	Experiment title: 3D micro-tomographic investigations of shaped catalyst objects	**Experiment number**: CH-5610/IH-CH-1192
Beamline: ID15A	**Date of experiment**: from: 2/5/2017 to: 8/5/2017	**Date of report**: 10/9/2020
Shifts: 18	**Local contact(s)**:Marco Di Michel	*Received at ESRF:*

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Report:

Abstract/figures from manuscript to be submitted: We have used *operando* X-ray diffraction computed tomography (XRD-CT) analysed by rigorous crystallographic methods to reveal the behaviour of an industrial-type methanol-to-hydrocarbon catalyst extrudate under working conditions. The cylindrical extrudate is deactivated during the process by filling with coke from the outer surface towards the core, a process we have fitted with a kinetic model. However, both the operando experiment and post mortem XRD-CT of fully deactivated extrudates from a test reactor show clearly that the core of the catalyst body, around 1/3 of its volume, remains completely untouched by the reaction, even when the reactor output indicates zero activity. Our findings suggest that catalyst efficiency could be significantly improved by more effective structuring of the extrudates.

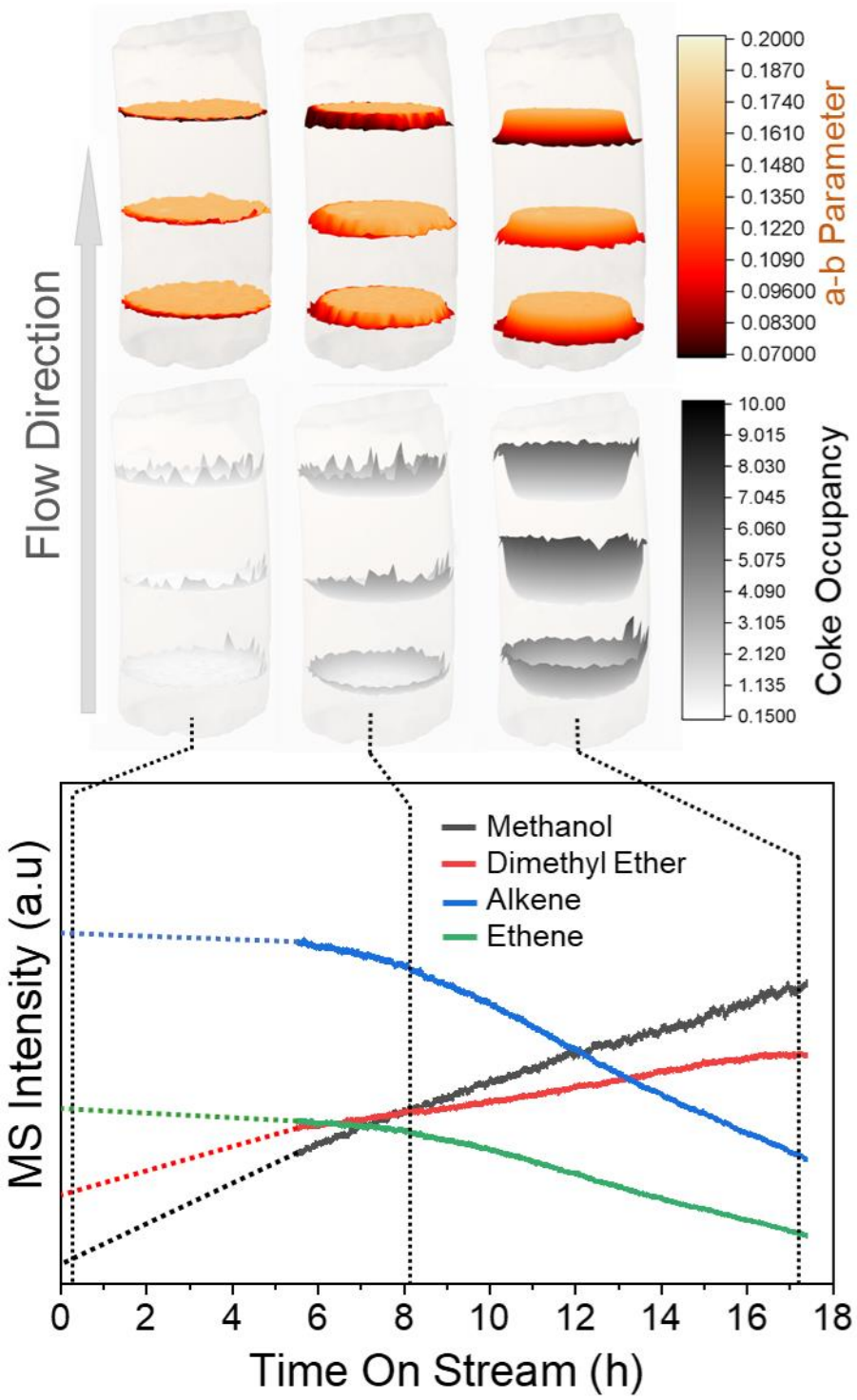

