

Intrinsic Reactivity of Gold Nanoparticles: Classical, Semi-Empirical and DFT Studies

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Abstract

Gold nanoparticles used in most experiments (1-10 nm) in gold catalysis show varying degrees of reactivity, with particles below 5 nm generally being more reactive. The origin of this activity is a subject of a number of model experiments and theoretical studies on either clusters of a few atoms in size or extended surfaces (smooth or stepped). In the work described here, a classical theory for the variation of the metal workfunction with cluster size, Extended Hückel Theory (EHT) calculations combined with DFT calculations, as well as a carbon monoxide (CO) chemisorption model are combined to develop a relationship between metal particle size and the particle's reactivity towards CO. For gold, it is shown that while the contribution of the d-band hybridization energy to the total CO chemisorption energy is unfavourable for bulk gold, this is not true for gold particles below 5-6 nm. That is, the d-band hybridization energy is negative for small gold particles. This is believed to be explanation of the onset of high reactivity for small gold particles.

Keywords

Gold catalysis, Chemisorption, Nanoparticles, Fermi level

Introduction

Gold nanoparticles are very active catalysts for a wide range of chemical reactions (1, 2). Since the position of the d-band centre relative to the Fermi level is a good indicator of chemical reactivity when comparing many metal surfaces (3, 4), it is interesting to establish whether a size-dependent shift in this parameter is responsible for the high intrinsic reactivity of small gold particles relative to an extended gold surface. Using chemisorption of CO onto Au particles, it is shown that the onset of catalytic activity corresponds to the particle size where the d-band contribution to the chemisorption energy switches from being unfavourable (positive energies of interaction) to being favourable (negative energies of interaction) as the d-band centre shifts upwards relative to the Fermi level. It is the main objective of this paper to show that simple models can be used to obtain quantitative estimation of energetics of molecule adsorption onto gold particles of practical size (~ 1–10 nm), where state of the art calculations are often prohibitively expensive. The intrinsic size effects are investigated (as opposed to combined size and support effects).

Computational details

Dependence of the Fermi energy on particle size: Classical, EHT and DFT calculations

Wood (5) derived an expression for the variation of the metal workfunction as a function of the metal radius. The expression was derived by considering the difference between a sphere and a plane in their classical image potentials' contributions to the workfunction of a metal. The final result is:

$$\varphi_{\text{im}}^{\text{sphere}} - \varphi_{\text{im}}^{\text{plane}} = \frac{5 \cdot e^2}{8 \cdot R} \quad (1)$$

$$W(R) = W_{\infty} - \frac{5 \cdot e^2}{8 \cdot R} + \frac{e^2}{R} = W_{\infty} + \frac{3 \cdot e^2}{8 \cdot R}$$

where W_{∞} is the bulk metal workfunction (= 5.10 eV for Au), and R is the particle radius. Assuming a zero vacuum level, Equation 1 then represents the variation in the Fermi energy with crystallite size. Snider and Sorbello (6) reproduced the form of Equation 1 using a variational calculation based on density functional theory formalism, although in their work the 3/8 factor was replaced by a factor in the range 0.4-0.5, and for very small R deviations from the form in Equation 1 were observed in some cases. The origin of at least two different factors, 3/8 and 0.5, was recently discussed classically by Halas (7). Snider and Sorbello (6) also note that Cini (8) observed similar numerical values using the same approach, although Cini (8) did not use a 1/R expansion to interpret the results. From a general electronic structure point of view, the lower Fermi energy for small clusters is a coordination effect. The

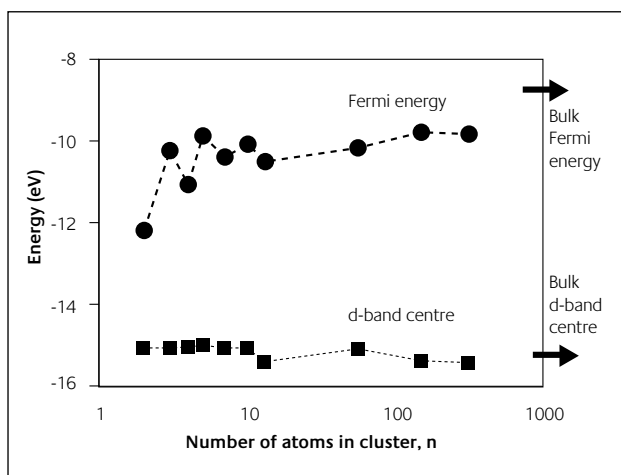


Figure 1
EHT-calculated Fermi energies (●) and the d-band centre energies (■) of Au_2 - Au_{309} clusters. Arrows show the values calculated for bulk gold. Au_2 - Au_4 clusters were pre-optimised at the DFT B3LYP level. The Au-Au distance was fixed at the bulk value for Au_5 , Au_7 , Au_{10} , Au_{13} , Au_{55} , Au_{147} and Au_{309} clusters. Au_{13} - Au_{309} clusters represented the first to the fourth geometrical shells of an fcc cuboctahedron

average metal-metal coordination in small particles is lower than in large particles. This results in increased localisation of frontier electrons to individual atoms (due to reduced degree of overlap of the atomic orbitals), an increase in electron-nuclear interaction, and hence a deeper lying Fermi level. This will occur until the Fermi energy lies near the HOMO of the atom (not necessarily a monotonous approach).

