Structural, Electronic, and Impurity-Doping Effects in Nanoscale Chemistry: Supported Gold Nanoclusters**

Hannu Häkkinnen,* Stéphane Abbet, Antonio Sanchez, Ulrich Heiz,* and Uzi Landman

Metal clusters exhibit unique size-dependent physical[1] and chemical properties[2] that differ from those of bulk materials. While inert as a bulk material, gold nanoparticles and clusters have attracted considerable interest lately as active catalysts for a number of industrially relevant reactions.[3–6] Unlike supported particles of larger size or extended solid surfaces,[7–10] size-selected small metal clusters adsorbed at specific sites of a support material (e.g. oxygen vacancies in the case of a MgO(100) surface) exhibit unique properties that originate from the highly reduced dimensions of the individual metal aggregates. These properties underlie the remarkable, newly found catalytic activity of small gold clusters, and they include: 1) dynamic structural fluxionality that exhibits itself through the propensity of small clusters to transform, in the course of chemical reactions, between various energetically accessible structural isomers, thus enhancing the rates for overcoming reaction barriers, 2) quantum size effects that are reflected in size-dependent characteristics of the electronic spectra of small gold clusters, and in charge transfer from the support to the clusters, 3) impurity-doping effects that allow modification and control of the electronic structure, and consequently the chemical reactivity, of small supported clusters, through incorporation of judiciously chosen impurity atoms in otherwise inert clusters. Herein, we focus on gaining fundamental insights into the above size-dependent “nanocatalytic factors”, and illustrate through experimental and theoretical investigations the manner in which such fundamental understanding may guide the design and atomic-scale modifications of nanocatalysts.

Recently, a set of model catalysts have been prepared by soft-landing[11] of mass-selected Auₙ and AuₙSr cluster ions onto well-characterized MgO(100) thin films. These substrate films contained a low concentration (typically 5 × 10¹³ cm⁻²) of oxygen vacancies (surface F-centers, FC), that act as strong trapping sites for the clusters at low temperatures.[12–14] Temperature-programmed reaction (TPR) measurements of CO oxidation (CO + 1/2O₂ → CO₂) have shown that the smallest gold cluster that catalyzes the reaction is Au₉. Furthermore, it has been found that while Au₉ is catalytically inert, the doped cluster Au₉Sr is active. These findings, in conjunction with ab initio calculations, have revealed that underlying the aforementioned remarkable chemical size-sensitivity is the nature of bonding and the activation of molecular oxygen by these nanocluster catalysts.

The measured chemical activity is summarized in Figure 1, which shows typical TPR spectra for selected samples (a–e). The total CO₂ yield per cluster obtained in a one-cycle heating experiment for Auₙ and AuₙSr with 1 ≤ n ≤ 9 is shown in the inset. The active model systems (n ≥ 8) for the pure Auₙ and...
Au₈, Au₄, and Au₃Sr clusters, respectively.

regardless of the order of deposition of O₂ and CO, that is, no 
ref. [15] and the Supporting Information). The optimized 
model catalysts were studied by ab initio calculations (see 
noble character of bulk gold.

MgO(100) are catalytically inert, the latter reflecting the 
MgO(100) surface as well as multilayer gold films grown on 
larger particles occurs during the heating phase. The clean 
MgO(100) surface as well as multilayer gold films grown on 
MgO(100) are thermally stable up to 450 K, that is, no agglomeration to 
process,[16,17] and thus understanding the structural, dynamic, 
electronic, and compositional factors that govern these 
processes is the key to explaining the observed size-depend-
ent activity of the Au₄/MgO(FC) and Au₃Sr/MgO(FC) model 
catalysts. Indeed, our ab initio calculations show that the 
binding energy of O₂ to the supported Au₄ and Au₃Sr clusters 
and the degree of O–O bond activation are strongly depend-
ent on the cluster size (see below). In contrast, the adsorption 
energy of CO to the supported clusters is higher than that of 
oxidation and is relatively insensitive to the cluster size (0.7– 
1.0 eV per CO molecule, depending on coverage). Conse-
quently, we focus on the adsorption and activation of O₂ by 
the supported gold nanoclusters, and illustrate the aforemen-
tioned nanocatalytic factors that govern this key reaction step.