Figure 1. Mapping the coke formation within a zeolite catalyst extrudate in space and time by *operando* computed X-ray diffraction tomography. Top and middle: Tomograms showing the evolution in the *a-b* parameter and the degree of coking with increasing reaction time, respectively. Bottom: Mass spectrometry traces showing the catalyst activity and deactivation with increasing reaction time. Black = methanol, m/z 31; red = DME, m/z 45, green = ethene, m/z 28; blue = higher alkenes (C3 and above), m/z = 41. The first 5.5 h of data have been retrospectively extrapolated due to technical challenges with the MS during synchrotron experiment, and are consistent with similar experiments carried out in our catalyst test lab. The reaction conditions were WHSV = 12 g_{MeOH} $g_{extrudate}^{-1}$ h^{-1} and 440 °C.

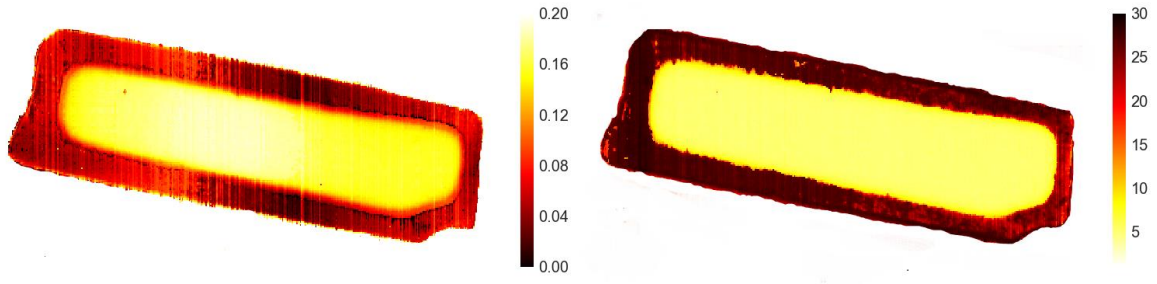

Figure 2. XRD-CT slices through a horizontally mounted extrudate. Left: The *a*-*b* parameter for a severely deactivated extrudate. Right: The degree of coking from the residual electron density. ZSM-5/alumina extrudates were deactivated *ex situ* at WHSV = 12 g_{MeOH} $g_{extrudate}^{-1}$ h^{-1} and 400 °C prior to XRD-CT analysis. Note that as around ¾ of the catalyst body is not used (pristine), the WHSV calculated on the total catalyst mass is not accurate.

