Cluster-Dependent Catalysis

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

Hannu Häkkinen, 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 Au_n and Au_nSr cluster ions onto well-characterized MgO(100) thin films. These substrate films contained a low concentration (typically 5×10^{13} cm^{-1}) 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 ($CO + {}^1\!/_2O_2 \rightarrow CO_2$) have shown that the smallest gold cluster that catalyzes the reaction is Au_8. Furthermore, it has been found that while Au_4 is catalytically inert, the doped cluster Au_3Sr 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 CO_2 yield per cluster obtained in a one-cycle heating experiment for Au_n and Au_nSr with $1 \leq n \leq 9$ is shown in the inset. The active model systems ($n \geq 8$ for the pure Au_n and

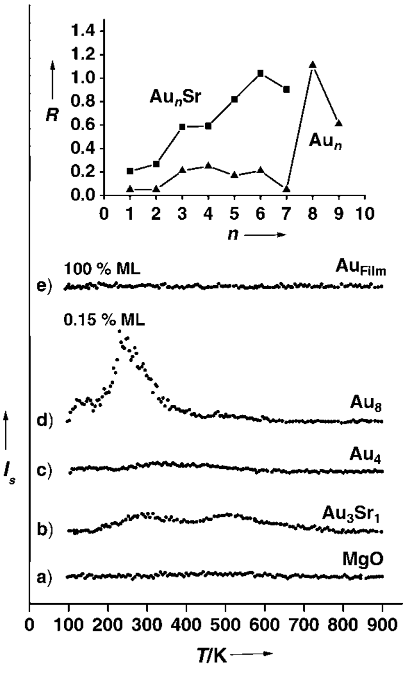

Figure 1. TPR spectra of CO_2 formation on: a) MgO(100) film, b) Au_3Sr/MgO(FC), c) Au_4/MgO(FC), d) Au_8/MgO(FC), and e) multilayer Au film grown on MgO(100). The Au_4/MgO(FC), pure MgO film, and the multilayer Au film are catalytically inert. The inset shows the chemical reactivity R of pure Au_n and doped Au_nSr clusters, with $1 \leq n \leq 9$, expressed by the number of product CO_2 molecules per deposited cluster. The TPR spectra are recorded after exposure of the model catalyst to isotopically labeled $^{18}O_2$ and $^{13}C^{16}O$ at 90 K. Only the production of the $^{13}C^{16}O^{18}O$ isotopomer was detected (by measuring its ion current (I_s)), which indicates that no oxygen from the MgO substrate is involved.

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[*] Prof. Dr. U. Heiz, Dr. S. Abbet
Abteilung für Oberflächenchemie und Katalyse
Albert-Einstein-Allee 47
University of Ulm
89069 Ulm (Germany)
E-mail: ulrich.heiz@chemie.uni-ulm.de
Dr. H. Häkkinen, Prof. Dr. U. Landman
School of Physics, Georgia Institute of Technology
Atlanta, Georgia 30332-0430 (USA)
E-mail: hannu.hakkinen@physics.gatecs.edu
Dr. A. Sanchez
Credit Suisse
Paradeplatz 8, 8070 Zürich (Switzerland)

[**] The experimental work was supported by the Swiss National Science Foundation and by the "Deutsche Forschungsgemeinshaft". The theoretical work was supported by the U.S. Air Force Office of Scientific Research and by the Academy of Finland. Simulations were performed at the National Energy Research Scientific Computing Center (NERSC), Berkeley, CA, and in the Georgia Tech Center for Computational Materials Science. We thank J.-F Jeanneret for the fabrication of the AuSr targets, Bokwon Yoon for his contribution to the graphical work, and W.-D. Schneider for his support at the early stages of this research.

Supporting information (experimental and theoretical details) for this article is available on the WWW under http://www.angewandte.org or from the author.

1433-7851/03/4211-1297 $ 20.00+.50/0

$n \geq 3$ for mixed Au$_n$Sr clusters) yield the same TPR spectra regardless of the order of deposition of O_2 and CO, that is, no CO poisoning occurs. The reproducibility of the TPR cycle has been verified, which indicates that these model systems are thermally stable up to 450 K, that is, no agglomeration to larger particles occurs during the heating phase. The clean MgO(100) surface as well as multilayer gold films grown on MgO(100) are catalytically inert, the latter reflecting the noble character of bulk gold.

