

Effect of adsorbed water molecules on reaction profile of CO oxidation catalyzed by Au₅ nanoclusters

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CO oxidation is an important reaction from the perspective of environment remediation techniques. The improvised, better end-of-pipe solution are desired to reduce the impact of anthropogenic activities on the environment. CO oxidation can take place at the surface of gold nanoparticles even at low temperatures, thereby providing solution to cold-emission problem. In this study, we explore the effect of water in adsorbed state on the reaction profile of CO oxidation catalysed by gold nanoclusters. It has been found that the main effect of water adsorbed onto gold nanoclusters is to reduce the barrier for carbonate formation. The carbonate formation is reported to negatively impact the catalytic properties of gold nanocluster. Here, we also report an alternative pathway through which the carbonate decomposition can be accomplished leading to the regeneration of the catalyst surface. This Eley – Rideal pathway involves reaction between CO and nanocluster-carbonate adduct. No effect of adsorbed water on energetics of carbonate decomposition at the surface of gold nanocluster has been observed.

Keywords: CO oxidation, Gold nanoclusters, Reaction profile, DFT, Catalysis

Carbon-monoxide oxidation reaction is an important but simple and, computationally most explored reaction. CO oxidation on the surface of catalyst is a bimolecular gas-phase surface reaction. A number of papers focused on understanding adsorption and catalytic properties of various supported and unsupported pure metal¹⁻¹⁵ or mixed metal nanoclusters¹⁶⁻¹⁹ highlighting the complexities involved in understanding the underlying reaction mechanism of any heterogeneously catalyzed chemical reaction. The heterogeneously catalyzed reactions involve three main steps: (i) Adsorption of reactants (ii) Surface reaction and (iii) Desorption of products. The study of any heterogeneously catalyzed reaction involves in detail, the study of adsorption energetics of different reactants on distinct adsorption sites of nanoclusters/ nanoparticles. This is followed by identification of various possible surface reactions. The bimolecular gas-phase surface reactions can proceed *via* two types of mechanisms. One is the Langmuir-Hinshelwood (LH) mechanism and another is Eley-Rideal (ER) mechanism^{20,21}. In LH mechanism both reactant species for example, CO and O₂ in current case chemisorb on the catalyst surface and form an adsorbed activated species. Then a reaction between these species gives product which

gets desorbed from the catalyst surface in the last step. In ER mechanism, the surface reaction occurs between reactants with one reactant molecule chemisorbed on the catalyst surface while the other is in the gaseous form. Subsequently, the reaction between these two reactant species that is, one in adsorbed state and another in gaseous state results in formation of product which desorbs from the catalyst surface^{20,21}. The energy profile of a reaction is beyond doubt influenced by the nature of catalyst. In addition, the presence of other adsorbates as well as the support significantly modifies the involved activation energies. Here, in present study we discuss the effect of presence of water in adsorbed state on reaction profile of CO oxidation reaction catalyzed by Au₅ cluster. The gold nanoparticles can oxidize CO at low temperatures which has important implication in regard to cold start emissions problem²². The computational studies show that even in large-sized nanoparticles, it is the small units that are the site of actual reaction³ which is our motivation behind selecting Au₅ nanocluster for the study.

