ESRF	**Experiment title:** Diagnosing sulphur poisoning of emission control catalysts with quantitative hard X-ray nanotomography	**Experiment number**: CH-6482
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Report:

Pd-based methane oxidation catalysts may suffer strong deactivation from sulphur poisoning, originating from odorant additive, lubricating oils, and in natural gas itself. While numerous studies on sulphur poisoning and catalyst regeneration strategies are reported in literature, the specific impact of sulphur deposition on the 3D structure of applied monolitic catalysts have rarely been explored. [1,2] Technical CH_4-oxidation catalysts are usually metal- or ceramic substrates coated with catalytic material in the form of a washcoat. Mass and heat-transport limitations in these hierarchical structures brings additional complexity compared to model systems. Exposure to sulphur will not only trigger molecular changes [3], but sulphur deposition may also affect mass transport within the catalyst pores. Moreover, concentration gradients can develop across the catalyst layer and along the monolith channels. Therefore, identifying the location of sulphurous species in structured catalysts is key to understanding the poisoning mechanism and its impact on catalyst performance.

Hard X-ray tomography at synchrotron radiation sources offers a unique capability to visualize and quantify the interior structure of catalytic materials in a non-invasive manner. This study involved hard X-ray holotomography as one specific application for high resolution nanoscale imaging combined with quantitative analysis of the local electron density in the sample [4], which is indicative of the presence and severity of sulphur deposition.

Coated Pd/Al_2O_3 catalyst honeycombs were poisoned in SO_2-containing gas feed, and regenerated by short exposure to 2% H_2. These two treatments mimic the fuel-lean operating conditions of a natural gas combustion engine followed by a fuel-rich catalyst regeneration step. Honeycomb catalysts with different degrees of sulphur poisoning, representative of variable time on stream, were then studied by hard X-ray holotomography at multiple length scales at ID16A. The 3mm long samples were prepared manually for measurements, extracting from inlet and outlet regions of whole washcoated monolith to validate the observed decrease in catalyst performance as tested in our home laboratory. Holotomography was used first for a macroscopic view of 280 x 280 μm^2, followed by zooming in to specific regions of interest of 50 x 50 to 100 x 100 μm^2 (e.g. honeycomb carrier, interface of catalyst/carrier, different catalyst washcoat depths and positions along the monolith channel) at 17.1 keV to directly image features such as macropores, mechanical integrity, and the distribution of such features in 3D space. This consisted of 'high throughput imaging' with a high resolution, allowing us to measure 10 samples that can be used to compare the effect of different time on stream poisoning and regeneration on the structure of the technical catalysts.

The structure of the samples could easily be resolved in the images collected as shown in Figure 1. depicting a clear contrast between the different parts i.e. washcoat, corderite and pores. The phase shift obtained from this technique was used to calculate the electron densities using the formulaa given in Figure 1. Thus, each pixel corresponds to a certain value of electron density that very well differentiated between the alumina honeycomb, open pores and dense sulphur deposits.

