ABSTRACT

One of the major air pollutants in the world, nitrogen oxides (NO_x) which primarily consist of nitric oxide (NO) and nitrogen dioxide (NO_2) are responsible for acid rain, photochemical smog, and ozone depletion [1, 2]. Serious respiratory conditions are brought on by nitric oxide (NO), which makes up about 90% of NO_x [3]. Prior to emission, it is crucial to chemically convert NO to N_2 in order to prevent air pollution. Despite the apparent irony, the catalytic oxidation of NO is a critical phase of its catalytic reduction. In NO_x abatement systems like selective catalytic reduction (SCR), continuously regenerating trap (CRT), and NO_x storage and reduction (NSR), one of the most important processes is the conversion of NO to NO_2. When it comes to reducing NO_x emissions in the presence of abundant oxygen, NH_3-SCR is generally considered to be the most effective approach available [4, 5]. The rate of the NH_3-SCR reaction can be considerably boosted if a fraction of the NO is transformed into NO_2. Hence, it has been established that the oxidation of NO to NO_2 is a critical step in NH_3-SCR. Moreover, compared to other oxidants used for oxidation, molecular oxygen acts as a green, non-toxic and inexpensive oxidant.

Recently, a new approach has been used to build particular catalysts for selective oxidation processes, that is, to use small metal clusters made up of only a few atoms [6-8]. These nano and subnanometer cluster's catalytic properties are unique and distinct from their bulk counterparts due to high surface-to-volume ratio, quantum confinement, etc. Metal atoms and clusters are highly reactive in variety of chemical processes [9] and serve as ideal platforms for investigating the mechanisms of complex reactions. Moreover, the formation of clusters on a support material bridges the gap between fundamental gas-phase investigations and the traditional field of heterogeneous catalysis study [10]. Therefore, it is highly crucial to examine the specific structural motifs of such clusters, which can be done by advanced computational methods. Precious metal nanoclusters, particularly, platinum nanoclusters are very much important for oxidation processes due to their high activity, selectivity, stability and poisoning resistance. Although a lot of previous literatures are present on NO oxidation, a detailed mechanism study is somewhat lacking on this topic. Hence, the adsorption pattern of NO and O_2 followed by extensive mechanism study for NO oxidation on small metal clusters have been investigated using density functional theory (DFT). The findings from our studies

will help to clarify the molecular mechanisms of the oxidation process and open up new avenues for the creation of a class of catalysts with high catalytic activity and maximum atom utilization.

This thesis consists of seven chapters viz. introduction of present work, overview of computational methods, four computational working chapters followed by conclusion and future prospects.

Chapter 1: Introduction of present work

The thesis is introduced in Chapter 1 and offers a comprehensive overview of the work that has been done to address the selected challenge. The significance of nanoscience and nanotechnology in the recent advancement of scientific study is covered in the opening section of this chapter. It was found that metal nano- and sub-nanoclusters have distinct physicochemical characteristics from their bulk counterparts which makes them quite interesting. Hence, it becomes imperative to understand their precise structural morphology, which can only be done by theoretical treatment. Moreover, among metal nanoclusters, precious metal nanoclusters are found to have potential applications across various fields, namely in heterogeneous catalysis. They act as an effective catalyst to convert NO to NO_2. However, the proper mechanism for NO oxidation on these small metal clusters are still unexplored. As a result, we decided to investigate the chemical and structural characteristics of precious metal nanoclusters at the theoretical level. Through this process, we learned more about how the reactant's (NO and O_2) adsorption patterns impact the reaction mechanism.

Chapter 2: Overview of the computational methods

Chapter 2 includes a detail description of computational tools that are used to carry out the work in this thesis. It contains two major methods; density functional theory (DFT) (most popular tool of quantum mechanics) and molecular mechanics (MM). We have also described various functionals and basis sets that are used to obtain structural and chemical properties of the clusters presented in the thesis. Additionally, the chapter also lists the software programs utilized to conduct the research work.

Chapter 3: Mechanistic insights on catalytic oxidation of NO to NO_2 on $[Pt_2]^{0,\pm}$ monometallic dimers using O_2

In Chapter 3, a comprehensive density functional theory (DFT) investigation of the catalytic oxidation of NO to NO_2 on neutral and charged $[Pt_2]^{0,\pm}$ dimers has been considered employing M06L/def2TZVP level of theory. Single as well as co-adsorption energies of NO and O_2 molecules suggest that the traditional Langmuir Hinshelwood (LH) mechanism and less explored termolecular Eley-Rideal (TER) and termolecular Langmuir Hinshelwood (TLH) mechanisms, are suitable for a full catalytic reaction pathway in which two NO molecules are converted to two NO_2 molecules, initiated by an activated O_2 molecule. Activation barrier reveals that the TER mechanism is found to be more reliable in converting two NO molecules into two NO_2 molecules on $[Pt_2]^-$ dimer. In addition to shedding light on the intrinsic characteristics of Pt_2 dimers, the study will serve as a benchmark for investigating the oxidation process of NO to NO_2 utilizing models of termolecular chemical processes.

