PHYSICAL REVIEW B **81**, 195443 (2010)

Catalytic activity of small MgO-supported Au clusters towards CO oxidation: A density functional study

Martin Amft[*] and Natalia V. Skorodumova
Department of Physics and Materials Science, Uppsala University, P.O. Box 530, S-751 21 Uppsala, Sweden

(Received 24 September 2009; revised manuscript received 1 April 2010; published 28 May 2010)

In order to explain the experimentally found catalytic characteristics of $Au_{1–4}/MgO(100)$ we have performed a comprehensive density functional study of these systems and their ability to (co)adsorb CO and O_2 molecules. Starting from the carefully determined ground-state structures we have analyzed binding mechanisms, the influence of spin-orbit coupling, and charge redistributions in $Au_{1–4}/MgO+CO(O_2)$. Experimentally $Au_{1,2}/MgO$ were found to be inactive under a mixed atmosphere. We show that O_2 strongly binds to Au_1/MgO that prevents coadsorption. Although a catalytic reaction cycle towards CO oxidation, analogous to the gas phase reaction involving Au_2^-, is energetically possible for Au_2/MgO, the cluster will get blocked by a strongly bound CO. On the other hand, the catalytic activity of $Au_{3,4}/MgO$ could be explained by their ability to coadsorb CO and O_2, hence indicating the occurrence of a Langmuir-Hinshelwood-type reaction mechanism for these clusters.

DOI: 10.1103/PhysRevB.81.195443 PACS number(s): 68.47.Jn, 68.43.Fg, 68.35.Np, 82.65.+r

I. INTRODUCTION

Nanometer-sized gold particles received much attention after the discovery of their substantial catalytic potential for the low-temperature oxidation of carbon monoxide.[1–4] Even really small gold clusters in the gas phase and on a metal-oxide support, e.g., Au_2^- and Au_8/MgO, show an interestingly high CO oxidation activity.[5–8] During recent years much, predominantly theoretical, work has been carried out on small supported gold clusters revealing the importance of the cluster/substrate interaction.[9,10] In particular, the charging of gold clusters as a result of an electron redistribution in the cluster/substrate system has been found to be crucial for the chemical reactivity.[11–14] It has also been established that the presence of surface oxygen vacancies[8,15,16] and underlying metal support[17] can play an important role in charging the gold clusters.

Magnesium oxide is one of the most studied substrates used for gold cluster deposition because of its stability and simplicity to be handled both in theory and experiment.[7,18] Although MgO is considered a comparably inert substrate, Sanchez *et al.*[7] found a surprisingly high catalytic activity of Au_8 on defective MgO(100). This finding was later on explained in greater detail by Yoon *et al.*,[8] who suggested that MgO color centers, i.e., oxygen vacancies, under the cluster donated extra charge to Au_8 and hence led to the observed enhanced catalytic activity. Despite a number of studies devoted to the CO and O_2 adsorption on very small free[6,19–23] and supported gold clusters[7,8,14,24–26] their catalytic properties for CO oxidation are not fully understood yet. To our knowledge very few studies exist[25,27] where the adsorption of CO on Au adatoms on a regular MgO support has been studied, although experimental data exist for the whole range of Au_n/MgO clusters (up to $n \leq 20$).[7]

Here, we concentrate on the four smallest gold clusters and offer an explanation of the experimental observations in Ref. 7 why the two smallest systems, $Au_{1,2}/MgO$, have not shown any catalytic activity at all and why the next bigger ones, $Au_{3,4}/MgO$, have demonstrated a very limited activity only. We address these issues by performing a detailed theoretical study based on density functional theory (DFT) of the adsorption of CO and O_2 molecules on $Au_{1–4}/MgO(100)$. We have chosen to work with a perfect MgO surface as it seems doubtful that an oxygen vacancy beneath a cluster as small as $Au_{1–4}$ could survive under an atmosphere containing substantial amounts of O_2. Moreover, recent infrared spectra measurements on CO adsorbed on Au_1/MgO have revealed that the activation of CO is stronger when the Au adatom is bound to a regular terrace site compared to Au_1 on a MgO color center.[25] Recent combined theoretical and experimental investigations of single Au adatoms on 20 monolayers (ML) MgO on Mo and of small Au_n clusters on 2 ML MgO on Ag have shown that theoretical results based on DFT calculations correctly describe the properties of these systems.[28,29] DFT methods have also been employed successfully to study the catalytic CO oxidation cycle.[6,30] Therefore, we feel confident that DFT is an appropriate theoretical tool to study the adsorption and activation of CO and O_2 molecules on supported gold clusters.

The paper is outlined as follows. Section II presents the computational details. In Sec. III the ground-state properties of $Au_{1–4}$ on a regular MgO surface are discussed. The following section (Sec. IV) shows the results for carbon monoxide and oxygen molecules absorbed on the $Au_{1–4}/MgO$ systems. In Sec. V the catalytic potential of these systems is analyzed in greater detail. Finally, Sec. VI gives a summary and conclusion.

