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Catalytic CO Oxidation by a Gold Nanoparticle: A Density Functional Study

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Gold is usually considered extremely noble. It does not oxidize, and the surface of gold cannot adsorb most molecules from the gas phase.[1,2] Yet it has been found that nanometer size gold particles on different oxide supports can act as catalysts even at or below room temperature.[3] This has started a search for the factors making nanosized gold particles catalytically active. Suggestions include quantum size effects,[4] charging of the gold particles by interaction with defects in the oxide,[5] availability of low coordinated sites, and strain[6] or combined effects of the gold particles and the oxide support.[7]

In the present paper, we present self-consistent density functional calculations showing that an isolated Au_{10} cluster should be able to catalyze the CO oxidation reaction even below room temperature. We use the calculations to analyze the origin of this effect and suggest that the extraordinary reactivity can be traced back to special reaction geometries available at small particles in combination with an enhanced ability of low coordinated gold atoms to interact with molecules from the surroundings.

Our starting point is a complete mapping of the CO oxidation process on the Au_{10} cluster. Following detailed scanning tunneling microscopy studies of gold nanoparticles deposited on a single-crystal $TiO_2(110)$ support,[4] we have chosen a disklike geometry of our Au particle, cf. Figure 1. The lower layer contains seven atoms, while the top layer contains three. The basal plane is an fcc(111) face, in accordance with experiment.[8] By choosing this geometry (which is not the equilibrium structure for an Au_{10} free particle[9]), we mimic in an indirect way the influence of the support because direct electronic effects are small for $TiO_2(110)$.[10]

The calculations are based on density functional theory with exchange-correlation effects described by the generalized gradient approximation.[11] A periodic array of clusters each in a cubic unit cell with a side length of 15 Å is used to expand the Kohn−Sham one-electron valence states in a basis of plane waves. The ionic cores are described by ultra soft pseudopotentials,[12] and convergence with respect to the basis set is obtained by using plane waves with kinetic energies up to 340 eV. Because the unit cell is large enough that there are no interactions between clusters, the Brillouin zone is sampled by only the Γ point. The self-consistent electron density is determined by iterative diagonalization of the Kohn−Sham Hamiltonian. Fermi population of the KS states ($k_BT = 0.2$ eV) and Pulay mixing of the resulting electronic density[13] have been used. Total energies have been extrapolated to $k_BT = 0$ eV. All structures are completely relaxed, and to model the presence of the substrate only positive values of z have been allowed for the adsorbates excluding the volume occupied by the support. The minimum reaction paths for the elementary reactions considered have been found using the nudged elastic band method.[14]

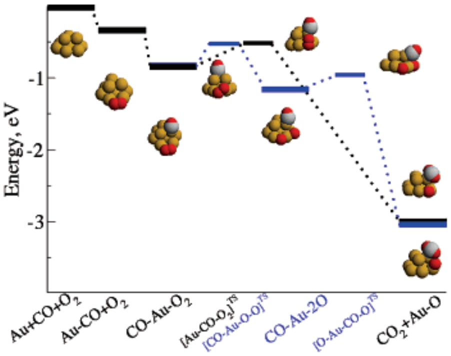

Figure 1. Reaction profiles for CO oxidation on Au_{10} particles. All energies are given with respect to CO and O_2 in the gas phase. Black color, direct path; blue, indirect path. Thicker lines represent stable states, while thinner lines correspond to transition states. Yellow spheres represent Au atoms, red spheres represent O atoms, and gray spheres represent C atoms.

The results are summarized in Figure 1. We have considered two different reaction paths, one where O_2 dissociates and one where adsorbed O_2 reacts directly with adsorbed CO. Both reactions are found to be extremely facile on the Au_{10} cluster, with reaction barriers less that 0.4 eV indicating that the reactions should be possible well below room temperature.

In both reaction paths, O_2 is first adsorbed into an O_2^- superoxide-like state with an O−O distance of 1.37 Å. This is in accordance with results from recent FTIR and EPR experiments and DFT calculations.[15]

O_2 dissociation is extremely facile on Au_{10}, and, contrary to the case on a Au(111) surface,[6] atomically adsorbed O is stable relative to O_2 in the gas phase. The stronger bonding of oxygen to low-coordinated Au atoms is in accordance with recent experiments indicating nascent oxygen atoms and oxide formation on a very sharp Au tip and for small neutral clusters.[16]

Once O_2 is dissociated, the barrier for CO_2 formation is also small, considerably smaller than on Pt(111), for instance.[17] We suggest that the key to this difference is that atomic oxygen is bound considerably weaker on the gold cluster than on Pt(111), so that it is easier for it to react further.[18]

After the first CO_2 molecule has left the surface, a second CO molecule can adsorb and react with the remaining O atom with a barrier similar to the one for the first oxidation step.

