Real-time regeneration of a working zeolite monitored *via operando* X-ray diffraction and crystallographic imaging: How coke flees the MFI framework

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1. Basic material characterization

a) Brønsted acidity, Si/Al ratio

Table S1. Si/Al ratio and Brønsted acidity for the H-ZSM-5 sample.

Sample	Si/Al*	Brønsted Acidity (mmol/g)**
H-ZSM-5	37	0.416

* Determined by in-house ICP analysis.
**Determined by in-house FTIR measurements.

b) Textural properties defined by N_2 physisorption and SEM.

Table S2. Summary of the BET surface area, external surface area, total pore volume and micropore volume of the H-ZSM-5 system as calculated by the N_2 physisorption measurements. The particle size has been averaged from SEM images.

	N_2 physisorption				SEM
Sample	BET (m^2g^{-1})	External area (m^2g^{-1})	Total pore volume (cm^3g^{-1})	Micropore volume (cm^3g^{-1})	Particle size (μm)
H-ZSM-5	414	4	0.20	0.18	2-4

c) Scanning Electron Microscopy (SEM)

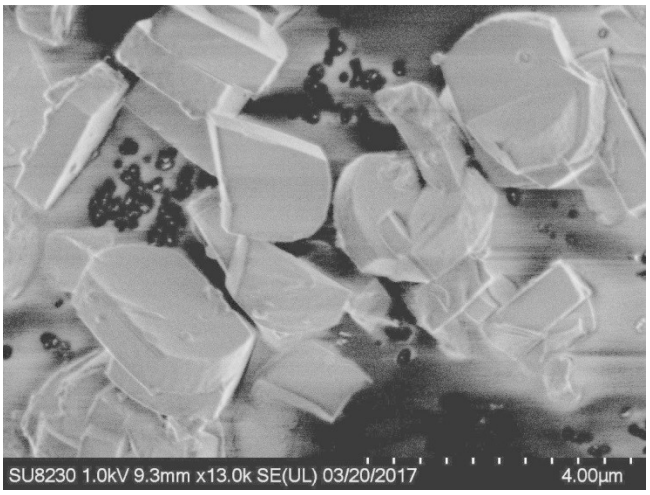

Figure S1. SEM image of the H-ZSM-5 sample.