Computational Details and Methodology

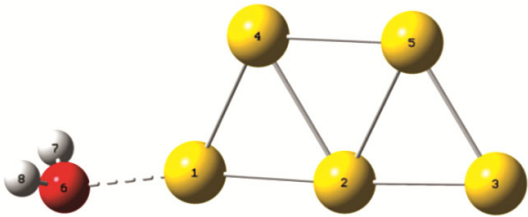
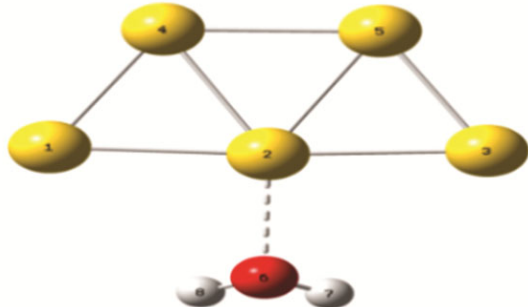
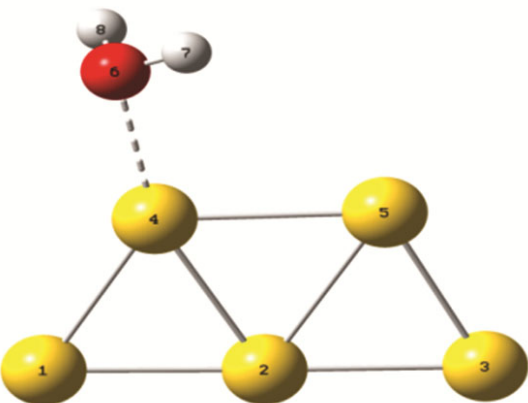
The quantum calculations have been carried out using density functional theory as implemented in

GAUSSIAN 09 package²³. To treat heavy atoms, relativistic effective core potential (ECP) has been used²⁴. For the study, we have employed LANL2TZ(f) ECP²⁵ and PW91 xc functional for Au atom while for carbon, hydrogen and oxygen atoms 6-311+G* basis set is used²⁶. The geometries of neutral clusters are optimized for doublet spin state. The clusters formed after adsorption of O₂ and CO *i.e.* Au₅O₂ and Au₅CO are optimized for different spin-multiplicities. The clusters with doublet spin multiplicity are found to be the most stable. During structure optimizations no symmetry constraints are imposed and all calculations are spin-unrestricted (UDFT). The spin contamination for UDFT calculations is found to be within the acceptable limits. Also, to identify the most preferred site for adsorption, CO and O₂ molecules are adsorbed at all distinct sites of the clusters. The calculations

suggested both CO and O₂ prefer to adsorb at 3-coordinated sites of Au₅ with Au₅CO adduct (adsorption energy, A.E. = -1.26 eV) being more stable than Au₅O₂ (A.E. = -1.04 eV in top geometry). The reason for considering the adsorption of O₂ in top geometry is explained in our previous study²⁷.

To understand the reaction profile of CO oxidation on Au₅ cluster, the starting geometry as taken in current study is Au₅COO₂ adduct, where both O₂ and CO are adsorbed on adjacent 3-coordinated sites. For the further study of effect of water in adsorbed state on the reaction profile, firstly water is adsorbed on all sites of Au₅ cluster. The most stable geometry for Au₅H₂O adduct is identified; which is H₂O adsorbed on 2-coordinated site of Au₅ (Table 1). A second water molecule is also subsequently introduced at second 2-coordinated site. This geometry of Au₅2H₂O is

Table 1 — H₂O adsorbed at different sites of Au₅ and the corresponding adsorption energies

Structure	Adsorption energy (eV)
	-0.50
	-0.30
	-0.44

selected to facilitate the comparative study. The reaction profile is computed for these two cases as well *i.e.* for Au₅.H₂O and Au₅(H₂O)₂ with CO and O₂ adsorbed at 3-coordinated Au sites as a starting geometry.

The harmonic vibrational frequencies are calculated to confirm whether the optimized geometry is ground-state or transition-state. The intrinsic reaction coordinate (IRC) calculations are carried out to validate the corresponding transition state for a given set of reactant and product. All energies reported in here, include zero-point energy (ZPE) corrections.

Results and Discussion

Reaction profile of CO oxidation catalyzed by Au₅ nanocluster

A single molecule of O₂ can oxidise two molecules of CO. The oxidation of first CO molecule on surface of bare Au₅ cluster takes place *via* LH mechanism and has been discussed in our previous study²⁶. It is developed that CO adsorption on Au₅ cluster is more favourable compared to O₂ adsorption therefore, the probability of CO binding first to the cluster is greater. For oxidation of CO, O-O bond activation is required therefore, attack of O₂ onto adsorbed CO (CO*) *via* ER mechanism is not a viable option. Hence, in our study we have considered only LH mechanism for the oxidation of first CO molecule on Au₅ surface. The oxidation of second CO molecule takes place on Au₅.O surface and both LH and ER pathways are likely. A set

of possible surface reactions which are considered in the present study are listed below.

