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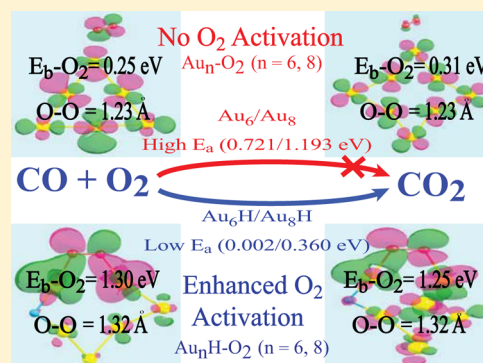
Hydrogen Atom Chemisorbed Gold Clusters as Highly Active Catalysts for Oxygen Activation and CO Oxidation

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S Supporting Information

ABSTRACT: Using oxygen activation and carbon monoxide oxidation as a probe, we have carried out density functional theory (DFT) calculations to investigate the effect of hydrogen atom chemisorption on the reactivity and catalytic activity of gold nanoclusters. In the present work, we particularly focus on the closed shell neutral Au_n ($n = 2, 4, 6, 8$) gold clusters which are reported to be chemically inert and catalytically less active. The results confirm that the hydrogen atom chemisorption activates the inert clusters, thereby leading to enhanced binding and activation of the O_2 molecule. A significant amount of increase in the O—O and decrease in the Au—O bond lengths together with a pertinent red shift in the O—O stretching frequencies clearly indicates the stronger binding and activation of oxygen molecule in the case of Au_nH clusters. Further, our results reveal that the hydrogen atom chemisorbed gold clusters are catalytically more active with low activation barriers for the CO oxidation reaction compared to the parent less active closed shell gold clusters. Thus, in short the current theoretical observation provides key inputs for enhancing the reactivity and catalytic activity of inert gold clusters through the adsorption of a small atom or a molecule.



1. INTRODUCTION

Gold clusters continue to attract a great deal of interest, owing to their interesting electronic and catalytic properties in comparison to the bulk gold. The various reactions that the gold clusters catalyze are carbon monoxide oxidation, selective oxidation of hydrocarbons, alkene epoxidation, and so on.^{1–5} Among the above-mentioned reactions, the CO oxidation^{6–9} has been studied extensively and is considered to be a bottleneck for predicting the catalytic activity of nanogold. The enhanced catalytic behavior has motivated a number of experimental and theoretical researchers to elucidate and confirm the atomic structure and bonding of gold clusters with 3–35 atoms.^{10–20} The important factors that have been shown to affect the reactivity and catalytic activity of the gold clusters include size and shape of the cluster, charge on the cluster, interaction with the supporting material, adsorption of ligands, and doping with other atoms.^{21–25} Recent advances in the characterization techniques and theoretical methods have revealed that the size and shape of gold clusters are the key parameters determining the unexpected catalytic activity of gold.^{26–29} Recently, Zeng and co-workers³⁰ using ab initio calculations have shown that the adsorption energy of O_2 and CO molecules, and the catalytic activity decreases with the increase in the cluster size in the size range of 16–35 atoms. Regarding the effect of charge, various interesting studies^{31–34} using density functional based theoretical calculations have shown that anionic gold clusters are more reactive and catalytically active compared to the neutral and cationic gold clusters. The cluster–support interaction is a subject of great

interest and plays an important role on the catalytic activity of gold clusters.^{35–38} Gold clusters supported on various reducible oxide supports such as TiO_2 and MgO have been synthesized and show exceptional catalytic properties at room temperatures.