It is assumed, in this study, that the *absolute* energy of the d-band centre remains unchanged as the particle size changes. This assumption was made on the basis of our Extended Hückel Theory (EHT) (9, 10) calculations on Au_2 - Au_{309} clusters (shown in Figure 1), which suggested that the Fermi energy changes with size but the absolute d-band centre energy remains unchanged as the particle size changes. The ability of EHT to give reliable orbital energies was checked by comparing Fermi energies calculated for Au_2 - Au_{13} clusters with those calculated by Density Functional Theory (DFT), and the Fermi energies (not presented here for brevity) showed the normal (11) odd-even oscillation. The Wood curve is not shown in Figure 1 because it is not applicable in the extreme quantum regime where odd-even oscillations are still observed.

CO chemisorption model

Nørskov et al. (3,4,12) propose, following extensive validation by high-level DFT calculations, the following model for estimation of the d-band hybridization energy contribution to the total CO chemisorption energy:

$$E_{d\text{-hyb}} = -4 \cdot \left[f \cdot \frac{V_{\pi}^2}{\epsilon_{2\pi} - \epsilon_d} + f \cdot S_{\pi} \cdot V_{\pi} \right] - 2 \cdot \left[(1-f) \cdot \frac{V_{\sigma}^2}{\epsilon_d - \epsilon_{5\sigma}} + (1+f) \cdot S_{\sigma} \cdot V_{\sigma} \right] \quad (2)$$

where: f = fractional filling of the d-band, V and S are the coupling matrix element and the overlap respectively of the metal d-states and the appropriate CO orbitals (5σ and $2\pi^*$). Filling in the relevant values for Au:

$$E_{d\text{-hyb}} \text{ (eV)} = \frac{-20.1}{2.5 - \epsilon_d} + 3.41 \quad (3)$$

The variation of the d-band contribution to the total chemisorption energy as the gold particle size changes can be calculated from Equations 1 and 3. The d-band centre was assumed to lie 3.56 eV below the Fermi level (12). Calculations by Ruban et al. (12) over different metals suggested that the total CO chemisorption energy when the d-band contribution is 0 eV is about -36 kJ/mol. In our calculations, the d-band hybridization energy calculated for different metal sizes was therefore converted to total CO chemisorption by adding -40 kJ/mol as the sp contribution.

Results and discussion

Relative upshift of the d-band centre

Figure 2 shows the calculated position of the d-band centre relative to the Fermi level. The relative position of the d-band centre is ~ 1 eV higher for gold nanoparticles compared to bulk gold. Note that this upshift is *relative*, as it is in fact the Fermi level that downshifts.

The key question is why a relative upshift of the d-band centre should, from an electronic coupling point of view, cause an increase in reactivity (as will be shown below). This has to do with the four-electron interactions between filled d-orbitals of the metal and the filled orbitals of the adsorbate (13). Under normal circumstances for metals with filled d-orbitals, the bonding and the antibonding orbitals that result from the metal d - adsorbate sp interaction will be filled and the interaction will subsequently be repulsive. If, on the other hand, the Fermi level is very close to the centre of the d-band

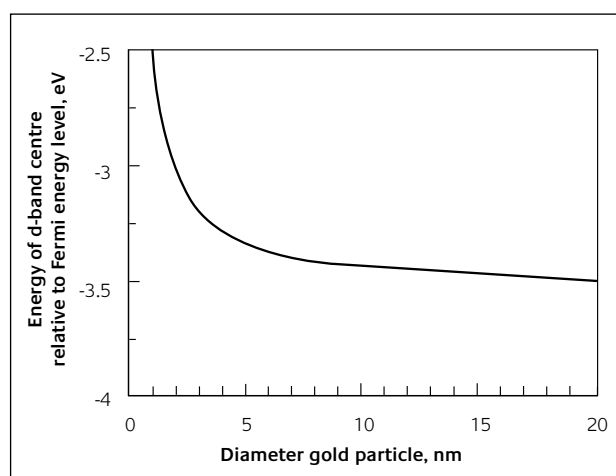


Figure 2
Variation of the d-band centre energy relative to the Fermi energy for gold as a function of the diameter of the gold particle

