1 Single-Atom Catalyst: An Introduction

J. J. Berzelius first used the term "catalysis" in 1836[1]. Broadly, a catalyst accelerates the rate of a reaction by lowering the activation energy of the reaction, without being consumed itself or undergoing any permanent chemical change in the process, and this whole process is called catalysis. The enormously increasing scale of basic human needs globally, the availability, recyclability and sustainability of energy resources and its carbon footprint to the environment, altogether put forward a complex endeavour in front of the scientific community. In this regard, catalysed chemical conversion plays has huge role to play to meet the human demands in all sectors and thus, catalysis becomes the corner-stone of modern living society as it is integral in addressing global challenges and advancing scientific knowledge. Economically, catalysis contributes more than 35% in the global gross domestic product (GDP) and this figure will get more significant considering the impact it is going to have in upcoming time. Here, we'll discuss about the types of catalysis, historical background of heterogeneous catalysis, fundamental principles governing heterogeneous catalysis, our motivation and objectives of the thesis and thesis organization.

1.1 Types of Catalysis

Broadly, the catalysis is divided into three major categories depending upon the phase of the reactants and catalyst as shown in Fig 1.1[2].

- Homogeneous catalysis: In this form of catalysis, the catalyst and the reactants are in the same phase (state), generally liquid or gaseous. Homogeneous catalysis contributes about 15% of all catalytic processes.
- **Heterogeneous catalysis:** In such catalytic process, the catalyst (usually solids) and the reactants (usually liquid or gas) are in different phase with respect to each other. Heterogeneous catalysis has great share, about 85% among all forms of catalysis, owing to the easiness in recovery of catalyst and robustness. Having such a significant impact, this branch of catalysis earned heightened attention by the scientific community. In our study too, we will be talking and studying about heterogeneous catalysis.
- Bio/enzymatic catalysis: Here, the catalysts are commonly known as enzymes that accelerates the biochemical reactions in living bodies. This kind of catalysis contribute about 5% among all catalytic processes.

1.2 Heterogeneous Catalysis

1.2.1 An Overview

Catalysis as a whole has a long history, defined by important discoveries, theoretical advances, and practical applications. Catalytic phenomena were first seen in ancient times, when natural catalysts such as enzymes in biological systems and specific minerals were unknowingly employed to speed chemical reactions. However, significant empirical observations about catalytic processes occurred during the 17^{th} and early 18^{th} centuries. But, the scientific study of heterogeneous catalysis began in the late 18^{th} and 19^{th} centuries as shown in Fig.1.1, laying the framework for modern catalytic science. After early exploration of catalysis, in late 1800, the industrialisation of the catalyst took place significantly in ammonia synthesis, oil reforming, three-way auto convertors etc... But it was more of a