2. MTG monitored *via operando* PXRD

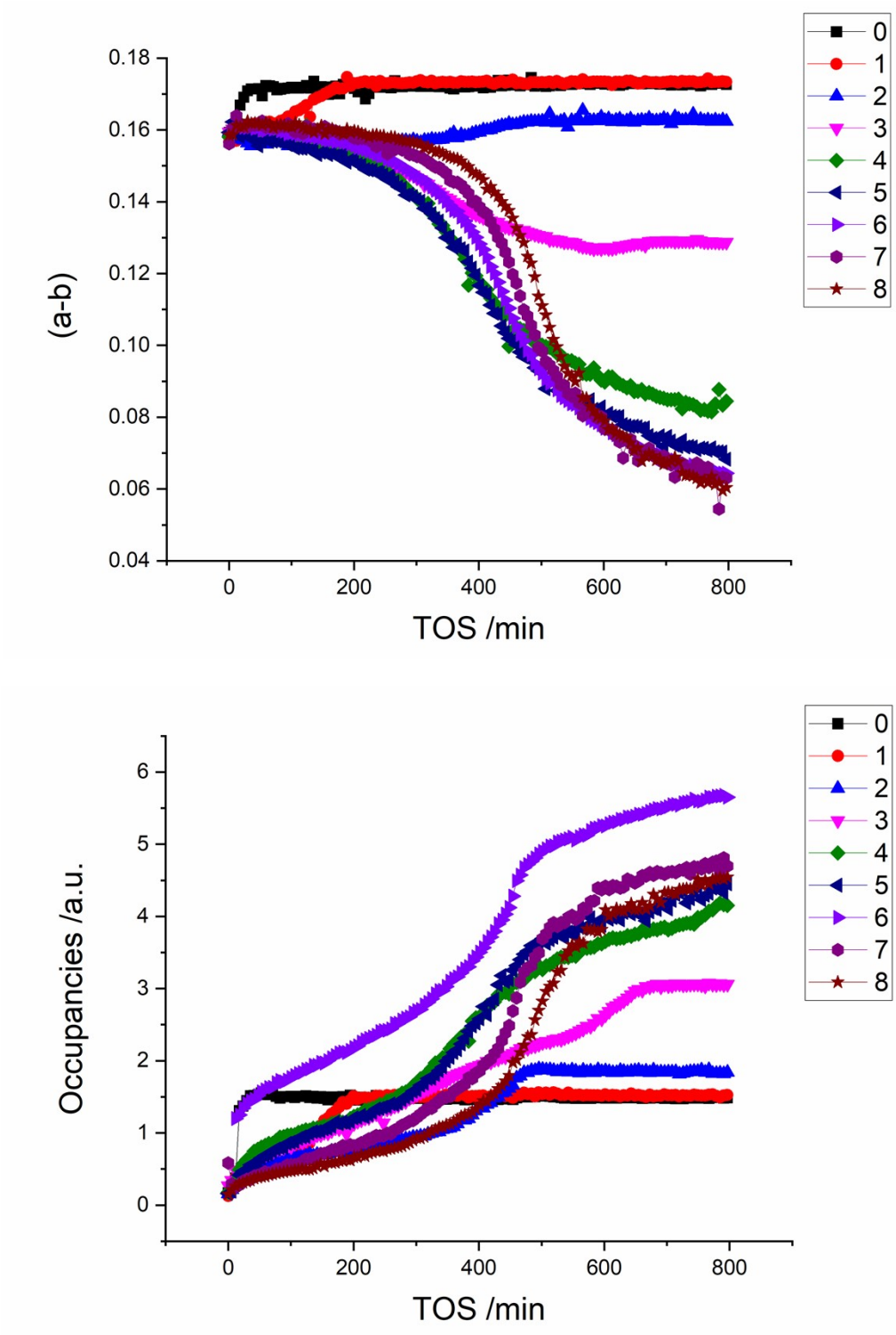

Figure S2. The *a* minus *b* parameter for the different layers of the catalytic reactor at increasing TOS (top). The total coke occupancies at increasing reaction times for the 10 reactor slices (bottom).

3. Temperature-programmed oxidation (TPO) monitored *via operando* XRD
   a. MS signal for CO_2, evolution of the (*a*-*b*) parameter and unit cell volume evolution at increasing TOS for the H-ZSM-5 catalyst

