improved d-band model in order to gain meticulous understandings of the role of d-states in enhancing catalytic properties of TM-SACs for screening and designing an efficiently functional SACs. These are discussed in detail in respective sections/chapters. The chapter wise (for chapter 3 to chapter 5) key outcomes and conclusions are discussed below:

In chapter 3, we discussed our investigation on catalytic activity of cobalt (Co) single-atom supported over $2 \times 2 \times 1$ supercell of Ψ -Graphene (PG) (unit cell containing 12 carbon atoms) substrate towards poisoning-free carbon monoxide (CO) oxidation reaction. Firstly, we computed binding energy (E_b) of Co-atom over all 14 possible inequivalent anchoring sites of PG to identify the most stable site (H4: with E_b value of 3.37 eV) and it is named as Co@PG for further calculations and analysis. The strong overlapping of Co-4d and C-2p states (near the Fermi level) observed in projected density of states (PDOS) corroborates the

strong interaction of Co-atom with the substrate. Further, the ‘cluster formation tendency’ of Co-atoms over PG is analysed by examining the diffusion of Co-atom from most stable site to neighbouring most stable site and corresponding diffusion barrier is found to be 3.18 eV. Furthermore, the calculated diffusion rate using theory of absolute velocities, is 10^{-41} s^{-1} at 300K and 10^{-9} s^{-1} at 750K. These all combinedly confirm the slow kinetic mobility and stoned-stability of Co@PG even at higher temperatures, also neglecting the cluster formation possibilities. Moreover, calculated relative energy of cluster formation which is the difference between energy of Codimer and two Co-atoms separately bound at most stable sites, shows that the Co-atoms prefers to bind individually rather than forming a cluster, thereby confirming no cluster formation possibility of Co@PG. We further performed adsorption/co-adsorption of reactant species like CO, O₂, CO₂, O, CO+O₂, CO + CO etc., over Co@PG and computed adsorption energy (E_{ads}) and analysed it using PDOS and electronic reactivity descriptors (ERDs) to gain detailed insight into adsorption mechanistic of reactants. It was found that $E_{ads}(\text{CO}) < E_{ads}(\text{O}_2)$, shows that Co@PG have greater affinity towards O₂ than CO, which suggest that O₂ molecule will prefer to bind with Co@PG rapidly than CO, shows that Co@PG will not be exposed directly to CO, thereby reducing CO poisoning and degrading effect of catalyst. Further, it was found that co-adsorption of reactants (CO+CO, CO+O₂) is preferred by Co@PG, shows that Co@PG is capable of handling both reactants simultaneously. We used this analysis for the screening of reaction mechanism as discussed in chapter 3 and, we selected Langmuir-Hinshelwood (LH) and Eley-Rideal (ER) mechanisms of CO oxidation reaction and complete reaction profiles are discussed in detail. The examination of reaction profiles suggests that the Co@PG prefers ER mechanism over LH mechanism with the activation energy (E_a) of 0.19 eV and 0.27 eV for the 1st and 2nd half of CO oxidation reaction, respectively via ER mechanism. Thus, Co@PG could be a potent, non-noble, CO poisoning free candidate for efficient CO oxidation reaction.

In chapter 4, we discussed our work on examining catalytic properties of nickel (Ni) single-atoms supported over various kinds of two-dimensional (2D) substrate like carbon-based, nitrides and oxides (Ni@2D) towards electrocatalytic HER. We considered $4 \times 4 \times 1$ supercell of Graphene and AlC (carbon-based), h-BN and AlN (nitrides) and BeO and MgO (oxides) as a support for Ni-atom. We considered various anchoring sites like top, bridge, hollow and vacancy sites to anchor the Ni-atom and computed E_b over all 34 anchoring sites. Having large number of

systems, we screened most stable sites using criteria $E_b < -3.00$ eV for H-adsorption and further analysis. Out of 34, 17 configurations of Ni@2D were screened out and H-adsorption was carried out computing E_{ads} of H-atom over these configurations. Further, we calculated Gibbs free energy change of H-adsorption (ΔG_H) as a HER activity descriptor in our case, ΔG_H value ranges from -1.57 eV to 0.49 eV. We also plotted volcano like structure between exchange current density (i_o) and ΔG_H , and as per the classical volcano theory, the top of volcano is occupied by the systems with excellent HER activity. In our case it is Ni@AlN and Ni@h-BN occupies the top, with optimum ΔG_H value of -0.06 and -0.09 eV, respectively. Then we calculated the computed theoretical overpotential (η) which is absolute value of ΔG_H is found to be as low as 60 mV and 90 mV for Ni@AlN and Ni@h-BN, respectively which is quite low. Further, applying Sabatier principle of optimum interaction ($|\Delta G_H| \approx 0$) for efficient HER activity, we applied a screener that only systems falling in $|\Delta G_H| \leq 0.5$ eV, is considered for investigation of complete HER. Out of 17, 10 configurations were falling in the range of $|\Delta G_H| \leq 0.5$ eV, and we performed complete reaction calculation of HER via two mechanisms i.e., Volmer-Heyrovsky (VH) and Volmer-Tafel (VT) and analyses the reaction profile as discussed in chapter 4. The investigation of complete reaction profiles shows that overall, the VT mechanism is more preferable than the VH mechanism. Specifically, the Ni@AlN and Ni@h-BN are found to have lowest E_a values i.e., 0.12 eV and 0.21 eV, 0.28 eV and 0.26 eV via VT and VH mechanisms, respectively. Thus, Ni@AlN and Ni@h-BN are the two best possible efficient and low-cost non-noble candidates to replace Pt-based catalyst for proficient HER.

