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Reactivity of anionic gold oxide clusters towards CO: experiment and theory

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Abstract. In this paper, we present results from our joint experimental and theoretical study of the reactivity of anionic gold oxide clusters $Au_{2,3}O_{1-4}^-$ towards CO. We provide clear evidence that, although O–O bond weakening/dissociation is important to enable CO oxidation, the presence of atomic oxygen can be favorable but is not always sufficient. Furthermore, we show that with the addition of a single gold atom the reactivity channels can be changed. As a consequence, in contrast to CO oxidation in the case of anionic gold dimer oxides, association of CO or replacement of O_2 by CO become the dominant reaction channels for $Au_3O_n^-$. This demonstrates the nonscalable properties of gold clusters in the size regime in which each atom counts.

PACS. 31.15.Qg Molecular dynamics and other numerical methods – 31.15.Ar Ab initio calculations

1 Introduction

Due to the findings of Haruta and coworkers [1–4] the oxidation of CO in the presence of gold has been a topic of numerous condensed and gas-phase studies [5,6]. However, the roles of size, charge state, support effects, the nature of the active site, and responsible mechanisms are still not fully clear. Many past studies have focused on the weakening of the molecular oxygen bond to promote the oxidation reaction. The general view is that neutral gold clusters alone cannot activate the O–O bond without influences from the substrate such as a charge transfer [7].

Recent literature has revealed that gold oxides with both atomic and molecular oxygen may play a role as the active site in supported gold catalysts [8–10]. Therefore, a fundamental question can be raised as to whether it is sufficient to have an atomic oxygen in order for the oxidation reaction to proceed. Our joint experimental and theoretical study is aimed at examining the role of atomic oxygen in the oxidation reaction. Our findings presented herein offer evidence of the fundamental processes and characteristics that accompany the oxidation of CO in the presence of $Au_{2,3}O_n^-$ ($n = 1$–4). Furthermore, theoretical exploration allows the identification of reactive centers and the proposal of viable general reaction mechanisms. Along with previously reported results for the CO oxidation reaction in the presence of AuO_n^- [11] we wish to show that a peripheral O-atom is the most effective center for the oxidation reaction. Moreover, while O–O bond weakening/dissociation is important to enable CO oxidation [7], we provide clear evidence that the presence of atomic oxygen is not always sufficient.

2 Experimental and computational

A fast flow reactor and a guided ion beam mass spectrometer were utilized to experimentally investigate the interactions between CO and gold oxides with both atomized and molecular oxygen [11,12]. Preoxidized gold oxide cluster ions were formed by passing oxygen seeded in helium over the metal plasma in the laser vaporization source. With the fast flow reactor, the gold oxides were then subjected to increasing amounts of CO (0–200 std cm^3 min^{-1}) added at a reactant gas inlet (RGI) located downstream of cluster formation. Moreover, fluctuations in ion intensity were monitored by alternating between the CO being turned on and off over the course of the reaction. The guided ion beam apparatus was employed to confirm the results from the flow tube studies and allowed mass-selected species to undergo reactions with CO. Collisional studies were used to confirm the presence of atomic versus molecular oxygen in the guided ion beam mass spectrometer. In these experiments, the gold oxides produced in the laser vaporization source were subjected to a flow of inert nitrogen in the octopole.

The resulting fragments verified structural features, such as the existence of molecular or atomized oxygen. Geometrical properties and the reactivity of the gold oxide

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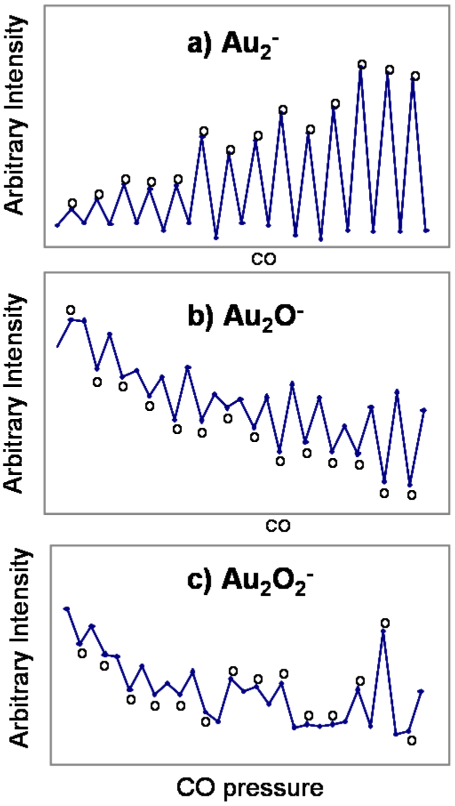

Fig. 1. "On/off" plots of the intensity of (a) Au_2^-, (b) Au_2O^-, and (c) $Au_2O_2^-$. In the plots, "o" always represents when CO is being added at the RGI and corresponds to the labels on the x-axis. The points not labeled represent when no CO is added. Other plots for $Au_2O_3^-$ and $Au_2O_4^-$ are similar to (b), having a decreasing pattern as CO is added, indicative of a species reacting away.