II. COMPUTATIONAL DETAILS

The *ab initio* DFT calculations were performed using the projector augmented wave method[31,32] as implemented in VASP.[33,34] The exchange-correlation interaction was treated in the general gradient approximation (GGA) in the parametrization of Perdew *et al.*,[35] which was found to be most appropriate for the systems under consideration.[36]

The MgO(100) surface was modeled in a supercell approach with a 2 ML thick 3×3 MgO slab. The repeated slabs were separated from each other by 27 Å, of vacuum. Such a large separation between the surfaces was necessary to ensure that it did not become smaller than 20 Å once gold clusters with adsorbed CO and O_2 molecules were attached to one side of the slab.[37] The unit cell was constructed using the equilibrium lattice parameter of MgO (4.235 Å) obtained in the corresponding bulk calculations. In order to show that the two layer thick slab adequately represented the MgO(100) surface for the considered systems we carefully checked the convergence of the adsorption energy (E_{ads}) of the Au_n clusters with respect to the slab thickness and lateral size. Convergence of E_{ads} within 2 meV/Au atom with respect to the number of k points and cutoff energy was reached for the Monkhorst-Pack $2\times2\times1$ mesh and 450 eV, respectively. All the atoms in the unit cell were allowed to fully relax without any constraint and the relaxation cycle was stopped when the Hellman-Feynman forces had become smaller than 10^{-2} eV/Å. In order to minimize the computation time the structural relaxation was initially performed without spin polarization. We carefully checked that the resulting structures were virtually identical to those obtained with spin polarization, and even spin-orbit coupling (SOC), taken into account during relaxation. The total energies of thus obtained ground-state structures were recalculated with SOC included. The charge distributions and transfers were analyzed by means of the Bader method.[38]

III. MgO-SUPPORTED SMALL GOLD CLUSTERS

As an initial step in our study we determined the favored binding sites and ground-state geometries of the Au_{1-4} clusters on the regular MgO(100) surface (see Fig. 1). In accordance with earlier studies[10,11,17,39,40] we found that gold prefers to bind on top of the surface oxygen atoms O_s. In the search for the ground-state configurations of Au_3 and Au_4 we started the relaxation procedures from four different initial cluster configurations already adsorbed on the surface. For some selected cases a soft landing of free cluster structures onto the surface was tested and did not give any new geometry. All the Au_{1-4}/MgO structures earlier reported in the literature[15,16,41] were also calculated.

Our results for the $Au_{1,2,4}/MgO$ systems, i.e., binding sites, adsorption energies, and geometries, agree very well with earlier theoretical works (see Table I).[15,16] The situation for Au_3/MgO is more delicate since two groups previously reported two different ground-state configurations for this system.[16,41] Our results, however, suggest yet another structure. Having calculated the geometries proposed in previous works we found that the one from Ref. 41 was just 25 meV higher in energy, whereas the geometry from Ref. 16 was 230 meV higher in energy than the Au_3/MgO structure found by us.

Figure 2(a) shows the calculated adsorption energies E_{ads} of Au_{1-4} on MgO. Clearly E_{ads} increases the bigger the cluster becomes. However, when recalculated per Au-O_s bond (not shown) the binding energy oscillates indicating a stronger bonding for the clusters containing an even number of Au atoms. Accordingly, Au-O_s bond distances also oscillate being shorter for "even" clusters and longer for "odd" clusters (see Table I).

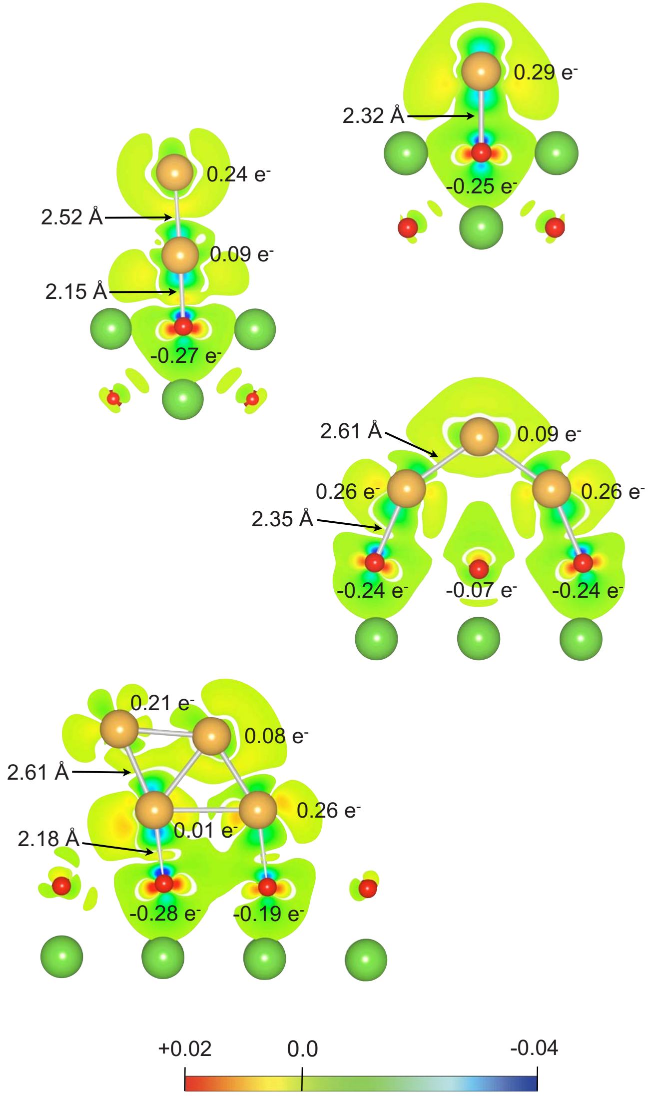

FIG. 1. (Color online) The ground state geometries of Au_{1-4} (yellow balls) on top of a regular MgO(100) terrace (green and small red balls, respectively). Also shown are the Bader charges (Ref. 38) and relevant interatomic distances. Additionally, cuts through the charge density redistribution $\Delta\rho$ are shown. They were calculated by subtracting the sum of the charge density of the cluster, $\rho(Au_n)$, fixed in the positions corresponding to the adsorption geometry, and surface, $\rho(MgO)$, from the total charge density of the cluster/substrate system, $\rho(Au_n/MgO)$.

