SYNOPSIS

Clusters are building blocks of nano-structured materials and constitute an intermediate state of matter between atoms (or molecules) and solids\(^1\). They are aggregates of atoms (or molecules) and show properties between those of individual atoms (with discrete energy states) and bulk matter (characterized by bands of states). The size of nanoclusters ranges from sub-nanometer to about 10 nanometers in diameter and are of technological importance in numerous areas of applied science (\textit{e.g.}, materials science, catalysis, (opto) electronics). The properties of nano-clusters gradually approach to those of bulk materials or extended surfaces, which are scalable with size. Nanoclusters, however, have properties and structures which are very sensitive to their composition and size (i.e. “every atom counts”), can lead to new and interesting properties which are not realized in the corresponding bulk material\(^2\).

Bimetallic clusters composed of elements with different atoms have gained considerable attention\(^3\) because by controlling the composition one can tune the electronic, optical, and chemical properties. Moreover, binary clusters are challenging for (i) better understanding of the characteristic properties of impurities or defects in solids (ii) the elucidation of the role of heterogeneous bonding in mixed clusters which provides understanding of fundamental effects responsible for the stability of covalent or metallic clusters and (iii) the effect of mixing on the electronic shell structure.

Understanding the electronic structure of metal clusters supported on solid substrates is of fundamental to the heterogeneous catalysis. Much effort is devoted to understand this phenomenon and to create a tailor-made catalyst with high efficiency and selectivity\(^4,5\). The size dependent electronic structure of these clusters is of great importance in the catalytic properties of these systems\(^6\). The unique size-dependent properties of these supported clusters are only one part of a more complex problem. The oxide supports on which the metal clusters
are chemically active suggests that careful understanding is required to separate the effects of cluster and support. Charge transfer between support and cluster and diffusion of reactant molecules from support to cluster are some of the important and complex roles of the support materials in these catalytic systems. In addition, metal clusters exhibit dynamic structural transformations, during a chemical reaction to optimize the catalytic pathway. Moreover, selective doping changes their electronic structure, their relationship to the oxide support, and their catalytic activity.

The goal of the present thesis is to gain fundamental understanding on isolated and supported metallic clusters and their interactions with gas molecules. These studies have implications towards designing new materials for heterogeneous catalysis. Throughout the work standard codes of density functional theory, within the plane-wave based pseudo-potential framework were used as a tool to illustrate the physico-chemical behavior of all systems in this study. The first part of this thesis involves understanding the quantum size effect on the equilibrium geometries and energetics of small lead clusters in the neutral and charged states. In addition, the effect of an impurity dopant on the geometric and electronic structure of lead clusters was investigated. The second part dealt with the interactions of $O_2$ with Al doped Au clusters. This work was further extended to study the $O_2$ interaction with Al – Au nano-composites. The primary objective of these works was to investigate the influence of an electro-positive element like Al on the bonding characteristics of electro-negative Au atoms. The results showed an improved oxidation behavior of Au in presence of Al atoms, be it inside the core for core-shell type structure or at the sub-surface layer for periodic slabs. As a natural continuation of the $O_2$ adsorption, the CO oxidation mechanism on the Au – Al nano-composites was also investigated. In the third part of the thesis, the role of support on the structure and reactivity of metal clusters was investigated. This was carried out by studying the interaction of Au$_n$ clusters on Al$_2$O$_3$ surface and subsequent molecular
Chapter 1:

The work described in this thesis is theoretical and its main objective is to look into the fundamental understanding of three important aspects of different types of clusters, namely the atomic structure, bonding and electronic properties. In this introductory chapter, the subject of cluster science is introduced, followed by a brief description on driving force for cluster science and some aspects of the evolution of size dependent properties of clusters so as to provide the necessary background for this thesis. This chapter also covers few experimental methods used for the generation and detection of clusters. In addition, role of theoretical calculations in understanding the experimental results and to predict the geometry and electronic properties of clusters has been described. In this chapter we have also described how theoretical data can be useful for the elucidation of the cluster structure and to interpret the experimental results. At the end of this chapter, a brief outline of the thesis is presented.

Chapter 2:

This chapter describes the general theoretical approach used throughout this thesis. Firstly, an overview is given of the underlying DFT quantum-mechanical approach and the computational details of the level of theory employed for the calculations. Technical aspects of the calculations viz. initial guess wave function or basis set, pseudo-potentials, simulation cell, geometry optimization techniques, utilized computer systems configuration etc. are discussed. Emphasis has been laid on the philosophy behind the methods rather than the concrete mathematical basis of different methods.

