



Experiment title: Combined XRD/XRF tomographic studies of multicomponent Bismuth Molybdate catalysts for acrolein synthesis		Experiment number: CH-4713
Beamline: ID16B	Date of experiment: from: 16.06.16 to: 23.06.16	Date of report: 19.09.16
Shifts: 18	Local contact(s): Jussi-Petteri Suuronen	<i>Received at ESRF:</i>
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Report:

Multicomponent bismuth molybdate (Bi-Mo) catalysts are known to be selective and active for conversion of propylene to acrolein, an important and industrially-relevant precursor to the amino acid methionine. Although 2-component (Bi-Mo) catalysts are generally used for this process [1], four-component systems (Bi-Mo-Co-Fe) show higher activity and selectivity with respect to pure molybdate systems. These catalysts consist of multiple metal oxide phases, forming a composite of active species, spectator species and support material. The catalyst synthesis method has been shown to significantly affect catalyst performance, and by extension the structure present [2]. Previous studies have also shown the influence of microcrystalline phase changes on catalytic activity. Under working conditions, active catalysts need several hours to reach constant conversion and selectivity on a lab scale, and even months on an industrial scale. Furthermore, BET analysis and Raman spectroscopy have shown drastic and permanent changes in surface area and component phases following the application of several conditions (e.g. catalytic treatment). Previous attempts to observe and characterise microcrystalline phases by lab-based XRD and Raman spectroscopy have proven difficult. Some questions therefore remain about metal distribution, identification and classification of the phases present (active, spectator, etc). The application of synchrotron tomography at ID16B was intended to result in a detailed structural study of various 4-component catalysts, improving understanding of the structure-activity relationship which is critical to catalyst function [3].

The proposed experiment had two objectives: (a) to obtain high resolution images (nm scale) of a single catalyst grain, allowing determination of microcrystalline phase distribution, metal speciation and general structure; (b) to perform initial tests with a new (quasi) *in situ* apparatus for tomographic measurement, allowing sequential analysis of the same catalyst grain following various heat and gas treatment conditions (Figure 1). Originally, the proposed plan was to perform XRF-CT to render 3D volumes of the catalyst particle according to the metal species present, and complement this with 2D renderings of individual slices by XRD-CT to reveal phase distribution. An optimised measurement strategy was later developed in discussion with the beamline staff, as described below.

Samples were first prepared with a sieve fraction of 50-100 µm and inspected under an optical microscope. Suitable particles (simple geometric shapes) were then fixed to a 2 mm steel pin with a planed tip via ceramic glue, with the majority of the particle volume exposed. The pin was either placed in a standard holder during beamline measurements, or attached to the custom-designed *in situ* sample holder for heat and gas treatment (Figure 1). In this way, an identical field of view of each particle could be obtained before and after the various treatments, allowing direct observation and relation of any changes in 3D space. Tomographic data was therefore acquired *ex situ* for the catalyst in the following states: (a) freshly prepared; (b) after catalytic treatment in He/O₂/propylene/H₂O at 380 °C for several hours.

Two types of measurement were performed at ID16B: full-field holotomography (phase-contrast imaging) of the entire catalyst particle, and nanofocused XRF-CT of several slices equivalent to approx. 20-30 % of the entire particle. Holotomography measurements were performed with a minimum field of view of approx. 50 x 60 µm and spatial resolution of approx. 100 nm (Figure 2). XRF-CT was performed by rastering with a step size of 100 x 500 nm (H x V). Complementary information was obtained regarding the general structure of the catalyst grain via holotomography, and specific elemental speciation and crystalline phase behaviour via XRF-CT. Despite the heavy and thus strongly absorbing matrix, the images acquired were of high quality. The ceramic glue was easily separated from the reconstructed data due to phase/fluorescence contrast obtained and therefore did not interfere with the final 3D renders. The energy resolution available was sufficient to accurately measure the individual fluorescence behaviour of each metallic component.

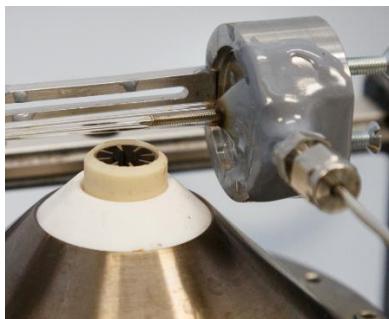


Figure 1 - Photo of the quasi *in situ* setup, consisting of sample supported on a pin, placed in a capillary over a hot air blower.

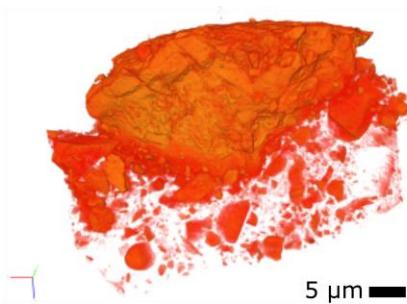


Figure 2 - 3D render of 4-component oxide catalyst after holotomography reconstruction. Approximate spatial resolution = 100 nm.

Due to the high amount of tomographic data recorded 2 months ago, processing and analysis of the data is still underway. The first inspection of the results has shown promising data, an example of which is shown in Figure 2. Furthermore, the beamtime served as a proof-of-principle study for a novel experimental apparatus, which is expected to further the goal of acquiring routine *in situ* tomographic data with X-ray microscopy in future, allowing multi-scale *in situ* characterization [3]. Such *in situ* tomographic studies of heterogeneous catalysts are an evolving area of research [3-5], and the overall aim herein of obtaining high quality 3D data on a complex multiphasic catalyst system, while moving towards the development of a full *in situ* measurement methodology, was met. The successfully acquired datasets are presently being further processed, and a publication will be prepared in collaboration with the local contact and ESRF staff.

References

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