Chapter 1

Introduction

1.1 Clusters

The famous talk entitled "There's Plenty of Room at the Bottom", presented by Richard Feynman to the American Physical Society in Pasadena on December 1959 focussed on the wide range of possibilities of manipulation at the atomistic level. His talk is considered to be a groundbreaking event in the history of nanoscience. In the early 1960s, F. A. Cotton coined the term 'cluster' to define aggregates of three to several hundreds of thousands atoms or molecules with interactions ranging from very weak van der Waals contacts to strong ionic bonds. Nowadays, in a broader purport, aggregates with two to several hundreds of thousands entities are defined within the realm of clusters. Clusters form an intermediate state between atomic and bulk size regime. This is depicted in Figure 1.1. In addition, they serve as a bridge among various disciplines by combining ideas of atomic, molecular, and condensed matter and nuclear physics as well as among physical, organic, and analytical chemistry [1,2]. The earliest investigations on clusters by
Rayleigh recognized that the colour of stained glasses was due to the scattering of light by small metal particles embedded in the glass [3]. The independent works of Bentley [4] and Henkes [5] in 1961 detected jet-generated clusters of carbon dioxide using mass spectrometers which marks the beginning of the modern era of cluster science. In the following years, field of cluster science gained momentum with the development of new experimental sources for production of clusters [6-10]. In 1974, Prof. Norio Taniguchi coined the term nano-technology to describe semiconductor processes such as thin film deposition and ion beam milling exhibiting characteristic control on the order of a nanometer.

The physical and chemical properties of clusters differ significantly from their bulk counterparts. The size-dependent specificity and selectivity of their physical and chemical properties or in other words, the ability to modify the cluster properties by changing the size of the system, one at a time, makes them particularly interesting. Delocalization of electrons in bulk metals which imbue them with high electrical and thermal conductivity, light reflectivity and mechanical ductility may be wholly or partially absent in metal nanoclusters, while new properties develop in them [12]. Metal clusters have lower melting point compared to the corresponding bulk material. The unique relationship of cluster properties with the size has been attributed to physical aspects such as high surface to volume ratio, quantum size effects etc. The increased surface to volume ratio in clusters compared to the bulk materials enhances their reactivity towards reactions occurring on the surfaces. Moreover, the low-coordinated atoms present in the surface of clusters have a tendency to form additional bonds with ligands which impart extra stability to clusters. Within the realm of the nanoscale, the electronic nature of the clusters
differs considerably from the macroscopic particles and quantization effects due to confinement of the electron movement appear. This leads to discrete energy levels intrinsic to every cluster size which can be modelled by quantum mechanical treatment of a particle in a box. The phenomenon is defined as quantum size effect that leads to new electronic properties in metal clusters.

Clusters find wide range of applications that include photonic devices [13,14], electronic devices [15,16], ultrasensitive biological detection and fluorescent biological imaging [17,18]. Thus, clusters form one of the most fascinating materials and the interest in cluster science to identify potent applications in different areas is ever increasing with the improvements in experimental techniques and computational tools.

1.1.1 Types of Clusters

Clusters can be classified according to the constituents in the aggregate and the nature of bonding present in the cluster which can be ionic, covalent, metallic, van der Waals etc. Table 1.1 summarizes the various cluster types according to the nature of bonding [11]. According to the nature of the constituents, clusters can be classified as:

*Homo-atomic (or Homo-molecular) clusters:* Clusters with identical constituent atoms/molecules. Example: \( \text{Au}_n \), \((\text{H}_2\text{O})_n\) \((n\) is the number of atoms/molecules).

*Hetero-atomic (or Hetero-molecular) clusters:* Clusters with two or more different constituents. Example: \( \text{Pd}_n\text{Pt}_m\) \((n\) and \(m\) are the number of atoms). Figure 1.2 shows some of the cluster types.

![Figure 1.2: Examples of different clusters](image-url)
**Table 1.1:** Classification of clusters according to the nature of bonding

<table>
<thead>
<tr>
<th>Type</th>
<th>Example</th>
<th>Nature of Binding</th>
<th>Binding Energy/Mole (kcal)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ionic Clusters</td>
<td>(NaCl)$_n$, (CsI)$_n$</td>
<td>Ionic Bonds</td>
<td>~ 50 – 100 (Strong Binding)</td>
</tr>
<tr>
<td>Covalent Clusters</td>
<td>C$_{60}$, Si$_n$</td>
<td>Covalent Bonding (Strong Binding)</td>
<td>~ 20 – 100</td>
</tr>
<tr>
<td>Metal Clusters</td>
<td>Na$_n$, Fe$_n$, Au$_n$</td>
<td>Metallic Bonding</td>
<td>~ 10 – 50 (Moderate to Strong Binding)</td>
</tr>
<tr>
<td>Molecular Clusters</td>
<td>(H$_2$O)$_n$</td>
<td>Molecular interactions, hydrogen bonding, Van der Waals, etc.</td>
<td>&lt; 10</td>
</tr>
<tr>
<td>Van der Waals</td>
<td>Ar$_n$, Xe$_n$</td>
<td>Polarization Effects (Weak bindings)</td>
<td>&lt; 5</td>
</tr>
</tbody>
</table>

**1.2 Gold Clusters**

Gold has fascinated mankind since ages. It finds widespread consumption in jewellery across the world owing to its excellent properties that it does not tarnish on exposure to atmosphere and retains its beautiful lustre undiminished for years.
Its resistance to oxidation and corrosion in air as well as its chemical inertness towards various reactions contributes largely to the noble behaviour of gold.

What makes gold particularly very interesting is the fact that the most noble metal losses its nobility to become one of the excellent catalyst for reactions such as low temperature CO oxidation, direct formation of hydrogen peroxide etc, when the size is reduced to nano dimension. The use of nanogold dates back to ancient ages and the most famous example is the Lycurgus Cup which was manufactured in the 5th to 4th century B.C and is now exhibited in the British Museum. It is ruby red in transmitted light and green in reflected light, due to the presence of gold particles [20]. In the Vedic period of ancient India, gold containing ashes (gold bhasma) was prepared for medicinal purposes by usually secret recipes [21]. In 1857, the legendary work of Michael Faraday [22] on the formation of deep red solutions of colloidal gold by reduction of an aqueous solution of chloroaurate (AuCl$_4^-$) using phosphorus was the first scientific investigation on finely divided gold. Since then, synthesis and application of gold nanoparticles in fields such as biological labelling, optical and electronic devices etc have been steadily growing. In addition, very large relativistic effects and the presence of aurophilic interactions, makes gold unique compared to the other coinage metal counterparts. These effects are discussed in the following sections.

