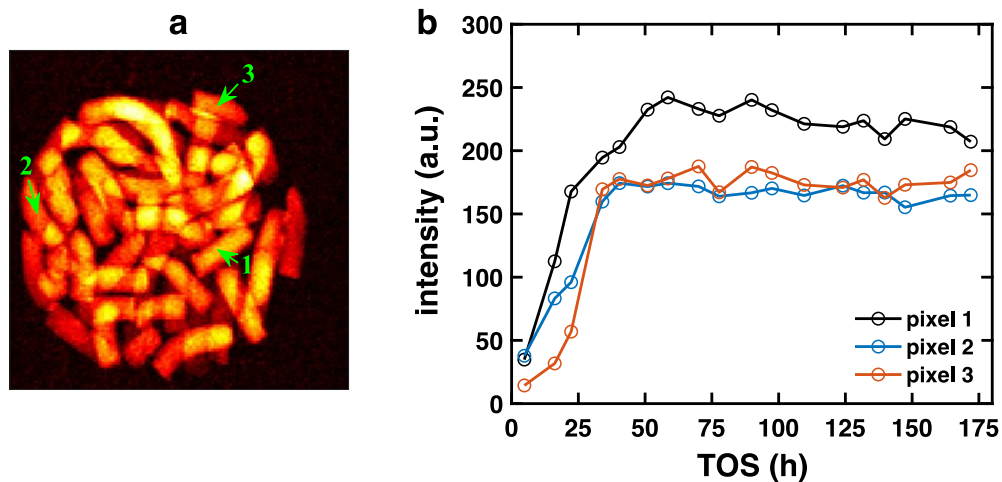


Operando magnetic resonance imaging of product distributions within the pores of catalyst pellets during Fischer–Tropsch synthesis

