Electronic Supplementary Information for

Rapid Nanoparticle-Catalyzed Hydrogenations in Triphasic Segmented Flow Millireactors with Facile Catalyst Recovery

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1. Experimental Images

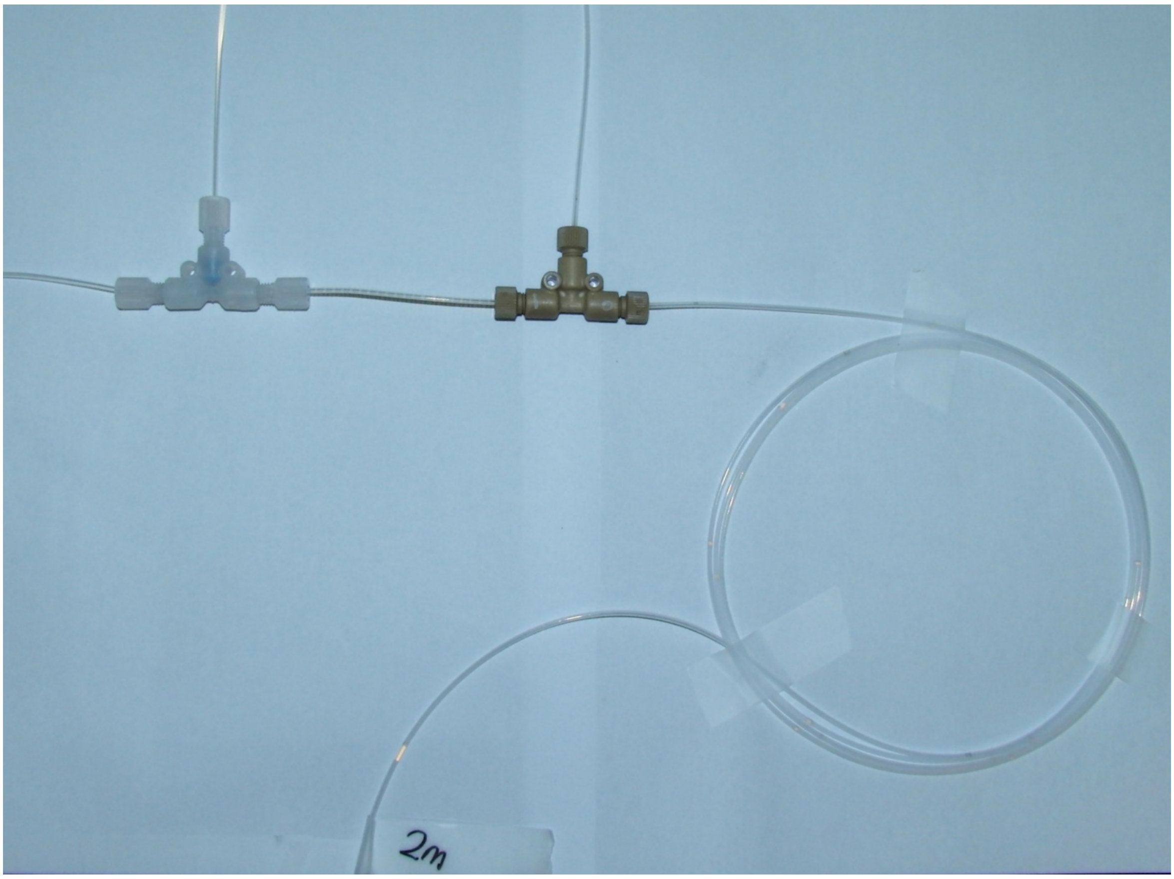


Fig. S1: Photographic image of experimental setup.

