EUROPEAN SYNCHROTRON RADIATION FACILITY

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ESRF

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:

https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do

Reports supporting requests for additional beam time

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** Operation and poisoning of hydrogenation catalysts as determined by (1) combined X-ray diffraction and Raman imaging; (2) combined X-ray diffraction and XAFS	**Experiment number**: CH-3295
Beamline: ID15A	**Date of experiment**: from: 22/6/2011 to: 28/6/2011	**Date of report**: 14/8/2013 *Received at ESRF:*
Shifts: 18	**Local contact(s)**: Dr. Marco Di Michiel	

Names and affiliations of applicants (* indicates experimentalists):

Andrew M. Beale (Inorganic Chemistry and Catalysis, Utrecht University)*

Matthew O’Brien (Inorganic Chemistry and Catalysis, Utrecht University)*
Matthijs Zandbergen (Inorganic Chemistry and Catalysis, Utrecht University)*
Simon Jacques (Manchester University)*

Report:

In an industrial reactor catalysts are used in pre-shaped forms, i.e. as millimetre-sized catalyst bodies. As such, a study examining deactivation in real catalyst samples needs to consider the problem from a spatial perspective in order to assess quantitatively, macroscopic effects leading to catalyst deactivation e.g. ‘shell progressive’, ‘shrinking core’ and ‘pore mouth’ effects. To the best of our knowledge, such a spatially-resolved systematic study on the S-poisoning of pre-shaped catalyst materials is not available in the open literature. The results contained in this report details a study using both invasive and non-invasive characterization techniques in order to understand the process by which sulfur poisoning leads to a loss in catalytic activity of Cu/ZnO catalysts for the water gas shift reaction. We demonstrate in particular how the technique of XRD-CT revealed that these catalysts deactivate via the solid-state transformation of the active Cu/ZnO phase(s) to the inactive CuS/ β-ZnS phases respectively.

In order to determine the spatial distribution of the phases present in the extrudate samples, 2D intensity distribution maps were produced using the following ‘diagnostic’ peaks: Cu (111), ZnO (002), CuO (111), CuS (103), Cu_2S (102) and β-ZnS (111) although the data are of sufficient quality that these maps could equally be produced by using a Rietveld phase scale factor. The colour maps show the distribution of the phases presented in the 1D plot and furthermore revealed changes in 2D spatial distribution with increasing [H_2S]. The first key observations concern the phases initially present in the sample and their consumption with increasing [H_2S] in the feed. The metallic Cu phase lost intensity and began to shrink towards the core of the extrudate (Figure 1 left hand side). The distribution of CuO (111) matches closely that of the metallic Cu phase although the intensity of this signal increased between 200 – 350 ppm before being observed at its weakest and smallest (in terms of spatial distribution) at 500 ppm. This increase in CuO content between 200 to 350 ppm [H_2S] relative to the amount of metallic Cu is most likely caused by differences in the passivation process. A similar distribution/intensity profile was seen for the ZnO response (although the profiled peak comprises a contribution for both CuO (-111) and ZnO(101)). Conversely then the new phases that evolved possess an inverse distribution (a broad shell around a core) to that of the initial phases with increasing [H_2S]. With increasing [H_2S] the shell of CuS and β-ZnS became thicker, concentrating further into the sample. Interestingly the 'egg white' distribution is itself non-uniform with greater signal intensity seen at the very periphery of the sample (termed an 'egg-shell' distribution). The Cu_2S phase in contrast is very much concentrated as an egg-shell.

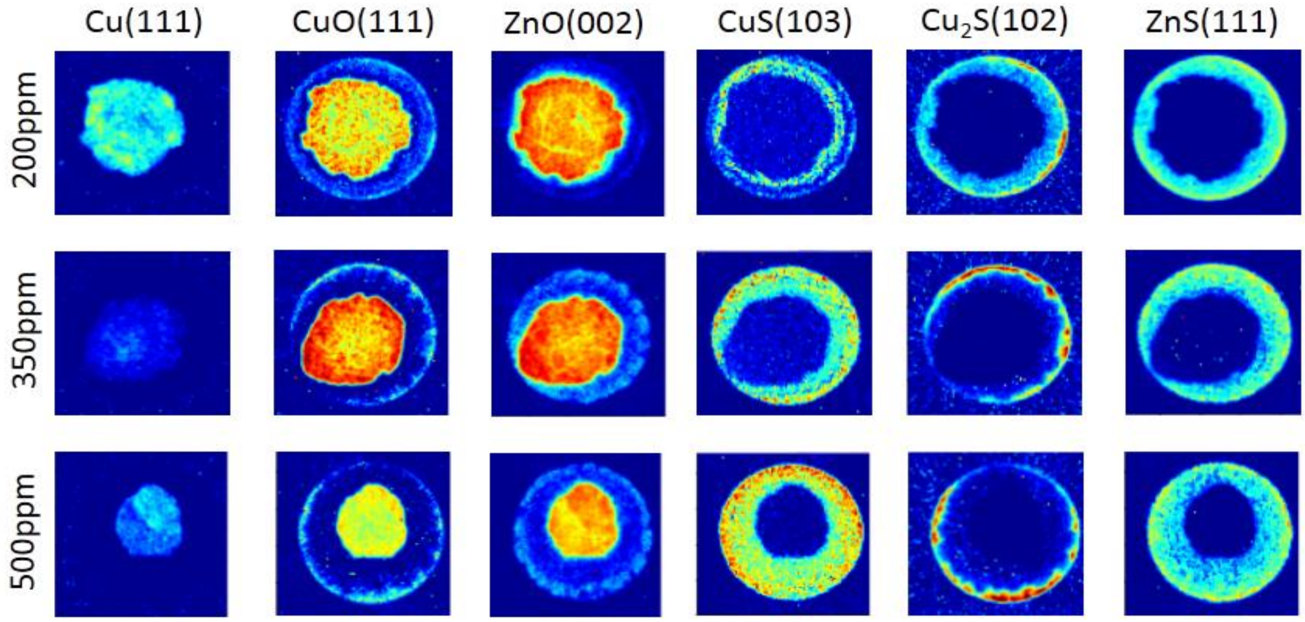

Figure 1. 2D XRD intensity colour maps produced from diagnostic peaks for the various Cu and Zn containing crystalline phases. The intensities have been scaled to the maximum and minimum values for the data presented since the absolute values for each phase vary.

Tomographic XRD-CT confirmed that the formation of the β-ZnS phase and previously unobserved crystalline CuS and Cu_2S sulfided phases, formed via the reaction between H_2S and the initial Cu and ZnO phases is the principle mode by which sulfur poisons $Cu/ZnO/Al_2O_3$ catalyst bodies for the WGS reaction. The resultant sulfided CuS phase is also mobile leading to Cu redistribution towards the sample edge, leading to promoted growth (sintering) of the Cu species which will also adversely affect activity. The ability of the Cu/ZnO catalyst body material to act as a H_2S trap ensures against a rapid loss of catalyst activity although it appears that the catalyst body becomes inactive before all Cu/ZnO (that which remains in the core) has been sulfided. This suggests a diffusion problem related caused by the formation of Cu/Zn sulfided phases (from the Cu/ZnO phases) either by the blocking of pores by mobile sulfides or else through destruction of the internal pore structure.