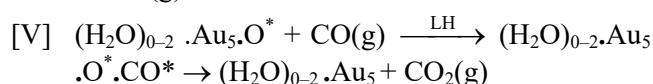
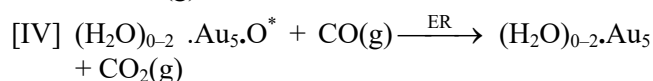
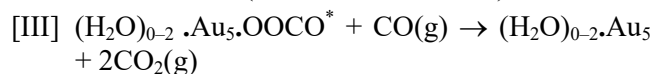
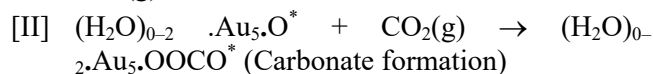
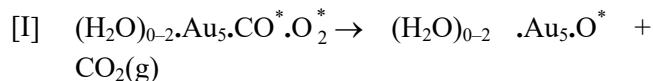


Fig. 1 shows the LH pathway of the oxidation of first CO molecule. The starting adduct of our study is CO and O₂ molecules adsorbed on adjacent three-coordinated sites of Au₅ cluster. An energy barrier of 0.50 eV exists for the transformation of adduct Au₅.CO.O₂ into Au₅.O and CO₂. Here the possibility that subsequent to desorption of CO₂; Au₅.O and CO₂ can further react to form carbonate on the cluster surface has also been considered. The formation of carbonate species can poison the catalyst surface as it is a highly stable complex. For example, the Au₅OOCO* complex has energy -4.52 eV with respect to reactants and catalyst (Au₅, O₂ and CO).

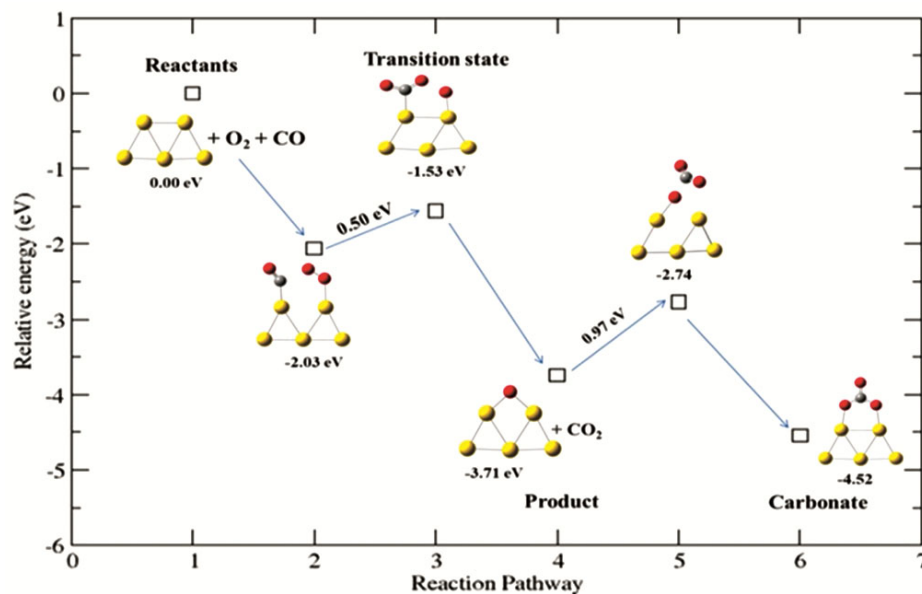


Fig. 1 — Reaction pathway of oxidation of first CO molecule on Au₅ nanocluster *via* Langmuir-Hinshelwood mechanism and formation of carbonate *via* Eley-Rideal mechanism. ("Reproduced from [Saini, S.; Yadav, J.; Parkash, J. "Mechanistic investigation into CO oxidation catalyzed by Au₅ gold cluster" AIP Conference Proceedings 2142, 190002 (2019); <https://doi.org/10.1063/1.5122634> Published Online: 29 August 2019], with the permission of AIP Publications.")