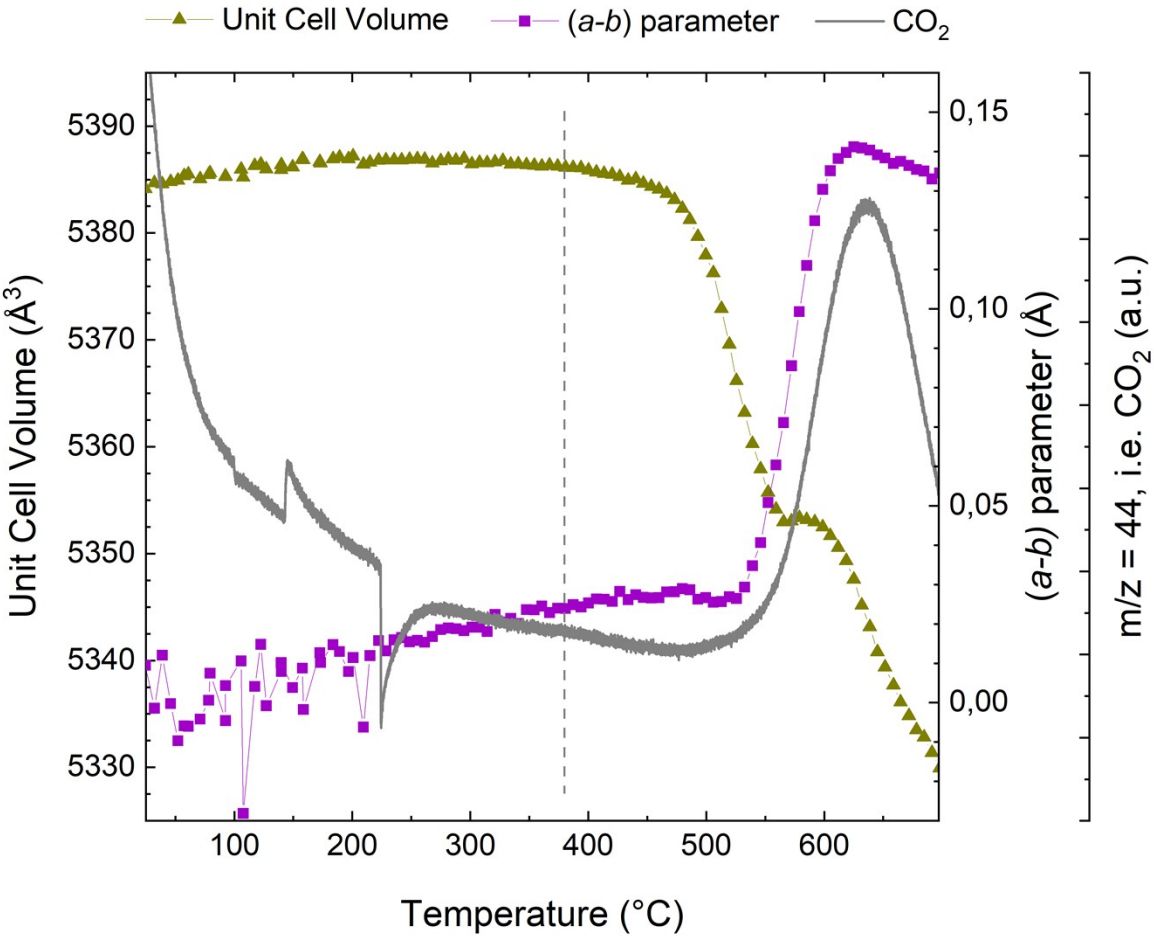

Figure S3. MS signal for CO_2, evolution of the (a-b) parameter and unit cell volume evolution at increasing TOS for the H-ZSM-5 catalyst. The vertical dashed line indicates the data selected for Figure 2 in the main manuscript.

b. Full scale evolution of individual coke occupancies within the H-ZSM-5 framework at increasing TOS and increasing temperature for the H-ZSM-5 catalyst.

