

“I made the decision that it was not enough to just do the science, but also try to do something about directly applying scientific research to social problems. That's how I became interested in environmental issues”

-Mario Jose Molina

Nobel Prize recipient in 1995 for detailing the threat that chlorofluorocarbon gases (CFC) pose to Earth's ozone layer

INTRODUCTION

1.1 OXIDES OF CARBON AND NITROGEN: THREAT TO ENVIRONMENT

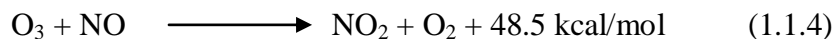
The introduction of clean air act in 1970 made substantial improvements in reducing the engine out and tail pipe emissions via the applications of catalysis technologies. Most of the automobiles use a spark ignited gasoline engine to provide power and it is the widest form of transportation. The incomplete combustions of fuel results exhaust pollutants mainly carbon monoxide (CO), unburned hydrocarbon (HC) and nitrogen oxides-NO_x (NO and NO₂) [1]. HC and CO are formed due to incomplete mixing of gases. NO_x forms at very high temperature (>1500⁰C) of combustion process which result thermal fixation of nitrogen in air [2]. The oxides of carbon and nitrogen are very harmful to our environment. They are green house gases due to the presence of IR active bonds which make them responsible for global warming. CO is also harmful for living organism as it forms carboxyhemoglobin with combination of hemoglobin and thus prevents the transport of oxygen in the body resulting anoxia [3,4].

Nitric oxide is a free radical and chemically unstable with a lifetime of 5 second. In low dose, it is beneficial to human body as it is essential for regulation of blood pressure and neurotransmission [5,6]. However, in high dose it can promote health problems like septic shock, Parkinson's as well as Alzheimer's disease [7]. The Zeldovich mechanism which describes the formation of NO as given below [2]:



NO is a major atmospheric pollutant. It can generate secondary contaminants through interaction with other primary pollutants which also results from the combustion of fossil fuels in stationary sources. Moreover it also contributes in the photochemistry of the troposphere and stratosphere. NO reacts with photochemical pollutants such as ozone, formaldehyde, organic hydroperoxides and peroxyacyl

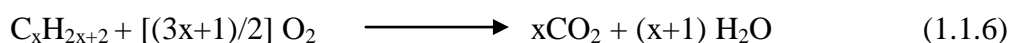
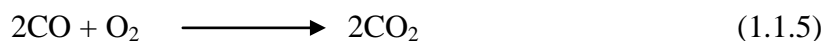
nitrates. The normal average content of ozone in the atmosphere is decreasing due to its interaction with NO [8,9].



The chemical depletion of ozone, is a prolong phenomenon. Toxic carcinogenic products are formed during these reactions. NO is also responsible for acid rain as well as photochemical smog formation.

Considering the adverse effect of these toxic gases towards our environment, various methodologies have been applied in different times. The most acceptable one is the three way catalytic converter (TWCC) which was introduced in 1981 in vehicle emission control systems. TWCC uses precious metals such as Rh, Pt and Pd as catalyst [10-12]. Rh catalyzes the reduction of NO_x to N_2 and also contributes to CO oxidation, while Pt and Pd can simultaneously catalyze CO and hydrocarbon conversion [13]. The main reactions occur in TWCC can be divided into two types-oxidation and reduction reactions.

Oxidation reactions:

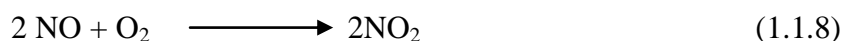


Reduction reactions:



However, TWCC is not effective in reducing NO_x in the highly oxidizing 'lean' exhaust. Thus current NO_x removal techniques include the lean NO_x trap [14,15]. During steady-state driving, engines operate lean to improve fuel economy upto 15-20% in comparison to continuous stoichiometric operations. In such cases, NO is first converted into NO_2 . On the other hand, the catalytic reduction of nitrogen oxides in effluent residual gases from various industries, mainly nitric acid plants, can be carried out selectively using ammonia or urea. This process is known as selective catalytic reduction (SCR) process [16,17]. The kinetic study reveal that oxidation of NO to NO_2 is a key rate determining step in SCR [18-21]. The advantage of oxidation of NO is that hydrocarbons are assumed to react with NO_2 more readily [22-23]. Control of soot and

particulate matter emitted from diesel vehicles is also one of the most important and challenging problems. Diesel exhaust contains excessive oxygen due to the high air-fuel ratio combustion condition. Diesel particulate Filter (DPF) used here oxidized the soot by NO_2 derived from the oxidation of NO available with diesel exhaust [24-27]. Considering, NO is predominantly present in diesel exhaust and the exhaust temperature is quite low for diesel vehicles, it is important to oxidize NO to NO_2 . Thus both NO_x trap, SCR as well as soot oxidation in diesel engines involve the following reaction of oxidation of NO.



Because of such importance, the oxidation of NO is established as a major topic of research in scientific community.

1.1.1 Transition metals in reducing toxic gases

In the field of removal of toxic gases like CO and NO, transition metals find wide applications due to their catalytic behavior towards environmentally significant reactions. Among transition metals, precious metals like Au, Ag, Pd, Pt show great potential towards the removal of the toxic gases [28-31]. Single Au atom was reported to effectively catalyze the CO oxidation reaction [32] while single Rh atom can catalyze the reaction between CO and NO [33]. Torres *et al.* [34] theoretically studied the adsorption and oxidation of NO molecules with O on Au(111) surfaces at the low-coverage limit. They proposed that adsorbed NO reacts with pre-adsorbed oxygen by the Langmuir–Hinshelwood (LH) mechanism, in which the reaction occurs between chemisorbed oxygen atoms and NO molecules. Sementa *et al.* [35] carried out density functional theory (DFT) calculations to show that $\text{Ag}_3/\text{MgO}(100)$ can work as the catalyst in the selective oxidation of NO to NO_2 . Getman and Schneider [28] developed a coverage-dependent, mean-field microkinetic model of catalytic NO oxidation at a Pt(111) surface based on large supercell density functional theory (DFT) calculations. Metkar *et al.* [36] performed a comprehensive experimental and kinetic modeling study on NO oxidation reactions using Fe-ZSM-5, Cu-ZSM-5 and Cu-chabazite catalysts.

