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ID-12-P-1569 Combining ESTEM and Kinetic Monte Carlo simulations to investigate sintering of Cu

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Combining an improvement in the environmental sustainability of energy solutions, whilst also remaining economically feasible, is obviously of great importance. Catalysis could provide part of the solution for realising environmentally friendly, economical processes for the conversion of fossil fuels to energy. Methanol synthesis has attracted interest due to its potential for use in fuel cells and because it is one of the most important basic components in the chemical industry (worldwide production ~45 million tons in 2010). Methanol synthesis is catalysed by Cu based systems and an improved understanding of thermal deactivation mechanisms (Ostwald Ripening (OR) and Particle Migration and Coalescence (PMC), Figure 1) is of importance to improve both catalyst efficiency and lifetime.

Development of new catalysts is inhibited by a limited understanding of these processes. Through knowledge of the atomic scale mechanisms that govern catalytic properties it is possible to improve control of catalyst sintering. Computer simulation and theoretical models have increasingly been used in combination with experiments in order to further understand known catalytic processes and in the design of new ones[1].

The development of a double aberration corrected environmental scanning transmission electron microscope (ESTEM) which has the ability to image single atoms in situ allows for the exploration of deactivation mechanisms (such as OR) of heterogeneous catalysts in a gas environment [2]. Imaging of the OR mechanism at an atomic scale requires understanding of the interplay of temperature, gas pressure and the metal-support interaction with the imaging capability of the electron microscope. Prediction of the number and visibility of single atoms undergoing OR is achieved using Kinetic Monte Carlo simulations.

ESTEM experiments in the 200-350˚C range with 3Pa of H_2 have shown that deactivation of the Cu catalyst on a C support occurs primarily via OR (Figure 2). There is a general lack of atomic scale understanding of the OR mechanism, but important observations have recently shown [1]that sintering particles undergo periods of size stability followed by rapid decay. This is hypothesised to be due to particle morphology. The effect of particle shape and degree of perturbation from the minimum surface energy state can be modelled using KMC to further understand the OR mechanism.

The ability of KMC to provide atomic detail (and macroscopic trends) combined with Angstrom level resolution of ESTEM at York [2] allows a different approach to investigating catalyst sintering. Experiments have allowed some of the first images of catalyst single atoms in situ and this provides a different perspective in terms of verifying theoretical models at the atomic scale.

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References:

1. Hansen, T.W., et al., Accounts of chemical research, 2013.

2. Boyes, E.D., et al., Annalen der Physik, 2013. 525(6): p. 423-429.

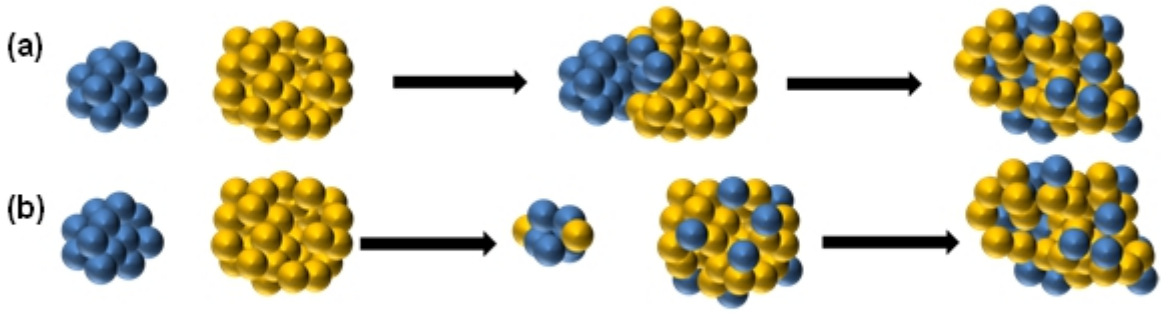

Fig. 1: : Diagram of 2 sintering mechanisms: (a) Particle Migration and coalescence and (b) Ostwald Ripening where single atoms/small clusters migrate from smaller to larger particles. Sintering is driven by reduction of free surface energy.

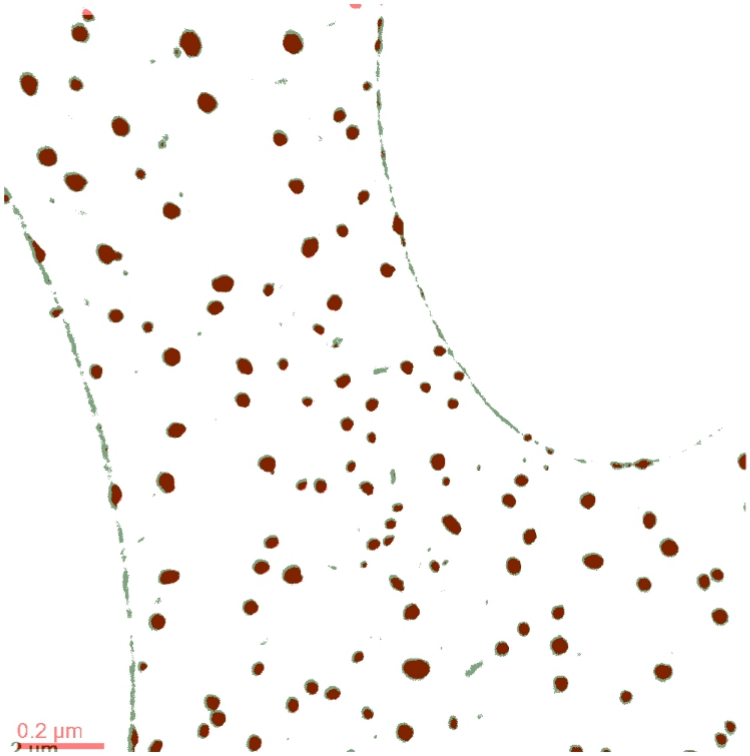

Fig. 2: Overlay showing that facetted particles have increased in size, but not changed position with temperature and pressure increase, suggesting OR mechanism. Overlay (red): after heating at 312˚C at 2Pa H2, Underlay (green) after heating at 361˚C at 3Pa H2.