On the effect of atomic structure on the deactivation of catalytic gold nanoparticles

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Abstract. Here we present atomic scale studies into the nature of both the internal structure and external surfaces of catalytic Au nanoparticles using aberration corrected in-situ electron microscopy. The activity of catalytic nanoparticles is thought to be highly sensitive to the particles’ structure, meaning typical local atomic rearrangements are likely to significantly affect the overall performance of the catalyst. As-deposited Au nanoparticles are found to exhibit a variety of morphologies, with many being internally strained or highly stepped at the surface. Upon heating, surface atoms are observed to minimise the particles’ surface energy by restructuring towards planar (111) facets, resulting in the removal of low co-ordinated sites thought to be crucial in catalysis by Au nanoparticles. These results suggest the process of surface energy minimisation made possible by heating may lead to a loss of active sites and consequently contribute to the deactivation of the catalyst.

1. Introduction

Traditionally believed to be inert, it was not until the mid 1980s and the pioneering work of Haruta et al [1] and Hutchings et al [2] that gold was discovered to be catalytically active. Haruta et al went on to show that when reduced to less than 5nm in diameter, gold is in fact a more active catalyst than other noble metals for many applications, and that even at low temperatures, small Au nanoparticles exhibit extremely high activity for CO oxidation [3]. As the activity of gold has been shown to be strongly dependent on particle size, properties that vary as a function of size have been proposed as the fundamental cause behind gold’s activity. In particular quantum size effects [4], perimeter sites [5], particle-support interfaces [6] and low co-ordinated atoms [7-9] have all been suggested to be the reason behind the catalytic properties of small gold nanoparticles.

The chemical activity of gold has been described as being strongly dependent on the co-ordination number of the gold surface atoms, and it has been shown that the strength of the Au-CO and Au-O bond varies with Au co-ordination number [10]. This is explained by the weak bonding between Au(111) and O relative to the stronger interaction between O and Au atoms of lower co-ordination number found at steps and corners of small particles. The $d$ states of atoms in the Au(111) surface are too low in energy to interact with the O $2p$ valence states, and are therefore unable to disassociate O$_2$. In contrast, the lower co-ordination atoms have $d$ states closer to the Fermi level, resulting in a stronger interaction. This effect can be further explained by the $d$ band model [11-13], in which both
tensile strain and reducing co-ordination numbers can modify the $d$ band, causing a narrowing and subsequent increase in the band’s population.

The inherent instability of small nanoparticles is one of the major problems with the widespread application of nano-catalysts, with sintering via particle coalescence or Ostwald Ripening processes being well documented [14-16]. Whilst sophisticated supporting materials can be used to minimise such processes; in time a loss in overall surface area can cause significant deactivation. However, it seems clear that there is a strong structural sensitivity of the catalytic properties of gold nanoparticles, and that any induced change in an individual nanoparticle’s internal structure or external surfaces may also result in a loss of activity.

2. Experimental Procedure

*In-situ* aberration corrected electron microscopy is a powerful tool for studying catalytic nanoparticles at the atomic scale under simulated reaction conditions. The removal of spherical aberration allows for a consistent phase contrast throughout the image, whilst operating at close to zero defocus helps to minimise delocalisation effects; allowing direct interpretation of inter-atomic distances, internal structure and external surfaces from a single image. This is crucial for *in-situ* studies, as the dynamical nature of the system means it is rarely possible to obtain a through-focal series. Furthermore, the exposure times necessary for imaging and hence the effects of the beam on the sample are minimised. In the present study a double aberration corrected JEOL 2200FS microscope has been used, with the wider gap pole piece made possible by correction of the spherical aberration allowing for an extended tilt range and the use of a regular hot stage [17].

Colloidal gold nanoparticles in the size range of 1–10 nm have been deposited on to 3.5nm thin amorphous carbon supports. The continuous amorphous carbon films provide a well defined substrate whilst the 3.5nm thickness allows for reduced noise and improved resolution of weak phase objects such as small nanoparticles.