The introduction of the SOC term does not change the Au_{1-4} cluster geometries on MgO or the amount of the transferred charge but influences their adsorption energies [Fig. 2(a)]. The difference between the adsorption energies, $\Delta E_{ads}=E_{ads}^{SOC}-E_{ads}^{sp}$, shown in Fig. 2(b), decreases rapidly with increasing cluster size, i.e., for Au_4 the difference is already smaller than 10 meV. At first glance the gold trimer seems to be at variance with the general trend of E_{ads}^{SOC} being a bit lower than E_{ads}^{sp}. But its exceptionally high adsorption energy for the spin-polarized calculation without SOC arises solely from the different ground-state geometries in the gas phase found in spin-polarized calculations with SOC (regular triangle) and without SOC (stretched base triangle), whereas

TABLE I. Compilation of calculated quantities for Au_{1-4}/MgO and, for comparison, available data from the literature. E_{ads} is the adsorption energy of Au_n (eV), $d(Au_n\text{-}O_s)$ is the gold-surface bonding length (Å), and ΔQ is the charge donation from the substrate into Au_n calculated by the Bader analysis (e^-) (Ref. 38). Note that all values are obtained for spin-polarized calculations including spin-orbit coupling.

Au_n	E_{ads} [a]		$d(Au\text{-}O_s)$		$\Delta Q(Au_n)$	
1	−0.89	$(-0.89)^b$	2.32	$(2.28)^b$	0.29	$(0.29)^c$
2	−1.44	$(-1.49)^b$	2.15	$(2.18)^b$	0.33	$(0.31)^c$
3^d	−1.52	$(-1.69,-1.15)^{c,e}$	2.35		0.61	$(0.36)^c$
4	−1.75	$(-1.45)^c$	2.18, 2.28		0.57	$(0.52)^c$

[a] References 15 and 41 used the Perdew-Wang 91 GGA parametrization and Ref. 16 used the revised Perdew-Burke-Erzernhof parametrization (Refs. 42 and 43).

[b] Reference 15.

[c] Reference 16.

[d] References 16 and 41 found different ground-state geometries that are at least 25 meV higher in energy in our calculations.

[e] Reference 41.

the geometries of Au_3/MgO obtained from both types of calculations are identical. In conclusion, neglecting the SOC term for bigger gold clusters, as it is routinely done in the majority of work, appears to be justified. The most important change in the electronic structure due to SOC occurs for the Au 5*d* states, whose center of mass moves upward in energy, promoting the contribution of these states to chemical bonding.

As a general trend we observe the formation of negatively charged clusters, $Au_n^{-\delta}$, in agreement with previously reported results.[17] Figure 2(c) and Table I show the total charge donation ΔQ to the clusters. Note that for the small clusters considered here the charge transfer scales roughly linear with the number of $Au\text{-}O_s$ bonds, i.e., $\approx 0.3e^-$ per bond. The analysis of the charge redistribution (Fig. 1) shows that the charge donation from the surface to the gold clusters is well localized to the binding surface oxygen atoms O_s, i.e., between 80% and 87% of the extra charge on the clusters comes from these atoms.[15] For $Au_{2,4}$ one can observe a noticeable charge accumulation along the $Au\text{-}O_s$ bond, indicative of covalent bonding. This explains the relatively high binding energies per $Au\text{-}O_s$ bond and shorter $Au\text{-}O_s$ bonding distances observed for the adsorbed $Au_{2,4}$ clusters.

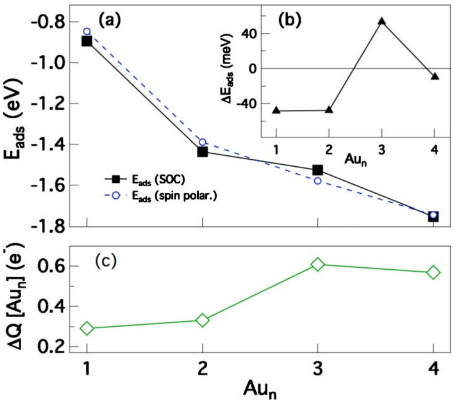

FIG. 2. (Color online) (a) Adsorption energies E_{ads} of Au_{1-4} on a regular MgO(100) terrace. For comparison the results of spin-polarized calculations including spin-orbit coupling (squares) and those of spin-polarized calculations without SOC (circles) are shown. Inset (b) $\Delta E_{ads}=E_{ads}^{SOC}-E_{ads}^{sp}$. (c) Total charge transfer from the MgO substrate to Au_n.

