MECHANISM OF CATALYTIC OXIDATION OF NITRIC OXIDE AND DECOMPOSITION KINETICS OF HYDROFLUOROETHERS: A DENSITY FUNCTIONAL APPROACH

Abstract

Oxides of carbon and nitrogen such as carbon monoxide (CO) and nitrogen oxides (NO_x) find considerable interest in recent years due to their contribution towards green house effect. They are responsible for global warming, which subsequently results climate change that causes sea levels to rise, increases salinity in ocean ecosystems, and affects rainfall patterns. In addition to global warming, these substances possess harmful effects in the living organisms as well. Thus they are seriously threatening our environment today. These oxides are mainly emitted from automobile exhausts due to incomplete combustion in the engine. According to U.S. Environmental Protection Agency (EPA), the largest emissions of NOx came from on road motor vehicles. The three way catalytic converters (TWCC) are widely used today in the removal of these toxic gases. But it possesses some problems including more fuel consumption, emission of carbon dioxides so on. Thus researchers are still working on further improvements of these TWCC.

Among the oxides of nitrogen, nitric oxide is a free radical, chemically unstable and has a lifetime of 5 seconds. It gains considerable attention in the last two decades due to its impacts on the environment such as acid rain and photochemical smog formation. Due to the toxic effects of these gases, research is widely going on today for the removal and conversion of these gases using the concept of catalysis. As a new kind of catalyst, nanoclusters of transition metals particularly that of precious metals Au, Ag, Pd, Pt show great potential towards the removal of environmentally toxic gases. Gold is one of the inert materials with an ionization potential of 9.2 eV. For this reason, catalysis by gold has received limited attention in the past. But the revolutionary work of Haruta on unusual catalytic abilities of gold nanoclusters considerably increases the attention in the study of gold at the nano level. In addition to the pure Au clusters, bimetallic

nanoclusters like Au-Ag also have shown novel catalytic behavior. They are more promising than the monometallic nanoparticles because synergestic effect is expected. Similar to monometallic clusters, they also can effectively catalyze the environmental friendly reactions of oxides of C and N. The knowledge on complete picture of the mechanisms of these catalytic processes is very important from environmental point of view.

Like the oxides of carbon and nitrogen, volatile organic compounds (VOC) also possess tremendous adverse effects towards our environment. VOCs used in daily life like chlorofluorocarbons (CFC) are responsible for ozone layer depletions and hence their commercial production was banned as per Montreal protocol. Hydrochlorofluorocarbons (HCFC) and hydrofluorocarbons (HFC) have been developed as first and second generation alternatives of CFCs for short term use. However, they also seem to possess green house effect. The third generation replacement of CFCs is hydrofluoroethers (HFE) which are now widely used in cleaning of electronic equipments, heat transfer fluid in refrigerators, lubricant deposition and foam blowing agents. HFEs do not contain chlorine and bromine atoms that cause the ozone depletion. The rate constant for the reaction of HFEs with OH radical suggest that their atmospheric lifetime should be relatively short and thus HFEs have less impact for the global warming. The tropospheric oxidation of HFEs generate corresponding hydrofluorinated esters (FESs) which on hydrolysis produce environmentally burdened product like trifluoroacetic acid (TFA) and COF_2. Thus, it is important to improve our knowledge about atmospheric degradation and lifetimes of these compounds in order to get a complete evaluation of their environmental impact. Atmospheric lifetime is determined primarily by the reaction rate constant of these molecules with OH radicals. Experimental studies on these HFEs provided only the total rate constant and it is difficult to predict the mechanism and thermo chemistry. Thus, for better understanding of mechanistic pathways, kinetics and thermochemistry we must rely on quantum chemical methods.

Considering the above facts, in this present thesis, we have employed density functional theory (DFT) to explore the structure, electronic and topology on pure and doped neutral

and charged small gold nanoclusters. The catalytic activity of Au and Au-Ag binary systems towards nitric oxide oxidation has also been studied here. The atmospheric chemistry of two important HFEs- HFE-365mcf3 and HFE-7000 is also investigated using DFT method.

The contents of the thesis consist of six chapters. Brief overviews of which are given below:

Chapter 1 gives brief introduction, importance and motivation of the present work along with the review of literature of small pure and doped gold clusters, oxidation of CO and NO by pure and binary gold systems and reaction kinetics of HFEs. The chapter describes the types of clusters and the variation of their different properties with increase in size. Unique large surface to volume ratio and quantum size effects results increase interest of nanoclusters in industrial applications such as catalysis. The transition metal based nanoclusters are widely used in catalysis due to the presence of unfilled d-orbitals which helps in tuning their electronic structure. Next we emphasize on gold nanoclusters and its unique properties such as presence of aurophilic interactions and large relativistic effect. At first, Au_2^- was found as the smallest units which can effectively catalyze CO oxidation. However, recent studies prove that single Au atom can oxidize CO as well. The gold based bimetallic clusters also have wide applications in catalysis. The chapter also includes a brief discussion on atmospheric chemistry of HFEs. Their tropospheric degradation is expected to be initiated mainly by H abstraction reaction with OH radicals in the gas phase. Finally the objectives of the present work are included in this chapter.

Chapter 2 describes the computational tools like molecular mechanics (MM), quantum mechanics (QM), density functional theory (DFT), and various basis sets and functionals used within the framework of DFT. We have also included the concept of quantum theory of atoms in molecules (QTAIM) in this chapter.

