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Crystal size and shape analysis of Pt nanoparticles in two and three dimensions

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Abstract. The majority of industrial catalysts are high-surface-area solids, onto which an active component is dispersed in the form of nanoparticles that have sizes of between 1 and 20 nm. In an industrial environment, the crystal size distributions of such particles are conventionally measured by using either bright-field transmission electron microscope (TEM) images or X-ray diffraction. However, the analysis of particle sizes and shapes from two-dimensional bright-field TEM images is affected by variations in image contrast between adjacent particles, by the difficulty of distinguishing the particles from their matrix, and by overlap between particles when they are imaged in projection. High-angle annular dark-field (HAADF) electron tomography provides a convenient technique for overcoming many of these problems, by allowing the three-dimensional shapes and sizes of high atomic number nanoparticles that are supported on a low atomic number support to be recorded. Here, we discuss the three-dimensional analysis of particle sizes and shapes from such tomographic data, and we assess whether such measurements provide different information from that obtained using two-dimensional TEM images and X-ray diffraction measurements.

1. Introduction

Crystal nucleation and growth processes give rise to a variety of possible crystal size distributions (CSDs) and particle shapes. CSD measurements of particle sizes are performed routinely in industrial environments with a requirement for statistically meaningful data. Two techniques are commonly used to provide this information. Bright-field transmission electron microscopy (TEM) is used to study small areas of a specimen, and to provide local information about individual particles [1,2,3]. In contrast, X-ray diffraction (XRD) yields information averaged over large numbers of particles. Here, an approach for measuring CSDs with improved accuracy when using TEM is presented. The use of high-angular annular dark field (HAADF) electron tomography, a technique that allows a sample to be imaged in three dimensions, to obtain similar information is discussed. CSD measurements performed using small-angle X-ray scattering (SAXS) and TEM are then presented. It is suggested that low-angle annular dark field tomography can be used to determine the degree of crystallinity of individual nanoparticles, which may be responsible for the differences observed between CSD measurements performed using SAXS and TEM. Experimental data in this work are presented from platinum nanoparticles on graphitic carbon, with an average size of 5 nm.

2. Local thresholding of TEM images

It is often challenging to measure the sizes of small particles from greyscale TEM images. Similar particles can have very different intensities as a result of diffraction contrast, while the carbon support has a thickness that changes locally, and variable contrast that affects the mean intensity values of the particles. Conventionally, a greyscale image is converted into a binary image, in which pixels with a greyscale value higher than a chosen threshold are separated from those with values below the threshold. This transformation is applied to the whole picture, using a single threshold value. This procedure rarely works across an entire image. Here, we propose using an adaptative threshold that is automatically adjusted in different parts of an image. Figure 1 shows a comparison between the two approaches.

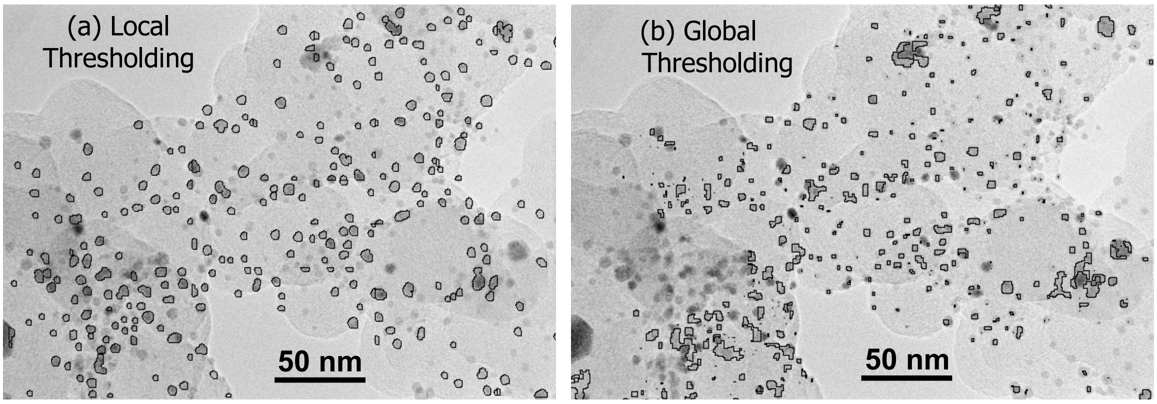

Figure 1. (a) local and (b) global thresholding applied to a bright-field image of a distribution of Pt particles on a carbon support.