### 1.2.1 Aurophilicity

Aurophilicity or Aurophilic Interactions play a central role in the area of gold chemistry [23,24]. The terms, introduced in 1987 by Schmidbaur, is used to describe various kinds of Au-Au interactions within and between gold compounds [25]. Aurophilic interactions are cohesive interactions occurring among formally closed shell gold atoms (Au$^+$ centres with 5d$^{10}$ configuration) inside a molecule, or between such atoms in different molecules. These interactions are characterized by metal-metal distances shorter (2.7-3 Å) than the sum of two van der Waals radii (3.7 Å) and that the bond energy is usually small but higher than the energy of standard van der Waals contacts. An outcome of aurophilicity is that several gold atoms can assemble in polynuclear gold species resulting in dimers, oligomers or infinite two-dimensional sheets. Temperature dependent NMR spectroscopy mea-
surement of the strength of interaction between per Au pair of atoms is observed in the range of 29-46 kJmol$^{-1}$, comparable to hydrogen bond [26] and such interactions has been suggested to be intermediate between conventional covalent/ionic and van der Waals interactions [27]. The behaviour of aurophilic interaction varies as a function of R$^{-6}$ at large distances which provide evidence for the dispersion character of these interactions [28]. Aurophilic interactions can coexist with other kind of bonding such as covalent bonding [29] and hydrogen bonding [30]. Theoretical studies have indicated that when an aurophilic attraction is present, the hydrogen bonding losses strength and directionality to retain the gold-gold interaction [31]. From a theoretical point of view, the aurophilic interaction has been attributed to electron-correlation strengthened by relativistic effects rather than classical theory of chemical bonding [26,32,33].

1.2.2 Relativistic Effects

The unique chemistry of gold has been largely attributed to the impact of large relativistic effects (larger than any other element with Z<100). Relativistic effects occur due to the high speeds of all electrons when they move near a heavy nucleus and as a consequence of relativity, will lead to an increase in mass. This mass increase results in radial contraction observed predominantly in case of s and p orbitals. Thus, contraction of these orbitals leads to a stronger screening of the nuclear attraction, and consequently destabilization and expansion of d and f orbitals. The relativistic effects scale roughly as $Z^2$ (Z is the full nuclear charge), thus becoming more important in the heavier elements. Large relativistic effects in gold accounts for the differences in properties between gold and the other coinage metals, most notably silver. Schmidbaur and co-workers established the smaller size of Au(I) compared to Ag(I) [34,35]. The high electron affinity of gold relative to silver and the existence of aurides (eg, Cs$^+$Au$^-$) which are non-metallic semiconductors have been attributed to relativistic effects [36]. Moreover, these effects are responsible for much higher first ionization potential of gold than silver (IP1 for Au 9.225 eV, IP1 for Ag 7.576 eV) [37]. The tighter binding of the s electron of gold accounts for higher cohesion energy of gold metal and higher melting point. The yellow colour of gold (absorption beginning at 2.38 eV) associated with tran-
sitions from the 5d orbital to the Fermi level (largely 6s in character) results from
the raising of the Au 5d orbital and the lowering of the valence 6s orbital unlike
absorption observed in the ultraviolet region in case of silver [38]. Over the years,
impact of relativistic effect on the chemistry of gold has been studied in detail
[39-42].

1.2.3 Structure of Gold Clusters

A unique feature of gold clusters is the presence of relativistic effect which induces s-d hybridization by reducing the 6s-5d energy gap thereby making gold clusters
strikingly different from Cu and Ag counterparts. Thus, investigating the structure
of gold clusters has been an interesting aspect of both experimental [43-50] and
theoretical studies [51-57]. For neutral and anionic Au clusters, the transition
from planar to three dimensional structure has been observed in the size range
n=11-14 [58-63]. The crossover size in case of neutral gold clusters is constantly
debated by different groups and no definite consensus has been achieved. Li et
al. [58] studied the structure and stability of Au clusters with up to 14 atoms
using DFT and suggested that the transition from planar to 3D structure for
neutral gold clusters occur at Au_{12}. However, Deka et al. [59] indicated the lowest
energy structures to be planar till Au_{13} in their study on Au clusters with 2-13
atoms using DFT. In a recent study by Johansson et al. [61], the transition for
neutral Au clusters was suggested to occur at Au_{11} (Figure 1.3) from the global
optimizations of Au_n, n = 9 – 13 clusters using a genetic algorithm and a meta-
generalized density functional theory. On the other hand, Assadollahzadeha and
Schwerdtfeger [62] observed Au_{14} to be the first cluster size where 3D structure is
the global minimum.

Unlike neutral Au clusters, the transition from 2D to 3D structure for anionic
clusters has been suggested to occur at Au_{12} by different studies. Häkkinen et
al. [63] observed the 2D to 3D transition for anionic gold clusters at n = 12
from combined experimental and theoretical investigation in agreement with ion
mobility measurements conducted earlier [64]. For cationic clusters, planarity was
retained till n = 7 and three dimensional structures form at Au^{+}_{7} as revealed from
ion mobility and density functional calculations [65]. In agreement with the above
Figure 1.3: Optimized TPSS/7s5p3d1f structures of the lowest energy 2D and 3D isomers of Au$_{11}$ [61].

Figure 1.4: Ground state geometry of Au$_{19}$ and Au$_{20}$ [71].

observations, Madsen and co-workers [66] observed 2D-3D transition at n=8 and n=12, respectively for cationic and anionic Au clusters from density functional calculations using meta-GGA functional. Johansson et al. [61] also observed the 2D-3D crossover for cationic and anionic clusters at Au$_8^+$ and Au$_{12}^-$, respectively.

On moving to the higher clusters, it has been observed that the structure of gold clusters undergo transition to flat-cage structures observed for Au$_{15}$, Au$_{16}$ while spherical hollow cage structures have been found to dominate in case of Au$_{17}$, Au$_{18}$ [52,67-69]. This transition from flat cage to hollow cage structure has been suggested to take place at Au$_{17}$ for neutral clusters and at Au$_{16}^-$ for anionic clusters. Studies have shown that Au$_{19}$ and Au$_{20}$ possess pyramidal structures with Au$_{20}$ having a tetrahedral symmetry. Au$_{19}$ differs from Au$_{20}$ by a single missing vertex atom of the tetrahedron and has C$_{3v}$ symmetry (Figure 1.4). The symmetries of both the clusters have been found to same in the anionic counterparts [70-73].

