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Catalysis by Gold: Why Size Matters

Jeroen A. van Bokhoven[§]*

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Abstract: Bulk gold is the most inert metal of all, however, when gold is finely dispersed on a support, it can be a very active catalyst for oxidation and hydrogenation reactions. X-ray absorption spectroscopy showed that the smaller the gold particles are, the shorter the gold–gold bond length is. The smaller particles also have an altered electronic structure, as they undergo less hybridization between the s, p, and d orbitals than the larger particles. The d band narrows and moves closer to the Fermi level. As a result, hydrogen, oxygen, and CO adsorb on the metal surface and the nano-sized metal particles can become catalytic.

Keywords: Catalysis by gold · Heterogeneous catalysis · *In situ* characterization · X-ray absorption spectroscopy

Jeroen van Bokhoven has been SNF-Professor in Heterogeneous Catalysis at the Institute for Chemical and Bioengineering, ETH Zürich, since April 1st 2006. He was born December 22nd 1971 in Maassluis, The Netherlands. He completed his studies in 1995 in chemistry at Utrecht University (NL). He obtained his PhD with distinction in 2000 in inorganic chemistry and catalysis. From 1999 until 2002 he was head of the XAS (X-ray absorption spectroscopy) users-support group at Utrecht University. In 2002, he moved to the ETH, where he worked as senior researcher in the group of Professor Prins. Van Bokhoven works in the field of heterogeneous catalysis and (X-ray) spectroscopy. The goal is the determination of structure–performance relationships, which aid the design and construction of better catalysts for cleaner and more efficient processes. His main interests are heterogeneous catalysts and developing advanced tools in X-ray spectroscopy to study the catalyst structure under catalytic relevant conditions. Their combination provides insight into the structure and function of the catalytically active sites.

Introduction

Catalysis by gold is a rapidly developing field in heterogeneous catalysis.[1] Many reactions that are catalyzed by gold have the potential to be developed into new applications in pollution control, sensors, chemical processing, and fuel cell technology. Gold is active in both oxidation and hydrogenation reactions and often surprises by showing very high activity and selectivity. It displays its unique performance when it is finely dispersed on a support as (sub)nanometer-sized particles.[2] Gold is appreciated as a precious metal and for this reason it is used in jewelry. For example, the golden mask of Tutankhamun, the boy-king of Egypt who lived from 1341 to 1323 BC is still as shiny as it was over 3000 years ago, which illustrates the inertness of gold. The reason why gold is the most inert metal of all is based on the high binding energy of its d band, which prevents molecules from adsorbing and thus reacting (*vide infra*).[3]

Although the inertness of bulk gold is well understood, the origin of its catalytic activity when finely dispersed as nano-particles over a support is much less known. Over the years, we have studied the catalytic performance of gold in the oxidation of carbon monoxide[4–7] and in hydrogenation reactions, such as the hydrogenation of cinnemaldehyde.[8,9] Gold is very active in the oxidation of carbon monoxide; the smaller the particles, the more active it becomes.[2,10] Similar behavior was observed in hydrogenation reactions.[8,11] In addition to higher activity with decreasing size, smaller particles showed different selectivities.[12] For example, the smaller the gold particles, the higher the selectivity to hydrogenation of the aldehyde group in unsaturated aldehydes such as cinnemaldehyde. This has been ascribed to the preferred adsorption of the aldehyde bond on the highly coordinatively unsaturated atoms in a nano-sized particle. The smaller particles have more such sites and a higher degree of unsaturation.[13] In addition to size effects, the nature of the support strongly affects the catalytic performance of the nano-sized gold particles. Various supports actively participate in the catalytic conversion.[14,15] To understand the origin of the exceptional performance of gold catalysts, we have determined the changes in gold structure as a function of its size, the interaction of reactants with the surface of nano-sized gold, and the structure of gold while it performed a reaction. *In situ* X-ray absorption spectroscopy (XAS) thus provided insights into particle size, electronic structure of gold, and the interaction of reactants with the gold catalytically active sites.

Heterogeneous Catalysis

A catalytic reaction that occurs on the surface of a heterogeneous catalyst consists basically of three fundamental steps (Fig. 1). The first is adsorption of the reactant(s), the second is reaction, and the third is desorption of the product(s). If any of these steps fails, the catalytic cycle is incomplete and no catalytic reaction takes place.

