Rational Design of Transition Metal Single-Atom Catalyst Using Density Functional Theory

Synopsis

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By

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Abstract

In this thesis, we have studied the geometric, electronic and electrocatalytic properties of various transition-metals (TMs) single atoms catalysts (SACs) like Co, Ni, Pd, Pt, Au, Cu, Ag for some prime chemical reactions like CO oxidation, hydrogen evolution reaction (HER) and water-gas shift (WGS) reaction first-principles based density functional theory calculations. To begin with, we studied electrocatalytic behaviour of Co-SACs supported over Ψ-graphene substrate towards poisoning-free CO oxidation reaction. Further, we explored Ni-SACs supported over various kinds of substrates like graphene, AlC, AlN, h-BN, BeO and MgO for efficient HER. Then, we investigated different TMs-SACs comprising of Ni, Pd, Pt, Cu, Ag, Au embedded into AlN substrate for WGS reaction. The stability of the considered SACs are examined by computing binding energy of atoms over substrate. Further, the diffusion barrier and diffusion rate of atoms over substrate is computed to analyse the stability and also the cluster formation possibilities of the SACs. The change in electronic properties of the SACs brought by its interaction with the substrate is examined by analysing the projected density of states and Lowdin charge analysis. For a feasible chemical reaction, the interaction of reactants with the SACs plays critical role. The strength of the reatants is investigated using adsorption/co-adsorption energy calculations. Further, the analysis of adsorption energy with the d-band properties of TMs SACs like d-band centre(ε_d), d-band width (W_d) and fractional filling of d-band (f_l) is carried out to predict the catalytic behaviour of the SACs. At the end, the calculation of minimum energy path, activation energy and reaction energy for all the reaction with different mechanisms is examined by employing climbing-image nudged elastic band (CI-NEB) method. Overall, this thesis theoretically describes the way to design a rational SACs for some important chemical reactions and provides a potential candidates to further explore them for the practical applications.

Contents

Introduction

Catalysis is of paramount importance having its affirmative impact in various scientific, industrial, environmental and daily-life domains. The term 'catalysis' was introduced by Berzelius in 1836 and defined it as catalyst have special powers that alters the affinity of chemical substances. In 1895, Ostwald redefined the definition of catalyst as 'it accelerates the chemical reaction without affecting a chemical equilibrium'. Thus, catalyst and catalysis are two long-standing terms having ever-increasing impact on society demands an unceasing research and development in the field. In this regard, there is a persistent advancement in tools, techniques and technologies in both theoretical as well as experimental ways for designing an efficient catalyst for various catalytic reactions. [1]

Traditionally, metals, especially transition metals (TMs) and their alloys have been extensively studied for catalytic purpose due to their excellent catalytic activity and selectivity, owing to their partially filled d-orbitals and variable oxidation states [2]. Also, the fact that catalytic properties of TM-based catalysts influenced enormously by the particle size. As the particle size is reduced from bulk to 2D to nanoparticles (NPs) and nanoclusters (NCs), the catalytic activity enhances greatly [3]. This approach of reducing the particle size from bulk to NPs/NCs, took one-step ahead by reducing the size to an atomistic scale, wherein an atomically dispersed atoms over a substrate that act as an active site to perform the reaction. This way of designing a catalyst is termed as single-atom catalysts (SACs), the word coined by in 2011, where they investigated Pt SACs on FeO_x for CO oxidation reaction [4–6]. They reported amplified activity of Pt-SACs compared to the respective NPs/NCs or higher dimensional catalyst. Thereafter, this strategy acquired heap of interest and attention from the researchers across the globe in the last decade or so. There has been exponential growth in exploring SACs, specifically SACs comprising of TMs like Pt, Pd, Ag, Au, Cu, Ni, Co and others are at the core interest of scientists and are widely investigated for prime environmental and industrial and chemical reactions like CO oxidation reaction, CO_2 reduction reaction, hydrogen evolution reaction (HER), oxygen evolution reaction (OER), water-gas shift (WGS) reaction, ammonia (NH_3) synthesis and many more and are found to exhibit exemplary catalytic activity [7]. The origin of the enhanced catalytic activity of TMs based

SACs is the emergence of frontier orbitals (FOs) arising due to the introduction of quantum confinement effect at an atomistic scale. The examination of interaction of FOs of the SACs with the adsorbate is of central prominence to gain profound insight of catalytic behaviour of the SACs [2, 8].

