

References

- [1] T. Egami and S.J.L. Billinge. *Underneath the Bragg peaks: structural analysis of complex materials*. Vol. 16. Newnes (2012).
- [2] K.M. Jensen, C. Tyrsted, M. Bremholm and B.B. Iversen, *ChemSusChem* 7, 1594-1611 (2014).

The structures found to best describe these structural stages are shown in **Figure 143**. The local structure found in the pre-nucleation stage is proposed to consist of polymeric zirconia species, formed during dissolution or present in the solid precursor from the beginning. At the point of nucleation, the data indicate that the polymeric species are rapidly fragmented into smaller species which cluster together and precipitate out as an amorphous network. The atomic network of the precipitate is not entirely randomised despite the apparent chaotic nucleation process, but has a local ordering which may be described as monoclinic in nature. The local bonding environment of the precipitate is therefore not too

far from the cubic lattice structure of the end product, yet lacks the correct long range topology. Over time, bond reforming ensures that the local domains order within themselves and in relation to each other thereby forming the desired cubic lattice structure.

Numerous simplified models exist to describe crystal nucleation and growth phenomena. The present study provides the first experimental atomistic insight into the very complex chemical processes that take place during crystallisation, and the total scattering technique provides a new approach to truly understanding nanomaterial formation.

Principal publication and authors

- A.M. Beale (a,b,c), E.K. Gibson (b,c), M.G. O'Brien (a), S.D.M. Jacques (c,d), R.J. Cernik (d), M. di Michiel (e), P.B. Cobden (f), O. Pirgon-Galin (f), L. van de Water (g), M.J. Watson (g) and B.M. Weckhuysen (a), *J. Catal.* 314, 94 (2014).
- (a) *Inorganic Chemistry and Catalysis, Debye Institute for Nanomaterials Science, Utrecht University (The Netherlands)*
- (b) *Department of Chemistry, University College London (UK)*
- (c) *UK Catalysis Hub, Research Complex at Harwell, Rutherford Appleton Laboratory, Didcot (UK)*
- (d) *School of Materials, University of Manchester (UK)*
- (e) *ESRF*
- (f) *Energy Research Centre of the Netherlands (ECN), Petten (The Netherlands)*
- (g) *Johnson Matthey Technology Centre, Billingham (UK)*

ILLUMINATING THE PHYSICAL PROCESS OF CATALYST DEACTIVATION

Synchrotron-based X-ray diffraction computed tomography (XRD-CT) is a technique developed at the ESRF for the purpose of revealing detailed chemical compositional information in solid materials in 2 and 3 spatial dimensions [1]. Much of this 'chemical imaging' has focused on the study of pre-shaped catalyst bodies often as a function of time. Here we demonstrate how the technique has been used to understand the importance of spatial variation during the process of sulfur-induced solid-state deactivation of low temperature Cu/ZnO/Al₂O₃ water-gas shift catalysts.

Catalyst deactivation by sulfur poisoning is a common problem for a wide range of catalytic processes and which is likely to become more problematic as the chemical industry moves from relatively clean feeds, such as natural gas and crude oil, to alternative feedstocks, such as bitumen tars and some forms of biomass. Cu/ZnO catalysts represent the industrial standard for the production of methanol and the water-gas shift (WGS) reaction. The catalysts are however very susceptible to sulfur poisoning (ZnO for example is often used as a 'sulfur scrubber'). However the process by

which sulfur poisons these catalysts is still up for debate. It is thought that sulfur, in the form of either H₂S or similar compounds, accumulates on the surface of the metallic Cu species blocking the active sites or else induces a phase transformation of the Cu and ZnO into the respective sulfides and oxy-sulfides. Since catalysts are used in pre-shaped forms, *i.e.* as millimetre-sized catalyst bodies, to understand deactivation in real catalyst samples needs consideration of the spatial perspective in order to assess macroscopic effects leading to catalyst deactivation. XRD-CT is ideal for assessing crystalline phase distribution at the μm scale, whereas XAFS/XRD mapping can be used to determine the relative importance of poisoning via sulfur adsorption vs. solid-state transformation of the active Cu/ZnO phase(s) into sulfide phases.

Sulfur, in the form of H₂S, was added to the catalytic feed during the WGS reaction and the results of the XRD-CT data recorded as a function of increasing sulfur concentration are given in **Figure 144**. The initial crystalline Cu and ZnO phases disappear with increasing [H₂S] in the feed and both phases lose intensity and 'shrink'

towards the core of the body. New sulfide phases evolve on the outside, while the increasing $[H_2S]$ leads to a thicker sulfide shell. Consequently, the thicker the sulfide shell, the greater the loss in catalytic activity. In the sample poisoned using 500 ppm H_2S , over 80% of the cylinder volume is converted into sulfide-containing phases and almost all catalytic activity is lost.

