Chapter 7

Conclusions and Future Scopes

Conclusions

The work presented in this thesis aims at: first, to investigate the structure, electronic and reactivity properties of hydrogenated gold clusters and the phenomenon of reverse hydrogen spillover on zeolite supported Pd$_6$ and Au$_6$ clusters; second, to study the adsorption of carbon monoxide and oxygen on gas phase gold cluster and carbon monoxide oxidation on neutral and charged gold clusters; third, to study the adsorption of carbon monoxide and oxygen on zeolite supported gold monomer in three oxidation states and to incorporate the effect of pre-adsorbed water on their adsorption; fourth, to investigate the activity of zeolite supported gold monomer in three oxidation states towards carbon monoxide oxidation and water gas shift reaction. Density functional theory (DFT) has been employed to carry out the calculations. The calculations associated with gas phase gold clusters as well as the phenomenon of reverse hydrogen spillover has been performed with the help of DMol$^3$ program while hybrid QM/MM method, SIMOMM implemented in GAMESS program has been used to study zeolite supported gold clusters. Gaussian 09 program has been used for natural bond orbital (NBO) analysis.

At the outset of this work, we present a general definition of clusters, their properties and classification based on nature of constituents and the type of bonding. Special emphasis has been laid on gold clusters and their structures in various
The unique properties of gold such as aurophilic interaction and relativistic effect have been also considered. Bulk gold is a noble metal however, its unusual and unanticipated catalytic properties when the size is reduced to nanometre range, makes it very interesting. Gold clusters, whether supported or unsupported, find widespread application as catalysts for reactions such as carbon monoxide oxidation, water gas shift reaction. The numerous reports on such catalytic activity of bare and supported gold clusters as well as adsorption of small molecules such as CO, O₂ on gold clusters have been discussed elaborately. Above all, we have also reviewed the recent developments in the field of single atom catalysis.

Various computational methods used for modelling surfaces, nanoparticle etc. have been discussed under two categories- Molecular Mechanics and Quantum Mechanics. A brief overview of the molecular mechanics method along with its advantages and disadvantages has been laid out. Quantum mechanics has been particularly stressed upon, since our calculations are mostly based on it. One of the most popular electronic structure methods, density functional theory (DFT) has been discussed in detail with reference to various functionals, basis sets available in the domain of computational chemistry. A part of our work related to zeolite supported gold systems utilizes hybrid QM/MM method and thereby, we have also included hybrid methods along with the various computational methods.

The geometric structures, electronic and reactivity properties of \( \text{Au}_6\text{H}_n \) (\( n=1-12 \)) clusters have been studied at the generalized gradient approximation level using the PBE functional and DNP basis set. In all the hydrogenated \( \text{Au}_6 \) clusters, the low spin state structures are found to be more stable than their high spin counterparts. Adsorption of H atoms stabilizes the \( \text{Au}_6 \) cluster which is reflected from the high binding energies. Our calculations indicate that planarity is retained till \( \text{Au}_6\text{H}_9 \) but the triangular structure of \( \text{Au}_6 \) distorts in \( \text{Au}_6\text{H}_7, \text{Au}_6\text{H}_8 \) and \( \text{Au}_6\text{H}_9 \). Further addition of H atoms removes planarity of the clusters such that one of the base Au atoms of the \( \text{Au}_6 \) triangle protrudes out of the plane of \( \text{Au}_6 \) in \( \text{Au}_6\text{H}_{10}, \text{Au}_6\text{H}_{11} \) and \( \text{Au}_6\text{H}_{12} \) cluster rendering these clusters non planar. The H atoms are found to be negatively charged in all the clusters indicating charge transfer from Au to H atoms. Clusters with even number of H atoms possess higher
HOMO-LUMO gap, chemical hardness, vertical ionization potential, adiabatic ionization potential and binding energy and are thus, suggested to be more stable than their congeners with odd number of H atoms. The Au atoms forming the vertices of the outer triangle in Au$_6$ have higher relative electrophilicity value while those forming the vertices of the inner triangle have higher relative nucleophilicity value as revealed by the DFT based reactivity descriptors. However, in Au$_6$H$_6$, two nearby Au sites forming the vertices of the inner and outer triangle have the highest relative electrophilicity and relative nucleophilicity values, respectively while in Au$_6$H$_{12}$, these are located in the inner triangle.

