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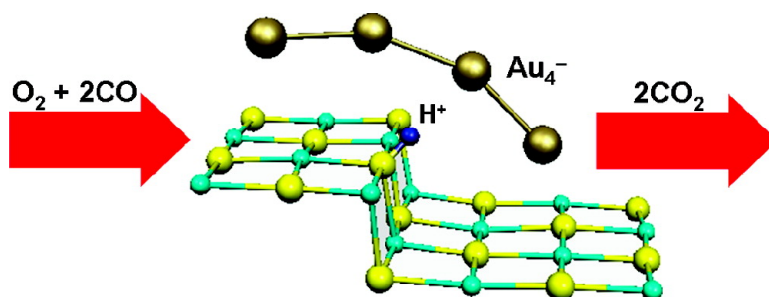# A Route toward the Generation of Thermally Stable Au Cluster Anions Supported on the MgO Surface

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A Route toward the Generation of Thermally Stable Au Cluster Anions Supported on the MgO Surface

Gianfranco Pacchioni,*,† Sabrina Sicolo,† Cristiana Di Valentin,† Mario Chiesa,‡ and Elio Giamello‡

Dipartimento di Scienza dei Materiali, Università di Milano-Bicocca, Via R. Cozzi, 53 - 20125, Milano, Italy, and Dipartimento di Chimica IFM and NIS Centre of Excellence, Università di Torino, Via P. Giuria, 7 - 10125, Torino, Italy

Received December 12, 2007; E-mail: gianfranco.pacchioni@unimib.it

Abstract: On the basis of experimental evidence and DFT calculations, we propose a simple yet viable way to stabilize and chemically activate gold nanoclusters on MgO. First the MgO surface is functionalized by creation of trapped electrons, $(H^+)(e^-)$ centers (exposure to atomic H or to H_2 under UV light, deposition of low amounts of alkali metals on partially hydroxylated surfaces, etc.); the second step consists in the self-aggregation of gold clusters deposited from the gas phase. The calculations show that the $(H^+)(e^-)$ centers act both as nucleation and activation sites. The process can lead to thermally stable gold cluster anions whose catalytic activity is enhanced by the presence of an excess electron.

1. Introduction

Gold is certainly the metal which in the past decade has attracted more interest in the field of catalysis by supported metal clusters.[1] The surprising discovery that, once prepared in the form of nanoparticles, even this chemically inert metal becomes an active catalyst, e.g. in CO oxidation,[2-5] has stimulated an enormous activity aimed at the elucidation of the role of the dimensions of the metal particle, of the support where it is deposited, and of the charged state of the cluster.[6-21] Despite these efforts, the origin of the activity of nanostructured gold remains debated. It depends on the preparation of the sample,[5] on the form and nature of the oxide substrate, and on the particle size and shape.[3,4,22-24] For instance, it has been suggested that flat, two-dimensional gold clusters are more active than thicker three-dimensional aggregates.[1,25] Also the charge state of the nanocluster plays a controversial role. Some studies suggest that the active catalyst is cationic gold;[26-30] however, it is possible that the positively charged gold nanoparticles are produced in the course of catalytic oxidation reactions.[31,32]

Other model studies, on the contrary, have shown that negatively charged gold clusters are chemically more active.[12,14,33,34] The presence of an extra negative charge on a small supported Au cluster results in an easier breaking of bonds of adsorbed molecules, O_2 in particular, and in an enhanced catalytic activity. Charging is supposed to occur through the interaction with specific sites of the oxide surface such as oxygen

† Università di Milano-Bicocca.
‡ Università di Torino.