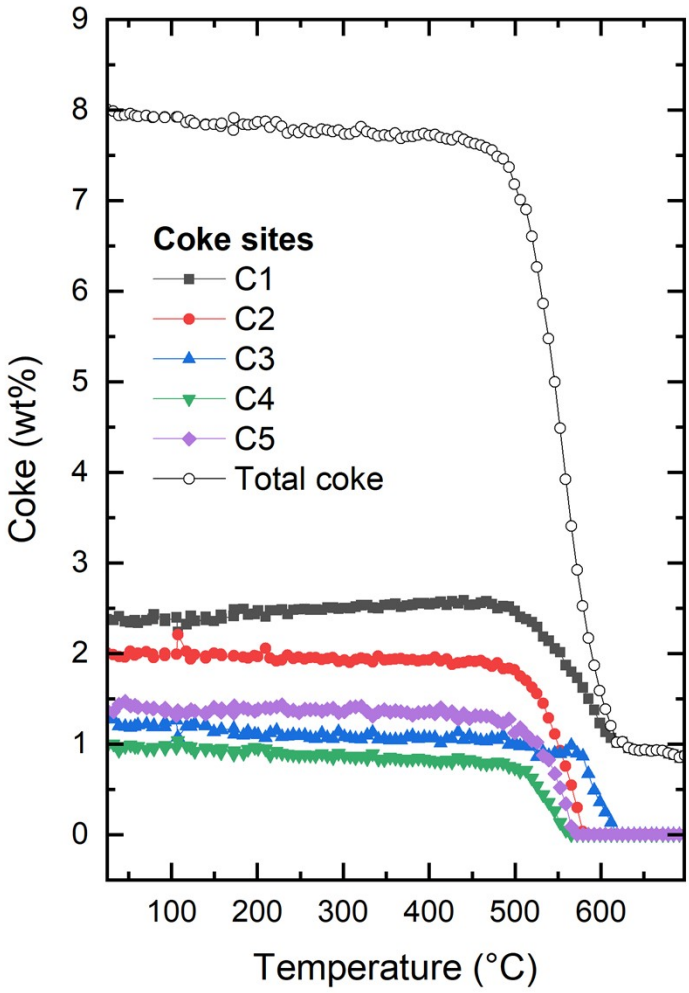

Figure S4. Full scale evolution of total coke and individual coke site occupancies within the H-ZSM-5 framework at increasing temperature.

c. Preferred sites of coke accumulation within the MFI framework.

