

Type of presentation: Oral

## **IT-7-O-1567 In situ Scanning Transmission Electron Microscopy study of CuO reduction**

Martin T. E.<sup>1</sup>, Lari L.<sup>1</sup>, Gai P. L.<sup>2</sup>, Boyes E. D.<sup>3</sup>

<sup>1</sup>The York Nanocentre and Department of Physics, University of York, UK, <sup>2</sup>The York Nanocentre and Departments of Chemistry and Physics, University of York, UK, <sup>3</sup>The York Nanocentre and Departments of Physics and Electronics, University of York, UK

Email of the presenting author: tm526@york.ac.uk

Methanol is one of the most important basic components in the chemical industry (worldwide production approx. 45 million tons 2010). Furthermore, it has potential as an in situ source of hydrogen for fuel cells [1, 2]. Cu is one component used to catalyse methanol synthesis and consequently, understanding of the activation and deactivation mechanisms of Cu is necessary to improve both catalyst activity and lifetime. Due to the scale of methanol production, small improvements in catalytic technology can lead to large economic impacts and make green technologies, such as fuel cells, more financially viable whilst also providing improved function. The activation process (in this case reduction) required to transform the precursor, CuO, into catalytically active Cu is very significant in determining the final size, structure and distribution of catalytic nanoparticles [1]. Subsequent to reduction, deactivation mechanisms (such as sintering) cause the catalyst activity to reduce with time. Single atom imaging under reaction conditions in ESTEM (Environmental Scanning Transmission Electron Microscope) can provide insights into activation and deactivation mechanisms, as well as the basis for improved catalyst designs.

The ESTEM at the York JEOL Nanocentre has recently been modified to provide the unique capability to directly visualise single atoms and the atomic structure of heterogeneous catalysts, such as Cu, in a gas environment [3]. This has allowed the in situ reduction of CuO in H<sub>2</sub> (Figure 1) and investigation of the temperature-pressure parameter space to ascertain effects on particle morphology and size. As temperature is increased the Particle Size Distribution becomes bimodal with the particles divided into two distinct categories (facetted and unfacetted, Figure 2). Using ESTEM combined with EDXS, CuO particles and the more facetted Cu particles are seen to coexist. This suggests that reduction is dependent on the characteristics of the particle in question and thus that an atomic scale observation is required to fully understand the reduction process. Subsequent deactivation of the Cu particles is driven by reduction of the surface free energy and is shown to be primarily via the Ostwald Ripening (OR) mechanism (Figure 2). Understanding of the OR mechanism at the atomic level is currently lacking and the single atom resolution of the ESTEM, combined with Kinetic Monte Carlo simulations, provide a unique perspective on the factors affecting sintering such as particle size, temperature, activation energy and particle distribution.

Acknowledgement: The authors thank the EPSRC for support from critical mass grant EP/J018058/1

References:

1. Hansen, P.L., et al., *Science*, 2002. 295(5562): p. 2053-2055.
2. Avgouropoulos, G., et al., *Applied Catalysis B: Environmental*, 2009. 90(3): p. 628-632.
3. Boyes, E.D., et al., *Annalen der Physik*, 2013. 525(6): p. 423-429.

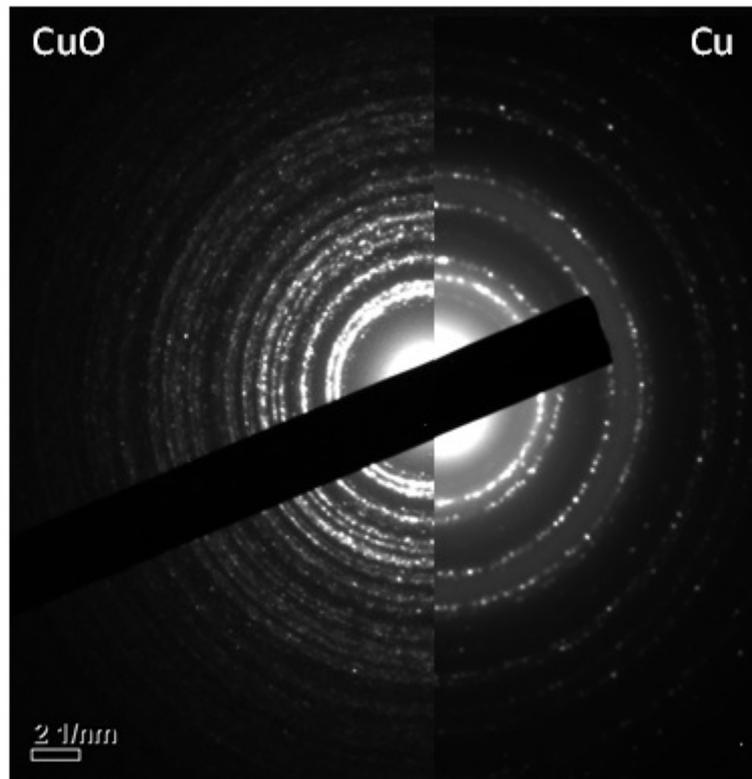


Fig. 1: Reduction of CuO particles in situ using ESTEM at 3Pa Hydrogen, 361 °C to Cu. Diffraction patterns observed before and after reduction in UHV TEM.

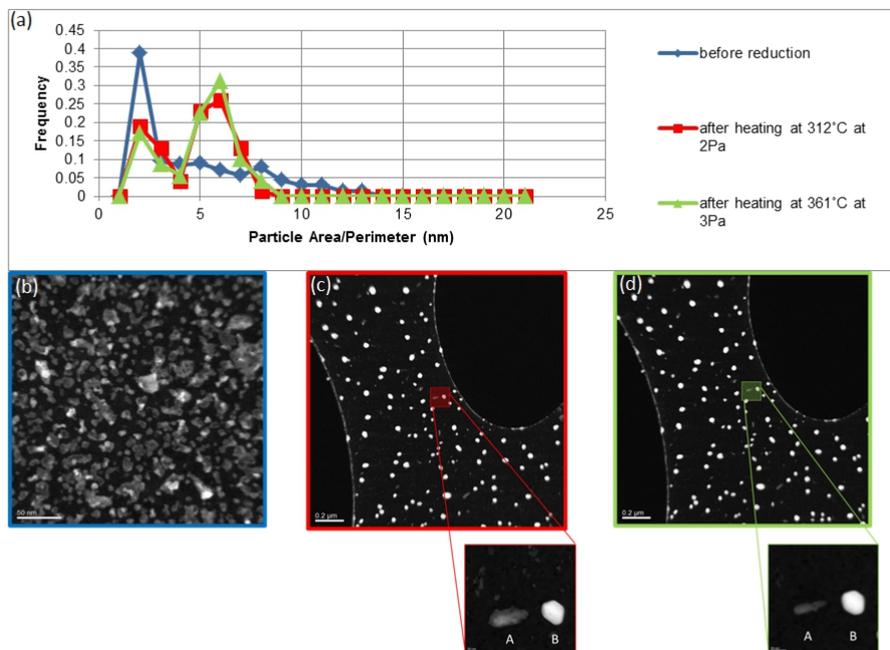


Fig. 2: (a) Bimodal distribution suggests 2 groups of particles. These can be seen as grey (A) and white (B-more faceted) particles, (b) before reduction (c) after heating at 312 °C at 2Pa, (d) after heating at 361 °C at 3Pa. Particles become more faceted with reduced surface area as sintering process occurs.