In-situ heating studies of gold nanoparticles in an aberration corrected transmission electron microscope

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Abstract. Gold nanoparticles have a high catalytic activity for CO oxidation at low temperatures providing they remain less than 5nm in diameter. Their structure and stability and the growth processes that occur during heating have been investigated using Angstrom resolution in-situ double aberration corrected transmission electron microscopy with a JEOL JEM-2200FS. Colloidal Au nanoparticles suspended in water, with mean diameters of 2nm and 5.6nm, have been deposited onto 3.5nm thin carbon supported on holey carbon grids and onto Si₃N₄ membranes. Dynamic in-situ high resolution AC-TEM images show competitive sintering processes on the different supports. Whilst the 5.6nm particles were observed to be very stable on the carbon, the 2nm particles showed sintering predominantly through particle migration and coalescence, with particle migration occurring as early as ~200°C, peaking at ~500°C. In contrast Au nanoparticles on Si₃N₄ membranes were observed to coalesce at ~180°C, before Ostwald Ripening became the dominant growth process at higher temperatures. It is believed that atoms and small clusters migrate away from their original particle before becoming trapped on the Si₃N₄ substrate. These trapped clusters then build up to form the small particles observed, before having sufficient energy to continue to migrate and join another larger particle at ~500°C.

1. Introduction

Despite the known catalytic properties of platinum and other noble metals, gold was traditionally believed to be inert until the pioneering work of Haruta et al [1] and Hutchings et al [2] in the 1980’s. 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 these Au nanoparticles exhibit extremely high activity for CO oxidation at low temperatures [3]. The exceptional catalytic activity of such gold nanoparticles has direct applications in automotive and industrial emission control [4, 5] whilst also being of great interest for the removal of CO from hydrogen streams in PEM fuel cells [6] and within the fuel cell itself as an electrocatalyst [7].

Further studies have investigated the properties of Au nanoparticles key for high catalytic activity, with differing conclusions. Perimeter sites [8], charge transfer [9] and low-coordination atoms [10-12] have all been attributed to enhance activity. However, it is commonly agreed that for Au nano-catalysts, particle size plays a crucial role [13-17], with an optimum diameter occurring at 3.2nm for CO oxidation [17]. Also the effect of the support has been widely investigated, with much of the focus on metal oxide supports such as TiO₂ and Fe₂O₃. Grunwaldt et al found significantly different CO oxidation activities for Au nanoparticles with the same mean diameter on different supports [18], and later related this to a change in support interactions leading to a difference in the number of low-coordinated gold sites [19]. Also it is clear that the substrates defects or vacancies play a significant role in the ripening process of catalytic nanoparticles, especially under atmospheric conditions [17].
One of the major problems with the application of nano-catalysts is their inherent instability and tendency to sinter and deactivate [20, 21]. Currently, the stability of promising new catalysts needs lengthy testing under reaction conditions before being further developed and implemented in industry. In order to speed up this process and improve our ability to develop highly active but stable catalysts, a greater understanding of the sintering processes is needed. It is generally accepted that there are two main mechanisms that give rise to cluster and particle growth. These are migration and subsequent collision and coalescence of particles, and Ostwald Ripening, in which one particle will grow at the expense of another through inter-cluster transport [21-23].

The earliest models of such sintering mechanisms were based on the Gibbs-Thompson relation, in which particle energy is dependent on particle size [21], and this relationship is still used today in current atomistic models [17, 24]. However, studies have shown that the stability of metal atoms decreases more rapidly than predicted when the particle diameter approaches the few nanometres range [25]. With a rise in the proportion of surface atoms, the melting temperature falls and the mobility of the surface atoms increases. Surface atoms also start to behave more independently, as the average number of bonds between atoms decreases and the band structure is weakened [26].

2. Experimental Procedure

The angstrom resolution double aberration corrected JEOL JEM-2200FS with wider gap (HRP) objective lens polepiece in the Nanocentre at the University of York is uniquely equipped to carry out in-situ studies of the structure and stability of small nanoparticles [27]. The nature of in-situ work means that it is rarely possible to obtain a complete through focal series of images. By including in the CTF of each image frame a complete range of spatial frequencies, and by minimising delocalisation effects by operating at close to zero defocus, AC-(S)TEM allows us to accurately observe inter-atomic spacings, crystal structures, interfaces and external surfaces from a single image, whilst the wider gap pole piece gives high stage capabilities and an increased specimen tilt range [27-29]. Also, AC-TEM under low electron dose imaging and ‘blank’ calibration experiments (without the beam and with the beam switched on only to record the final reaction end point and compared to in-situ data) are used to ensure no effects of the electron beam [30].

The use of 3.5nm thin carbon as a well defined substrate on holey carbon grids gives reduced background noise and improved resolution of Au nanoparticles; especially for those less than 2nm in diameter. Colloidal Au nanoparticles suspended in water, with mean diameters of 2nm and 5.6nm, have been deposited onto the thin carbon and onto Si$_3$N$_4$ membranes. Initial AC-HRTEM studies into the structure of the particles were carried out, before dynamic in-situ AC-TEM was used to find the developing particle size distributions and particle number density as a function of temperature. Finally in-situ AC-HR(S)TEM was used to study the structure of the Au particles throughout the sintering process.

3. Results and Discussion

It was found that the 2nm Au colloid suspension contained particles in a size range of 1-8nm, see figure 3, whereas the larger 5.6nm Au colloids showed a much narrower size distribution. Particles less than 2nm in diameter were observed to be predominantly single crystals, whereas as above this multiply twinned particles (MTP) were much more common. Figure 3 shows a classical MTP on the right, a decahedron made up of five tetrahedral planes, bound by (111) twin planes [31] and a small, single crystal particle on the left. Figure 4 is an aberration corrected ultra high resolution TEM (AC-UHRTEM) image showing clear inter-atomic spacings, crystal structure and external surface detail.
Samples prepared using 2nm Au colloids supported on thin carbon showed clear sintering, predominantly through particle migration and coalescence, with an increase in mean particle diameter from 3.37nm to 5.22nm and a 53% reduction in the number of particles present in the area observed in figure 5. However, the larger 5.6nm Au colloids deposited on to the same carbon support proved very stable, with little to no sintering observed throughout heating. In contrast, the same colloidal suspension deposited on to Si₃N₄ membranes showed firstly particle migration and coalescence at ~180°C, followed by sintering predominantly via inter-cluster transport. It is clear that between 200-500°C there is a significant increase in the number of small particles and clusters approximately 1nm in diameter (circled in red in figure 6). Atoms or small clusters may leave a particle in order to reduce the original particles surface energy; however before joining another larger particle the clusters appear to become trapped on the Si₃N₄ surface, thus leading to the increase observed in figure 6.
Above 500°C, the trapped clusters and small particles have sufficient energy to continue to migrate across the surface and rejoin a larger particle, (as seen in the marked reduction of 1nm particles present) thus completing the process of Ostwald Ripening. From 200°C onwards both the total number of particles present and the mean particle diameter is constant, within error, whilst the standard deviation of the particle size increases from 1.15nm to 1.36nm, before reducing back to 1.09 nm at 670°C, consistent with the above conclusions.

Studies of the structure of the particles after heating showed many particles had undergone surface reconstruction and internal recrystallisation in order to minimise surface area and surface energy. Many larger particles that would have been typically multiply twinned were observed to have become single crystals, with an average increase in crystal size, whilst agglomerates of particles that had coalesced were observed to minimise their surface area by reconstructing towards more spherical shapes, as can be seen in both figures 5 and 6.

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