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Nano-Sized Intermetallics: Unraveling Intricacies of $GaPd_2$ Catalysts Using Aberration-Corrected STEM

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The ability to perform selective hydrogenation is of considerable importance in many industrially-relevant applications such as polyethylene production. Recently, a promising new class of selective hydrogenation catalyst has emerged based on intermetallic Ga-Pd compounds [1]. The well-ordered crystal structures and covalent bonding in these intermetallics can result in effective active site isolation and a strong modification of the electronic structure, yielding superior performance to the conventional monometallic Pd or Ag-Pd alloy catalysts. With the aim of achieving systems that may be applicable industrially, attention is now being given to the development of high-performance nanoparticulate Ga-Pd systems. In this work we have exploited the specific advantages offered by aberration-corrected scanning transmission electron microscopy (AC-STEM) to elucidate the nature of unsupported Ga-Pd catalysts in nanoparticulate form, $GaPd_2$ in particular [2].

A key result of the AC-STEM analysis is a direct visualization of the crystal structure of the intermetallic compound $GaPd_2$. The Ga-Pd phase diagram contains a number of possible phases, many of which have similar crystal structures, making unambiguous verification of the phase in nanoparticulate form challenging. Through a spatially resolved analysis however, and using the chemically sensitive annular dark-field (ADF) imaging mode in particular, it is possible to identify individual nanoparticles oriented such that the electron beam is parallel to particular crystal zone axes where the image of the structure is unique to the $GaPd_2$ phase. A prime example is the [010] $GaPd_2$ zone axis, shown in Figure 1. At the [010] orientation in particular, it can be seen that there is a close relationship of the $GaPd_2$ structure to that of a face-centered cubic (fcc) lattice, and this is true of other Ga-Pd phases, but the observed chemical ordering and 'distortions' from a perfect fcc lattice are distinct to $GaPd_2$.

Conversely, the ADF imaging also revealed deviations from the 'bulk' intermetallic structure, particularly at the surface/near-surface regions. Many nanoparticles were found to be decorated by a patchy disordered over-layer (Figure 2). Electron energy-loss spectrum imaging identified the over-layer as oxidic in nature, and overall the AC-STEM analysis corroborates the notion [3] that a partial decomposition of the intermetallic surface may occur following exposure to ambient (oxidizing) conditions, resulting in Pd rich regions and partial coverage by Ga_xO_y. The directly interpretable ADF imaging also rendered visible more subtle crystallographic deviations from the 'bulk' intermetallic structure. The nanoparticle in Figure 2, for example, is viewed close to the [120] $GaPd_2$ zone axis, where the distinct characteristic of the intermetallic structure is the undulating (or 'wavy') nature of the lattice planes, but in the near-surface regions the lattice planes are seen to 'relax' to a straighter form - potentially towards an 'undistorted' fcc-like arrangement. Focusing on the smaller (sub-10 nm) nanoparticles, the ADF imaging revealed a variety of morphologies and nanocrystalline defects

including well-faceted single crystalline, single twinned and, notably, five-fold twinned nanoparticles. It is well-known that five-fold twinned nanoparticles are inherently strained and there must therefore be some deviation from the 'bulk' crystalline structure. The extent to which the intermetallic $GaPd_2$ structure may be maintained in such morphologies and the precise nature of the resultant catalytically active sites is an important aspect to be addressed *en route* to well-defined Ga-Pd nanocatalysts.

References

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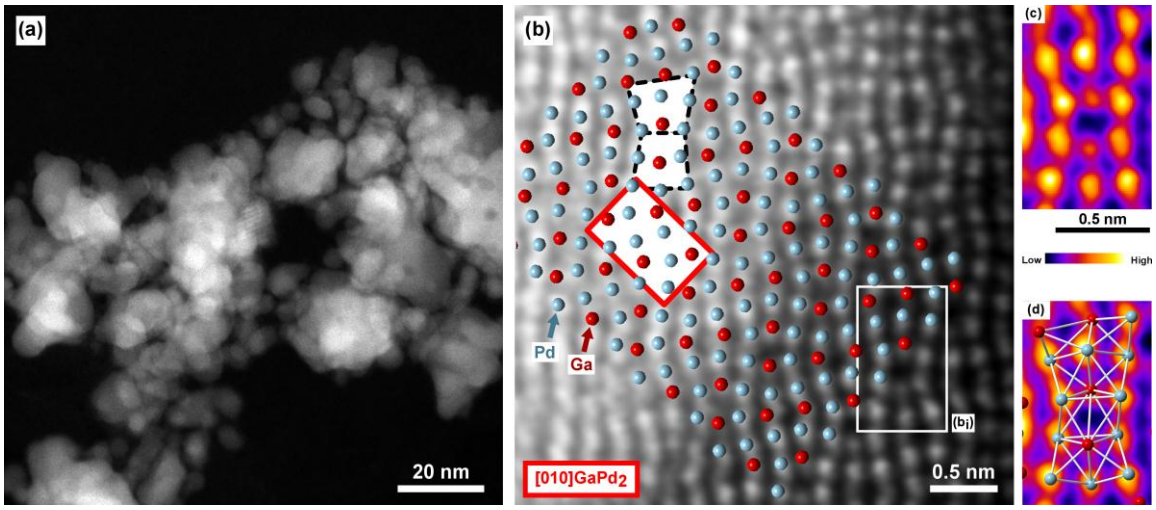
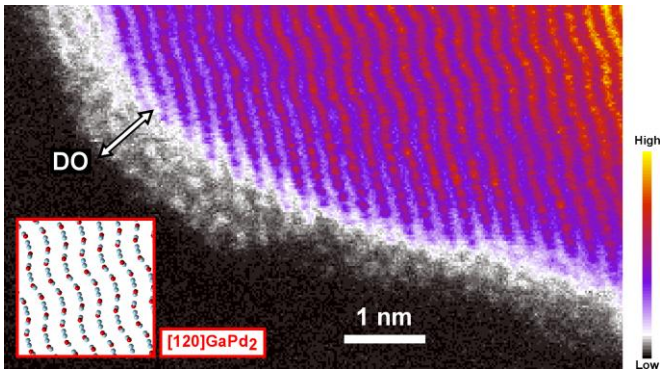


Figure 1. (a) Low magnification ADF image of the Ga-Pd nanoparticles. (b-d) Identification of nanoparticulate $GaPd_2$ via the [010] zone axis. (b) Atomically resolved ADF image (low-pass filtered) on which the structure of $GaPd_2$ in [010] projection is overlaid. The orthorhombic unit cell is outlined in red, and two 'fcc-like' units by dashed black lines. (c) A selected region (b_i) from (b) over which the thickness of the nanoparticle is sufficiently constant to enable a relative comparison of the intensities of the atomic columns in the image. A portion of the $GaPd_2$ structure in [010] projection is overlaid in (d), confirming that the lower and higher intensity atomic columns in the image correspond to those in the [010] projection of $GaPd_2$ that exclusively contain Ga or Pd respectively.

Figure 2. ADF image of a nanoparticle that is consistent with $GaPd_2$ viewed close to the [120] zone axis. The structure of $GaPd_2$ in [120] projection is shown inset, where the lattice planes form an undulating ('wavy') arrangement. In the ADF image, the lattice planes can be seen to 'relax' to a straighter form towards the surface of the nanoparticle. The disordered over-layer on the surface of the nanoparticle is rendered in white by the false color map and is labeled DO.



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