Aberration Corrected (S)TEM and Nano Beam Diffraction (NBD) of Pt and Pd on Al$_2$O$_3$ Catalysts

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Abstract. Nano-beam electron diffraction (NBD) has been used in addition to HAADF-STEM and HRTEM analyses of Pd-Al$_2$O$_3$ and Pt-Al$_2$O$_3$ catalysts. NBD and its STEM nanodiffraction counterpart are not widely used for nanoparticle catalysts but the more common SAD method does not offer the same level of structural information for individual ultrafine (<10 nm) nanoparticles, even with aberration correction. Here, NBD has been applied to commercially relevant catalysts for added information and to investigate defect structures in sintered particles.

1. Introduction
Pt nanoparticles loaded onto $\gamma$-Al$_2$O$_3$ are popular catalytic systems used in automobile emission treatment catalysts [1,2] and various other industrial processes [3,4]. Although there have been many studies of the Pt-Al$_2$O$_3$ system, including in-situ and ex-situ HRTEM, there seem to be relatively few that concentrate on the nanostructures of the individual nanoparticles. This may be related to the complex structure of $\gamma$-Al$_2$O$_3$ which can often coexist with $\delta$, $\theta$ [5,6] and $\gamma'$ phases [7]. HAADF-STEM is the ideal choice for the study of small clusters and atomically dispersed Pt because it’s $Z$ (atomic number) image contrast is ideally suited to the system [8,9]. However, the defective spinel structure of Al$_2$O$_3$ and the weakly scattering nature of Al and O often result in images of commercial Al$_2$O$_3$ being poorly resolved. With HRTEM, it is possible to gather structural information from nanoparticles on Al$_2$O$_3$ but clusters and atomically dispersed metal remains elusive in the image.

Here, we apply nano-beam diffraction (NBD) in addition to HRTEM and HAADF-STEM to Pd and Pt-Al$_2$O$_3$ systems. To investigate potential metal-support interactions under an O$_2$ atmosphere, we also examine catalysts which have been treated at elevated temperatures in air. We found that on these catalysts there is no fixed epitaxy between the support and nanoparticles. NBD also provided insights into structural intricacies in nanoparticles containing defects which would be unlikely to be detectable in a normal SAD pattern.

2. Technique
The Pt-Al$_2$O$_3$ and Pd-Al$_2$O$_3$ catalysts were provided by Johnson Matthey. A powder and pellet variant of the Pt-Al$_2$O$_3$ catalyst was provided in addition to a Pd-Al$_2$O$_3$ powder catalyst.
Figure 1. TEM images with corresponding SAD diffraction patterns of the labelled untreated fresh catalysts. The nanoparticles on the Pt-Al₂O₃ pellet specimen can be barely seen and the Al₂O₃ crystals are much larger than in the powder catalysts. The diffraction pattern in (a) is δ-Al₂O₃ [1 1 0] whereas the other two SAD patterns are dominated by the γ-Al₂O₃ {4 0 0} and {4 4 0} rings.

Portions of the fresh catalyst powders and pellets were heat treated in a furnace (held in a Al₂O₃ crucible) in air at 250 °C and 500 °C for 3 h and 15 h in addition to 750 °C for 3h prior to (S)TEM specimen preparation. (S)TEM specimens were prepared by suspending some of the powder in ethanol. The pellets required crushing. The powder suspensions were deposited using 2.5 µl drops onto a holey-C film suspended by a Cu grid.

The microscope used for these studies was a double aberration corrected JEOL 2200FS. Aberrations were corrected using a reference sample (Au nanoparticles on 2.5 nm amorphous C) in HRTEM mode. Nano-beam diffraction (NBD) mode was used for acquiring diffraction patterns from individual nanoparticles. A beam diameter of 2 nm was used with the smallest condenser aperture. The resulting diffraction patterns were indexed like a SAD pattern.