The $Au\text{-}O_s$ bonds show an odd-even hybridization pattern: $Au_{1,3}$ have an unpaired 6*s* electron, which constitutes the highest occupied states for these clusters hybridizing with the $2p_z$ states of O_s. In the case of $Au_{2,4}$ the highest occupied states are 5*d* states, which, in particular the d_{z^2} states, hybridize with the p_z states of O_s. The oscillations of properties due to the changing parity of the number of Au atoms were previously observed for low-dimensional gold structures.[44,45]

IV. ADSORPTION OF CO AND O_2

We studied the adsorption of single carbon monoxide and oxygen molecules on $Au_{1-4}/MgO(100)$ starting from the earlier determined ground-state geometries (cf. Fig. 1). The fully relaxed structures of $Au_{1-4}/MgO+CO(O_2)$ are shown in Fig. 3. The figure also shows cuts through the charge redistribution due to the adsorption of a molecule, $\Delta\rho=\rho(Au_n/MgO+CO,O_2)-\rho(Au_n/MgO)-\rho(CO,O_2)$. A compilation of the most interesting properties calculated for the systems is given in Tables II and III. Note that for comparison the binding energies of CO and O_2 molecules on MgO(100) are shown in the tables as well. In agreement with previous studies[46–48] both molecules are found to bind on top of a surface magnesium atom. These studies also found a high mobility at finite temperatures for both molecule species.

In accordance with previous studies of CO adsorption on bigger gold clusters supported by MgO, e.g., Ref. 9, we found that the carbon atom binds to Au and the oxygen atom points away from the cluster. The Au adatom donates almost all the additional charge received from the MgO support to the CO molecule. Although the bigger clusters, Au_{2-4}, donate a smaller fraction of their extra charge, CO appears to bind significantly stronger to these clusters than to Au_1 [cf. Fig. 4(a)]. A substantial fraction of the charge assigned to CO by

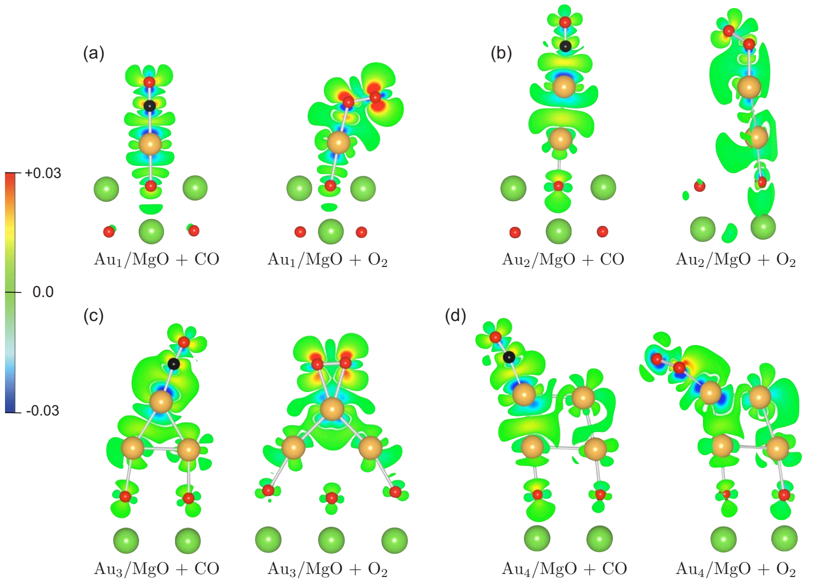

FIG. 3. (Color online) The ground-state geometries of $Au_{1–4}/MgO+CO(O_2)$. Also shown are cuts through the charge density redistribution $\Delta\rho$. They were calculated by subtracting the sum of the charge density of the cluster, $\rho(Au_n)$, the molecule $CO(O_2)$, fixed in the positions corresponding to the adsorption geometry, and surface, $\rho(MgO)$, from the total charge density of the cluster/substrate plus molecule system $\rho(Au_n/MgO+CO,O_2)$.

the Bader analysis is actually located in between Au and C (cf. Fig. 3) indicating the formation of a covalent bond. Furthermore, due to the adsorption on the cluster, an intramolecular charge redistribution from oxygen towards carbon is seen for the CO molecule. This is somewhat different from the electron distribution in the free CO molecule, where the two carbon $2p$ electrons, forming the bond with oxygen, have a higher expectation value in the vicinity of O.

The binding mechanism is different for the oxygen molecule adsorbed on $Au_{1–4}/MgO$. Except for $Au_3/MgO+O_2$, where both oxygen atoms bind to the top Au atom, only one of the O atoms binds to gold. Due to the much higher electron affinity of O_2 (1.16 eV) compared to that of CO (0.29 eV) more charge is transferred from $Au_{1–4}/MgO$ to O_2 than to CO [Fig. 4(c)]. In the case of $Au_1/MgO+O_2$ this charge even exceeds the charge transferred from the substrate to the Au adatom almost by a factor of 2. The substrate oxygen still donates $0.27e^-$, but now also the Au adatom donates additional $0.22e^-$ to the adsorbed O_2. For the other three clusters between 70% and 80% of the additional charge received from the substrate is passed onto the O_2 molecule. Most of this donated charge tends to concentrate as far away from the cluster as possible (Fig. 3).

The adsorption of CO and O_2 on the gold clusters leads to a stretching of their intramolecular bonds (Tables II and III), as the extra charge fills antibonding molecular orbitals. Although the intramolecular bond of O_2 is stretched by up to 8%, thereby substantially exceeding the oxygen-oxygen separation in O_2^- in the gas phase (1.26 Å), we could not find any trace of a dissociation of the O_2 molecule upon adsorption. For comparison we also present the corresponding values for Au_2CO^- and $Au_2O_2^-$ (Tables II and III) as the CO oxidation cycle with Au_2^- in the gas phase has previously been studied in detail.[5,6,30] Au_2^- has one extra electron, which is significantly more extra charge compared to the amount Au_2 gets from the substrate. Therefore, it is not surprising that the charge donation from Au_2^- to CO and O_2 is about $0.3e^-$ larger than that from the supported Au dimer. Consequently, the molecular bond stretching was found to be more pronounced for CO and O_2 adsorbed on Au_2^-.