Chapter 3 is divided into two sections: *Section 3.1* presents the DFT investigations on geometrical structures and relative stabilities of neutral and charged double berylium atoms doped gold clusters, $Au_nBe_2(n=1-5)$ and their comparison with pure gold clusters. The relative stabilities of the clusters are compared on the basis of average binding

energies, fragmentation energies and second order difference of energies. The nature of bonding interaction is studied by using Bader's quantum theory of atoms in molecules (QTAIM) which suggest strong covalent interaction between the gold and beryllium metal centres. *Section 3.2* summarizes the results of double Mg atom doping in neutral and charged Au_n (n=1-7) clusters using DFT. Classical annealing simulation is applied using the Forcite Plus code as encoded in the MATERIAL STUDIO software to generate the initial structure. The most stable structures obtained by this simulation used as input for DFT studies. Parameters like vertical ionisation potential, vertical electron affinity values are used here to calculate the electronic properties. The relative stabilities are compared on the basis of average binding energies, fragmentation energies and second order difference of energies. QTAIM analysis is also used to study the topology of the clusters. The population analysis is performed to search the transfer of electrons in Mg and Au atoms. *Section 3.3* describes the DFT study to observe the effect of double Al atoms doping in neutral and charged Au_n (n=1-7) clusters. Classical annealing simulation is also applied for initial structures. The Universal force field (UFF) was adopted to perform this simulation The electronic preoperties are calculated by using vertical ionisation potential, vertical electron affinity values and these parametrs show even-odd alternation pheneomenon. QTAIM analysis is also applied to study the nature of bonding.

Chapter 4 investigates the catalytic activity of Au_2^- and $Au\text{-}Ag^-$ binary systems for NO oxidation. The chapter is divided into two sections. *Section 4.1* focuses on DFT study on mechanistic details of NO oxidation ($2NO + O_2 \rightarrow 2NO_2$) promoted by anionic gold dimer (Au_2^-). The reaction is studied along three possible pathways. To ensure reliability of the reaction path, the connections between the transition state and the corresponding minima have been verified using an intrinsic reaction coordinate (IRC) calculations. The thermochemical parameters like standard reaction enthalpy (ΔH_r) and Gibbs free energy (ΔG_r) at a temperature T are also calculated to observe the feasibility of the reaction paths. In order to determine the nature of different stationary points on the potential energy surface, vibrational frequency calculations are also performed. The transition states are characterized by the occurrence of only one imaginary frequency. The

construction of energy profile diagram suggests the most favorable path for NO oxidation. The results of DFT study on NO oxidation by Au-Ag$^-$ dimers are included in *Section 4.2.* Two most plausible pathways of NO oxidation are considered here. No symmetric constraints are imposed during geometry optimization. IRC calculation has been performed to study the reliability of the reaction path. The binding orientations of Au-Ag$^-$ with NO and O$_2$ are studied by observing the HOMO and LUMO isosurfaces. Various possible geometries where the O$_2$ and NO molecules approach the dimer with different orientations as well as different possible spin combinations between the dimer with O$_2$ and NO molecule are considered here. The reaction paths have been studied along both Au and Ag site to reveal the most active site of the dimer. In order to access the multi-reference characteristics, T1 diagnostic calculations at CCSD(T) level of theory is employed. The most favorable pathway and the barrier heights of the reaction paths are determined by constructing the energy profile diagram.

Chapter 5 presents the atmospheric chemistry of two different HFEs. It is splits into two parts. *Section 5.1* describes the mechanism and kinetics of the gas-phase reactions of CF$_3$CF$_2$CH$_2$OCH$_3$ (HFE-365mcf3) with the OH radicals using DFT. Meta-hybrid modern density functional M06-2X in conjunction of 6-31+G(d,p) basis set have been applied here. Reaction profiles for OH-initiated hydrogen abstraction are determined including the formation of pre-reactive and post-reactive complexes at entrance and exit channels. Vibrational frequencies are calculated to observe the formation of stable structures and transition states. The rate constants of the titled reactions are computed over the temperature range of 250–450 K. The atmospheric life time of HFE-365mcf3 is estimated and compared with experimental results. Same level of theory is used to study the atmospheric fate of the alkoxy radicals, CF$_3$CF$_2$CH(O$^\bullet$)OCH$_3$ and CF$_3$CF$_2$CH$_2$OCH$_2$O$^\bullet$ generated from the HFE. The standard enthalpy of formation ($\Delta_f H^\circ_{298}$) has been computed by using the group-balanced isodesmic reactions. *Section 5.2* reports the mechanism of the hydrogen abstraction reaction between HFE-7000 (i-C$_3$F$_7$OCH$_3$) and the OH radicals using M06-2X functional with 6-31+G(d,p) basis set. The pre-reactive and post-reactive complexes from intrinsic reaction coordinate calculations are validated at entrance and exit channels, respectively. The

thermochemical data for the reaction of i-$C_3F_7OCH_3$ with OH radicals, the rate constants of the titled reactions over the temperature range of 250–450 K and the atmospheric life time are also computed. The atmospheric fate of the alkoxy radical, (i-$C_3F_7OCH_2O^\bullet$) is explored using the same level of theory. The standard enthalpy of formation ($\Delta_f H^\circ_{298}$) at 298 K for i-$C_3F_7OCH_3$ and i-$C_3F_7OC^\bullet H_2$ radical generated from hydrogen abstraction are calculated with the help of isodesmic reactions.

Chapter 6 finally review the salient observations of the entire work presented in the thesis and presents future prospects to refine and strengthen the research work.