When reactants adsorb on metal surfaces, they form bonding and anti-bonding or-

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*Correspondence: Prof. Dr. J. A. van Bokhoven
ETH Zurich
Institute for Chemical and Bioengineering
HCI E127
CH-8093 Zurich
Tel.: +41 44 633 4372
Fax: + 41 44 632 1162
E-mail: j.a.vanbokhoven@chem.ethz.ch

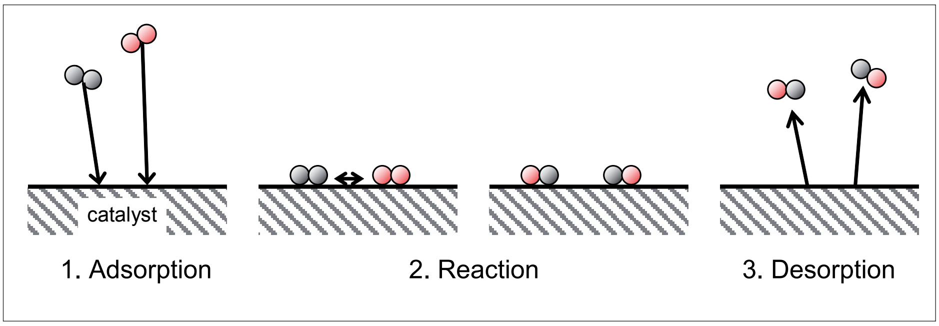

Fig. 1. A catalytic reaction on the surface of a heterogeneous catalyst generally consists of three essential steps: adsorption, reaction, and desorption. If any of these steps does not occur, there is no catalytic conversion. Massive gold is characterized by a very weak adsorption and is generally inactive because its surface remains empty.

bitals with the metal. Chemisorption occurs when the bonding orbitals are positioned below the Fermi level and the anti-bonding orbitals are depopulated and pushed above the Fermi level (Fig. 2). A universal model of adsorbate bonding on transition metals based on the energy position of the d band has been proposed.[16,17] The closer the d orbital energy is to the Fermi level, the stronger are the bonds. The coupling of adsorbates with the metal s states varies moderately for each metal. The interaction of the adsorbate with the d band is much stronger and the bonding and anti-bonding states form. From left to right in the periodic table, the d band is increasingly filled and moves away from the Fermi level (if more than half-filled) because of the higher nuclear charge. As a consequence, the anti-bonding state is pulled down as well. Going down a row in the periodic table, from 3d to 4d to 5d, there is increased Pauli repulsion because of the more extended nature of the 5d orbitals than the 4d orbitals, which are more extended than the 3d orbitals. Electrons in overlapping orbitals repel each other, which leads to repulsion between the adsorbate and the metal surface. Bulk gold is a bad catalyst, because most reactants do not adsorb on its surface, because the d band of gold is too low in energy to empty the anti-bonding state and no bond is formed. Thus, one way to increase the reactivity of gold is to move the d band closer to the Fermi level.

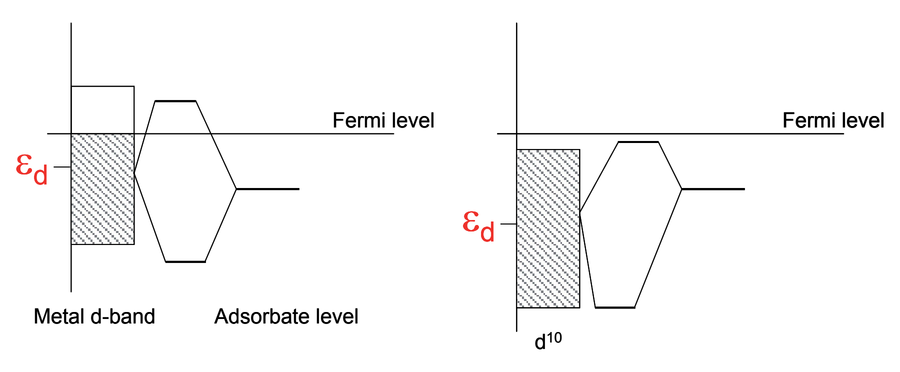

Fig. 2. Formation of bonding and anti-bonding orbitals after adsorption of an adsorbate on the surface of a metal. When the anti-bonding state is pushed above the Fermi level and depopulated, bonding of the adsorbate occurs; if the anti-bonding state is below the Fermi level, it is filled and no bonding takes place. Such a model explains why massive gold is inert and for example does not react with oxygen and hydrogen. Nano-sized gold particles have depopulated anti-bonding states with hydrogen, oxygen, and CO, which makes them catalytically active (see text).