Apart from surface and oxide supported metals, bare nanoclusters of transition metals also show tremendous catalytic activity towards oxidation of CO and NO. DFT

study by Wang *et al.*[37] for CO oxidation promoted by cationic, neutral, and anionic Au₃ clusters revealed that all the three Au species facilitates the CO oxidation via different mechanisms. The CO oxidation reactivity of negatively and positively charged isolated cuboctahedron (COh) and icosahedron (Ih) Ag₁₃ nanoparticles were reported by Kim *et al.* [38]. They found that catalytic activity of the nanoparticle with a (-2) negative charge is as good as an Au nanoparticle. Thus they confirmed that we can use excess charge to control the catalytic reactivity of a nanocatalyst. Tang and Hu [39] investigated the charge effect and multi state reactivity for CO oxidation catalyzed by neutral and charged Au₅₅ cluster. They found that the catalytic activity of the anionic Au₅₅ nanocluster was better than that of the neutral and cationic counterparts. Xie *et al.* [40] have investigated the reaction mechanism of NO reduction on the Rh₇⁺ cluster by DFT calculation and showed that dissociation of the first NO molecule is the rate-determining step of the whole catalytic cycle. Xu *et al.* [41] investigated the effect of cluster size on the reactivity of small Pt_x clusters (x = 1–5 and 10) toward the oxidation of CO and NO using periodic DFT calculations. They observed Langmuir–Hinshelwood-type CO and NO oxidation reactions and found that binding of all the individual species was markedly enhanced compared to the corresponding Pt bulk levels. Thus it is high time to extensively use different nanoclusters for removal of toxic gases. In the following section, we will discuss a brief overview on the basics of metal clusters and nanoclusters.

1.2 CLUSTERS AND NANOCCLUSERS

Clusters are aggregates of atoms or molecules which may contain any number of component particles from three to ten or hundreds of millions. When such aggregates reach sizes with diameters of nanometers, we refer them as nanoscale particles [42]. Clusters are systems of bound atoms or molecules, existing as an intermediate form of matter, with properties that lie between those of atoms (or molecules) and bulk materials. The origin of the word cluster comes from a German word “*Klustro*” which means a pile of material or nanomaterials [43]. The phrase cluster was used by F.A. Cotton in early 1960s to represent compounds containing metal–metal bonds. Irish-born chemist Robert Boyle first proposed the importance of clusters

in his book, *'The Sceptical Chymist'* where he thought of “*minute masses or clusters that were not easily dissipable into such particles that composed them.*” Clusters include species existing only in the gas phase or in the condensed phase or in both. Clusters differ from bulk materials in terms of the presence of a magic number of atoms or molecules they contain. Magic numbers signify electronic and structural stability [44]. Clusters bridge the gap between molecules and materials. Thus they help in the evolution of properties of molecules when they become materials. Properties such as chemical reactivity and catalysis depend strongly on specific geometry, electronic structure, etc., and can help us to understand such basic phenomena.

Figure 1.1 depicts clusters as a state between isolated atoms or bulk solid [43]. It also implies that it is possible to find them from either side, from atoms or molecules (bottom up approach) or from the bulk (step down approach). One of the most important properties of clusters is that their physical and chemical properties can be modified by varying the size of the system. It facilitates the design of systems for specific applications. This characteristic makes clusters particularly interesting.

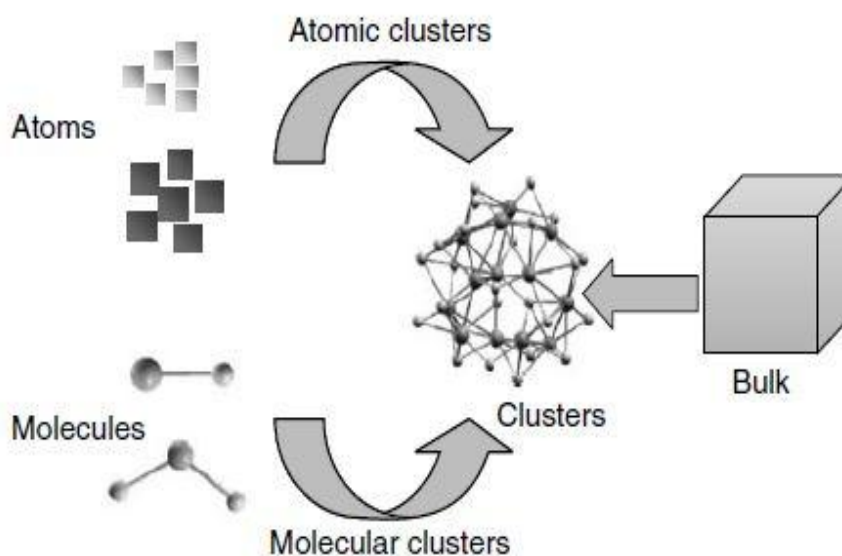


Figure 1.1 Schematic representation of cluster placed in between atom, molecule and bulk material.

1.2.1 Types of clusters

Clusters can be formed either from similar constituents or from the combination of different types of constituents. Depending on the nature of constituents clusters may be classified in the following types [41]:

Homo-atomic clusters: Here the constituent particles are identical. Examples are: C_{60} , Au_n , $(H_2O)_n$ etc.

Hetero-atomic clusters: Here constituent particles are of two or more types. Examples are: Pd_nPt_m , $FeAlAu_n$ etc.



