Gas-Phase Catalytic Oxidation of CO by Au$_2$-

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Chemical reactivity of transition metal clusters toward various molecules in gas phase has been a subject of numerous investigations,1,2 motivated by search of analogues to adsorption mechanisms and reactivity at bulk metal surfaces. However, the full catalytic cycle, involving detection of a product molecule XY, as a result of reaction between reactants X and Y in the presence of the metal cluster M (possibly through an intermediate compound MXY), has been demonstrated experimentally only in a handful of studies.2

While it is well-known that gold is chemically inert as bulk material, nanometer-sized dispersed gold particles often show remarkable catalytic activity.3 Most recently it was found that mass-selected deposited gold clusters Au$_n$ (N = 2 - 20) on MgO(001) exhibit extremely sensitive size-effects in the catalytic activity to oxidize CO: only clusters with eight or more atoms catalyzed the reaction, and the CO$_2$ yield had a nontrivial dependence on the cluster size for N ≥ 8.4 A concurrent theoretical study revealed that charging effects (by electrons trapped in surface color centers of MgO) are important in activating the gold cluster and the adsorbed O$_2$.5 It is then of interest to study also the reactivity and catalytic properties of small negatively charged gold clusters with O$_2$ and CO.

We present here a detailed investigation, based on the density functional theory, on the interactions of oxygen and carbon monoxide with the gold dimer anion, which is the smallest gold cluster found to react with oxygen in the gas phase.5 We find that oxygen should bind molecularly to Au$_2$$^-$.

Furthermore, we studied a full catalytic cycle, producing two carbon dioxide molecules, and identified a key intermediate state, di-gold--carbonate, which should be detectable in the experiments.6

In this study the Kohn–Sham (KS) equations were solved using the Born–Oppenheimer local-spin-density molecular dynamics (BO-LSD-MD) method,7 including generalized gradient corrections (GGA),8 with nonlocal norm-conserving pseudopotentials9 for the 5d$^{10}$6s$^2$4p$^2$, and 2s$^2$2p$^4$ valence electrons of Au, C, and O atoms, respectively. Bonding in gold clusters requires a relativistic treatment;10,11 a scalar-relativistic pseudopotential was used here. From comparison of several calculated properties of basic dimers Au$_2$, Au$_{2}$-, AuO, AuO$^-$, and molecules O$_2$, CO, as well as CO$_2$, to available experimental values in Table 1, we judge that calculations at the GGA level give a rather satisfactory description of the energetics and structure of these systems. The same methodology was used recently by us to study oxidation of CO at a single Pd atom adsorbed on a surface color center on a MgO(001) film,13 and the calculated reaction barriers agree favorably with the ones deduced from the experiment.13

We found two bonding configurations for Au$_2$CO$^-$, shown in Figure 1. In the ground-state (GS) “end-bonded” configuration (Figure 1a) both the Au–Au and C–O bonds are significantly stretched. The calculated adsorption energy of CO is 0.96 eV. In the “side-bonded” configuration (Figure 1c), which is 0.41 eV less stable than the GS, the CO induces a break-up of the Au–Au bond. This illustrates the ability of CO to bind to different sites of the metal cluster, reminiscent of various adsorption sites on transition metal surfaces (e.g., on-top, bridge, etc.).

The bonding of CO to transition metal surfaces is generally characterized by charge transfer from the metal (donation) to the antibonding CO($\pi^*$) orbital, and back-donation to the metal mainly from the bonding CO($\sigma^*$) orbital.15 Similar concepts apply

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<tr>
<th>Table 1. GGA vs Experimental Data of Bonding</th>
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*(b) Shown are spin $S$, bond length $d$, dissociation energy $D$, and (b) vertical ionization potential, vIP, or (c) vertical electron detachment energy, vDE, for neutral and anionic systems, respectively. The experimental data is shown in parentheses. Reference 14.  
Reference 15 (adiabatic value).  
Adiabatic EA from refS 14, 16 is 1.94 eV to be compared to 2.02 eV from theory.  
Reference 17.  
Reference 18.  
Atomicization energy.

Figure 1. (a) Ground-state (GS) structure (S = 1/2) of Au$_2$CO$^-$; (b) contour plot of density difference, $\Delta\rho = \rho({\text{Au CO}}^-) - \rho({\text{Au}}^-) - \rho({\text{CO}})$.  
(c) “side-bonded” isomer (S = 1/2). BE is the binding (adsorption) energy of CO. vDE is the vertical electron detachment energy. The contours of $\Delta\rho$ are shown in the range of −0.015–0.015 au with 0.006 au intervals. Dashed (solid) line denotes depletion (accumulation) of the density. The indicated bond lengths are given in Å.
Au₂CO complex, for which the Au—O bond is stretched by 8%, whence the Au—O—di-oxygen is pulled together, with a donation to Au₂O₂ and the extra electron of the anionic complex promotes occupation of the initially half-filled O₂(π*) antibonding orbitals (by 0.4e), making oxygen a superoxo-like species. The stability of the GS molecular complex suggests that molecular oxygen adsorption to gold should be realizable under common experimental conditions.