The CO and O_2 adsorption also influences the structure of the gold cluster/substrate system. For instance, the Au-O_s

TABLE II. Compilation of calculated quantities for $Au_n/MgO+CO$ and, for comparison, available data from the literature. E_{ads} is the adsorption energy of CO (eV), d is the interatomic distances (Å) [note that d(C-O)=1.14 Å in gas phase], and ΔQ is the charge donation from Au_n/MgO into CO calculated by the Bader analysis (e^-) (Ref. 38). Note that all values are obtained for spin-polarized calculations including spin-orbit coupling. For comparison CO on pure MgO is included in the last row.

Au_n+CO	E_{ads}		d(Au-C)	d(C-O)	ΔQ(CO)
1	−0.73	(−0.64)[a]	1.90	1.18	0.31
2	−1.34		1.95	1.15	0.05
Au_2^-(GP)	−1.07	(−0.96)[b]	2.02	1.19	0.37
3	−1.33		1.94	1.16	0.10
4	−1.14		1.94	1.16	0.08
CO on MgO	−0.17	(−0.2)[c]		1.14	0.10

[a] Reference 27.
[b] Reference 5.
[c] Reference 46.

TABLE III. Compilation of calculated quantities for $Au_n/MgO+O_2$ and, for comparison, available data from the literature. E_{ads} is the adsorption energy of O_2 (eV), d is the interatomic distances (Å) [note that d(O-O)=1.23 Å in gas phase], and ΔQ is the charge donation from Au_n/MgO into O_2 calculated by the Bader analysis (e^-) (Ref. 38). Note that all values are obtained for spin-polarized calculations including spin-orbit coupling. For comparison O_2 on pure MgO is included in the last row.

Au_n+O_2	E_{ads}		d(Au-O_m)	d(O-O)	$\Delta Q(O_2)$
1	−1.32		2.02	1.32	0.54
2	−0.23		2.10	1.28	0.24
Au_2^-(GP)	−1.40	(−1.39)[a]	2.10	1.33	0.60
3	−0.64		2.23, 2.27	1.32	0.41
4	−0.09		2.01	1.30	0.47
O_2 on MgO	−0.03	(0.01)[b]		1.23	0.00

[a] Reference 5.

[b] Reference 48.

distance decreases by more than 10% for the Au adatom, whereas it increases by 5% for the dimer, when CO is adsorbed. For $Au_{3,4}/MgO$ the molecule adsorption leads to a geometry change that is best seen for Au_3/MgO [Fig. 3(c)]. In this case it results in the shrinkage of the triangle base, which is most prominent for CO adsorption, where one of the gold atoms even changes the binding oxygen site. The shape variation of Au_4 due to molecular adsorption is less dramatic but still noticeable [Fig. 3(d)].

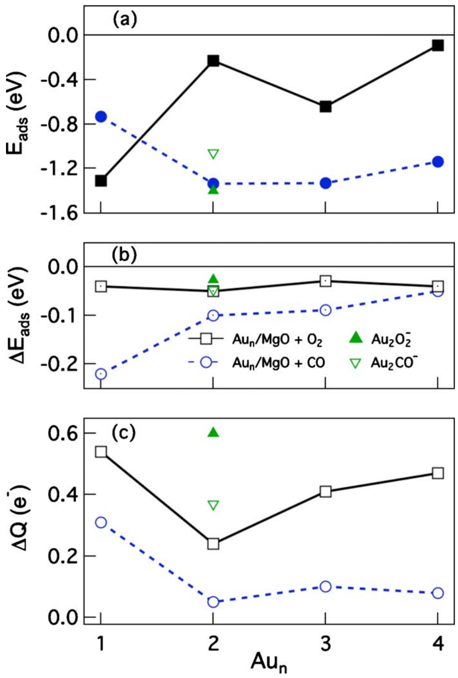

FIG. 4. (Color online) Adsorption energies and charge transfers. (a) E_{ads} of a single CO (circles) and O_2 (squares) molecule on $Au_{1\text{–}4}/MgO(100)$. Also shown are E_{ads} for CO (open triangle) and O_2 (solid triangle), on the Au dimer anion in the gas phase. (b) Difference ΔE_{ads} between the calculations including spin-orbit coupling and calculations only taking spin polarization into account. (c) Charge transfer ΔQ to the CO (circles) and O_2 (squares) molecules from Au_n/MgO. Note that in the case of Au_2CO/O_2^- (open and solid triangles, respectively) the available extra charge is one electron, compared to a maximum of $0.61e^-$ in the case of Au_4/MgO; hence, the significantly higher charge transfer to the molecules takes place.

The analysis of binding energies shows that CO binds stronger to $Au_{2\text{–}4}/MgO$ than O_2 does [Fig. 4(a)]. For $Au_{2\text{–}4}/MgO$ the adsorption energies of CO are rather similar and significantly higher than those for Au_1/MgO. Oxygen molecules, on the other hand, bind much weaker to $Au_{2\text{–}4}/MgO$ than to the supported Au adatom. Furthermore, the adsorption energies of oxygen follow an odd-even oscillation pattern that is not observable for CO. The spin-orbit coupling term has the highest impact on the adsorption energies of the molecules on the smallest clusters [see Fig. 4(b)]. SOC plays a much smaller role for $Au_n/MgO+O_2$, $\Delta E_{ads} \leq 50$ meV, than it does for $Au_n/MgO+CO$, $\Delta E_{ads} \leq 220$ meV. Furthermore, the effect of SOC for $Au_n/MgO+O_2$ is rather independent of the cluster size, whereas it is most significant for $Au_1/MgO+CO$ and quickly diminishes as the cluster size increases.