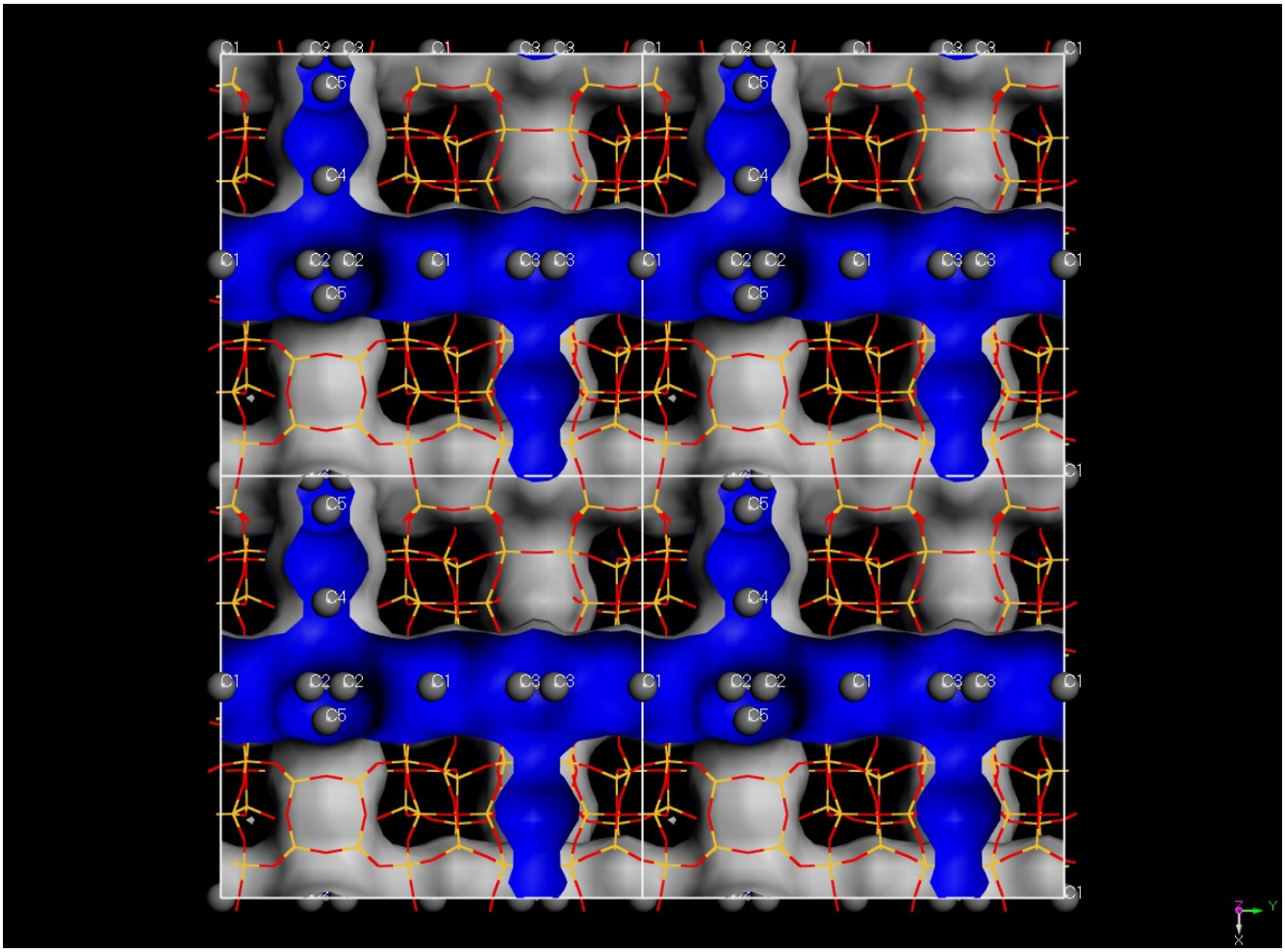

Figure S5. Preferential residing sites of coke in the straight channel and intersections of the MFI framework. The sites have been identified by extra-framework electron density distribution in the framework calculated by difference Fourier maps analysis during the Rietveld refinement analysis in TOPAS.