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vacancies and other point defects. MgO[35–37] and TiO$_2$[1,22,38–41] are certainly the supports which have been studied in greater detail. While the nature of charge transfer between Au and TiO$_2$ is not universal and may depend on cluster size,[42] on MgO there is ample evidence that oxygen vacancies (F centers) act both as nucleation and activation centers for supported Au nanoparticles.[12,14,17] The problem is the abundance of these centers. Differently from what has been assumed for many years, the number of F centers on MgO single crystals, powders, or thin films is low, often below the detection limit.[43,44] Their number has to be artificially increased (e.g., by electron bombardment or by producing substoichiometric oxides) in order to obtain a defect-rich surface where the Au clusters can form and be stabilized from self-assembling of deposited gas-phase atoms. The low natural abundance of F centers represents a problem in the design and preparation of these systems for practical purposes. Furthermore, even the interaction with F centers may not be sufficient to enhance the chemical activity: there is both theoretical and experimental evidence that a Au$_4$ cluster supported on an F center of the MgO surface binds only weakly the O$_2$ molecule and is inert in the catalytic oxidation of CO,[45] at variance with Au$_8$ which, when adsorbed on the same defect, converts CO and O$_2$ into CO$_2$.[12]

Charging of supported gold can be obtained in a completely different way when an ultrathin oxide film (MgO, AlO$_x$) is grown on a metal substrate (Mo, Ag, NiAl).[46–48] Under special conditions, electrons can tunnel through the thin oxide film to supported gold, leading to negatively charged atoms or nanoclusters. The shape and the reactivity of these charged gold clusters differ substantially from those of the corresponding neutral species.[16,49–51] In this way one can prepare a collection of negatively charged nanoparticles by properly selecting the metal/oxide substrate. The problem is the thermal stability of these species which tend to coalesce and form large aggregates for temperatures of 150−200 K. The stabilization of charged Au nanoclusters in order to prevent diffusion and aggregation is a key aspect in this technology.

In this paper we propose, on the basis of the results of density functional theory (DFT) calculations and of existing experi-

mental evidence, a simple, yet viable method to generate negatively charged and thermally stable gold nanoclusters. First, we briefly review the experimental and theoretical evidence that shows the possibility to selectively generate electron-rich MgO surfaces. This implies the functionalization of the surface by exposure of MgO polycrystals or thin films to hydrogen, alkali metals, or in general, to electron donors. Then we show that these centers act as efficient sites for nucleation and growth of gold nanoclusters from diffusion of deposited Au adatoms, and that the resulting nanoclusters are catalytically active in the CO oxidation.

For many years, it has been assumed that surface electron trapping on oxides was due to the population of empty sites naturally present on the surface, as for instance empty oxygen vacancies (F^{2+} centers). However, work from our group[42,52–55] has clearly shown the different nature of the chemically generated surface color centers. Exposure of MgO[44,56] or CaO[54] surfaces to H atoms or to H$_2$ under UV light results, in fact, in the spontaneous ionization of H$^\bullet$, at temperatures as low as 77 K, with the subsequent formation of excess electrons and extra protons on the surface, as schematically represented in eq 1.

$$H^\bullet + -Mg-O- \rightarrow -\overset{e^-}{Mg}-\overset{H^+}{O}- \qquad (1)$$
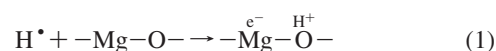
These centers are named (H$^+$)(e$^-$)[52] to indicate that they result from the ionization of the H atom with subsequent stabilization of the electron on low-coordinated cation sites, and of the proton on surface oxide anions. Reaction 1 leads to surface excess electron color centers, thermally stable up to 373 K, fully characterized by EPR, IR, UV measurements and theoretical calculations.[44,52–55] Recently, we have shown that residual OH groups present on partially hydroxylated MgO, CaO, or SrO surfaces act as potential electron traps which can be populated by the deposition of tiny amounts of donors such as alkali metals, leading to the formation of exactly the same kind of (H$^+$)(e$^-$) centers.[57] This provides an alternative way to generate electron-rich centers on the MgO surface. The density of (H$^+$)(e$^-$) centers can be obtained by evaluating the integrated intensity of the EPR absorption signal and comparing it to that of a standard reference (diphenyl-2-picrylhydrazyl, DPPH) with known concentration, according to standard procedures.[58] In this way the density of (H$^+$)(e$^-$) centers was found to range between 10^{14}/cm^2 and 10^{15}/cm^2.[59] For high surface area MgO, with average crystallite size of about 7 nm, this figure implies that the majority of edges and corners is populated by (H$^+$)(e$^-$) centers. Recently, our group has found evidence of magnetic interactions between surface (H$^+$)(e$^-$) centers. This is consistent with a phenomenological model of interacting paramagnetic centers which are separated by no more than a few lattice parameters.