Structural transition from pyramidal to hollow tubular type has been observed in Au$_{24}^-$ and further to compact core-shell structure at Au$_{25}^-$ (Figure 1.5)[74]. For clusters larger than Au$_{25}^-$, experiments in conjugation with theoretical investigation
have indicated low-symmetry core-shell structures as the global minimum with the number of core atoms increasing as the cluster size increases [75]. Jalbout et al. [76] have suggested higher stability of low symmetry (disordered) isomers for Au$_{32}^-$ unlike the most stable cage structure as proposed by others [75,77]. It was observed that Au$_{32}^-$ possess a three-atom triangular core while Au$_{33}^-$ to Au$_{35}^-$ and Au$_{36}^-$ to Au$_{38}^-$ possess a four-atom tetrahedral core [75,78]. Cage like structure has also been identified as the global minimum for neutral Au clusters [79,80].

![Figure 1.5: Compact core shell of Au$_{25}^-$ [74]](image)

### 1.2.4 Magic Number Clusters

One key concept in the field of cluster science is the magic number clusters which was originally introduced in alkali metal clusters with (ns)$^1$ configuration [81]. The electronic magic-number clusters are near-spherical metal clusters with specific number of valence electrons, e.g., 8, 18, 20, 34, 40, 58, ..., and are very robust because of their closed electronic shells. These clusters possess high stability and much higher abundance in mass spectrometric studies than other sizes of metal clusters. The electronic magic-number clusters typically have much larger HOMO-LUMO gap than their neighbouring-size clusters. The highly symmetric clusters such as those clusters with icosahedral symmetry may be viewed as geometric magic-number clusters [82]. It has been established that magic number gold clusters are obtained when the number of valence electrons is equal to or near the value of 2, 8, 18, 32, 50, ... that stabilizes the spherical structures. The magic gold clusters have been studied using experimental techniques as well as theoretical methods [83,84]. Au$_{20}$ is a near-double magic cluster with a large HOMO-LUMO gap and a highly symmetric tetrahedral structure [85] while among the medium sized gold clusters, the electronic magic cluster Au$_{34}$ has a large HOMO-LUMO gap but a low symmetry structure [45].
1.3 Adsorption of small molecules on gold clusters

1.3.1 Adsorption of O$_2$ and CO on gas phase gold clusters

The exceptional catalytic activity of gold at the nanoscale regime prompted interest in understanding the chemical reactivity of gas-phase gold clusters towards adsorption of various molecules. CO oxidation is one of the most extensively studied reactions in which gold clusters exhibit excellent catalytic activity. Among the various factors affecting the catalytic activity, adsorption of CO and O$_2$ on gold clusters is one of the key issues and has been a subject of numerous experimental and theoretical investigations. An oft-studied process is the variation of the adsorption behaviour of O$_2$ with the number of electrons in the host gold cluster and consequently its activation which is essential for CO oxidation. This is apparent from the large number of experimental [86-91] and theoretical [92-101] studies on O$_2$ adsorption on gold clusters. Salisbury et al. [86] investigated the adsorption-desorption equilibria of di-oxygen (O$_2$) on gold cluster anions (Au$_N^-$, N=2-22) in the high-pressure limit by pulsed flow-reactor methods at ambient temperature. They observed measurable adsorption of single O$_2$ molecule for certain clusters (N= 2, 4, 6, 8, 10, 12, 14, 18, 20). Their results suggested that O$_2$ acts as a single electron acceptor yielding adsorbed superoxide (O$_2^-$) species. However, from density functional calculations, Metiu and co-workers [92] observed binding of the second O$_2$ molecule to clusters with odd number of electrons with binding energy lower than the first O$_2$ molecule. The anionic gold clusters with odd number of electrons bind O$_2$ more strongly than neutral clusters with odd number of electrons and clusters with even number of electrons. The effect of surface roughness on the binding of O$_2$ on Au clusters and Au(111) surface was studied by Mills et al. [93] using DFT. From the calculations, they observed that O$_2$ does not bind to a flat facet while roughening of the Au(111) surface by depositing Au clusters, leads to binding. Localization of the HOMO in clusters and in rough surfaces provides higher electron density at site where O$_2$ binds; thus facilitates the charge transfer to the $\pi^*$ of O$_2$. Over the years, exploring the adsorption characteristics
of O₂ remains an interesting topic of research. Boronat and Corma [97] considered different conformations for O₂ adsorption on extended gold surfaces, isolated gold nanoparticles and small gold clusters supported on TiO₂ and concluded that the mode of O₂ adsorption and its activation does not depend on particle size but on particle morphology. They suggested that the dissociation of O₂ depends on the arrangement of gold surface atoms. For Au/TiO₂ catalysts, it was observed that O₂ preferentially adsorbed on the metal-support interface rather than the gold particles and are the most active sites for O₂ dissociation (Figure 1.6).

Figure 1.6: Optimized structures of O₂ adsorption complex on metal-support interface [97].

On the basis of density functional calculations, Roldán et al. [98] suggested that the presence of charge has a small effect on the bond strength and activation of O₂ for up to about 20-25 atoms. While for larger clusters such as Au₅₅ and Au₇₉ considered in their work, it was observed that the nuclearity and the shape of the gold cluster are much more important than the charge state, such that bond strengths and activation modes are independent of their charge. Larger nanoparticles with more than 30 atoms consist of positively charged core and a negatively charged shell and were found to simultaneously activate several oxygen molecules owing to the negative charge on the surface [99]. Sun et al. [100] proposed that atomic oxygen prefers multifold hole sites on gold surfaces and forms the most stable linear O – Au – O structure which accounts for the observed high diffusion barrier of an oxygen atom. Spectroscopic evidence for the formation of a superoxo species bound to a formally cationic gold cluster as a result of charge-transfer complex in odd sized AuₙO₂ (n=7,9,11,21) was presented by Woodham et al. [91]. DFT calculations indicated that the charge transfer induces significant rearrangement of the gold cluster such that it more closely resembles the structure of the cation. Thus, they suggested that structural flexibility plays an important role for oxygen activation by small gold particles.
The adsorption behaviour of CO on gold clusters has been another important issue of experimental [102-105] and theoretical [106-114] investigations. The CO adsorption is affected by the cluster charge as reflected from the study by Wu et al. [106] where they observed stronger CO adsorption on cationic clusters than on neutral and anionic counterparts. Neumaier et al. [103] studied room temperature CO adsorption on isolated gold cluster cations (Au^+_N, 1<N<66) in a Fourier transform ion cyclotron resonance mass spectrometer. The binding energies were found to decrease with increasing cluster size and at cluster sizes beyond 30 atoms, CO binding energies appeared to approach those found for gold single-crystal surfaces. The decreasing bond energy was attributed to the increasingly "diluted" charge in the metal particle. CO binding to Au atoms with low coordination number of two or three in the head-on fashion has been characterized as the most stable isomer.