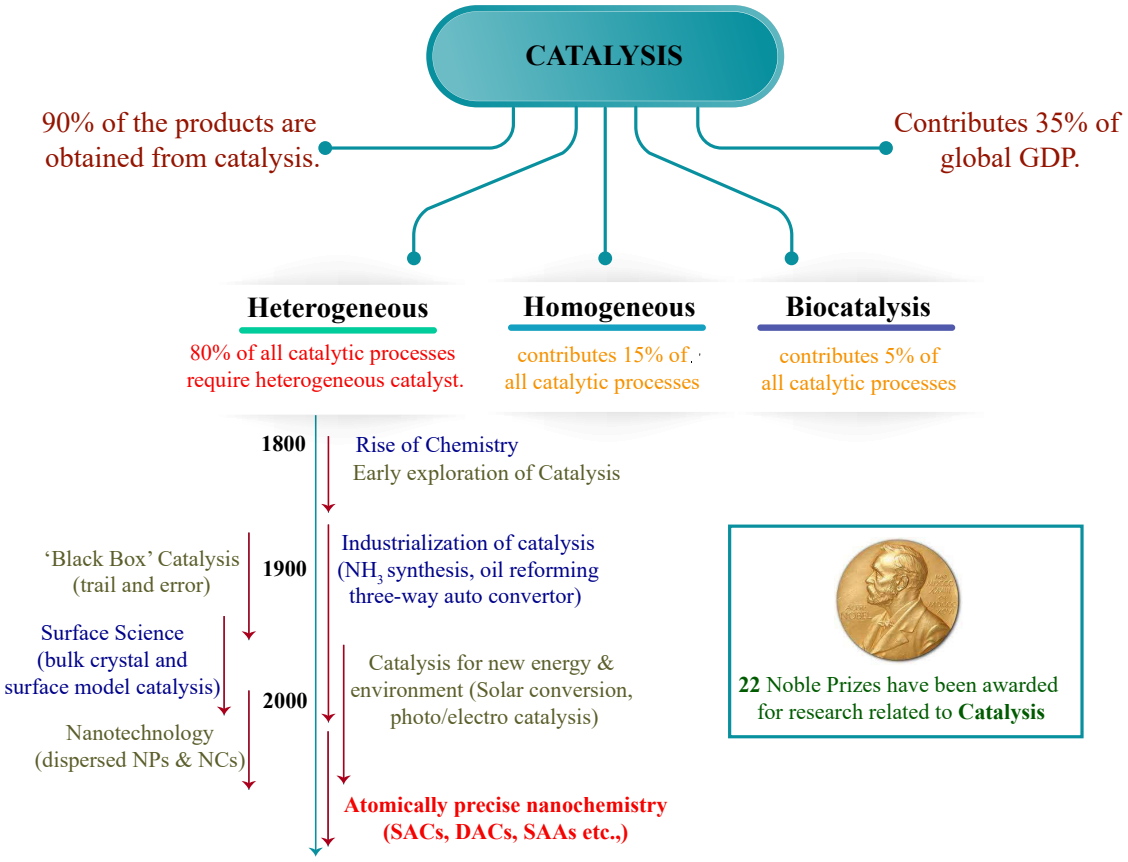

FIGURE 1.1: A schematic representation about catalysis, its types and evolution of heterogeneous catalysis[2, 3].

'black box catalysis', i.e., it is like a trial-and-error method wherein, all the components taking part in the reaction were known but the how they interact at an atomic scale was not exactly known. For example, Johann Wolfgang Döbereiner observed in the early 19^{th} century that platinum black accelerated the breakdown of hydrogen peroxide[4]. Then the rise of surface science field unfolded the bulk and surface model of catalysis in mid-1900, which opened up new areas of studies like active sites identification, adsorption and desorption studies, surface reactivity and kinetics, catalyst-substrate interaction, surface modification and engineering, catalyst deactivation mechanisms etc. Soon after, catalysis find its usefulness in new energy generation and environmental remediation applications via solar conversion, photo/electro catalytic processes etc[5]. Further, the emergence of nanotechnology brought the concept of nanoparticles (NPs) and nanoclusters (NCs) based catalysis, wherein free and supported NPs/NCs are used as a catalyst[6, 7]. Subsequent advancements in synthesis technologies, characterization techniques and computational models and methods lead us to notion of an atomically precise nano-chemistry, wherein the minusculely spread atoms behaves as an active site for

a catalytic reaction, such designs of catalysis are known as single-atom catalysts (SACs), dual-atom catalysts (DACs), single-atom alloys (SAAs) etc...[3, 8].

1.2.2 Physical Phenomenon Occurring on the Surface of Catalyst

In heterogeneous catalysis, several physical phenomena occur during the catalytic process like;

(i) Adsorption:

As the reaction process begins, the reactant(s) (usually gas molecules) interact with the catalytic site and depending upon the affinity of catalyst towards the reactant(s), the strength of interaction varies. In general, adsorption is classified as either physisorption, in which the interaction is very weak, predominantly involving van der Waals forces and usually does not occur at any specific site on the surface of catalyst or chemisorption, in which there is a strong interaction between reactant(s) and surface atom of the catalyst involving formation of strong chemical bonds and this kind of adsorption is site specific.

(ii) Diffusion:

The movement of the adsorbed species (atoms, molecules etc.) over the surface of catalyst, known as diffusion, plays critical role in catalytic process. The efficiency of diffusion ascertain that the reactant(s) reaches the active site in timely manner, sustaining the high reaction rates and also it enhances the product desorption and prevent reaction inhabitation by product accumulation. There are various types of diffusion like surface diffusion, bulk diffusion and there are different laws and concepts to study and analyse the diffusion mechanism. In general, the diffusion properties depend upon the porosity and morphology of the material, pore size and pore distribution, reactant(s) size and reaction conditions.

(iii) Dissociation and Recombination:

The dissociation and recombination are two crucial processes in a heterogeneous catalytic reaction. Firstly, dissociation means when a molecule breaks into two or more smaller species (atoms, ions, molecules) on the surface of catalyst. In the process, the molecule adsorbs on the surface of catalyst and then the breaking of chemical bonds within the molecule due to interaction with catalyst takes place. The key role of dissociation is the activation of reactant molecules(s) to make it more reactive and undergo further transformations. Recombination, on

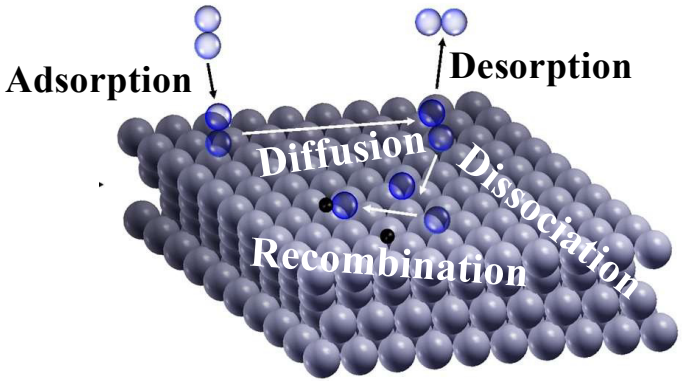

FIGURE 1.2: A schematic representation about physical phenomena occuring over the surface of heterogeneous catalyst.

the other hand, is the process in which the dissociated molecules migrate over the catalyst surface and combine with the suitable partners to make new bond(s) and form new molecule(s). Recombination is the key process in product formation. The dissociation and recombination process depends greatly on catalyst surface morphology, affinity of catalyst towards molecules, surface coverage of molecules, diffusion and reaction conditions. Dissociation and recombination are the key process of breaking-and-making of bonds in any catalytic process.