Whilst XRD-CT is able to identify the distribution of crystalline components over the 2D cross-section, it is insensitive to the presence of small amounts of adsorbed sulfur species on the surface of metallic Cu, which may block the active site. For this purpose, a chemical map derived from the fitting of the Cu-NN (nearest neighbour) contribution from XAFS spectroscopy on a section of the microtomed catalyst is given in Figure 145. The main Cu nearest neighbour component is $< 2 \text{ \AA}$ at the core and $> 2.1 \text{ \AA}$ towards the edge, consistent with the presence of CuO at the core and CuS at the edge. There was no clear evidence for the presence of either Cu-S or Zn-S phases in the centre of the sample [2].

The formation of sulfide phases at the sample edges is highly detrimental to the catalytic activity of the sample since the catalyst deactivates before all Cu/ZnO has been lost. Although industrial Cu/ZnO/ Al_2O_3 catalysts are unlikely to see anything like the

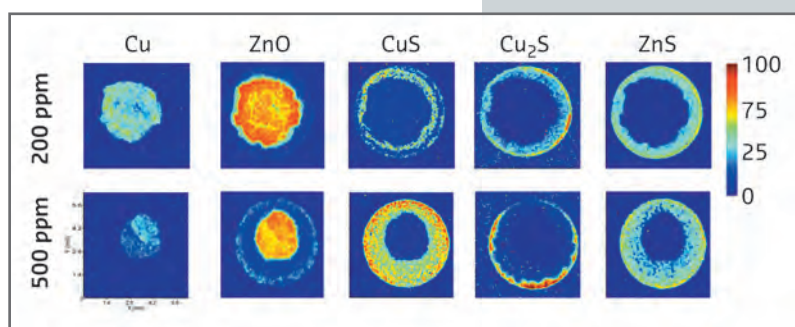
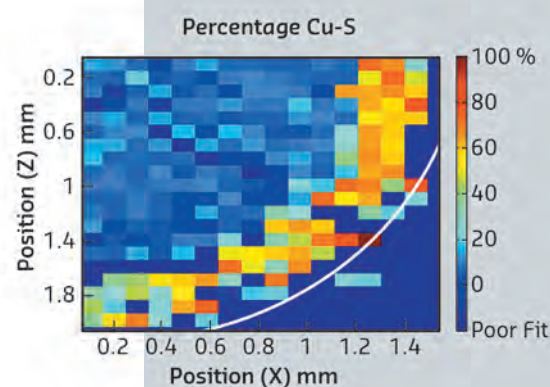


Fig. 144: 2D XRD intensity colour maps for various crystalline phases (top) after two concentrations of H_2S (left) were introduced in the WGS reactant feed. Right – colour scale map.

Fig. 145: Derived composition data from the Cu-'O' bond distance map of a microtomed cross-section of a Cu/ZnO/ Al_2O_3 catalyst body treated with 200 ppm H_2S . Right – colour scale map.



amount of H_2S used in this study, the tendency for Cu and Zn to adsorb S does mean that, over time, sulfide phases will accrue in much the same way as observed here. Clearly it is important to consider the spatial component when trying to determine the structure-activity relationships in real heterogeneous catalyst samples with imaging methods critical for such purposes.

References

- [1] A.M. Beale, S.D.M. Jacques, E.K. Gibson and M. Di Michiel, *Coord. Chem. Rev.* 277, 208 (2014).
 [2] A.M. Beale, E.K. Gibson, M.G. O'Brien, S.D.M. Jacques, R.J. Cernik, M. di Michiel, P.B. Cobden, O. Pirgon-Galin, L. van de Water, M.J. Watson and B.M. Weckhuysen, *J. Catal.* 314, 94 (2014).

SHORT-RANGE CORRELATIONS IN MAGNETITE ABOVE THE VERWEY TEMPERATURE

Magnetite, Fe_3O_4 , is the first magnetic material discovered and utilised by mankind in Ancient Greece, yet it still attracts attention due to its puzzling properties. Discovered in the first half of the twentieth century, the Verwey transition in magnetite [1] remains one of the most intriguing phenomena in solid-state physics. Magnetite is a ferrimagnet with an anomalously high Curie temperature $T_C = 850 \text{ K}$. Hence, it

is viewed as an ideal candidate for room-temperature spintronic applications. It crystallises in the inverse spinel cubic structure, with two types of Fe sites: the tetrahedral A sites and the octahedral B ones. At $T_V = 124 \text{ K}$, a first-order phase transition occurs as the electric conductivity drops by two orders of magnitude with the simultaneous change of the crystal structure from the cubic to monoclinic symmetry and with

Principal publication and authors

A. Bosak (a), D. Chernyshov (b), M. Hoesch (c), P. Piekarczyk (d), M. Le Tacon (e), M. Krisch (a), A. Kozłowski (f), A.M. Oleś (e,g) and K. Parlinski (g), *Phys. Rev. X* 4, 011040 (2014).

(a) ESRF

(b) SNBL, ESRF

(c) Diamond Light Source, Didcot (UK)

(d) Institute of Nuclear Physics, Polish Academy of Sciences, Kraków (Poland)

(e) Max-Planck-Institut für Festkörperforschung, Stuttgart (Germany)

(f) AGH-University of Science and Technology, Kraków (Poland)

(g) Marian Smoluchowski Institute of Physics, Jagellonian University, Kraków (Poland)