2D-3D transition of gold clusters as a result of CO binding was reported by Li and co-workers [108] where they showed that on adsorption of two CO molecules, the planar structure of Au^+_4 is no longer retained; thus signifying a 2D-3D transition. Moreover, DFT based molecular dynamics calculations by Manzoor et al. [109] shed light on the effect of cluster charge and ligand on the temperature behaviour of Au_6 cluster. Their simulations revealed that the neutral cluster is stable up to much higher temperature (1100 K) compared to charged clusters (500 K). Higher stability of the neutral cluster has been attributed to enhanced s-d hybridization, higher HOMO-LUMO energy gap and the bonding of the negatively charged inner triangle atoms to the positively charged outer atoms. Their work demonstrated that on chemisorption of CO, the neutral and anionic ground state conformations are stable up to nearly 800K whereas the cationic counterpart collapses at room temperature.

Thus, the charge state, cluster size and presence of specific low coordination binding sites in gold clusters are some of the factors that have been identified on which the adsorption of O_2 and CO depends as revealed by the various experimental and theoretical studies. Presence of supports such as metal oxides, zeolites etc. might alter the adsorption behaviour and has been a subject of investigations. Moreover, the presence of moisture in practical catalytic systems can also affect the adsorption of O_2 and CO and in turn influence the catalytic properties of
supported gold clusters.

1.3.2 Adsorption of O$_2$ and CO on supported gold clusters

One of the rudimentary processes in understanding the catalytic activity of supported gold clusters towards CO oxidation is the adsorption of O$_2$ and CO on these catalysts and activation of O$_2$ is an essential step in CO oxidation. Thus, various experimental [115-119] and theoretical [97,120-126] studies have been made on O$_2$ adsorption on supported gold clusters. Stiehl et al. [115] provided evidence for the presence of molecularly chemisorbed O$_2$ on both TiO$_2$(110) supported gold clusters and Au(111) using thermal desorption (TDS), adsorption/reaction-induced desorption and collision-induced desorption (CID). It was observed that O$_2$ adsorbs much more readily on Au particles than on the Au(111) surface possibly due to the higher concentration of low coordinated sites in the former. From DFT calculations, Rasmussen et al. [120] suggested that the adsorption of O$_2$ on reduced rutile surface was possible only in the presence of bridging oxygen vacancies unlike on stoichiometric rutile TiO$_2$(110) surface where adsorption was observed to be endothermic. Molina and Hammer [121] observed weaker binding of O$_2$ and lesser charge transfer on Au$_6$ cluster supported at a MgO-F$^+$ centre compared to free anionic Au$_6$.

Adsorption of CO on various supported gold clusters has also been investigated by both experimental [127-130] and theoretical [131-136] studies. Gates and co-workers [128] provided the first evidence of Au$^0$(CO)$_3$ species present on the low-coordinated zerovalent Au atoms at the surface of zeolite supported gold nanoclusters from IR data. The sample initially prepared by them consisted of mononuclear gold complexes in zeolite NaY and observed the formation of zero-valent gold nanoparticles during CO treatment. Three new $\nu_{\text{CO}}$ bands were observed during CO treatment; characteristic of Au$^0$-carbonyls and have been assigned to Au$^0$(CO)$_3$ species. Using quantum mechanics/molecular mechanics method, Thomson and co-workers [131] reported favourable adsorption of CO on the Au clusters in TS-1 but the adsorption energies are weakly dependent on the cluster size and on the TS-1 site. Activation of the C-O bond as indicated by the red-shift in CO vibrational frequency results from the electron back-donation.
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into antibonding orbital in CO. The charge transfer mechanism as proposed by the authors involves first losing of electron density by the TS-1 framework to the adsorbed Au clusters. This excess negative charge on the clusters is then donated to the antibonding CO orbital upon its adsorption. Sierraalta et al. [132] studied the interaction of CO molecule with Au-exchanged mordenite catalysts, Au/MOR using hybrid quantum mechanics/molecular mechanics method. It was perceived from their study that the position of Al in the mordenite affects the degree of the back bonding between Au$^+$ and the CO molecule such that different $\nu_{\text{CO}}$ are obtained for CO adsorbed on Au at sites T1 and T4. Moreover, for Au-T1 site, the CO adsorption energy was observed to be slightly greater than for the Au-T4 site because of the stronger overlap between the Au and the CO orbitals. Deka et al. [133] studied the adsorption of CO on gas phase and faujasite supported gold monomer in three oxidation states 0, +1 and +3 using DFT. They observed an increase in CO binding energy in gas phase monomer with increase in Au oxidation state. The calculations revealed red-shift in CO vibrational frequency for AuCO and Au$^{3+}$CO complex while blue-shift for Au$^+$CO. In case of supported clusters, CO facilitated stronger interaction of gold with the support which increased with oxidation state. The strongest binding of CO to the gold monomer was observed in the +1 oxidation state and $\nu_{\text{CO}}$ value increases with increasing Au oxidation state.

The studies so far reported thus imply that with sufficient charge transfer, activation of O$_2$ to superoxo state (O$_2^-$) is observed, and O$_2$ preferentially adsorbs on the metal-support interface rather than the gold particles. On zeolite supported gold clusters, red-shift in $\nu_{\text{CO}}$ value was observed that indicates CO activation and CO adsorption energy increases with Au oxidation state. Both CO and O$_2$ prefer low coordination sites of Au clusters for adsorption.