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The important consequence of reaction 1 is that it provides a way of "dropping" electrons on specific surface sites, hence to prepare a chemically modified (functionalized) MgO surface. These trapped electrons are available to be donated to deposited metal particles, and to increase their chemical reactivity. The interaction of Au atoms and clusters with these specific sites is the topic of this paper. The energetics, structure, and stability of the resulting supported cluster anions have been investigated theoretically by means of embedded cluster models and hybrid DFT calculations (B3LYP exchange-correlation functional).[60,61] In order to properly account for the occurrence of charge transfers at metal/oxide interfaces, hence of strong dipoles, we have used a computational method which allows us to take into account the electronic relaxation of the substrate in a wide region using a shell-model approach.

2. Computational Details

The surface of MgO is represented by a finite nanocluster containing about 5000 atoms. The central part of the cluster, treated quantum mechanically (QM), is surrounded by a region of about 300 classical ions whose polarizability is described by a shell-model (SM).[62] Cations in the SM region at the interface with the QM region are replaced by ions (hereafter indicated as Mg*) on which a semilocal effective pseudopotential (ECP) is centered, in order to reproduce the Pauli repulsion and avoid the nonphysical polarization of QM interface anions. Region I, QM and SM, is then surrounded by a large array of point charges (PC) in order to correctly reproduce the long-range electrostatic potential.

This scheme is implemented in the GUESS code[63] interfaced with the Gaussian03 code,[64] and the total energy of the hybrid system is calculated as a sum of classical QM contributions. Forces acting on all centers in region I, both QM and classical (cores and shells), can be calculated, allowing the simultaneous optimization of their position. All centers in QM region and Mg* interface atoms have been allowed to move during the optimization, while only shells, not cores, have been relaxed in the SM region. Thus, the electronic polarization has been included in a large portion of the surface, while ionic polarization is restricted to a few tens of atoms. The total energy and the electronic structure of the QM cluster are calculated within density functional theory (DFT) using the hybrid B3LYP exchange-correlation functional.[60,61]

The following QM clusters have been considered to model edge, step, corner, and reverse corner sites, respectively, on the MgO surface: $Mg_{10}O_{10}Mg^*_{14}$ (edge), $Mg_8O_8Mg^*_{12}$ (step), $Mg_{10}O_{10}Mg^*_9$ (corner), and $Mg_{17}O_{17}Mg^*_{22}$ (reverse corner). A larger $Mg_{11}O_{11}$-Mg^*_{17} QM cluster has been used to model a step site for the adsorption of Au_4.

The basis sets used are: 6-311+G** on H, 6-31G* on Mg, 6-31G on O. For the CO molecule we used a 6-311+G* basis set. Au was treated using the lanl2 scalar relativistic effective core potential[65] (ECP), which explicitly includes the $5s^2 5p^6 5d^{10} 6s^1$ electrons in the valence. The basis set used is lanl2dz.[65] For the O_2 molecule we used a 6-311+G* basis set; with this basis the O–O distance, 1.21 Å, coincides with the experimental value. The O_2^- anion has an O–O distance of 1.35 Å (exp. 1.34 ± 0.01 Å[66]).
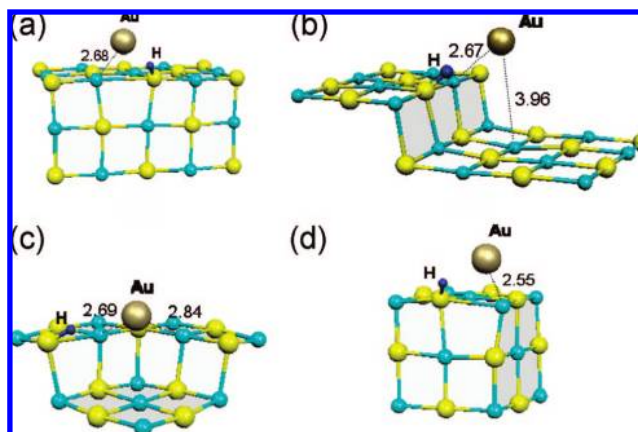
Figure 1. Structure of $(H^+)(Au^-)$ surface complexes formed by trapping a diffusing neutral Au atom on a $(H^+)(e^-)$ center. (a) edge; (b) step; (c) reverse corner; (d) corner. Selected distances are given in Å.