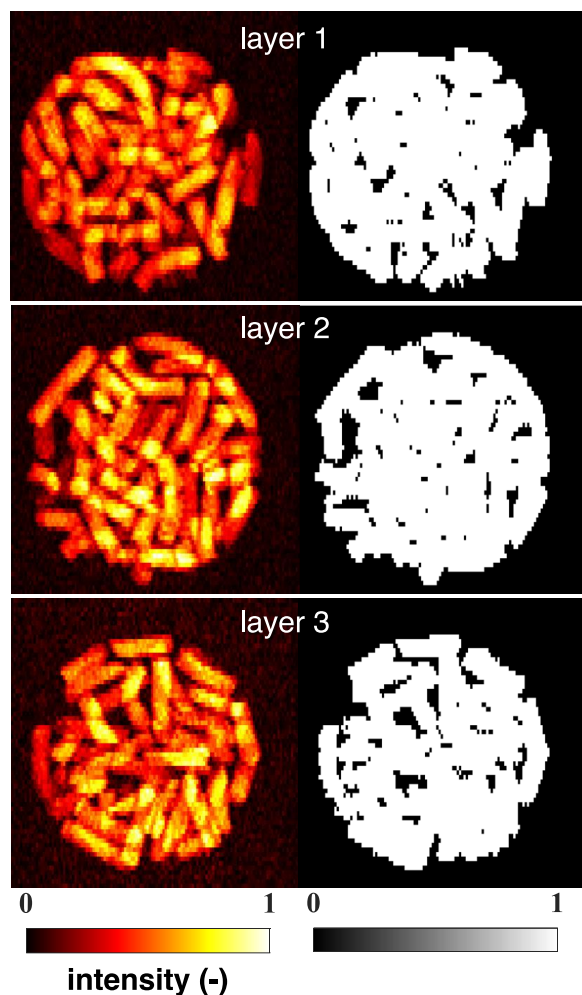
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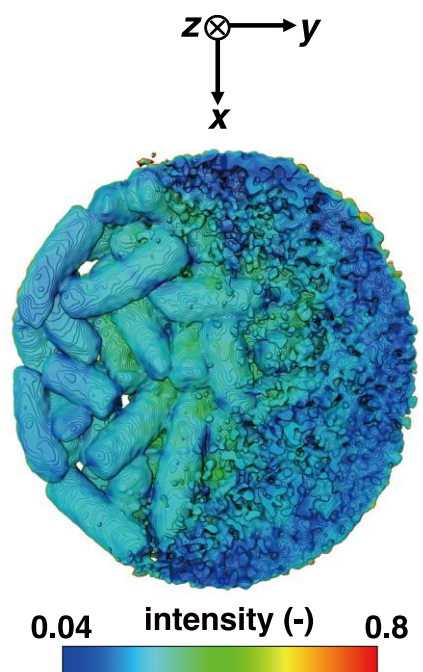
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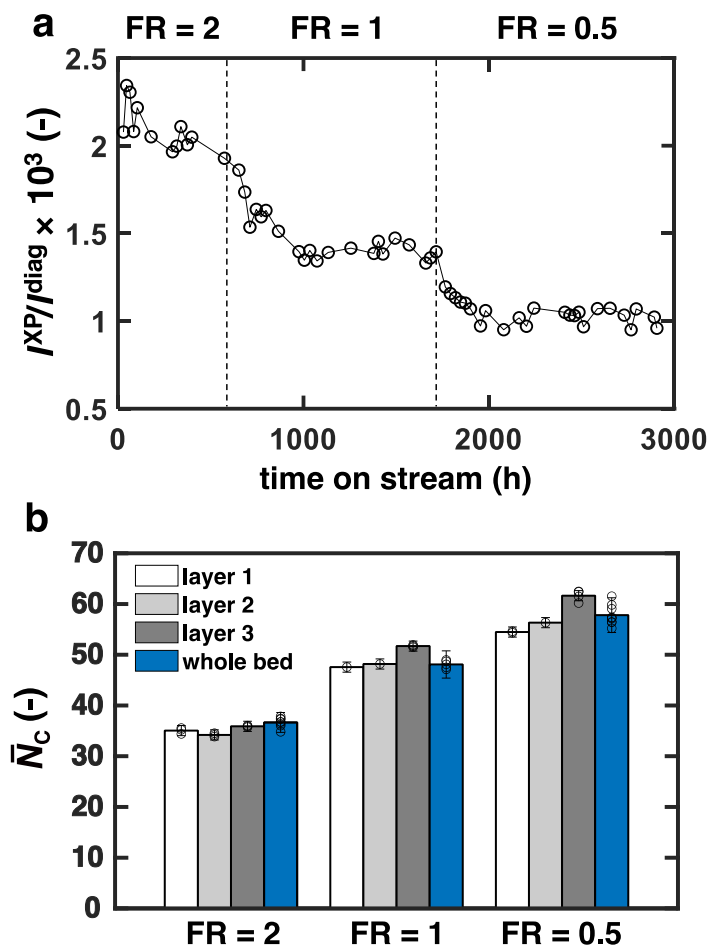
Supplementary Figure 1. Pore filling in intra-pellet pixels. (a) 2D ^1H intensity image of catalyst layer 1 acquired at TOS = 51 h in which 3 intra-pellet pixels (1-3) are identified. (b) Variation of signal intensities with time in the 3 selected pixels identified in (a), showing that the catalyst pores are saturated after TOS $\sim$ 50 h.