We turn now to study the full catalytic cycle of oxidation of CO in the presence of Au₂⁻: Au₂⁻ + O₂ + 2CO → Au₂ + 2CO₂ (Scheme 1). (I) is the elementary step of O₂ adsorption, which we predict to occur molecularly as shown in Figure 2a and discussed above. Adding CO from the gas phase may lead to several intermediate complexes, out of which a carbonate complex is formed thermodynamically the most stable. The formation of the carbonate involves an activation barrier of 0.3 eV. This di-gold carbonate is the key intermediate compound in the reaction cycle, and its experimental verification would be most interesting. Since it has a distinctively high electron detachment energy, 4.67 eV, reflecting its stability, and setting it apart from the other possible compounds of the same mass, it should be detectable experimentally by photoelectron studies. From the carbonate, the reaction cycle can proceed along two branches, corresponding to steps (IIIa) or (IIIb). Step (IIIa) includes reaction of a gas-phase CO with Au₂CO₂, which requires an activation barrier of 0.5 eV but produces simultaneously two CO₂ molecules. Step (IIIb) is endothermic, requiring 1.12 eV to detach the CO₂ molecule from the carbonate; however, the remaining linear Au₂O⁻ is highly reactive with another gas-phase CO, producing CO₂ without an activation barrier (step IV). In both cases, the total exothermicity of the oxidation reaction is 3.25 eV per CO₂.

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Figure 2. Four lowest-energy structures of Au₂O₂⁻.

![Diagram of Au₂O₂⁻ complexes](image)

The optimized structures of several Au₂O₂⁻ complexes are shown in Figure 2a–d. As evident from Figure 2a, binding of dioxygen to Au₂⁻ can take place in various ways, which may involve both Au—Au and O—O bond breaking. However, in the GS configuration (Figure 2a) oxygen is clearly molecularly and rather strongly (BE = 1.39 eV) bound to gold. In this “end-bonded” configuration, which is energetically 0.6 eV more stable than the first isomer (Au—O—Au—O linear chain) the O—O bond is stretched by 8%, whence the Au—Au bond length is intermediate between that of the neutral and anionic Au₂. Spatial analysis of the electronic charge indicates a net transfer of 0.26e to oxygen, while the electron density of the anionic complex promotes occupation of the initially half-filled O₂(π*) antibonding orbitals (by 0.4e), making oxygen a superoxo-like species. The stability of the GS molecular complex suggests that molecular oxygen adsorption to gold should be realizable under common experimental conditions.

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(23) Written formally as Au₂—Au—O(O)—CO—O—O⁻. The bond lengths are: d(Au—Au) = 2.36 Å; d(Au—O(1)) = 2.09 Å; d(O(1)—C) = 1.29 Å; and for the two C—O bonds d(C—O) = 1.27 Å. The O—CO₂ plane has an angle of 127.4° with the Au–Au–O(1) axis, ζ(O(CO₂)) = 118.3°, and ζ(Au—O(1)) = 123.8°.

(24) Three other structures are also energetically feasible: (i) Another carbonate, which could be formed by inserting CO in the middle of the O—O bond of Au₂O₂⁻. In Figure 2d, (ii) a coadsorbed OC—Au—Au—O, and (iii) a coadsorbed Au—(CO)—Au—O⁻ structure. The energy difference ΔE of the GS and VDE for these structures are: (i) ΔE = 1.04 eV; VDE = 3.38 eV; ζ(Au—O) = 1.27 Å; and for the two C—O bonds d(C—O) = 1.27 Å. The O—CO₂ plane has an angle of 127.4° with the Au–Au–O(1) axis, ζ(O(CO₂)) = 118.3°, and ζ(Au—O(1)) = 123.8°.

(25) Reaction barriers were determined by constrained optimizations, where the reaction coordinate x (distance between chosen atoms, e.g., the C atom of the approaching CO molecule and one of the O atoms of the Au₂O₂⁻ in step II), was changed by increments of 0.1—0.2 Å, with all other degrees of freedom fully relaxed for each value of x. This procedure yields the shape of the reaction barrier along the reaction path, and with the discretization of x used here the barrier height (and the transition state) is estimated within 0.1 eV. The connectivity between the transition state and the products in steps (II), (IIIa) was verified using first-principles dynamical simulations, releasing the system from the transition state.