The preadsorption of small molecules and atoms on gold clusters provides an efficient way of modifying the electronic and catalytic properties of gold clusters. However, there are limited number of such reports where the precise role played by a small molecule or an atom on the catalytic activity of gold clusters has been explored. In this regard, Wallace et al.³⁹ showed that the adsorption of OH moiety enhances the binding and activation of O_2 molecule on small gold clusters. Gao et al.⁴⁰ revealed using density functional based calculations that a single water molecule adsorbed on the gold clusters can play an important role in catalyzing the dissociation of O_2 molecule. Similarly ethylene adsorbed gold clusters bind and activate O_2 molecule strongly as compared to parent gold clusters.⁴¹ These studies have shown that the preadsorption of small molecules activates the gold clusters and leads to enhancement in their reactivity with small molecules such as O_2 . Moreover, recently in an interesting study, Zeng and co-workers⁴² demonstrated that coadsorption of CO molecule at a specific site acts as a promoter for the cleavage of the O—O bond and thereby considerably reduces the activation barrier for CO and styrene oxidation reactions.

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The hydrogen–gold cluster interaction is extremely important in the field of heterogeneous catalysis. For example, Haruta and co-workers⁴³ illustrated that the presence of hydrogen enhances the propylene oxidation and epoxidation on gold clusters. In order to understand the effect of hydrogen (H) atom chemisorption on the structure and electronic properties of gold clusters, a number of experimental as well as theoretical works^{44–46} have been carried out. Phala et al.,⁴⁷ for the first time studied the chemisorption of hydrogen atom on gold clusters using density functional theory. It was found that the H atom prefers bridged type of bonding with two Au–H bonds on the gold clusters. Buckart et al.⁴⁸ from photoelectron spectroscopy examined the effect of hydrogen atom adsorption on the electronic structure of anionic gold clusters. The authors found that hydrogen atom donates an electron to the valence electron pool of gold clusters. It is important to mention here that gold clusters do not react with H₂ molecule but only react with atomic H indicating that the gold cluster–H atom interaction can be of paramount importance in real time catalysis.

In the present work, we have investigated the effect of H atom chemisorption on the reactivity and catalytic activity of closed shell gold clusters (Au₂, Au₄, Au₆, and Au₈) which are reported to be highly stable and catalytically less active. Our results demonstrate that H atom chemisorption leads to a significant increase in the binding and activation of oxygen molecule, as compared to parent gold clusters. Further, CO oxidation was used as a chemical probe to understand the effect of H atom chemisorption on the catalytic activity of pristine closed shell gold clusters. The results confirm that the H atom chemisorption significantly improves the catalytic activity of the closed shell gold clusters by reducing the activation barriers for the CO oxidation reaction.

2. COMPUTATIONAL DETAILS

Density functional Theory (DFT) with PBE exchange and correlation potential as implemented in the Gaussian 09 was used to perform all the calculations.⁴⁹ For each cluster, a number of conformers were used as a starting guess to find the ground state geometry. Geometry optimizations were carried out by using the Berny algorithm with the default convergence criterion. The LANL2DZ basis set and the corresponding Los Alamos relativistic effective core potential (RECP) was used to take into account scalar relativistic effects for the gold atoms. For the hydrogen, oxygen and carbon atoms, the TZVP basis set was used. To locate the energetically most favorable configurations of O₂ adsorbed gold cluster complexes, we considered the various possible adsorption patterns, including the bridge (with two Au–O bonds) and atop (with single Au–O bond) adsorption of O₂ on the Au_n and Au_nH clusters at the various possible sites. Vibrational frequency calculations were carried out to guarantee the optimized structures are local minima. The O₂ binding energies have been calculated as the difference between the energy of O₂ adsorbed complex and its constituents (i.e., O₂ and cluster). The basis set superposition error (BSSE) has not been considered for calculation of O₂ binding energies, as it has been demonstrated recently that the BSSE has a negligible effect on the O₂ adsorption energies on gold clusters.^{50,51} The transition states were found by using the linear synchronous transit method and were characterized by the presence of one imaginary frequency.