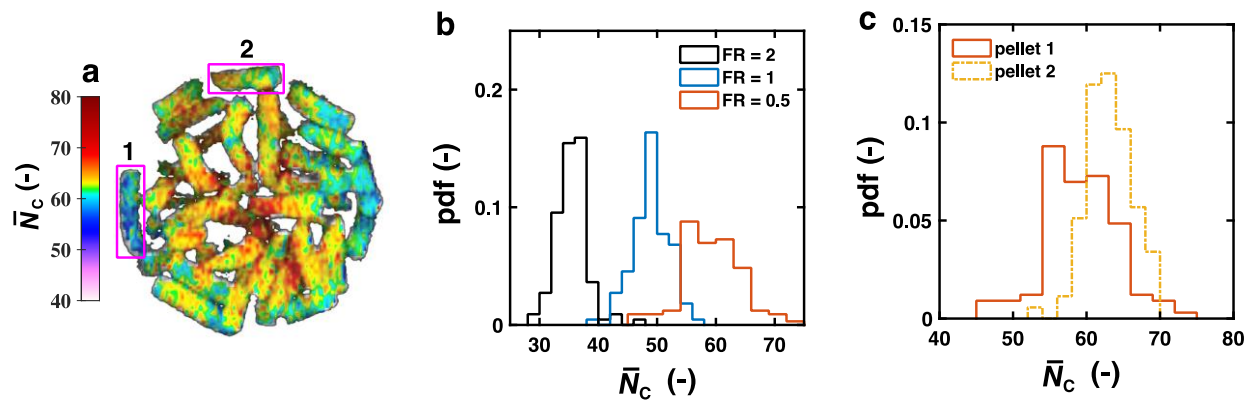
Supplementary Figure 2. Creation of masks for selecting intra-pellet pixels. 2D ^1H intensity images of the 3 catalyst layers acquired at pore saturation, when the pores are saturated by liquid while the liquid accumulation in the inter-pellet space is negligible. The binary images created using the intensity images are shown and they are used as the masks to discriminate intra- and inter-pellet spaces. The imaging parameters are the same as for the images in Fig. 3a.



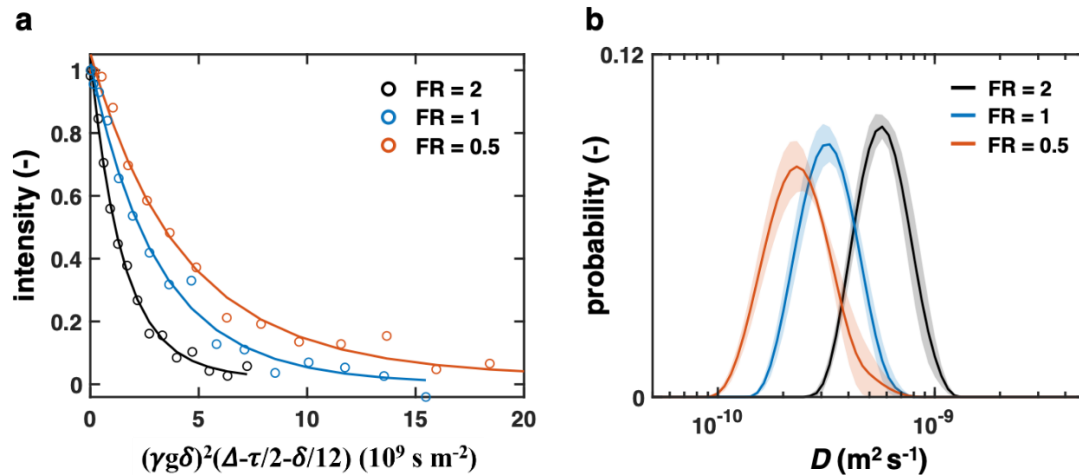
Supplementary Figure 3. Maldistribution of liquid above catalyst layer 1. Top view of the 3D image of the reactor acquired at steady state for a feed ratio of 1. The imaging parameters are the same as for Fig. 2. The liquid maldistribution could arise from factors such as bed structure or channelling of the feed gas mixture at the reactor entrance.