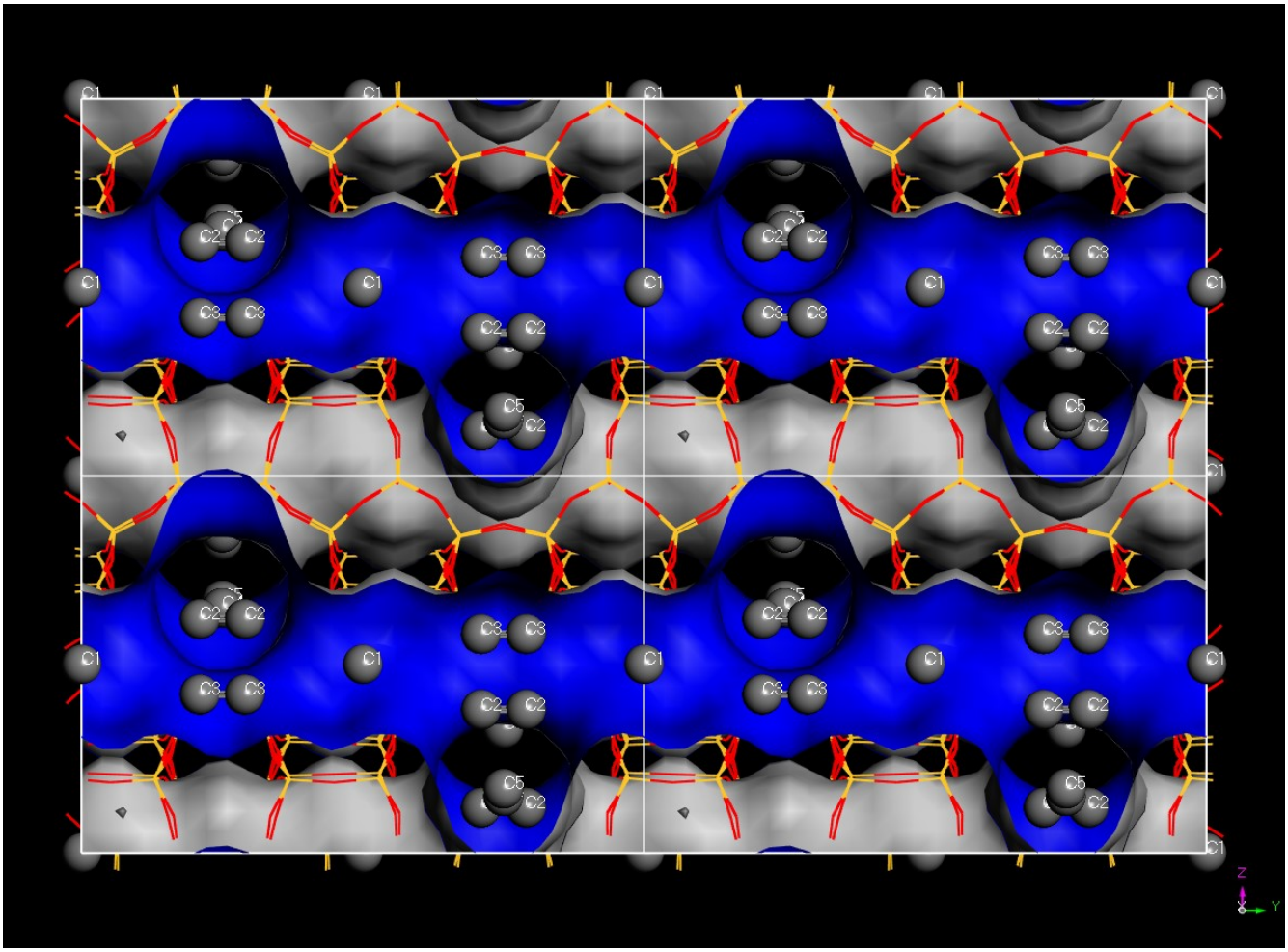

Figure S6. Preferential residing sites of coke in the straight channel and intersections of the MFI framework. The sites have been identified by extra-framework electron density distribution in the framework calculated by difference Fourier maps analysis during the Rietveld refinement analysis in TOPAS.