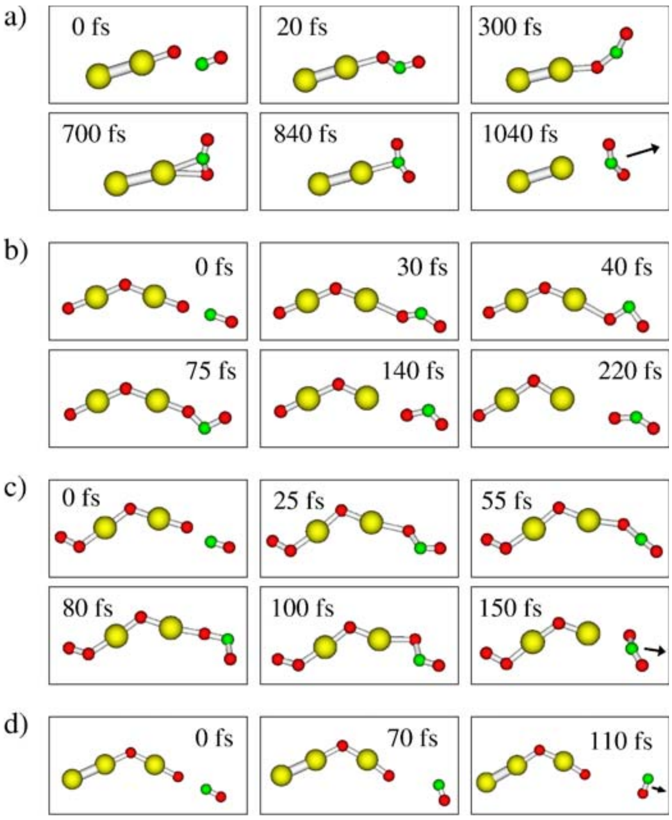

Fig. 2. (Color online) MD snapshots for the reaction of (a) Au_2O^-, (b) $Au_2O_3^-$, (c) $Au_2O_4^-$ and (d) $Au_3O_2^-$ with CO. (a), (b), and (c) show CO reacting with a peripheral oxygen atom on the gold oxide cluster to produce CO_2. Note in (d) for $Au_3O_2^-$, the CO molecule does not react with the peripheral oxygen.

clusters $Au_mO_n^-$ ($m = 2, 3$; $n = 1–5$) have been studied using a DFT method with the B3LYP [13,14] functional employing the Stuttgart scalar relativistic 19-electron effective core potential (19e$^-$ RECP) with corresponding basis set for gold [15] and 6-311G* basis set for C and O. The choice of functional, effective core potential, and AO basis set allows for a proper description of binding energies and reactivity patterns as has been demonstrated for the adsorption of O_2 and OH onto anionic gold clusters [16] and the oxidation reaction of gold oxide clusters with CO [11,17]. The reaction mechanism has been also revealed by performing ab initio MD simulations.

3 Results and discussion

Our flow tube experiments revealed that Au_2O^-, $Au_2O_3^-$, and $Au_2O_4^-$ decrease in intensity with CO addition, while the intensity of $Au_2O_2^-$ remains relatively unaffected [17]. Furthermore, the intensity of Au_2^- increased with CO addition. Experiments were also conducted in which CO was turned on and off in order to confirm that reactions are occurring for $Au_2O_{1,3,4}^-$. As shown in Figure 1, the intensity of those species considered to be reactive decreases when the CO is flowing. This is the case for the example of Au_2O^-. There is no consistent oscillatory pattern for the unreactive species in the "on/off" plots (cf. Fig. 1c for $Au_2O_2^-$). Notice the overall ion signal decreases slightly for all species as the gold rod is ablated.

In order to determine the specific type of reaction taking place, we present our theoretical results. Based on the structural properties of the gold oxides reported elsewhere [17], three kinds of reaction centers are considered for the oxidation reaction of CO with gold oxide clusters. These include a peripheral O-atom, a bridging O-atom, and a molecular O_2-group. We previously reported that AuO^- and AuO_3^- react to promote CO oxidation via transfer of a peripheral oxygen atom [11]. Since the lowest energy structures of Au_2O^-, $Au_2O_3^-$, and $Au_2O_4^-$ possess a peripheral O-atom, these species are also good candidates for the CO oxidation reaction. We present MD snapshots for Au_2O^-, $Au_2O_3^-$, and $Au_2O_4^-$ in Figures 2a–2c. These snapshots illustrate that the CO oxidation reaction also proceeds for these species.

As illustrated in Figure 3, the oxidation reactions follow a general mechanism which is also valid for the anionic gold monomers [11]. The oxidation channel involves initial formation of complex I with a weakly bound CO molecule, followed by a charge transfer from the cluster to CO, giving rise to the formation of structure II with a CO_2 subunit. Subsequently, this complex fragments via either rotation of the O−CO group (TS_3) or a bond rearrangement channel which involves breaking of the Au−O bond and simultaneous formation of a Au−C bond. The final emanation of CO_2 is accompanied by a charge transfer from the CO_2 subunit back to gold.