3. RESULTS AND DISCUSSION

We begin with a discussion on the structure of pristine and H atom chemisorbed gold clusters. The structures of the pristine and H atom chemisorbed gold clusters are presented in Figure 1 and are in close agreement with the earlier reported

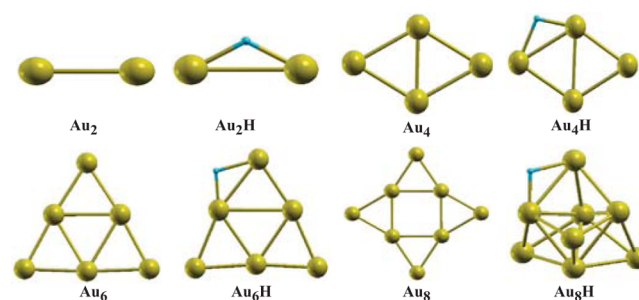


Figure 1. Optimized geometries of pristine Au_n and Au_nH clusters ($n = 2, 4, 6, 8$).

results.^{46,47} We note that the hydrogen atom prefers a bridged type of bonding with two Au–O bonds, with all the gold clusters considered in the current study. The overwhelming number of experimental and theoretical works on the gold clusters during the past decade have revealed that interaction and binding of molecular oxygen with gold clusters is the most critical and important step in the catalytic oxidation reactions involving gold nanoclusters. The optimized geometries of the O₂ adsorbed complexes of the Au_n clusters ($n = 2, 4, 6, 8$) are presented in Figure 2 and are in accordance with the earlier

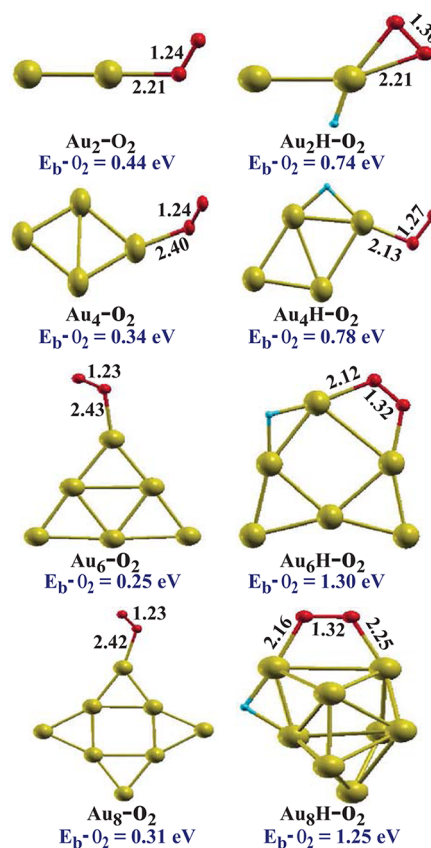


Figure 2. Optimized geometries of Au_n–O₂ and Au_nH–O₂ complexes ($n = 2, 4, 6, 8$).

studies of O_2 adsorption on gold clusters.^{29,52} Figure 2 also depicts the O_2 adsorbed complexes of the Au_nH clusters. Oxygen adsorption was studied both in the atop (superoxo) as well as in the bridged (peroxo) modes at various sites in all the clusters. For the Au_n clusters, O_2 molecule prefers an atop (peroxo) mode of bonding with a single Au—O bond and for the Au_nH clusters, three different modes of O_2 bonding are seen. In the case of Au_2H , both the oxygen atoms of the O_2 molecule interact with a single gold atom. The O_2 molecule adsorbs in an atop mode on the Au_4H cluster with a single Au—O bond, where as, the O_2 molecule prefers bridged/peroxo mode of bonding with two Au—O bonds with the Au_6H and Au_8H clusters. The O_2 binding energies on the parent and hydrogen atom chemisorbed gold clusters are also presented in Figure 2. For the pristine gold clusters, the binding energy is highest for Au_2 cluster (0.44 eV). The binding energies for the Au_4 , Au_6 , and Au_8 clusters are 0.34, 0.25, and 0.31 eV, respectively. The obtained O_2 binding energies are in close agreement with the earlier reported results of Yoon et al.²⁹ The low binding energies of O_2 molecule with Au_n clusters indicates that the above-mentioned clusters are less reactive and thus can not activate the O_2 molecule. However, the hydrogen atom chemisorbed gold clusters interact strongly with the O_2 molecule leading to higher binding energies and significant activation of the oxygen molecule. The Au_6H and Au_8H clusters show significantly larger binding energies (1.30 and 1.25 eV respectively) among the hydrogen atom chemisorbed gold clusters. The O_2 binding energies on Au_2H and Au_4H clusters are 0.74 and 0.78 eV, respectively, which are again nearly two times as compared to the parent gold clusters. Thus, the hydrogen atom chemisorption on the aforementioned less reactive gold clusters leads to a substantial enhancement in the binding energy of O_2 molecule which in turn leads to the activation of O_2 molecule.