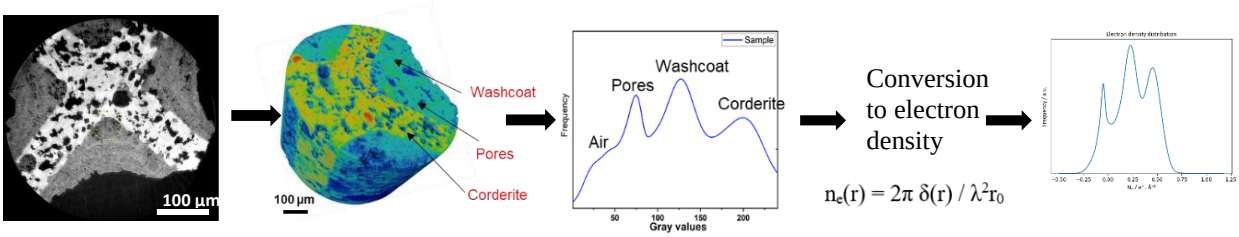

Figure 1. Methodology to obtain quantitative information from images

For preliminary analysis, different ROIs from the whole resonstructed volumes of tested and long poisoned samples were extracted as shown in Figure 2 and were compared for the variation in electron densities. We could interpret that sulphur deposition leads to structural changes in the washcoat that was also depicted by comparing different ROIs for same sample (Figure 3). The effect is non-uniform along the monolith channel, inlet being more poisoned than the outlet. Also, the electron density calculations confirm the structure regeneration after treatment in H_2- containing feed. These outcomes can serve as the basis for a more rational preparation of sulphur-resistant catalysts and facile catalyst regeneration.

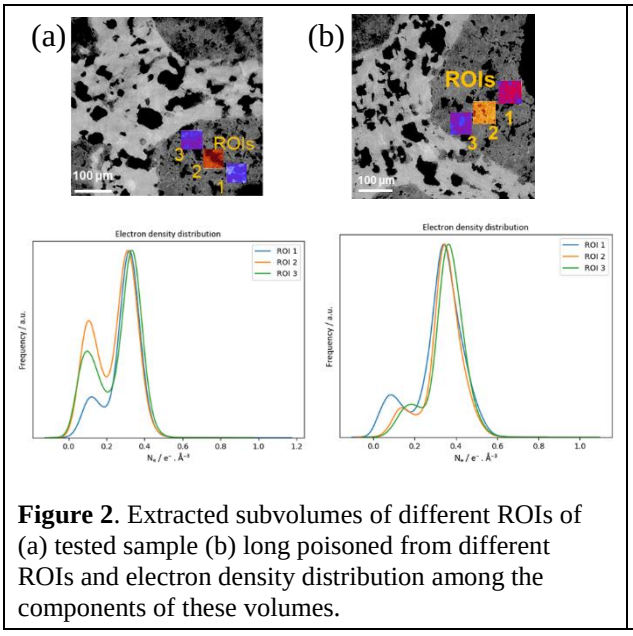

Figure 2. Extracted subvolumes of different ROIs of (a) tested sample (b) long poisoned from different ROIs and electron density distribution among the components of these volumes.

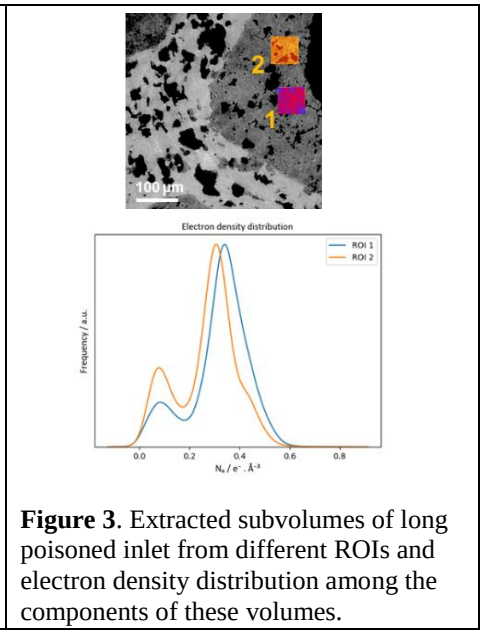

Figure 3. Extracted subvolumes of long poisoned inlet from different ROIs and electron density distribution among the components of these volumes.

A detailed analysis is needed to establish the effects of sulphur poisoning and regeneration on the structure of the technical catalysts. The direct comparison of catalytic activity measurements (performed at KIT) and tomographic data with a fresh reference catalyst, sulphur poisoned catalysts, and a H_2-pulse regenerated catalyst, will give valuable inside into the sulphur-poisoning process. The outcomes will serve as the basis for a more rational preparation of sulphur-resistant catalysts, e.g. by tuning the pore structure, washcoat thickness, and catalyst synthesis procedure to minimise sulphur poisoning and facilitate catalyst regeneration. We expect to publish the results together with our ESRF local contact, whose assistance was essential to ensure a successful experiment.

References

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