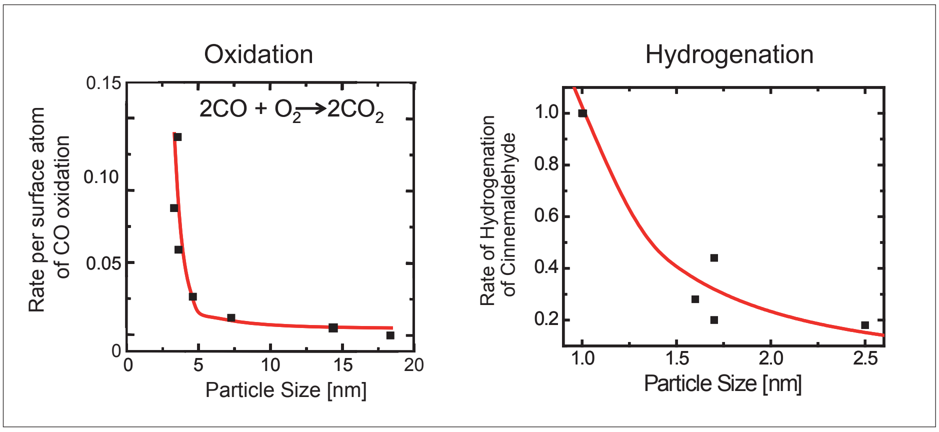

Fig. 3. Size-dependent activity of gold catalysts. The left figure shows the increasing rate of surface atoms of gold with decreasing particle size in the oxidation of CO;[2] The right figure shows the rate dependence of hydrogenation of cinnemaldehyde as function of particle size.[8]

Size Effects on Catalytic Performance and Structure of Gold Catalysts

Gold can be a very active catalyst when finely dispersed on a support. Therefore the particle size and the support strongly affect its performance. The rate per surface exposed gold atom in the oxidation of CO increased significantly when the particle size decreased below 4–5 nm (Fig. 3).[1] Sometimes an optimum in conversion as a function of size was observed.[10]

We have systematically investigated the structure of gold catalysts of different size and on various supports using XAS. XAS at the Au L$_3$ edge provides the empty d density of states and the gold local structure, such as coordination number, bond length, and Debye-Waller factor. Au L$_3$ edge XAS spectra were recorded on many gold catalysts of various particle sizes and using six different supports. The spectra were recorded after reduction at 450 to 525 K for 1 h in 4% H$_2$/He. No cationic gold was detected in any of the spectra after this treatment. Fig. 4 shows the averaged Au–Au bond length as function of particle size on various supports.[5] The particle size was determined from the Au–Au coordination number using known relations. All catalysts followed the same correlation equally well. As the dispersion[18] increased to above about 30%, which correlates to particles of about two nm, a noticeable contraction in the metallic bond length occurred. For the smallest particles, the contraction was about 0.16 Å, or about 5.5%. The data agree quantitatively to those obtained from X-ray diffraction data on unsupported gold particles.[19] Fig. 4 shows a single correlation for all supports, which apparently do not affect the relation between Au–Au coordination number and bond length. This suggests that under the measurement conditions, there is no variation in particle shape over the different supports, which would affect the correlation between particle size and coordination number.

The white line, which is the first intense feature in a spectrum, in L$_3$ absorption edges of transition metals reflect the number of holes in the d band. The more intense, the larger the number of holes in the d band. The L_3 edge of bulk gold shows a small white line, which originates from hybridization of s, p, and d orbitals, which pushes some d density of states to above the Fermi level.[20–22] This is shown in Fig. 5a which shows the L_3 edge absorption near-edges of bulk gold and that of gold particles of identical size (1.1 nm) on varying supports. The spectrum of bulk gold showed the small white line intensity. All near-edge spectra of the nano-sized particles were identical within the limits of accuracy and had much lower white line intensity. Fig. 5b shows the difference in white line intensity of all samples compared with that of bulk catalysts that were represented in Fig. 4. The smaller the particles are the lower the white line intensity. As expected, the largest particles had white line intensity equal to that of bulk gold. The number of holes in the d band thus decreased with particle size, caused by decreased s, p, and d hybridization in the smaller particles, which was corroborated by theoretical multiple scattering calculations.[23] Interestingly, the electronic structure of the particles varied with size, but no visible variation with support occurred.

