Some recent advances in gold-based catalysis facilitated by aberration corrected analytical electron microscopy

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Abstract. The recent availability of aberration corrected analytical electron microscopes (ACAEM) is revolutionizing our ability to characterize nanostructured catalyst materials. Some recent case studies are presented whereby the application of the high angle annular dark field (HAADF) imaging technique, coupled with STEM-XEDS analysis, has given us a more detailed and realistic view of the catalyst morphology. The examples chosen include supported Au catalysts for low temperature CO oxidation and supported AuPd bimetallic alloy catalysts for the direct production of H2O2.

1. Introduction
Supported gold clusters and gold-palladium nanoparticles are intensely studied materials primarily because of their exciting potential applications in catalysis. The recent availability of aberration corrected analytical electron microscopes (ACAEM) is revolutionizing our ability to characterize the morphology, crystallography and chemical composition of such nanoscopic volumes of materials and for the first time are giving us more realistic views of these catalyst systems. In this paper, we present a short review of some of the recent developments in gold catalysis that have been facilitated by ACAEM.

2. Supported gold catalysts for low temperature CO oxidation
The oxidation of CO to CO2 at low temperature is the most studied reaction in the field of gold catalysis [1]. Bond and Thompson have summarized the most up-to-date understanding of the CO oxidation mechanism over Au in their recent review [2]. This particular reaction is crucial for the removal of carbon monoxide from enclosed spaces such as submarines and space craft, prolonging the life of fuel cells, and extending the usable lifetime of a fire fighters mask. There is a consensus building that a small particle size (which introduces more low coordination number Au atoms), Au oxidation state, the choice of support, particle-support interactions and experimental conditions (e.g. moisture level) are all important parameters to control in this reaction. Previously researchers believed that 2-4 nm size Au nanoparticles are the active species for CO oxidation, however experiments in aberration corrected electron analytical electron microscopes are now beginning to alter that view.
2.1 The multiplicity of supported gold species in conventional catalyst preparations

Conventional bright field and phase contrast lattice imaging experiments are effective for characterizing Au particle size distributions, provided that the supported metal particles are greater than ~1nm in size. However HAADF imaging in an aberration corrected STEM indicates that the true nature of the Au distribution on oxide supports is far more complex than previously imagined. For instance, five distinct gold morphologies have been identified by STEM-HAADF to co-exist on ZnO supports; namely (i) isolated Au atoms, (ii) sub-nm Au clusters, (iii) ordered monolayer rafts of Au atoms, (iv) assemblies of Au at step edges and (v) epitaxial Au nanoparticles greater than 1nm in diameter, as shown in Fig.1. Interestingly, the relative population density of these various Au species, as well as the overall catalytic activity of the material, can vary considerably with the calcination temperature to which the Au/ZnO material is subjected [3]. The challenge is to devise experiments that will allow us to deduce the relative catalytic activities of these various supported Au species. Once this is known, sample preparation strategies may be developed to maximize the number of the most active entities so that the precious Au metal can be utilized more efficiently. This has been achieved for the Au/FeO$_x$ system where sub-nm bilayer Au clusters have been identified as the key active species for CO oxidation [4].

![Figure 1. Aberration corrected STEM-HAADF (z-contrast) images showing the various Au species co-existing on a ZnO support in a sample made by co-precipitation; (a), (b) 3-dimensional Au nanoparticles; (c) sub-nm Au clusters (arrowed); (d) sub-nm Au clusters and isolated Au atoms (circled); (e) ordered monolayer Au rafts and isolated Au atoms; (f) assemblies of Au at step edges [2].](image)

2.2 Sol-immobilized gold nanoparticles

An alternative technique that allows more precise control over particle size and structure, is to preform the Au nanoparticles in a colloidal solution before depositing them onto the support. The only disadvantage to this method arises from the fact that during fabrication the nanoparticles are coated with organic molecules – ligands– which prevent them from clumping together (Fig. 2(a)). Once they
are deposited onto a support, these ligands tend to impair the nanoparticle’s catalytic performance by blocking the approach of molecules to active sites on the metal surface. Previous methods for stripping away these ligands have involved heat treatments of up to 400°C, which caused sintering and a loss of activity. We have recently discovered a milder alternative for removing the ligands from polyvinyl alcohol (PVA) stabilized gold nanoparticles deposited on a titanium oxide support—a simple hot water wash [5]. HAADF imaging (Fig. 2(b) shows this mild treatment has fewer detrimental effects on the particle morphology or size, and results in a doubling its CO oxidation activity.

