3D-printed Capillary Force Trap Reactors (CFTRs) for Multiphase Catalytic Flow Chemistry

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ELECTRONIC SUPPLEMENTARY INFORMATION

S1. Study of solvent effects on agglomeration/deactivation of rhodium nanoparticle (RhNP)

We first performed transmission electron microscopy (TEM) analysis on the RhNP catalysts to observe the effects of reaction and mixing on the catalysts, as shown in Fig. S1(d) and Fig. S1(e), compared to freshly synthesized catalysts in Fig. S1(a). We observed that the RhNP catalysts agglomerated from their initial sizes of ~3 – 4 nm to ~20 nm after a 5-hour reaction (τ = 20 s), and also after a 1-hour batch mixing of 1-hexene with the RhNPs under the no reaction condition, where hydrogen gas reactant was replaced with inert nitrogen gas. This latter RhNP mixing experiment with no reaction was also extended to decane (solvent) and n-hexane (product), there were no observable changes to the RhNP in thse cases as shown in Fig. S1(b) and Fig. S1(c).

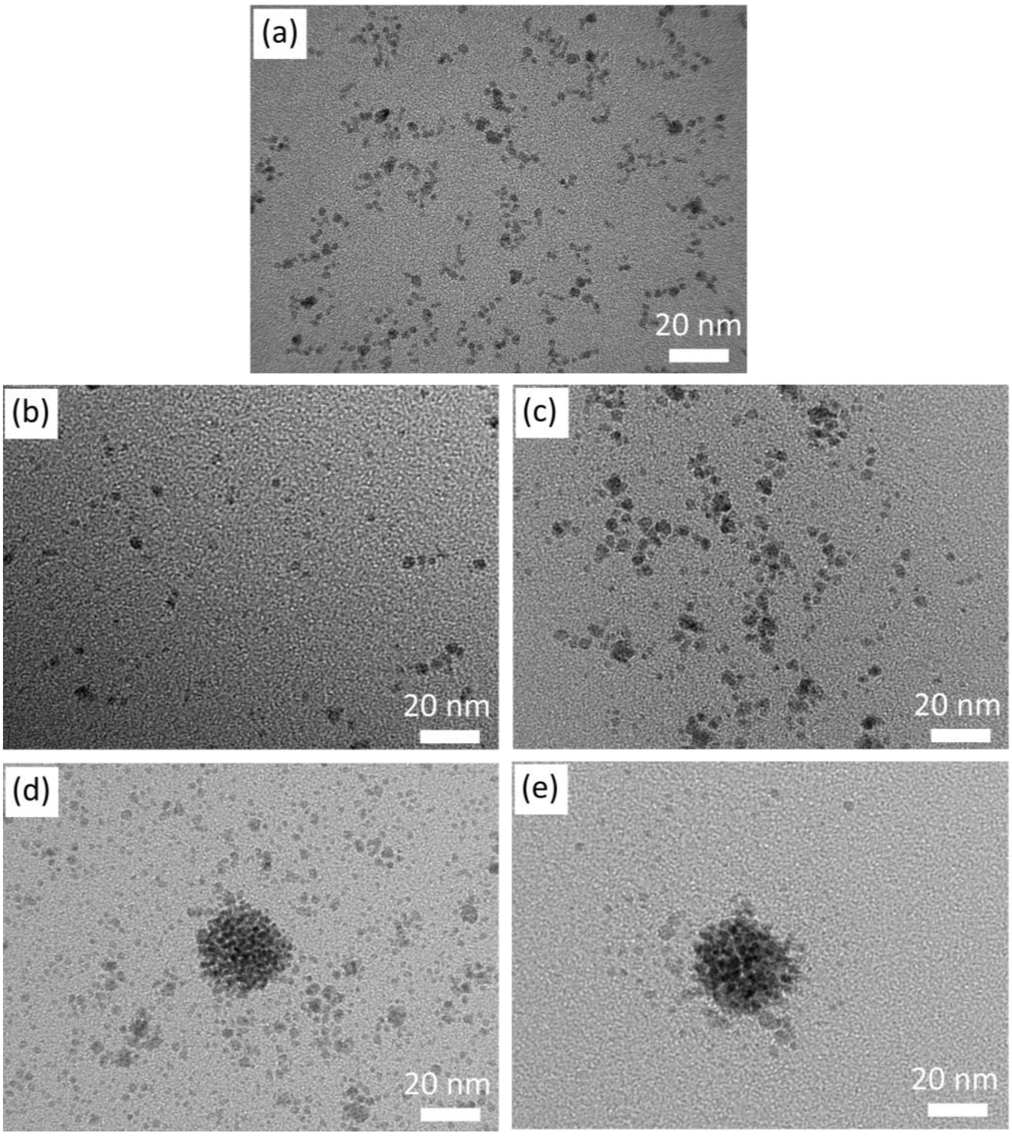

Figure S1. (a) Transmission electron microscopy (TEM) image of rhodium nanoparticle (RhNP) catalysts before hydrogenation of 1-hexene (substrate) (3 – 4 nm). (b) Transmission electron microscopy (TEM) image of rhodium nanoparticle (RhNP) catalysts contacting with n-hexane (product) via mixing (no reaction) (3 – 4 nm). (c) Transmission electron microscopy (TEM) image of rhodium nanoparticle (RhNP) catalysts contacting with decane (solvent) via mixing (no reaction) (3 – 4 nm). (d) Transmission electron microscopy image (TEM) of rhodium nanoparticle (RhNP) catalysts after hydrogenation of 1-hexene (~20 nm). (e) Transmission electron microscopy (TEM) image of rhodium nanoparticle (RhNP) catalysts contacting with 1-hexene via mixing (no reaction) (~20 nm).

S2. Study of the effect of substrate (1-hexene) concentration, $C_{hex,0}$ on catalyst deactivation

We examined the effect of varying 1-hexene concentration during hydrogenation on the catalyst deactivation rate. Fig. S2 is a plot of substrate conversion, X as a function of CFTR operation time with the associated error bars. The normalized conversion, X' plot is obtained by obtaining the normalization of the instantaneous conversion, X by the initial conversion X_0 at each 1-hexene concentration. The motivation to normalize Fig. S2 is to be able to observe each curves respective deactivation rate more clearly regardless of their initial conversions.

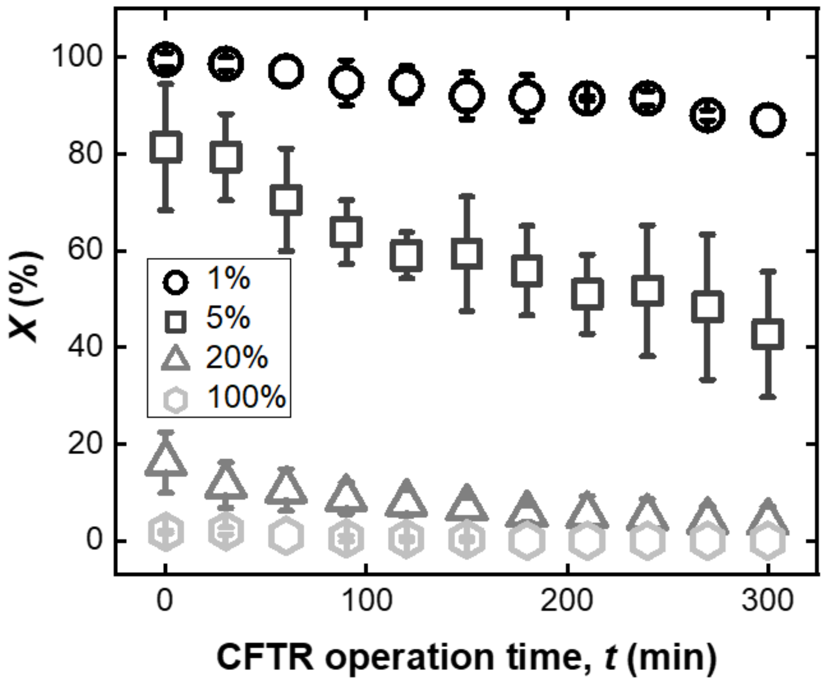

Figure S2. Substrate (1-hexene) conversion, X *vs.* CFTR operation time, t. $C_{hex,0}$ = 0.08 M (1% 1-hexene in decane), $C_{hex,0}$ = 0.4 M (5% 1-hexene in decane), $C_{hex,0}$ = 1.6 M (20% 1-hexene in decane), $C_{hex,0}$ = 8.1 M (100% 1-hexene in decane), C_{cat} = 2 mM, precursor to stabilizer molar ratio: $RhCl_3$:PVP = 1:100, Q_{org} = 20 µL/min, τ = 50 s: Q_{gas} = 0.04 mL/min.