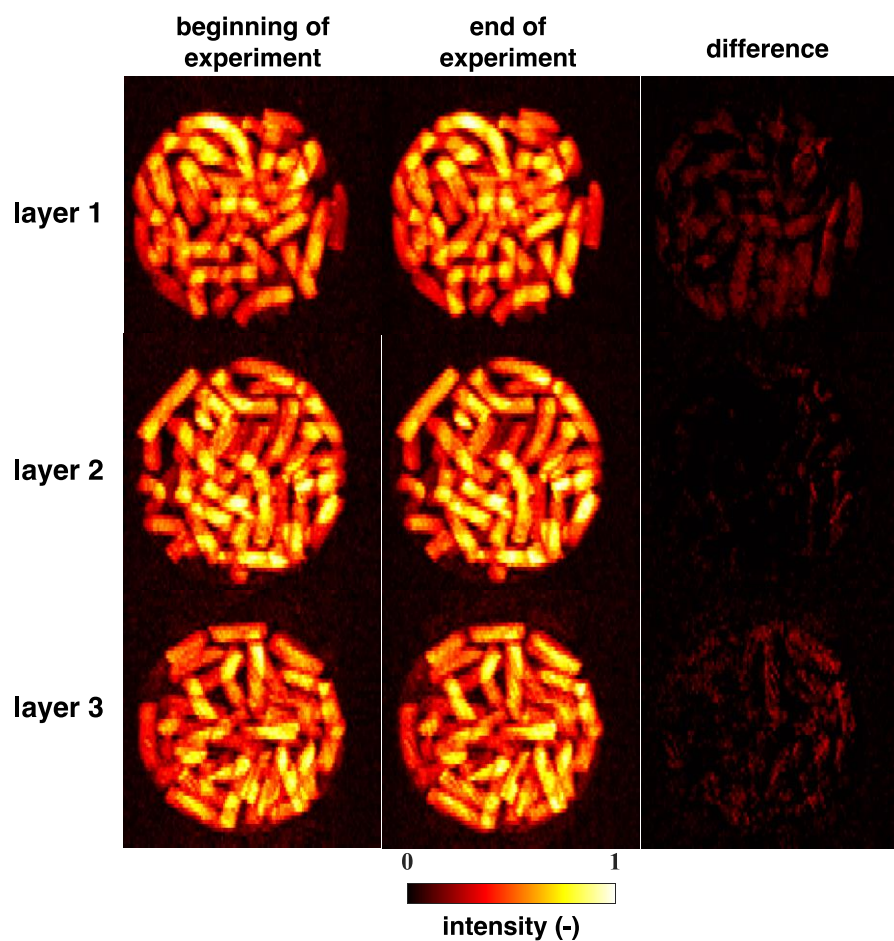
Supplementary Figure 4. Average carbon numbers determined by 2D NMR. (a) Ratio between intensities of the cross peak and diagonal peak of 2D DQF-COSY and COSY spectra acquired throughout the experiment. The decrease in the intensity ratios indicates an increase in product carbon number. (b) Comparison between the average carbon number, $\bar{N}_C$, for the whole catalyst bed determined by 2D NMR and the $\bar{N}_C$ for the 3 catalyst layers determined based on measurement of molecular diffusion. The error bars indicate standard errors (SE) estimated using repeat measurements and the data are presented as mean values $\pm$ SE. The errors of the $\bar{N}_C$ obtained based on diffusion coefficients are estimated using 3 repeat measurements ($n = 3$). The errors for the $\bar{N}_C$ obtained based on 2D NMR spectra are estimated by considering both the errors of the fit parameters in equation (3) and the errors associated with the 2D NMR experiments (Error analysis in Methods). The experimental errors are estimated using repeat measurements with $n = 8, 5$ and 9 for feed ratios of $2, 1$ and 0.5 , respectively.