The theoretical oxidation channel has been confirmed by mass selected experiments involving individual cluster species [17]. The findings for Au_2O^- show that the reaction is selective for the oxidation of CO. As will be reported in a longer detailed paper [17], mass selected experimental plots also support an oxygen atom transfer pathway for $Au_2O_3^-$ and $Au_2O_4^-$.

The fact that the presence of a peripheral oxygen atom is not sufficient in promoting the oxidation reaction is most evident for $Au_3O_2^-$, for which DFT calculations show that the stable structures possess a peripheral oxygen atom [17]. Even though the overall reaction of this species would be exothermic, the energy of the transition state is higher than those of the reactants and thus creates a bottleneck for the reaction. This is evidenced by MD snapshots in Figure 2d which show repulsion of CO in the presence of $Au_3O_2^-$, and it is further supported by mass selection experiments in which no reaction has been found. Moreover, in spectra recorded by our flow tube technique, no increase in the intensity of the possible product species, Au_3O^-, has been observed. In the case of $Au_3O_4^-$, no oxidation has been observed or predicted [17]. To summarize, although the presence of a peripheral oxygen atom is an important feature, it is the synergistic effect with the energy barriers that is crucial for the oxidation of CO.

A second type of reactive center, the bridging O-atom, seems to be less effective for the oxidation reaction. In the case of Au_3O^-, no oxidation reaction has been observed experimentally [17]. Calculations find that the transition states are comparable in energy with the reactants, which suggests that, if a reaction involving a bridging oxygen atom occurs, it will be very slow. In the case that the Au−O bond strength is enhanced due to a polarization effect introduced by binding an electron acceptor group to the gold atom (e.g. O-atom, O_2-group), the reaction will not proceed.

The third type of reactive center is the molecular O_2-group. For $Au_2O_2^-$, the reaction in which a single CO is oxidized by a molecular O_2 cannot proceed under our experimental conditions due to the high barriers necessary to break the strong O−O bond (3.19 eV), as identified by DFT calculations. If cooperative effects are not present, the barriers involved in the oxidation reaction are too high to be surmounted. In accordance, our experiments have not shown any oxidation reactions involving species with the molecular O_2-group. However, they can be observed under different experimental conditions [17–19] in which cooperative effects can take place. There are other possible reaction pathways involving association onto the $Au_3O_n^-$ and/or replacement of a molecular oxygen group which will be considered in a later paper [17].

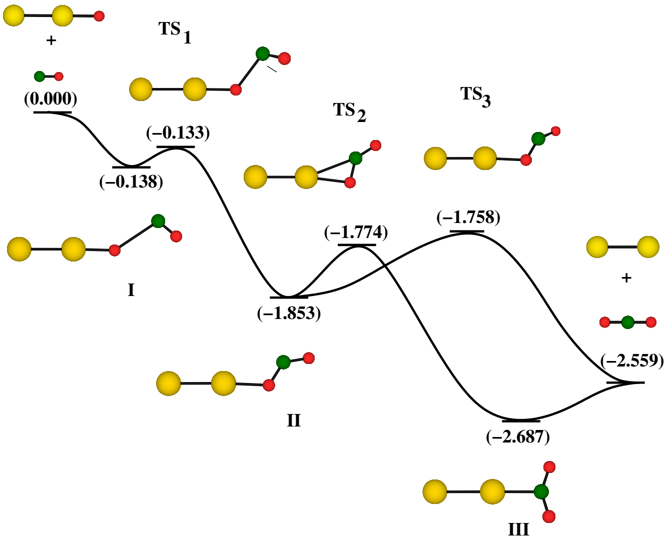

Fig. 3. (Color online) Reaction profile for the reaction of Au_2O^- with CO. Local minima are labeled with I-III, transition states with TS_1-TS_3. The atom colors are: green for C, red for O, and yellow for Au. Energies in eV relative to the reactants are given in parenthesis.

4 Conclusion

In conclusion, we propose a mechanism and have revealed structure-reactivity relationships in which the presence of a peripheral oxygen atom is necessary, under our experimental conditions, for the oxidation of CO to take place in the presence of gold cluster anions. However, the existence of a peripheral oxygen atom does not ensure that the reaction will proceed. Hence, it is the presence of the peripheral oxygen atom along with surmountable reaction barriers that enables the oxidation of CO in the presence of gold oxide cluster anions. Only those species with a favorable TS with respect to the reactants can react to oxidize CO. Our joint gas phase experimental and theoretical results presented herein provide valuable insight into the role of gold and atomic oxygen in the oxidation of CO. Moreover, our results show that the effect of "each atom counts" is present in going from dimer to trimer oxide clusters; by adding a single gold atom, different reaction channels, such as association and replacement as opposed to oxidation, can be preferable. Furthermore, these studies have shed light onto some of the fundamental processes and relationships that may be essential for the reactions to proceed.

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