3. Results and Discussion

Figure 1 shows a montage of TEM images of the untreated fresh catalysts along with a section of their SAD patterns. Using HAADF-STEM, the average nanoparticle diameters were determined to be as follows. Pt-Al₂O₃ pellet: 1.57 ± 0.02 nm, Pt-Al₂O₃ powder: 2.69 ± 0.04 nm and Pd-Al₂O₃ powder: 3.43 ± 0.04 nm. These randomly orientated ultrafine particles gave virtually no contribution to the SAD patterns as shown in Figure 1. Figure 2 shows a NBD pattern, HRTEM image and its FFT from a nanoparticle located on the edge of a Al₂O₃ crystal. It is known that HRTEM contrast from thin oxide crystals can be ambiguous [10] and the crystal quality varies considerably in the presented Al₂O₃ powder catalysts. The NBD pattern shows the nanoparticle approximately 2° from the exact [1 1 2] zone axis. Intricacies in the diffraction pattern can be found on the upper reflections. Here, an array of spots can be seen near the main reflections. Such intensity phenomena have been shown to originate from the effect of the crystal’s finite size [11]. The additional reflections, in the 2D projection extend in the [3 1 1] direction, so the nanoparticle is likely a thin wedge based on the expectations of size effects from a cube (see, for example [11]). Such intricacies would be missed in a SAD pattern and FFT. Work continues to deduce epixial relations between the support and nanoparticles.
Figure 2. NBD pattern with HRTEM image and FFT of a small Pt nanoparticle on the Pt-Al$_2$O$_3$ powder catalyst. Scale bar is 2 nm.

Figure 3. Example of a large structure on the Pt-Al$_2$O$_3$ catalyst treated for 3 h at 750 °C. Nano-area diffraction reveals the presence of additional diffraction phenomena caused by the presence of a series of stacking faults. Measurements in nm$^{-1}$ in diffraction pattern A.
Figure 3 shows a series of NBD patterns from a large Pt structure on the Pt-Al$_2$O$_3$ powder catalyst which has been treated at 750 °C in air for 3 h. Although defects have been studied in nanoparticles by dark field TEM they have generally been analysed in very large particles. With NBD it is possible to obtain diffraction patterns from defects on the nano-scale. The diffraction pattern from region A shows what appears to be a highly distorted Pt lattice. The pattern resembles the [2 1 3] zone axis but the spatial frequencies of most of the reflections are wrong for this zone axis. A dark field image is shown as an inset in the HRTEM image which implies that the structure observed is an overlap between two differently aligned nanoparticles approximately each 20 nm in diameter at their widest point measured from left to right in the dark field image. We believe the pattern in A is a highly distorted Pt [1 1 2] zone axis where the distortion is facilitated by the presence of a tilted grain boundary in region B which may have induced defects between the two nanoparticles.

The diffraction pattern from region B shows near continuous intensity along the [1 1 1] direction (with respect to C) and this type of contrast is consistent with the presence of stacking faults but it may also be caused by the presence of a tilted gain boundary which may induce its own shape effects into the diffraction pattern. The main reflections in B originate from an overlap of the diffraction patterns in A and C. In diffraction pattern C, Pt [1 1 0] can be seen. A key feature shown in these diffraction patterns is the alignment of different directions in each crystal, namely [1 1 1] in A with [1 1 3] in C.

4. Conclusions
Our NBD investigation on Pt and Pd-Al$_2$O$_3$ has provided additional structural insights of small particles as well as larger particles that contain defects. Such features are likely to be missed using SAD patterns. For the smallest particles, such as those on the Pt-Al$_2$O$_3$ pellet catalyst shown here, nanodiffraction, pioneered by Cowley and co-workers [12] would be the most practical diffraction technique. Recent developments at the York-JEOL Nanocentre regarding in-situ environmental microscopy [13] could allow diffraction techniques to be combined with traditional imaging techniques that could allow dynamic structural changes to be investigated in more detail than before.

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