1) Dynamic structural fluxionality: The capability of small 
clusters to exhibit several structural forms (isomers) of 
comparable energies, and to interconvert between such 
isomers at finite temperature, is one of the hallmarks of 
cluster science. This unique structural variability may 
influence the chemical reactivity of nanocatalytic systems 
in two main ways. First, at finite temperature, the model 
catalyst (and in particular the cluster component) will 
form an equilibrium of coexisting structural configura-
tions, with various isomers exhibiting different chemical 
reactivities. This situation is illustrated here by the properties of two structural 
isomers of the Au₄ cluster. One isomer has a 
two-layered structure (Figure 2b) and is thermodynamically less stable (by 
0.29 eV) than the other isomer which has a 
stable geometric isomer (Figure 2a). The 
two-layered structure binds an oxygen 
molecule more strongly (energy gain 
upon oxygen adsorption 0.47 eV com-
pared to 0.28 eV for the latter isomer). 
Second, and most importantly, is the 
dynamic structural fluxionality of clusters 
which is the ability of a given isomer to 
adapt its structure so as to allow the 
reaction to evolve on the most favorable 
energy path. Such fluxionality is illus-
trated in Figures 2b and 2f where the 
more reactive two-layered Au₄ cluster is 
shown to undergo a large structural trans-
formation upon adsorption of molecular 
oxidation at the “periphery site”. The 
approximate bccapped octahedral ge-
ometry of Figure 2b) is transformed to a bicap-
pered trigonal-prismatic structure (Figure 
2f). This structural fluxionality is 
essential for the reaction to occur, since 
we have found that constraining the cluster 
to maintain its original geometry (Figure 
2b) prevents the adsorption and activa-
tion of O₂.

2) Electronic size effects: Understanding the 
size-dependent electronic structure of the
Au$_4$/MgO(FC) model catalysts, which is fundamental for elucidation of their size-dependent reactivity, is facilitated by analysis of the spectra of the local density of electronic states (LDOS) of the oxygen molecule and the metal cluster. A similar analysis is often employed in the context of the interaction of adsorbates with extended surfaces.\(^{(18)}\) Figure 3a shows the LDOS of the O$_2$ molecule which is adsorbed at the periphery site (Figure 2f) of the more reactive isomer of the Au$_4$/MgO(FC) model catalyst. All the prominent peaks of the LDOS spectrum in Figure 3a can be unambiguously assigned to orbitals of the (free) molecular oxygen. In addition, these states overlap with the entire d band of the Au$_4$ cluster (shown in Figure 3b) in the range of $-7$ eV $\leq E \leq E_F$ where $E_F$ is the Fermi energy. Bonding of the oxygen molecule to the gold octamer mainly involves hybridization of the $5\sigma$, $1\pi^*$, and $1\pi_1$ oxygen states with the gold d band (Figure 3b). Most importantly, all the antibonding $2\pi^*$ spin-states of O$_2$ are located below the $E_F$, which results in strong activation of the absorbed O$_2$ molecule through occupation of the antibonding orbitals. This leads to weakening of the O–O bond that is reflected in a significant increase of its length (1.43 Å in Figure 2f) compared to that of the free molecule (1.25 Å). Accompanying the activation process is a change in the spin state of the molecule from a triplet state in the gas phase to a peroxo-like adsorbed state with a zero net spin. A drastically different scenario is found for the interaction of O$_2$ with the smaller gold cluster, Au$_6$/MgO(FC), where molecular oxygen adsorbs in an “on-top” configuration, with one oxygen atom binding to a single gold atom (Figure 2g). This system exhibits rather weak bonding of the molecule to the metal cluster (0.18 eV), an almost unperturbed O–O bond length (1.28 Å), and, like the free molecule, is in a triplet spin state (see Figure 3c). The weak binding is attributed to the narrower d band of the adsorbed Au$_6$ cluster compared to that of Au$_4$ (see Figures 3b and 3d), with a consequent lack of overlap between the states at the bottom of the d band of the gold cluster (Figure 3d) and the molecular oxygen states ($E < -5$ eV). Moreover, the spin-down antibonding $2\pi^*$ orbitals of the adsorbed oxygen molecule are located above the $E_F$ (unlike the case of the larger cluster, compare Figures 3c and 3a) which results in no activation of the adsorbed molecule by the Au$_6$ cluster.