(iv) Desorption:

It is the process of detachment of adsorbed species from the catalyst surface to return into gas phase, after reacting and forming product. The efficient desorption mechanism ensures quick product release and cycle continuation. It also prevents catalytic poisoning that degrade the catalytic activity over the time. The desorption process primarily depends upon the catalyst affinity towards reactant(s) and product(s), surface coverage of reactants and reaction conditions[9–11].

A schematic representation of all the processes is presented in Fig1.2.

1.2.3 Fundamental Principles Governing Heterogeneous Catalysis

In heterogeneous catalysis, as discussed above, the adsorption, diffusion, dissociation, recombination, and desorption are the key processes occurring over the surface of the catalyst. Qualitatively, these processes affect and governs the catalytic performance of the catalyst to a large extent. But these are not an accurate quantitative parameter through which one can reliably claim the degree of performance of a catalyst[12–14]. Moreover, obtaining first-principles calculations data

for large number of catalysts and identifying a superior catalyst by performing reaction kinetics calculation is gruelling and computationally infeasible task. In computational heterogeneous catalysis, the development of predictors/descriptors-based models/methods to predict the activity and reactivity of a catalyst rather than performing first-principles calculations of high computational cost, is one of the central research topics in recent years[15–17]. There has been surge in research related to the predictor-based catalysis and some of the models have appreciable accuracy in terms of predicting catalyst performance or even drawing a conclusive trend out of it, which not only save time and efforts of researchers but also assist them in designing a potential catalyst. Here, we discuss some theoretical/-computational models that are often used as a predictor/descriptor for large-scale catalyst screening like[18, 19];

(i) Binding Energy Linear Scaling Relations:

Binding energy linear scaling relations are empirical observations that describe how the adsorption energies of different species on a catalyst surface are linearly related to each other. These relations provide significant insights and are of great help for understanding and predicting catalytic behaviour, facilitating the design of new catalysts, and improving the efficiency of computational screening processes. Early research by Abild-Pedersen et al. showed that the atom via which a small molecular species is adsorbed on a surface largely controls the binding characteristics of that species[20]. The computed binding energies of CH_x^*, NH_x^*, OH_x^*, and SH_x^*, for instance, have linear correlations with those of C^*, N^*, O^*, and S^*, correspondingly. Remarkably, the adsorbate's valence electron count affects the slopes of the linear scaling relations. The valencies of CH^*, CH_2^*, and CH_3^* are 3, 2, and 1, respectively, whereas atomic C^* has four valence electrons. As a result, the slopes of the scaling relations of the binding energies of CH^*, CH_2^*, and CH_3^* vs those of atomic C^* are around 0.75 (3/4),0.50 (2/4), and 0.25 (1/4), respectively. Because scaling relations may anticipate the binding energies of a group of surface intermediates given the binding energy of one or more structurally similar intermediates, they are particularly important for simplifying more complex chemical systems. This makes it possible to quickly build the thermochemical profiles of reaction mechanisms. For instance, Studt et al. used only one binding energy that of CH^* to estimate the thermodynamics for the selective hydrogenation of acetylene to ethylene on different transition metal alloy surfaces by applying C_2 scaling relations[21]. This enabled them to rapidly select catalyst with favourable reaction thermochemistry. By examining the conversion of synthesis gas to higher alcohols,

which has a complicated reaction mechanism including many $C_xH_yO_z^*$ reaction intermediates, Medford and colleagues provide another illuminating example of the application of scaling relations. In particular, they were able to reduce the number of factors required to characterise the total reaction thermo-chemistry to two by scaling the binding energies of the $C_xH_yO_z^*$ species with the binding energies of simply C^*, O^*, or a linear mixture of the two[22, 23].

While scaling relations have been discovered for many catalytic systems and are valuable for lowering system complexity, it is important to note that these relationships are heavily influenced by the binding geometries of the adsorbates. In a previous study by Abild-Pedersen et al., the offsets (but not slopes) of the scaling relations for the binding energies of CH_3^* against that of C^* differed depending on whether they were constructed using (1) binding energies obtained on optimal binding sites or (2) binding energies obtained on top sites only. This demonstrates that scaling relationships are site-specific[20].

(ii) Bronsted-Evans-Polanyi (BEP) Relations:

In addition to scaling relationships between binding energies, there are linear connections between the thermochemistry of elementary chemical steps and their associated transition state energies. These are the BEP relations, that connect a reaction's activation energies with reaction energies. Early examples of BEP relations were found for noncatalytic or homogeneous catalytic systems. The initial hypothesis by Brønsted was developed for acid- and base-catalyzed reactions[24], while Evans and Polanyi discovered comparable correlations for radical reactions[25]. However, computational approaches have also uncovered numerous examples of BEP interactions in heterogeneous catalysis. Nørskov et al. found a BEP connection for dissociation processes of N_2, NO, CO, and O_2 on transition metal surfaces[26]. Other examples are the BEP relations constructed for methanol decomposition[27], CO_2 reduction reaction[28], glycerol decomposition[29], and the water-gas shift reaction[30, 31].