S3. Scale-up of the dimpled CFTR – concept for a monolithic dimpled CFTR insert

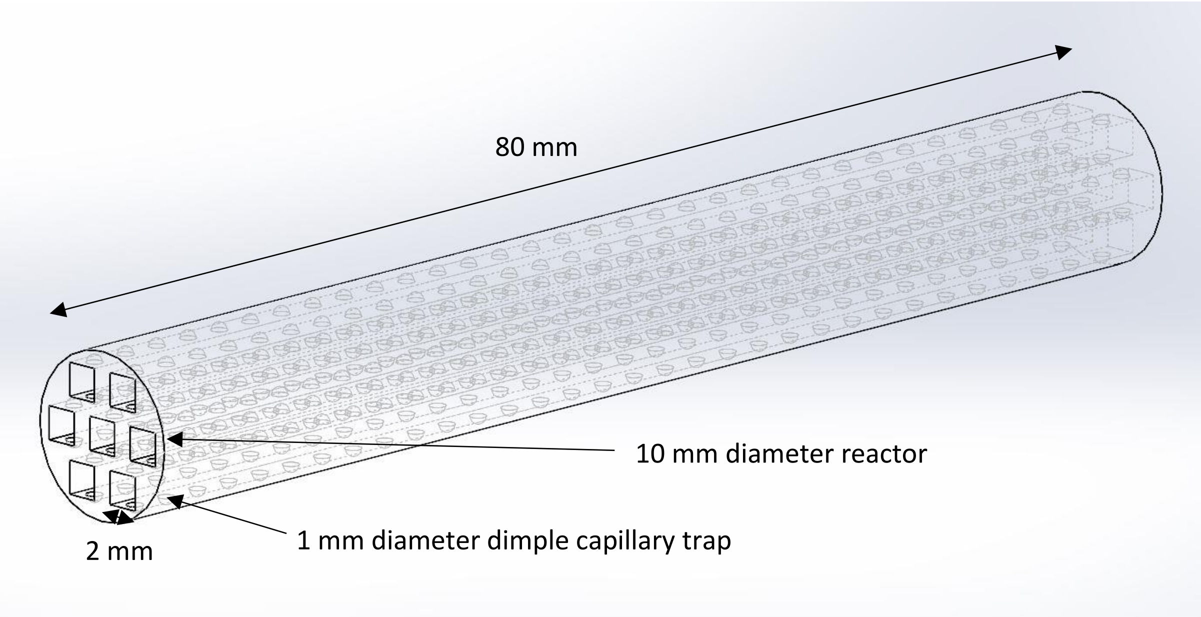

Figure S3 Monolithic dimpled Capillary Force Trap Reactor (CFTR) (see main text for details)

Reactor	τ	Conversion (%)	Substrate Flow rate	Throughput (g/day)	Space-time Yield ($g_{product}/g_{cat}\cdot min$)
50 mL round bottle flask [1]	60 min	100	5 mL 800 mM 1-hexene	8.25	108
1 mm ID G-L-L single triphasic milli-reactor [2]	~1 min	82	10 µL/min 800 mM 1-hexene	0.8	585
Square dimpled CFTR (64 dimples)	~50 s	100	20 µL/min 403 mM 1-hexene	~2	394
Monolithic dimpled CFTR (448 dimples) *Hypothesized	~50 s	100	7 × 20 µL/min 403 mM 1-hexene	~14	395

Table S1 Comparison of reactors for the same model reactions in terms of throughput and space-time yield. [3]

References

1. S. K. Yap, Y. Yuan, L. Zheng, W. K. Wong, N. Yan and S. A. Khan, *Journal of Flow Chemistry*, 2014, **4**, 200-205.
2. S. K. Yap, Y. Yuan, L. Zheng, W. K. Wong, J. Zhang, N. Yan and S. A. Khan, *Green Chem.*, 2014, **16**, 4654-4658.
3. D. Karan, PhD Thesis, 2019.