Figure 4 also contains results for Au_2CO^- and $Au_2O_2^-$. Opposite to what we find for Au_2/MgO oxygen binds stronger to the anion dimer compared to CO. Interestingly, the inclusion of SOC has a little effect on molecular E_{ads} only, lowering them by less than 50 meV.

V. COADSORPTION ON $Au_{1\text{–}4}/MgO$ AND CATALYTIC ACTIVITIES

After studying the adsorption of single CO and O_2 molecules on $Au_{1\text{–}4}/MgO(100)$, we look upon the coadsorption of these molecules and attempt to shed some light on the experimentally found catalytic characteristics of the clusters. In a systematic experimental study of Au_n clusters ($n=1,\ldots,20$) Au_8/MgO has been discovered to be the smallest effective catalyst for CO oxidation.[7] Thereby it has also been found that $Au_{1,2}/MgO$ do not show any catalytic activity at all, whereas $Au_{3\text{–}6}$ show at least some activity. In contrast, the free gold dimer anions have been shown to exhibit a considerable catalytic activity.[5,6,30] In particular, in the joint experimental and theoretical study[6] the following the Eley-Rideal reaction mechanism for the CO oxidation with Au_2^- as a catalyst has been suggested,

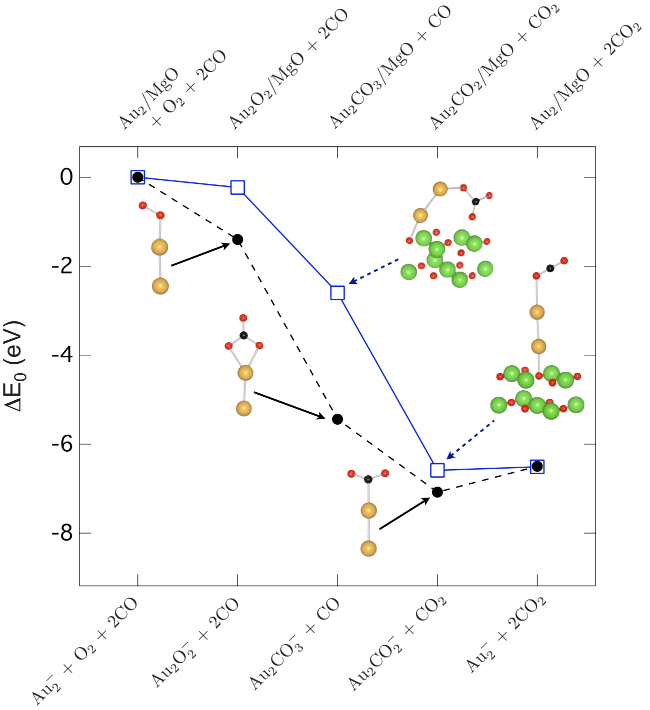

FIG. 5. (Color online) Differences ΔE_0 in the total energy for all steps during a catalytic cycle for the carbon monoxide oxidation by means of Au_2^- in the gas phase (circles) and Au_2/MgO (squares).

$$Au_2^- + O_2 \rightarrow Au_2O_2^-,$$

$$Au_2O_2^- + CO \rightleftharpoons Au_2(CO)O_2^-,$$

$$Au_2(CO)O_2^- + CO \rightarrow Au_2^- + 2\,CO_2.$$

For supported clusters a Langmuir-Hinshelwood (LH) reaction scheme, where adsorbents can thermalize and long-lived transition species exist, would be expected instead. We compare in detail the energetics of a CO oxidation reaction path for the free anionic Au dimer and an analogous reaction path for Au_2/MgO. Since the suggested reaction mechanism demands the coadsorption of O_2 and CO molecules on the gold dimer, forming a carbonatelike state, we started with $Au_2^-+O_2$ and coadsorbed an additional CO molecule on $Au_2O_2^-$. The intermediate carbonatelike product, $Au_2CO_3^-$, has also been found in experiment.[6] The energies for the reaction path, including the intermediate steps, i.e., energy gains and products, are shown in Fig. 5. Except for the geometry of $Au_2CO_3^-$ and its binding energy our results agree very well with those reported in Ref. 6. On the other hand, the authors of Ref. 30 found the same structure for $Au_2CO_3^-$ as we did.

Figure 5 illustrates that all but the final dissociation step, i.e., $Au_2CO_2^- \rightarrow Au_2^- + CO_2$, are exothermic and barrier free. The endothermic release of the second CO_2 demands 0.58 eV according to our calculations. This value should be compared to 0.53 eV from Ref. 6 and 0.28 eV reported in Ref. 30. This endothermic step has usually not been considered an obstacle for the reaction since the energy gained in the previous reaction steps is an order of magnitude higher and our calculations did not show an additional barrier, in agreement with Refs. 6 and 30.

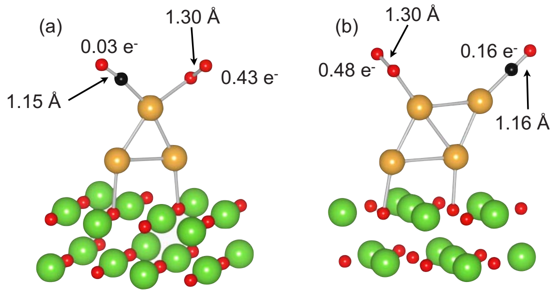

FIG. 6. (Color online) Carbon monoxide and molecular oxygen coadsorbed on Au_3/MgO (left) and Au_4/MgO (right). O_2 was adsorbed after CO. Also shown are the intramolecular distances and the extra charges gained due to the adsorption on the gold cluster. The Au atoms binding to the molecules were depleted by an according amount of charge.