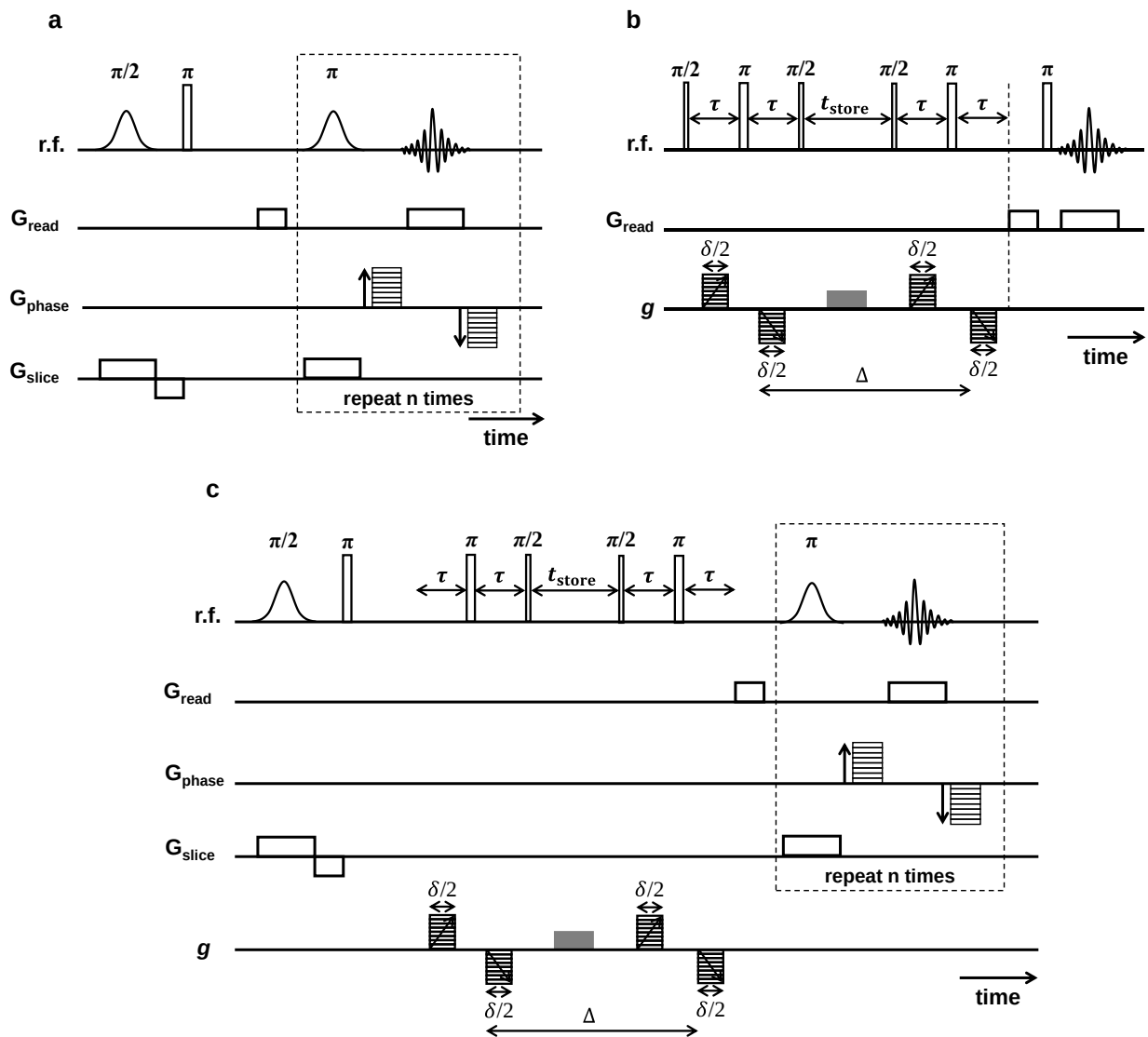
Supplementary Figure 5. Distributions of average carbon number in individual pellets. (a) Intra-pellet $\bar{N}_C$ map of catalyst layer 3 acquired at a feed ratio of 0.5 in which two pellets are identified. The results for pellet 2 are shown in Fig. 6. (b) Pdfs of the $\bar{N}_C$ from within pellet 1 for the three feed ratios. (c) Comparison between the pdfs of $\bar{N}_C$ in pellets 1 and 2 measured at FR = 0.5.



