



| | | |
|---------------------------|--|--------------------------------------|
| | Experiment title: High resolution X-ray fluorescence tomography of a bi-functional catalyst system: a <i>quasi in-situ</i> study | Experiment number: CH4285 |
| Beamline: ID16b | Date of experiment: from: 26/08/2014 to: 02/09/2014 | Date of report: 10/09/2015 |
| Shifts: 18 | Local contact(s): Remi Tucoulou | <i>Received at ESRF:</i> |

Names and affiliations of applicants (* indicates experimentalists):

A. Rochet¹, S. Baier^{1*}, F. Benzi^{1*}, P. Sprenger^{1*}, P. Pfeifer², S. Lee³, M. Klumpp^{4*} and J.-D. Grunwaldt^{1,3}

¹ Institute for Chemical Technology and Polymer Chemistry, Karlsruhe Institute of Technology, D - 76131 Karlsruhe, Germany

² Institute for Micro Process Engineering, Karlsruhe Institute of Technology, D - 76344 Eggenstein-Leopoldshafen, Germany

³ Institute of Catalysis Research and Technology, Karlsruhe Institute of Technology, DE - 76344 Eggenstein-Leopoldshafen, Germany

⁴ Nurnberg Institute of Chemical Reaction Engineering, Universitaet Erlangen, DE - 91058 Erlangen, Germany

Report:

Finding energy sources alternative to fossil fuels has become a very urgent matter of our society. Among the new sources, dimethyl ether (DME) is a promising alternative since it can be produced starting from syngas (CO + H₂) either directly or through the dehydration of methanol. In the so called bioliq-process, which is a two step process, DME is produced from methanol which is synthesised by syngas. To improve the the yield of the reaction a bi-functional catalyst is suitable since it permits a one step synthesis.

The system analysed in this study is based on a micrometer sized core/shell particle. The core, composed by copper and zinc, catalyzes the methanol synthesis from syngas, while the acidic shell, composed by a zeolite (H-ZSM5), permits gas exchange and catalyzes the dehydration of methanol to form DME.

Sample particles (sieved fraction 50-100 µm) have been inserted in 100 µm capillaries, pre-reduced in hydrogen and sealed with glue. The aim of this experiment was to study the particles in a *quasi in situ* fashion, *i.e.* by measuring on a particle non destructively, performing gas/heat treatment *ex situ* and then measuring on the same particle to see the changes occurred. By this experimental procedure we aimed to follow the structural changes in the core due to reduction/oxidation (*i.e.* shrinking of the core due to reduction) as well as elemental distribution inside the particle.

XRD, XRF and phase shift resolved tomography have been collected at the ID16b beamline. The storage ring operated with a current of around 90 mA in 16-bunch mode. The beamline operated with a pink beam at 17 keV with a beam size of FWHM around 100 nm. XRF spectra have been collected by means of a multielement silicon drift detector, while XRD and phase shift images have been collected with a FReLoN camera.

The main issue we had during the experiment was due to the particle size. Our particles were far too big to collect a full 3D tomogram; thus we had to collect a single slice making the *quasi in situ* approach impossible. We were unable to find the same 100 nm thick slice under the beam after removing the capillary

for the treatment. Moreover, due to the frequent refill of the storage ring during the 16-bunch mode (6 hours), the acquisition of XRD slices, which took about 16 hours per slice, was seriously compromised. Despite these experimental issues, we have been able to gather information about the sample and the feasibility of such an approach. By mapping the Cu K_{α} and the Zn K_{β} fluorescence lines we have been able to perform reconstructions of the particle slice before and after treatment. Unfortunately, due to its composition, the shell of the particle is invisible to the fluorescence and thus only the core was mapped (Fig. 1).