3. Tomography for the determination of crystal sizes and positions

The uncertainty of using two-dimensional images of three-dimensional crystals to infer their shapes can make conventional TEM, even with subsequent image processing, inconclusive. The application of HAADF tomography to the measurement of CSDs may overcome the limitations of conventional TEM images [4]. Figure 2 shows a three-dimensional HAADF reconstruction of a distribution of PtCr nanoparticles, obtained at 200 kV using a Tecnai F20 TEM equipped with a field emission gun (FEG). Images were acquired over a sample tilt range of –68 to +68 degrees in steps of 2 degrees, and a magnification of 640 kx. Quantitative measurements of the volumes and spatial distributions of the particles in three dimensions are possible from such datasets. Alternatively, the reconstructed information can be reprojected in any direction, and the resulting CSDs measured conventionally. Figure 3 shows plots of CSD measurements performed on two projections of the particles shown in Figure 2. The graphs illustrate the danger of interpreting CSD measurements performed on small datasets consisting of

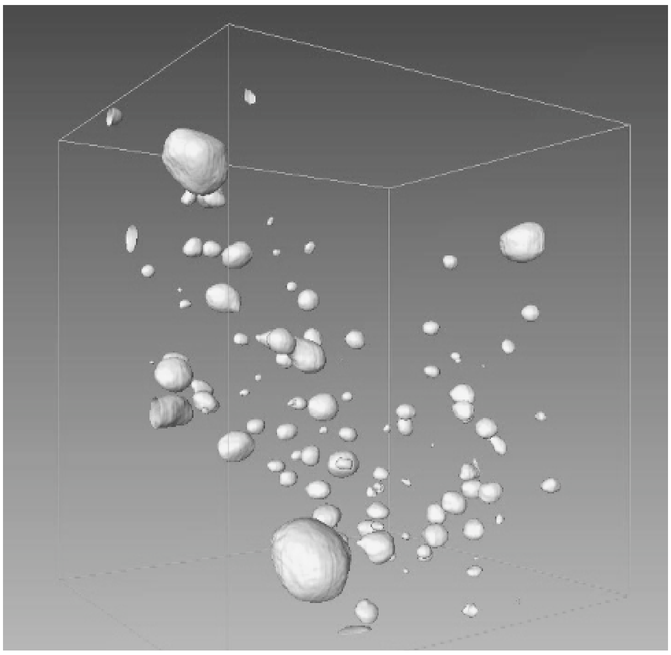

Figure 2. HAADF tomographic reconstruction of a distribution of PtCr nanoparticles.

two-dimensional projections of three-dimensional particles. In Figure 3 mean particle sizes differs by 21%.

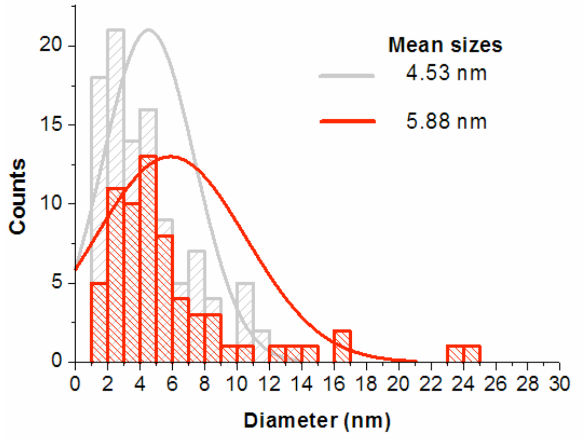

Figure 3. Histograms and fitted curves fitting for two different CSD measurements corresponding to two different projections of the Pt particles shown in Figure 2.

4. CSD measurement by SAXS and TEM

CSD measurements from TEM images are usually performed on at least 1000 particles. However, larger particles are often deliberately omitted from the measurements. SAXS, instead, provides information indiscriminately from much larger number of particles. Figure 4 shows CSD measurements obtained from two different samples, and illustrates the differences that arise when using different techniques.