Chapter 3:

The structural and physicochemical properties of the Group IV elemental clusters have been the subjects of intense research because of the fundamental interest to understand
their bonding and growth patterns and the possibility of applications in nanotechnology. Their growth behavior and the nature of bonding differ considerably as one goes down from C to Pb. In this chapter we elucidate the evolution of geometric and electronic structure of $\text{Pb}_n$ and $\text{Pb}_n^+$ clusters ($n = 2–15$) and compared it with other Group IV elemental clusters. The results suggest that unlike Si, Ge, and Sn clusters, which favour less compact prolate shape in the small size range, Pb clusters favour compact spherical structures consisting of fivefold or six fold symmetries. The difference in the growth motif can be attributed to their bulk crystal structure, which is diamond-like for Si, Ge, and Sn but fcc for Pb. The relative stability of $\text{Pb}_n$ clusters analyzed based on the calculated binding energies and second difference in energy suggests that $n = 4,7,10$ and 13 clusters are more stable than their respective neighbours. This is in good agreement with experimental observations\textsuperscript{7}. Charged $\text{Pb}_n^+$ clusters also showed compact growth pattern as those observed for neutrals with small local distortions. Based on the fragmentation pattern it is seen that small clusters up to $n = 12$ favour monomer evaporation, larger ones fragment into two stable daughter products. The experimental observation of a large abundance for $n = 7$ and lowest abundance of $n = 14$ have been demonstrated from their fragmentation pattern. The chemical stability of these clusters was analyzed by evaluating their energy gap between the highest occupied and lowest unoccupied molecular orbitals and adiabatic ionization potentials. Albeit higher binding energy of $\text{Pb}_{13}$, the lower ionization potential was explained based on its electronic structure through the density of states and electron shell filling model of spherical clusters. A good agreement of our theoretical results with that of the experimental findings reported earlier implied accurate predictions of the ground state geometries of these clusters.

**Chapter 4:**

Introduction of an impurity atom can play a very important role in the modification of electronic and geometrical properties of homoatomic clusters\textsuperscript{3}. However, these studies are
relatively few due to difficulties in the experimental arrangements and more number of isomeric structures that needs to be evaluated from theoretical side. In this chapter we report the structural and electronic properties of $\text{Pb}_nM$ ($M = C, Al, In, Mg, Sr, Ba,$ and $Pb; n = 8, 10, 12$ and $14$) clusters. Extensive search based on large number of initial configurations has been carried out to locate the stable isomers of $\text{Pb}_nM$ clusters. The results revealed that the location of the impurity atom depends on the nature of interaction between the impurity atom and the host cluster and the size of the impurity atom. While the impurity atoms smaller than $Pb$, favor to occupy the endohedral position, the larger atoms form exohedral capping of the host cluster. The stability of these clusters has been analyzed based on the average binding energy, interaction energy of the impurity atoms and the energy gap between the highest occupied and lowest unoccupied energy levels (HLG). Based on the interaction energy of the $M$ atoms with $\text{Pb}_n$ clusters, it is found that $p – p$ interaction dominates over the $s – p$ interaction and smaller size atoms interact more strongly. The stability analysis of these clusters suggests that while the substitution of $Pb$ by $C$ or $Al$ enhances the stability of the $\text{Pb}_n$ clusters, $Mg$ lowers the stability. Apart from geometrical effects, it is found that the stability of these clusters can be tuned by the ordering of their energy levels. The energy gap analysis revealed that while the substitution of $Mg$ atom widens the HLG, all other elements reduce the gap of the $\text{Pb}_nM$ clusters. The unusual increase in the interaction energy of $Mg$ with $\text{Pb}_{12}$ and the largest HOMO–LUMO gap of $Mg\text{Pb}_{12}$ cluster has been explained based on the 50 electrons rule for icosahedral structures. Further investigations of the stability of $\text{Pb}_nM$ clusters revealed that the interplay between the atomic and electronic structure is crucial to understand the stability of these clusters.

Further in this chapter, fragmentation behavior of the bimetallic cluster ions $Sn_nPb^+$ and $\text{Pb}_nSn^+$ has been investigated. A systematic theoretical study of the structure and electronic properties of $Sn_{n-1}Pb$ and $\text{Pb}_{n-1}Sn$ ($n = 2 – 13$) clusters and comparison with
pure $Sn_n$ and $Pb_n$ to understand the influence of the dopant elements was presented. Fragmentation studies have revealed that, for $Sn_nPb^+$ first the single lead atom is split off; in contrast the $Pb_nSn^+$ clusters dissociate mainly in fragments retaining the single tin atom, which is in full accordance with the low-energy surface-induced dissociation patterns of $Sn_nPb^+$ and $Pb_nSn^+$ clusters. For larger collision energies the complete set of smaller tin fragment ions $Sn_{n-m}^+$ with $m < n$ is found for $Sn_nPb^+$, whereas the $Pb_nSn^+$ clusters decay into two series of $Pb_{n-m}Sn^+$ and $Pb_{n-m}^+$ fragments with $m < n$.