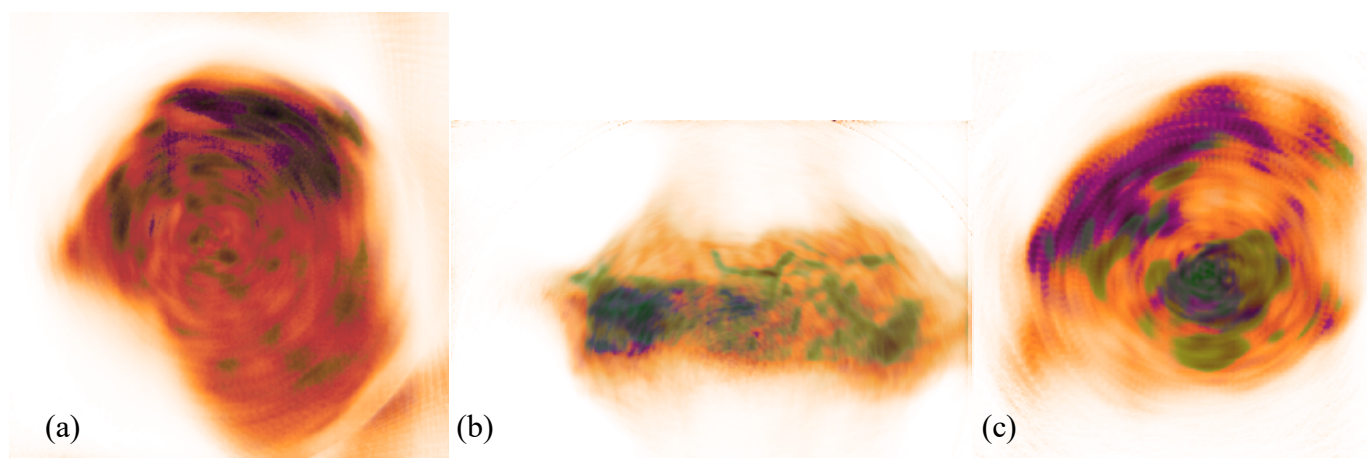


Figure 1: 2D XRF maps of particle slices before and after treatment. The colours represent the Cu K_{α} (green) and the Zn K_{β} (violet). The pictures represent (a) a calcinated sample, (b) the reduced particle, (c) the re-oxidised particle. From the maps we can see a structural change between the states, but unfortunately comparisons are no possible.

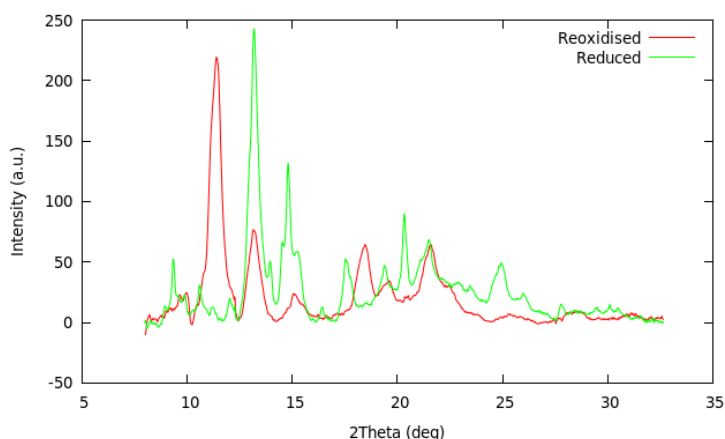


Figure 2: Azymutally integrated diffraction patterns obtained by averaging a set of images from the reduced and the re-oxidised slices.

In a similar way, XRD data were able to detect significant phase changes between the reduced and the oxidised particles. In Fig. 2 it is possible to observe the difference in the diffraction patterns obtained by azimuthal integration of the 2D powder diffraction images. Works are in progress to identify and quantify the phases present in the samples. Only the core of the particle could be resolved by powder diffraction since the shell had crystallite sizes bigger than the beam size and thus the powder diffraction condition could not be met (only spots instead of rings were visible in the diffraction images). Again, due to the impossibility of performing the *quasi in situ* measurements, the slices are different and thus no precise information can be gained by

comparing the sample before and after reoxidation.

The present study gave us a preliminary insight of the possibilities offered by scanning diffraction with such a high resolution. Combining XRF and XRD scanning tomography is a powerful and valuable tool to gain deep insights into the elemental and phase distribution of complex system such as our core/shell particles. The *quasi in situ* approach can be the only way to obtain meaningful comparison of a system before and after a treatment when a standard *in situ* approach is not possible. This was the case of the present experiment, since the system stability can be heavily compromised by thermal fluctuations in the experimental hall. Future experiments in this direction should be performed on smaller particle sizes (of the order of 10 μm) so a full 3D tomogram can be recorded in a reasonable time.