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Priority Communication

On the origin of the catalytic activity of gold nanoparticles for low-temperature CO oxidation

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Abstract

It is suggested that there may be several effects contributing to the special catalytic properties of supported nanosized gold particles, and that it is useful to order them in a hierarchy. The most important effect is related to the availability of many low-coordinated gold atoms on the small particles. Effects related to the interaction with the support may also contribute, but to a considerably smaller extent. We base the analysis on a new set of experimental results comparing the CO oxidation rates over gold supported on different reducible and nonreducible oxides, on an analysis of a large number of published activity data, and on an analysis of density-functional calculations of the effect of metal coordination numbers in comparison to the role of charge transfer, layer thickness, and interactions with the support.

Keywords: Gold; Nanoparticles; CO oxidation

Nanometer-size gold particles on oxide supports are active for a number of reactions including low-temperature catalytic combustion, partial oxidation of hydrocarbons, and reduction of nitrogen oxides [1]. It is generally agreed that the catalytic activity of gold catalysts depends on the size of the gold particles, but the nature of the support material, the preparation method, and the activation procedure have also been suggested to play a key role [1–5]. Exceptionally high activities for oxidation of CO have been reported for highly dispersed Au on reducible oxides, such as TiO_2, Fe_2O_3, and NiO, and therefore it has been proposed that the support supplies oxygen to form active oxidic gold sites [6]. Sites at the gold-support interface have also been claimed to be responsible for the activity in CO oxidation [7–11]. Other explanations focus on the charge transfer between the support, particularly negatively charged defects (F centers), and the Au particles [12]. In addition, positively charged gold particles with a few atoms have been shown to be catalytically active [2,13–15]. Strain in the Au particles due to the mismatch of the lattices at the interface with the support [16,17] and the presence of a metal to nonmetal transition in very small, two-dimensional Au particles [18] have also been suggested. Finally, several groups have pointed to the effect of low-coordinated sites and roughness [10,16,19–22].

In the present Communication we focus on the low-temperature CO oxidation reaction. We show that a number of the effects discussed above may contribute to the catalytic activity of nanosized gold particles, and that it is useful to order the different effects into a hierarchy of contributions. The contributions can be ordered according to the effect they have on the stabilization of reaction intermediates, such as CO or oxygen on the surface of gold. Based on such an analysis the largest effect is proposed to be associated with the presence of a high concentration of low-coordinated sites on the surface of very small particles. On top of this, interactions with the support, charge transfer, strain, and other effects may also contribute, albeit to a lesser extent.

The hierarchy of contributions to the catalytic activity is based on two observations. The first observation is that particle size seems to have considerably more influence on the catalytic activity of gold particles for CO oxidation than

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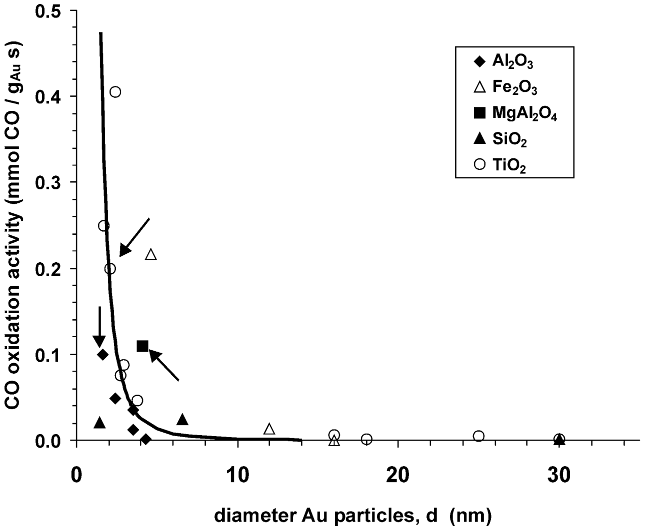

Fig. 1. Measured activities (in mmol CO/(g_{Au}s)) for CO oxidation at 273 K over different Au-based catalysts as a function of the average particle size (d, in nm). Supports are indicated by the symbol shape. Open symbols are used for reducible supports; solid symbols for irreducible supports. The curve shows a $1/d^3$ guide to the eye, showing that the activity of gold catalysts is approximately proportional with the number of low-coordinated atoms at the corners of the gold particles. The three points marked by an arrow are from our measurements, and the rest are collected from Refs. [1, 6,23–29] as described in the text. A full account of the data and references can be found at http://www.fysik.dtu.dk/CooxidationGoldNano.pdf.

effects due to the support. Fig. 1 compiles a number of measured CO oxidation activities for different gold catalysts, as a function of the average Au particle size. The arrows indicate our measured CO oxidation activities for a Au/TiO_2, a Au/$MgAl_2O_4$, and a Au/Al_2O_3 catalyst at 0 °C, using a feed of 1% CO, 21% O_2, and 78% Ar. The other data points are collected from a number of publications [1,6,23–29], corrected for temperature effects using the activation energies listed. Taking into account that the catalysts have been prepared with a variety of methods, and measured using quite different methods, these data show a remarkable consistency.