NaCl cluster

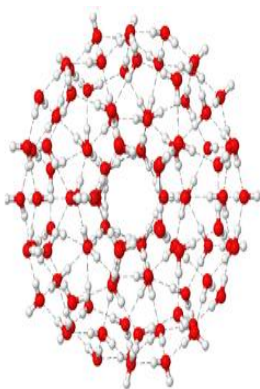
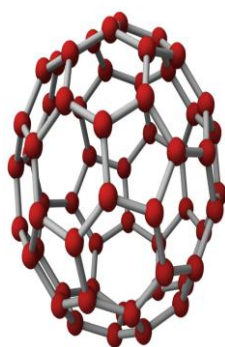
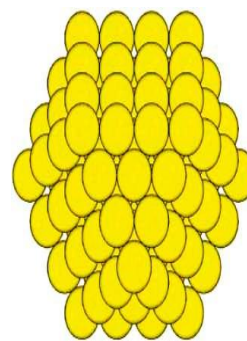
H₂O clusterC₆₀ clusterPd₁₄₇₁ cluster

Figure 1.2 Examples of various types of clusters

Depending on the nature of chemical bonding in the constituents, clusters can be further divided into various types as provided in Table 1.1[43].

Table 1.1 Types of clusters according to chemical bonding

Cluster type	Examples	Nature of bonding	Binding energy/mole(kcal)
Ionic	(NaCl) _n	Strong ionic bonding	~50-100
Covalent	C ₆₀ , Si _n	Strong covalent bonding	~20-100
Metal	Al _n , Au _n , Pd _n	Moderate to strong Metallic bond	~10-50
Molecular	(H ₂ O) _n	Molecular interactions, hydrogen bonding, van der Waals etc	<10
van der Waals	Ar _n , Xe _n	Polarization	<5

1.2.2 Cluster generation in gas phase

Most of the methods of cluster formation are based on homogeneous nucleation in the gas phase and subsequent condensation and coagulation. There are various kinds of cluster sources from which gas phase clusters are generated. Few of them are as follows:

(a) Supersonic source

Seeded supersonic nozzle sources are used to generate clusters of low boiling point metals. Here the metal is vaporized in oven and mixed with inert carrier gas like helium (He) to promote cluster formation and cooling.

(b) Laser vaporization source

It is the most widely used method to produce nanoclusters of various size and polarity [45]. Here pulse laser is used to heat the target metal rod causing its vaporization. Evaporation is cooled by using He as carrier gas.

(c) *Gas aggregation source*

It utilizes the property of aggregation of atom in inert media. Metal is vaporized and introduced in a flow of cold inert gas which makes the vapor highly supersaturated [46]. These sources produce continuous beams of clusters of low to high boiling metals.

(d) *Sputtering source*

In this method, material is vaporized from a solid surface by bombardment with high velocity ions of an inert gas. Sputter source such as ion gun is normally used. Electron from electron gun can also be used. TiN and AlN particles are reported to produce in this method [47].

1.2.3 Variation of cluster properties with size

The physical and chemical properties of clusters are largely varies with size. Thus it is possible to design them for specific applications [48]. Important properties like stability, reactivity etc depends on clusters size.

(a) **Binding energy:** Binding energy (BE) of clusters generally increases with increase in cluster size. Figure 1.3 shows that the BE increase gradually from 1-7 for Pd clusters [49].

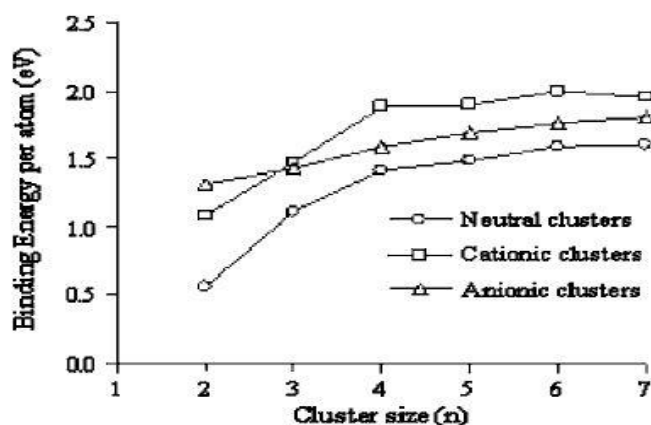


Figure 1.3 Variation of BE with cluster size for Pd_n (n=1-7) clusters

(b) **Ionization potential:** Ionization potential (IP) of metal clusters varies with cluster size. Figure 1.4 shows the variation of IP with cluster size for metal (M=Ti, Zr, Hf) doped Si_n ($n=9-20$) clusters [50]. It is seen from the plot that ionization potential of Si clusters have an oscillatory nature with higher values for $n=11$ and 16.

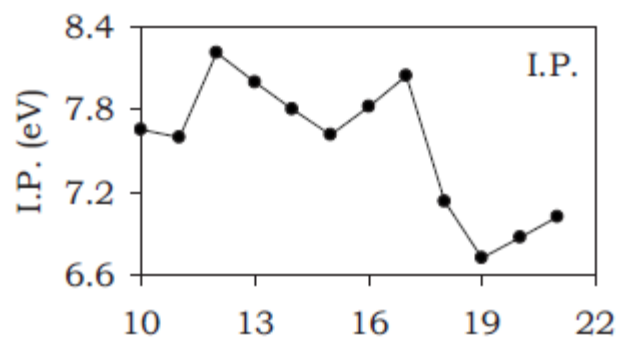


Figure 1.4 Variation of IPs of the most stable isomers with $N=n+1$.

(c) **Reactivity:** Reactivity of the cluster also depends on size and charge. Figure 1.5 shows the plot of extent of reaction of anionic gold clusters towards molecular oxygen [51]. The plot shows even-odd alternation in reactivity. Molecular oxygen absorbs more strongly on even number of gold atoms and reactivity is highest for Au_6^- .