The atomic structure and the electronic spectra of these model catalysts were studied by ab initio calculations (see ref. [15] and the Supporting Information). The optimized structures of Au$_8$ (with two relevant isomers), Au$_4$, and Au$_3$Sr adsorbed on MgO(FC) are shown in Figure 2. The Figures 2a–d show the structures before, and Figures 2e–h after O_2 adsorption. These clusters bind to the MgO(FC) surface quite strongly (calculated binding energy of 2.65 eV to 4.06 eV), and their binding is significantly enhanced (typically by about 2 eV) by the F-center defects. These high binding energies and the "anchoring" effect of the F-centers correlate well with the observed thermal stability of the supported clusters. Another important finding pertains to the charge state of the adsorbed clusters—in particular, our calculations predict that the interaction with the surface is accompanied by a charge transfer[6] of 0.5 e, 0.3 e, and 0.3 e to the adsorbed Au$_8$, Au$_4$, and Au$_3$Sr clusters, respectively.

Binding and activation of molecular O_2 by the model catalyst are necessary elementary steps in the CO oxidation 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-dependent activity of the Au$_n$/MgO(FC) and Au$_n$Sr/MgO(FC) model catalysts. Indeed, our ab initio calculations show that the binding energy of O_2 to the supported Au$_n$ and Au$_n$Sr clusters and the degree of O—O bond activation are strongly dependent on the cluster size (see below). In contrast, the adsorption energy of CO to the supported clusters is higher than that of oxygen and is relatively insensitive to the cluster size (0.7–1.0 eV per CO molecule, depending on coverage). Consequently, we focus on the adsorption and activation of O_2 by the supported gold nanoclusters, and illustrate the aforementioned 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 configurations, with various isomers exhibiting different chemical reactivities. This situation is illustrated here by the properties of two structural isomers of the Au$_8$ 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 quasi-planar structure (Figure 2a). The two-layered structure binds an oxygen molecule more strongly (energy gain upon oxygen adsorption 0.47 eV compared 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 free-energy path. Such fluxionality is illustrated in Figures 2b and 2f where the more reactive two-layered Au$_8$ cluster is shown to undergo a large structural transformation upon adsorption of molecular oxygen at the "periphery site". The approximate bicapped octahedral geometry (Figure 2b) is transformed to a bicapped 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 activation of O_2.

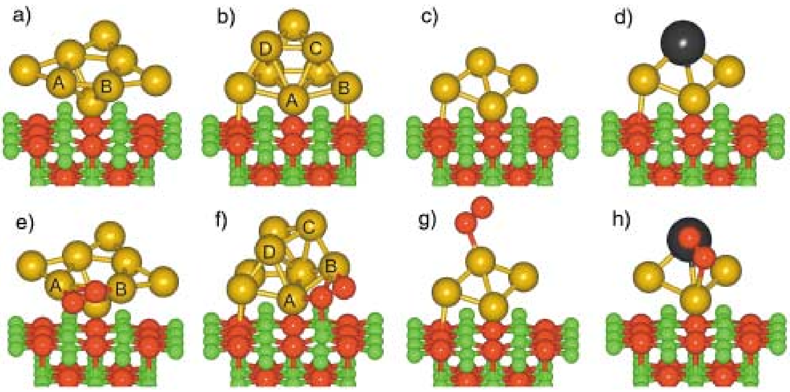

Figure 2. The optimized atomic structures of model catalysts comprising a) and b) Au$_8$, c) Au$_4$, and d) Au$_3$Sr clusters adsorbed at a F center (FC) defect on MgO(100). For Au$_8$ two relevant isomers, separated by an energy difference of 0.29 eV, are shown, with the more stable cluster (a) having a quasi-planar geometry with one atom bound to the F center and the remaining seven atoms defining a plane tilted slightly away from the MgO-surface plane. The higher-energy isomer (b) has a "two-layer structure" where the bottom layer consists of five atoms with one of the atoms strongly interacting with the F center. The adsorption energies of these clusters are 3.92 eV (a) and 3.45 eV (b). The adsorbed Au$_4$ and Au$_3$Sr clusters have rhombic structures, with adsorption energies of 4.06 eV and 2.65 eV, respectively. The adsorption induces an average strain of 3% (Au$_8$), 3% (Au$_4$), and 5% (Au$_3$Sr) in the bond lengths of the clusters, compared to their corresponding gas-phase structures. The optimal geometries for the adsorption of the O_2 molecule on these model catalysts are shown in the panels e–h. Although the dissociation of O_2 is thermodynamically favored, the dissociation process involves a large activation barrier (of the order of 1.5 eV) and is thus kinetically precluded. The corresponding O—O bond lengths and adsorption energies are: e) 1.45 Å and 0.28 eV, f) 1.43 Å and 0.47 eV, g) 1.28 Å and 0.18 eV, and h) 1.37 Å and 1.94 eV. Selected interatomic distances [Å]: a) A-B 2.62, b) A-B 2.94, A-C, A-D 3.14, e) A-B 3.48, f) A-B 2.90, A-C 4.28, A-D 2.95. Note the significant structural rearrangement of the more reactive Au$_8$ cluster (b) upon oxygen adsorption, reflected in the modified bond lengths *d*(A-C) and *d*(A-D) in (b) and (f). Mg green, O red, Au yellow, and Sr black.

