Supporting Information

Operando Nuclear Magnetic Resonance (NMR) Studies of a Trickle-bed Reactor Using *D*-*T*2 Correlations

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S1 Monitoring of Wetting Profile During TBR Start-Up

1D axial (*z*) signal intensity profiles were used to monitor the liquid distribution during start- up, using the 1D spin echo imaging pulse sequence shown in Figure S1a. The strength of the phasing and dephasing read gradients was 4.6 G cm^{-1} with duration 0.1 ms within an echo time of 0.5 ms, giving a FOV of 100 mm. Figure S1b shows the typical wetting profile acquired during reactor start-up prior to reaction monitoring experiments; t=0 is 9 mins after liquid is introduced and after a further 5 mins for equilibration.

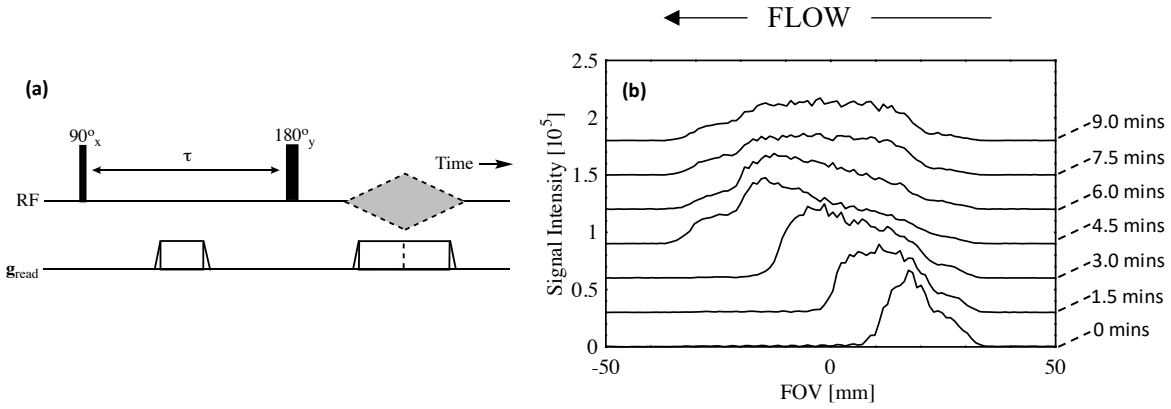

Figure S1. (a) A schematic of the 1D imaging profile pulse sequence and (b) typical qualitative profiles observed during the initial wetting process.

S2 Liquid Distribution Measurements during TBR Operation

The standard Topspin multislice spin-echo imaging pulse sequence (imsems) was used to ensure the liquid distribution was consistent within transverse slices of the reactor and the signal was derived from inter-pellet liquid. The field-of-view (FOV) of the images was 30(x) × 30(y) mm and 5 slices were acquired with 1.5 mm thickness, separated by 6 mm. The number of phase encoding steps was 64, such that the data array was 256 × 64. The data set was zero filled such that the images contained 256 × 256 pixels and a spatial resolution of 235 μm. The total acquisition time was 1.5 h. The echo time for the multislice spin-echo imaging pulse sequence was <3 ms, which was smaller than the echo time in the *D*-T_2 measurements (~15 ms including *D* preconditioning and T_2 encoding); this ensured no signal was detected from inter-pellet liquid during *D*-T_2

experiments. Figure S2 shows a typical multislice imaging measurement acquired at steady-state during BN hydrogenation. Total signal intensity in each image was calculated by summing over all pixels.