In order to understand the interaction of the molecular oxygen with pristine and hydrogen atom chemisorbed gold clusters, we have studied the frontier molecular orbitals of the Au_n-O_2 and Au_nH-O_2 complexes ($n = 2, 4, 6, 8$). The degree of charge transfer and hence the activation of molecular oxygen depends on the spatial overlap between frontier molecular orbitals of the gold clusters and the O_2 molecule. Figure 3 depicts the molecular orbitals of the Au_n-O_2 and Au_nH-O_2 complexes ($n = 2, 4, 6, 8$). The SOMO's (singly occupied molecular orbitals) in the case of all Au_nH-O_2 complexes show a considerable in phase overlap between the d-orbital of Au atom and the p-orbital of the adsorbed O_2 molecule, resulting in the formation of strong Au—O bonds in the case of the hydrogen atom chemisorbed gold clusters. However, this type of d–p overlap is not seen in the frontier orbitals of O_2 adsorbed complexes of Au_n clusters. Also it is known that O_2 molecule acts as an electron acceptor and interacts strongly with clusters which can donate electrons easily to the $2\pi^*$ antibonding orbitals of the O_2 molecule. The ionization potential provides an easy way of calculating the electron donating capability of a cluster. Figure 4 presents the ionization potentials of Au_n and Au_nH clusters. Interestingly, the hydrogen atom chemisorption leads to a reduction in the ionization potential by about 2 eV for all the clusters. The low ionization potential in the case of hydrogen atom chemisorbed gold clusters facilitates the electron transfer from the cluster to the O_2 molecule. This enhanced charge transfer is clearly reflected from the natural bond orbital (NBO) charge analysis of Au_n-O_2 and Au_nH-O_2 complexes (see Table 1). The net

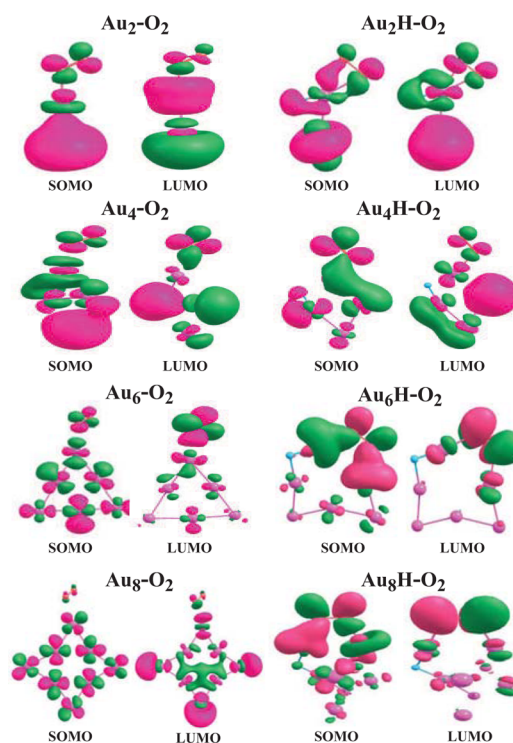


Figure 3. Frontier molecular orbitals of Au_n-O_2 and Au_nH-O_2 complexes ($n = 2, 4, 6, 8$).