However, kinetically the formation of this carbonate complex is hindered as the barrier for the carbonate formation is 0.97 eV which is much higher therefore, the probability of carbonate formation on Au₅ surface seems improbable.

In rare case if it is formed, it can further be made to react with another carbon monoxide molecule *via* ER mechanism leading to release of two carbon dioxide molecules as shown in Fig. 2. The release involves an initial barrier of 0.32 eV followed by a rotational barrier of about 0.24 eV. With the release of two CO₂ molecules, the catalyst Au₅ is regenerated for the next cycle.

The other possible pathway which in terms of energetics is more favourable is the surface reaction of CO molecule with Au₅O which can either proceed *via* ER or LH mechanism. The ER pathway is single-step, barrier-less reaction with transition state being slightly more stable than the reactants (Au₅O and CO)²⁶.

An equally likely alternative route is through LH mechanism as here as well the first step that is; chemisorption of CO on Au₅O nanocluster leading to formation of Au₅CO.O is a barrier-less process (Fig. 3).

To summarize, the first CO molecule oxidation on Au₅ takes place *via* LH mechanism and a barrier of 0.50 eV is involved. The formation of carbonate on Au₅ surface is unlikely (barrier height = 0.97 eV). The second CO molecule oxidation which takes place on

the surface of Au₅O is equally likely to take place either *via* LH or ER pathway. In the next sub-section, the effect of adsorbed water molecules on the above discussed reaction profile is discussed.

Effect of water co-adsorption on energy profile

Haruta *et. al* in 2004 observed from his experiments that moisture enhances the rate of CO oxidation on a surface reducible and non-reducible oxides by activating O-O bond²⁸. Here, water participated in the catalytic reaction and promoted the dissociation of O₂. Here, we discuss the reaction profiles for CO oxidation on different system which is hydrated nanoclusters, *i.e.* Au₅.H₂O and Au₅.2H₂O.

In our study, the role of water is passive. It does not directly participate in the reaction but it is expected to influence the reaction through the modification of density of states profile.

CO Oxidation Catalysed by Au₅.H₂O Clusters

Likewise, the previously discussed mechanism on Au₅ cluster, for Au₅.H₂O also three coordinated gold atoms are the site for CO oxidation. The oxidation of first CO takes place *via* LH mechanism while the oxidation of second CO can proceed either *via* LH or ER mechanism. In aforesaid first step, CO and O₂ molecules are adsorbed on the surface of gold atoms at 3- coordinated sites in top form and the complex is stabilized by -2.14 eV with respect to reactants. The surface reaction between CO and activated O₂ on Au₅.H₂O cluster has a barrier height of 0.47 eV similar