Single atoms have atomic orbitals of distinct energy. Bulk metals have bands in which the energy levels of the orbitals show very little variation. The more atoms present in the metal, the more orbitals contribute to the band and the larger the band width becomes. Because the number of electrons in the d band for gold is close to ten and varies only slightly as a function of size, the narrowing of the band means that it will shift up in energy. Such behavior has been shown by full multiple scattering[23] and DFT[13] calculations. This makes the d band in nano-sized gold particles more reactive. Such higher reactivity is shown by the interaction with reactants such as CO,[6] O_2,[4,5,7] and H_2.[8] We showed that hydrogen chemisorbs on gold, provided that the particles are nano-sized.[24] The gold–hydrogen bond was weak, however the anti-bonding state could be observed in the L_3 edge XAS spectrum. Fig. 6 shows the L_3 absorption near-edges of nano-sized gold measured under an inert gas after reduction and under oxygen. The spectrum after reduction is typical of fully reduced gold (Fig. 5); that taken under oxygen showed a small white line and decreased intensity at energies directly above the white line, which is indicative of about 10–15% oxidic gold in the sample.[6] Thus, although bulk gold is inert towards oxygen, nano-sized gold supported on alumina partially oxidizes. Such oxidation was observed for particles that were supported on alumina and titania, the two supports that were investigated, however, only when the particles were smaller than about two nm. No interaction with oxygen was observed for larger particles. This indicates that supported nano-sized gold particles activate oxygen. Exposing such partially oxidized particles to CO re-reduced the gold and formed CO_2, which completes a catalytic cycle. Under a mixture of CO and O_2, no oxidation of gold was observed, because the CO kept the particle reduced.[4,6] Any activated oxygen will be directly converted to CO_2 with the CO that co-adsorbs on the surface. Recent theoretical calculations have confirmed that such a cycle, in which a short-lived activated oxidized gold is an intermediate, can occur catalytically over supported nano-sized gold particles.[25]

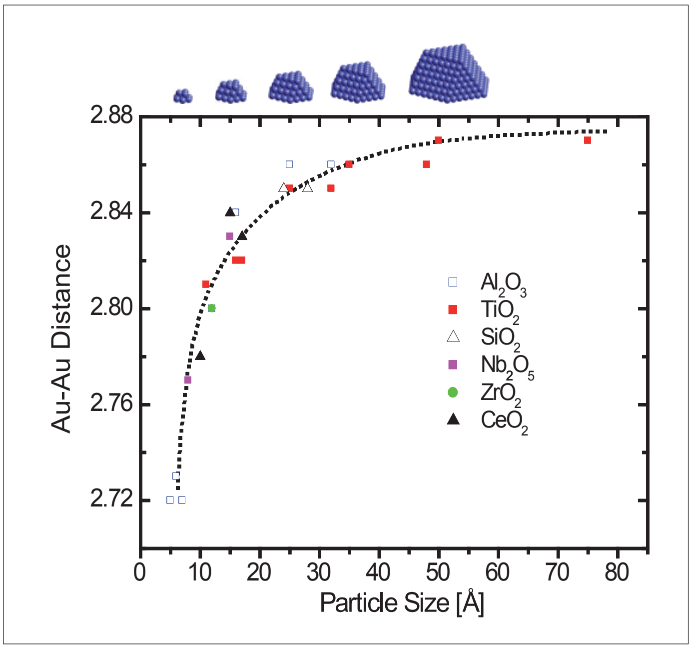

Fig. 4. Averaged Au–Au bond length as function of particle size. The particle size and Au–Au bond length are strongly correlated. The support did not show a noticeable effect. The particle size was derived from the Au–Au coordination number determined by EXAFS analysis.