The structures of faujasite supported bare Pd$_6$ and Au$_6$ clusters and their interaction with the bridging OH groups of the zeolite support to form hydrogenated Pd$_6$ and Au$_6$ clusters has been studied using density functional theory. During calculations, the optimized positions of the terminal hydrogen atoms have been fixed. The faujasite supported bare metal clusters, Pd$_6$ and Au$_6$ interact with the support through three close M-O bonds (M=Pd, Au) whereas in their hydrogenated counterparts, Pd$_6$H$_3$/FAU and Au$_6$H$_3$/FAU, respectively there are overall six close M-O contacts. This implies that interaction of the metal clusters with the zeolite is enhanced as a consequence of stepwise reverse spillover. The hydrogenated Pd$_6$ and Au$_6$ clusters supported on faujasite are more stable than the dehydrogenated clusters and exothermic $E_{RS}$ values indicate that the process of proton transfer from the zeolite support to the metal cluster is energetically favourable in both the metals. Our calculations reveal that Pd$_6$H$_2$/FAU(H) and Au$_6$H$_2$/FAU(H) are the most stable among other hydrogenated congeners. Proton transfer leads to partial oxidation of the metal atoms with a concomitant reduction of H$^+$ to H$^-$. In case of both the metals, atoms which are in close proximity with the zeolite oxygen atoms are more strongly oxidized compared to the metal atoms that do not interact directly with the zeolite framework and thus there exists metal centres with different oxidation states within the same cluster in both bare and hydrogenated metal clusters.

With a view to delineate the effect of cluster charge on the catalytic activity of gas phase gold cluster towards CO oxidation, we have considered the conventional bi-molecular Langmuir-Hinshelwood CO oxidation mechanism on Au$_6^0$, Au$_6^-$ and
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Au$_6^+$ clusters using density functional theory (DFT) calculations. Adsorption of CO and O$_2$ has been considered initially and our calculations indicate that both CO and O$_2$ prefer the low coordination apex site for adsorption in the Au$_6$ clusters irrespective of the cluster charge. On considering their co-adsorption on the three clusters viz. Au$_6^0$, Au$_6^-$ and Au$_6^+$, it is observed that CO preferentially adsorbs at the apex Au site and O$_2$ at the nearest lateral site. However, O$_2$ activation is observed in the case of Au$_6^0$ and Au$_6^-$ but not in the cationic counterpart. Investigation of the CO oxidation pathway on the three clusters reveal that the barriers observed for the reaction on Au$_6^-$ are much lower than those with the neutral and cationic counterparts. CO oxidation over anionic gold hexamer does not require thermal activation unlike in Au$_6^0$ and Au$_6^+$ clusters which is reflected from the stability of all the species including the transition states with respect to the interacting species. It can be thus concluded that Au$_6^-$ exhibits better catalytic activity compared to neutral and cationic clusters.

We have employed hybrid quantum mechanics/molecular mechanics method to treat the faujasite supported gold monomer in three oxidation states viz. 0, +1 and +3 model system considered in our work. Initially, we have investigated the adsorption of CO and O$_2$ on faujasite supported neutral and cationic (+1 and +3) gold monomer. CO adsorption was found to be favourable in all the oxidation states and the highest CO binding energy is observed in Au$_3^{3+}$/FAU. On the neutral monomer, CO adsorbs in a bent fashion while in the cationic systems, it adsorbs linearly. O$_2$ adsorption was considered in three modes viz. top, bridge and dissociative. Our calculations indicate that the top mode of O$_2$ adsorption is favourable in the cationic systems and higher O$_2$ binding energy is observed in Au$_3^{3+}$/FAU. Charge transfer to O$_2$ results in O-O bond elongation and consequently its activation. On the other hand, O$_2$ adsorbs in the bridge mode with high binding energy in both neutral and cationic systems. This mode of O$_2$ adsorption is favourable in the three oxidation systems and involves substantial O-O bond activation. Adsorption of O$_2$ as two dissociated O atoms is designated as the dissociative mode and is quite interesting. In Au$_0^0$/FAU, the dissociative mode is observed to be favourable albeit with low binding energy. However, in cationic systems, the dissociative mode reverts back to the bridge mode rather
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than remaining as dissociated O atoms. The present calculations imply that the bridge mode is preferred over top and dissociative modes of O\textsubscript{2} adsorption on faujasite supported neutral and cationic Au monomer which also accompanies substantial O\textsubscript{2} activation.

Further, as a certain amount of moisture is inevitably present in practical catalytic systems, we have investigated the effect of water on the adsorption of CO and O\textsubscript{2} on faujasite supported neutral and cationic gold monomer. Our calculations indicate that the adsorption of CO on faujasite supported monomer in presence of pre-adsorbed water results in cleavage of the Au-H\textsubscript{2}O bond and no interaction exists between CO and H\textsubscript{2}O. The binding energy of CO increases with the Au oxidation state. In the optimized structures, bonding of CO on water pre-adsorbed Au\textsuperscript{n}/FAU changes from bent to linear mode with increase in Au oxidation state. This can be correlated with the decrease in $\nu_{C-O}$ value observed in the neutral monomer and blue shift in case of cationic systems. In presence of pre-adsorbed water, the top and bridge modes of O\textsubscript{2} adsorption are favourable in all the oxidation states and the highest binding energy is observed in Au\textsuperscript{0}/FAU. The dissociative mode reverts back to the favourable bridge mode in Au\textsuperscript{0}/FAU while in the cationic systems where it remains in the dissociative mode, the adsorption of O\textsubscript{2} is observed to be unfavourable. Activation of H\textsubscript{2}O observed in our calculations can be attributed to the hydrogen bonded interaction that prevails between O\textsubscript{2} and H\textsubscript{2}O and also between the nearest zeolite oxygen atoms and the H atoms of H\textsubscript{2}O. Further, we consider the feasibility of dissociation of the adsorbed H\textsubscript{2}O molecule and consequently formation of a hydroperoxyl and hydroxyl species from the transfer of the dissociated H atom from H\textsubscript{2}O to O\textsubscript{2} when O\textsubscript{2} and H\textsubscript{2}O are in close proximity. Transfer of a proton from H\textsubscript{2}O to O\textsubscript{2} that results in a hydroperoxyl-hydroxyl species was found to involve a barrier as low as 0.20 eV.