Complex reaction systems can be made much simpler by combining scaling and BEP relations, which effectively reduces the number of parameters needed to fully describe the thermochemistry and reaction kinetics of these systems to just a few. As will be covered in more detail in the following section, these relations can be used to create reactivity volcano plots, which facilitate effective early catalyst design and screening. However, readers should be aware of the shortcomings of scaling and BEP relations. These correlation techniques naturally introduce fitting errors, which when combined with the inherent error of DFT binding energies,

may rapidly propagate throughout the multiscale modelling pipeline and lead to significant errors in the reaction rates and selectivity that are predicted[32]. Hence, even though scaling and BEP relations are effective tools for preliminary catalyst design and screening, comprehensive DFT-based reaction mechanism analyses on particular catalyst surface models might still be required to confirm the suitability of suggested catalysts before starting any in-depth experimental verification.

(iii) Sabatier Principle and Volcano Plots:

The 1912 Nobel Prize winner in Chemistry, Paul Sabatier, postulated that the

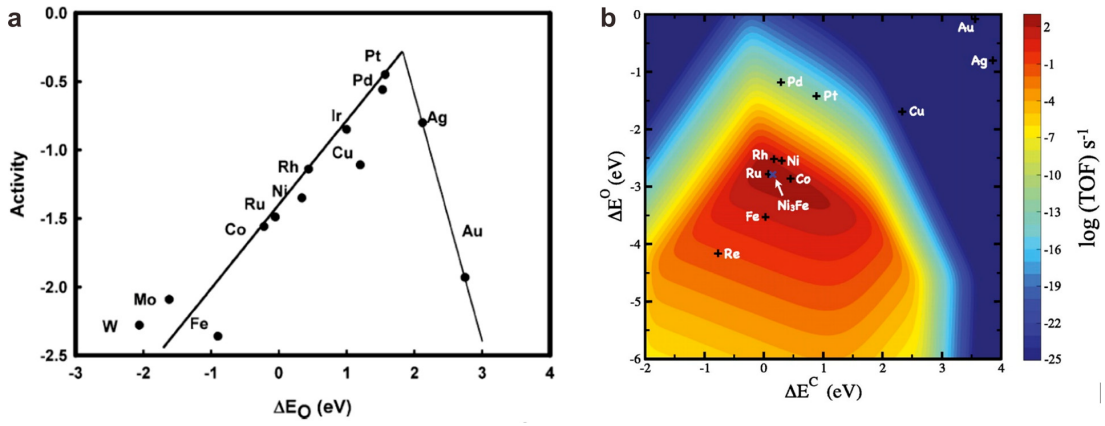

FIGURE 1.3: (a) Volcano plot of the predicted oxygen reduction reaction (ORR) activity of close-packed transition metal surfaces as a function of thecalculated binding energy of O*[33]. (b) Two-dimensional volcano plot of the predicted CO methanation turnover frequencies (TOF) as a function of thecalculated binding energies of O* and C* on the (211) stepped surfaces of transition metals[34].

perfect catalyst binds reaction intermediates at just the optimal strength—neither too strong nor too weak[35]. We term this the Sabatier principle. Volcano plots, which relate a catalyst's activity to the binding energies of important intermediates, provide a quantitative illustration of this idea, made possible by recent developments in computational catalysis. In heterogeneous catalysis, the work of Nørskov et al. on the oxygen reduction reaction (ORR) provides a famous example of volcano plots[33]. They discovered that a volcano with a peak at intermediate O* binding energies forms when the estimated ORR activity of different transition metal surfaces is plotted against how strongly they bind atomic O* (Fig4.3). Nonetheless, the use of volcano plots in catalyst design and catalytic activity rationalization has proven to be quite effective[36, 37]. However, when it comes to using volcano plots to find new catalysts, there are a few seldom addressed presumptions. First, across the descriptor space, it is typically assumed that the mechanism remains unchanged. Still, novel paths might emerge, particularly in

areas remote from the studied descriptor space. Additionally, when searching for novel catalyst candidates, descriptor values are usually calculated near the edge of poor adsorbate coverage. This is true for weakly binding surfaces; but stronger binding surfaces might be contaminated by contaminants[38], have a high concentration of adsorbates, or even experience state transitions like oxidation and carburization[39, 40]. Put another way, the active site environment might vary significantly even under similar reaction conditions, depending on the type of catalyst surface. Volcano plot analysis must therefore be done carefully in order to account for any trustworthy predictions.

(iv) d-band Model:

While scaling relations have been applied to computational heterogeneous catalysis with great success, their precision still needs to be further improved. This has led to an increased quest for more fundamental quantities, especially for transition metal surfaces, that may be used to more accurately characterize the reactivity of catalysts. Rodriguez and Goodman's early experimental work suggested that the electronic structure of the surface atoms might be used as a potential descriptor[41]. Theorists looked for surface reactivity descriptors that were simpler to calculate than core-level modifications as electronic structure computations became more prevalent. The d-band model, first developed by Hammer and Nørskov in 1995, is currently one of the most important descriptors of electronic structural reactivity[42, 43]. They developed the concept of d-band centre (ε_d), defined as the average energy of d-states, is well known for being a very precise and easy to calculate reactivity descriptor for transition metals and their alloys used in heterogeneous catalysis. This descriptor's effectiveness has been supported by both theory and experiments[44]. In addition to ε_d, there are other reactivity descriptors like d-band width (W_d) and fractional filling of d-band (f_l). are proved to be an accurate electronic reactivity descriptor (ERDs) for TM-based catalysts[45, 46] and thus, we have used these ERDs extensively in our study and the complete formalism of these ERDs is separately discussed in chapter 2.