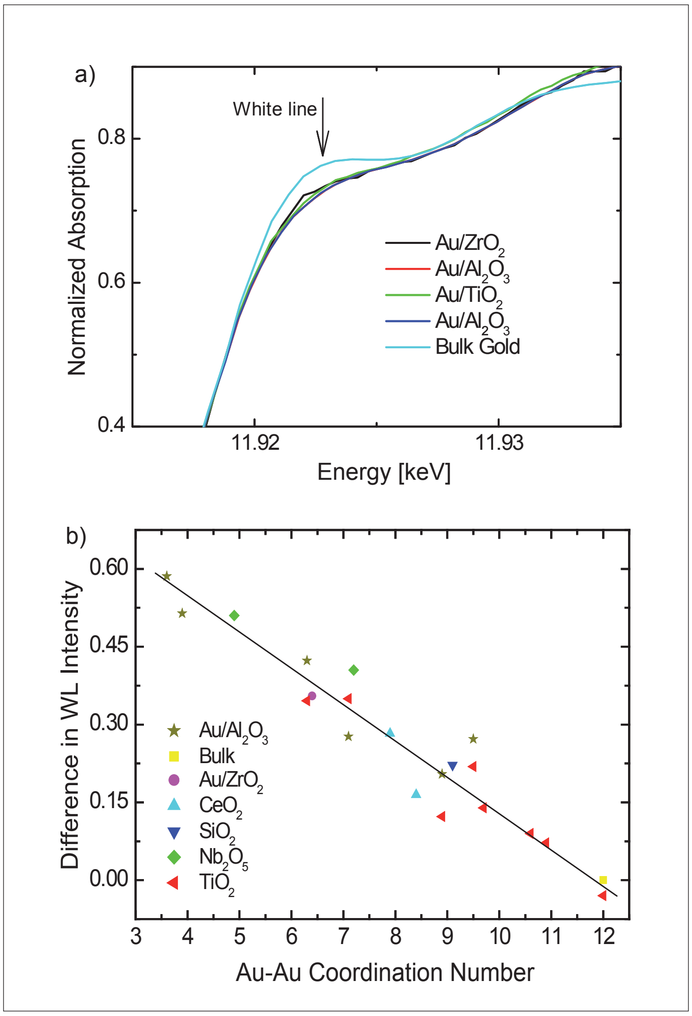

Fig. 5. a) L_3 near-edge X-ray absorption spectra of 1.1 nm particles on various supports compared to that of massive gold (light blue);
b) Difference of white line intensity of all catalysts that were presented in Fig. 4 compared to that of bulk gold. Larger differences indicate a lower number of holes in the d band that originate from hybridization of the s, p, and d bands. The change in structure correlates to particle size *via* the gold–gold coordination number.

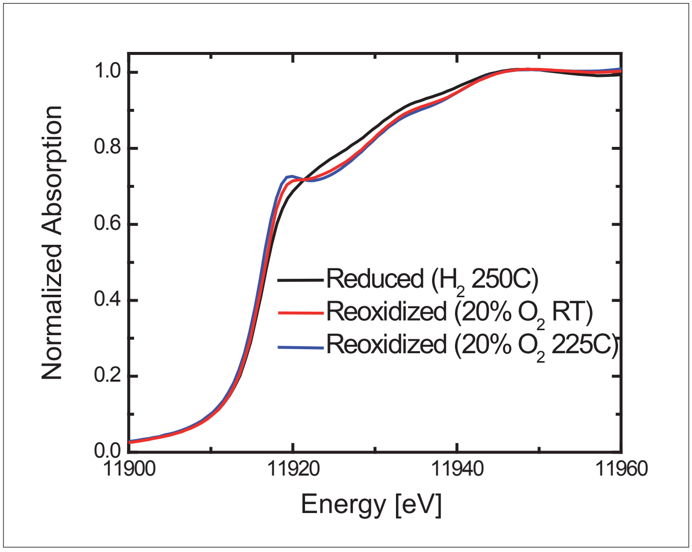

Fig. 6. *In situ* Au L_3 near-edge spectra of a 1.3 wt% Au/Al_2O_3 catalyst after reduction (black) and after exposure to oxygen at room temperature (red) and 225 °C (blue). The differences in the spectra originate from partial oxidation of the gold in the samples that were taken under oxygen.

Thus, unlike bulk gold, nano-sized gold is able to adsorb and activate reactants such as CO, O_2, and H_2. The surface of bulk gold remains empty, which prevents any catalytic reaction occurring as the first step in Fig. 2 will not happen. This alters when the particles decrease in size into the nanometer domain, which enable such particles to be catalytically active. Recent DFT calculations suggested that gold particles of 13 atoms will show a maximum interaction with reactants such as oxygen and CO and will thus be an optimum catalyst for the oxidation of CO.[13]

Conclusion

Gold catalysts show a unique catalytic performance, which is related to the changes in structure of nano-sized particles. Nano-sized particles are intrinsically more reactive because of the increased coordinative unsaturation of the surface atoms, which makes them active in the oxidation of carbon monoxide. The anti-bonding states of gold with oxygen, hydrogen, and carbon monoxide can be directly observed in L_3 edge X-ray absorption data, which also indicated a modification of electronic and geometric structure with size, irrespective of the underlying support. The oxidation of CO could be performed stepwise by first exposing gold to oxygen followed by CO. Nano-sized gold is the partially oxidized and subsequently reduced by CO to form CO_2.

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