Full 3D-XRF-tomography of catalyst particles using the Maia detector at P06

U. Boesenberg, F. Meirer,[1] S. Kalirai,[1] B.M. Weckhuysen,[1] M. Alfeld, G. Falkenberg

Deutsches Elektronen- Synchrotron DESY, Notkestr. 85, 22607 Hamburg, Germany

[1] Inorganic Chemistry and Catalysis, Utrecht University, Universiteitsweg 99, 3584 CG Utrecht, The Netherlands

Catalysis is the backbone of modern gasoline production, converting crude oil into usable transportation fuels via a 'cracking' process. During this 'cracking' heavy oil fractions, i.e. large molecules, are split into lighter (smaller molecules), more valuable products. For this, multi-component catalyst particles, consisting of active Zeolite material embedded in a matrix of clay, silica, and alumina are used. One important issue is 'aging' of these particles, observed as a decrease of the 'cracking' capability with time. This deactivation is directly linked to the accessibility of the particle for oil molecules, which need to reach the catalytically active zones within. Therefore an understanding of the complexity of catalyst deactivation at the single particle level is mandatory. The localization and change in the distribution of poisoning elements in the feedstock, such as Ni and Fe, especially in correlation with structural information, will give valuable insight about the degradation behavior.

High resolution X-ray fluorescence (XRF) tomography correlates the distribution of multiple elements inside the structures of interest, meaning that the distribution of different elements such as e.g. Fe, Ni, La, Ca can be acquired in a single measurement. This reduces measurement time and also facilitates processing, since sample alignment and corrections for sample drift only have to be performed once. Furthermore, XRF is sensitive to trace elements and therefore the distribution of elements in low concentrations, which would be below the detection limit even in a dedicated absorption tomography, can be determined.

To collect full 3 dimensional data sets with micro-XRF, both fast data acquisition and streamlined processing are mandatory. The newly integrated Maia detector system at P06 allows for count rates exceeding exceeding 10^7 photons/s and pixel transit times as small as 50 µs [1,2]. The integrated routine for online data analysis via Dynamic Analysis [3] allows easy optimization of the measurement parameters as well as close monitoring. The experiments were performed in the micro-endstation of P06. A KB mirror system was used to focus the beam down to 500x500 nm^2 at an incident energy of 10keV. Integrated readout of the encoder positions ensures accurate localization of each pixel. Particles of approximately 50µm in diameter were imaged as "projections" and the combination of 180 projection images used for tomographic reconstruction of each element. Such a tomographic measurement took approximately 8h with a resolution of about 1µm in the reconstructed datasets. A dwell time of 1ms was used for each pixel. Simultaneous acquisition of the primary beam signal was used to normalize for fluctuations in the incoming beam. The software suite GeoPIXE[4] was used to analyse and fit the XRF spectra of each pixel, the software suite of the TXMWizard [5] was used for alignment and tomographic reconstruction of the dataset.

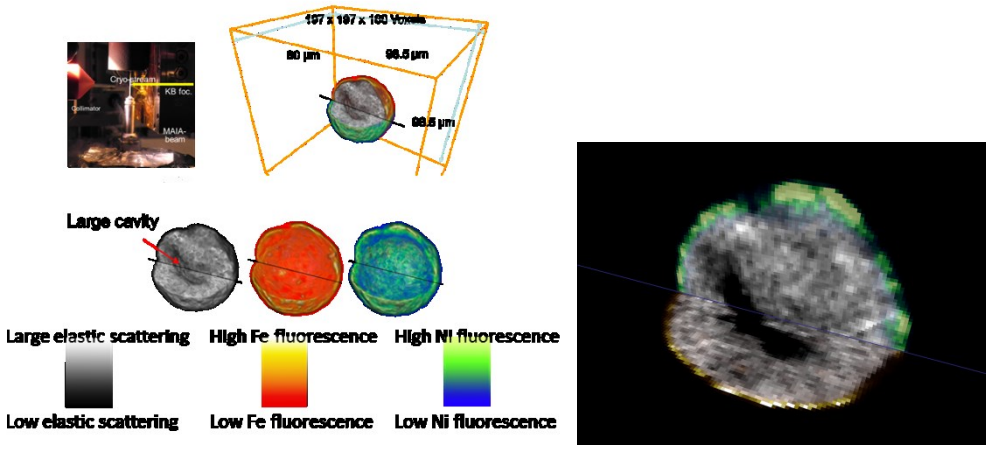

Figure 1: Setup of the experiment at the P06 micro-endstation and the results from tomographic reconstruction of an aged catalyst particle for multiple elements and the elastic scattering (structural information)

The results show a high concentration of Fe and Ni at the surface but Fe shows a higher minimum concentration within the particle in comparison to Ni; this is due to its presence in the particle matrix (clay). It is obvious that Fe introduced by the feedstock is mainly deposited at the surface of the particle. In contrast, Ni penetrates deeper into the particle which can be explained by a higher mobility of the Ni containing species in the feedstock. The signal of the elastic scattering was used for reconstruction of the microstructure, revealing pores and in this case, a large cavity in the center of the particle. For the future we envision a combination of multi-element XRF data with high resolution ($50nm^3$) full-field X-ray microscopy to reveal structural properties with even higher resolution and correlate structural changes due to the presence of metals (e.g. pore clogging).

References

[1] C.G. Ryan, et al., Nucl. Instrum. Methods Phys. Res., Sect. A, **619**, 37 (2010).
[2] C.G. Ryan, et al., Proc. SPIE, **8851,** 88510Q (2013).
[3] C.G. Ryan, et al., Nucl. Instrum. Methods Phys. Res., Sect. B, **104**, 157 (1995).
[4] C.G. Ryan, D.R. Cousens, S.H. Sie, W.L. Griffin, G.F. Suter, E. Clayton, Nucl. Instr. and Meth. B 47 (1990) 55
[5] Y. Liu, F. Meirer, P.A. Williams, J. Wang, J.C. Andrews and P. Pianetta, J. Sychrotr. Rad. **19**, 281 (2012).