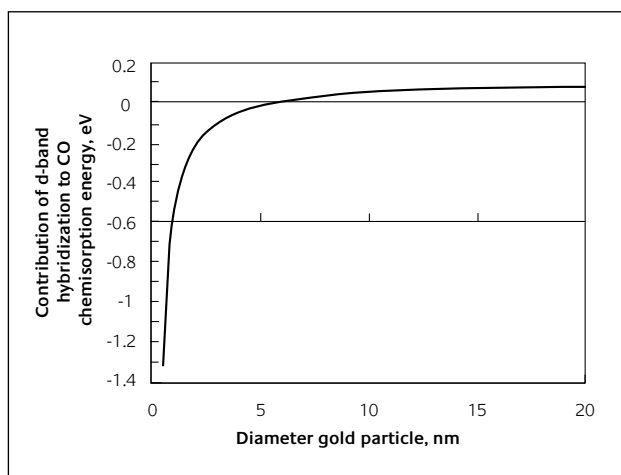


Figure 3
Size dependency of the contribution of the d-band hybridization energy to the total energy of CO chemisorption onto gold particles

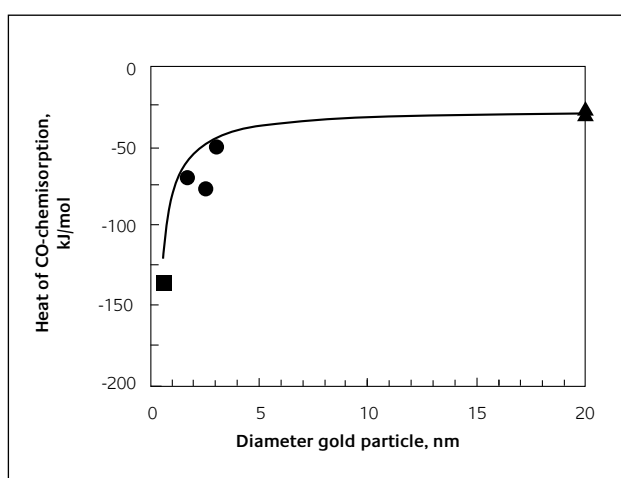


Figure 4
The total CO chemisorption energy onto Au particles, obtained by adding the *sp* contribution to the energies indicated in Figure 3. ●: experimental measurements on Au nanoparticles supported on TiO₂ (15); ■: DFT calculation on Au₁₃ (11); ▲: DFT calculations on Au(111) surface (16-17)

following a relative upshift of the d-band centre (e.g. by lowering the Fermi level), the antibonding orbital can be raised above the Fermi level and electrons can consequently flow from the antibonding orbital to the metal Fermi level, changing the four-electron interaction from being repulsive to being attractive.

Reactivity of gold nanoparticles

Figure 3 shows the variation of the d-band hybridisation energy contribution to the CO chemisorption energy as a function of gold particle size. It is seen that the d-band contribution to the total chemisorption energy becomes attractive at a gold particle size of around 5-6 nm. In Figure 4, the *sp* contribution (-40 kJ/mol) was added to the d-band hybridisation energy in Figure 3 to obtain the total CO chemisorption energy. Literature values are also indicated for comparison. Despite recent doubts expressed on the d-band centre model (see e.g. 14), it is shown that a combination of this model and a classical model for

workfunction variation with particle size can still help rationalise the high intrinsic reactivity of gold particles at the nanometre range. Note that it is, in fact, computationally difficult to calculate the properties of metal nanoparticles at the practical size ranges typically employed in catalytic reactions (~1-10 nm) using quantum mechanics. The semi-classical calculations presented here span that practical range. Use of a bulk Fermi level instead of a site dependent maximum orbital energy does not limit the applicability of the model as reliable trends can still be calculated for a given *reference* d-band centre energy.

Conclusion

Using CO as a test molecule, it has been shown that the d-band contribution to the total energy of CO chemisorption onto Au nanoparticles is favourable for particle sizes typically employed in catalytic studies (below 5-6 nm), but remains unfavourable above these sizes. This is due to the higher *relative* energy of the d-band centre for small particles compared to bulk gold. The intrinsic reactivity of gold nanoparticles is therefore rationalised for size ranges typically used in most experiments in gold catalysis.

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About the authors



Dr Noko Phala is a Lead Research Scientist at Anglo Research, a division of Anglo Operations Limited. He obtained a PhD in Chemical Engineering at the University of Cape Town in 2004, for a thesis entitled 'a theoretical investigation in heterogeneous gold catalysis'. His areas of research include

(i) search for novel metal mining/extraction technologies, and (ii) application of metals as catalysts in chemical processing. In both these fields a significant portion of his time is spent seeking to understand, rationalize, and predict surface-molecule interactions by applying theoretical methods.



Prof Eric van Steen is the Head of the Department of Chemical Engineering at the University of Cape Town and is part of the Centre for Catalysis Research. His research interest is in heterogeneous catalysis and his current focus is on the catalytic activity of nano-sized metal particles.

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