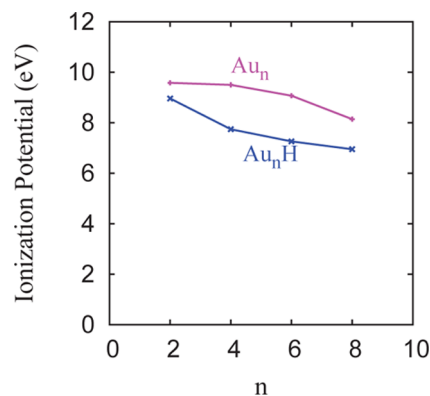


Figure 4. Ionization potential of the Au_n and Au_nH ($n = 2, 4, 6, 8$) clusters.

negative charge on the O_2 molecule in the case of Au_nH-O_2 complexes is around 0.3 electrons where as the net negative charge on O_2 molecule in the Au_n-O_2 complexes is around 0.07 electrons. Thus, a clear correlation of the ionization potential and the degree of charge transfer is found with the calculated binding energy of the O_2 molecule on these clusters. To further validate our results, we have computed the relevant geometrical parameters such as O—O bond length (r_{O-O}) and Au—O bond length (r_{Au-O}). The various geometrical parameters are enlisted in Table 1 and lead to two interesting observations. First, the hydrogen atom chemisorption enhances the interaction of oxygen with these clusters, which is reflected in the decrease in the Au—O bond length for the Au_nH clusters as compared to that of Au_n clusters. Second, a significant increase in the O—O bond length on the hydrogen atom chemisorbed gold clusters clearly indicates the activation of O_2 molecule on these clusters. It can also be seen from Table 1

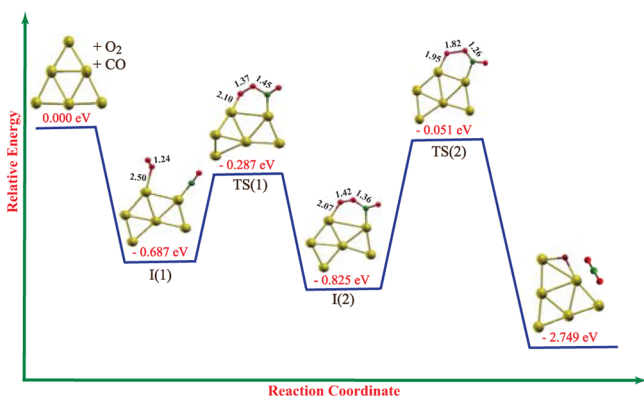
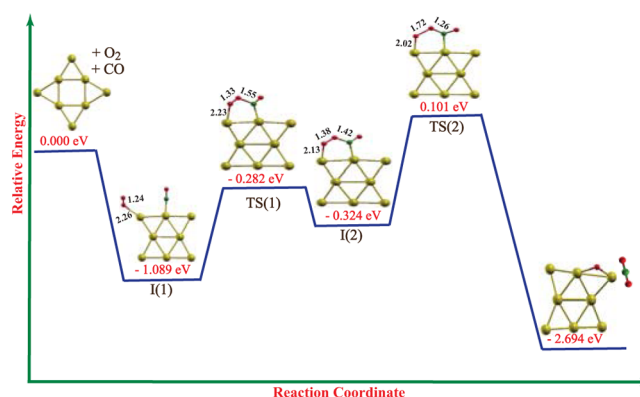
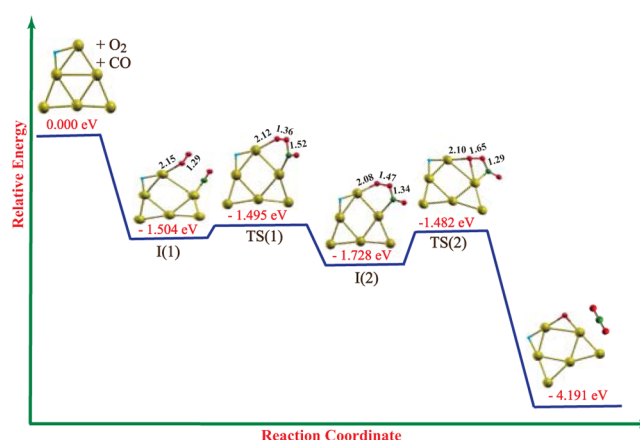
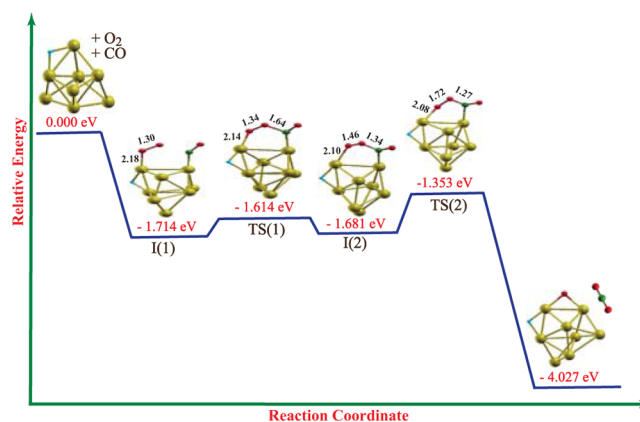
Table 1. Optimized Geometrical Parameters Such As O—O bond length ($r_{\text{O—O}}$), Au—O bond length ($r_{\text{Au—O}}$), Au—O—O bond angle ($\angle\text{AuOO}$) and O—O stretching frequency ($\nu_{\text{O—O}}$)

