Gold Clusters

DOI: 10.1002/anie.201003851

Formation of Gold(I) Edge Oxide at Flat Gold Nanoclusters on an Ultrathin MgO Film under Ambient Conditions**

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Intensive experimental work since the early 1980s has revealed that gold nanoparticles exhibit unexpected catalytic activity in many industrially important chemical reactions that involve activation of O–O, C–C, and C–H bonds.[1] Low-temperature CO oxidation is one of the most extensively studied processes, and a number of different factors have been suggested to contribute to the ability of gold particles to activate the O–O bond, which is considered to be the key reaction step.[2] Many active gold catalysts are prepared on reducible oxides, and strong interactions between the support and the gold particle may create active sites at the periphery close to the particle–support interface. These interactions may also include charge transfer to or from the particle. For purely geometric reasons, small particles have a high proportion of low-coordinated edge and corner atoms that might act as reaction centers. Also, thermal effects from localized soft phonon modes at particle edges may contribute to the lowering of critical reaction barriers.

Lately, a large amount of work has been conducted to elucidate the properties of gold clusters on ultrathin (a few monolayers (ML) thick) MgO films supported by metal, typically silver.[3,4] On thin MgO films, Au clusters become multiply negatively charged by charge transfer from the support through the ultrathin oxide, they wet the film effectively by growth of two-dimensional islands, and they bind strongly to the support. The excess electron charge on the clusters is located at the edge atoms,[5] which possibly makes the edge sites reaction centers for activation of the O–O bond by charge transfer to the antibonding $2\pi^*$ orbital of O_2. Density functional theory (DFT) studies have recently considered the adsorption and dissociation of a single O_2 molecule at these sites and its relevance for CO oxidation.[6]

While studies of CO oxidation at a minimal reactant coverage on a gold cluster over MgO/metal can yield valuable information regarding the reaction mechanism,[6] attempts to bridge the materials and pressure gaps are essential to discover potential morphology changes of the catalyst particle under ambient conditions. Herein, we report a joint DFT and ab initio thermodynamics (AITD) investigation on adsorption and dissociation of multiple O_2 molecules at the edges of a nanometer-sized flat Au_{14} cluster supported by MgO(2ML)/Ag. Our results highlight a novel ability of the gold cluster to act as an exothermic center to adsorb multiple O_2 molecules, activating each adsorbed molecule by charge transfer from the support. The low molecular dissociation barrier leads to a kinetically favorable and exothermic oxygen-induced reconstruction of the cluster edge, where alternating O-Au-O-Au-O chains are spontaneously formed. Atom charge and bonding analysis of such reconstructed gold clusters indicates formation of a novel one-dimensional edge oxide of gold in which the edge Au atoms are formally Au^I. AITD calculations show that this reconstructed edge oxide state of the cluster is the Gibbs free energy minimum for a large range of oxygen chemical potentials, including ambient conditions ($T = 300$ K, $p = 1$ atm).

Our previous DFT investigations together with scanning tunneling microscopy imaging and spectroscopy studies by Freund's group have identified the atomic and electronic structure of a few flat gold clusters formed on the MgO-(2ML)/Ag support.[4h] We selected two clusters, Au_{14} and Au_{18}, from the previous work and subjected them to a variable number of O_2 molecules and O atoms. Herein we discuss primarily results obtained for the smaller cluster; the calculations for the larger cluster show that our conclusions are independent of the cluster size in this size region. Figure S1 in the Supporting Information shows a number of favorable adsorption sites of O_2 molecules at $Au_{14}(O_2)_N$ with $N = 1$–6, 10, and the energetically best configurations for $N = 1$, 2, 6, and 10 are collected in Figure 1. The Au_{14} cluster has an idealized C_{2v} symmetry with ten atoms at the edge and four inner atoms forming a rhombuslike pattern. All the favorable adsorption sites reside at the periphery of the cluster; adsorption on top of the cluster is endothermic. The adsorption energies for all the studied cases range from -1.15 eV per O_2 molecule ($N = 1$) to -0.6 eV per O_2 molecule ($N = 10$; Figure 2). Depending of the orientation of the molecule with respect to the cluster edge, two adsorption modes are identified: perpendicular or parallel, where either one or two oxygen atoms interact with the periphery Au atoms. In both adsorption geometries, O_2 molecules also seek to interact with the Mg^{+2} ions at the film surface (Figure S2 in the Supporting Information). In the perpendicular mode, the O–O bond length is typically 1.31–1.37 Å, the Bader charge in the molecule is about -0.7 $|e|$, and the magnetic moment is approximately 1.0 μ_B. In the parallel mode, the O–O bond lengths are considerably longer than in the first case, varying from 1.44 to 1.53 Å, the Bader charges are higher (-1.0 to -1.3 $|e|$), and the magnetic moment is zero. Previously we discussed a linear correlation

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[**] We thank the Academy of Finland for financial support and CSC, the Finnish IT Center for Science, for generous computational resources and support.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201003851.