The CO oxidation rate for 2- to 4-nm particles is more than two orders of magnitude larger than for 20 to 30-nm particles. For example, the CO oxidation activity of Au/TiO_2 or Au/Fe_2O_3 increases from about 0.001 mmol CO/(g_{Au} s) for Au particles larger than 15 nm to about 0.2–0.4 mmol CO/(g_{Au} s) for Au particles in the range 2–5 nm, a factor of 200–400. This is an enormous effect of particle size

The effect of the interaction with the support can be judged from Fig. 1 by comparing data from reducible (TiO_2, Fe_2O_3) and irreducible (Al_2O_3, $MgAl_2O_4$, SiO_2) supports. The latter are generally less reactive than the former, but only by a factor of 2–4. Therefore, the data in Fig. 1 suggest that effects related to the reducibility of the support can be important, but also that they are not essential for a large activity. If we had only included a couple of different supports the fact that the activities are roughly the same at a given particle size might be a coincidence given by a fortuitous cancellation of different effects, but the large number of different supports (and synthesis procedures) collected in Fig. 1 should rule out this possibility. This means that effects related to exchange of oxygen between the gold and the support and effects due to charge transfer from oxygen vacancies to the gold particles cannot be the main effect. Furthermore, support specific interactions between adsorbates or reaction intermediates on gold close to the perimeter with the support are apparently not the main contribution to the activity in gold catalysts either.

This leads to the conclusion that a property directly related to the size of the gold particles is the dominant effect in the exceptional catalytic activity of nanometer gold particles, while other effects due to the support may have an additional, possibly important, but considerably smaller effect.

Our second observation is that the chemical activity of gold is strongly dependent on the coordination number of the gold atoms—see Fig. 2. We have calculated the adsorption energy of CO and O on a number of different gold surfaces and analyzed the origin of the bonding trends.[1] It is well known that gold dimers and other small clusters, unlike close-packed gold surfaces [30], are able to make strong chemical bonds to adsorbates [21,22,30–33]. Fig. 2 shows that the strength of the Au–CO and Au–O bond varies strongly with the Au coordination number. The figure also indicates why: The Au atoms in the surface of an Au(111) have d states that are so low in energy that they are unable to interact strongly with the O 2p valence states. This gives a weak bond—so weak that O bonds stronger to another O atom than to the Au(111) surface, and O_2 does not dissociate on Au(111) [34,35]. Au atoms at steps and corners of small particles, on the other hand, have a lower coordination number and d states that are closer to the Fermi level, giving a stronger interaction.

The effect of a low-coordination number is enormous. Both the O and the CO adsorption energies are lowered (stronger bonding) by up to ~ 1 eV going from Au(111) where the Au atoms have a coordination number of 9 to the Au_{10} cluster where the most reactive Au atoms have a coordination number of 4. These differences in binding energy mean that, for instance, the CO coverage on the gold surface at a pressure of 1 bar and a temperature of 300 K is 10^{-13} on Au(111) while it is ~ 1 on the Au_{10} cluster. This is clearly important for the ability for the catalyst to oxidize CO. It has been shown that activation barriers for the surface reactions closely follow the trends in the adsorption energies [36–39], suggesting that the ability of low-coordinated gold atoms to

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[1] Calculations have been performed with the DFT-RPBE functional on slabs representing a regular Au(111) stepped (211) and the Au_{10} cluster. In all cases sufficiently large k-point sample $4 \times 4 \times 1$ has been employed for the slabs (Monkhost–Pack scheme) and a single k-point for the molecules; together with a cutoff of 340 eV. For the cluster a sufficiently large $15 \times 15 \times 15$ Å unit cell has been used. Coupling between dipole moments on different cells has been removed.