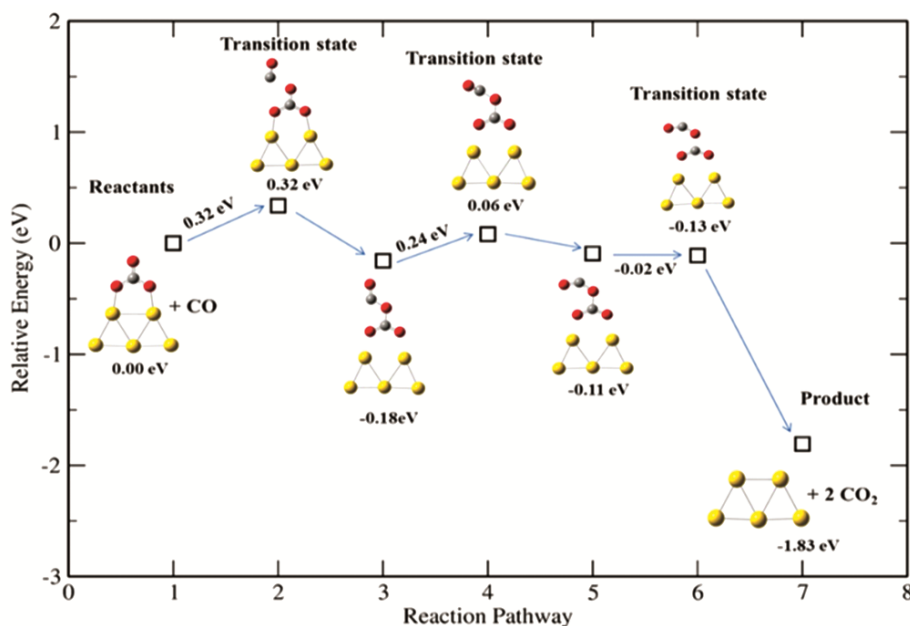


Fig. 2 — Reaction pathway of CO attack on Au₅ carbonate cluster *via* Eley-Rideal mechanism leading to decomposition of carbonate.

to that obtained for Au₅ cluster (0.50 eV). The difference lies in the activation energy required for carbonate formation. The barrier for carbonate formation on surface of Au₅.H₂O is 0.15 eV, much less compared to 0.97 eV observed for Au₅ cluster (Fig. 4). The energy profile concerning the attack of

CO molecule on carbonate Au₅.H₂O complex and its subsequent conversion into two CO₂ molecules with the regeneration of Au₅.H₂O surface is similar to the one for Au₅ cluster with energy barriers of 0.34 eV and 0.24 eV. In both Au₅.H₂O and Au₅, the decomposition of carbonate takes place *via* ER

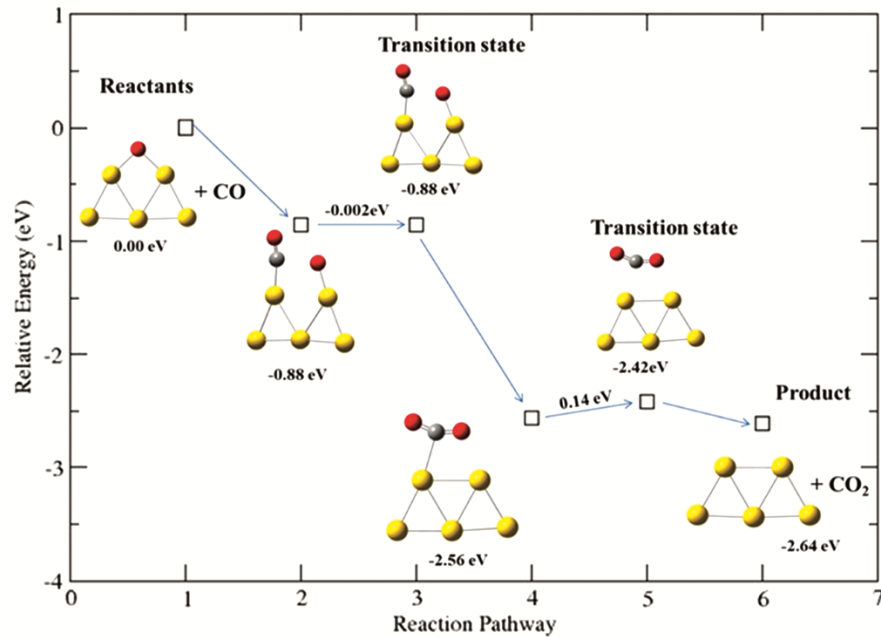


Fig. 3 — Reaction pathway illustrating the oxidation of second CO molecule on Au₅ nanocluster *via* Langmuir - Hinshelwood mechanism. A barrier of 0.14 eV is involved. ("Reproduced from [Saini, S.; Yadav, J.; Parkash, J. "Mechanistic investigation into CO oxidation catalyzed by Au₅ gold cluster" AIP Conference Proceedings 2142, 190002 (2019); <https://doi.org/10.1063/1.5122634> Published Online: 29 August 2019], with the permission of AIP Publications.")