3. Results and Discussion

The as-deposited particles exhibit a variety of internal structures, often multiply twinned, and it is clear that the small difference in energy terms between such structures [18] means that small variations in the number of atoms or the local environment can result in vastly different morphologies. An example of a multiply twinned particle can be seen in figure 1. This crystallographically forbidden Marks decahedral structure [19] consists of five tetrahedra adjoined by \{111\} twin planes, meaning significant internal strain has to be incorporated into the non-space filling structure. In the Marks decahedral, \{111\} re-entrant facets act to further minimise the particles surface energy, even at the expense of an increase in surface area.

Figure 2 is again as-deposited and shows a single crystal of gold with a (twin) dislocation in the AC-HRTEM image in [011] orientation. Such dislocations may arise due to internal stresses during the crystal growth or during the initial crystallisation. Preliminary displacement vector (Burgers vector) of the dislocation can be inferred based on the atomic scale planar image. Due to the small size of the nanoparticle, tilting the sample to different zone axes is difficult and requires prolonged exposure to the electron beam. Such exposures are avoided due to concerns over beam induced surface atom movement and possible modifications of the internal structure, meaning determination of the component of the displacement vector in the third crystal direction ($z$) has not been possible. The measurements suggest that the Burgers vector of the dislocation is of the type 1/6 [21]. Such dislocations lie on adjacent twinning planes of \{111\} type leading to stacking faults.

Also clear from the image is the highly stepped nature of the surface. The internal dislocation terminates in a partial terrace at the surface, whilst the rest of the surface is regulary stepped throughout the perimeter of the particle in the image. Such a disordered surface structure generates an abundance of low co-ordinated surface sites thought to be crucial for the catalytic activity of gold nanoparticles. However, whilst surface atoms with reduced co-ordination are likely to provide active
sites for catalysis, they are also likely to be inherently unstable as they result in an increase in total surface energy. This can be represented by the expression for surface energy [20]:

\[ \sigma_{hkl} = \frac{1}{2} \frac{N_{hkl}}{Z_B} E_{coh} \]

where \( Z_B \) is the bulk co-ordination number, \( E_{coh} \) is the cohesive energy between two neighbouring atoms and \( N_{hkl} \) is the number of broken bonds. Clearly low co-ordinated ad-atoms, steps and terraces result in a greater number of broken bonds and hence increased surface energy.

The effect of heating on these low co-ordinated sites is shown in figure 3, where exposure to the electron beam over the course of a minute causes movement of the surface atoms and minimisation of surface energy terms via restructuring towards planar \{111\} surfaces. These low energy surfaces exhibit much higher co-ordination, with density functional theory calculations predicting very weak adsorption of CO and consequently much reduced activity [13].

In-situ heating to 600°C provides further evidence of such effects, as is demonstrated in figure 4. Here we can see a single crystal cuboctahedral particle bound predominantly by \{111\} surface facets. Such large single crystal structures with almost atomically clean facets were only produced as a result of heating to elevated temperatures. Nearly all surface step sites have been removed; with heating having an annealing effect on both the surfaces and the internal structure, as any twin boundaries or dislocations have been removed. Added effects due to gas adsorption may further modify the nature

**Figure 1.** As-deposited Marks Decahedral Au nanoparticle with \{111\} re-entrant facets.  
**Figure 2.** As-deposited single crystal Au nanoparticle with internal dislocation and surface steps.  

**Figure 3.** Re-arrangement of Au surface atoms towards planar \{111\} surface facets and increased co-ordination as a result of heating by 200kV electron beam.
of both the surface and internal structure [21].

Whilst the origin of gold’s remarkable catalytic activity is still being debated in the literature, a consensus seems to have been reached that under co-ordinated surface atoms provide highly active binding sites for incoming adsorbates, and clearly any reduction in the number of such sites will have a detrimental effect on the nanoparticles activity. Here we have demonstrated the effect of heating on these sites, showing a tendency for the nanoparticle to minimise its surface energy by restructuring towards planar \{111\} surface facets. These studies suggest that as well as maintaining the catalysts surface to volume ratio by preventing conventional sintering processes, it is necessary to identify the actual active sites and consider their evolution under typical operating conditions.

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