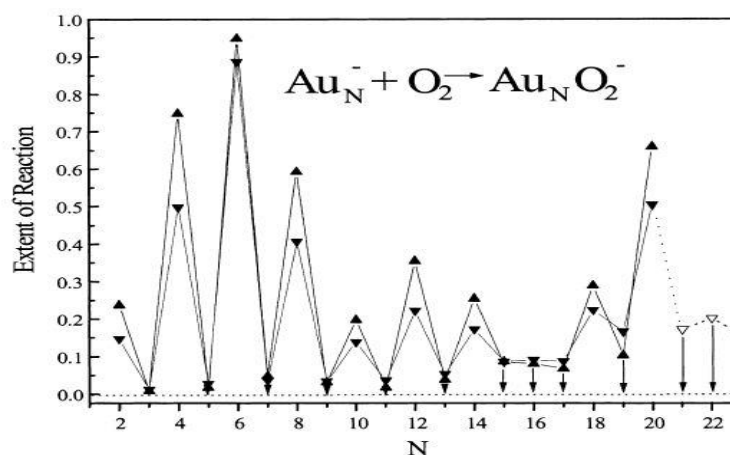


Figure 1.5 Cluster size (N) dependence to the extent of reaction of Au_N^- and O_2 . Separate plots correspond to different O_2 concentrations.

(d) **Melting temperature:** Melting temperature of clusters generally increases with cluster size. The change in the melting temperature of gold with the particle size is illustrated graphically in figure 1.6 [41]. The graph shows that for lower clusters, the melting temperature increases gradually with size. However for large clusters, the rise is steady.

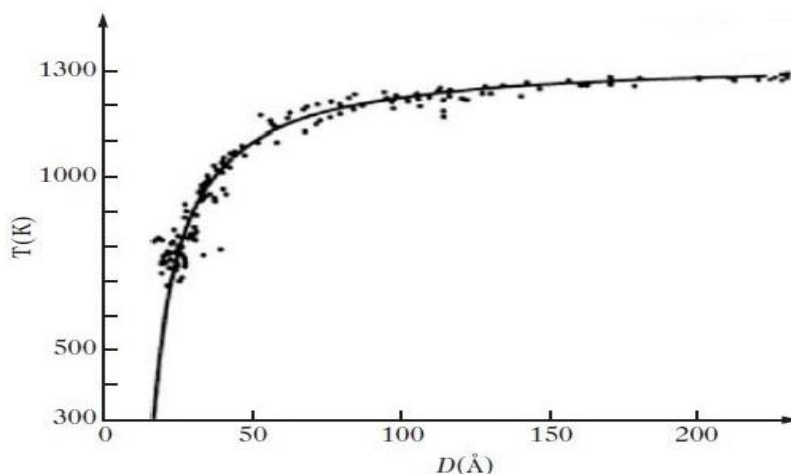


Figure 1.6 Dependence of melting temperature (T) on the size of Au nanoparticles

1.2.4 Importance of metal nanoclusters

The prefix “nano”, derived from the Greek “nanos,” signifying “dwarf,” is becoming increasingly common in scientific community [52,53]. Although the idea of nanotechnology, *i.e.* manufacturing nanoscale objects and carrying out nanoscale manipulations, has been around for quite some time, the birth of the concept is usually linked to a speech by Feynman at the December 1959 meeting of the American Physical Society [54], where he asked, “*What would happen if we could arrange the atoms one by one the way we want them?*” Metal nanoparticles, in the form of colloids or sols, have been used by man since the middle ages. One of the oldest of this use is in the fourth Century AD *Lycurgus cup* (Figure 1.7) made by the Romans which is still present at the British Museum in London. The cup appears red in transmitted light (if a light source is kept within the cup) and appears green in reflected light (if the light source is outside) due to the presence of nanometric inclusions of gold and silver in the glass [43,45]. In the mid 17th century, Andreus Cassius discovered Purple of Cassius—a coated gold colloid, used as a pigment in glass enamel and chinaware. A few years

later, Johann Kunchel perfected the technique of making ruby-coloured stained glass [55]. Michael Faraday [56] in 1857 elucidated the mechanism of formation of colloidal metals and prepared stable sols and called them divided metals.



Figure 1.7 Fourth Century AD *Lycurgus cup*

Till today nanoclusters prominently possess a lot of areas of application due to their unique optical, electrical, magnetic and reactivity properties. They have fascinating potential uses including quantum dots, chemical sensors, light emitting diodes, industrial lithography, medical science etc[51,57-64]. The unique reactivity properties and the ability to control the size and number of atoms in nanoclusters have proven to be a useful approach for increasing activity and tuning the selectivity in a catalytic process. Metal nanoparticles have much larger surface area per unit volume or weight of metal than the bulk material. The electrons in a nanocluster are confined to spaces that can be as small as a few atom-widths across, giving rise to quantum size effects. These properties provide nanoclusters to find wide applications in the field of catalysis [65-67].

1.2.5 Transition metal clusters

Among different nanoclusters, transition metal clusters are generally finds wide applications in various areas and mainly in the field of catalysis. They have already

been found to catalyze various reactions like hydrogenations, dehydrogenations, hydrosilylations, hydrolysis, oxidation of CO, oxidative acetoxylation, coupling, cycloaddition reactions etc [68-76]. Transition metals contain unfilled d shells and it gives rise to a large number of low-lying excited states due to the different possibilities of arranging the electrons among the unfilled shells. The huge possibility of varying the electronic structure and properties makes the study of transition metal clusters particularly interesting. As the energy gap between $(n+1)s$ and nd levels is very small, the electronic and chemical properties of these clusters are determined by the interplay between s and d electrons. On account of their variable valency, transition metal clusters can form unstable intermediate compounds quite readily. Therefore, they are widely used in catalysis [77]. Among the transition metals, clusters of coinage metals have been widely studied mainly because of their industrial applications. These metals with their filled d shell and singly occupied s shell (outer electronic configuration $nd^{10}(n+1)s^1$), can be considered as a bridge between the "simple" s-only alkali metals and the more complicated transition metals [78]. They may be regarded as perturbed s^1 -electron systems with the (filled) d-shell influence.