Next, we attempted to investigate the activity of faujasite supported neutral and cationic Au monomer towards CO oxidation using hybrid QM/MM method. Initially, we considered different CO-O\textsubscript{2} containing configurations and the corresponding interaction energies were determined. It was observed that high barriers are involved in the pathway initiating from the most favourable initial CO-O\textsubscript{2} configuration (Eley-Rideal mechanism with dissociated O\textsubscript{2}) compared to the pathway
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with initial CO-O$_2$ containing configuration having moderate interaction energies. Our calculations indicated that the Eley-Rideal mechanism with CO adsorbed on the supported Au centre and O$_2$ in the gas phase is the preferred pathway. Among the three faujasite supported Au systems, Au$^{3+}$/FAU exhibits better catalytic activity and the stability of all the species including the transition states with respect to the interacting species indicates no thermal activation. Superior activity of NaY supported mononuclear Au$^{III}$ complex towards CO oxidation as compared to Au$^I$ has also been observed in experiments. The conclusions drawn from this simple model of zeolite supported Au catalyst for CO oxidation may be inherent for understanding the catalytic activity of larger realistic catalytic system so as to apprehend the mechanism involved.

The study was further extended to investigate the activity of faujasite supported neutral and cationic gold monomer towards water-gas shift reaction using hybrid quantum mechanics/molecular mechanics calculations. Initially, two different CO-H$_2$O co-adsorbed configurations have been considered and our calculations indicated that CO adsorption on Au$^n$/FAU (n=0, +1 and +3) in presence of pre-adsorbed H$_2$O is more favourable than the adsorption of H$_2$O on Au$^n$/FAU (n=0, +1 and +3) in presence of pre-adsorbed CO. Subsequently, this configuration has been appraised as the starting configuration for investigating water-gas shift reaction mechanism. The reaction involves formation of a carboxyl intermediate in all the oxidation states from the recombination of CO and OH. However, carboxyl formation is above the entrance channel in Au$^+$/FAU and is thus, the rate limiting step. The overall reaction is found to be endothermic in both the cationic systems while is exothermic in Au$^0$/FAU. Comparing the activity of the three Au monomer species, it is observed that neutral Au exhibits better catalytic activity towards water-gas shift reaction and the dissociation of H$_2$O into OH and H is the rate limiting step. Substantially high barriers associated with the cationic systems and endothermicity of the reaction will inhibit their catalytic activity. Stability of all the species including the transition states with respect to the interacting species indicates no thermal activation in faujasite supported neutral Au monomer. However, reducing the water dissociation barrier observed in the neutral monomer will improve the catalytic activity further.
Our calculations indicate that faujasite supported Au monomer posses the potential to act as a catalyst for CO oxidation but significantly high barrier involved in water dissociation will inhibit its catalytic activity towards water gas shift reaction. It is believed that designing improved catalysts with enhanced potential for water gas shift reaction will open up a new dimension for water gas shift reaction catalysts. The conclusions drawn from this study may be inherent for understanding the catalytic activity of larger realistic catalytic system so as to apprehend the mechanism involved.

Future Scopes

With the emerging advancement in the field of material research and nanotechnology, there has been a growing interest in diverse applications of nanoclusters. Gold nanoclusters are appreciated largely because of their appealing role as a catalyst for a large number of both industrially and environmentally important reactions such as CO oxidation, propene epoxidation, water gas shift reaction and so on. The work presented in the thesis attempts to provide an insight into the structure, energetics and properties of gas phase and zeolite supported hydrogenated gold clusters. Moreover, we have investigated the catalytic activity of gas phase and zeolite supported gold cluster towards CO oxidation and water gas shift reaction. The effect of moisture on the adsorption of CO and O₂ on zeolite supported Au and consequently the process of proton transfer between H₂O and O₂ has also been considered. This work can be further extended in various directions, some of which are:

1. Single gold atom or small gold clusters supported on materials such as graphene can be utilized to study reactions such as NOₓ reduction, alkene hydrogenation etc.

2. Reaction mechanisms can be modelled on small gold clusters entrapped in a larger zeolite cavity to obtain a more realistic model.

3. The detailed mechanism of H atom transfer during the process of reverse hydrogen spillover from bridging OH groups of zeolite to metal clusters can
be investigated.

4. The study can be extended to gold clusters doped with other transition metals such as Ag, Pt etc.

5. Molecular dynamics simulations can be implemented to study reaction mechanisms on gold clusters.