The path without dissociation is governed by the reactivity of the O_2 molecular precursor. Adsorbed O_2 can rotate and bind with only one oxygen atom to the gold edge, while the other atom gets closer to the already adsorbed CO molecule. Both the adsorption energies and the reaction barriers are considerably smaller than on Au(111) and on the stepped Au(211) surface;[6,18] see Figure 2.

Our calculations provide clear evidence that an Au nanocluster can perform interesting catalytic chemistry, and we are now in a position to investigate in more detail what the origin is of this effect.

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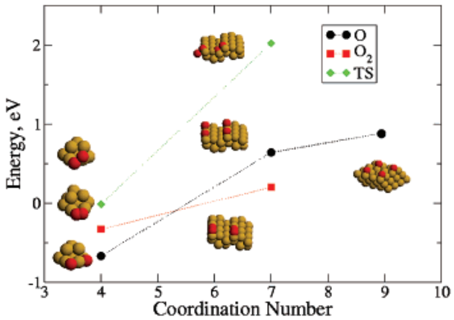

Figure 2. Binding energy of different oxygen species, versus gas-phase O_2, plotted with respect to the coordination number of the Au atoms of the site. Yellow spheres represent Au atoms, red spheres represent O atoms, and gray spheres represent C atoms.

Before doing so, we note that our cluster is neutral. A charged cluster is therefore not necessary for a large reactivity, but of course charging may also help.[5] There are two possible explanations of the high catalytic activity of the Au_{10} cluster. One is that the electronic structure of the Au atoms in the cluster is significantly different from Au atoms at the surface of a large crystal. The other is that the small clusters offer special geometrical configurations that cannot be found on extended surfaces.

To investigate the role of electronic effects, consider the adsorption energies of O_2 and O on Au_{10} in comparison to similar values for Au(111) and (211) from the literature.[6,18,19] The local adsorption geometries are essentially the same in the systems considered; O_2 is adsorbed in a bridge configuration with the two O atoms coordinating to one Au atom each, while the O atoms coordinate to two Au atoms at the step. On Au(111), the O atoms coordinate to three Au atoms, though. In Figure 2, the adsorption energies are plotted as a function of the Au coordination number, and a very strong dependence on this parameter is observed. This behavior is well known from other adsorbates and metal substrates and can be related to changes in the Au electronic structure with coordination number. In particular, it has been shown that the average energy for the d electron states is a good descriptor, the underlying physical reason being that the higher in energy the d electron states are, the better they can interact with adsorbate states.[2] In accordance with this, the d states of Au_{10} are 0.75 eV higher in energy than the d states of the surface atoms of an Au(111) surface. The large differences in adsorption energies can thus be traced back to an electronic effect: Au atoms with low coordination numbers have higher lying d states, which interact stronger with the adsorbate states. This effect has been observed at steps and kinks on the surface of extended crystals[19,20] and clearly operates even for a 10-atom cluster.

We now turn to the energy of the transition state for the O_2 dissociation reaction. Here the variation with coordination number is much stronger than that for the adsorption energies; see Figure 2. This could be due to a stronger coupling to the d states, but an inspection of the transition state geometry in Figure 1 indicates an additional explanation: The small cluster has low coordinated Au atoms in positions such that the O atoms in the transition state can coordinate to three low coordinated Au atoms at the same time. This geometry is characteristic of corners of the small particle and cannot be found at a straight step of an extended surface, for instance. The Au_{10} cluster thus offers both very low coordinated atoms *and* a very favorable dissociation geometry.

The Au_{10} particle we have studied here is only a model system. Yet the calculated potential energy diagram for the CO oxidation reaction shows good agreement with available experiments concerning adsorption properties, and it indicates energy barriers consistent with a CO oxidation process running at temperatures below room temperature.[3,4] We have identified two factors making the Au_{10} cluster considerably more reactive than extended Au surfaces: It has very low coordinated Au atoms which are able to interact stronger with adsorbates, and it has sites with a geometry which is particularly well suited for reactions involving bond breaking (and formation) in small molecules where two atoms or molecules close to each other both need to be stabilized. This picture offers an immediate explanation of the special reactivity of nanosized Au clusters. Only clusters in the nanoscale regime have the very low coordinated Au atoms *and* a sufficiently large fraction of corner sites.[6] The present calculations also suggest that having small particles is not enough. The particles must have a high fraction of special geometries. This implies that size and shape of the particles are both important parameters.

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