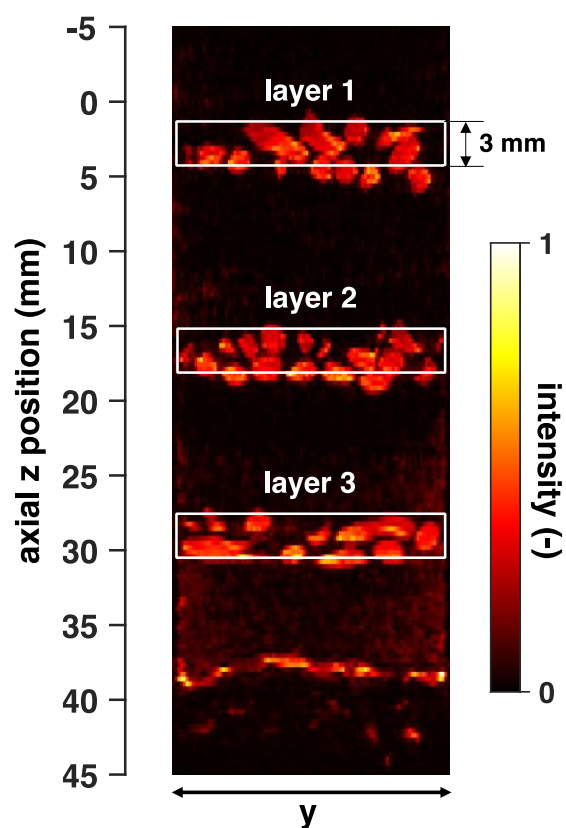
Supplementary Figure 6. Analysis of the diffusion data from a single pixel. (a) PFG signal decays from the single pixel identified in Fig. 6a, acquired at the 3 feed ratios. The solid lines indicate the regularisation fit to the data. (b) Distributions of diffusion coefficient D obtained by inverse Laplace transformation of the data in (a). The shadow regions in (b) indicate the standard errors (SE) of the distributions estimated using 3 repeat measurements ($n = 3$). The data are presented as mean values $\pm$ SE.



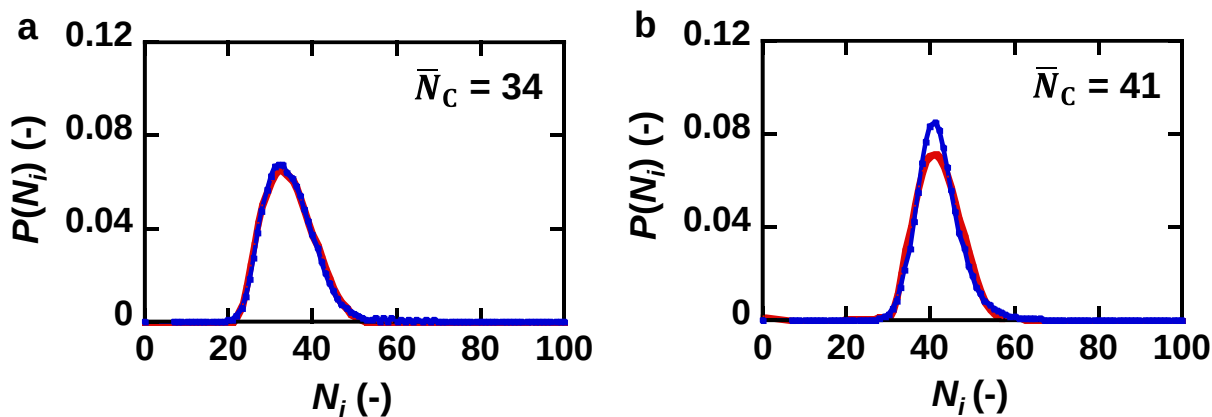
Supplementary Figure 7. Confirmation of no change of bed structure and position. The first two columns from the left show the 2D ^1H intensity images acquired towards the beginning (TOS = 500 h) and end of the series of experiments performed in this work (TOS = 3000 h). The third column shows the difference between the first two columns. These images confirm no change in bed position and structure. The slight variation of signal intensity between the images shown in the first two columns is the result of a slight change in liquid accumulation at the two different times-on-stream.