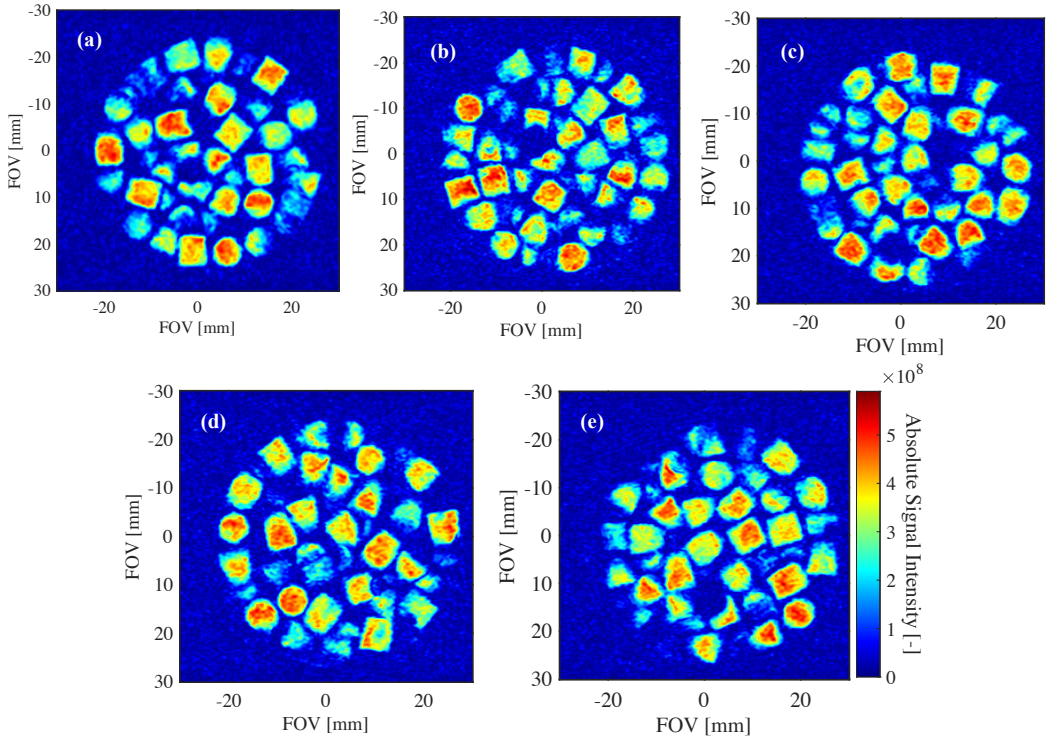

Figure S2. Multislice images of 1.5 mm slices of the reactor acquired at steady-state during BN hydrogenation. Images (a)-(e) are from top to bottom of the reactor, respectively.

S3 NMR Relaxation and Diffusion Characterisation

The global and local D-T_2 distributions during reaction conditions were supported by separate 1D and 2D measurements of T_1, T_2, and diffusion measurements conducted under non-reactive conditions of various model/phantom samples the species of interest in the catalyst pellets with the external liquid removed. The bulk liquids were also characterised.

Model/Phantom Sample preparation

Benzonitrile (BN), benzylamine (BA), toluene (all 95%) and H_2SO_4 (98%) were purchased from Alfa Aesar. CD_3OD (99.8%) was purchased from Goss Scientific. Individual solutions of BN, toluene, and BA were prepared by addition of BN/BA/toluene to CD_3OD (0.35 M), followed by dropwise addition of 1.4 eq. H_2SO_4. Mixtures of solutions were prepared by combining equal volumes of the individual solutions.

For initial characterisation of the relaxation and diffusion behaviour of species within the catalyst pores, five catalyst pellets were soaked in a pore volume amount of liquid for 12 h in a sealed NMR tube. The external liquid

of the pellets was then removed by placing them on pre-soaked filter paper. The pellets were then placed in a 5 mm NMR tube which was subsequently flame sealed. To reach equilibrium, the tubes were placed in the spectrometer for 30 mins before any NMR measurements were conducted.

All relaxation and diffusion characterisations on model/phantom samples were acquired using a Bruker Biospin WB DMX 300 spectrometer operating at a ^{1}H frequency of 300.13 MHz, equipped with a 7.05 T vertical superconducting magnet and an 8 mm ^{1}H/^{2}H i.d. r.f. coil. Standard inversion recovery (IR), Periodic Refocusing of J-Evolution by Coherence Transfer (PROJECT), and 13-Interval Alternating Pulsed-Gradient Stimulated Echo (APGSTE) were used to acquire T_1, T_2, and diffusion coefficients, respectively.[1–3] T_1-T_2 correlations were made by combining IR and PROJECT sequences into one pulse sequence; the D-T_2 correlations were performed by combined PROJECT and APGSTE pulse sequences. For model/phantom samples, the SNR of the raw data exceeded 2000. For bulk liquid and imbibed liquid in pellets model/phantom experiments, the recycle delay was set to 60 and 8 s (>5×T_1) respectively, to ensure the magnetisation was fully relaxed between steps in the indirect dimension. Tables S3.1, S3.2, and Figures S3, S3.1 show selected results of the T_1, T_2 and D analysis of individual model/phantom samples for mixtures of BN, BA, and toluene, both in pure liquid (bulk) samples and liquids imbibed in the catalyst pellets.

