Heterogeneous Catalysis

CO Oxidation on Rutile-Supported Au Nanoparticles**

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Gold is usually catalytically inert in chemical processes.[1] On the other hand, nanometric gold particles supported on oxides have been found to be catalytically active, even at low temperatures.[2,3] A number of effects may contribute to the enhanced reactivity of small gold clusters: an odd or even number of electrons, a metal–insulator transition below a certain cluster size,[3,4] charge transfer from the support,[5,6] strain,[7] or the presence of undercoordinated step and corner atoms.[4,7–11] The catalytic properties of gold are also reported to be affected by the supporting oxide and the method of preparation, which suggests that atoms near the boundary between the gold cluster and the oxide may have a key role in the oxidation of CO.[12,13] In addition, defects in the support can stabilize the metal particles and may change their catalytic properties.[10]

In a pioneering work, Molina et al. calculated the energetics of CO oxidation on an infinite array of Au rods supported on TiO_2.[14] They found that in the minimum-energy oxidation path, CO and O_2 are adsorbed near the gold/support interface. Similar results, for a two-layer gold strip were found by Liu et al.[15] Herein, we take one further step and present the first theoretical study of CO oxidation on a finite gold nanoparticle supported on rutile (TiO_2). On this basis, we propose an additional mechanism for the oxidation of CO that takes place on corner Au atoms and does not directly involve the gold/support interface. The $[Au_{10}]$ cluster that we have studied has a size of approximately 0.7 nm, which is at the lower end of the size-range for active nanoparticles reported in experiments.[3] This model system has most of the important features that have been suggested to contribute to the catalytic activity of gold: it has a 3D structure with two layers, it contains the characteristic (111) and (100) facets of gold clusters, and, most importantly, it takes into account both the finite size of the cluster and the redox character of the support.

The relaxed structure of the $[Au_{10}]$ cluster supported on rutile $TiO_2(110)$ is shown in Figure 1. CO binds above the highest Au atom (labeled 1 in Figure 1) with an adsorption energy of −0.95 eV. Adsorption is significantly more exothermic compared with that calculated for a free, disk-shaped gold cluster (−0.6 eV).[8] This difference is mainly due to the decrease in the coordination number of the Au atom in the supported cluster.[10] Recently, Meier and Goodman[16] reported a binding energy of 0.8 eV for CO on TiO_2-supported Au bilayer clusters and 0.5 eV for CO on unsupported Au clusters. Within the error range associated with experimental and calculated values, these results are essentially the same as those calculated. For co-adsorbed CO and O_2, the minimum-energy structure (−1.59 eV, relative to gas-phase CO and O_2) involves CO adsorbed on top of Au(1) (Figure 1) and O_2 bonded between Au(5) and Ti(7). This structure is 0.4 eV lower in energy than the best co-adsorption geometry for CO and O_2 that involves Au atoms only (see below).

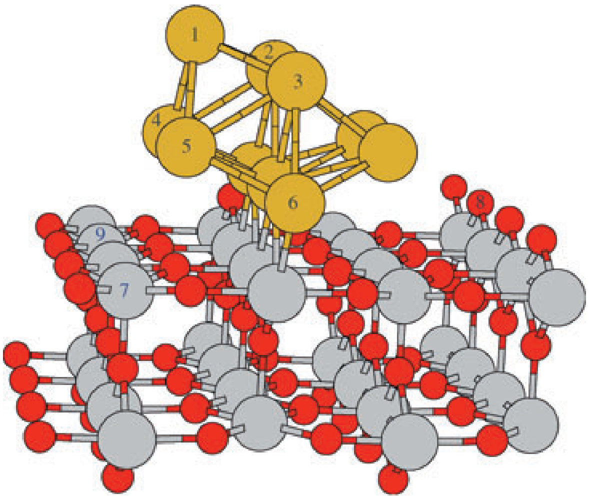

Figure 1. Relaxed geometry for an $[Au_{10}]$ cluster supported on reduced rutile $TiO_2(110)$. Au, Ti, and O atoms are represented by yellow, gray, and red spheres, respectively. The structure is periodic in both lateral dimensions.