Although, ample amount of work has already been done towards SACs in both theoretical as well as experimental domains, yet there are lots of vague questions in front of research community. The fundamental challenge is to understanding the role the support/substrate on which the single-atoms are deposited plays [9]. As the support used to anchor the single-atoms in designing SACs plays significant role in stabilizing the atoms but it also alters the electronic structure of the atom, there by impacting the electrocatalytic behaviour of the SACs greatly. Thus, it is of foremost importance to investigate and interpret the impact of role to design an effective SACs. So far, two dimensional (2D) sheets of various kinds of materials like carbon-based materials like, oxides, nitrides, chalcogenides etc., are explored as a support for designing the SACs. Although, these materials are examined comprehensively for various SACs towards different chemical reaction, but the vast reservoir of these substrates combining with various TMs and large number of reactions to study, makes this area of research always inquisitive to the researchers [10–12].

Exhilarated by the above-mentioned fact, we decided to delve into the pool of options at disposal in the field of SACs. In this thesis, we present an extensive and exhaustive computational inquest of electrocatalytic behaviour of TMs based SACs supported over 2D sheets towards some cardinal chemical reactions like CO oxidation reaction, WGS reaction and HER. Firstly, we investigated catalytic activity of cobalt (Co) single-atom spread over the newly predicted graphene allotrope; Ψ-graphene towards electrocatalytic CO oxidation reaction [13]. In the next work, we explored different TMs like Ni, Pd, Pt, Cu, Ag and Au SACs atomically embedded into 2D AlN substrate for efficient WGS reaction. In another work, we examined the catalytic performance of Ni SACs injected into various kinds of 2D materials like graphene, AlC, AlN, h-BN, BeO and MgO towards HER. For all of the considered reactions, we considered various reaction mechanisms and the catalytic efficiency is contemplated in terms of minimum energy path and activation energy calculations by employing CI-NEB method. The works presented in thesis are comprehensively investigated and are systemati-

cally analysed to draw an accurate and upright conclusion. This thesis provides a meticulous computational approach of designing a potent and industries-applicable TMs based SACs towards prime chemical reactions and possesses an ample scope to be inspected experimentally.

Objectives

The main aim of the study was the computational designing of TMs-based SACs for some prime chemical reactions. In view of that, we systematically worked over specific objectives that are mentioned here.

1. Ground state geometry: We considered 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: The stability of considered SACs are analysed 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: The change in electronic properties of the SACs arising due to the interaction with support is examined by analysing electronic band structure, projected density of states (PDOS) and Lowdin charge transfer.

4. Effects of d-states: As the considered SACs are comprising of TMs, the effect of d-states on catalytic behaviour is examined by employing spin-polarized d-band model to compute d-band centre (ε_d) and fractional filling of d-band (f_l) to predict catalytic properties of SACs.

5. Effects of defects: The effect of creating defects on the stability, electronic properties and catalytic properties of SACs is examined.

6. Activation barrier and minimum energy path (MEP): The activation energy and MEP for different mechanisms of considered reaction like CO oxidation, HER and WGS

reaction are examined by employing climbing-image nudged elastic band (CI-NEB) method over selected SACs.

Thesis Outline

This thesis has been divided into six chapters starting with introduction comprising of basic idea about background of heterogeneous catalysis, origin and advances of SACs, challenges in designing SACs and work done on the proposed objectives. In chapter 2, the computational methodology to study the geometric, electronic and catalytic properties of considered system for various catalytic reactions is discussed in detail. In chapter 3, we presented our work about catalytic performance of cobalt (Co) SACs supported over Ψ-graphene substrate (Co@PG) towards electrocatalytic CO oxidation reaction. Further, the catalytic behaviour of nickel (Ni) SACs spread over graphene and graphene like 2D materials like AlC, AlN, h-BN, BeO and MgO (Ni@2D), towards hydrogen evolution reaction (HER) is investigated and presented in chapter 4. Chapter 5 presents the study catalytic activity of various TMs like Ni, Pd, Pt, Cu, Ag and Au supported over AlN (M@AlN), for water-gas shift (WGS) reaction. The conclusion and the future aspects of the work presented in thesis is discussed in chapter 6.