1.3 GOLD NANOCCLUSERS

Gold (Au) is a noble metal and termed as "the king of elements." It finds extensive utilization in jewellery across the world because of its exceptional properties that it does not tarnish on exposure to atmosphere and retains its attractive luster undiminished for years. The noble behavior of gold is mainly owing to its resistance to oxidation and corrosion in air as well as its chemical inertness towards various reactions. Gold metal and gold alloys are used in electrical and electronics industry for various applications including electroplating. In addition, there appears to be a potential for exploitation of gold nano particles for a variety of applications including environmental pollution abatement, sensors and various other chemical and biochemical applications [79]. Gold exhibits properties very different from the other two coinage metals, viz, copper and silver. This is mainly due to the presence of large relativistic effect and aurophilic interactions that makes it unique.

1.3.1 Auophilic interactions

In the area of gold chemistry, auophilic interactions or auophilicity plays a central role [80]. Schmidbaur introduce the term in 1987 to describe various kinds of Au-Au interactions within and between gold compounds [81]. This term is derived from the Latin word "Aurum" (gold) and the Greek word "Philos" (with an affinity for). Auophilic interactions are cohesive interactions occurring among formally closed shell Au^I centres (with 5d¹⁰ valence electronic configuration) inside a molecule, or between such atoms in different molecules. These interactions are characterized by metal-metal distances shorter (2.73 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. Due to the effect of auophilicity, several gold atoms can assemble in polynuclear gold species resulting in dimers, oligomers or infinite two-dimensional sheets. Temperature dependent NMR spectroscopy measurement to study the strength of interactions between pairs of gold atoms resulted values in the range 29-46 kJ/mol which is comparable to that of a hydrogen bond, [82] and is intermediate between ionic/covalent bonding and van der Waals interaction [83]. Theoretical studies suggest that when an auophilic attraction is present, hydrogen bond loses strength and directionality in order to retain the gold-gold interaction [84]. A better theoretical explanation of auophilic interactions requires the inclusion of relativistic effects.

1.3.2 Relativistic Effects

The unique chemistry of gold particularly the initial resistance of gold to oxidation, and its greater extent of oxidation once oxidize can be recognized largely due to relativistic effect. As atomic nuclear charge (Z) increases, electrons that penetrate to the nucleus (the s electrons) increases their average velocity and as a consequence of relativity their mass also increases. This causes the radial contraction in s electrons and to a lesser extent, the p electrons. Therefore the s electrons are more strongly bound and shield the nuclear charge from the other electrons (especially d and f) more effectively in the heavier elements. As a consequence, the d and f electrons are destabilized and occupy larger orbitals. Expansion of the 5d orbital and contraction of the 6s orbital lead to change in the corresponding energy levels and increases the

interaction between them [85]. These effects scale roughly with Z^2 and become important for elements heavier than the lanthanides [86]. Schmidbaur and his coworkers [87] reported smaller size of Au(I) in comparison with Ag(I) as a result of relativistic effect. The high electron affinity and first ionization potential of gold are much higher than that of silver [88] and the existence of the aurides (e.g.; Cs^+Au^-) which are non-metallic semiconductors are also due to this effect [89]. The tighter binding of the s electrons of gold also explain the greater cohesion energy of gold and higher melting point. The raising of the Au 5d electron energies and the lowering of the valence 6s associated with transitions from the 5d band to the Fermi level (largely 6s in character) which in turn responsible for the yellow color of gold [90].

1.3.3 Catalysis by gold

Gold is an inert material with an ionization potential of 9.2 eV. For this reason, catalysis by gold seemed to be unimportant and has received limited attention in the past. However the revolutionary work of Haruta [91,92] on low temperature CO oxidation opened up new aspects towards catalytic activity of supported gold clusters. He reported the exceptionally high reactivity as well as selectivity of ultrafine gold particles ($2\text{nm} \leq \text{diameter} \leq 5\text{nm}$) supported on certain metal oxides towards the oxidation of CO to CO_2 at temperatures as low as -70°C . This work of Haruta stimulated gold catalysis in a wide range of applications, such as hydrogenation of unsaturated hydrocarbons [93,94], propylene epoxidation [95], water-gas shift [96,97], selective oxidation [98], catalytic combustion of methanol [99] etc. The catalytic activity is characterized by the cluster size of gold particles [49,100]. However, other properties like site-specificity [101,102], morphology [103] and electronic state [104] of gold clusters are also contribute to the activity of gold. The difference of small particles from the bulk gold is due to more reactive electronic structures results from low coordination atoms and the adoption of geometries [105,106].

The oxidation of CO and NO is an important process concerning the environmental protection and safety. Various experimental and theoretical studies have proved that free and supported nanosized gold clusters can efficiently catalyze the CO oxidation reaction [107-113]. Socaciu *et al.* [114] used temperature-dependent rf-ion

trap mass spectrometry to study the reaction mechanism of the catalytic gas-phase oxidation of CO by free Au_2^- ions. They observed a key metastable intermediate with a mass of Au_2CO_3^- . They also used first-principle simulation and reported that intermediate Au_2CO_3^- have two alternative structures-digold carbonate or peroxyformate like structures. As gold at nano level can effectively catalyse CO oxidation, it is both natural and promising to study their catalytic activity towards the NO oxidation as well. Citra *et al.* [115] reported an experiment in which laser-ablated gold clusters reacted with NO in excess argon and neon, yielding the neutral nitrosyl complexes AuNO and Au(NO)₂ as the main products. Ding *et al.* [116] investigated NO molecule adsorption on the gold clusters with DFT and observed a strong ability to adsorb NO molecules for the majority of gold clusters. However, compared to CO oxidation, the study on catalytic oxidation of NO by Au clusters is relatively less. With advanced computational methods and experimental techniques, the study of catalytic properties of gold towards NO oxidation seems worthy. The systematic computational approach to unveil the plausible mechanism as well as the knowledge of structure and properties of various intermediated and transition states formed during the oxidation process can provide powerful platform for upcoming research in the concern field.