The ensemble, which gives rise to such strong bonding for O_2, is a corner gold atom in the basal plane of the gold particle and a neighboring "bare" Ti atom of the support. The energy of co-adsorbed CO and O_2 does not seem to be affected by redox conditions. We repeated the calculation for two different cases, one in which an extra oxygen vacancy was formed by removing O(8), and another in which an O_2 molecule is adsorbed above Ti(9). In both cases, the co-adsorption energy of CO and O_2 changed by less than 0.05 eV. Co-adsorbed CO_2 and O have an energy of −3.95 eV relative to gas-phase CO and O_2. The energy of the transition state for the reaction $CO + O_2 \rightarrow CO_2 + O$ is −1.19 eV relative to gas-phase reactants and yields an energy barrier of 0.40 eV. The relaxed structures and energies associated with this CO oxidation path are shown in Figure 2.

We then considered a second oxidation pathway, which does not directly involve the support and is similar to that

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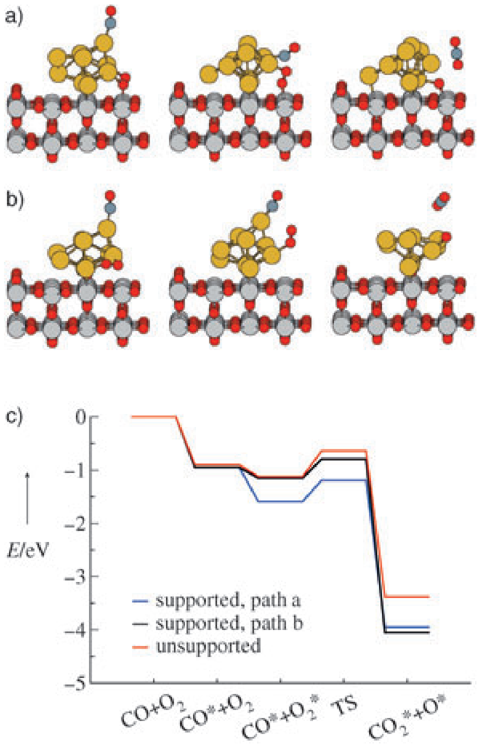

Figure 2. a, b) Relaxed geometries of the initial, transition, and final states, and c) energy profiles for CO oxidation on a [Au$_{10}$] cluster. Blue line: [Au$_{10}$] supported on TiO$_2$(110), CO oxidation takes place at the Au/TiO$_2$ interface (path a); black line: [Au$_{10}$] supported on TiO$_2$(110), CO oxidation takes place solely on the Au particle (path b); red line: unsupported cluster with the bottom three atoms kept fixed at the positions as they would be if the oxide were present.

proposed for a model [Au$_{10}$] cluster.[8] To obtain an adsorption energy for co-adsorbed CO and O$_2$ on the low-coordinated gold atoms without any direct bonding to the oxide, we performed a calculation with O$_2$ bonded to the bridge site between the Au atoms 5 and 6 (Figure 1) in a geometry that is very similar to the minimum-energy geometry described by Lopez and Nørskov, [8] but with the extra constraint so that the z coordinate of the O atom bonded above the bare Ti(7) is kept within a range of 0.5 Å to Au(5). This configuration is metastable, but can still contribute to the kinetics. It has an energy of −1.15 eV relative to gas-phase CO and O$_2$, which is in agreement with −0.9 eV calculated for a stand-alone [Au$_{10}$] cluster.[8] The use of a constraint to get a realistic configuration is necessary, because for such a small particle it is difficult to have a co-adsorption geometry that involves low-coordinated Au atoms and no interaction with the support. Co-adsorbed CO$_2$ and O have an energy of −4.06 eV relative to gas-phase CO and O$_2$. The transition-state energy is −0.79 eV relative to gas-phase CO and O$_2$ and yields an oxidation barrier of 0.36 eV. The relaxed structures and energies associated with this oxidation pathway of CO are also shown in Figure 2. As can be seen from this figure, in both oxidation pathways, the cluster changes its shape slightly to minimize the total energy.

To gain insight into the role of the oxide in this pathway, we repeated the same calculations, this time without the presence of TiO$_2$, and with the bottom three Au atoms fixed at the positions they would have if the oxide were present. The comparison between the unsupported and the supported cluster is shown in Figure 2. The energy of co-adsorbed CO and O$_2$ is −1.12 eV, only 0.03 eV higher than the energy of the same configuration for the supported cluster. The transition-state energy is 0.15 eV higher for the unsupported cluster and yields an energy barrier of 0.48 eV. There is a significant difference in the final state (CO$_2$ and O) energy. This difference is an artifact related to the restructuring of the supported cluster induced by the O atom, as can be seen in Figure 2. The binding energy of the O atom is −0.9 eV, relative to gas-phase O$_2$, which is 0.6 eV lower than the binding energy of the O atom to the unsupported cluster, where relaxation is not fully allowed.

