ESRF	**Experiment title:** In situ energy-dispersive X-ray tomography: combining high spatial and time resolution for the study of dynamic catalyst systems under working conditions	**Experiment number**: CH-5475
Beamline: ID24	**Date of experiment**: from: 3rd to: 9th May 15th 23th June	**Date of report**: 17/08/2018
Shifts: 18 / 21	**Local contact(s)**: Debora Meira / Sakura Pascarelli	*Received at ESRF:*

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Report:

The aim of this experiment was twofold: (i) to exploit the energy-dispersive capabilities of beamline ID24, allowing acquisition of entire XANES/EXAFS data ranges in a single shot acquisition with high time resolution; (ii) to commission and test a new reactor setup (Figure 1) designed for spatially-resolved microtomography measurement of catalysts under appropriate operating conditions. The combination of spatial- and time-resolution is suggested to be particularly advantageous for the study of catalysts, where dynamic operating conditions are often present during real-life applications. The operando tomography setup was used for the first time at ESRF ID24 and based on the preliminary results was considered to be highly successful, The setup, named aRCTIC (Rotating Capillary for Tomographic In situ Catalysis), is now expected to be easily adaptable for use at other microtomography beamlines.

Two experimental sessions were scheduled for commissioning of the setup and delivering proof-of-principle for operando energy-dispersive XANES tomography (tomoXANES):

(i) in the first session, we focused on Catalytic Partial Oxidation of methane (CPO) to synthesis gas ($CO + H_2$) over Pt/Al_2O_3 catalysts. As a potential alternative to large-scale steam reforming of natural gas, the CPO reaction is suggested as an important stepping stone towards hydrogen synthesis, carbon neutral energy generation and green chemical synthesis, particularly when methane is sourced from biomass or other renewable sources. Platinum is thought to promote CPO via two distinct mechanisms: direct conversion of methane to syngas; and combustion-reforming where methane is first oxidised to CO_2 and H_2O followed by further reaction with unburnt methane to form syngas. This reaction displays clearly distinct zones within the catalyst bed, where Pt is oxidised in the combustion zone and reduced in the reforming zone.

(ii) in the second session, we attempted to visualise single cut channels from an exhaust gas monolith catalyst, whereby the catalyst material (Cu deposited on SSZ-13 zeolite) is washcoated onto the monolith

surface, forming an active layer of µm to mm thickness. Such catalysts are currently a strong focus in industrial and automotive exhaust systems as a means of pollution control and abatement of harmful exhaust gases such as NO and NH_3. A central research question concerns the efficiency of the washcoated catalyst, where mass transport effects or diffusion limitations on the gaseous reagents may inhibit catalyst performance. This may lead to oxidation state gradients within the catalyst washcoat.

While the CPO investigation was based on a model packed-bed capillary geometry (Figure 2), the SCR monolith investigation concerns a realistic catalyst form (a monolith channel) with industrial applications. In combination, the success of these two studies demonstrates the flexibility of the apparatus for examining various types of sample, and under a variety of gas and temperature conditions.

The so-called energy-dispersive tomoXANES method has only been demonstrated in an extremely limited number of studies, and on both occasions under ambient or ex situ conditions [1,2]. This experiment achieved full functionality of the aRCTIC setup, including temperatures up to 500 °C and controlled gas environments (3%/1.5% CH_4/O_2 and 1%/1%/10% $NO/NH_3/O_2$, up to 50 ml/min) relevant to CPO and NH_3-SCR reactions, while monitoring gas phase products by online mass spectrometry. The ability to maintain such enviornmental conditions in a closed system while performing tomography constitutes a significant conceptual and experimental advance. While operando studies with XRD and XANES tomography are known in the literature [3,,4], the application of time-resolved and spatially-resolved energy-dispersive tomoXANES in a single measurement is distinctly novel.

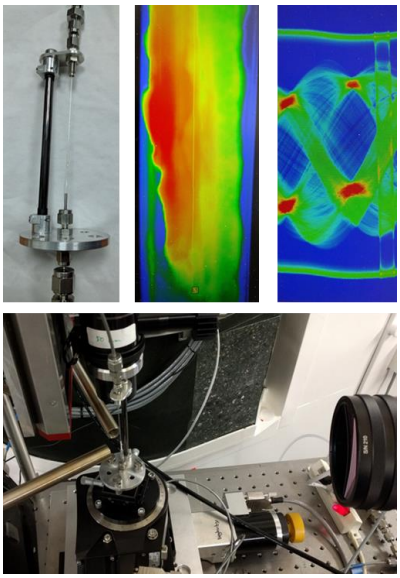

Figure 1. Clockwise from top left: the capillary reactor, an IR thermography image of Cu-SSZ-13 at 400 °C, a typical tomoXANES sinogram prior to reconstruction, the aRCTIC setup installed at ID24

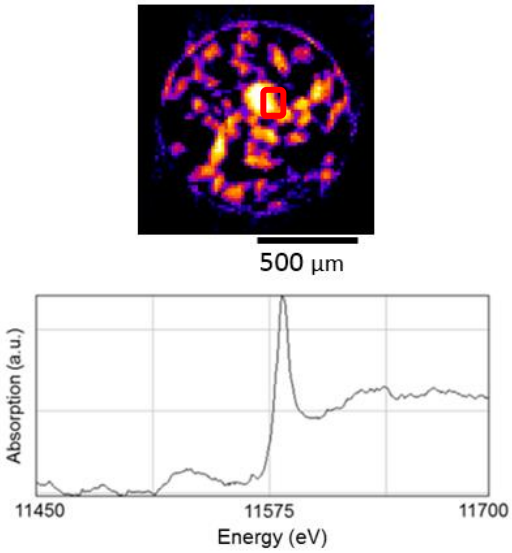

Figure 2. A typical reconstructed tomoXANES slice showing the Pt/Al_2O_3 CPO catalyst with spatial resolution of around 5 µm, and a Z-plot along the energy axis within the red-highlighted region.

The results are currently in the late stage of processing. Tomographic reconstruction is complete and the individual tomograms are now being analysed for chemical information. Specifically, the presence of oxidation state gradients will be examined in a spatially-resolved manner, as a function of the reaction conditions for each sample system. The structural data will be linked to the chemical environment applied, and considered together with product analysis to draw conclusions about catalyst structure-activity relationships. The results are expected to be published separately for each experiment, in collaboration with the local contacts, ID24 staff and external collaborators involved in data analysis. Further opportunities to develop operando tomoXANES as a viable technique would be welcomed following the EBS upgrade.

References:

[1] J. Ihli et al, *Angew. Chem. Int. Ed.* **2017** 56 (45), 14031-14035.
[2] D.F. Sanchez et al, *Sci. Rep.* **2017** 7 (1), 16453.
[3] S.W. Price, *Sci. Adv.* **2017** 3 (3), e1602838.
[4] J.C. Andrews B.M. Weckhuysen, *ChemPhysChem* **2013** 14 (16), 3655-3666.