NO oxidation over bare and zeolite supported precious transition metal clusters using quantum mechanical approach

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By

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Chapter 7: Conclusion and Future Prospects

7.1 Conclusion

Nitrogen oxides (NO_x), which are mostly composed of nitric oxide (NO) and nitrogen dioxide (NO_2), are one of the main air pollutants in the world, causing acid rain, ozone depletion, and photochemical smog. Nitric oxide accounts for more than 90% of NO_x and is the cause of serious respiratory ailments. As a result, chemically converting NO to N_2 is crucial for preventing air pollution. A crucial step in NO_x abatement systems like NO_x storage and reduction (NSR), continuously regenerating traps (CRT), and selective catalytic reduction (SCR) is the conversion of NO oxidation to NO_2. Recently, a different strategy has been used to create customized catalysts for selective oxidation processes: small subnanometric metal clusters, consisting of a few atoms, and their catalytic properties are different from those of bulk metals. Metal atoms and clusters are highly reactive in a wide range of chemical reactions. They are also ideal platforms for investigating the mechanisms of complicated chemical reactions. For NO oxidation, the activation of both the reactants is a crucial step. Hence, it is necessary to study the interactions between metal subnanometric clusters and the reactants (NO and O_2). Recent experimental as well as theoretical studies have shown small gas-phase Pt clusters to be reactive in the field of selective oxidation catalysis. Moreover, if alloying is done, the catalytic activity of metal clusters can be adjusted. According to studies, Pt metal exhibits more catalytic activity than its monometallic counterparts when combined with metals like Au and Pd. Lastly, well-defined metal clusters on a support, like zeolites, provide as a link between gas-phase studies and the conventional field of heterogeneous catalysis research. It was found that the metal-support interaction can have a major impact on the adsorption energies of NO and O_2. In this thesis, our aim was to investigate in detail the adsorption pattern of NO and O_2 on small metal clusters as well as exploring the various mechanisms for NO oxidation.

The work of the thesis has now been concisely summarized chapter by chapter.

In Chapter 1, we gave a brief overview of the history of nanoscience and nanotechnology. The chemical and physical characteristics of nanoparticles as well as their possible uses in various fields have also been addressed. This review has shown that, in comparison to their bulk counterparts, nanoparticles exhibit notably distinct physical and chemical properties because of the quantum confinement effect and high surface to volume ratio. Additionally, we have included a brief overview of the top-down and bottom-up approaches for the synthesis and classification of nanoparticles. Going forward, the importance of transition metal clusters in catalysis is discussed. Molecular-level comprehension of catalytic active sites can be obtained by treating well-defined metal clusters using the most advanced density functional theory (DFT) methods. These approaches can also serve as a foundation for subsequent theoretical and experimental research. At last, based on single as well as co-adsorption, various mechanisms for NO oxidation is thoroughly investigated.

In Chapter 2, the several computational techniques that are employed to carry out the tasks described in the thesis have been thoroughly addressed. Some of the several computational chemistry tools accessible are molecular mechanics, semi-empirical, *ab-initio* techniques, such as the HF approach and density functional theory. Among these, the density functional theory is given greater importance as it is mainly employed to obtain the results presented in this thesis. We have discussed the history and development of DFT, as well as its evolution to the most current modification, beginning with the local density approximations (LDA). Moving forward, a significant advancement in the DFT was realized with the development of generalized gradient approximations (GGA). To improve the accuracy of the exchange-correlation energy, further functional development has been performed in the approximation, termed as hybrid and double hybrid functionals. We have also provided an overview of the basis sets that were employed in the thesis's work.

In Chapter 3, an extensive density functional theory (DFT) analysis of the catalytic oxidation of NO to NO_2 on neutral and charged $[Pt_2]^{0,\pm}$ dimers has been examined using the M06L/def2TZVP level of theory. Based on single as well as co-adsorption energies, the conventional Langmuir Hinshelwood (LH) mechanism and the less explored termolecular Eley-Rideal (TER) and termolecular Langmuir Hinshelwood (TLH) mechanisms are used for a full catalytic reaction pathway in which two NO molecules are converted to two NO_2 molecules, which is initiated by an activated O_2 molecule. The activation barrier indicates that on $[Pt_2]^-$ dimer, the TER mechanism is found to be effective in converting two NO molecules into two

NO_2 molecules. In this work, the oxidation process of NO to NO_2 at the atomistic level is investigated, and the significance of models of trimolecular chemical reactions is highlighted.