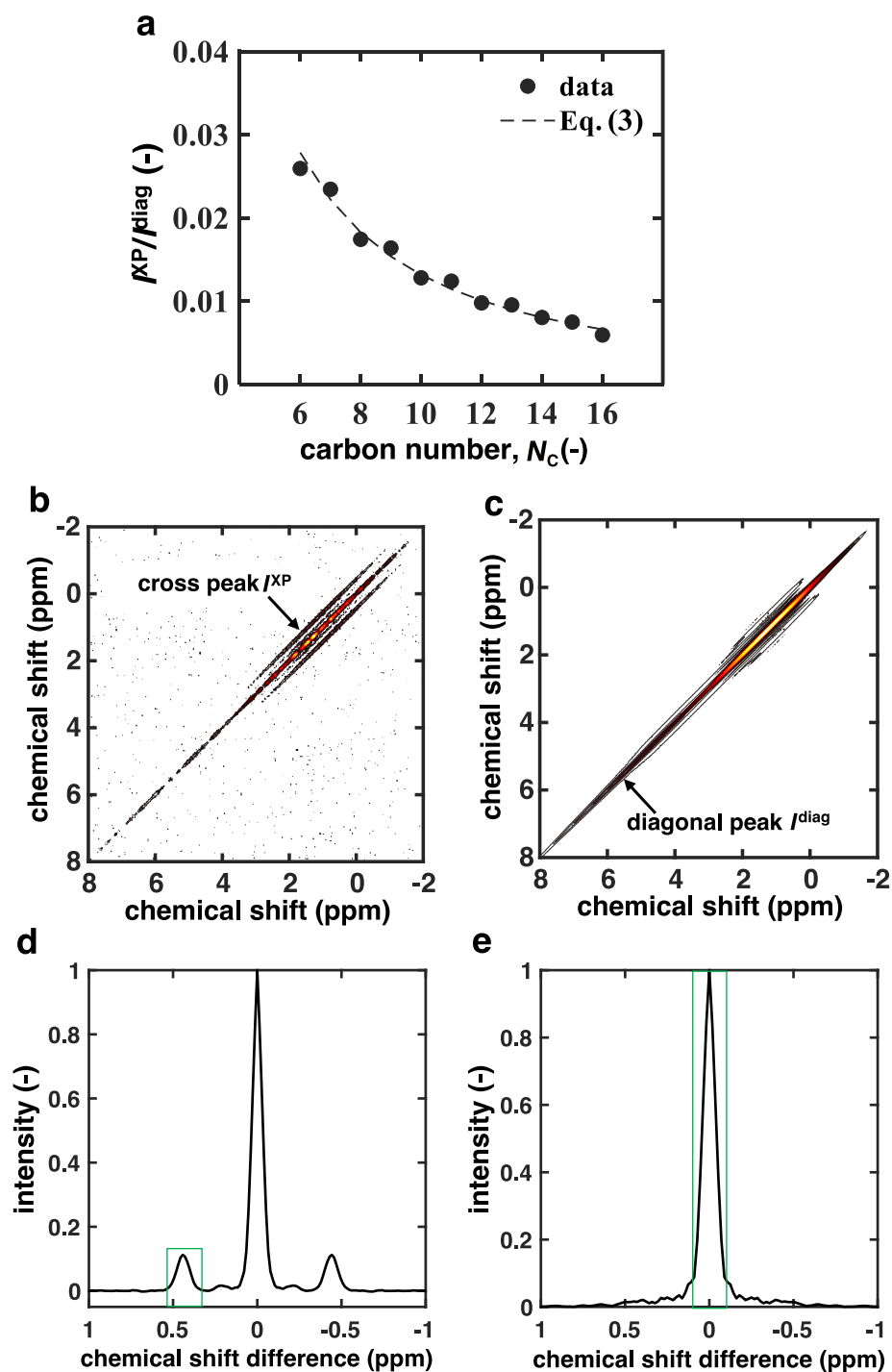
Supplementary Figure 8. Pulse sequences. (a) Slice-selective RARE. (b) 1D frequency encoding imaging preconditioned with the 13-interval APGSTE sequence. (c) Slice-selective RARE preconditioned with the 13-interval APGSTE sequence.