1.3.3 Effect of water on CO and O$_2$ adsorption

The presence of moisture is inevitable in practical catalytic systems such as supported gold clusters and can affect the adsorption of O$_2$ and CO on such catalytic systems; in turn, altering their catalytic activity towards CO oxidation. Various studies have investigated the co-adsorption of O$_2$/CO and H$_2$O or the effect of pre-
adsorbed water on adsorption of O₂ and CO [137-146]. Gao et al. [139] suggested that the promotional effect of water on the catalytic activity of TiO₂ supported Au particles is mainly due to activation of molecular oxygen rather than carbonate decomposition. It was suggested that the binding energy of CO decrease in presence of water. DFT calculations by Zhang and Lindan [140] on the co-adsorption of water and oxygen on the TiO₂ (110) surface indicated enhancement in water binding in presence of co-adsorbed O and a new feasible path for water dissociation was observed. First-principle investigations by Bongiorno and Landman [142] revealed a significant enhancement of the binding and activation of O₂ resulting from the co-adsorption of O₂ and water on small Au clusters (Au₈) supported on defect-free MgO(100), as well as on gas-phase neutral clusters (Au₈ and Au₃₀). The water enhanced activity of gold clusters towards CO oxidation has been attributed to the formation of a complex which involves partial sharing of a proton between the co-adsorbed molecules resulting in a hydroperoxyl-like intermediate. The O-O bond is observed to be highly activated in this complex attaining bond length values characteristic of superoxo or peroxo like states. Reaction with a gaseous CO molecule either via Eley-Rideal or Langmuir-Hinshelwood mechanism (depending on the adsorption site) involved low reaction barriers. Su et al. [143] studied the effect of water on the adsorption of O₂, O, CO, dissociation of O₂ and CO oxidation on the Ag(111) and Au(111) surfaces using density functional theory. For the co-adsorption of H₂O and atomic oxygen, significant stabilization with respect to the adsorption of atomic oxygen was observed in presence of water. Strong lateral interaction between water and atomic oxygen on both Ag(111) and Au(111) surfaces has been attributed to the formation of the H bonds and the charge transfer from H₂O to the atomic O mediated through the substrate. For the co-adsorption of H₂O and O₂, the stabilization of the adsorbates has been attributed to the charge transfer mediated through the substrate rather than H bonding interaction which was found to be modest. For H₂O and CO co-adsorption, they observed moderate stabilization of the adsorbates as compared to O₂ and atomic O. Recently, Ito et al. [145] demonstrated the enhancement in the adsorption of CO and O₂ molecules on gold dimer cation, Au₂⁺ due to pre-adsorption of a H₂O molecule using tandem mass spectrometry and ion trap methods. They observed adsorption
of up to two \( O_2 \) molecules in presence of pre-adsorbed \( H_2O \) and has attributed the enhancement effect to partial electron transfer from O atom in \( H_2O \) to \( Au^+ \).

1.4 Catalysis By Gold

Traditionally, gold is viewed as an element of beauty and wealth and has been appreciated for its luster, malleability and nonreactivity and noncorrosive durability. The earliest report on the use of gold as a catalyst dates back to 1906 when Au gauzes were reported as catalysts for \( H_2 \) oxidation [147]. The work of Bone and Andrew [148] in 1925 is one of the earliest reference where Au has been reported as catalyst for CO oxidation. Years later, Huber et al. [149] in 1977 reported CO oxidation on Au atom based model and attempted to interrelate the results with actual heterogeneous oxidations of CO to \( CO_2 \). In the subsequent years, pioneering work by Haruta et al. [150,151] on low temperature CO oxidation opened up new dimension towards catalytic activity of supported gold clusters. Their work showed that ultrafine gold particles dispersed on transition metal oxides were highly active for CO oxidation at temperatures as low as \(-70^\circ C \). The catalytic activity has been attributed to cluster size [152-154] of gold particles. Apart from this, morphology [155], site-specificity [156,157] and electronic state [158-160] of gold clusters are identified as other physicochemical parameters which contribute to the activity of gold. A striking difference of small particles of gold from the bulk is the presence of low coordination atoms [161] and the adoption of geometries which lead to more reactive electronic structures [162]. Thus, catalytic properties of gold nanoparticles can be attributed partly to their geometric structures [163]. In case of supported gold clusters, modification of the electronic properties by the support has been considered as an important factor [150,164,165]. A focus on all the above mentioned factors and the important features in gold catalysis has been well documented [166,167].

1.4.1 Bare gold clusters in CO oxidation

The sensational catalytic performance of bare gold clusters for CO oxidation has been a subject of a number of experimental [168-170] studies. Using pulsed flow
reactor and mass spectrometric techniques, Wallace and Whetten [168] observed cooperative co-adsorption of CO and O$_2$ on anionic gold clusters in the gas phase, Au$_n^-$. Under CO and O$_2$ co-adsorption conditions, the new peaks that arise in the mass spectrum of Au$_6^-$ has been attributed to CO$_2$ and it is found that Au$_6^-$ is capable of oxidizing CO at 100 times higher rate than reported for commercial or model gold catalysts. The evidence for low temperature catalytic oxidation of CO by Au$_2^-$ was provided from the combined experimental and theoretical study of Landman and co-workers [169].

Density functional theory based studies [171-177] have played an important role in the exploration of underlying facts and understanding the mechanism involved in CO oxidation on gold clusters. The catalytic activity of a single gold atom has been demonstrated by Fang et al. [171] at the CCSD(T)/aug-cc-pVTZ//mPW2PLYP/aug-cc-pVTZ level of theory. They observed a barrier of 4.8 kcal mol$^{-1}$ at 0K for the first oxidation step and 1.6 kcal mol$^{-1}$ for the second step. An associative mechanism was observed to be more favourable for CO oxidation while breaking of the O-O bond (dissociative mechanism) involves a very high energy barrier of 68.8 kcal mol$^{-1}$. Häkkinen and Landman [172] identified di-gold-carbonate as the key intermediate in CO oxidation on Au$_2^-$ from the density functional calculations. Reaction of a CO molecule with this intermediate Au$_2$CO$_3^-$ produces two CO$_2$ molecules simultaneously and an activation barrier of 0.5 eV was identified. On subnanometer Au$_{16}$-Au$_{35}$ clusters, Gao et al. [173] observed stronger adsorption of O$_2$ as well as the co-adsorption of CO and O$_2$ in the anionic clusters and consequently lower reaction barrier as compared to the neutral counterparts. Relatively small cone angle (<110°) associated with each surface site has been identified as another important geometric indicator of relatively strong adsorption strength of CO or O$_2$. To provide an insight into the catalytic activity of large-sized nanoclusters, Tang and Hu [174] studied the charge and spin state effect on the catalytic activity of Au$_{55}$ towards CO oxidation. The formation of a peroxo-type (OOCO) intermediate was predicted as the rate limiting step in the Langmuir-Hinshelwood mechanism and the catalytic activity of the anionic cluster was better than the neutral and cationic counterparts. However, the triplet pathway involved lower barriers than the singlet pathway in case of
Au\textsubscript{55}. DFT study on three decahedral Au clusters (Au\textsubscript{75}, Au\textsubscript{101} and Au\textsubscript{146}) by Liu et al. [175] included the effect of an external electric field on their catalytic activity. Au\textsubscript{75} corresponds to the moderate stable structure while Au\textsubscript{146} is the most stable. Their work showed that looser binding of the reactants could benefit for catalyzing CO oxidation. Among the three clusters, Au\textsubscript{75} performs the best in this catalytic reaction due to the weakest adsorption capacity and the large activation barriers in the higher clusters. A moderate intensity negative field balances between exothermic adsorption and low activation energy; thus making it a better option. With the advancement in computational methods and experimental techniques, the urge to study the catalytic properties of gold clusters ranging in size from small to large clusters continues so as to obtain an improved realistic catalyst.