1.3 Single-Atom Catalyst

Heterogeneous catalysis as a branch has always evolved and is evolving as faster as ever, owing to its colossal impact on the society[47, 48]. Over the course of years,

researches oriented to enhancement in catalytic behavior of a heterogeneous catalyst has acquired heightened consideration[49]. In the context of this, downsizing the catalyst, as from bulk to 2D to 1D and NCs/NPs, is the well-trodden approach by the research community, due to the fact that reducing size of the particle results in better catalytic properties, predominantly due to increased surface-to-volume ratio[50, 51]. Although, the NCs/NPs shows excellent performance as a catalyst but the approach of downsizing along with the technological advancements in synthesis and characterization techniques and accurate and fast computational models enabled us to further mitigate the size of the particle, this time to an a sub-nanometric scale, wherein the isolated spread atoms stabilized on some kind of substrates act as a catalyst[52, 53], scientifically known as 'single-atom catalyst', the term first coined by Qiao et al., where they investigated Pt-SACs over FeOx for CO oxidation reaction[54]. Since then, there is an escalated researches and continuous progress in the field of SACs as the timeline of progress in SACs shows in Fig.1.4[55]. The researches related to SACs has attracted the heaps of heed as it offers first-rate advantages like;

(i) Maximize atomic utilization efficiency: In SACs each atom acts as an active site, offering maximum utilization of precious metals, thereby reducing the cost of the catalyst.

(ii) Enhanced catalytic activity: The isolated metal atoms possess unique electronic structure, due to the emergence of quantum confinement effect at atomic-scale, consequently enhancing catalytic activity and reactivity.

(iii) Improved selectivity: The unique active sites and tailored electronic structure of SACs due to the variation in the interaction of SACs with the supports allow us to oversee the selectivity of SACs for specific reaction.

(iv) Stability and Durability: Often, the supports having high porosity offers a strong binding and favorable coordination environment to the SACs, thus enhancing its stability and also improve the durability of the SACs.

(v) Environmental benefits: The lower metal utilization to form SACs reduce the usage of precious metals, lowering the environmental impact associated with the metal mining and processing and high efficiency of SACs leads to lesser byproducts and wastes during catalytic cycle.

Overall, SACs exhibit combined advantage of heterogeneous catalysis like robustness, easy separation, reusability, operational simplicity and homogeneous catalysis like high activity, maximized usage efficiency, broad applicability etc.,

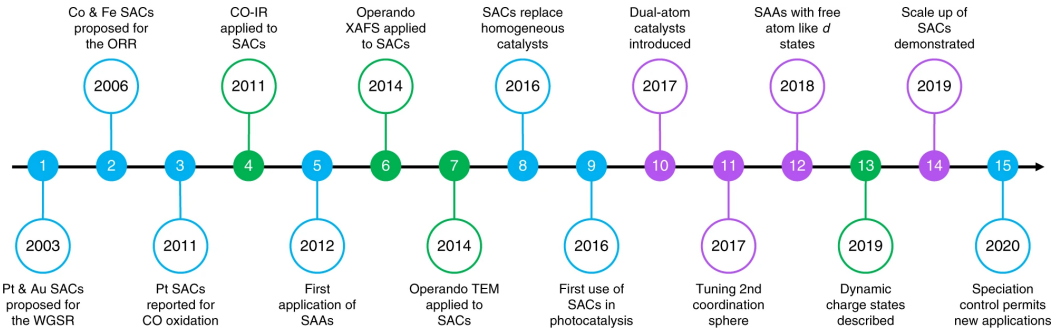

FIGURE 1.4: Progress in single-atom catalysis[55].

thus, SACs present unparalleled efficiency, selectivity, stability and longevity[56–58]. Their unique properties stem from the atomic-level dispersion of metal atoms, which maximizes the utilization of active sites and allows for precise control over catalytic performance[59, 60]. Although, the SACs exhibit eye-popping properties, it do come with certain limitations and challenges as of now, which hinders its widespread application like; (i) the complexity in SACs structures makes the synthesis and characterization of SACs a process that requires advanced techniques which comes with delicate machineries, that poses the challenge in obtaining precise control over synthesis, time-consuming and high production cost, that makes SACs difficult in scaling up for commercial use. (ii) The stability of SACs is one of the key issues to address as it varies significantly with the reaction conditions, type of support and its compatibility. Apart from this, there are other lighter issues like reaction specificity, reproducibility and environmental concerns also need to be addressed to design an all-round SACs[61–63].