1 Single-Atom Catalyst: An Introduction

This chapter begins with the introduction and importance of catalysis for sustainable world, followed by the thorough discussion over the subject, its development from the initial to the origin of single-atom catalysts (SACs), its current status of research by providing some examples of recent research. This chapter will certainly build the foundation of the thesis, providing a thorough background about the topic, the motivation behind working over the problem and the objectives of the thesis.

2 Computational Methodology

In this chapter, we discussed the background and development of the first-principles based density functional theory (DFT) implemented as an elementary tool in the investigation of all the work presented in the thesis. In order to find the ground state energy and geometry of the considered system, we employed Quantum ESPRESSO (QE) simulation package [14,15], which basically solves the famous Kohn-Sham equation by solving the self-consistent field cycle as shown in Fig.1. For the accurate prediction of interaction between substrate and adsorbates, the dispersion corrections D3 within implemented in the QE is employed in all calculations [16]. The improved d-band model for the spin-dependent properties of TMs is considered to compute electronic reactivity descriptors like d-band centre, d-band width, and higher moments of d-band [17, 18]. The minimum energy path (MEP) and transition state for the considered reactions is sketched using the climbing-image nudged elastic band (CI-NEB) method proposed by Henkelman et al. (implemented in the QE) [19, 20].

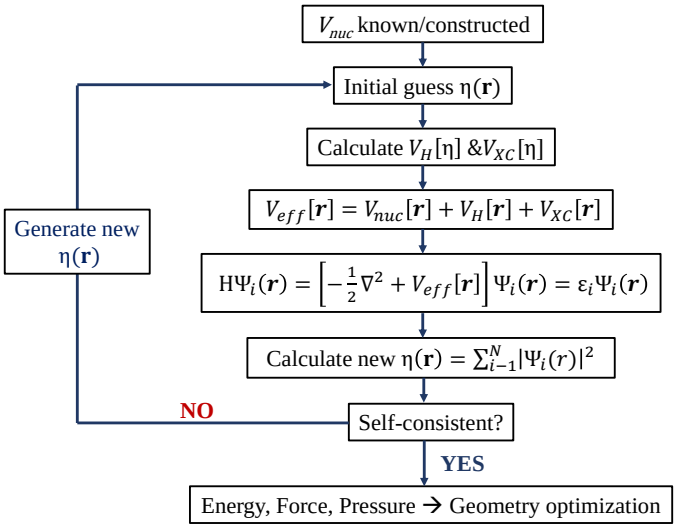

Figure 1: A typical self-consistency loop implemented in Quantum ESPRESSO code to compute the ground state of a material by solving the Kohn-Sham equations..

3 Cobalt Supported Ψ-Graphene: A Proficient SACs for CO Oxidation Reaction

In this chapter, we present our work on investigation of catalytic behaviour of Co SACs supported over recently predicted Ψ-graphene substrate (Co@PG) towards poisoning-free CO oxidation reaction which is the reaction between CO and O_2 molecule to produce CO_2. Here, we will discuss about the change in electronic properties of Co-atoms brought by its interaction with the substrate, that resulted in enhanced catalytic activity as predicted by the d-band data analysis. Further, we will discuss about the reduced CO poisoning effect of Co@PG, as the Co@PG prefers O2-adsorption rather than CO adsorption, which increases the longevity of Co@PG. Based on the adsorption/co-adsorption energy criteria of CO, O_2 molecules, we shortlisted Langmuir-Hinshelwood (LH) and Eley-Rideal (ER) mechanisms of CO oxidation reaction. We performed complete CO oxidation reaction over Co@PG by both the mechanisms and computed minimum energy path (MEP) and activation energy (E_a) by employing CI-NEB method. Accordingly, Co@PG is found to be a potent, non-noble transition metal SACs for CO oxidation reaction preferring ER mechanism with E_a values are 0.19 eV and 0.27 eV for 1st and 2nd half reaction of CO oxidation, respectively.