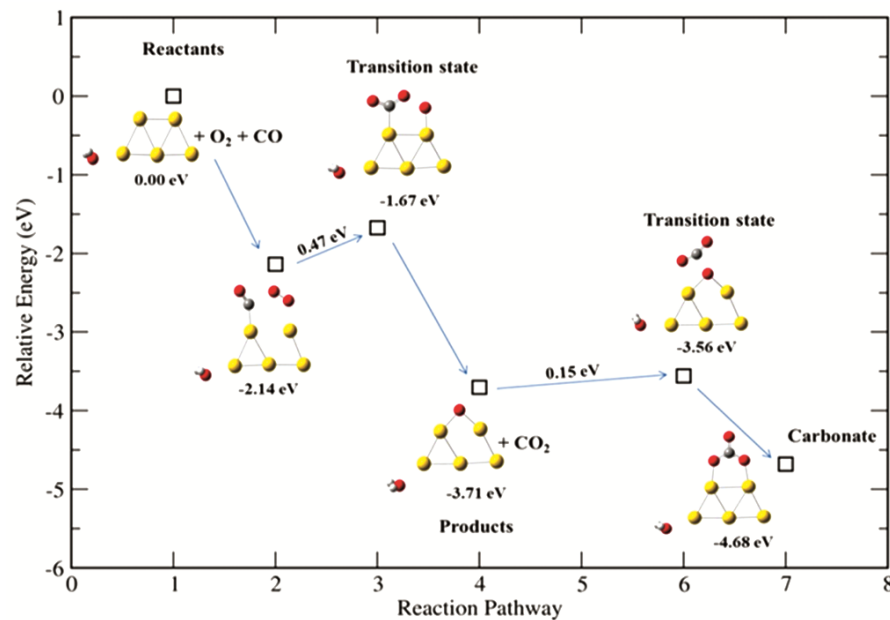


Fig. 4 — Reaction pathway of oxidation of first CO molecule on Au₅.H₂O nanocluster *via* Langmuir - Hinshelwood mechanism and formation of carbonate *via* Eley-Rideal mechanism.

mechanism and involve almost similar energy barriers.

An alternative pathway to carbonate formation available for $\text{O.Au}_5\text{.H}_2\text{O}$ following the release of first CO_2 molecule *via* LH mechanism is the surface reaction between $\text{O.Au}_5\text{.H}_2\text{O}$ and CO molecule. As before, this reaction can either proceed *via* LH or ER mechanism. In ER mechanism the reaction of $\text{O.Au}_5\text{.H}_2\text{O}$ takes place with CO in gaseous state

involving an energy barrier of 0.12 eV leading to release of CO_2 molecule (Fig. 5). Another possibility is that CO can also get adsorbed on $\text{O.Au}_5\text{.H}_2\text{O}$ and then the surface reaction between adsorbed CO and O takes place *via* LH mechanism finally releasing CO_2 molecule. ER is a single step reaction involving energy barrier while LH mechanism is multistep with first step that is adsorption of CO on $\text{O.Au}_5\text{.H}_2\text{O}$ being barrier-less (Fig 6).