3. Results and Discussion

Let us start by briefly summarizing the characteristics of $(H^+)(e^-)$ sites on the MgO surface. First of all they form only at low-coordinated sites (steps, edges, kinks, corners, reverse corners, etc.). This means that the method proposed here can be applied to high surface area MgO powders. Model studies can also be performed on MgO thin films provided that they have a sufficient roughness. The formation of the $(H^+)(e^-)$ pair from atomic hydrogen is exothermic by 1.5–1.7 eV, depending on the site (edge 1.48 eV, corner 1.89 eV, step 1.77 eV, reverse corner 1.73 eV). The plot of the spin density of the electron trapped near an adsorbed proton on an edge site (Supporting Information) clearly shows that this is separated from the OH group. Notice that these trapped electrons are very stable, as their ionization energies are of the order of 3 eV and more.[44,52]

The interaction of a Au atom ($5d^{10}6s^1$ valence configuration) with a $(H^+)(e^-)$ center leads to a spin coupling and a diamagnetic complex. We denote this as $(H^+)(Au^-)$:

$$(H^+)(e^-) + (Au^0)_{ad} \rightarrow (H^+)(Au^-) \qquad (2)$$

The high electron affinity of gold, 2.17 eV (theory) and 2.3 eV (exp.), favors the formation of an adsorbed Au^- anion near the surface OH group. The process is very exothermic: the addition of a gas-phase Au atom to the $(H^+)(e^-)$ defect leads to an energy release of 3.5–3.8 eV, depending on the location (edge 3.65 eV; step 3.83 eV; reverse corner 3.67 eV; corner 3.49 eV; see also Figure 1). However, it is much more likely that Au atoms will thermally diffuse on the surface. In fact, the barrier for diffusion of Au on MgO terraces is estimated to be of about 0.2–0.3 eV, which guarantees rapid diffusion above liquid nitrogen temperature.[67,68] In their diffusion path the Au atoms can find and bind to a $(H^+)(e^-)$ site with a large energy gain, of the order of 2.5–3 eV. This is determined as the difference in stability between a Au adatom bound to the O_{5c} anion of a