Next we studied an analogous reaction path for Au_2/MgO (Fig. 5). Obviously the start and end points must be the same since their difference is the energy released during the oxidation of two CO molecules. Interestingly, here the last endothermic step of the reaction demands only 80 meV, which is much less than the corresponding value for Au_2^-. Similar to the dimer in the gas phase no additional barrier exists for this endothermic step.

According to these results a catalytically enhanced reaction should work for both systems, i.e., the free Au_2^- and the supported dimer. So why has no catalytic activity been observed for Au_2/MgO? The answer is twofold. First, the binding energy of CO to Au_2/MgO is more than 1 eV higher than that of O_2. Hence, in a mixed CO/O_2 atmosphere one could expect CO to more readily adsorb on the gold dimers. Second, in our calculations we find carbonatelike states starting from preadsorbed O_2 and adding a CO molecule. But all our attempts to find a similar state starting from preadsorbed CO and then adding oxygen failed. Thus, we can expect that in a mixed CO/O_2 atmosphere the gold dimers on MgO surface are to a large extent blocked by CO hindering the coadsorption of O_2.

We obtain similar results for Au_1/MgO: when either O_2 or CO is preadsorbed on the adatom it appears to be impossible to coadsorb a second molecule. This blocking of the supported gold adatom and dimer by the initially adsorbed molecule inhibits a reaction and could explain the absence of any catalytic activity for these systems.[7]

Looking at the adsorption energies of the molecules on the two bigger clusters (Fig. 4), one might again assume that in a mixed CO/O_2 atmosphere CO binds first on $Au_{3,4}/MgO$. But in contrast to the two smaller clusters it is now possible to coadsorb a second molecule onto the cluster+molecule/substrate system (Fig. 6). However, we could not find a carbonatelike configuration in these cases either.

The adsorption energies for the additional O_2 were -0.32 eV (-0.13 eV) for Au_3 (Au_4). Hence, the coadsorbed oxygen molecule actually binds stronger to Au_4 than O_2 adsorbed alone (see Fig. 4 and Table III). In Fig. 6 also the intramolecular distances of the adsorbed molecules and their additional charge due to adsorption are shown. These values are comparable to what was found earlier for single adsorbed molecules (Tables II and III). The additional charges on the molecules were donated from the Au atoms they bind to. Our findings indicate that LH-reaction-type mechanism, i.e., coadsorption of two molecules on different sites of the cluster and their reaction with each due to their movement on the clusters, as suggested for Au_8/MgO,[8] could be possible. By means of a LH reaction path it is understandable that $Au_{3,4}/MgO$ showed at least some catalytic activity in Ref. 7. We therefore suggest that a LH reaction type becomes increasingly important for bigger clusters.

VI. SUMMARY AND CONCLUSIONS

Small gold clusters on regular MgO(100) and the adsorption of CO and O_2 on these systems have been studied. The obtained ground-state properties of the Au_n/MgO clusters are in good agreement with available experimental data and earlier calculations. We show that the impact of SOC is most important for the smallest clusters and it quickly diminishes as the cluster size increases. We find that the charge transfer from the MgO substrate to the clusters scales approximately as $0.3e^-$ per cluster/substrate bond and it plays an important role for molecular adsorption and activation. We have carefully studied the CO and O_2 adsorption on Au_n/MgO analyzing binding sites and energies, charge redistribution, bond stretching in the molecules, and changes in the cluster/substrate geometries. We show that the coadsorption of CO and O_2 on Au_1/MgO is not possible, whereas a carbonatelike state can form on Au_2/MgO if oxygen could adsorb first. However, due to the higher binding energies of CO on Au_2/MgO the adsorption of carbon monoxide is likely to be preferred in a mixed CO/O_2 atmosphere that should block the formation of the carbonatelike state. These findings suggest that a LH-type catalytic cycle is not possible for the $Au_{1,2}/MgO$ systems. Although a carbonatelike state could not be formed on $Au_{3,4}/MgO$ either, it appears to be possible to coadsorb CO and O_2 at different sites of these clusters indicating that a LH reaction could occur in these systems. This would explain the catalytic activity experimentally found for these systems.

ACKNOWLEDGMENTS

This research was supported by the Swedish Energy Agency (Energimyndigheten) and the Swedish National Infrastructure for Computing (SNIC).

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*martin.amft@fysik.uu.se

[1] M. Haruta, T. Kobayashi, H. Sano, and N. Yamada, Chem. Lett. **16**, 405 (1987).

[2] M. Haruta, Catal. Today **36**, 153 (1997).

[3] S. Chrétien, S. Buratto, and H. Metiu, Curr. Opin. Solid State Mater. Sci. **11**, 62 (2007).

[4] R. Coquet, K. L. Howard, and D. J. Willock, Chem. Soc. Rev. **37**, 2046 (2008).

[5] H. Häkkinen and U. Landman, J. Am. Chem. Soc. **123**, 9704 (2001).

[6] L. Socaciu, J. Hagen, T. Bemhardt, L. Woste, and U. Heiz, J. Am. Chem. Soc. **125**, 10437 (2003).