1.4.2 Supported gold clusters in CO oxidation

Gold clusters supported on various transition metal oxides and zeolites have been recognized as exceptionally active catalysts for low temperature CO oxidation. The major breakthrough in understanding the catalytic activity of supported gold clusters originated with the work of Haruta et al. [150,151] on 3d-transition metal oxide supported ultra-fine gold particles. Since then, the activity of gold clusters supported on various oxides towards CO oxidation has been studied with different experimental techniques [178-185]. Among the various factors such as particle shape, nature of support etc. on which the catalytic activity of Au nanoparticles for CO oxidation depends, particular emphasis has been laid on the size of Au clusters. A marked increase in the catalytic activity of supported Au clusters was observed when the diameter of the Au clusters is decreased below \(\sim3.5\) nm. However, a further decrease in the cluster diameter to below \(\sim3\) nm decreases the catalytic efficiency [185]. Aguilar-Guerrero and Gates [178] observed the initially synthesized mononuclear cationic gold species on CeO\textsubscript{2} to be slightly active as a catalyst for CO oxidation. But after a short period of operation, the catalyst underwent activation to form clusters as small as Au\textsubscript{6}, on average, and was inferred to be non-metallic. Their work proposed better catalytic activity of the clusters, at least on the CeO\textsubscript{2} support. Gold octamer cluster Au\textsubscript{8} supported on defect
rich MgO(001) has been identified as the smallest cluster to catalyze the low
temperature CO oxidation to CO$_2$. The catalytic activity has been attributed to
the charging of the metal cluster caused by partial transfer of charge from the
substrate oxygen vacancy F-centre defect into the deposited cluster. On the other
hand, the same cluster bound to a MgO surface without oxygen vacancy has been
found to be catalytically inert for CO oxidation [180,181].

Over the years, density functional theory based calculations have helped in
understanding the various factors influencing the catalytic activity of supported
gold catalysts such as the importance of low coordinated sites [186-188], size and
shape of supported gold clusters [189], role of oxide support [190-193], perimeter
sites [194], oxidation state of Au [195] etc. The urge to investigate the catalytic
activity of various gold-based catalysts supported on different metal oxides con-
tinues and everyday new research has been focused in developing such catalysts.

1.4.3 Zeolite supported gold clusters

1.4.3.1 Zeolites-Structure and Property

An appealing and unique class of host materials with well-defined cavities and
channels is zeolites which bestow them with excellent shape- and size-selectivity
property. Zeolites are crystalline aluminosilicates with the general composition

$$M^{n+}_{x/n}[(AlO_2)_x(SiO_2)_y]zH_2O$$

where $M^{n+}$ is a cation with charge $n+$ and $x$, $y$, $z$ are numbers [196]. The
term zeolite, originally coined by Swedish mineralogist Axel Fredrik Cronstedt in
1756 means boiling stone. These porous crystalline materials are composed of SiO$_4$
and AlO$_4$ tetrahedra which combine in a variety of ways to give rise to different
structures. When twenty-four primary building blocks, SiO$_4$ and AlO$_4$ arrange to
form a truncated octahedron, the resulting secondary building block is known as
sodalite cage (Figure 1.7).

In faujasite zeolites, each sodalite cage is connected to four other sodalite cages
and each connecting unit is six bridging oxygen ions (form hexagonal prism) that
link the hexagonal faces of two sodalite cages. Sometimes, the tetrahedra can arrange to form chain-type building block which then connect to form a layer. Such structure consists of rings with five O atoms and hence the name pentasil is used to describe them. Examples of zeolites included in this category are: Silicalite, ZSM-5, ZSM-11. Faujasites find largest-scale application in catalysis and includes Zeolite X and Zeolite Y. The three-dimensional pore structure is relatively large with a diameter of 0.74 nm and comprises of twelve membered oxygen rings such that selective transport of molecules are allowed. The supercage has a diameter of 1.2 nm and is surrounded by 10 sodalite cages. The framework structure of faujasite zeolite is shown in Figure 1.8. When a Si atom of the zeolite framework is replaced with an Al atom, it generates an excess negative charge which when compensated with a proton attached to the oxygen atom connecting neighbouring Si and Al atom results in a Brønsted acid site. Four positions in the faujasite zeolites have been identified for charge compensating cations: in the centers of hexagonal prisms, in the sodalite cages across the hexagonal faces, in the supercages near unjoined hexagonal faces and in supercages but farther from hexagonal faces.
The cations located in the supercages are easily accessible to reactants and hence are involved in catalysis [197]. These cations act as Lewis acid site and the negative charge bearing framework oxygen atoms behave as basic sites. As the amount of aluminium in the zeolite structure increases the concentration of acid sites also increases while the strength of the acid sites is greater when the amount of aluminium is lower. Thus, the Si/Al ratio is an important factor in acidity of zeolites. Zeolites find widespread application as cracking catalysts of higher hydrocarbons [198-202]. Over the years, both experimental [203-206] and theoretical [207-211] studies have been made on various aspects of zeolites.

1.4.3.2 CO oxidation on zeolite supported Au

With pores and cavities of molecular dimensions and adjustable acidic properties, zeolites form a fascinating class of solid support. Their ability to disperse gold, because of the internal distribution of the pores and the aptness to control particle size, makes them a promising type of solid support for gold nanoparticles. The catalytic activity of gold nanoparticles supported on zeolites towards CO oxidation has been studied using different experimental methods [212-222]. The earliest report concerning zeolite supported gold clusters was the work of Boudart and Meitzner [212]. The size of the gold particles in Y-zeolite was found to be compatible with their location inside the zeolite lattice. The size of the clusters increased with thermal treatment and the authors attributed this to the migration of the particles to the outside of the zeolite crystallite. Later, Fraissard and co-workers proposed [213], for the first time, a method to prepare small, thermally stable gold particles located inside NaHY zeolite. The effects of preparation conditions such as chloroaauric acid concentration, pH of gold solution, solution temperature, and mixing time on zeolite supported gold (Au/Y) for CO oxidation was studied by Lin and Wan [214]. Higher catalytic activity of Au/Y catalyst was found with gold species prepared in the supercage of Y-type zeolite. Chen et al. [215] prepared nano-gold in Y, β and mordenite zeolites and observed that Y-zeolite with more aluminium loading showed no aggregation of the gold particles with size around 1 nm. The high activity of Au/Y catalyst and its stability for CO oxidation has been attributed to the cage-like pores in Y-zeolite with high aluminium content.
that prevented sintering of gold and the hydrophilic surface favoured activation of gold species. Roduner and co-workers [216] observed the stabilization of the unusual Au(II) oxidation state in zeolite Y supercage for the first time using electron spin resonance (ESR). The authors concluded that confinement within the zeolite pores stabilized this unusual oxidation state of Au and prevented it from undergoing disproportionation.