1.3.4 Bimetallic nanoclusters of gold

Bimetallic nanoparticles composed of two different metal elements are more promising than the monometallic nanoparticles because synergistic effect is expected. They show novel catalytic behavior based on the effect of second metal element added. This effect can often be explained in terms of an ensemble or a ligand effect in catalysis [117-120]. The ligand effect represents the electronic modifications resulting from the additional metal, while the ensemble effect refers to the fact that the addition of metal may block certain sites, reducing or eliminating the formation of an inhibiting species or an important intermediate. If we consider doped gold clusters, its chemical activity can also be tuned as the introduction of a dopant atom induces charge transfer, electronic energy level splitting, and geometric reorganization [121,122]. Till today, lots of studies on doped clusters have been carried out both experimentally as well as theoretically. Bouwen *et al.* [123] investigated the time-of-flight mass abundance

spectrometry on Au_nCu_m^+ clusters. They reveals that doped clusters exhibit the same electronic shell effects as Au_m^+ which make the study on Au_nCu_m^+ system interesting. Ji-Xian *et al.* [124] carried out DFT calculations on Au_nRh ($n = 1-8$) and found that even number atom clusters are more stable than that of odd number atom clusters. Binary clusters such as Au–Ag found importance in catalysis, colloidal chemistry, and medical science [125]. New molecular nanocrystalline materials with gold and silver nanoclusters and nanowires, which would be considered as prototypes for electronic nanodevices and biosensors, have also been synthesized [126]. Due to difference in relativistic effects and geometric structures of pure gold and silver clusters, the structural and electronic properties of gold–silver binary clusters are expected to be dependent strongly on the cluster size and mixing ratio of gold and silver atoms. Since the Ag-5s orbital is energetically much higher than the Au-6s orbital, partial charge transfer from Au to Ag takes place in Au–Ag binary clusters [127]. In the field of catalysis, Au-Ag binary system shows potential activity towards CO oxidation [127,128]. Liu *et al.* [129] studied the detailed mechanisms of catalytic CO oxidation catalyzed by Au–Ag⁻ dimer in the gas phase and compared it with the pure Au₂⁻ dimer. They found that anionic Au–Ag⁻ dimer has good catalytic activity towards CO oxidation and also the activity is higher compared to that of pure Au₂⁻. As Au–Ag⁻ promotes CO oxidation in the gas phase, it is both natural and promising to investigate its catalytic activity for NO oxidation as well.

Although extensive studies are performed on single metal doped Au clusters, only few studies have been carried out on doubly metal doped clusters. Zhao *et al.* [130] applied DFT on small bimetallic M_2Au_n ($\text{M} = \text{Ag}, \text{Cu}; n = 1-10$) and pure gold Au_n ($n \leq 12$) clusters. The optimized geometries revealed that M_2 substituted Au_{n+2} clusters and one Au atom capped $\text{M}_2\text{Au}_{n-1}$ structures are dominant growth patterns of the stable alloyed M_2Au_n clusters. Jun *et al.* [131] performed DFT to the low-lying isomers of Au_nY_2 ($n = 1-4$) clusters. They reveal that the gold–yttrium interaction is strong enough to modify the growth pattern of bare gold clusters.

The interaction of Au clusters mostly focused on transition metal atoms. But researchers now also look forward towards the interactions of s- and p-block elements with Au clusters. Balducci *et al.* [132] reported the dissociation energy, vibration

frequency and bond energy of bimetallic AuBe, AuMg and AuCa dimers by using mass spectrometry and DFT. The systematic analysis by Li *et al.* [133] on the equilibrium geometries, relative stabilities and electronic and magnetic properties of anionic Au_nMg ($n = 1-8$) clusters inferred that lowest energy structures for the Mg-doped clusters are different to that of the bare Au clusters and $[\text{Au}_3\text{Mg}]^-$ cluster has the most enhanced chemical stability. Hu *et al.* [134] applied DFT to study the geometric structures, stabilities, and electronic properties of bimetallic Rb_2Au_n ($n = 1-10$) clusters. Their study revealed that doping gold clusters with two Rb atoms dramatically affects the ground-state geometries of the pure gold clusters. The doped Rb atoms prefer to locate on the surface and mirror symmetry positions, and the Au-capped $\text{Rb}_2\text{Au}_{n-1}$ clusters are the dominant growth pattern. The detailed investigation of structures, stability and electronic properties of small bimetallic clusters can provide an insight into understanding the larger doped clusters of gold as well as other metals.

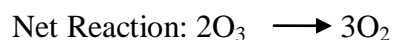
1.4 VOCs: ANOTHER THREAT TO ENVIRONMENT

As the automobile exhaust gases like CO, NO are harmful to our environment, there are some other compounds used in our daily life which also possess adverse effect towards environments. These are volatile organic compounds (VOC). The most commonly used halogenated VOCs are chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), hydrofluorocarbons (HFCs), hydrofluoroethers (HFEs) etc. CFCs were among the first commodity chemicals which possess physical properties matching for particular uses. Prior to 1930s, ammonia, chloromethane, carbon tetrachloride, isobutene and propane were used as common refrigerants [135]. However, concerning about the toxicity and flammability of these compounds, in 1928, an American Chemist, T. Migdley, predicted that Dichlorodifluoromethane (CCl_2F_2) might be a useful cooling medium. CCl_2F_2 has been manufactured since the 1930's by consortiums of DuPont and General Motors [136]. Originally it was introduced as the cooling medium in refrigerators to replace the highly toxic and odorous SO_2 , CH_3CCl_3 and NH_3 which have been used for this purpose. This compound is insoluble in water, chemically and thermally stable, non-flammable, non-explosive, non corrosive, non-toxic, volatile in ambient air, has a low thermal conductivity, and surface tension [137].