Chapter 4: Catalytic Oxidation of NO on $[Au\text{-}M]^-$(M=Pd & Pt) Bimetallic Dimers: An Insight from DFT Approach

In our previous chapter, we have reported catalytic oxidation of NO to NO_2 on $[Pt_2]^{0,\pm}$ dimers in which it was found that anionic Pt_2 system is the most efficient catalyst. However, it is important to improve the design of a suitable catalytic system that could perform the catalytic activity of the oxidation process more efficiently. Herein, in Chapter 4, a comprehensive theoretical investigation of the catalytic oxidation of NO on anionic bimetallic dimers $[Au\text{-}M]^-$(M=Pd, Pt) has been considered here using Density Functional Theory (DFT) method at M06L functional along with def2TZVP basis set. The adsorption of NO and O_2 on bimetallic dimers are studied and adsorption energies has been calculated to understand the stability of the adsorbed species. Our calculations show that M-sites are found to be the preferred site for adsorption than Au-site. Further, full catalytic reaction pathways using Langmuir-Hinshelwood (L-H), Termolecular Eley- Rideal (TER) and Termolecular Langmuir-Hinshelwood (TLH) mechanism are investigated in which two NO molecules are converted to two NO_2 molecules in the presence of an activated O_2 molecule. On comparing the activation barriers for all the three mechanisms, it can be concluded that L-H mechanism is the favored pathway for catalytic NO oxidation. Moreover, energetic span model has justified that conversion on $[Au\text{-}Pd]^-$ catalyst possesses a lower apparent activation energy than $[Au\text{-}Pt]^-$ which make $[Au\text{-}Pd]^-$ more efficient catalyst towards the catalytic conversion of NO into NO_2. Thus, the present study reveals that the presence of Au in a bimetallic system reduces the activation barrier for NO oxidation.

***Chapter 5:* Mechanistic DFT investigation of catalytic oxidation of NO to NO_2 on pristine and doped $[Au_nPd_{3-n}]^-$ (n=0-3) clusters.**

In our previous chapter, it was found that $[Au\text{-}Pd]^-$ acts as an efficient catalyst towards the catalytic conversion of NO into NO_2. Hence, in Chapter 5, pristine and doped anionic $[Au_nPd_{3-n}]^-$ (n=0-3) trimer clusters were chosen to comprehend the oxidation mechanism of NO into NO_2 at the molecular level using density functional theory (DFT) approach. Gas-phase Au clusters are ideal model systems for imitating gold catalysts as they have electronic structure similar to active supported gold catalysts. The detailed reaction routes under the Langmuir Hinshelwood (LH), termolecular Eley-Rideal (TER), and termolecular Langmuir Hinshelwood (TLH) mechanisms were explored, in which two NO molecules are converted to two NO_2 molecules using molecular O_2. Results shows that on doping Pd on anionic $[Au_3]^-$ clusters, adsorption of both NO and O_2 increases. Our calculations shows that Pd site on bimetallic clusters is more preferable for adsorption than that of Au site. Moreover, energetic span model reveals $[Au_2Pd]^-$ cluster to be the most efficient cluster towards conversion of NO to NO_2 via L-H mechanism. Hence, the addition of one atom decreases the activation barrier and increases the efficiency.

***Chapter 6:* Adsorption and activation of nitric oxide (NO) and oxygen (O_2) on bare and supported M_n/ZSM-5[M=Au, Pd, Pt] (n=1-2) using ONIOM method**

In Chapter 6, we have investigated the adsorption and activation pattern of nitric oxide (NO) and oxygen (O_2) on bare and supported M_n/ZSM-5[M=Au, Pd, Pt] (n=1-2) using DFT based ONIOM method. Well defined metal clusters on a support material such as zeolites serves as a link between the traditional field of heterogeneous catalysis studies and fundamental gas-phase investigations. Zeolite is a great host material with outstanding size and shape selectivity and well-defined cavities and channels. They can conduct reactions in both the gas and liquid phases in challenging circumstances because of their relatively high thermal stability. Here, wB97XD functional along with 6-31G(d,p) for nonmetals and LANL2DZ for precious metals were chosen for ONIOM calculations. In this study, the impact of support on the activation and adsorption energies of NO and O_2 was investigated.

Chapter 7: Conclusion and Future Prospects

In Chapter 7, the key findings from the entire thesis are finally summarised, along with future directions and opportunities to further develop and consolidate the research.