Chapter 5:

Gold, which is inert in the bulk, is found to be highly active in its nano form. Their potential as active catalysts for a large number of reactions (e.g., CO oxidation) has been elucidated earlier. Moreover the chemical reactivity of the $Au$ clusters can be tuned by the incorporating a dopant in it. In this chapter, we have presented the atomic and electronic structure of $Au_{n-1}Al$ clusters ($n = 2 - 7$) and elucidated the results with a view to understand how chemical bonding influences the stability and structure of small size $Au$ clusters. This work is divided into two parts: (i) the equilibrium structures and stability of $Al$ doped $Au_{n-1}$ clusters ($n = 2 - 7, 21$) and (ii) the interaction of $O_2$ with stable clusters. The optimized geometries of $Au_{n-1}Al$ clusters indicate that the substitution of $Au$ by $Al$ results an early onset of three-dimensional structures from tetramer onwards. The stability of $Au_{n-1}Al$ clusters has been analyzed based on the binding energy, second difference in energy, and the energy gaps between the highest occupied and lowest unoccupied molecular orbital energy levels. Based on the energetics, $Au_2Al$ and $Au_5Al$ clusters are found to be extraordinary stable. The oxidation of $Au_{n-1}Al$ clusters undergoes via dissociative mechanism, albeit significant charge transfer from $Al$ to $Au$. Moreover, the $O_2$ molecule prefers to attach at the $Al$ site rather than at the $Au$ site.

On the basis of the above results it is envisaged that it will be of interest to investigate
the CO oxidation behavior of Au – Al nano-composites. Al – Au nano-composites in three
different size ranges; (i) a small cluster Al₆Au₈, (ii) a mid-sized cluster Al₁₃Au₄₂, and (iii) a
periodic slab of Au(111) surface, where the Au atoms in the second layer is substituted by
Al atoms have been modelled. While the Al₆Au₈ forms a cage like structure with both the Au
and Al atoms on the surface of the cage, Al₁₃Au₄₂ forms core-shell type symmetric
icosahedral structure. For the Al substituted Au(111) surface, the ionic relaxation results in
compression between the interlayer separations. The charge distribution analysis suggests
that in all cases Al atoms donate electronic charges to the Au atoms. This has been
corroborated by the red shift in the density of states spectrum, a signature of more negative
charge state whence a higher chemical reactivity. The CO oxidation on these nano-composite
systems was investigated through both Eley -Rideal (E-R) and Langmuir Hinshelwood (L-H)
mechanism. The interaction of O₂ molecule with these systems occurs non-dissociative way
with elongation of the O – O bond. Further interaction with CO molecule leads to the
formation of CO₂ spontaneously. On contrary, the CO₂ evolution by co-adsorption of O₂ and
CO molecules undergoes through an intermediate complex of higher energy. On the basis of
the results it is inferred that the efficient CO oxidation of the Al – Au nanocomposite is due
to negatively charged surface Au atoms.

Chapter 6:

The pioneering work of Haruta et al.⁸⁸,⁹,¹⁰ which showed low temperature CO
oxidation of supported Au clusters has resulted in the surge of theoretical and experimental
studies to understand the mechanism of CO oxidation on these deposited clusters. Motivated
by these studies, we have carried out a systematic study on the adsorption of Auₙₙ (n = 1 – 6)
clusters on a regular α – Al₂O₃ (0001) surface. The results have been divided into four major
sections (i) Ground state geometries of the adsorbed Auₙₙ clusters (ii) Energetics of
adsorption as a function of cluster size (iii) Charge transfer analysis and the resultant
electronic structure changes of the adsorbed $Au_n$ clusters and (iv) interaction of $Au_2$ cluster adsorbed on $Al_2O_3$ with $O_2$. The above results are compared with neutral and anionic $Au_n$ clusters at the appropriate context. The results reveal a considerable resemblance of the deposited $Au_n$ with their gas phase anionic counter parts. The adsorption energies of $Au_n$ clusters showed strong odd-even variations on $Al_2O_3$ surface, with local maxima at $n = 2, 4, 6$ which are established to be stable by both experiment and theory. A qualitative understanding of the nature of the bonding characteristics was obtained by the charge difference analysis. Further, a red shift of the Fermi energy levels of the deposited $Au/Al_2O_3$ surface when compared to the $Au_n$ was observed. Upon adsorption, $O_2$ is observed to strongly interact with deposited $Au_2$ cluster molecularly with an elongated $O − O$ bond. This activated $O_2$ molecule is expected to facilitate the oxidation of $CO$.

**Chapter 7:**

This chapter consists of conclusions and future directions. This gives a brief outline about the possible outcomes and future directions that can be charted out from the present studies on designing new materials for catalysis applications, which have been discussed in the present work.

**References:**


