Nano-metrology of platinum-ruthenium bimetallic catalysts and the cluster-to-crystal transformation

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Abstract. We have used atomic number, Z-contrast, imaging, performed using high-angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) to study bimetallic ruthenium-platinum nanoparticles anchored within silica nanopores, a system that shows great promise as a catalyst for single-step hydrogenation reactions. By exploiting the ultra-high spatial resolution obtained with aberration-corrected STEM, it is possible to study the internal structure of individual nanoparticles within the support, and to analyze their size distribution. Specimens examined before catalysis showed evidence for coalescence of the precursor units (12-atom clusters) during loading into the silica support. An indication of the stability of the system during catalysis is given by the similarity of pre- and post-catalysis size distributions, whilst the multimodal nature of each distribution suggests certain preferred (‘magic’) particle sizes. Some larger particles appear facetted, and exhibit image periodicity characteristic of crystalline structures.

1. Introduction

Bimetallic RuPt and RuPt nanoparticles, anchored along the inner walls of nanoporous silica supports, have been shown to provide excellent selectivity and activity for the hydrogenation of key organic compounds, including precursors in the more environmentally benign syntheses of polyester fibres and Nylon [1]. These nanoscale particles may exhibit high catalytic activity as a large fraction of the atoms in the nanoparticles are on the surface and consequently are available to participate in the heterogeneous catalysis of reactant species. Furthermore, catalytic activities and selectivities are highly dependent on electronic and structural characteristics, and these properties can differ significantly between bulk, surface, and nanoparticulate systems [2]. An analysis of the distribution of particle sizes, accompanied by characterisation of their atomic structures, is therefore an essential step in understanding and optimising the properties of these important materials.

An ideal substrate for the support of these bimetallic particles is MCM-41 mesoporous silica [3]. This material is produced via a templated synthesis route involving the calcination of
aluminosilicate gels in the presence of surfactants. The resulting anisotropic structure has regular hexagonal arrays of uniform channels, with high surface areas and a narrow pore size. In order to investigate the distribution of particles throughout this support, as well as determining the properties of the individual nanoparticles, any characterisation technique must provide near-atomic spatial resolution throughout the specimen volume. In this work, the results of high resolution scanning transmission electron microscopy (STEM) using the SuperSTEM [4] are presented, and the distribution and nature of supported Pt-Ru nanoparticles are discussed. Analysis of samples taken before and after catalysis gives important clues as to the processes occurring during catalysis. Furthermore, the distribution of particle sizes allows for the direct observation of fundamental trends in the structural properties of small particles, such as the transition between clusters and crystallographic structures, and suggests possible preferred ‘magic’ numbers of atoms.

2. Method

MCM-41 mesoporous silica supports loaded with Ru\textsubscript{p}Pt\textsubscript{q} particles [1] were obtained before and after catalysis; a sample containing Ru\textsubscript{p}Pt prior to catalysis was also studied. High spatial resolution STEM using a HAADF detector (STEM HAADF) was performed at the SuperSTEM facility. The SuperSTEM is a dedicated aberration corrected STEM, consisting of a VG HB 501 FEG STEM corrected to third order using a combination of dipole, quadrupole and octupole elements [4]. Collection of the incoherent HAADF signal, which is approximately proportional to the square of the atomic number, gives excellent contrast when imaging the metal particles within the lighter silica support [5]. For STEM observation, samples were suspended on holey carbon films.

Software scripts written in IDL [6] were developed for quantification of the particle distribution from STEM HAADF images. A semi-automatic data collection strategy involved manual identification of particles, integrated with the automatic calculation of particle projected areas and their total intensities. The Laplacian of Gaussian (LoG) filter was found to be effective in accurately detecting particles against the modulated, noisy background present in STEM images of interest, such as in figure 1. The LoG filter, which was applied as a single discrete 9x9 kernel in image space, involves the convolution of the edge-finding Laplacian with a Gaussian smoothing operator [7]. The kernel values were calculated for a Gaussian standard deviation, $\sigma$, of 1.4, with matrix values given by

$$\text{LoG}(x, y) = -\frac{1}{\pi\sigma^4} \left[1 - \frac{x^2 + y^2}{2\sigma^2}\right] \exp\left(-\frac{x^2 + y^2}{2\sigma^2}\right).$$

In order to estimate particle volume from projected area, particles were assumed to be spherical, and calculation of the number of atoms within a cluster was accomplished using the bulk density of the majority species, such that the volume occupied by a single Ru atom was assumed to be 13.6 Å$^3$.

![Figure 1](image1.png)

**Figure 1.** STEM-HAADF image of the Ru\textsubscript{p}Pt/MCM-41 system after catalysis. An inhomogeneous spatial distribution of particles and a range of nanoparticle sizes are in evidence.

![Figure 2](image2.png)

**Figure 2.** Frequency against estimated number of atoms for the Ru\textsubscript{p}Pt/MCM-41 system (a) before and (b) after catalysis. The overlay represents the best-fit Poisson distribution, constrained to have the same integrated volume as the original particle distribution.
3. Results and Discussion

3.1. General observations and sample stability
The MCM-41 support had a very narrow pore size distribution, with a mean pore diameter of 3 nm. However, the presence of particles within the pores is often accompanied by the expansion of these pores, causing a narrowing of adjacent pores. This may have been the cause of the inhomogeneous distribution of particles within the structure, whereby some regions contain a high density of particles while other regions are sparsely populated, as in figure 1. Alternatively, this inhomogeneous distribution may be due to defects created during the synthesis of the templated support.