Figure 2. (a) A schematic diagram of a Au particle stabilized with PVA ligands; (b) an HAADF image of a colloidal Au particle after the ligands have been removed by hot water washing. [5]

2.3 Gold re-dispersion by chemical methods
The practical application of gold catalysts has often been limited due to low stability and irreversible deactivation during reaction or thermal pre-treatment. Many studies have investigated the underlying causes behind the loss in activity and have reported surface poisoning, loss of metal support interaction, and nanoparticle sintering as potential contributing factors. Re-activation of the catalysts is problematic, particularly in cases where the gold particles have increased in size, and, therefore, if it were possible to devise an effective method to re-disperse the Au metal, this would be of significant benefit. In a recent study, we have shown that methyl iodide can be used to disperse large (~20 nm)

Figure 3. A standard World Gold Council Au/C catalyst displaying large Au nanoparticles (a), which after a mild chemical treatment with CH₃I becomes atomically dispersed (b) on the support [6].
gold nanoparticles supported on carbon into dispersed gold atoms/dimers at low temperature and atmospheric pressure [6]. The process occurs via the progressive removal of gold-halogen entities from the metal nanoparticles and a gradual decrease in the size of the gold on the minute timescale.

3. Bimetallic Au-Pd alloys for the direct production of H$_2$O$_2$

There is a growing interest in using supported bimetallic AuPd alloy nanoparticles for the direct production of H$_2$O$_2$ from H$_2$ and O$_2$. In our first reports on this topic [7, 8] the metal nanoparticles were prepared via a co-precipitation route using HAuCl$_4$ and PdCl$_2$ as precursors. This generated AuPd alloy particles having a broad particle size distribution, with the larger particles being Au-rich and the smaller ones being Pd-rich [9]. Interestingly we found that on oxide supports the AuPd particles tended to adopt a Pd-rich shell/Au-rich core structure, whereas on activated carbon they remained as random homogenous AuPd alloys [10]. The following sub-sections present some specific examples of how STEM-HAADF imaging is increasing our understanding of Au-Pd bimetallic alloy systems.

3.1 Bimetallic Au-Pd colloidal particles with designer morphologies

In a recent study [11], a systematic series of AuPd bimetallic particles have been prepared by colloidal synthesis methods, which gives us better control over the particle size distribution and structure. Particles having random alloy structures, as well as ‘designer’ particles with Pd-shell/Au-core and Au-shell/Pd-core morphologies, have been prepared and immobilized on both activated carbon and TiO$_2$ supports. These materials have subsequently been compared as catalysts for the direct production of H$_2$O$_2$ in an attempt to elucidate the optimum particle morphology/support combination for the H$_2$O$_2$ reaction. The Au-core/Pd-shell nanoparticle variant was found to be the most effective catalyst of the three morphologies for the direct H$_2$O$_2$ reaction on both activated C and TiO$_2$ supports [11]. HAADF imaging can be used to clearly distinguish these three types of colloidal nanoparticle as shown in Figure 4. In fact, with some basic knowledge of the particle structure (i.e. cub-octahedral, decahedral or icosahedral) the composition of individual core-shell particles can also be estimated from images such as Figs. 4(b) and (c) by measuring the core diameter and shell thickness [11].

![Figure 4](image_url)

**Figure 4.** HAADF ($z$-contrast) images of sol-immobilized catalyst particles: (a) a random alloy AuPd nanoparticle; (b) a Au-core/Pd-shell nanoparticle, and (c) a Pd-core/Au-shell nanoparticle [11].