Pure (bulk) Liquid Characterisations

The T_1 experiments used 16 linearly spaced intervals from 0.1-20 s in the indirect dimension. The T_2 experiments used an echo time of 2.5 ms and 16 linearly spaced refocusing times from 0.01-20 s. The diffusion experiments used δ=1ms, Δ=100 ms, and 16 linearly spaced gradient steps from 5-100 G cm^{-1}, such that the signal attenuated to <1%. An echo time of 14 ms was used in diffusion encoding. The bulk solutions contained spectrally resolvable peaks, the 1D relaxation and diffusion coefficients for each compound were calculated by taking the relevant peak integral from the series of spectra acquired. This data was then fitted to the standard Bloch (relaxation) or Sketsjal-Tanner (diffusion) equations.[4,5]

Imbibed Liquid in Catalyst Pellets Characterisations

For imbibed liquids, the 1D D and 2D D-T_2 experiments used δ=1 ms, Δ=50 ms, and 16 gradient steps from 5-200 G cm^{-1}, such that the signal attenuated to <1%. For samples with two diffusion components, gradient strengths were optimised using Cramér-Rao Lower Bound (CRLB) theory, incremented linearly.[6] The shortest possible echo time of 2.8 ms was used during diffusion encoding. The 1D T_1 and 2D T_1-T_2 experiments used 16 linearly spaced intervals from 0.001-10 s in the indirect dimension. 2D correlation experiments used 1024 points and a 0.5 ms echo time during T_2 encoding. 1D relaxation and diffusion coefficients experiments were calculated integrating over the entire spectrum and fitting multiple components to the standard Bloch (relaxation) or Sketsjal-Tanner (diffusion) equations.[4,5] In certain cases, for example imbibed toluene in pellets and benzylamine in pellets shown in Figure S3, the T_2-relaxation of different functional groups on the molecule could be observed, supporting the use of multiple component relaxation fitting. The OH peak data is omitted in Table S3.1 for clarity.

Table S3.1. The T_1, T_2, and D coefficients for the individual components of model/phantom samples from both bulk and imbibed liquids in catalyst pellets. Values are from 1D experiments.

		T_1 [s]			T_2 [s]			D [10^{-9} m^{2}s^{-1}]	
	Individual	ArH	Alkyl	OH	ArH	Alkyl	OH	ArH/Alkyl	OH
Bulk	BN	3.7	-	2.0	3.6	-	1.3	2.5	2.5
	BA	5.0	4.1	1.8	4.8	3.9	0.5	2.4	2.2
	Tol	4.4	3.9	1.9	4.3	3.9	1.2	2.7	2.8
		T_1 [s]			T_2 [ms]			D_{eff} [10^{-10} m^{2}s^{-1}]	
		ArH	OH	Alkyl	ArH	OH	Alkyl	ArH/Alkyl	OH
Imbibed	BN	1.8	0.8	-	36	2	-	2.0	24
	BA	2.4	0.4	2.4	43	1	4	1.8	19
	Tol	2.7	0.8	2.7	77	1	78	2.3	9.0

Table S3.2. The T_1, T_2, and D coefficients for the 1:1 imbibed liquid mixtures 2D correlation experiments. Uncertainties are calculated from the standard error of three BN:BA:Tol samples prepared the same way.

		T_1 ±0.1 [s]*	T_2 ±0.3 [ms]†	D_{eff} ±0.2 [10^{-10} m^{2}s^{-1}]	Contour Integral ±0.05 [-]‡
Imbibed	BN	0.9	18	2.3	0.53
	BA	1.3	36	3.5	0.47

	BN	1.0	25	2.3	0.42
	Tol	1.3	202	7.2	0.58
	BA	1.7	41	2.7	0.39
	Tol	1.8	92	7.2	0.61
	BN	1.4	28	3.3	0.26
	BA	1.3	99	10.1	0.28
	Tol	1.3	478	8.5	0.46