The oxidation state of the active gold species in zeolite supported gold catalysts remains controversial [217-219]. The role of cationic gold in CO oxidation catalysis was investigated by Fierro-Gonzalez and Gates [218] in their work on mononuclear Au$^{III}$ and Au$^{I}$ complexes bonded to NaY zeolite but without zerova- lent gold. It was observed that reduction of Au$^{III}$ to Au$^{I}$ was accompanied by the consequent decrease in catalytic activity which implied that Au$^{I}$ is less reactive than Au$^{III}$ at 298 K under the studied reaction conditions. The EXAFS spectrum indicated that gold remained in the mononuclear form without forming clusters. The crystalline structure of the zeolites limited the migration of the entrapped gold clusters (formed when the supported gold complexes were treated at very high temperatures) [220]. However, Simakov et al. [219] have identified two types of active sites of gold in Y-zeolite for CO oxidation- partly charged gold clusters Au$^{δ+}_n$ and gold nanoparticles Au$^0_m$. Using aberration corrected scanning transmission electron microscopy (STEM), Lu et al. [221] demonstrated that zeolite serve as a suitable catalyst for dispersed gold catalyst with a high degree of uniformity. The catalytic sites were identified as site-isolated gold complexes and that the site-isolation of the gold complexes was retained after CO oxidation catalysis which supports the inference that the gold species were stabilized by their confinement in the zeolite channels.

In comparison to the large volume of the experimental work on the catalytic activity of zeolite supported Au towards CO oxidation, theoretical investigations are quite scarcer and some studies have been focused on CO adsorption on zeolite supported gold [135, 223-225]. Griffe et al. implemented density functional calculations to study CO oxidation on silicoaluminophosphates (SAPO) molecular sieves supported Au, Au$_2$ [224] and Au$_{3-5}$ [225]. Their results indicated exothermicity of the oxidation reaction on both Au/SAPO-11 species and an Eley-Rideal
mechanism where gas phase $O_2$ reacts with adsorbed CO [224]. CO adsorption and oxidation was studied on $Au_{3-5}$/SAPO-11 using hybrid QM/MM method [225]. Lack of theoretical understanding of the catalytic CO oxidation on zeolite supported Au clusters necessitates it to be properly addressed. The present thesis attempts to provide a theoretical insight into the CO oxidation mechanism over zeolite supported small Au clusters.

1.4.4 Activity of gold clusters towards water-gas shift reaction

The water gas shift reaction, WGS ($CO + H_2O \rightarrow CO_2 + H_2$) plays a pivotal role in providing high-purity hydrogen for fuel cell and numerous industrial applications [226,227]. The commercially available low-temperature heterogeneous WGS catalysts do not meet the stringent requirements of high activity and structural stability in air and in cyclic operations [228]. The commercially used WGS catalyst, Cu-ZnO suffers from drawbacks such as its sensitivity to temperature excursions, air exposure (pyrophoric), and water condensation during shutdown; thus making it unsuitable for fuel cell applications [229]. Alternative to Cu-ZnO, cerium oxide based catalysts have been investigated for WGS. Presence of a small amount of a transition metal significantly enhances the reducibility and catalytic activity of ceria and platinum (Pt) was one of the earliest metal additives with considerable effect on ceria reducibility [230]. The high cost associated with Pt-based catalysts and the deactivation of Pt – CeO$_2$ catalysts when used in realistic WGS streams [231] made it desirable to develop useful alternatives to it. Li et al. [232] have reported a Cu-ceria catalyst that is more stable than Cu-ZnO-based LTS catalysts and exhibits high WGS activity and structural stability at temperatures as high as 600°C.

The unusual and unanticipated catalytic properties of nano sized gold in contrast to bulk gold makes it one of the central tenant in the field of catalytic research. The high activity of gold catalysts towards WGS reaction was first made by Andreeva et al. [233,234] using Au/Fe$_2$O$_3$ at low temperatures. Under same conditions, Au/Fe$_2$O$_3$ catalyst exhibited better activity than the most efficient low temperature WGS catalyst, CuO/ZnO/Al$_2$O$_3$. Excellent WGS catalyst
resulting from Au supported on ceria was first reported by Fu et al. [235] and since then this catalytic system has been extensively studied [228,236-239]. Experimental evidence pertaining to the role of oxidized Au in the WGS reaction was provided and it was proposed that the metallic Au\(^0\) particles are mere spectators [228]. They characterized the active species as Au cations using x-ray photoelectron spectroscopy (XPS). Liu et al. [240] concluded from DFT studies that the active sites in the Au-ceria catalysts are neither single Au atoms nor sizeable Au particles, but ultra-small Au clusters. In a recent work by Song and Hensen [241], it was shown that the CeO\(_2\)(110) supported Au nanorod exhibits better activity than the single Au atom for WGS reactivity. The carboxyl mechanism has been proposed as the dominant pathway for the low temperature reaction instead of the redox mechanism. A novel and more active Au/TiO\(_2\) catalyst which exhibits low temperature activity for both forward and reverse water-gas shift reactions was reported by Haruta and co-workers [242]. Apart from this, catalytic activity of gold particles dispersed on titania has been investigated by different experimental and theoretical studies [242-244]. In addition, Au particles supported on various other oxides such as ZrO\(_2\), Al\(_2\)O\(_3\) etc. as well as mixed oxides have been used as catalysts for WGS reaction [245-247]. Although the WGS reaction on different supported gold catalysts has been extensively studied, no definite consensus on the mechanism as well as the active gold site has been reached. The various factors affecting the WGS reaction on supported gold catalysts such as the effect of particle size, effect of the support, preparation method, active site [248,249], location of the gold species which is critical both in terms of stability and low temperature activity, detailed insight into the reaction mechanism [250] have been reviewed in detail.