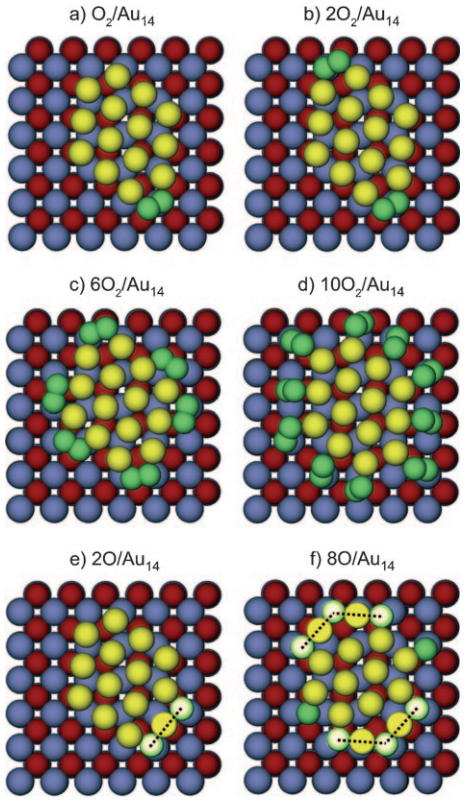

Figure 1. Optimal adsorption geometries of one, two, six, and ten O_2 molecules and two and eight O atoms at Au_{14}/MgO(2ML)/Ag. Mg blue, Au yellow, O in MgO red, O adsorbed at gold green.

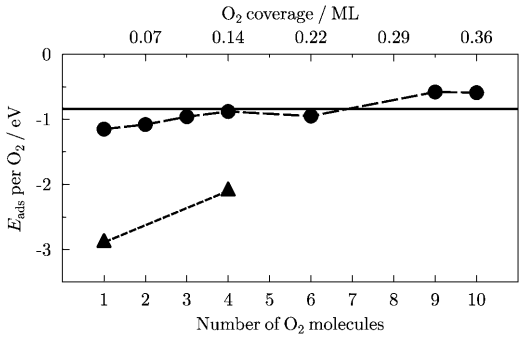

Figure 2. Adsorption energy E_{ads} of molecularly (●) and dissociatively (▲) adsorbed oxygen at Au_{14}/MgO(2ML)/Ag. The horizontal line denotes E_{ads} for O_2 on a clean MgO(2ML)/Ag film.

of the O_2 Bader charge and the degree of O–O bond elongation;[4i] it can be noted that a clear correlation between the magnetic moment and O–O bond length also exists here, as shown in Figure S3 in the Supporting Information. Analysis of the electronic density of states projected on the adsorbed O_2 (Figure S2) gives a clear indication of filling of one additional $O_2(2\pi^*)$ orbital in the perpendicular adsorption mode, which reduces the magnetic moment to 1 μ_B and two orbitals in the parallel mode quenching the magnetic moment. All these analyses support an interpretation that the electronic state of O_2 is superoxo-like in the perpendicular mode and peroxo-like in the parallel mode.

Interestingly, our calculations show that it is possible to adsorb up to ten O_2 molecules on the Au_{14} cluster, corresponding to a full coverage on the ten edge Au atoms. Different local environments at the edge lead to a slight variation of the O_2 adsorption energy, which can be characterized in two ways, by evaluating either the average adsorption energy per molecule as shown in Figure 2 or the differential adsorption energy of the *N*th molecule. Figure 2 shows that for up to six O_2 molecules, the average adsorption energy is favorable compared to our calculated value of −0.84 eV[7] for a single O_2 molecule on clean MgO(2ML)/Ag. The differential adsorption energy of the tenth O_2 molecule is still considerable (−0.75 eV). Consequently, a clear thermodynamic force exists to enable the Au_{14} cluster to act as an exothermic "sink" for the adsorption of multiple O_2 molecules. The ability of the gold cluster to simultaneously bind several O_2 molecules, reported herein for the first time, is clearly at variance with the well-known propensity of the "on–off" adsorption of O_2 at anionic gas-phase gold clusters, where only gold clusters with an even number of Au atoms and odd number of valence electrons can adsorb one O_2 molecule.[8] Adsorption of multiple O_2 molecules has not been observed in gas-phase experiments. This behavior is well understood, since adsorption of O_2 on the gas-phase gold cluster anion "consumes" the single excess electron and makes the cluster inactive for further O_2 adsorption.[9] In this case, the presence of the support Ag metal enables tunneling of multiple charges through the MgO(2ML) film to the $Au_{14}(O_2)_N$ complex, thus enabling adsorption of multiple O_2 molecules.