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(68) The determination of the diffusion barrier has been done by optimizing the vertical position of the diffusing anion for fixed *x* and *y* coordinates, corresponding to the ion in the center of the four-fold hollow position, which provides an approximation to the real transition state. The computed adsorption energy of Au^- in the four-fold hollow site, 0.55 eV, is 0.27 eV smaller than the adsorption energy on a Mg_{5c} cation, the preferred adsorption site. Thus, the estimated diffusion barrier, 0.27 eV, is similar to that computed for the neutral Au atom, 0.24 eV.
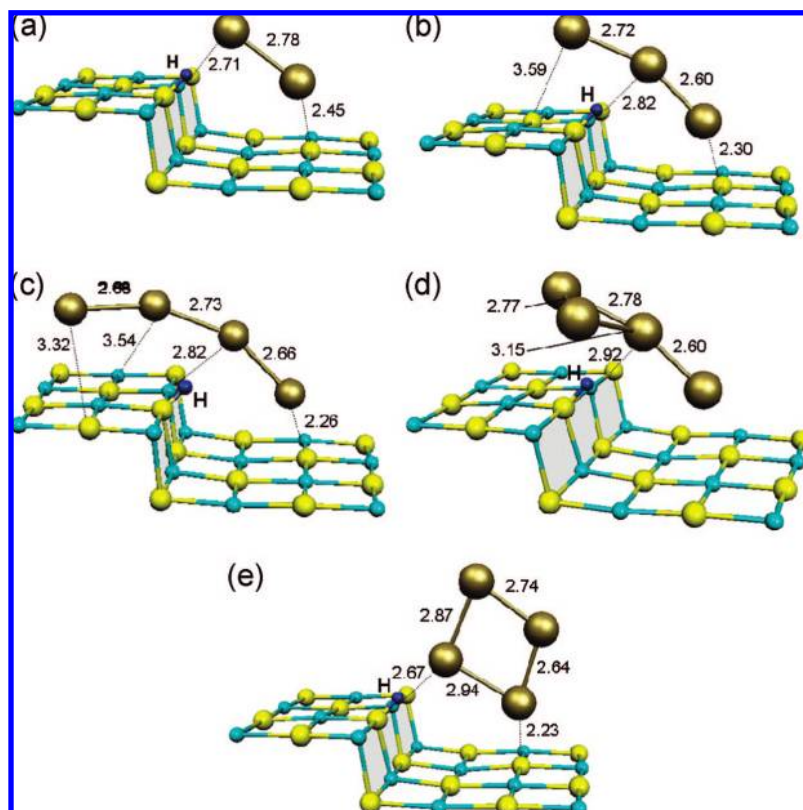
Figure 2. Structure of Au dimer (a), trimer (b), and tetramers (c−e) formed on $(H^+)(e^-)$ sites of the MgO surface. Selected distances are given in Å.

MgO terrace, 0.82 eV, and that of Au bound to a $(H^+)(e^-)$ center. The process is barrierless: once the diffusing Au atom is at a few lattice parameters from the trapping site, it will be attracted by its deep potential to form the $(H^+)(Au^-)$ surface complex.

On the edge site the Au atom is adsorbed in a bridge position between the Mg_{4c} cation and the OH group, Figure 1a; and the corresponding distances are 2.68 and 2.25 Å, respectively. On the other sites the distances are similar, with a shorter distance from the proton and a longer distance from the closest Mg cation. Only on a corner site is the Au atom almost equidistant from the H and Mg atoms, Figure 1d. On a step and on a reverse corner, the Au^- anion can interact also with the Mg_{5c} cation of the basal plane, Figure 1 b and c.

These results show the ability of $(H^+)(e^-)$ centers to strongly bind gold atoms and form gold anions. The detachment of Au^- from these sites requires overcoming a substantial energy barrier. The process has been investigated in detail for an edge site:

$$(H^+)(Au^-) \rightarrow (H^+)\cdots(Au^-)_{ad} \quad (3)$$
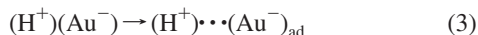
Reaction 3 leads to the formation of a Au^- species well separated from the OH group; on our model Au^- binds preferentially to a Mg_{4c} cation along the edge. In the calculation it was placed about 6.8 Å apart from the OH group, and the process has a $\Delta E = +1.35$ eV and an activation barrier of 1.52 eV; therefore, the back reaction occurs with a very small thermal activation, 0.17 eV, and leads again to the very stable $(H^+)(Au^-)$ species. Thus, $(H^+)(e^-)$ centers are strongly anchoring sites for the diffusing atoms; once bound to this center, gold will escape only at relatively high temperatures, well above 400 K, but in the form of Au^-, not of Au^0 (this second process costs in fact 2.5 eV or more).

The next aspect to consider is the possibility for these centers to act also as sites where nucleation and growth occur. The cluster binding energy, E_b, measures the stability of an adsorbed Au_n cluster with respect to a Au_{n-1} cluster bound to the $(H^+)(e^-)$ center, and a neutral Au adatom on a terrace O_{5c} site:

$$E_b(Au_n) = -E[(H^+)(Au_n^-)] + E[(H^+)(Au_{n-1}^-)] + \\ E(Au/O_{5c}) - E(O_{5c}) \quad (4)$$

Notice that in typical growth conditions E_b is a key quantity because dimerization and cluster growth are dominated by diffusion of adsorbed atoms and not by direct attachment from the gas phase.[37,69] A positive E_b value indicates a cluster stable toward fragmentation.

