Site-specific characterisation of an auto catalyst using EPMA, FIB and TEM/STEM

D Ozkaya, M Matthews, S Spratt, G Goodlet, P Ash, and D Boyd
Johnson Matthey Technology Centre, Sonning Common, Reading RG4 9NH UK

Abstract. Auto-catalysts are used to cut down harmful emissions from car exhausts. The catalysts are usually made up of platinum, rhodium and palladium nanoparticles supported on alumina and/or ceria zirconia. Particle size investigations of aggregation of the noble metal particles form an important part of the analysis of these systems. The aggregation, localised to only a few areas, can be detected using electron probe micro analyser or scanning electron microscopy, using an elemental mapping using an X-ray wavelength or energy dispersive spectrometer. Although these techniques spot the enriched areas it then becomes very difficult to characterise particle sizes from this specific area. This problem is addressed by extracting focused ion beam samples from these areas. The samples are then characterised using a combination of bright field and high angle annular dark field imaging in the transmission electron microscope.

1. Introduction

Autocatalysts have been around since 1970’s and are one of the most effective ways to reduce smog and related pollution due to car exhausts [1]. The catalyst is usually coated on a ceramic monolith that has a multi-channel structure. The catalyst coating is usually made of platinum group metal (PGM) nanoparticles supported by alumina and/or ceria zirconia. The general mechanism by which the catalyst deactivates is usually through metal surface area reduction caused by particle size enlargement. It is crucial to have an idea of the metal particle sizes of various PGM nano-particles as well as the way they intermix as a function of time.

The way the catalysts samples are prepared for examination in a transmission electron microscope (TEM) has always been through either a powder based grinding and dusting routine or embedding and ultra-microtome sectioning [2] routine. Although in most cases these techniques are adequate, if a specific part of a catalyst needs to be analysed then an alternative method needs to be used. FIB has been increasingly used in a diverse set of samples in recent years including catalysts [3]. Here we show how a combined effort by three microscopy techniques yields information from specific areas in a catalyst sample. The sample was first analysed using an electron probe micro analyzer (EPMA), which has showed how uniform the elemental distributions are to a very high sensitivity through wavelength dispersive X-ray (WDS) spectroscopy. EPMA is able to detect and map very low concentrations of elements and is generally much better than an equivalent energy dispersive X-ray spectrometer (EDX) on an SEM. The areas with high concentrations of PGM were marked so that these areas could be used to extract TEM samples to observe the particle size and intermixing.

Following the FIB stage, the sample was examined and characterized using TEM/STEM bright field microscopy and annular dark field microscopy with EDX line scan analysis.
2. Experiment and results.

The monolith sample was chosen specifically due to cracks in its washcoat, making it easier to relocate the areas identified for FIB sample extraction. It was embedded in resin, polished and carbon coated to be analysed in a CAMECA SX50 EPMA with the main aim of getting high sensitivity elemental maps. The resulting backscattered electron image and Pd map are shown in Figure 1. Pt and Rh elemental distributions were very uniform. Only Pd revealed higher concentration “hot spots”, indicating that Pd nano-particles are likely to be enlarged in that specific area.

![Figure 1](image)

Figure 1 Backscattered image of the polished monolith crossover point (a), and Pd map (b). Circled area indicates the area with highest Pd counts. This is where the FIB section was cut.

The circled area in the Pd map is the highest concentration area of Pd, where the focused ion beam (FIB) section was decided to be extracted. This area is also quite distinct due to the cracks in the washcoat. These features were used to recognize the area once the sample was in the FIB system. A 200nm conductive coating was deposited at the sample surface to eliminate charging from gallium ions during milling. The FIB sample was prepared using the “lift out” technique. The area where the sample was extracted is shown in figure 2a, with a larger view of the area mid-way through FIB process (figure 2b) before the final thinning.

The extracted membrane mounted on a holey carbon film can be seen in figure 3. The sample is very porous as would be expected from a washcoat type structure. Only a limited part of the Pt protection strap is left on the sample due to some parts being broken whilst handling.

The sample was examined in the Tecnai F20 field emission gun transmission electron microscope operating at 200KV. Images were acquired both in the TEM and STEM modes, with the EDX analysis being carried out in the STEM mode.

The Bright field image of a typical area of the section can be seen figure 4. The brighter area represents the alumina rich phase, where most of the PGM particles are visible, whilst the dark area is ceria zirconia rich. There are two different sets of particle sizes visible in the bright alumina rich area. The two largest, at the center of the image are around 100nm size, whereas the others are around 8-20nm. On other parts of the sample particles in the 20-30nm ranges were seen. The required particle size for this type of catalyst is in the region of 8-10nm, so some particle enlargement has taken place.
EDX analysis on the particles showed that these were Pd rich with some Rh present in them. The particles in the ceria phase are not easy to distinguish by conventional imaging. This is due to similarity in the scattering potentials of the PGM particles to the ceria zirconia for most of the diffraction conditions. Usually elemental maps are required to be able spot these particles.

Figure 2 Electron image of the area of the sample circled in fig1, showing the location of the FIB etched pit (a), and enlarged area showing the membrane just before the final thinning and cutting (b).

Figure 3 Low magnification image of the membrane lifted out of the FIB.

Figure 4 Bright field image showing different regions and large and small Pd rich particles (arrowed).

Some 20-30nm sized particles can be seen in the dark field image in figure 5a. Compositional data was obtained from these particles through acquisition of 30 EDX spectra from a line across the particles. The square area marked on the image (5a) represents the area used for drift correction. Intensity values at the individual points from the high angle annular detector are shown plotted in figure 5c. The Pd line scan confirms that these particles are Pd rich (figure 5d). Rh and Pt profiles are
also presented together with a background profile to show that particles hardly contain Pt or Rh. The presence of such large Pd particles explains the Pd rich areas identified in the EPMA elemental maps.

Figure 5 High angle annular dark field image showing Pd rich particles (a) with the EDX spectrum at a point marked on the line (b), the live HAADF intensity profile (c), and the elemental distributions along the line marked in the image (d-f). The dark lines in the elemental profiles and the mark on the line at the image match to the exact point where the spectrum (b) was taken. The shaded portions of the spectrum show the positions of the energy windows used to generate the line profiles.

3. Conclusion
An approach to catalyst characterization on two different length scales has been demonstrated by utilizing the site-specific sample extraction ability of FIB. Pd rich areas identified in the EPMA showed corresponding Pd rich large particles in the TEM analysis of exactly the same area.

Acknowledgements
We would like to thank Dr S Golunski from Johnson Matthey gas phase analysis group for providing the sample and Dr Chengge Jiao from FEI Company in Bristol for FIB sample preparation.

References
[1] Twigg M V 2003 Platinum Metals Review 47 (4) 157-162
[2] Blom DA, Dunlap JR, Nolan T A and Allard LF J. of Electrochem Soc. 2003 150 (4) 414-418
[3] Haswell R, McComb DW, Smith W 2003 J.of Microscopy-Oxford 211 161 - 166