Quantification of a Heterogeneous Ruthenium Catalyst on Carbon-black using ADF Imaging.

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Abstract. Using recent developments in ADF quantification techniques, we utilise a rapid atom counting procedure to document the evolution of a heterogeneous ruthenium catalyst on carbon black. Selected areas of the ruthenium catalyst were imaged for approximately 15 minutes. The imaged areas show that the Ru wets the support forming a thin amorphous layer that transforms to a crystalline layer under beam irradiation.

1. Introduction.
Ruthenium catalysts show promising results for many catalytic processes, however, their crystal structure (hexagonal closed packed) prevented them being considered as potential candidates for many reactions. With the recent discovery of fcc (face centred cubic) ruthenium nanoparticles[1], interest in ruthenium has picked up again. The fcc structure has been attributed to a substantial catalytic activity enhancement in CO oxidation reactions when compared to the more common hcp ruthenium nanoparticles[1].

Here we study a ruthenium on carbon catalyst using annular dark-field (ADF) scanning transmission electron microscopy (STEM). ADF STEM is particularly suited to the study of heterogeneous catalysts because of its strong dependence on atomic number and lack of contrast reversals with thickness and defocus. Particle stability under the electron beam remains a challenge with this approach, however.

In this paper, using recently developed quantification techniques, we present results of a pure heterogeneous ruthenium catalyst supported on carbon-black, changing structurally, as it was imaged under the electron beam. The images were normalised with the appropriate parameters and atomic column counts were obtained for the images.

2. Experimental and normalisation parameters.
The nanoparticles were imaged using a JEOL ARM 200CF EM at NTNU (Trondheim, Norway) was done at 200kV with 69.2mrad and 137.53mrad inner and outer detector angles respectively. Two areas of the catalyst were imaged (Figure 1) and labelled as nodule and ring, with their respective analysis regions highlighted by the yellow box.
33 and 44 frames were acquired for the nodule and ring regions respectively. The before and after labels indicate a change from amorphous to crystalline phase from the beginning to the end of the imaging period. In order to quantify each frame reliably there are certain normalisation parameters that have to be addressed.

**Scan-drift correction.** This correction ensures that the relative positions of the atomic columns we detect and measure lie within the analysis areas. We implemented the non-rigid technique here[2].

**Detector asymmetry.** Asymmetry of the ADF detector has to be compensated to make reliable correlations of scattering cross-sections to atomic counts using simulations[3]. This was addressed by using a technique proposed by Martinez et al.[4].

**Detector current normalisation.** Throughout the imaging process, the current the detector measures drops non-linearly due to the electron gun. The measured column intensity would therefore decrease when measured for many images over time. This deficit was compensated, and corrected, in our measurements by measuring the detector current at several imaging intervals.

After these corrections, the resultant frames were compiled into a movie (https://goo.gl/nII6dA). From this, the scattering cross-sections were measured using absolute integrator software[5]. Once the measured cross-sections were obtained they were then correlated to simulations. Simulations were run using the µSTEM software[6]. The simulation supercell was 2048x2048 pixels, tiled 8 times in x and y, then a multislice simulation was carried out using the frozen phonon model with 30 phonons.

3. **Correlating cross-sections to atom counts.**

The idea of using scattering cross-sections to estimate atomic column counts was first suggested by Retsky[7], and more recently expanded upon by E et al[8]. Scattering cross-sections can be correlated to atomic column counts through simulations. The measured cross-sections are robust to several microscope parameters such as: magnification, defocus, convergence angle, source size, astigmatism, scan noise and sample mis-tilt[8].

Using a technique demonstrated by Jones et al[5] the measured cross-sections were correlated to simulated atom counts. The simulated library for the ruthenium nanoparticles is shown in Figure 2. In some frames the atomic columns were difficult for Absolute Integrator to resolve. This was due to smearing of the intensities during scan-drift correction and the catalyst’s phase shifting constantly.