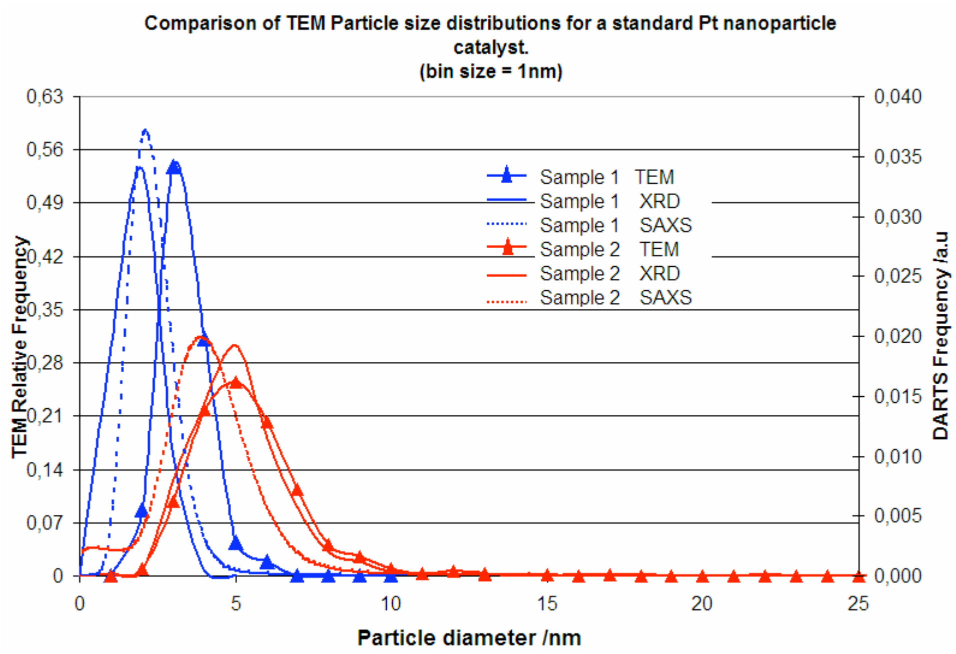

Figure 4. CSD measurements performed on two different Pt samples. Each sample was analysed using TEM with local thresholding, XRD and SAXS.

In addition, SAXS and XRD reflect the **average** size of a scattering element, which may be smaller than the crystal that contains it. Figure 5, shows low-angle annular dark field images that illustrate qualitatively the regions within individual Pt particles that diffract differently, and which would appear to be separate crystals when measured using XRD or SAXS.

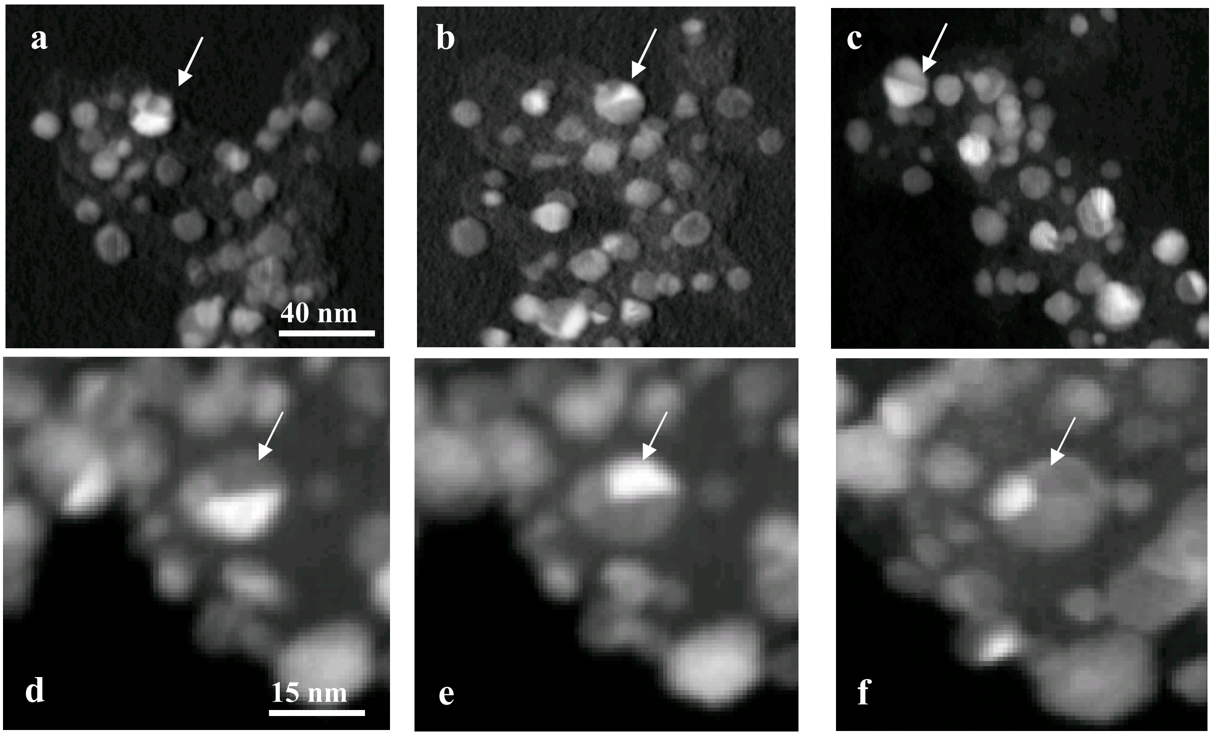

Figure 5. (a)-(c) Low-angle annular dar-field images of three frames taken from an ultra-high-tilt series of a distribution of Pt particles of average size 5 nm, showing crystalline domains in individual particles (arrowed). (d)-(f) Similar crystal domains in a 6 nm Pt nanoparticle.

5. Conclusions

An automated approach for particle detection from TEM images using local thresholding has been presented. This approach is based on adaptative thresholding. The application of HAADF electron tomography to crystal size distribution measurement of nanocatalysts supported in a low atomic number matrix has been illustrated. The use of a low-angle annular dark-field detector to examine the crystallinity of Pt nanoparticles has been used to highlight a possible source of discrepancy between crystal size measurements made from TEM images and similar measurements made using small-angle X-ray scattering and X-ray diffraction.

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