3.2 Interaction of Au-core/Pd-shell colloids with different supports

The effect of a 3h calcination treatment at 200°C on the Au-core/Pd-shell catalyst immobilized on C and TiO$_2$ supports was also analysed by STEM-HAADF imaging and an interesting support dependant phenomenon was observed [11]. The Au-core/Pd-shell nanoparticle structure was generally well preserved on the activated C support (Fig. 5(a)) as the particles were relatively non-wetting. However, the onset of sintering between neighbouring Au-core/Pd-shell particles was also commonly observed, suggesting that the nanoparticle/activated C interaction was not very strong. By way of contrast, the Au-core/Pd-shell particles on the TiO$_2$ support showed no strong evidence of sintering, but theirAu-
core/Pd-shell structure had been compromised (Figs. 5(b & c)). Presumably their better resistance to sintering is associated with the fact that the metal particles had formed extended flat interfaces with the TiO$_2$ support (Fig. 5(b)), which improved their overall adhesion and thermal stability. It is also fascinating to note that in those particles where a core-shell was still visible, it was not uncommon to find that the Au component had diffused towards, and attached itself preferentially to the TiO$_2$ support, while the Pd component was displaced outwards forming a hemispherical cap (Fig. 5(c)).

Figure 5. (a) HAADF image of a non-wetting Au-core/Pd-shell particle supported on activated C after 3h calcination at 200°C. An HREM image (b) and HAADF image (c) of a Au-core/Pd-shell particle strongly interacting with a TiO$_2$ support after 3h calcination at 200°C [11].

3.3 Thermally induced phase separation of Au-core/Pd-shell colloidal particles on TiO$_2$

The Au-Pd sols immobilized on TiO$_2$ that had an initial core-shell morphology responded very differently to a 400°C calcination treatment as compared to the random alloy Au-Pd sols on TiO$_2$. For the latter sample, all the metal particles remained as random AuPd alloys upon calcination. However, no core-shell structures were retained in either of the two core-shell variants on TiO$_2$ after calcination at 400°C. Instead, three distinct new particle morphologies were found to develop (see Fig. 6(a)), namely; (i) bright particles with extended 1-10 nm faint tails (arrowed blue), (Fig. 6(b)) (ii) isolated faint PdO$_x$ particles (arrowed red) (Fig 6(c)) and (iii) isolated bright Au particles (arrowed yellow) (Fig 6(d)). Localized XEDS measurements on those particles exhibiting extended tails (Fig. 6(b)), showed the faint tail features to be very Pd-rich, whereas the brighter end of the structure was Au-rich [11]. The tailed particles must therefore be a snapshot of ongoing phase separation of the Au and Pd components from the core-shell nanoparticles upon high temperature calcination.

It is indeed curious that Pd and Au components in the core-shell materials readily separate upon calcination at 400°C, whereas such behavior is not observed in the random alloy Au-Pd/TiO$_2$ variant. This suggests that an initial intimate mixing of the Au and Pd atoms in the nanoparticle (i.e. true alloy formation) imparts an initial degree of thermal stability as compared to the situation where one elemental component is simply coated upon the other in the core-shell bimetallic nanoparticles. For the core-shell particles, the Pd component (irrespective of whether it is the shell or the core material) prefers to phase separate to form PdO$_x$ rather than remain associated with the gold. Similarly the Au component prefers to form an extended interface with the TiO$_2$, rather than retaining its extensive AuPd interface. The combination of the desire of Pd to oxidize and the tendency of Au to wet the TiO$_2$ support seem to be the driving force for phase separation in the core-shell morphology particles upon calcination at 400°C.

In summary, the HAADF imaging technique has provided invaluable new (and often unexpected) information on the atomic structure, elemental distribution within particles, and compositional variations between Au-Pd particles. In addition, we have been able to compare their differing thermal stability and sintering behaviors, and to demonstrate that they have quite varying wetting interactions with activated carbon and TiO$_2$ supports.
Figure 6. (a) HAADF image of a Au-core/Pd-shell on TiO$_2$ catalyst after a 3h calcination at 400°C. Three distinct nanoparticle types were found to co-exist after this treatment, namely:- (b) phase separated, but connected, Au-PdO$_x$ particles, (c) PdO$_x$ nanoparticles and (d) Au nanoparticles [11].

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