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Electron holography reveals the internal structure of palladium nano-particles

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Phase images of palladium particles 5–15 nm in diameter were reconstructed from electron holograms acquired using the coherent beam of a field emission transmission electron microscope. The Pd particles were supported on amorphous silica microspheres, 0.2 μm in diameter. A central contrast feature, suggestive of an internal void, was visible on most of the Pd particles. The phase profiles obtained from the holograms matched computed phase profiles confirming the existence of an internal void in these nano-particles. This is the first observation where internal morphology at the nano-scale has been unambiguously determined. While the observed voids are similar in scale to those occurring in recently reported hollow nanometre-sized particles, such as graphite polyhedra [9, 10], this represents the first report of such voids in metallic particles that are single crystals.

1. Introduction

Studying the nano-scale structure of materials remains a daunting task despite continuing advances in instrumental techniques. The problem is compounded further when the object of study is finely dispersed within the tortuous pore structure of a high surface area matrix. Such is the case with nanometre-sized metal particles in heterogeneous catalysts, which are used for controlling emissions from automobile exhausts or in industrial processes such as the refining of crude oil to produce gasoline. The morphology of these nanoparticles is of great interest to catalytic chemists since it affects the activity and selectivity for a class of reactions known as structure-sensitive reactions [1]. The behaviour of finely divided metal particles has continued to fascinate researchers since the original work of Faraday [2].

While high resolution transmission electron microscopy (TEM) techniques have made it possible to image nanometre-sized particles at atomic resolution [3], the oxide support of a metal catalyst often obscures details of the morphology of such particles [4]. One way to circumvent the problem of studying finely dispersed supported metal particles is to use a model support of simple geometry such as silica microspheres. This model system permits metal particles deposited on the surface to be observed with the metal/support interface edge-on, so that information on particle morphologies and interface structures can be obtained [5]. Extracting details of structure and morphology on an atomic scale, however, is still a formidable challenge. Conventional high resolution TEM imaging methods permit the image intensity to be recorded, but the phase information in the complex image wave is lost. However, it is the phase information which is sensitive at the atomic scale to changes in specimen thickness and composition (i.e. as related to mean inner potential changes [6–8]), and thus analysis of the phase image can yield important information on morphological details down to the nanometre level. This phase information can be retrieved from a TEM image using the emerging technique of electron holography. Electron holograms are made possible by use of the coherent beam in the new generation of high resolution field emission gun TEMs.

In this paper it is shown how the internal structure of catalytic Pd particles, 5–15 nm in diameter, were unambiguously determined using electron holography.

2. Experimental procedure

Palladium was deposited on a model catalyst support consisting of 0.2 μm amorphous silica microspheres. The Pd particles formed after oxidation of the precursor in air, followed by hydrogen reduction, were roughly spherical, often faceted, single crystals (or "nanocrystals"), as determined by high-resolution electron microscopy. Most nanocrystals exhibit a central contrast feature, also often faceted, that typically extends over 1/3 the diameter of the particle. Phase images of these particles were reconstructed from electron holograms. The phase profiles confirmed that the nanocrystals had internal voids. The

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voids were comparable in scale to those occurring in recently described hollow nanometre-sized particles, such as graphite polyhedra [9, 10]. However, to the best of our knowledge, this represents the first report of nano-scale voids in metallic single crystal particles. The results show that electron holography can provide significant advances in understanding the nano-scale structure of materials.

The method of production of the amorphous silica microsphere support material has been described in detail in [11]. Pd was deposited on the silica surfaces by non-aqueous impregnation of the silica with Pd acetyl acetonate. Treatment temperature was 300 °C for oxidation in air and for reduction in H_2. The resulting powder was deposited on TEM support grids by simply dipping a grid in the powder and observing particle aggregates clinging to the grid bars. High resolution TEM images were recorded at 400 kV on a JEOL 4000EX, and electron holography and high spatial resolution energy dispersive spectroscopy (EDS) results were obtained at 200 kV using a Hitachi HF-2000 cold field emission TEM.

Fig. 1 is a high resolution TEM image of typical SiO_2-supported Pd nanocrystals. The nanocrystals were analysed by EDS techniques using the 1 nm probe of the field emission TEM, and no other elements besides Pd were found to be present. Most nanocrystals showed a distinctive central feature, suggesting the presence of a void. This structure was not affected by the electron beam at either 200 or 400 kV in the microscopes used. At high magnifications, the nanocrystals always showed a single crystal structure, with crystal lattice planes extending through the central contrast feature as seen in Fig. 1. This image also showed that the central contrast feature could have facets which were parallel to the crystal lattice. Such images represent all the information which can be obtained using conventional TEM imaging methods. Additional information on the particle morphology is provided by electron holography.

The geometry for holography using the coherent electron beam of a field emission TEM has been described in detail [12]. The electron wave that passes through the object is allowed to interfere with a reference wave that does not pass through the object. The superposition of these waves creates interference fringes in the image which carry information about the image phase. Fig. 2 shows the hologram of a typical Pd particle. From this hologram, the image phase was reconstructed, shown in Fig. 3 (see [13] for details of reconstruction methods).