Having established the adsorption characteristics of molecular O_2, we now turn our attention to dissociative adsorption. We calculated the dissociation barrier for dioxygen in the $Au_{14}O_2$ complex shown in Figure 1 a, in which the O_2 molecule is adsorbed in the peroxo-like state. Figure S4 in the Supporting Information shows the initial, transition, and final states of the reaction. The transition state is characterized by an O–O distance of approximately 2.1 Å and is only 0.5 eV higher in energy than the initial state. This low barrier was also found for a dissociation process at the larger $Au_{18}O_2$ complex (not shown here) and on a Au cluster supported on MgO/Mo.[6] A considerably higher barrier (1.5 eV) is obtained on a gas-phase Au cluster,[9a] and on a Au cluster supported on bulk MgO the barrier is close to 1 eV.[2e] The final state is strongly exothermic by 1.8 eV compared to the initial molecular state. A closer inspection of the final state (Figure 1 e) shows formation of a linear O-Au-O configuration at one edge of the cluster. Next, we studied the possibility of dissociation of multiple oxygen molecules at the edge of the Au_{14} cluster. We highlight a configuration (Figure 1 f) that forms after dissociation of four O_2 molecules. The energy of this state $Au_{14}O_{8,diss}$ is exothermic by 1.2 eV per O_2 molecule compared to the $Au_{14}(O_2)_4$ configuration (Figure 2).

As shown above, a strong thermodynamic driving force exists to dissociate multiple oxygen molecules at the edge of the Au_{14} cluster, and the low dissociation barrier renders this process kinetically accessible even at low temperatures. To assess the relative thermodynamic stability of calculated

structures, the Gibbs free energy of oxygen adsorption (ΔG_{ads}) is evaluated in oxygen atmosphere. We employ an AITD method to determine an equilibrium composition and geometry of the gold cluster in contact with an O_2 gas reservoir.[10] The calculation of ΔG_{ads} as a function of the O_2 chemical potential $\mu(O_2)$ utilizes the DFT computed total energies. Temperature and pressure effects are included through the value of $\mu(O_2)$ that has been calculated from first principles using appropriate partition functions.[10] Figure 3 shows ΔG_{ads} for the adsorption geometries shown in Figure 1 and discussed above for a large range of the oxygen chemical potentials. It is clear that among all the calculated structures the configuration $Au_{14}O_{8,diss}$ has the lowest value of ΔG_{ads} and is thus thermodynamically most stable. For example, at ambient conditions (O_2 pressure 1 atm and $T = 300$ K) ΔG_{ads} of $Au_{14}O_{8,diss}$ is 3.9 eV lower than that of the $Au_{14}O_{2,diss}$.

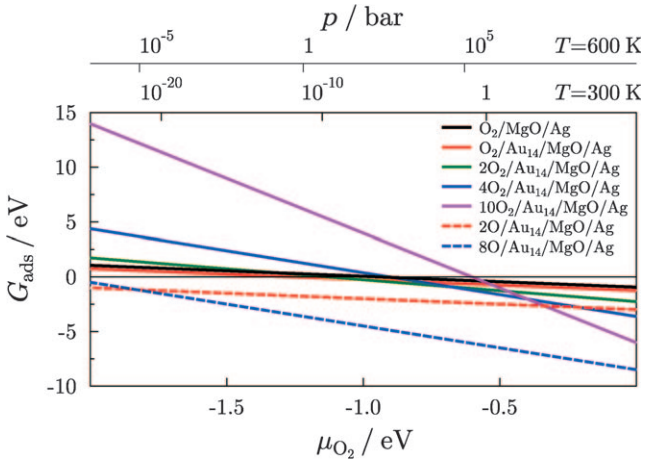

Figure 3. The free energy of oxygen adsorption, ΔG_{ads}, as a function of the oxygen chemical potential μ_{O_2}. The upper abscissas relate the values of the chemical potential to oxygen partial pressure at $T = 300$ and 600 K.