In comparison to the large volume of work reporting the activity of gold supported on different metal oxides towards WGS reaction, investigation of zeolite supported gold is very meagre. Mohamed and Ichikawa [251] used \textit{in situ} FTIR spectroscopy to identify the adsorbed species derived from CO + H\(_2\)O and CO + O\(_2\) reactions on H-mordenite-encapsulated gold catalysts. On Au/H-mordenite, they characterized a monodentate formate species while performing WGS reaction from the well-developed absorption bands in the 3000 to 2800 cm\(^{-1}\) range along with
the 1690 and 1340 cm\(^{-1}\) asymmetric and symmetric stretching bands of the COO\(^-\) group, respectively. Contrary to this, on H-mordenite WGS reaction proceeded through the formation of a bidentate formate species. It was observed that the activation energy for the formate decomposition to products, CO\(_2\) and H\(_2\), was lower in Au/H-mordenite (40.1 kJmol\(^{-1}\)) compared to H-mordenite (63.3 kJmol\(^{-1}\)) emphasizing the higher decomposition rate in the former. It was thus, suggested that the reaction is more facile when Au is encapsulated in the H-mordenite zeolite. In another study by the same group [252], reaction intermediates in the WGS reaction on Au\(^n+\)(1 ≤ n ≤ 3) incorporated into NaY, Na-mordenite, and Na-ZSM-5 zeolites has been studied by means of \textit{in situ} FT-IR spectroscopy. They have identified a unidentate formate species on Au\(^+\)/NaY from the characteristic bands observed at 1620 and 1340 cm\(^{-1}\) which further decomposed to CO\(_2\) and H\(_2\). Au\(^+\) has been identified as the active site that interacts with the dissociative H\(_2\)O molecules giving monodentate formate as the intermediate. They observed that on the Au/NaY surface, formate species formed exclusively while on Au/Na-mordenite, carbonate and organic-like carbonate species also formed. This has been attributed to the lower Si/Al ratio in NaY, leading to a lower average negative charge sitting on the lattice oxygen atoms to decrease considerably the amount of formed carbonate species. The highest activity towards WGS reaction was observed in NaY catalyst and involved activation energy of 64.1 kJ mol\(^{-1}\). Participation of the Au\(^+\) and Au\(^0\) dual site for WGS reaction when encapsulated inside NaY zeolite was suggested. Much higher concentration of water was found to decrease the catalytic activity because of the masking of the active sites.

A few theoretical studies have investigated the catalytic activity of unsupported Au nanoparticles such as Au\(_2\), Au\(_{38}\) etc. towards WGS reaction. DFT study by Wang \textit{et al.} [253] on the WGS reaction promoted by neutral and charged gold dimer clusters signified the role of cluster charge on the catalytic activity. The barriers calculated for the neutral and anionic clusters were higher than those in the cationic clusters and on all the three clusters, irrespective of the charge state; the formate mechanism was feasible rather than the redox mechanism. Liu and Rodriguez [254] have attributed the presence of low coordinated corner and edge sites in addition to the fluxionality of the particles as factors contributing to the
higher activity of nanoparticles \([\text{Au}_{29} \text{ and Cu}_{29}]\) than their parent bulk surfaces \([\text{Au}(100) \text{ and Cu}(100)]\). In all the systems, water dissociation remained the rate limiting step. DFT study on the catalytic activity of \(\text{Au}_{38}\) cluster towards WGS reaction indicated better activity of this cluster when compared to \(\text{Au}(100)\) and \(\text{Au}_{29}\) based on the lower barrier associated with the rate limiting water dissociation step (\(\text{Au}_{38}: 31.41 \text{ kcal mol}^{-1}\); \(\text{Au}(100): 35.28 \text{ kcal mol}^{-1}\) and \(\text{Au}_{29}: 32.05 \text{ kcal mol}^{-1}\)). Desorption of \(\text{H}_2\) was observed to occur more readily on the \(\text{Au}_{38}\) cluster [255].

**1.5 Single Atom Catalysis**

The concept of single atom catalysis has recently gained impetus and has become one of the central tenants in the field of catalytic research which is reflected from the numerous reports [256-259] on the activity of single atom supported on different materials towards reactions such as CO oxidation. The attraction towards single atom catalysis has evolved so as to maximize the efficiency of metal utilization. It has been proposed that catalysts with well-defined single active centres are necessary to understand the catalytic mechanisms better unlike the multiple active sites of subnanoclusters which are not always the most desirable centres for catalytic processes. Single atom catalysts have evolved as an effective way to utilize each and every metal atom of supported metal clusters [260]. A novel iron oxide supported single Pt atom catalyst was synthesized by Qiao et al. [261] which exhibited excellent stability and high catalytic performance for both CO oxidation and preferential oxidation of CO in \(\text{H}_2\).

Catalysis by single gold atom has also been reported for reactions such as CO oxidation, water gas shift reaction etc. Recently, Mao et al. [262] reported catalytic activity of a single Au atom embedded in a 2D h-BN monolayer using density functional theory along with molecular dynamics and microkinetic analysis. Activation of \(\text{O}_2\) involved low barrier and the rate determining step was the formation of two \(\text{CO}_2\) molecules from an \(\text{OOCAuCOO}\) intermediate obtained in their work. They concluded from their study that this supported single Au atom has a potential for CO oxidation. In another recent work, Li et al. [263]
observed the catalytic activity of single Au atoms supported on aluminium oxide clusters using mass spectroscopy and density functional calculations. Gates et al. [218,220] have identified single cationic Au centre as the active site for CO oxidation on mononuclear Au$^{\text{III}}$ and Au$^1$ complexes supported on faujasite using experimental techniques. Bare single gold atom has been demonstrated to be good catalyst towards CO oxidation by Fang et al. [171] at the CCSD(T)/aug-cc-pVTZ//mPW2PLYP/aug-cc-pVTZ level of calculation. The adsorption and catalytic activation of O$_2$ which is an important step for oxidation reactions has been observed on Au and Au$_2$ supported on h-BN surface as a consequence of charge transfer [264]. The catalytic activity of isolated Au atoms supported on titania has been reported for water gas shift reaction at low temperatures and the catalyst exhibited good stability at temperatures up to 473 K [244]. An important point that needs to be considered is that the availability of only a single site in these catalysts can at some times limit the applicability of single atom catalysts for processes requiring multiple active sites. However, deeper insight in utilizing the novel properties derived from single atom catalysts will provide new dimension in the field of heterogeneous catalysis. It is believed that investigation of such fundamental aspects at the atomic level will help understand these phenomena at larger clusters better.

1.6 Objectives of The Present Work

The present Ph.D. work was undertaken with the following objectives:

1. DFT studies on hydrogenated gold clusters and the phenomenon of reverse hydrogen spillover on zeolite supported gold and palladium clusters.

2. Theoretical studies of the adsorption of carbon monoxide and oxygen on gas phase gold clusters and carbon monoxide oxidation.

3. Theoretical studies of the adsorption of carbon monoxide and oxygen on zeolite supported gold monomer in three oxidation states and the effect of moisture on their adsorption using hybrid QM/MM methodology.
4. DFT studies of CO oxidation and Water-Gas Shift reaction on zeolite supported gold monomer in three oxidation states using hybrid QM/MM methodology.