Supplementary Figure 9. Positions of selected slices. The figure shows a 2D vertical z-y slice extracted from the 3D ^1H intensity image (Fig. 2) through the middle of the reactor. The three slices from which the signal of the catalyst layers was recorded are shown in the figures as rectangles. For the 2D images of intensity, average diffusion coefficient and carbon number, the signal integrated along the slice thickness was acquired.



Supplementary Figure 10. Calibration results of the diffusion model parameters. (a) and (b) show the results for two model wax mixtures characterised by average carbon numbers of 35 and 42, respectively. The compositions determined by GC are shown as the blue lines and the red lines represent the distributions estimated using equation (2) and the calibrated parameters ($A = 2.22 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$, $\beta = 0.27$, $\nu = 1.41$). The average carbon numbers of the mixture $\bar{N}_C$ computed from the predicted distributions are indicated in the figures. All data were acquired from waxes confined in the TiO_2 catalyst support and at 220 °C.



Supplementary Figure 11. Determination of average carbon numbers using 2D NMR. (a) Experimental data and the calibration curve given by equation (3). (b) and (c) show the 2D ^1H DQF-COSY and COSY spectra acquired at the steady state for feed ratio 2, respectively. (d) and (e) show the anti-diagonal spectra corresponding to the spectra in (b) and (c), respectively. The signal intensities in (d) and (e) were normalised to the maximum of each spectrum. The integration regions used to calculate I^{XP} and I^{diag} are highlighted in (d) and (e).

Supplementary Table 1. Time parameters used for the MR pulse sequences.

pulse sequence	echo time	recycle time	number of scans	acquisition time
1D imaging	6.7 ms	40 s	4	2.7 min
2D RARE imaging	40.7 ms	3 s	32	13.7 min
3D RARE imaging	34.4 ms	10 s	8	22.8 h
1D diffusion imaging	20.9 ms	3 s	8	26.8 min
2D diffusion imaging	56.4 ms	3 s	256	14.4 h
COSY	35.5 ms	3 s	8	1.9 h
DQF-COSY	35.5 ms	3 s	16	3.8 h
T_1 saturation recovery	0.4 ms	3 s	8	1 h

Supplementary Table 2. Imaging parameters used for the MRI pulse sequences.

Pulse sequences	field of view (FOV)	spatial resolution	RARE factor
1D imaging	100 (z) mm	392 (z) μm	N/A
2D RARE imaging	22 (x)×22 (y) mm^2	172 (x)×172 (y) μm^2	16
3D RARE imaging	80 (z)×25 (x)×25 (y) mm^3	313 (z)×195 (x)×195 (y) μm^3	16
1D diffusion imaging	100 (z) mm	392 (z) μm	N/A
2D diffusion imaging	22 (x)×22 (y) mm^2	172 (x)×344 (y) μm^2	16

Supplementary Table 3. PFG parameters used for the diffusion measurements.

parameters	1D diffusion imaging	2D diffusion imaging		
	FR = 2	FR = 2	FR = 1	FR = 0.5
δ (ms)	4	4	4	4
Δ (ms)	20	20	40	40
g (G cm ⁻¹)	0.1-80	2-60	2-60	2-70
number of g steps	64	16	16	16