The chemical inertness and high volatility make this material suitable for technological use but it also means that they remain in atmosphere for a long time. Production and emissions of CFCs 11 and 12 (trichlorofluoromethane, CCl_3F , and dichlorofluoromethane, CCl_2F_2), remained comparatively low till 1950s, then increased rapidly with the spread of refrigeration in the developed world and as new uses, such as in aerosol spray cans, became commonplace. They are used in modern society as the working fluids in refrigerators, air-conditioners and as the blowing agents for plastic foams and industrial solvents. Intense development of technology has extended the use of halocarbons e.g. in medicine for sterilization of surgical instruments ($\text{CCl}_2\text{FCClF}_2$) and as blowing agents in the fabrication of flexible and rigid foams (CCl_3F , CCl_2F_2 , $\text{CCl}_2\text{FCClF}_2$) used for thermal insulation for building engineering. Due to excellent cleaning and fat removing properties, they have been widely applied in the electronics industry ($\text{CClF}_2\text{CClF}_2$) and as industrial solvents.

1.4.1 Effects of CFCs on environment

CFCs are not destroyed by the common cleansing mechanisms that remove most pollutants from the atmosphere such as rain or oxidation by hydroxyl. Instead the CFCs decompose by shorter wavelength solar ultraviolet radiations but only after migrating to the stratosphere. CFCs are ozone depleting substance (ODS). By adsorbing solar radiation, the CFCs molecule rapidly releases their chlorine atoms which lead to ozone depletion as given by the following reactions [138]:



Ozone is one of the most important trace species present in the atmosphere. Ozone plays two critical roles. First, by absorbing solar ultraviolet radiation, it protects the biosphere from harmful effects. Second, as a strong oxidant and together with water vapor, as a precursor of the hydroxyl radical, ozone has a strong influence on the “oxidizing power” of the atmosphere and hence on the rate at which many natural and anthropogenic compounds are eliminated from the atmosphere [139]. In 1974, Molina

and Rowland [140] proposed that CFCs emitted by human activities at earth's surface could pass through the troposphere to the stratosphere because of its strong resilience towards oxidation. In the stratosphere, UV radiation from the Sun breaks the C-Cl bonds in CFCs leading to liberation of Cl atoms. The Cl atoms can participate in a catalytic cycle that leads to the conversion of ozone into oxygen molecules. The recognition that anthropogenic emissions of halogenated hydrocarbons especially CFCs and halons could lead to destruction of ozone layer in the stratosphere led to P. Crutzen, M. Molina and F.S. Rowland to win the Nobel Prize in Chemistry in the year 1995.

The consequences of ozone layer depletion (OLD) are skin cancers, cataracts, blindness and other eye diseases, immunosuppression, reduced growth, photosynthesis and flowering in plants, damage to marine lives, degradation of construction materials like wood, plastic, rubber, fabrics etc. The first international agreement limiting the production of CFCs was approved in Sept 1987 under the auspices of the United Nations Environment Program [141]. This agreement, '*The Montreal Protocol*', was initially called for a reduction of only 50% in the manufacture of CFCs by the end of the century and signed by 24 countries [142]. Subsequently it has been modified in scope as a result of additional scientific assessments and ratified by 165 countries and now the manufacture of such CFC has been phased out.

1.4.2 Effects in Global warming

Global warming is an average increase in the temperature of atmosphere near the earth's surface and in the troposphere. The cause of global warming is due to the increase of greenhouse gases in the atmosphere. Carbon-halogen bonds absorb strongly the infrared wavelengths and this is why halogenated organic compounds are designated as strong greenhouse gases. The effectiveness of these compounds as greenhouse gases depends on two factors: (i) the number of carbon-halogen bonds in the molecule and (ii) the atmospheric life time of the molecule. They can trap heat up to 22,000 times more effectively than CO₂ and they can stay in the atmosphere for thousands of years.

1.4.3 Substitutes for CFCs

The research for substances which could replace the most widely used CFCs started with an investigation of the physic-chemical and thermodynamic properties of a number of aliphatic fluoro derivatives containing up to three carbon atoms from the point of view of their potential use as cooling agent. Two classes of halocarbons have received particular attention as replacements for CFCs; hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs) [143]. HCFCs and HFCs retain many of the desirable properties of CFCs such as low or zero flammability, low gas phase thermal conductivity, good chemical stability, reasonable cost etc. Each molecule of these classes of compounds has at least one C-H bond susceptible to attack initiated by hydroxyl radical, the naturally occurring radical in the troposphere, thereby eliminating the compound with its potential to produce ozone depleting Cl atoms before it reaches the stratosphere [144, 145].

1.4.3.1 HCFCs, the first generation replacement of CFCs

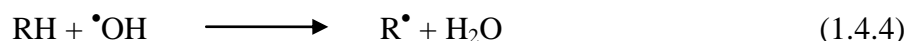
HCFCs are compounds containing carbon, hydrogen, chlorine and fluorine. The HCFCs have shorter atmospheric lifetimes than CFCs and releases less number of reactive chlorine to the stratosphere where the "ozone layer" is found [145]. Hence, it is expected that these chemicals will contribute much less to stratospheric ozone depletion than CFCs. HCFCs are less stable than CFCs because HCFC molecules contain carbon-hydrogen bonds. Hydrogen is attacked by the hydroxyl radical (OH) in the lower part of the atmosphere known as the troposphere [146]. HCFCs having shorter atmospheric residence time have been proposed as interim (transitional substances) CFCs replacement compounds. However, despite their shorter lifetimes they still have the potential to transport Cl to the stratosphere and there is concern that their substantial use could soon add significantly to the atmospheric Cl burden and prolong the period of high Cl levels. Due to these factors, their production has been restricted and they are planned to be completely phased out by 2020 under the current (Vienna 95) version of the Montreal Protocol.