In Chapter 4, an extensive theoretical investigation of the catalytic oxidation of NO on anionic bimetallic dimers $[Au\text{-}M]^-$ (M=Pd, Pt) has been performed utilizing the def2TZVP basis set at M06L functional. In order to determine the stability of the adsorbed species, the adsorption of NO and O_2 on bimetallic dimers is investigated and adsorption energies are calculated. According to our calculations, M-sites rather than Au-sites are the preferred sites for adsorption. Complete catalytic reaction pathways involving the conversion of two NO molecules to two NO_2 molecules employing the Langmuir-Hinshelwood (L-H), Termolecular Eley-Rideal (TER), and Termolecular Langmuir-Hinshelwood (TLH) mechanisms are studied. Comparing the activation barriers for the three mechanisms, it was found that the preferred route for catalytic NO oxidation is via L-H mechanism. Additionally, the energetic span model supports the idea that $[Au\text{-}Pd]^-$ catalyst has a lower apparent activation energy than $[Au\text{-}Pt]^-$, making it a more effective catalyst for the catalytic conversion of NO into NO_2.

In Chapter 5, the adsorption properties of NO and O_2 as well as the mechanism for oxidation of two NO molecules to two NO_2 molecules on $[Au_nPd_{3-n}]^-$ (n=0-3) clusters, were thoroughly investigated. Adsorption energy analysis showed that the adsorption energy of both NO and O_2 increases when a Pd atom is added to a pure $[Au_3]^-$ cluster. Furthermore, it was found that the reactants have a preference for binding to the Pd site of the bimetallic $[Au_2Pd]^-$ and $[AuPd_2]^-$ clusters. The findings further advocate that the co-adsorption energy values of two NO molecules on the catalyst are more negative when compared to NO and O_2 and two O_2 molecules. The detailed reaction path under L-H, TER and TLH mechanism were investigated in which L-H mechanism was found to be the most effective for catalyzing NO oxidation on $[Au_2Pd]^-$ cluster using molecular O_2. According to the energetic span model calculation, with the lowest δE value and the highest TOF value, $[Au_2Pd]^-$ is the most efficient catalyst. Therefore, it has been found that the reactivity of a pure $[Au_3]^-$ cluster is enhanced by Pd alloying.

In Chapter 6, 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) is investigated. We have used density functional theory (DFT) with ONIOM2 (QM: MM) (wB97xd/LANL2DZ/6-31G(d,p):UFF) calculations to examine the adsorption properties. The findings demonstrate that, in contrast to bare single metal atoms, the adsorption energies of NO and O_2 on ZSM-5 supported single metal atoms are higher. According to Mulliken charge analysis, a significant amount of charge transfer occurs from the support to the metal, assisting the metal in donating electrons to the antibonding orbitals of NO and O_2. In contrast to the monomers, Au_2 and Pt_2, on the other hand, show lower adsorption energies in the dimer system inside ZSM-5 than they do in the bare dimer system. Our investigation of the supported monomer and dimer structures reveals that the interaction with the support leads to significant changes in the framework's deformation as well as the geometric and electronic properties of the clusters. When compared to gas-phase clusters, the results demonstrate that the interactions between the cluster-framework and molecule-cluster result in a change of the adsorption energies of NO and O_2.

7.2 Future Prospects

Given the rapid advancements in the fields of nanoscience and nanotechnology, the comprehensive knowledge gained from the work on single atoms and sub-nanometre clusters could aid in the construction of appropriate catalysts for applications in various scientific fields. Platinum nanoclusters are becoming more and more attractive in both commercial and ecological contexts. Research on nanoclusters provides reliable insight into the smallest features, the local chemistry of the sites, and the catalyst's electronic environment. Furthermore, nanocluster tuning is a straightforward way to create relevant catalyst material by adjusting atom size or alloying. Our research presented in the thesis aim to provide a comprehensive understanding of the NO oxidation process by examining the energetics, structure, and other properties (electronic and thermochemical) of both bare and doped gas-phase Pt sub nanoclusters. While study on subnanometre clusters has been carried out, there are still a number of issues that require investigation. As a result, our work can be expanded to offer fresh perspectives in the field of catalysis.

1. Since NO oxidation was successfully carried out for smaller clusters of pure and doped precious transition metal clusters, it can be extended to larger clusters in order to understand the atom by atom dependency and evaluate the transition border to bulk properties during the course of the reaction.
2. Our adsorption pattern and mechanism for NO oxidation in small clusters can be compared with large surface systems in order to find whether studies in small cluster can actually provide reference for surface systems.
3. In our work, doping Pd cluster with Au proved to be an efficient method for bringing adsorption energies of the reactants to optimal range which helped in minimizing the activation barrier of the oxidation process. This may prove beneficial to experimentalist for building efficient NO oxidation catalyst.
4. Our work with metal supported zeolite can be investigated further for co-adsorption of NO and O_2 and exploring the minimum energy pathway for oxidation of NO.