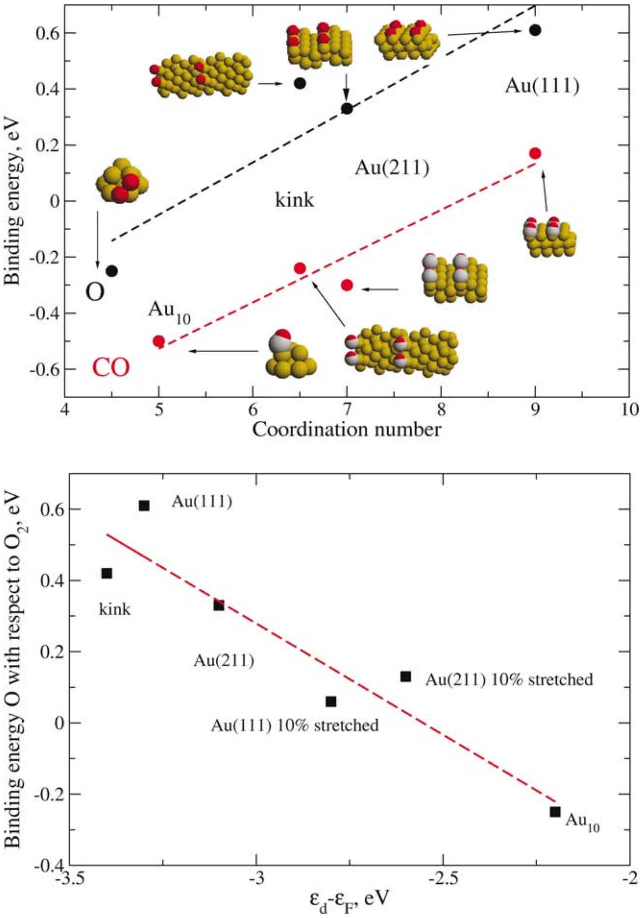

Fig. 2. (Top) The correlation between the binding energies, for CO molecules and O atoms, with respect to the coordination number of Au atoms in a series of environments. Binding energies, in eV, reported are referred to gas-phase CO and O_2, for O_2 the energies are given per O atom. The kink configuration falls outside the general trend as noted in Ref. [43]. (Bottom) The dependence of the binding energy of O atoms with the position of the d band of Au atoms in different environments.

bind adsorbates also means that the barriers for surface reactions are also lower at these sites. We therefore conclude that one effect which *must* contribute to the support-independent increase in the catalytic activity of gold particles with size is the concentration of low-coordinated sites, which increases steeply with decreasing particle size [16]. The tendency that small particles bind CO more strongly than larger ones has recently also been observed experimentally [19,40]. The scaling of the low-coordinated sites with particle size is not straightforward—it will depend on the particle shape, which is given by the adhesion between the gold particle and the support. If we assume that only corners contribute to the activity the activity should scale roughly with particle size d as $1/d^3$. Fig. 1 shows that this is indeed consistent with the experimental data.

The contribution from effects other than low-coordinated sites can be evaluated and compared to the effect due to coordination number by comparing the effects on CO and O_2 adsorption energies and effects on activation barriers. Many of the effects have been quantified by DFT calculations.

The intrinsic particle size dependence of CO and O_2 adsorption energies (excluding coordination number effects) is quite large with even-odd oscillations for clusters containing 1–5 atoms, but the effect levels out as the cluster size increases. For molecular O_2 the binding energy oscillates less than 0.2 eV for clusters containing 5–8 atoms, and 0.3 eV for O atoms [31]. A similar behavior is observed for CO; the binding energy to gold clusters saturates when the clusters contain 5–6 atoms [32]. The diameter of the clusters considered in these studies is 0.5–0.8 nm, well below the 2–5 nm size range of the gold catalysts considered in Fig. 1. In addition, the intrinsic effect of cluster size (quantum size effects) for a given metal cluster (0.2–0.3 eV) is considerably smaller than the coordination number effect ($\sim$ 1 eV), even for these small clusters.

The effect of metal-insulator transitions has been addressed by Metiu and co-workers [41] by comparing small clusters, which have large band gaps, with small clusters on a metal surface, which are completely metallic. For a Au_2 cluster, the difference in O_2 adsorption energy is only 0.2 eV, while it is 0.3 eV/O atom for Au_3.

The effect of charge transfer has been studied by considering adsorption on negatively and positively charged clusters. Negatively charged clusters generally show larger binding energies to oxygen than neutral ones, but for clusters containing more than 7 atoms the effect is small. For instance, for O_2 adsorption a 1 eV difference in binding energies was obtained for Au(111) and Au_7, while the effect of charging (to give $Au(111)^-$ and $Au_7{}^-$, respectively) was only 0.1 eV in both cases [41]. This is also true for CO, where the convergence toward the neutral case is present whether coming from larger binding energies (cations) or from lower binding energies (anions) [32]. When an oxide support with an oxygen vacancy provides the charge to the gold cluster, the transferred electrons are mainly localized at the interacting atom and the nearest neighbors [42]. A decrease of 0.3 eV in the barrier for CO oxidation has been found by Sanchez et al. [12] but only when the reaction takes place at the Au atom of a Au_8 cluster directly in contact with the defect site at the MgO surface.

A direct interaction between the adsorbates and the oxide surface for Au on MgO has been evaluated by Molina and Hammer to be less than 0.2 eV for both bond energies and transition state energies [10].

The strain effect has been evaluated by Xu and Mavrikakis to be of the order 0.2 eV for O adsorption for a 10% elongation on a stepped (211) surface and 0.1 eV for the molecularly adsorbed O_2 [17]. Since a 10% strain is very large this clearly sets an upper limit to this effect. All the effects considered above are thus a factor of 5–10 smaller that the effect of changing the Au coordination number from 9 to 4 [20]. The calculations thus point to a hierarchy of effects, where the largest is a change in reactivity due to changes in the metal coordination number followed by a range of effects, which can all contribute, but to a smaller extent. While the hierarchy is based on DFT calculations on idealized systems, it provides a consistent picture of the extraordinary chemical activity of gold nanoparticles. We note in this connection that the recent experiments by Freund and co-workers point in the same direction by showing that the CO adsorption properties seem to be dominated by coordination number effects [19].

In conclusion, we propose that the main effect of decreasing the gold particle size (Fig. 1) is to increase the concentration of low-coordinated Au atoms. On top of that, the important fine tuning provided by different supports is given by a range of effects, most of which are related to defects in the support. These effects also explain why reducible supports generally give more active catalysts that nonreducible ones.

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