*Values are from a T_1-T_2 experiment

†, ‡ Values are from a D-T_2 experiment

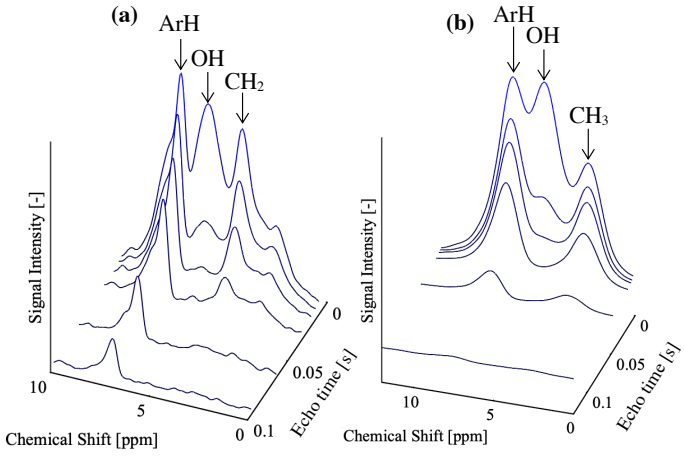

Fig S3. Six ^{1}H spectra taken from the T_2-PROJECT experiments for (a) BA and (b) toluene imbibed in pellets.

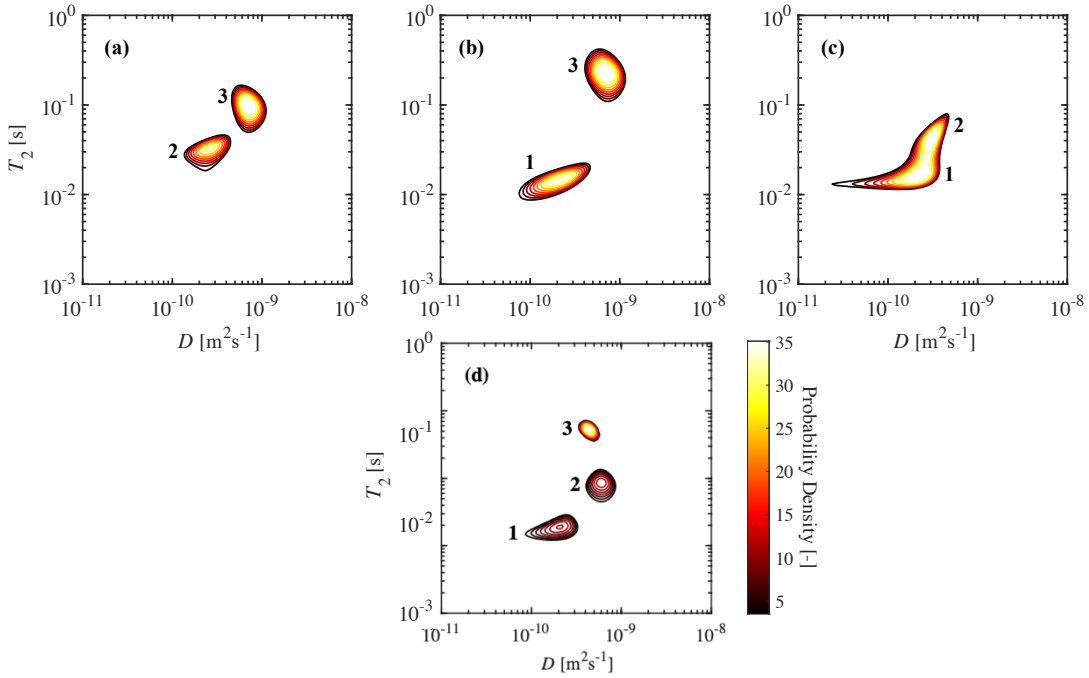

Fig S3.1. The (a) T_1-T_2 and (b) D-T_2 distributions for 1:1 imbibed mixtures in catalyst pellets of (a) BA:Tol, (b) BN:Tol, (c) BN:BA (c), and (d) D-T_2 distributions of a 1:1:1 imbibed mixtures of BN:BA:Tol. BN (ArH), BA (ArH), and toluene (ArH+CH_3) are represented by peaks **1**, **2**, and **3**, respectively.

S4 Reaction Monitoring during TBR Operation

Progression to steady-state was tracked using: a global D-T_2 (APGSTE-PROJECT) experiment; a phase encoded D-T_2 sequence (Figure S4(a)); a local chemical shift imaging (CSI) sequence (Figure S4(b)). Parameters for the global and local D-T_2 measurements are detailed in Table S4. For CSI, the echo time was 2.2 ms and gradient duration, $\mathbf{g}_{phase}$ was 0.5 ms with 64 linearly incremented steps reaching a maximum gradient strength of ±0.75 G cm^{-1}, giving a FOV of 100 mm. The recycle delay was set to 1 s and the experiment time was 10 mins.