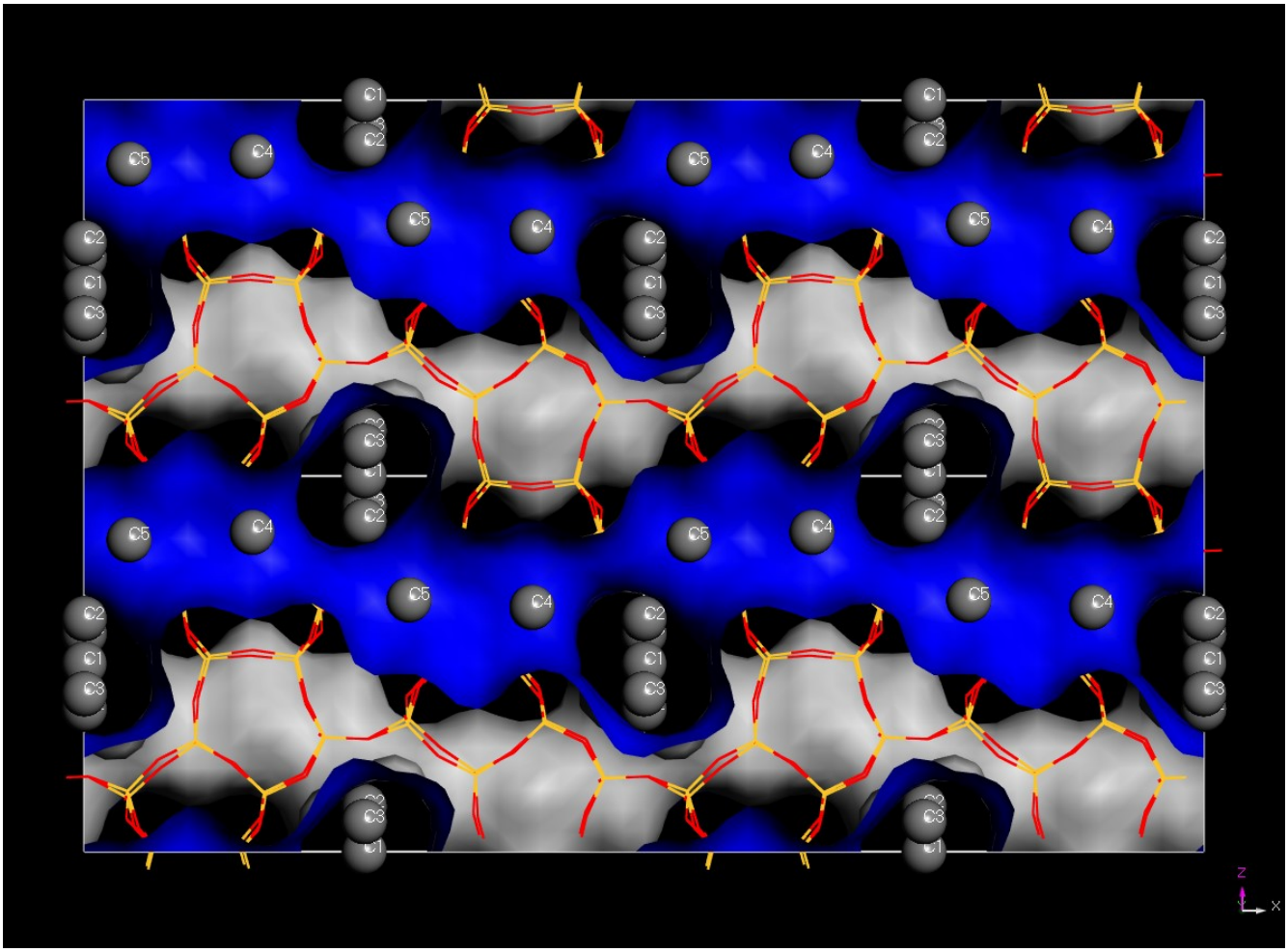

Figure S7. Preferential residing sites of coke in the zig zag channels and intersections of the MFI framework. The sites have been identified by extra-framework electron density distribution in the framework calculated by difference Fourier maps analysis during the Rietveld refinement analysis in TOPAS.

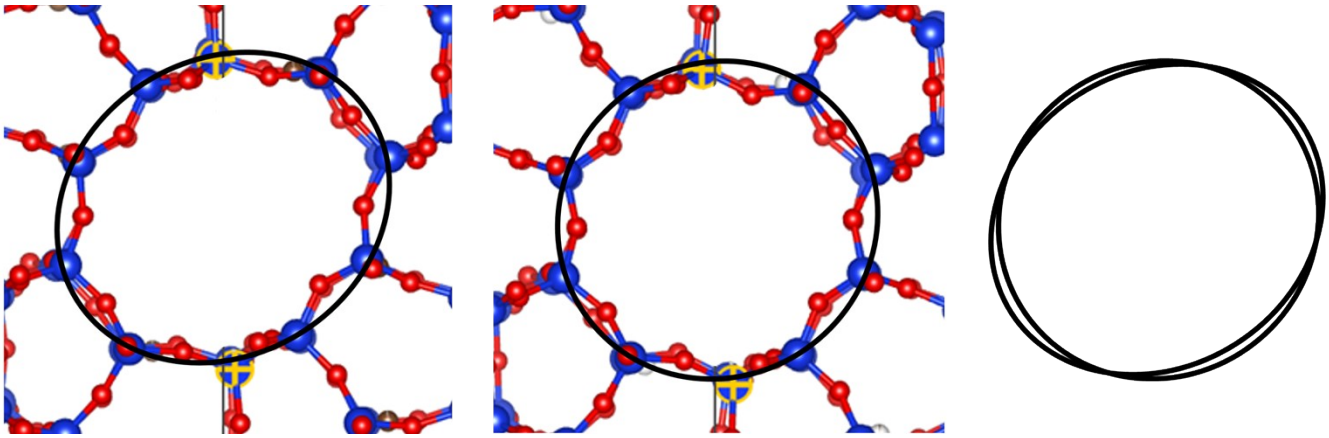

Figure S8. Detail highlighting the transition from an oval pore circumference of the straight channel to a more circular circumference upon coke removal. Left panel: Channel shape at 405 °C, i.e. fully coked. Middle panel: Channel shape at 625 °C, i.e. after removal of all coke by oxidation. Right panel: Overlay of the ovals used to outline channel shape in the two other panels.