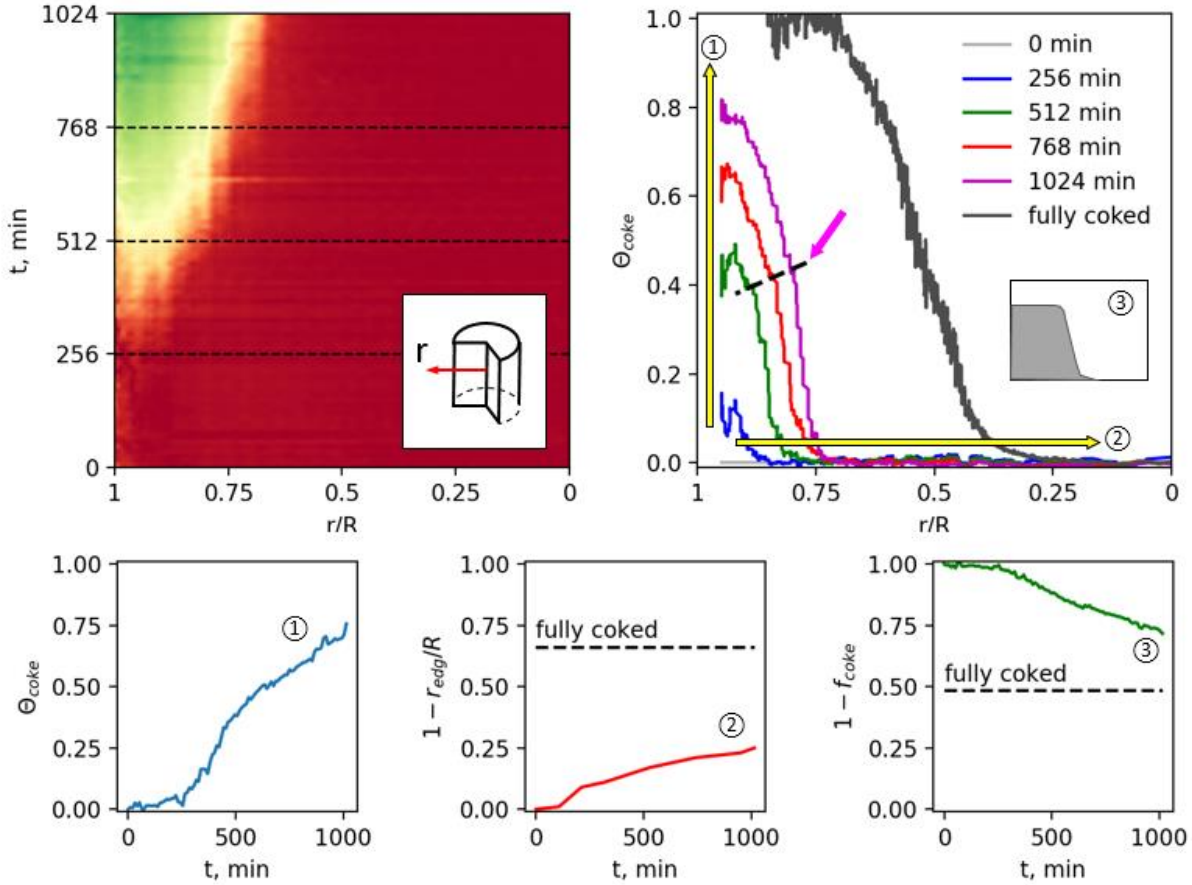

Figure 3. Top: Angle-averaged radial coke profiles from XRD-CT for the topmost slice of the catalyst extrudate. (Left) An overview of the central angle averaged coke content (orange – low, green - high) as a function of normalized radial coordinate (x-axis, r/R) and time (y-axis, t). (Right) Radial coke profiles at selected time points (indicated as black dashed lines on the left) along with the profile for a fully coked extrudate (black). Yellow

arrows are shown to guide the eye in the directions of coke growth, while the pink arrow points to the highly non-linear features of the coking profile (slope change). Bottom: Temporal evolution of coke content in the catalytic extrudate: (left) relative coke content within the outermost extrudate shell (see vertical arrow in the top right panel), (middle) relative radial position of the coking front (see horizontal arrow in the top right panel), (right) relative coke-free fractional volume of the catalyst extrudate. All data are normalized to the maximal amount of coke in the fully-deactivated extrudate.