4 Catalytic Activity of Ni-SACs Towards Hydrogen Evolution Reaction

We will discuss catalytic activity of Ni SACs supported over graphene and graphene like substrates for hydrogen evolution reaction (HER) in this chapter. Here, we considered various kinds of substrates like carbon-based (graphene and AlC), nitrides (h-BN and AlN) and oxides (BeO and MgO) to anchor Ni-atoms (Ni@2D), which acts as an active site for electrocatalytic HER which is basically the cathodic-half reaction of overall water-splitting method. In this chapter we will discuss about various anchoring sites like top, bridge, hollow and defects that lead to the stability of Ni SACs. Further, we will discuss about the differential Gibbs free energy of H-adsorption (ΔG_H) which provides quantitative idea about

the strength of H-adsorption. As having large number of systems and many anchoring sites, we shortlisted some of the configurations of Ni@2D on the basis of ΔG_H to further investigate complete reaction profiles of HER. We considered Volmer-Heyrovsky (VH) and Volmer-Tafel (VT) mechanism of HER and computed MEP and E_a for the shortlisted systems. Our study found that Ni@AlN and Ni@h-BN are potential, eco-operational candidates to replace the existing high-cost Pt-based catalyst.

5 Catalytic Performance of Transition Metal SACs for Water-Gas Shift Reaction

In this chapter, we will discuss about the catalytic behaviour of transition metals (TMs) based SACs supported over AlN substrate (M@AlN), M=Ni, Pd, Pt, Cu, Ag, Au, towards water-gas shift (WGS) reaction, which is the reaction between CO and H_2O to produce CO_2 and H_2 molecule as a product. Here we will discuss the significance of WGS reaction not only in production of ultra-pure H_2 but also in conversion of CO to CO_2. Here, we will discuss about the diffusion of considered M-atoms over AlN, to examine the cluster formation possibility of the SACs. Further, we have discussed the formate and OH-assistive mechanisms of WGS reaction over M@AlN and examined MEP to compute Ea using CI-NEB method. Overall, OH-assistive mechanism is found to be preferred over formate mechanism, with Au@AlN and Cu@AlN showing superior catalytic activity with E_a values 0.14 eV and 0.21 eV, respectively. The obtained Ea values are further validated with the linearity between Ea and co-adsorption energy of CO-OH molecule. Further the feasibility of the reaction is discussed in terms of relation between E_a and reaction energy (E_R) by employing energetic span model.

6 Conclusion and Future Prospects

This chapter will summarize and conclude the results and discussions done in the previous chapters. It also discusses about the motivation and objectives fulfilled which are presented in the chapter 1 of the thesis. Here, we will highlight the thesis in brief by emphasizing on

the extraordinary results we obtained from the first-principles calculations. The summary in this chapter will be followed by the future prospects of the work done here and future scope of the work in a way to extrapolate it further and the exploration of the work by experimental point of view, to check the possibility of designing a practicable SACs working with similar efficiency. This chapter will end with my plans to further explore the field of SACs and work on the possibilities and opportunities it brings from research perspectives.

Conferences and Workshops

- Participated and poster presentation in **International Conference on Condensed Matter and Device Physics-2021**.
- Participated and poster presentation in **65^{th} DAE Solid State Physics Symposium, 2021**.
- Participated and poster presentation in **66^{th} DAE Solid State Physics Symposium, 2022**.
- Participated and oral presentation in **International Conference on Condensed Matter and Device Physics-2023**.
- Participated in one-day symposium on **Application of Machine Learning Methods in Physics**.
- Participated in **2024 Catalysis Science** & **Technology Symposium by Royal Society of Chemistry**.

Publications

- "Co Implanted Ψ-graphene: A Non-Noble Metal Single-Atom Catalyst for Proficient CO Oxidation Reaction",**Hemang P. Tanna**, Bhumi A. Baraiya, Prafulla K. Jha, Molecular Catalysis 556, 113907.

- "Dressing of Cu atom over nickel cluster stimulating the poisoning-free CO oxidation: an ab initio study", Bhumi A. Baraiya, **Hemang P. Tanna**, Prafulla K. Jha, The Journal of Physical Chemistry A 125 (24), 5256-5272

- "A Theoretical Inquest of Atomically Injected Ni-atom over Graphene and Analogous Substrates for Hydrogen Evolution Reaction", **Hemang P. Tanna**, Prafulla K. Jha, Electrocatalysis 15 (5), 412-420

- "Water-Gas Shift Activity of Atomically Embedded Transition-Metals on AlN Support: A DFT Investigation ", **Hemang P. Tanna**, Prafulla K. Jha, Inorganic Chemistry Communications 169, 113075

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