1.4.3.2 HFCs, second generation replacement of CFCs

Hydrofluorocarbons (HFCs) are compounds containing carbon, hydrogen, and fluorine. Certain chemicals within this class of compounds are viewed by industry and the scientific community as acceptable alternatives to CFCs and HCFCs on a long-term basis. Because the HFCs contain no chlorine they do not directly affect stratospheric ozone [146]. All HFCs have an ozone depletion potential of zero. Like HCFCs, the HFCs contain hydrogen that is susceptible to attack by the hydroxyl radical. Oxidation of HFCs by the hydroxyl radical is believed to be the major destruction pathway for HFCs in the atmosphere. Although it is believed HFCs will not deplete ozone within the stratosphere, this class of compounds has other adverse environmental effects. It has been postulated that extensive use of these chemicals in the future could contribute significantly to enhance radiative atmospheric heating due to the presence of infrared active C-F bonds. Also, a number of the HFCs, for example HFC-134a, are expected to decompose in the atmosphere and produce a long-lived chemical called trifluoroacetic acid (or TFA) that is known to have adverse effects on certain biota. Concern over these effects may make it necessary to regulate production and use of these compounds at some point in the future.

1.4.3.3 HFEs, third generation replacement of CFCs

Volatile organic compounds like HFEs are widely recommended as a third generation replacement for CFC, HFC and HCFC in applications such as electronic equipments, heat transfer fluid in refrigerators, lubricant deposition and foam blowing agent [147-149]. HFEs contain C, F, H and O atoms. They do not contain Cl and Br atoms that cause ozone layer depletion. HFEs maintain many of the remarkable properties of similar perfluorinated compounds such as low vapour pressure, wide liquid interval and low dependence of viscosity on temperature but have a lower impact on environment [150]. The atmospheric degradation of HFEs initiated with the H-abstraction reaction with tropospheric hydroxyl (OH) radicals.



The rate constant for reaction of HFEs with OH radical suggest that their atmospheric lifetime should be relatively small. However the presence of great number

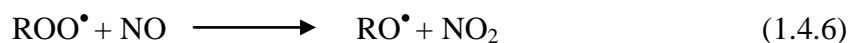
of C-F bonds drives to atmospheric long lived compounds with infrared adsorption features. Thus it may contribute to global warming but the impact is less in comparison to other VOCs. Hence it is necessary to improve our knowledge on the lifetime and global warming potential (GWP) of these compounds to get a complete picture of their environmental impact. The tropospheric oxidation of HFES produces corresponding hydro fluorinated esters (FES) [151,152] which on hydrolysis generate environmentally burdened product like trifluoroacetic acid (TFA) and COF₂.

1.4.4 Generation of alkoxy Radicals

The troposphere degradation of HFES which is initiated by attack of OH radicals leads to the formation of alkyl radical as shown in reaction 1.4.4. The latter reacts with atmospheric O₂ readily to form peroxy radical.



In a polluted atmosphere the peroxy radical thus formed may further reacts with other oxidizing species such as NO₂ and NO that ultimately leads to the formation of alkoxy radical [152].

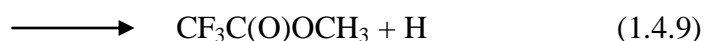
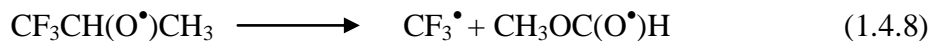


The experimental data suggests that nitrate formation from reactions of fluorinated alkylperoxy radicals with NO is of little, or no, significance. The product of the reaction between RO₂ and NO₂ is a peroxy nitrate, RO₂NO₂. Alkyl peroxy nitrates are thermally unstable and decompose to regenerate RO₂ radicals and NO₂ [146]. At room temperature in one atmosphere of air the peroxy nitrate derived from HFC-134a has a lifetime of < 90 second.

1.4.4.1 Atmospheric fate of alkoxy radical

The fate of the haloalkoxy radicals formed at the stage of the oxidation of HFES is especially interesting from the fundamental chemical view point and from the context of atmospheric chemistry. There are three potential pathways of decomposition of alkoxy radical that involve bond scissions and oxidation processes [153]. For

example, the decomposition of alkoxy radical $\text{CF}_3\text{CH}(\text{O}^\bullet)\text{CH}_3$ generated from HFE $\text{CF}_3\text{CH}_2\text{OCH}_3$ involves the following three pathways [154]:



1.4.5 Degradation Products of HFES

The primary products expected from HFES are given below:

Acid Halides	CF_3COOH , $\text{C}_4\text{F}_9\text{COOH}$
Carbonyl Halides	CF_2O
Aldehyde	CF_3CHO , HCHO

The atmospheric concentration of these products will be extremely small (\ll ppb). There are no known adverse environmental impacts associated with these compounds at such low concentrations. The ultimate removal mechanism for all products is incorporation into rain-sea cloud water where hydrolysis will take place [146]. With the possible exception of $\text{CF}_3\text{C}(\text{O})\text{OH}$, the hydrolysis products are naturally-occurring species that have no known adverse environmental impact [155]. $\text{CF}_3\text{C}(\text{O})\text{OH}$, has been detected in surface waters (oceans, rivers, and lakes) and in fog, snow, and rainwater samples around the globe and appears to be a ubiquitous component of the present hydrosphere. However, TFA appears to have been absent from the ancient freshwater hydrosphere [156]. While it is clearly established that there is a substantial environmental burden of $\text{CF}_3\text{C}(\text{O})\text{OH}$, the sources of this compound are unclear.

1.4.6 Importance of atmospheric chemistry of HFES

The rate constant for the reactions of OH radical with HFES have been studied in a number of laboratories by a variety of experimental techniques and have been critically evaluated and henceforth they are now reasonably well known [157,158]. To evaluate the atmospheric lifetime and environmental impact, accurate measurement of their OH reaction rate constant as well as the effect of temperature is necessary. These life times are important parameters in the calculation of Ozone depleting potential (ODP) and global warming potential (GWP). The experimental studies provided only

the total rate constant and it is difficult to predict the detailed mechanism and thermochemistry. Thus, for better understanding of mechanistic pathways, kinetics, and thermochemistry we must rely on quantum chemical methods. The atmospheric fate of alkoxy radical generated from HFEs is also necessary because they may lead to environmentally burdened products. The theoretical calculations can provide their most favourable pathway of degradation and thus helps to predict the major final product.

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