Highlight #3: METHODOLOGIES and DISORDERED AND MULTISCALE MATERIALS

Towards better industrial catalysts for reducing air pollution

Catalysts are materials that can promote chemical reactions. They can convert toxic components into non-toxic forms and play a fundamental role in cleaning up vehicle fuels. Nevertheless, optimization of industrial catalysts remains a challenge, mainly because they are relatively large multi-component bodies, consisting of active phases, supports, and additives. To better understand the relationships between their complex structure and their functionalities, it is crucial to characterize their inner structure with high resolution and high sensitivity. This also allows detection of defects or unexpected deposits of harmful materials, which can develop in a catalyst's structure during operation, thereby reducing its lifetime. For this purpose, we are developing Ptychographic X-ray Computed Tomography (PXCT), an emerging, non-destructive, 3D X-ray microscopy technique, which is revolutionizing the characterization of industrial catalysts.

The removal of sulphur from crude oil by hydro-desulphurization (HDS) is an essential catalytic process in the petroleum industry. It ensures production of clean refined-petroleum products, such as diesel, kerosene, and jet fuel. Especially It allows creation of ultra-low-sulphur diesel, which is critical to reducing the toxic sulphur dioxide (SO_2) emitted by trucks as well as automobiles.
To remove sulphur, the petroleum gas is forced under high pressure and high temperature through a support matrix, a highly porous material alumina (γ—Al_2O_3) that provides a very large interior surface area to carry the catalyst, the transition metals Molybdenum (Mo) and Nickel (Ni), which forms slabs of "NiMo". However, the effectiveness of this procedure depends on the microstructure of the HDS catalysts used in the oil refinery, which determines the accessibility of reactants to the active catalyst sites on the interior of the porous matrix.

Characterization of this microstructure is needed to differentiate the various zones of the sample. We have used Ptychographic X-Ray Computed Topography (PXCT) to characterize a series of HDS catalysts, at the Swiss synchrotron (the Swiss Light Source). PXCT combines ptychography (from the Greek: πτηξ= fold and: γραφη= writing) and computed tomography to obtain 3D imaging of the microstructure of our materials. In ptychography, the sample is scanned by a spatially-restricted highly coherent X-ray beam across a grid of partially overlapping target spots. This allows retrieving the phase shifts using advanced algorithms and enables us to achieve nanoscale spatial resolution independent of the X-Ray probe size. In PXCT, a ptychography experiment is repeated at each angle over 180 degrees-rotation of the sample. Afterwards, the phase-retrieved 2D images are combined into tomographic reconstruction algorithms to yield 3D images. We achieved a spatial resolution of about 50 nm with a voxel (volume pixel) size of 30 nm.

By probing the inner microstructure of an industrial alumina carrier: unloaded, loaded with a Mo catalyst, and loaded with both Mo and Ni catalysts, we obtained a wide range of valuable information about the carrier's porous structure and the distribution of the catalysts. Especially, and surprisingly, this work revealed a build of the alumina carrier consisting of two interwoven phases of the alumina matrix differing in the size of their nanopores regardless of the catalyst loading.

This first-time observation of a two-phase build of the alumina carrier has the potential to deepen our understanding of a wide range of hydroprocessing catalysts. Our results should enable further calculations of reactant diffusivities in the carrier's pores, and guide manufacturing methods to obtain a better distribution of the NiMo active phase in next-generation HDS catalysts.

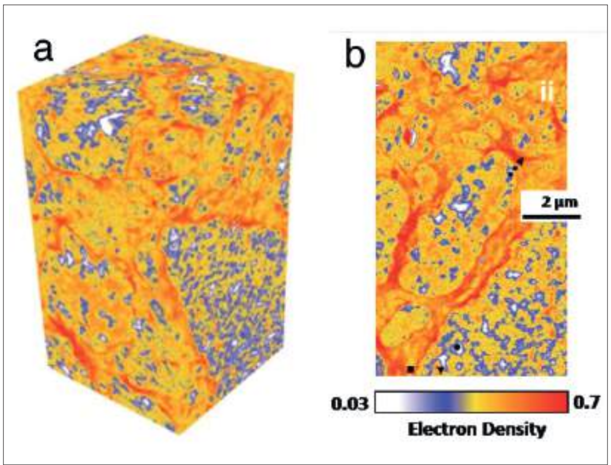

Fig.: *(a) A region of a 3D image, obtained by PXCT, of the electron density inside a sample of a Nickel-Molybdenum hydro-desulphurization catalyst.*
(b) A 2D image, which is a vertical cut through the electron-density volume of (a).
The Ni-Mo catalyst lies inside the nanoscale pores of an Al_20_3 support material. The colour scale-bar represents the electron density in units of electrons per angstrom cubed. These colours correspond to the fraction of air, Al_20_3 support and Ni-Mo catalyst in each 30 nm "voxel" (3D pixel). The less dense, most porous material, which contains much air, appears towards white, while the densest alumina and catalyst materials appear closer to red.

Reference

J. Ihli, L. Bloch, F. Krumeich, K. Wakonig, M. Holler, M. Guizar-Sicairos, T. Weber, J.-C. da Silva, & J.-A. van Bokhoven, "Hierarchical Structure of NiMo Hydrodesulfurization Catalysts Determined by Ptychographic X-ray Computed Tomography", *Angew. Chem. Int.* 59, 17266 (2020).