The Ru$_{10}$Pt$_2$ nanoparticles within the MCM-41 support were observed to be stable during imaging, although some loose particles on the holey carbon film were observed to disperse atoms and disintegrate over several scans. More significantly, smaller particles in the Ru$_5$Pt sample were susceptible to disturbance by the electron beam, and successive raster scans could show significant displacements and even coalescence of smaller particles, which may have distorted the lower end of the particle size distribution observed for the Ru$_5$Pt sample.

3.2. Particle size distribution
Histograms of nanoparticle size were calculated using the software described in section 2, and the results of this analysis are presented for the Ru$_{10}$Pt$_2$ samples in figure 2. The characteristic properties of the distribution of particle sizes for each specimen are detailed in table 1. It was immediately clear from the mean particle sizes that many of the initial 6- and 12-atom clusters had coalesced; this coalescence may involve atomic rearrangement to form sintered particles, or the agglomeration of individual clusters into larger weakly-bound structures.

A comparison of the distribution of particle sizes before and after catalysis suggested that the particles are quite stable during catalysis. While there may have been some degree of particle interaction leading to a slight shift in the particle distribution (such as the peak shifting from ca. 40 to 60 atoms in figure 2), the mean particle size remained unchanged (within the accuracy of the observation scheme). This is a promising result for the stability and true catalytic behaviour of this anchored catalytic system. The main trend in the data is in good agreement with a Poisson best fit, which would be expected if the formation of larger particles from the initial clusters was related to a stochastic process. This distribution would arise from the random partitioning of clusters into interaction volumes corresponding to a characteristic travel distance. The partitioning might be influenced by the constrained geometry of the discrete pores in the MCM-41 silica support. Additionally, the characteristic distance would be dependent on processing time and temperature during synthesis.

There was a statistically significant deviation of certain particle sizes from the best-fit Poisson distribution, including the peaks at around 40 and 60 atoms seen in figures 2a and 2b. Such peaks may be due to the formation of stable ‘magic number’ clusters, which are energetically favourable and exist as strongly cohesively bonded structures [8]. Preferred sizes might also be expected at integer multiples of cluster units. For example, the peak at around 60 atoms could correspond to an agglomeration of five individual clusters to form a (Ru$_{10}$Pt$_2$)$_5$ species, or a sintered single particle. It is interesting to note that agglomeration could lead to meso-scale clusters, such as the structure observed in figure 3, which may correspond to a ‘cluster of clusters’.

| Sample | Number of particles analysed | Mean volume /nm$^3$ | Mean number of atoms per particle |
|--------|-------------------------------|--------------------|----------------------------------|
| Ru$_5$Pt | 215                           | 0.48               | 36 ± 6                           |
| Ru$_5$Pt$_1$ before catalysis | 212                           | 1.88               | 140 ± 12                         |
| Ru$_{10}$Pt$_2$ after catalysis | 364                           | 1.66               | 120 ± 11                         |
3.3. Cluster-to-crystal transition
The various sizes of the bimetallic particles observed in this work span the transition between non-crystallographic and crystalline structures. For gold atoms, Cleveland et al [9] have used atomistic models to identify three regimes in the size evolution of gold. A transition from molecular to ordered non-crystallographic structures occurred when the number of atoms approached 40. A further transition to crystallinity and bulk lattice structure was predicted at around 250 atoms. In the present work on bimetallic Ru-Pt, we find a threshold at around 200 atoms. For volumes substantially below this, crystallinity is not detected. For some particles approaching a size of 200 atoms, the onset of ordering is apparent, while for many of the larger nanoparticles, clear crystalline character is observed, as observed in figure 4.

Figure 3. (left) STEM HAADF high-magnification image of Ru$_{10}$Pt$_{2}$ cluster before catalysis. The spot indicated a] is an individual atom that has escaped from a cluster such as b], which is itself part of a larger cluster formed from original 12-atom precursors.

Figure 4. (right) Nanocrystallite originating from Ru$_{10}$Pt$_{2}$ precursors prior to catalysis. The crystal lattice fringes, clearly resolved as shown in the inset Fourier transform, correspond to a spacing of 2.1 Å, compared to the (002) Ru spacing of 2.14 Å. Facets of the crystal can also be observed.

4. Conclusions
Using high resolution HAADF STEM, it is possible to study the internal structure of individual bimetallic nanoparticles within a mesoporous silica support. The coalescence of precursor units during loading was found to generate a distribution of particle sizes. The mean particle size was equivalent to the coalescence of between 6 and 12 precursor units, depending on the identity of the precursor. An analysis of the particle size distribution also permitted the investigation of the effects of catalysis on nanoparticle stability. The particles were found to be stable, with only minor differences in the distribution between samples studied before or after catalysis. The existence of certain preferred nanoparticle sizes was suggested, and characteristics of different size structures agree with the regimes of the cluster-to-crystal transitions identified by atomistic models.

5. References
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