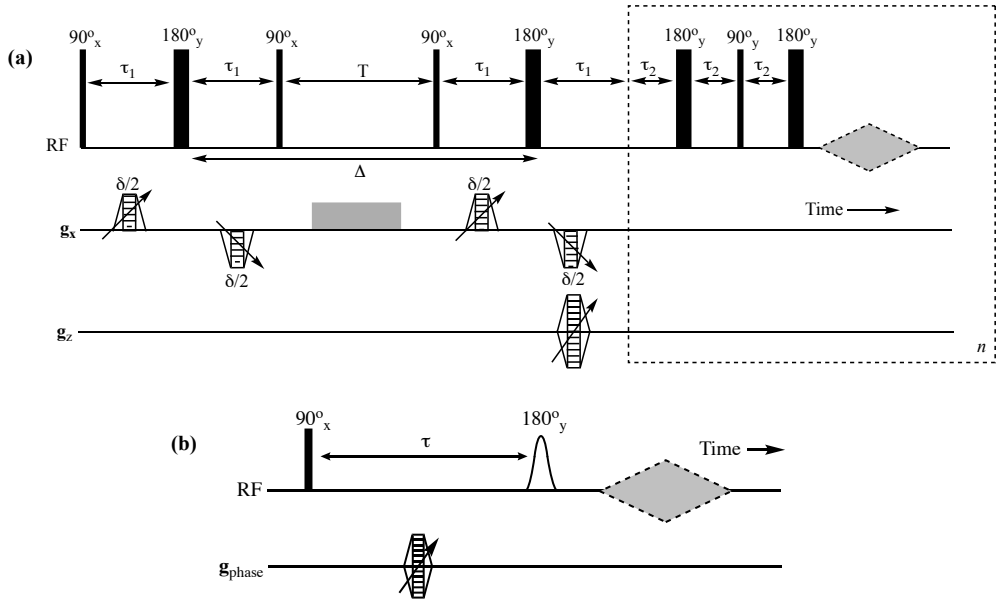

Figure S4. (a) A schematic of the (a) PE-D-T_2 (where n is the number of iterations over the PROJECT sequence before acquisition, and **g** is the applied magnetic field gradient) and (b) chemical shift imaging pulse sequences.

Table S4: List of experimental parameters used in the non-spatially resolved and spatially resolved D-T_2 experiments.

Parameter	D-T_2	Phase-encoded D-T_2
δ [ms]	1	1
Δ [ms]	80	80
Number of gradient steps for diffusion [-]	16	16
Diffusion gradient strength [G cm^{-1}]	5-80	5-80
τ_1 [ms]	2.8	2.8
τ_2 [ms]	0.5	0.5
Number of echoes [-]	256	256
Recycle delay [s]	6	6
Number of **k**-space points [-]	-	8

Spatial resolution [mm]	-	10000
FOV [mm]	-	80
Phase encoding gradient strength [G cm^{-1}]	-	-0.24-0.18

References

[1] G. M. Bydder, J. V. Hajnal, I. R. Young, *Clin Radiol* **1998**, *53*, 159, DOI: 10.1016/S0009-9260(98)80096-2.
[2] R. M. Cotts, M. J. R. Hoch, T. Sun, J. T. Markert, *J Magn Reson* **1989**, *83*, 252, DOI: 10.1016/0022-2364(89)90189-3.
[3] J. A. Aguilar, M. Nilsson, G. Bodenhausen, G. A. Morris, *Chem. Commun.* **2012**, *48*, 811, DOI: 10.1039/C1CC16699A.
[4] E. O. Stejskal, J. E. Tanner, *J Chem Phys* **1965**, *42*, 288, DOI: 10.1063/1.1695690.
[5] F. Bloch, W. W. Hansen, M. Packard, *Phys Rev* **1946**, *69*, 127, DOI: 10.1103/PhysRev.69.127.
[6] A. Reci, A. J. Sederman, L. F. Gladden, *J Magn Reson* **2018**, *294*, 35, DOI: 10.1016/j.jmr.2018.06.010.