2) Electronic size effects: Understanding the size-dependent electronic structure of the

Au_n/MgO(FC) model catalysts, which is fundamental for elucidation of their size-dependant 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_8/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_8 cluster (shown in Figure 3b) in the range of $-7\,\mathrm{eV} \le E \le E_F$, where E_F is the Fermi energy. Bonding of the oxygen molecule to the gold octamer mainly involves hybridization of the 5σ, $1\pi_{\parallel}$, and $1\pi_{\perp}$ 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_4/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 binding 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_4 cluster compared to that of Au_8 (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 $2\pi^*_{\perp}$ and $2\pi^*_{\parallel}$ 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_4 cluster.

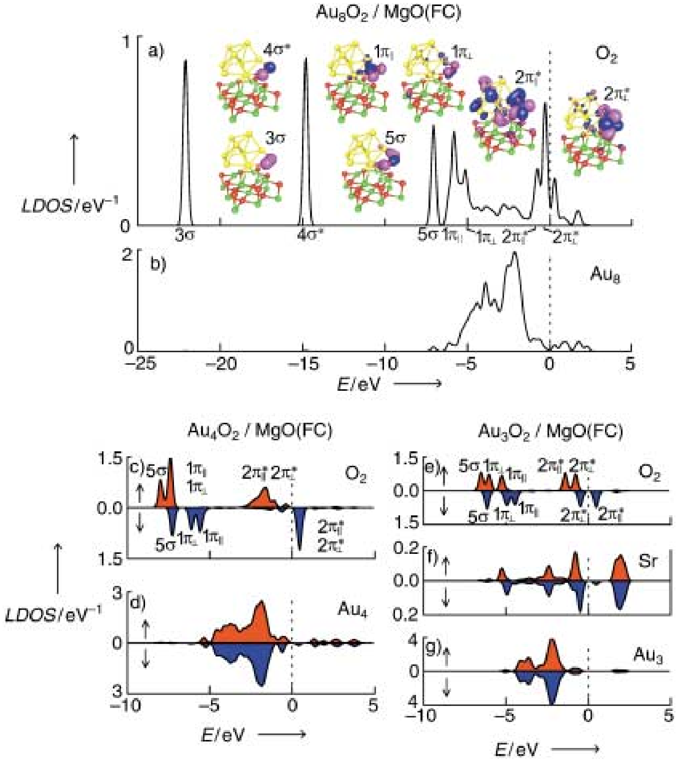

Figure 3. Local density of spin-up and spin-down electronic states (LDOS) of the model catalysts shown in Figure 2f–h for oxygen (a,c,e) and the metal cluster (b,d,f,g). The total spin is 0 in a and b, 1 in c and d and $^1/_2$ in e–g, and only spin-up states are shown in a and b since they are degenerate with the spin-down states. The prominent peaks of the oxygen LDOS are labeled following the conventional nomenclature for the molecular orbitals of the gas-phase O_2 molecule; assignment is by comparison with the free-oxygen orbitals (panel a). In (a) the notations $2\pi^*_{\perp}$ and $2\pi^*_{\parallel}$ denote, respectively, the perpendicular and parallel orientation with respect to the plane defined by the two atoms of the O_2 and the Au atoms closest to the FC. In (c) and (e) the orientation is given with respect to the plane defined by the atoms of the O_2 molecule and the metal atom closest to this molecule. The Fermi energy is at 0 eV.

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_3Sr/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_3Sr 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 $2\pi^*_{\perp}$ oxygen orbital (compare Figure 3e and 3c), which results in a superoxo-like state of the adsorbate. Bonding of the oxygen molecule to Au_3Sr/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 $1\pi_{\parallel}$ and $2\pi^*_{\perp}$ states, as well as with the spin-down $1\pi_{\perp}$ and $2\pi^*_{\perp}$ 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 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.

Received: August 22, 2002
Revised: December 10, 2002 [Z50026]

Keywords: CO oxidation · density functional calculations · gold clusters · magnesium oxide · nanocatalysis

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