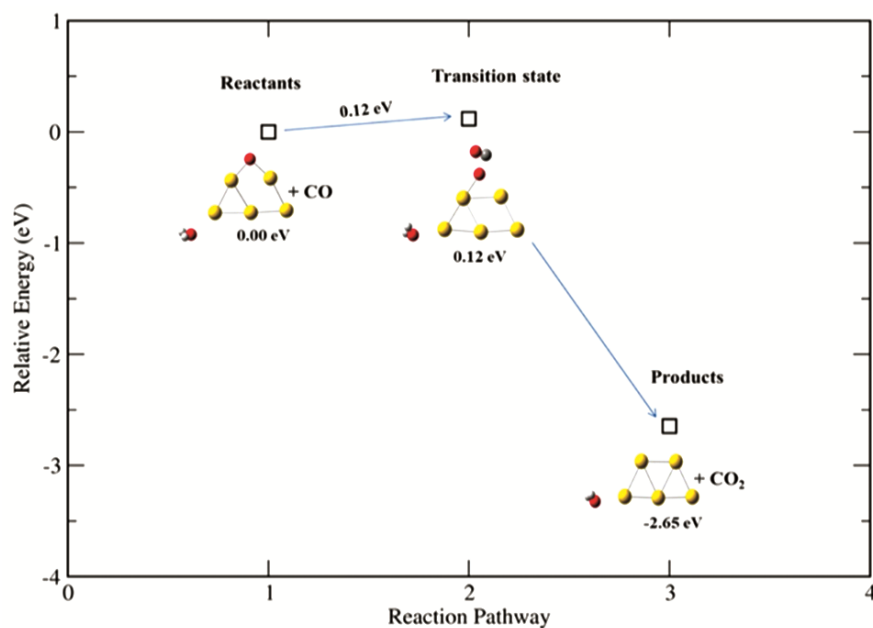


Fig. 5 — Reaction pathway illustrating the oxidation of second CO molecule on $\text{Au}_5\text{.H}_2\text{O}$ nanocluster *via* Eley-Rideal mechanism.

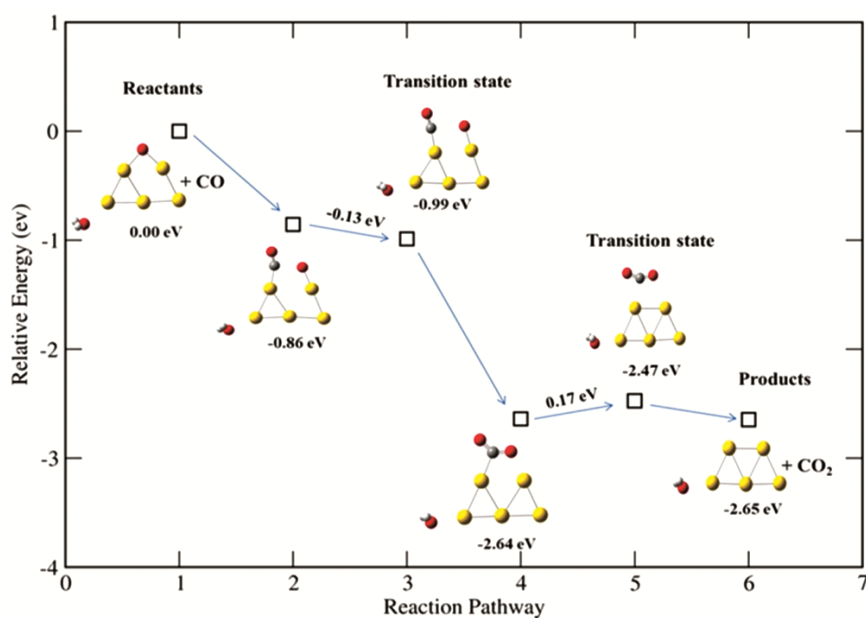


Fig. 6 — Reaction pathway illustrating the oxidation of second CO molecule on $\text{Au}_5\text{.H}_2\text{O}$ nanocluster *via* Langmuir-Hinshelwood mechanism. A barrier of 0.17 eV is involved for desorption of product, CO_2 .