3. Discussion

The phase change, $\Delta\phi$, of the electron wave caused by an object can be described in analogy to wave optics [6, 7] as follows:

$$\Delta\phi = t(n - 1)\,2\pi/\lambda + c$$

where n describes the refractive index of the object, t the local specimen thickness, λ the wavelength of the electrons and c is a constant related to the experimental set-up. Using the definition for the refractive index, it was also possible to express the phase change in terms of the mean inner potential of the particle

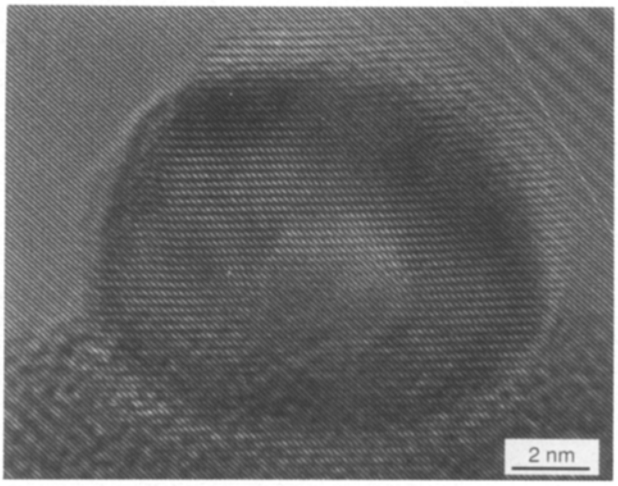

Figure 2 Hologram of one palladium nanocrystal. The modulations of the hologram fringes carry information on the morphology of the nanocrystal.

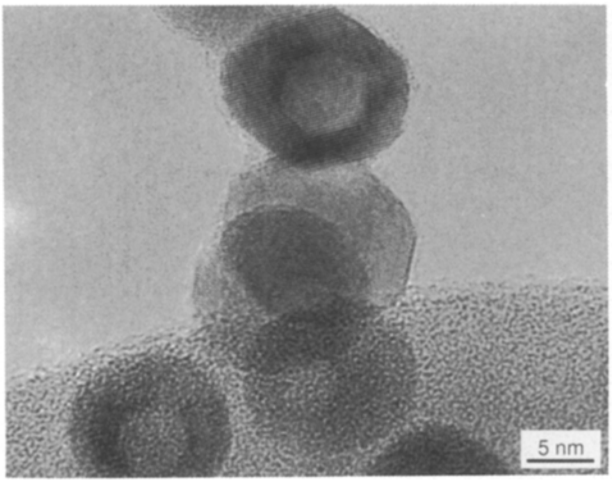

Figure 1 Palladium nanocrystals dispersed over amorphous silicon microspheres. The nanocrystals show a central contrast feature suggesting an internal void.

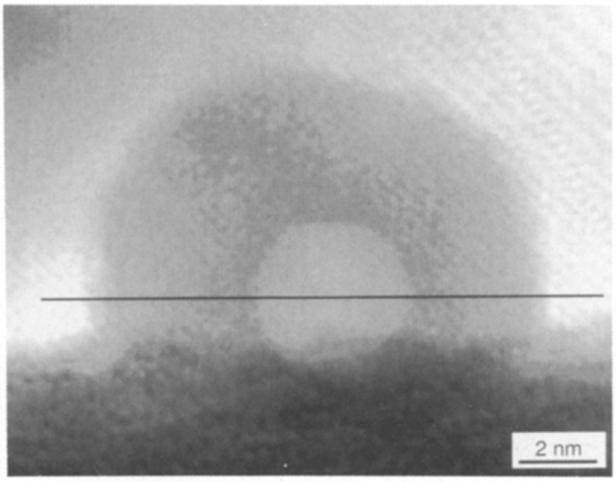

Figure 3 The phase image as reconstructed from Fig. 2. A phase profile across the nanocrystal yielded quantitative information on its thickness variation.

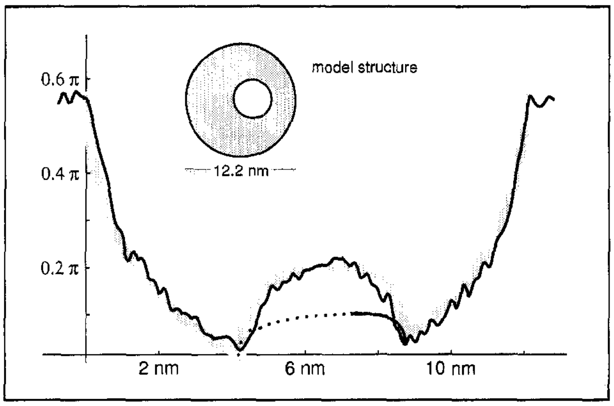

Figure 4 A phase profile of Fig. 3 (solid line) compared with simulated phase profiles over a model structure with both an empty void (grey line) and a void filled with, for example, a material having a mean inner potential different from Pd (dotted line) confirmed that the nanocrystals were hollow.

[6–8]. A comparison of the experimental profile with a simulated profile is shown in Fig. 4. The simulated profile assumed a spherical void of appropriate dimension and position, obtained from the experimental image. Also shown is a profile computed assuming that the void was filled with an amorphous material, showing the mismatch with the experimental results. The fact that no nanocrystals were observed having the central contrast feature intersecting the surface, coupled with the excellent match of simulated and experimental phase profiles, confirmed that the nanocrystals were hollow.

4. Conclusions

The electron holograms provide compelling evidence of nanometre-sized voids in these Pd particles. The voids were probably caused by the transformation of the Pd (acac) precursor into an oxide and its conversion at low temperature into a Pd hydride which eventually transformed to Pd metal at higher temperatures. Further work is underway to pinpoint the specific conditions responsible for void formation and its consequences on catalytic activity.

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