In chapter 5, we discussed our findings on investigation of catalytic activity of various TMs (M=Ni, Pd, Pt, Cu, Ag, Au) embedded into 2D AlN support towards WGS reaction which is the reaction between CO and H₂O to produce CO₂ and H₂. Here, we considered various sites like Al-top (Al-T), N-top (N-T), bridge (B), hollow (H), Al-defect (Al-d) and N-defect (N-d) sites of 4 x 4 x 1 supercell of AlN to anchor the M-atoms (M@AlN). The calculated E_b shows that M-atoms prefers to bind at Al-d sites with $E_b < -4.00$ eV for all M-atoms. Further, we computed diffusion of M-atoms from Al-d site to neighbouring Al-d site suggest high-stability of M@AlN with very high diffusion barrier for all systems. Then, we performed adsorption/co-adsorption of reactants like, CO, OH, H₂O, CO+OH and CO+H₂O and analysed the E_{ads} values. In order to gain exact reaction insights, we considered a traditional formate mechanism and a relatively novel OH-assistive

mechanism, by analysing the E_{ads} values of reactants, the complete reaction mechanisms are detailed in chapter 5. Overall, the OH-assistive mechanism is found to be more preferable over M@AlN than the formate mechanism. In particular, the Au@AlN and Cu@AlN shows excellent catalytic activity with lowest E_a values of 0.14 eV and 0.21 eV, respectively. To validate the CI-NEB results, we used the concept of optimum interaction of reactants, where the linear relationship between E_a and $E_{ads}(\text{CO}+\text{OH})$ supports the findings. However, the more accurate parameter to judge the reactivity of TMs is the d-band centre (ε_d), where the accurate linear plot between E_a and ε_d authenticate the CI-NEB results. Moreover, according to energetic span model, in order to have a sustainable catalytic cycle, the reaction energy (E_R) should be higher than that of activation energy so that the energy released in the first cycle can subsequently be used in the next cycle and the process continues. Thus, we plotted E_a with E_R and the plot shows that for Au@AlN and Cu@AlN, the E_R is significantly greater than E_a , shows that the WGS reaction is feasible over Au@AlN and Cu@AlN. Overall, Au@AlN and Cu@AlN can serve as practically applicable industrial WGS catalyst.

6.2 Future Prospects

Considering the rapid growth and constructive societal impact of SACs as a field in last decade or so, the future prospects and scope are very vast and promising. In the current scenario, where the energy demand and consumption are sky rocketing as with the increment in population and the detrimental environmental impact the current energy sources are having, the efficient chemical conversion of the environmentally noxious substances and generation of a new-age, ecofriendly energy source in abundance will only hold the key to have a sustainable future. The one thing that will act as an ‘Brahmastra’ here is an efficient catalyst for this conversion and generation and SACs is one such. Although, SACs is exhaustively explored subject recently, but there are yet some challenges, limitations and detailing which need to be examined thoroughly like enhanced synthesis techniques for precise and uniform dispersion of atoms, stability and durability improvements, exploring/creating new supporting materials, expanding the applicability of SACs over various reactions, understanding structure-activity relationship for tuning the SACs as our desires, advanced computational methods for ‘real-time reaction’ investigations, develop a multifunctional SACs etc... To make this possible, the

combined knowledge of physics, chemistry, material science, physical chemistry of surface, reaction kinetics, chemical reactivity and computational and experimental handling will be required.

In general, future research direction I propose is as follows:

- To work on developing an activity predictors/descriptors to assist the screening of materials.
 - To perform microkinetic modelling to gain insights of environmental variable like temperature, pressure, understanding the effect of surface coverage of reactants and products and reaction rates to analyse the exact reaction kinetics.
 - To understand the atomic architectures of SACs, to develop an active, stable, practicable and scientifically ideal SACs.
 - To work on developing the way/path of designing a rational catalyst.
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