cluster	$r_{\text{O—O}}$ (Å)	$r_{\text{Au—O}}$ (Å)	$\angle\text{AuOO}$	$\nu_{\text{O—O}}$ (cm^{-1})	$q_{\text{O}_2}^a$	cluster	$r_{\text{O—O}}$ (Å)	$r_{\text{Au—O}}$ (Å)	$\angle\text{AuOO}$	$\nu_{\text{O—O}}$ (cm^{-1})	q_{O_2}
Au ₂	1.24	2.21	120°	1387	−0.08	Au ₂ H	1.30	2.21	75°	1183	−0.32
Au ₄	1.24	2.40	119°	1385	−0.07	Au ₄ H	1.27	2.13	110°	1241	−0.26
Au ₆	1.23	2.43	120°	1425	−0.06	Au ₆ H	1.32	2.12	98°	1080	−0.33
Au ₈	1.23	2.42	119°	1420	−0.05	Au ₈ H	1.32	2.16	109°	1110	−0.32

^a q_{O_2} represents the net negative charge on the O₂ molecule in the O₂ adsorbed complexes of Au_{*n*} and Au_{*n*}H (*n* = 2, 4, 6, 8) clusters calculated using Natural Bond Orbital (NBO) charge analysis.

that the Au—O—O bond angle decreases in the case of Au_{*n*}H clusters as compared to the Au_{*n*} clusters. Furthermore, we have quantified the activation of O₂ molecule on the hydrogen atom chemisorbed gold clusters by looking at the O—O stretching frequencies in the Au_{*n*}—O₂ and Au_{*n*}H—O₂ complexes. In line with the above results, a significant decrease in the O—O stretching frequency provides a clear indication of O₂ activation in the case of Au_{*n*}H clusters. Thus, from the above discussion, we conclude that the hydrogen atom chemisorption plays an effective role in tuning the electronic environment in the gold clusters and thereby leads to the strong binding and higher degree of activation of the O₂ molecule.