1.3.1 Transition-Metal SACs

In the periodic table, groups 3-12 elements are regarded as transition metals (TMs), whose atoms have partially filled or incomplete d-sub shells. This can be further sub-divided into early (groups 3-7) and late (groups 8-12) TMs. Traditionally, TMs are known to exhibit exceptional catalytic properties owing to their partially filled d-orbitals and possessing variable oxidation states[64, 65]. Thus, TMs-based catalysts are always at the center of sphere for research community working in catalysis. As discussed in the above section, the understanding of size dependent catalytic activity brought the approach of downsizing the particle size and lead to designing the catalysts at an atomic scale, popularly known as SACs, has provided an additional dimension to design an efficient catalyst[66]. In

this context, the combined advantages of TMs like variable oxidation states and partially filled d-orbitals along with the advantages of SACs like introduction of quantum confinement effect at an atomistic scale has led to surge in the exploration of TMs-based SACs for various environmental and industrial chemical reactions like CO oxidation reaction[67], HER[68], OER[69], ORR[70], WGS reaction[71], CO2 reduction reaction[72], ammonia synthesis[73] etc. The detailed discussion over TMs SACs for CO oxidation reaction, HER and WGS reaction along with our investigations is presented in chapter 3-5, respectively.

1.3.2 Role of Support

As we discussed earlier, SAC is the atomically dispersed metal atoms over a surface that acts as an active site for a particular reaction. So, the surface/substrate is a vital cog in designing a practically operative catalyst[74]. As the substrate does not only stabilize and anchor the dispersed metal atoms but also alters its electronic properties consequently modifying its electro-catalytic properties[75, 76]. As in case of SACs, the adsorbate interacts with only one atom, examining the wave function overlapping between occupied/unoccupied orbitals of adsorbate and atomic orbitals near to fermi level of SACs, also known as frontier orbitals (FOs), becomes extremely crucial in order to understand origin of improved catalytic performance of SACs[77, 78]. The high surface free energy of the dispersed metal atoms in SACs is the reason that two-dimensional (2D) materials with high surface area to volume ratio and having ample number of porous sites are traditionally used as a substrate to anchor and stabilize the metal atoms and also to avoid the aggregation of atoms during synthesis of catalyst or during the catalytic reaction taking place.

Generally, carbon-based, oxides, nitrides, chalcogenides 2D surfaces are extensively investigated as a substrate to host the single-atoms for various catalytic reactions. The carbon-based materials like graphene, its allotropes, carbon nanotubes etc., offer exceptional attributes as a support like excellent mechanical, thermal and chemical stability, high porosity and tunable morphology, decent electronic and thermal conductivity, easiness in synthesizing, handling and operating during chemical reaction, its high abundancy and eco-friendly nature, all this makes carbon-based materials a first-choice as a support for designing SACs[79–81]. The oxides materials present some advantages like high specific surface area, strong interaction and large charge transfer with the dispersed metal atoms, the

oxygen-atom(s) of the oxide substrate greatly support the redox reactions, high chemical and thermal stability along with superior electronic conductivity and chemical inertness also support the applicability of oxide materials as a substrate for SACs[82–84]. The nitrides materials along with some of the above advantages, offers corrosion resistance and assist chemical reactions like ammonia synthesis with the nitrogen atoms of the substrate, also the ease of defect engineering helps in tailoring active sites to tune the catalytic properties of SACs[85, 86].
Overall, the substrate plays huge role in designing an efficient SACs and depending upon our requirements for a particular chemical reaction, we can tune the properties of SACs by altering the substrates. Thus, it is of fundamental necessity to incorporate the role of support in SACs.

1.4 Reactions under Investigation

1.4.1 CO Oxidation Reaction

CO Oxidation Reaction Carbon monoxide (CO) is one of the most detrimental gases as it has strong affinity with the hemoglobin and it has extremely inimical effects over living bodies even if its concentration is as low as 35 parts per million in atmosphere[87]. Thus, reducing CO gas is the need of the hour and one such efficient way of lowering CO concentration is the catalytic oxidation of CO by O_2 molecule, commonly known as CO oxidation reaction, $CO + 2O_2 \rightarrow 2CO_2$. The major source of CO is the industrial processes and incomplete combustion of fuels in automobiles[88]. Although, there exist catalysts for CO oxidation reaction, predominantly Pt-based, but the key issue in CO oxidation is the poisoning effect of CO that degrade and deactivate the catalyst over the time[89]. Thus, to design a poisoning-free catalyst for CO oxidation reaction is the serious challenge. The CO oxidation reaction proceeds via three reaction mechanism primarily viz., Langmuir-Hinshelwood (LH), Eley-Rideal (ER) and termolecular Eley-Rideal (TER) mechanism, depending upon the interaction of reactant(s) with the catalyst, the activity varies for different mechanism[90]. The reaction pathway and corresponding activity via different mechanism is discussed in detail in chapter 3.

1.4.2 Hydrogen Evolution Reaction

Hydrogen evolution reaction (HER) is basically a cathodic half reaction of overall water splitting method, that proceeds as $2H_2O \rightarrow 2H_2+O_2$[91]. HER is critical process for generating ultra-pure hydrogen, which is regarded as a clean and renewable energy carrier that can be used in fuel cells. H_2 as an energy source offer zero-carbon footprint and pollution free exercise in vehicles as well as industrial application[92]. H_2 is also a vital chemical feedstock in many chemical industrial processes like ammonia synthesis, syngas conditioning etc. The high-cost and inefficiency in breaking H-OH bond by already existing Pt-based catalyst offers an opening to look for an alternative[93]. To examine the HER activity, Volmer-Heyrovsky (VH) and Volmer-Tafel (VT) mechanisms are considered[94] and complete reaction investigation is presented in chapter 4.