The conclusion from the density functional calculations is that there are two possible reaction mechanisms for CO oxidation on a [Au$_{10}$] cluster that is supported on rutile TiO$_2$. The first pathway is similar to those previously reported,[14,15] and can only take place at a specific ensemble at the edge of the Au/TiO$_2$ interface. The other pathway takes place solely on the gold particle, with the support having a small effect on the energetics. Both pathways involve low-coordinated Au atoms to stabilize the reactants. The two pathways show similar activation energies for CO oxidation in the range 0.36–0.40 eV, which is very close to the activation energy of 0.36 eV measured by Haruta et al.,[17] close to the range of 0.15–0.25 eV reported by Valden et al. for STM-characterized catalysts,[18] and within the range of values between 0.16 and 0.60 eV reported by Bamwenda et al.[12] and Choudary et al.[19]

Our findings give further support to the notion that low-coordinated Au sites are essential to the reactivity of Au nanoparticles, as suggested in other theoretical and experimental works.[4,7–11] In addition, our results show why some experiments may uncover effects due to interface sites. Most importantly, the finding of the pure Au pathway shows that there is at least one reaction channel open for all supports, independent of the ability of the support to provide O$_2$ or to stabilize intermediates. This result explains why activities of several different gold catalysts have been found to depend mainly on the size of the gold particle or, equivalently, the concentration of corner atoms on the gold particle.[10] Finally, we note that oxygen-atom vacancies are clearly important in stabilizing Au atoms on the surface. Without them the Au particle hardly binds to the support.[20]

Our results suggest that the art of making Au atoms reactive can be reduced to the question of controlling the structure of Au particles at the nanoscale. One has to create many interface sites or maximize the number of low-coordinate Au atoms in the particles.

Experimental Section

The calculations were carried out by using density functional theory (DFT); the DACAPO package was employed.[21] The ionic cores and their interactions with valence electrons were described by ultrasoft pseudopotentials.[22] Exchange and correlation effects were taken into account by using the generalized gradient approximation (GGA) and the revised Perdew–Burke–Ernzerhof (RPBE) functional.[23] The wave function was expanded in a plane-wave basis with a kinetic-energy cutoff of 25 Ry. The ionic degrees of freedom were relaxed by using a conjugate-gradient minimization until the root of the mean squared-force component was smaller than $0.2\,\text{eV}\,\text{Å}^{-1}$. Further relaxation of selected structures resulted in insignificant changes in the calculated energies. The rutile $TiO_2(110)$ substrate was modeled by a two-layered slab, with a (4×2) surface unit cell. The TiO_2 slabs are separated by 15 Å of vacuum. First, we obtain a relaxed geometry for the supported cluster by allowing all Au and topmost Ti and O atoms to relax. In the calculations for adsorbed molecules on the cluster, only the coordinates of adsorbate and gold atoms were optimized. Three oxygen vacancies were placed on one of the bridging oxygen rows, with the cluster on top connected by three Au atoms of the basal plane. We used a ratio of about three Au atoms per vacancy as a consequence of experimental STM results.[20]

To find the activation energy for the first CO oxidation pathway, which involves the Au/TiO_2 interface, we located the transition state by decreasing the distance between the C atom of the CO molecule and the O atom of the O_2 molecule until we found a maximum in the energy at a C–O interatomic distance of 1.8 Å. To ensure that the actual transition state was reached, we repeated the series of calculations. We started this time from CO_2 and stretched the C–O bond until it started to break at 1.8 Å, which was at a very similar geometry to that of the reverse reaction. For the second CO oxidation pathway, which does not directly involve support atoms, we placed CO and O_2 on the cluster in a configuration similar to that found in the transition state reported in reference [8] and kept the C–O bond length fixed at 2.8 Å. All other degrees of freedom of the adsorbate and the gold atoms were allowed to relax. We validated this approximation in retrospect by checking that the forces on the atoms were very small, thus verifying that the system is at a saddle point. For both oxidation paths, we tried several initial geometries for the system to ensure that for each instance (initial, transition, or final state) the minimum-energy structure was found.

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