Both $Au_{14}O_{8,diss}$ and $Au_{14}O_{2,diss}$ geometries display an interesting structural detail (Figure 1e,f): atomic oxygen at the edge of the Au_{14} cluster seems to "etch" Au atoms away from the cluster and induce spontaneous formation of linear O-Au-O moieties (marked by dashed lines in Figure 1). The distance of the Au atoms that are doubly bonded to O atoms to some of their neighbors increases by roughly 10%. Bader charge analysis indicates that while the O atoms are negatively charged (close to -1 |e|), the Au atoms in the chains have a slight positive charge of $+0.3$ |e|. This result has to be contrasted with the excess negative charge of -0.2 to -0.3 |e| of edge Au atoms in Au_{14} in the absence of O_2, which indicates significant oxidation of Au atoms when they are contacted with O. The analysis of the density of electronic states projected onto the Au atoms at the edge, coordinated to O, and inside the Au cluster shows that these atoms have a different electronic structure (Figure S5 in Supporting Information). The geometric details, local charges, and electronic structure all support the interpretation that the $O^{-\delta}$-Au^{I}-$O^{-\delta}$ chains signal the propensity to form a one-dimensional edge oxide.

The linear coordination of Au^{I} between electron-withdrawing atoms or ligands in various molecular complexes is well known.[11] Metastable bulk and surface forms of gold(III) oxide Au_2O_3 are known to form under special conditions.[12,13] Previously, DFT coupled with AITD calculations has indicated that atomic oxygen on the Au(111) surface can induce the formation of a two-dimensional gold(I) oxide network as an overlayer on Au(111), predicted to be stable up to 420 K at atmospheric pressure. This network features linked O-Au^{I}-O chains.[14]

Herein we have shown, for the first time, that a one-dimensional counterpart of the two-dimensional gold(I) oxide[14] can form at ambient conditions at flat Au clusters on ultrathin metal-supported MgO films, where stabilization of the edge oxide can be enhanced by electrostatics from the underlying $Mg^{+2}O^{-2}$ film surface. The relevance of the gold(I) edge oxide is imminent for CO oxidation reactions considering the fact that the Au^{I} atoms in the O-Au^{I}-O chains can readily act as electrophiles to possibly enhance CO adsorption. Our findings may also be relevant in the case of larger, three-dimensional gold nanoclusters on oxide supports, where the presence and high activity of a one-dimensional oxide at the gold cluster perimeter has been speculated.[15] For other precious metals, it is known that one-dimensional metal oxide PtO_2 is the precursor phase for CO oxidation on stepped Pt surfaces.[16]

Experimental Section

The DFT calculations were carried out using the GPAW implementation[17] of the projector augmented wave (PAW) method[18] in real space grids. The exchange and correlation functional was approximated with the spin-polarized Perdew–Burke–Ernzerhof (PBE) formula.[19] The frozen core and projectors were generated with scalar relativistic corrections for Ag and Au. The details of the computational setup for the slab geometry used to model the Ag support, MgO film, and Au clusters are described in Ref. [4h]. Atom charges are analyzed with the Bader method.[20] The ab initio atomistic thermodynamics approach[10] is applied to calculate the oxygen free energy of adsorption using the expressions in Equations (1)–(3):

$$\Delta G_{ads} = \Delta E_{ads} - N\Delta\mu_{O_2}(T,p) \quad (1)$$

$$\Delta\mu_{O_2} = \mu_{O_2} - E^{tot}_{O_2} \quad (2)$$

$$\mu_{O_2} = (-k_B T \ln Z^{tot}_{gas} + pV)/N \quad (3)$$

where N is the number of O_2 molecules, Z^{tot}_{gas} is the total partition function, and E_{ads} and $E^{tot}_{O_2}$ stand for the zero-point corrected adsorption energy and the total energy of the gas-phase oxygen molecule, respectively. T and p refer to temperature and pressure. V is the volume, and k_B is the Boltzmann constant. We neglect the metal oxygen vibrations and slab phonon contributions, as they largely cancel each other in the free-energy expression.

Received: June 24, 2010
Published online: September 17, 2010

Keywords: gold · gold oxides · heterogeneous catalysis · O–O activation · thin films

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