1.4.3 Water-Gas Shift Reaction

The water-gas shift (WGS) reaction is a crucial chemical reaction in industrial chemistry and various energy applications. It involves the reaction of carbon monoxide (CO) with water vapor (H_2O) to produce carbon dioxide (CO_2) and hydrogen (H_2). The reaction is represented as $CO+H_2O \rightleftarrows CO_2+H_2$[95]. The WGS reaction holds great significance in converting lethal CO gas to relatively less harmful CO_2 gas, in production and purification of pure hydrogen and in maintaining syngas conditioning. Moreover, the high exothermicity of WGS reaction is also advantageous in generating and utilizing surplus energy in the form of heat. There are various mechanisms of WGS reaction like redox, formate, carboxyl and recently predicted OH-assistive mechanism[96]. The choice of mechanism primarily depends upon the form of catalyst, its interaction with the reactant(s) and the reaction conditions. Commonly used catalysts are Fe/Cr-based (at high temperature)[97] and Cu-based (at low temperature)[98]. The key challenge in WGS reaction is to manage slow kinetics and high thermodynamics of the reaction along with controlling the CO poisoning effect[99]. In our study, we performed complete WGS reaction via formate and OH-assistive mechanism and is presented in chapter 5.

1.5 Motivation and Objectives of the Thesis

Although, heterogeneous catalysis is the most explored branch of catalysis among all owing to its impactful consequences to the society, but it is also the fastest-growing branch as the advancements are happening rapidly and continuously aligning with upgradation in technology, in order to achieve a practically applicable catalyst towards energy and environmental applications[100]. Accordingly, the approach of designing of a rational catalyst is getting more and more contemporary. The most recent of them is the single-atom catalysts (SACs), has attracted researchers' interest thanks to its idiosyncratic peculiarities as a catalyst. As the field of SACs is relatively novel to the world and it possesses sea of opportunities and challenges at the same time like[101]:

1. The investigation and understanding of origin of enhanced efficiency and selectivity and its correlation with the altered electronic properties at an atomic scale.
2. The individually exposed atoms behave as an active site resulting in 100% atom utilization efficiency leading to design economic catalyst.
3. SACs offer a platform to explore the fundamentals of reaction mechanisms occurring and at an atomic scale.
4. SACs also have a potential of tailoring catalytic properties by designing a catalyst with precise control over active sites and altering the electronic properties by changing supports.
5. The strong interaction of spread atoms with substrates ensuring stead-stoned stability of SACs, presents a possibility of application of SACs in harsh reaction conditions.
6. The fact that the SACs comprising of TMs possesses exceptional catalytic behavior towards prime chemical reactions.

Moreover, a rational design of an efficient catalyst requires fundamental understanding of the origin of catalytic activity by virtue of the energetics of the system and its interaction with the reactants occurring at an atomistic scale, which is a

tedious task if done by experimentally, where the reactions are performed in real-time. But, the advancements in reliable computational tools and methods made it possible to simulate a particular system for a particular reaction in investigate and analyze every minute details like composition at atomic level, the structural variations, the alteration in electronic structure (atom wise orbital contribution in electronic band structure, density of states etc.), interaction of reactants with the catalyst, bonding characteristics and detailed reaction profile of particular reaction and it also enables us to examine high-energy intermediates or transition states which is of vital prominence and often go unnoticed during experimental characterization. Thus, all these combinedly provides valuable insights for drawing a path for an effective catalyst, which aids significantly in experimental designing rather than the traditional approach of trail-and-error which is time-sapping, labor-intensive and big-budget process. So, all these prospects inspired us to delve deep into the field to explore[19].

In the present thesis work, we aimed to achieve a rational design of TM SACs supported over various substrates, by investigating electro-catalytic activity for some key chemical reactions like CO oxidation reaction, hydrogen evolution reaction (HER) and water-gas shift (WGS) reaction, by employing first-principles based density functional theory (DFT) calculations. In order to organize the study, specific objectives were designed as

1. **Ground state geometry:** To examine various anchoring sites like top, bridge, hollow etc., over variety of 2D materials like carbon-based, oxides, nitrides etc., for different study to obtain ground state geometries of the system for further investigation.

2. **Stability:** To investigate the stability of considered SACs by computing binding energy of atoms with support, diffusion barrier and diffusion rate of atom over substrate and cluster formation possibility by computing relative energy of cluster formation.

3. **Electronic properties:** To inspect the change in electronic properties of the SACs arising due to the interaction with support by assessing electronic band structure, projected density of states (PDOS) and Lowdin charge transfer.

4. **Effects of d-states:** To contemplate the effect of d-states (important for TMs based catalyst) on catalytic behavior by employing spin-polarized d-band model to compute d-band center (ε_d) and fractional filling of d-band (f_l) to predict catalytic properties of SACs.

5. **Effects of defects:** To explore the effect of creating defects on the stability, electronic properties and catalytic properties of SACs.