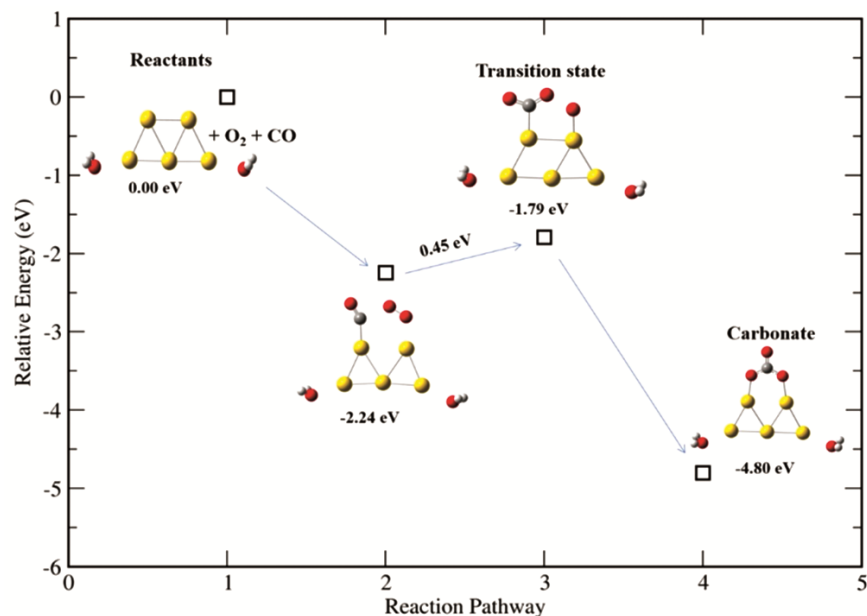


Fig 7—Energy profile of reaction between CO and O₂ molecules on Au₅.2H₂O cluster *via* Langmuir-Hinshelwood mechanism leading to formation of carbonate in a single step.

Therefore, the possibility of CO oxidation proceeding *via* LH mechanism on O.Au₅.H₂O surface is comparatively more. However, even for LH mechanism a barrier of 0.17 eV exists for desorption of formed product *i.e.* CO₂ from the surface of Au₅.H₂O. Another aspect to be noted is that (CO₂).Au₅.H₂O (cluster with CO₂ in adsorbed state) is nearly as stable as the end-products; Au₅.H₂O and CO₂ in gaseous state.

CO Oxidation Catalyzed by Au₅.2H₂O Clusters

For comparative study of CO oxidation on surface of Au₅, Au₅.H₂O and Au₅.2H₂O - two water molecules in Au₅.2H₂O are taken to be adsorbed at 2- coordinated sites leaving 3-coordinated sites free for CO oxidation.

Here, interestingly following CO and O₂ adsorption on Au₅.2H₂O, the surface reaction between these two adsorbed species leads directly to carbonate formation with an energy barrier of 0.45 eV. Fig. 7 shows the discussed reaction profile along with the geometries of clusters at different stages of reaction.

The energy profile suggests once again that the presence of water molecules in adsorbed state at sites of Au₅ favour carbonate formation. Here the only pathway available to regenerate Au₅.2H₂O surface is *via* ER reaction between Carbonate.Au₅.2H₂O adduct and CO molecule leading to release of two CO₂ molecules. Again, the energy profile for carbonate decomposition is nearly the same as for Au₅ and Au₅.H₂O clusters with two energy barriers of 0.35 eV and 0.25 eV, respectively.

Conclusion

The present study discusses the effect of water in adsorbed state on energy profile of CO oxidation at the surface of Au₅ nanocluster. The significant observation is that the presence of water reduces the energy barrier for carbonate formation. For Au₅ cluster with two water molecules adsorbed the carbonate formation takes place in single step with an energy barrier of 0.45 eV. However, carbonate formation on surface of Au₅ and Au₅.H₂O is a multistep reaction with energy barrier 0.97 eV and 0.15 eV, respectively. No significant effect of water is found on energetics of carbonate decomposition for ER reaction pathway in which CO in gaseous state interacts with carbonate species.

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