3) Impurity-doping effects: The possibility of enhancing the catalytic activity of a nanocluster by designed incorporation (doping) of an impurity is demonstrated here by the catalyzed oxidation of CO on Au$_3$/Sr/MgO(FC) (see Figure 1b and the inset). The LDOS spectra of the oxygen molecule, the Sr atom, and the Au$_3$ part of the metal cluster, are displayed in Figures 3e–g, respectively. Doping by a single impurity atom changes significantly the bonding and activation of O$_2$ compared to that in the pure gold tetramer, Au$_4$. The O$_2$ bonds mainly to the strontium atom of the Au$_3$/Sr cluster (Figure 2h), and this bonding is characterized by a substantially higher adsorption energy (1.94 eV compared to 0.18 eV for the configuration shown in Figure 2g) and a significant activation of the O–O bond that is reflected in an increased bond length of 1.37 Å. This activation results from occupation of the spin-down $2\pi^*$ oxygen orbital (compare Figure 3e and 3c), which results in a superoxo-like state of the adsorbate. Bonding of the oxygen molecule to Au$_3$/Sr/MgO(FC) occurs through resonances formed between the Sr states in the energy intervals (5–6) eV and (0–1) eV below the $E_F$, with the spin-up $1\pi_1$ and $2\pi^*$ states, as well as with the spin-down $1\pi_1$ and $2\pi^*$ orbitals, of the adsorbed activated O$_2$.

In summary, we have identified and illustrated some of the key physical factors that underlie the chemical activity of supported nanoclusters, with a particular focus on the adsorption and activation step of molecular oxygen, that is essential for the oxidation of CO on supported gold model nanocatalysts. First, the metal-oxide support, and in particular surface oxygen vacancy sites, were found to play a dominant role in anchoring the metal clusters, and in activating the clusters by (partial) charge-transfer. Second, the structural fluxionality of the model catalyst (and in particular the
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isomerization propensity of the metal-cluster component) is predicted to enable and promote binding and activation of the reactants and to allow propagation of the catalyzed reaction along an optimal path through concurrent structural rearrangements of the model catalyst. Third, size-dependent activation of the reactants by the model catalyst and the resulting reactivity, correlate with subtle features in the electronic structure of the catalyst (in particular the width and positioning of the d band of the model gold catalyst). Finally, we have shown that catalytically inert clusters (e.g., supported gold tetramers) can be activated by doping with impurity atoms (e.g. Sr) that strongly bind and activate the reactants. These results may form guiding principles for further endeavors in the growing field of nanocatalysis, aiming at atomic-scale design of nanocatalysts with desired chemical activity, specificity, and selectivity.

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[15] Simulations were performed using the Born-Oppenheimer local-spin-density-functional simulations (BO-LSD-MD, see R. N. Barnett, U. Landman, *Phys. Rev. B* 1993, 48, 2081) with self-consistent generalized gradient corrections[19] and employing pseudopotentials[20] with a scalar-relativistic treatment for gold.[21,22] The Kohn-Sham electronic states are expanded in a plane-wave basis set with a kinetic energy cutoff of 62 Ry. The relaxed configurations of the bare adsorbed clusters, and the clusters with O₂ have been obtained by a spatial- and spin-unconstrained gradient-optimization method; in the relaxation process the substrate Mg²⁺ ions which are nearest neighbors to the oxygen vacancy F-center (FC), the metal cluster, and the adsorbed O₂ molecule are treated dynamically. The metal clusters were initially placed about 4 Å above the surface plane and the system was relaxed to the nearest energy minimum; this procedure was repeated several times to explore the isomer space of the adsorbed clusters. In addition, the stability of the lowest energy structures was checked by short-time (a few ps) ab initio molecular-dynamics simulations. It is worth noting that while it was recently found that gas-phase gold clusters (particularly anions) favor planar (2D) optimal structures up to sizes beyond 10 atoms (see ref. [22] and ref. [15] therein), the strong attraction by the FC always anchors one gold atom close to it and distorts the planar structures; in fact, the Au₄/MgO(FC) catalyst shown in Figure 2a and 2b correspond to low-energy 3D isomers of Au₄ in the gas phase.