To determine the effect of hydrogen atom chemisorption on the catalytic behavior of gold clusters, we explored the environmentally important CO oxidation reaction on the Au_{*n*} and Au_{*n*}H clusters. By now, it is well-known that CO oxidation on gold clusters follows two types of reaction mechanisms,⁵³ (a) Langmuir–Hinshelwood (LH) mechanism and (b) Eley–Rideal mechanism (ER). In the LH type of reaction mechanism, both the O₂ and CO molecules adsorb on the cluster initially and then react with each other to form CO₂, while as in the ER type of reaction mechanism CO reacts with the chemisorbed O₂ molecule. However, a number of studies^{10,30,42,54,55} have revealed that the CO oxidation on the small and medium sized gold clusters effectively follows the LH type of reaction mechanism. We have also considered the LH type of mechanism for CO oxidation on the Au_{*n*} and Au_{*n*}H clusters. The reactants, transition states, and the products involved in the catalytic reaction pathways for CO oxidation on the Au_{*n*} and Au_{*n*}H clusters are presented in the Figures 5–8. As can be seen from the figures and reported earlier,^{30,54–56} the CO oxidation on gold clusters occurs via two steps. During the first step, one of the oxygen atoms of the O₂ molecule comes close to the carbon atom of CO, leading to the elongation of the O—O bond and formation of the O—O—

**Figure 5.** Reaction pathway for CO oxidation on the Au₆ cluster.**Figure 6.** Reaction pathway for CO oxidation on the Au₈ cluster.**Figure 7.** Reaction pathway for CO oxidation on the Au₆H cluster.**Figure 8.** Reaction pathway for CO oxidation on the Au₈H cluster.

C—O intermediate. The second step involves the breaking of the O—O bond of the O—O—C—O intermediate, leading to

the formation of the CO₂ molecule. From Figures 5 and 7, we note that the calculated activation barriers for the formation of O—O—C—O intermediate on the Au₆ and Au₈ clusters are 0.40 and 0.81 eV, respectively. The activation barrier for the second step involving dissociation of the O—O bond and formation of CO₂ molecule on Au₆ and Au₈ clusters are 0.77 and 0.42 eV, respectively. Intriguingly, the barrier height for CO oxidation on the hydrogen atom chemisorbed gold clusters is very low. The calculated barrier heights for the first and second steps in the case of Au₆H are 0.01 and 0.25 eV, respectively (Figure 7), where as in the case of the Au₈H cluster, the barrier heights for the first and second steps are 0.10 and 0.33 eV, respectively (Figure 8). Thus, the hydrogen atom chemisorption not only leads to stronger binding and activation of O₂ molecule but also improves significantly the catalytic activity of gold clusters.

4. CONCLUSIONS

In summary, we have carried density functional calculations to investigate the effect of hydrogen atom chemisorption on the reactivity and catalytic activity of the stable closed shell gold clusters. Our results affirm that the chemisorption of hydrogen atom on the gold clusters facilitates the electron transfer from the cluster to the O₂, leading to the activation of oxygen molecule. The enhanced binding energies and significant red shift in the O—O stretching frequency unequivocally confirm the activation of the O₂ molecule in the case of Au_nH clusters. These findings are also validated by a notable increase in the r_{O—O} distance and a concomitant decrease in the r_{Au—O} on the hydrogen atom chemisorbed gold clusters. Moreover, the hydrogen atom chemisorbed gold clusters show very low activation barriers and act as effective catalysts for the environmentally important CO oxidation reaction as compared to the catalytically inert Au_n clusters. Interestingly the CO oxidation reaction is almost barrierless in the case of the Au₆H, the cluster which shows the highest O₂ binding energy. Thus, the present computational study highlights the importance of preadsorption of a small atom or a molecule in the design of highly active gold nanocatalysts.

■ ASSOCIATED CONTENT

Supporting Information

Cartesian coordinates of reactants, intermediates, transition states, and products for the CO oxidation on the various gold clusters and a figure highlighting the effect of hydrogen atom chemisorption on the reactivity of CO molecule with Au_n (*n* = 2, 4, 6, 8) clusters. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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This paper was published to the Web on December 10, 2014, with errors in Table 1. These were fixed in the version published to the Web on December 16, 2014.