[7] A. Sanchez, S. Abbet, U. Heiz, W. Schneider, H. Häkkinen, R. Barnett, and U. Landman, J. Phys. Chem. A **103**, 9573 (1999).

[8] B. Yoon, H. Häkkinen, U. Landman, A. Worz, J. Antonietti, S. Abbet, K. Judai, and U. Heiz, Science **307**, 403 (2005).

[9] L. M. Molina and B. Hammer, Phys. Rev. Lett. **90**, 206102 (2003).

[10] L. M. Molina and B. Hammer, Phys. Rev. B **69**, 155424 (2004).

[11] G. Pacchioni, L. Giordano, and M. Baistrocchi, Phys. Rev. Lett. **94**, 226104 (2005).

[12] D. Matthey, J. Wang, S. Wendt, J. Matthiesen, R. Schaub, E. Laegsgaard, B. Hammer, and F. Besenbacher, Science **315**, 1692 (2007).

[13] S. Chrétien and H. Metiu, J. Chem. Phys. **127**, 084704 (2007).

[14] G. K. H. Madsen and B. Hammer, J. Chem. Phys. **130**, 044704 (2009).

[15] A. D. Vitto, G. Pacchioni, F. Delbecq, and P. Sautet, J. Phys. Chem. B **109**, 8040 (2005).

[16] P. Frondelius, H. Häkkinen, and K. Honkala, New J. Phys. **9**, 339 (2007).

[17] P. Frondelius, H. Häkkinen, and K. Honkala, Phys. Rev. B **76**, 073406 (2007).

[18] S. Schintke, S. Messerli, M. Pivetta, F. Patthey, L. Libioulle, M. Stengel, A. De Vita, and W. D. Schneider, Phys. Rev. Lett. **87**, 276801 (2001).

[19] N. Lopez and J. Nørskov, J. Am. Chem. Soc. **124**, 11262 (2002).

[20] B. Yoon, H. Häkkinen, and U. Landman, J. Phys. Chem. A **107**, 4066 (2003).

[21] A. Franceschetti, S. Pennycook, and S. Pantelides, Chem. Phys. Lett. **374**, 471 (2003).

[22] E. Fernández, P. Ordejón, and L. Balbás, Chem. Phys. Lett. **408**, 252 (2005).

[23] L. Molina, A. Lesarri, and J. Alonso, Chem. Phys. Lett. **468**, 201 (2009).

[24] L. Molina and B. Hammer, J. Chem. Phys. **123**, 161104 (2005).

[25] M. Sterrer, M. Yulikov, T. Risse, H.-J. Freund, J. Carrasco, F. Illas, C. D. Valentin, L. Giordano, and G. Pacchioni, Angew. Chem., Int. Ed. **45**, 2633 (2006).

[26] S. Sicolo, L. Giordano, and G. Pacchioni, J. Phys. Chem. C **113**, 10256 (2009).

[27] L. Giordano, J. Carrasco, C. D. Valentin, F. Illas, and G. Pacchioni, J. Chem. Phys. **124**, 174709 (2006).

[28] M. Yulikov, M. Sterrer, M. Heyde, H.-P. Rust, T. Risse, H.-J. Freund, G. Pacchioni, and A. Scagnelli, Phys. Rev. Lett. **96**, 146804 (2006).

[29] V. Simic-Milosevic *et al.*, Phys. Rev. B **78**, 235429 (2008).

[30] M. Kimble, N. Moore, G. Johnson, A. Castleman, C. Bürgel, R. Mitrić, and V. Bonačić-Koutecký, J. Chem. Phys. **125**, 204311 (2006).

[31] P. E. Blöchl, Phys. Rev. B **50**, 17953 (1994).

[32] G. Kresse and D. Joubert, Phys. Rev. B **59**, 1758 (1999).

[33] G. Kresse and J. Furthmüller, Comput. Mater. Sci. **6**, 15 (1996).

[34] G. Kresse and J. Furthmüller, Phys. Rev. B **54**, 11169 (1996).

[35] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).

[36] Y. Shen and J. BelBruno, J. Phys. Chem. A **109**, 512 (2005).

[37] N. V. Skorodumova, K. Hermansson, and B. Johansson, Phys. Rev. B **72**, 125414 (2005).

[38] W. Tang, E. Sanville, and G. Henkelman, J. Phys.: Condens. Matter **21**, 084204 (2009).

[39] G. Barcaro and A. Fortunelli, J. Chem. Theory Comput. **1**, 972 (2005).

[40] K. Honkala and H. Häkkinen, J. Phys. Chem. C **111**, 4319 (2007).

[41] L. Molina and J. Alonso, J. Phys. Chem. C **111**, 6668 (2007).

[42] J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, Phys. Rev. B **46**, 6671 (1992).

[43] B. Hammer, L. B. Hansen, and J. K. Nørskov, Phys. Rev. B **59**, 7413 (1999).

[44] N. V. Skorodumova, S. I. Simak, A. E. Kochetov, and B. Johansson, Phys. Rev. B **72**, 193413 (2005).

[45] A. Grigoriev, N. V. Skorodumova, S. I. Simak, G. Wendin, B. Johansson, and R. Ahuja, Phys. Rev. Lett. **97**, 236807 (2006).

[46] G. Pacchioni, G. Cogliandro, and P. S. Bagus, Int. J. Quantum Chem. **42**, 1115 (1992).

[47] M. Sterrer, T. Risse, and H. Freund, Appl. Catal., A **307**, 58 (2006).

[48] G. Pacchioni, A. Ferrari, and E. Giamello, Chem. Phys. Lett. **255**, 58 (1996).