Figure 2a shows the structure of a gold dimer formed at a $(H^+)(e^-)$ center on a MgO step. Au_2^- acts as a bidentate ligand, with one atom interacting with an oxide anion on the basal plane, and the other with a Mg_{4c} cation along the step. This is different from neutral Au_2 which binds to terrace sites with the molecular axis almost perpendicular to the surface.[67] The spin resides almost entirely on the gold dimer and the Au−Au bond, 2.78 Å, is elongated with respect to neutral Au_2, 2.57 Å, and is similar as in gas-phase Au_2^- (2.74 Å). $E_b(Au_2)$ is 0.7 eV, showing a clear tendency for diffusing Au atoms to bind to the $(H^+)(Au^-)$ complex and form a negatively charged Au dimer. Diffusion of Au_2 from this site is unfavorable: the $(H^+)(e^-)$ center is a strong anchoring point and nucleation site. In fact gas-phase Au_2 binds to the $(H^+)(e^-)$ site by 3.38 eV, and to the O_{5c} terrace site by 2.04 eV. This means that the displacement of a gold dimer from

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the $(H^+)(e^-)$ center is endothermic by 1.3–1.4 eV. The next step is the addition of a third atom, with formation of a gold trimer. Gas-phase Au_3 has a doublet ground-state and is a Jahn–Teller distorted triangle with an internal angle of 141° and $r(Au-Au) = 2.64$ Å; this is also the structure (apart from some distortion) found when neutral Au_3 is deposited on "clean" MgO.[36,70,71] In the presence of the trapped electron, however, the trimer, Figure 2b, assumes a much more open structure, ($\alpha = 158°$) closer to that of gas-phase Au_3^- which is linear. Attempts to start from a different structure, e.g. a triangle with two atoms interacting with the surface and the third one pointing toward the vacuum, failed and resulted in the structure illustrated in Figure 2b. The ground state of $(H^+)(Au_3^-)$ is diamagnetic, as a result of the addition of a Au atom to the pre-existing $(H^+)(Au_2^-)$ open-shell complex; $E_b(Au_3)$ is extremely large, 1.8 eV, due to the particular stability of the resulting Au_3^- (free Au_3 has a very large electron affinity, 3.68 eV). The Au–Au distances, 2.60 and 2.72 Å, are close to that of free Au_3^-, 2.65 Å.