6. **Activation barrier and minimum energy path (MEP):** To compute the activation energy and MEP for different mechanisms of considered reaction like CO oxidation, HER and WGS reaction by employing climbing-image nudged elastic band (CI-NEB) method over selected SACs.

1.6 Thesis Organization

The thesis is divided into six chapters. As discussed here, the **Chapter 1** presents brief introduction and background about the topic of the thesis, motivation and objectives. In Chapter 2, we discussed the theoretical framework of the methodology we used in our calculations. The details of specific studies are presented in Chapter 3-5. At the end, the conclusion of the thesis is included in chapter 6. In chapter 3-5, a brief summary about topic and major outcomes are scripted in the form of an abstract, followed by an introduction, followed by computational methodology, results and discussion and conclusion.

Chapter 2 presents a detailed discussion over the theoretical framework of the computational methodology we used in our study i.e., density functional theory (DFT) for all the energetics and electronic structure calculations. Also, the methodologies to compute the electronic reactivity descriptors, reaction barrier and minimum energy path of a reaction is discussed in detail.

Chapter 3 presents our investigation on the catalytic performance of cobalt (Co) single-atoms supported over psi-graphene (PG) substrate (Co@PG) for electrocatalytic CO oxidation reaction. In CO oxidation reaction, a noxious carbon monoxide (CO) reacts with oxygen molecule (O_2) to produce relatively benign carbon dioxide (CO_2) molecule. In the chapter we discussed the stability of Co

SACs in terms of binding energy of Co with Pg over various binding sites, diffusion barrier and diffusion rate of Co-atoms over the substrate. The relative energy of cluster formation is calculated to analyze the cluster formation tendency of Co SACs. Further the adsorption/co-adsorption mechanistic of CO, O_2, O, CO_2, CO+O_2, CO+CO etc., are studied and are with respect to electronic reactivity descriptors like d-band centre (ε_d) and fractional filling of d-band (f_l) in order to validate the adsorption performance of CO@PG and also to predict the reaction mechanism for CO oxidation reaction. Further, two reaction mechanism viz., Langmuir-Hinshelwood (LH) and Eley-Rideal (ER) mechanisms of CO oxidation reaction are investigated comprehensively and are presented in chapter-3. The study presented in this chapter have appeared in the following publication.

H.P. Tanna, B. A. Baraiya and P. K. Jha, Co Implanted Ψ-graphene: A Non-Noble Metal Single-Atom Catalyst for Proficient CO Oxidation Reaction, Molecular Catalysis 556 (2024): 113907, DOI: 10.1016/j.mcat.2024.113907.

Chapter 4 discusses our work on catalytic activity of nickel (Ni) atoms embedded into various class of two-dimensional (2D) substrates like carbon-based (graphene and AlC), oxide substrates (BeO and MgO) and nitride substrates (h-BN and AlN) (Ni@2D) towards hydrogen evolution reaction (HER). Here we explored various anchoring sites like top, bridge, hollow and vacancy of atoms for Ni-atoms and computed binding energy over all these sites of the above-mentioned substrates. Further, we examined adsorption of H-atoms over some stable configurations of Ni@2D and computed two important activity descriptors of HER i.e., differential Gibbs free energy of H-adsorption (ΔG_H) and volcano plot in order to predict configurations of Ni@2D that possibly shows good activity towards HER. Then, we performed complete HER over selected configuration of Ni@2D via two mechanisms i.e., Volmer-Heyrovsky and Volmer-Tafel mechanism and computed activation energy and validated it with the activity descriptors of HER. The research presented in this chapter is under communication.

Chapter 5 addresses our study on catalytic behavior of transition metal (TM) embedded 2D AlN substrate (M@AlN; M=Ni, Pd, Pt, Cu, Ag, Au) towards water-gas shift (WGS) reaction. The WGS reaction is between CO and H_2O to produce CO_2 and H_2. The WGS reaction holds great significance due to its energy and environmental application, as it converts CO to CO_2 and it also generate ultra-pure

H_2, which can be used as an energy carrier. Here, we computed binding energy of considered TM-atoms over various anchoring sites of AlN, like top, bridge, hollow and defect site. In order to gain more detail about stability of M@AlN, we computed diffusion of M-atoms over substrate and calculated diffusion barrier. The interaction of reactants, like CO, OH, H_2O, CO+OH and CO+H_2O is analysed via adsorption/co-adsorption energy calculations. Then, we performed complete WGS reaction over M@AlN via two mechanisms i.e., formate mechanism and OH-assistive mechanism. The analyses of minimum energy path and activation energy calculations are validated by applying Sabatier principle and correlating it with the co-adsorption energy of the reactants, and also by applying the concept of d-band centre (ε_d), which is more accurate parameter to analyse reactivity of TMs. Further, the feasibility of the reaction is examined by applying energetic span model (ESM) through the concept of activation energy and reaction energy. The findings of the research presented in this chapter is under communication.

Chapter 6 wraps up the thesis by summarizing key conclusions and potential applications of the study presented in chapter 3-5. The scope and future directions of research in the area of the rational design of TM-based single-atom catalyst for futuristic practical applications with enhanced performance.

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