Therefore, only frames where the atomic columns were reasonably well resolved, within the quantification areas, were used. From Figure 2, atomic maps of the quantification regions were created by assigning atoms of simulated cross-sections to closest matching measured cross-sections. A simulation library of fcc [110] was used ([100] and [110] orientations yield similar cross-sections for thicknesses of up to 8 atoms, as shown by Figure 2). From this, three-dimensional surface plots were derived, shown in Figure 4.
Figure 4 displays snapshots of the beginning, intermediary and final evolution phases of the catalyst. The carbon-black support, can be interpreted as the white surface the catalyst disperses on. The resolvable frames can be seen at (https://goo.gl/nlIi6A).

The crystal class of the structures in Figure 4 was determined by super positioning perfect fcc and hcp lattices. Overlaying several images in this manner suggested that the regions observed in this case were fcc 100 and 110 for nodule regions I and II respectively (Figure 3). Whereas, the ring region was a mixture of the hcp and fcc, continuously changing between the two throughout imaging.

Next, the mean thickness of the structure was measured by plotting the mean atomic column counts against imaging time, Figure 5. Figure 5, is a plot from nodule regions I and II. The plot indicates stabilisation of the raft after a certain imaging period. The ring region also yielded similar results.

Figure 2 μSTEM simulation library for fcc [100] and [110] used for correlating measured cross-sections to number of atoms within an atomic column. Simulated cross-sections between the two orientations are very similar for thicknesses up to 8 atoms.

Figure 3 a) and b): Images of regions I and II with perfect fcc (Black) and hcp (Yellow) candidate lattices.

Figure 4 a set of surface plots displaying how the structure changed under beam effects at different beam exposure times, t. The x and y axes represent the pixel coordinates of the atomic columns.
4. Discussion and conclusions.

We have presented quantification data of a ruthenium catalyst on carbon-black support as the sample was exposed to the electron beam. Our analysis suggests formation of raft-like structures forming under the electron beam. The crystal class was determined to be fcc for the nodule area (whereas a mixture of hcp and fcc for the ring area), this is particularly interesting as ruthenium is commonly known to possess a hcp structure in the bulk. Furthermore, Density Functional Theory and molecular dynamics calculations by Zhao et al.[9] indicate that it may be possible to obtain a stable fcc ruthenium raft-like structure if a carbon atom is added to the more common hcp ruthenium structure. Therefore, in conclusion the ruthenium atoms wet the carbon support and formed a stable fcc raft between 2 and 6 atoms thickness.

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6. References.

[1] Kusada K, Kobayashi H, Yamamoto T, Matsumura S, Sumi N and Sato K 2013 J. Am. Chem. Soc. 135 5493
[2] Jones L, Yang H, Pennycook T J, Marshall M S J, Van Aert S, Browning N D, Castell R and Nellist P D 2015 Adv. Struct. Chem. Imaging 1 8
[3] Findlay S D and LeBeau J M 2013 Ultramicroscopy 124 52
[4] Martinez G T, Jones L, De Backer A, Beche A, Verbeeck J Van Aert S and Nellist P D 2015 Ultramicroscopy [in press]
[5] Jones L, MacArthur K E, Fauske V T, Van Helvoort A T J and Nellist P D 2014 Nano Lett. 14 6336
[6] Allen L J, D’Alfonso A J and Findlay S D 2014 Ultramicroscopy, 151 1
[7] Retsky M 1974 Optik (Stuttg) 41 127
[8] E H, MacArthur K E, Pennycook T J, Okunishi E, D’Alfonso A J, Lugg N R Allen L J and Nellist P D 2013 Ultramicroscopy 133 109
[9] Zhao Z, Meng C, Li P, Zhu W, Wang Q, Ma Y, Shen G, Bai L, He H, He D, Yu D, He J Xu B and Tian Y 2014 Nanoscale 6 10370

Figure 5 Mean thickness plot for Nodule. The crosses represent counts in atoms whereas the dots represent mean fractional beam current. The mean fractional beam current was assigned to frames that were difficult to resolve. The plots indicated a mean thickness range between 2 and 4 atoms.