The last nanocluster considered is Au_4. On the MgO(100) surface this cluster assumes a slightly distorted rhombic structure with two atoms interacting with the surface and the cluster plane normal to the surface.[71] On a $(H^+)(e^-)$ center, however, the Au_4 cluster is no longer rhombic but is nearly linear, Figure 2c, although the gold chain bends to adapt to the step morphology. A T-shaped structure, Figure 2d, and the rhombus, Figure 2e, are respectively 0.12 and 0.53 eV higher in energy. The Au–Au distances in the chain are between 2.66 and 2.73 Å, and the cluster carries a net spin localized mostly on the terminal Au atoms (see Supporting Information). Notice that a slightly distorted chain or a T-shaped structure is the lowest isomer also for gas-phase Au_4^-, depending on the computational method used.[72,73] $E_b(Au_4)$ is 0.5 eV, again showing the tendency of diffusing Au atoms to add and aggregate on the supported nanoparticle. The interaction of the resulting Au_4^- (doublet ground state) with another Au atom to form a pentamer has not been considered here explicitly, but because of the spin coupling, $E_b(Au_5)$ is expected to be rather large, of the order of 1 eV or more. The growth process can continue, and the dimension of the particles formed will be determined by the amount of gold atoms deposited on the surface.
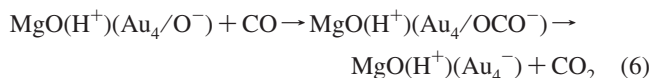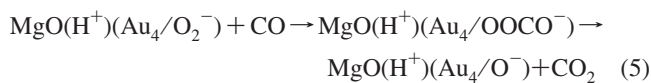
There is ample evidence that gold cluster anions are active species in promoting CO oxidation to CO_2,[74,75] or hydrogen peroxide formation from H_2 and O_2.[73] Both theoretical and experimental studies on gas-phase or oxide-supported gold cluster anions show that a key step in the reaction is the formation of a superoxo species, O_2^-.[76-79] In CO oxidation, this is followed by formation of an OOCO intermediate with
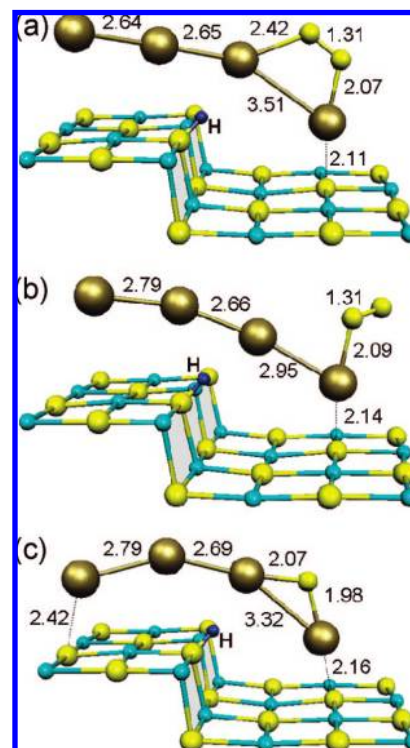
Figure 3. Structure of (a) and (b) MgO$(H^+)(Au_4/O_2^-)$ (two isomers) and (c) MgO$(H^+)(Au_4/O^-)$ complexes. Selected distances are given in Å.

no oxygen dissociation.[80,81] This leads to a transition state and then to the formation of CO_2 which desorbs from the cluster. The rupture of the O–O bond and simultaneous formation of the O–CO bond is the rate-determining step, and the formation of O_2^- a necessary prerequisite.

We have considered the adsorption of O_2 on Au_4^-; O_2 binds to Au_4^- by 0.45 eV, forming two nearly degenerate isomers, a side-on and a terminal conformation, Figure 3a and 3b, respectively (the side-on is more stable by 0.01 eV). The O–O bond activation due to the partial delocalization of the extra electron on the molecule is shown by the elongation of the O–O distance, 1.31 Å (1.21 Å in gas-phase O_2, 1.35 Å in free O_2^-). Thus, the Au_4^- cluster has the required characteristics of a chemically active gold catalyst in CO to CO_2 oxidation. It has been shown that the reaction of CO with activated O_2 can occur following a Langmuir–Hinshelwood (LH) mechanism, where CO is adsorbed on the Au cluster or at the cluster–oxide interface and then forms the OOCO activated complex, or an Eley–Rideal (ER) mechanism where gas-phase CO brought into the vicinity of the superoxo complex reacts spontaneously to form CO_2. In both cases, the activation barrier is low.[34,70,82,83] Our calculations indicate that indeed the following reactions occur according to an ER mechanism on Au_4^-:

$$MgO(H^+)(Au_4/O_2^-) + CO \rightarrow MgO(H^+)(Au_4/OOCO^-) \rightarrow$$
$$MgO(H^+)(Au_4/O^-) + CO_2 \quad (5)$$

$$MgO(H^+)(Au_4/O^-) + CO \rightarrow MgO(H^+)(Au_4/OCO^-) \rightarrow$$
$$MgO(H^+)(Au_4^-) + CO_2 \quad (6)$$

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Attempts to identify the same process according to a LH mechanism failed. Our results show that the process is only weakly activated and proceeds via formation of a OOCO intermediate (eq 5). Reaction 5 leads to the formation of $MgO(H^+)(Au_4/O^-)$, Figure 3c, and CO_2 with an energy gain of 3.2 eV; the barrier for CO_2 desorption is 0.41 eV. A second gas-phase CO molecule readily interacts with $MgO(H^+)(Au_4/O^-)$ to form a OCO intermediate (eq 6) and then CO_2 + $MgO(Au_4^-)$; the process is exothermic by 2.4 eV, and the barrier for CO desorption 0.21 eV only. Therefore, the gold clusters will not be "polluted" by the adsorbed oxygen. At the end of the cycle, the $(H^+)(Au_4^-)$ complex is regenerated and is ready for another catalytic cycle.

