Structural intricacies of unsupported intermetallic Ga-Pd catalyst nanoparticles studied by high resolution and three-dimensional electron microscopy

R Leary1, Z Saghi2, M Armbrüster3, G Wowsnick3, R Schlögl4, JM Thomas1 and PA Midgley1

1. Department of Materials Science, University of Cambridge, Pembroke Street, Cambridge, CB2 3QZ, UK.
2. BIONAND, Parque Tecnologico de Andalucía, c/Severo Ochoa, 35, 29590 Campanillas, Malaga, Spain.
3. Max-Planck-Institut für Chemische Physik fester Stoffe, Nöthnitzer Strasse 40, 01187 Dresden, Germany.
4. Department of Inorganic Chemistry, Fritz Haber Institute of the Max Planck Society, Faradayweg 4-6, 14195 Berlin, Germany.

Email: rkl26@cam.ac.uk
Keywords: selective hydrogenation catalysts, electron tomography, five-fold twinning.

Much promising information has emerged recently regarding Ga-Pd intermetallic compounds as highly stable and active selective hydrogenation catalysts. Fundamental research has shown that the efficacy of this new class of catalyst originates from covalent interactions in their well-ordered crystal structures [1]. These stabilise isolated Pd sites on the catalyst surface and strongly modify the electronic structure in comparison to elemental Pd. While many of the early studies used bulk or powdered materials, the highest catalytic activity has recently been achieved using nanoparticulate systems. The synthesis and characterisation of well-defined Ga-Pd nanoparticles is therefore an important goal in the pursuit of catalysts that are applicable industrially. Considerable progress has already been made in the development of preparatory routes [2,3], opening the way for an in-depth analysis of the active solid catalyst itself. We have undertaken studies of unsupported single-phase Ga-Pd nanoparticles using electron-optical methods, with particular interest in the so-called ‘nanometric’ properties of the nanoparticles; their distribution in size and shape, and characteristic morphologies, as well as the crystallographic factors underpinning their nanostructure.

To attain 3D morphological analysis of statistically relevant numbers of the polycrystalline nanoparticles (>1000), we have used scanning transmission electron microscope (STEM) electron tomography (ET) employing the high-angle annular dark-field (HAADF) imaging mode. Semi-automated image processing procedures have been developed to achieve segmentation of the densely-populated tomograms, facilitating extraction of 3D nanometrological information, such as measures pertaining to the size, shape and agglomeration state of the nanoparticles (Figure 1). The fidelity of the tomographic reconstruction and quantitative analysis is limited primarily by the finite and limited angular sampling in the ET data acquisition, but should be markedly improved with the development of advanced ET reconstruction techniques [4].

High resolution transmission electron microscopy and aberration-corrected (AC) STEM have provided direct verification of single-phase identity, and AC-STEM in particular has been used to enable atomically resolved analysis of the smaller (<5 nm) nanoparticles. These investigations have raised several aspects worthy of consideration, two examples of which are shown in Figure 2. The nanoparticle in Figure 2b (phase GaPd₂) shows terminating planes that have also been observed in abundance in our studies on carbon nanotube (CNT) supported nanoparticulate GaPd₂ [3]. This is despite the unsupported and CNT-supported GaPd₂ nanoparticles being produced by very different synthesis routes. Also consistent with the studies on CNT-GaPd₂, Figure 2c shows the occurrence of five-fold twinning in small GaPd₂ nanoparticles. In this case, the nanoparticle exhibits a structure indicative of a distorted decahedron. The observation of five-fold twinning in GaPd₂ nanoparticles presents an intriguing crystallographic puzzle regarding the mechanisms by which 3D space-filling is achieved in such morphologies. The GaPd₂ phase is usually considered to have an orthorhombic (Co₂Si-type) crystal structure, but it can also be interpreted in terms of a distorted face-centred-cubic (fcc) lattice. It is well known that the packing of tetrahedral sub-units of fcc structure around a five-fold axis results in a solid angle deficiency, meaning that some form of distortion is required to fill space. Given the close relationship between an fcc lattice and the orthorhombic GaPd₂ structure, it may be possible to apply many existing theories for fcc systems (which are still open to debate) in
the interpretation of the multiply twinned small nanoparticle structures formed in the case of GaPd$_2$; although consideration of subtly differing factors may also yield new insights.

These results show how electron microscopical characterisation of Ga-Pd nanoparticle catalysts can play a key role in an incremental knowledge-based development, where the aim is to obtain understanding from the bottom-up and thorough characterisation at each stage, leading to close control of nanostructure. This should pave the way towards high performance nanoparticle systems for applications in catalysis and more, including those with potential for industrial application [5].

References

[5] ZS and PAM acknowledge financial support from the Framework 6 program of the European Union under a contract for an Integrated Infrastructure Initiative, Reference 026019 ESTEEM. PAM acknowledges financial support from the ERC under grant number 291522 3DIMAGE.

![Figure 1](image1.png)

**Figure 1.** (a) HAADF-STEM image of a cluster of GaPd$_2$ nanoparticles from an ET tilt-series. (b) 3D voxel projection visualisation of the segmented 3D reconstruction in which each nanoparticle or agglomerate has been given a colour that differs from those of its nearest neighbours. (c) Statistical distribution and size filtered tomograms according to the equivalent diameter, d, of the nanoparticles and agglomerates, based on the segmented data.

![Figure 2](image2.png)

**Figure 2.** (a) AC-STEM image of GaPd$_2$ nanoparticles in the small (<5 nm) size range. In (b) the matching simulated diffraction pattern for the GaPd$_2$ phase is overlaid on the left of the local Fourier transform (FT) taken from the nanoparticle in region (b). (bii) Is a contrast adjusted image of the area in (b), where the terminating planes and approximate overall shape of the nanoparticle are indicated by solid white lines. (c) Shows a nanoparticle exhibiting five-fold twinning. Arrowheads mark the approximate positions of the boundaries between each twinned region or ‘sub-unit.’ (ci) Shows the FT for the entire nanoparticle, while FTs from each region labelled (1)-(5) in (c) are shown in (cii).