CH-2836 Report

(I) Reconstructive imaging of the formation and in-operando operation o f supported metal-oxide catalysts and (II) Watching the formation of zero-valent nano-iron using rapid angle dispersive diffraction.

As the title suggests, the proposal concerned two pieces of work for which 18 and 3 shifts (for I and II respectively) were requested and ultimately 18 shifts were allocated. Part II of the work was not completed due to lack of available time. Part I concerned the imaging of metal oxide supported catalysts both in preparation and under in-operando conditions and is a continuation from previous work we recently published [1]. The aim was to watch the formation and operating behaviour of the active catalyst of alumina supported Nickel catalysts prepared via two precursor routes. The preparation treatment and operation of the catalyst required inert and active gasses to be passed over the support at temperatures up to 500^{o}C. This was achieved by containing the supported catalyst in a gas tight environment which was externally heated using hot air guns as shown in figure 1. A CAT type approach was used to image the supported catalyst which necessitated rotation of the rig through 180^{o} while maintaining the gas seal. The samples were ca. 3.5 mm in diameter. Diffraction was measured at 0.1 mm translations across the sample (requiring 43 steps to account for, with good reason, a few steps outside the sample) at all angles from 0 ^{o} to 180 ^{o} in steps of 6 ^{o}; this equates to 43 x 31 = 1333 projections for each slice measured. At each projection, diffraction was acquired for 0.4 s and with dead time this equated to about 10 minutes to accumulate each measured slice. Static 3D data and time-resolved 2D data were collected under preparation and under reaction conditions (the methylation of synthesis gas (CO/H_2)). We have a bounty of very impressive results from both Nickel preparation routes. We are confident that these will be published in a high impact journal. By example, figure 2 shows some initial results of a Nickel catalyst precursor undergoing a calcinations treatment under helium. The results are interesting and show materials forming that were missed in our previous studies (due to both poorer time and peak resolution of the technique we previously used) [1]. Clearly, we still have some work to do in identifying phases and understanding the interplay between them. We consider the beam-time to have been a great success and are most grateful for the opportunity to carry out these experiments.

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[1] *Tomographic Energy Dispersive Diffraction Imaging To Study the Genesis of Ni Nanoparticles in 3D within γ-Al2O3 Catalyst Bodies* L. Espinosa-Alonso, M.G. O'Brien, S.D.M. Jacques, A.M. Beale, K.P. de Jong, P. Barnes and B.M. Weckhuysen, J. Am. Chem. Soc. 131 (2009) 16932

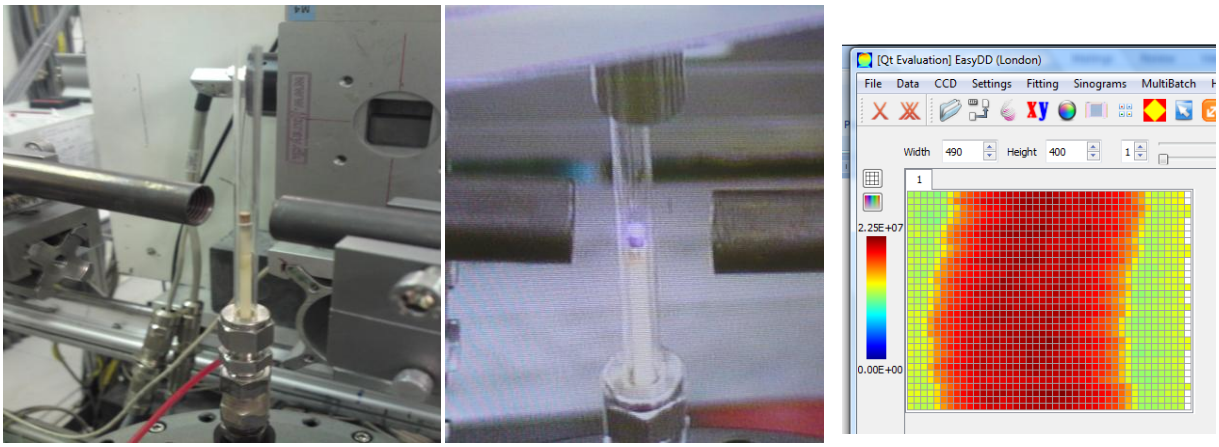

Figure 1 **A and B** Photographs of the setup. Alumina supported catalysts were ceramic cemented to a gas porous rod and contained in a quartz glass tube sealed to a gas stub. The latter was mounted to a goniometer for alignment. The sample-stub-goniometer was attached to a fast rotation stage with this itself mounted to translation stage, onto which was also mounted the hot-air guns. These stages provided the movements required for CAT scanning while maintaining constant position of the heating guns with respect to the sample. **C** Raw sinogram of summed diffracted intensity. At each point in the sinogram there is a recorded diffraction pattern. Features of which can be reconstructed into real space images.

Time/temperature ⟶

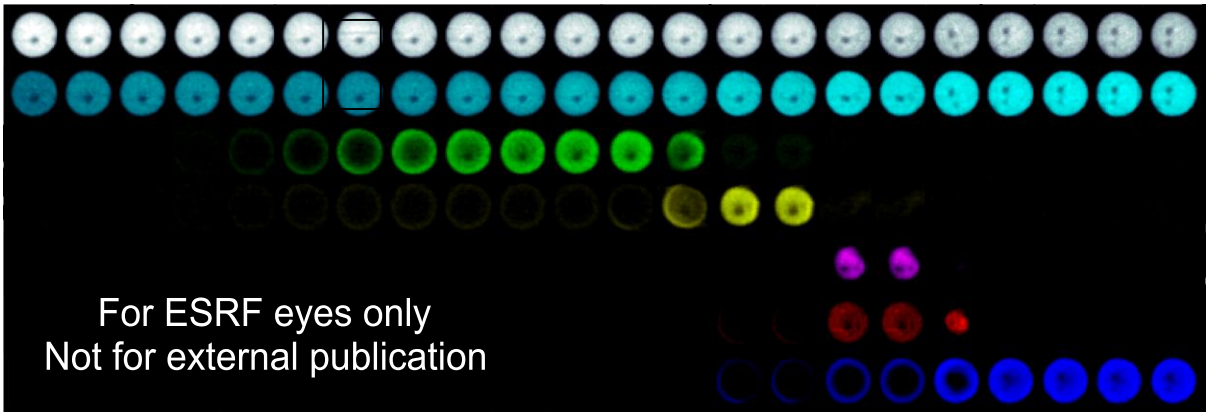

Figure 2 Reconstructed images of features found in recorded diffraction pattern as a function of time/temperature in the calcination of a alumina supported nickel catalyst precursor. Seven features have been mapped corresponding to at least six distinct different materials. The colour maps are described as follows. White = alumina; dark patches in the maps are voids in the alumina support material. Clearly there is sample movement between the 17th and 18th time slice, this is confirmed from the pre and post 3D scans of the sample. The cyan maps correspond to an unidentified 20Å feature which is increasing in concentration with time. The green and yellow phases are not yet identified. There evolution is interesting. They give rise to hexagonal close packed (HCP) nickel (shown in Red) which forms at the exterior moving with time to the interior. The spatial existence of which is short lived as it quickly converts to Face Centred Cubic (FCC) nickel (shown in Blue). The pink phase has not been identified, its formation is interesting as its existence is also brief and concurrent with the ‘egg-white’ distribution of HCP nickel, but itself having a more ‘egg-yolk’ distribution.