With respect to gold clusters activated on F centers, the present method has three important advantages. First, as we mentioned in the Introduction, interaction of a gold cluster with an F center is not sufficient to guarantee the activation of the O–O bond and the enhanced activity.[33] In fact, while Au_8 on a MgO F center leads to the formation of O_2^- and to the production of CO_2,[12] Au_4 deposited on the same site is inactive.[45] The excess of charge transferred from the F center is not sufficient to turn Au_4 into an active catalysts, O_2 is not activated, and the reaction does not occur.[45] The second, and more important advantage is that on $(H^+)(e^-)$ centers the process is catalytic as it implies the regeneration of the original supported cluster anion at the end of the cycle. This is different from F centers since atomic oxygen formed in the course of the reaction most likely migrates to the interface and fills the vacancy with elimination of the surface defect (the associated energy gain is of about 8–9 eV).[84] When this occurs, the catalytic cycle is broken, and the supported cluster is no longer activated. The third advantage is that the $(H^+)(e^-)$ defect centers can be easily produced by chemical methods, at variance with F centers, which must be produced under more severe conditions (electron bombardment, preparation of substoichiometric oxides, high thermal treatment in oxygen-poor atmosphere, etc.).

4. Conclusions

Making use of both existing experimental evidence and first principles DFT calculations, we suggest that it is possible to prepare thermally stable and chemically active gold nanoclusters on the surface of an ionic oxide like MgO. The preparation should follow a two-step procedure. First, one has to generate a properly functionalized MgO surface by "dropping" excess electrons at specific sites. A few well-established routes exist to create electron-rich surfaces, provided that a sufficient number

of low-coordinated sites exist.[44] In this respect, the method is ideal for high-surface area polycrystalline oxides, but it can be applied also to thin films when the lattice mismatch with the metal support is such to favor the grow of oxide islands or nanocrystals. Once the $(H^+)(e^-)$ surface electron centers have been generated, one can deposit low amounts of gold atoms. The theoretical results indicate that the atoms will diffuse on the surface and remain trapped at the $(H^+)(e^-)$ centers, forming thermally stable gold anions, and that nucleation and growth of gold nanocluster anions can easily occur on these sites.

This theoretical prediction needs to be validated by direct experimental measurements. This should best be done by deposition of very low amounts of gold (<0.1 monolayer) in a UHV chamber onto MgO thin films grown on a metal substrate (e.g., Ag or Mo). This would allow the use of scanning probes, STM in particular, to characterize the size and the shape of the formed gold clusters. EPR experiments in UHV could also be performed to verify the formation of paramagnetic defect centers and eventually of paramagnetic gold cluster anions. The possibility to perform EPR measurements in UHV conditions has been recently demonstrated for the case of deposited Au atoms on MgO.[15] The present study shows that $(H^+)(e^-)$ centers are potentially useful entities for the preparation of catalytically active charged gold clusters; however, while the presence of an excess electron can modify the chemical activity of a tiny metal particle, of 1 nm or less, it will hardly affect the chemistry of large metal particles of a few nanometers in size. This is also the reason why an investigation of the phenomenon in UHV conditions and on well-controlled substrates is a necessary step before attempting the preparation of these chemical entities on MgO powders under normal vacuum or even ambient conditions. If these systems can play a role as real catalysts is a question which cannot be answered at the moment. On the other hand, they can be extremely useful as model systems to shed light onto the origin of the catalytic activity of supported gold clusters.

Supporting Information Available: (1) Spin density plot of a $(H^+)(e^-)$ center; (2) spin density plots of Au_2 and Au_4 clusters formed on a $(H^+)(e^-)$ center; (3) complete ref 64. This material is available free of charge via the Internet at http://pubs.acs.org.

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