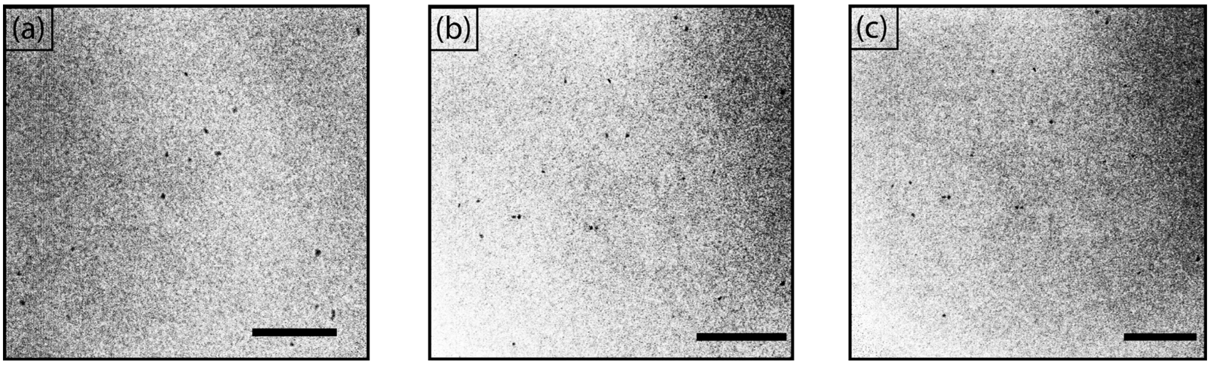
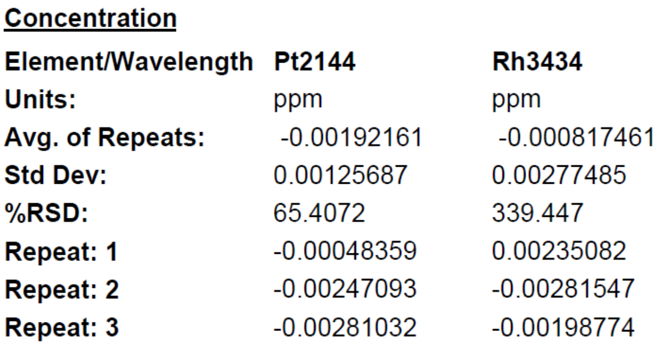


Fig. S2: Transmission electron microscope (TEM) images of PtNPs (a) before reaction, (b) after two catalytic cycles and (c) after three catalytic cycles for the hydrogenation of nitrobenzene. All scale bars represent 60 nm.

2. Metal Leaching

The organic phases collected from the hydrogenation of nitrobenzene catalyzed by PtNP and that collected from the hydrogenation of 1-hexene catalyzed by RhNP are both collected at the outlet of the millireactor and analyzed for the presence of any metal content. Inductively coupled plasma-optical emission spectrometry (ICP-OES) measurements reveal that metal leaching into the organic phase is negligible in the hydrogenation reactions performed in our millireactor system (Fig. S3).



Concentration

Element/Wavelength	**Pt2144**	**Rh3434**
Units:	ppm	ppm
Avg. of Repeats:	-0.00192161	-0.000817461
Std Dev:	0.00125687	0.00277485
%RSD:	65.4072	339.447
Repeat: 1	-0.00048359	0.00235082
Repeat: 2	-0.00247093	-0.00281547
Repeat: 3	-0.00281032	-0.00198774

Fig. S3: Inductively coupled plasma-optical emission spectrometry (ICP-OES) measurements of metal content in the organic phase for both PtNP-catalyzed and RhNP-catalyzed hydrogenation reveal the absence of metal leaching into the organic phase.

3. Reactor Model

A phenomenological model simulating the nanoparticle (NP) catalyzed hydrogenation of 1-hexene is developed to account for both the mass transport and reaction processes occurring within the millireactor. The following mass transfer controlled rate expressions are used for both hydrogen and hexene consumption in our pseudo biphasic segmented flow millireactor:[1-3]

$$r = \frac{D_{H_2}}{w_{org}} \underline{a}\, C_{H_2 sat} \qquad (1)$$

$$r = \frac{D_{hex}}{w_{org}} \underline{a}\, C_{hex} \qquad (2)$$

Where D_{H_2} and D_{hex} are the diffusivity of hydrogen and 1-hexene in the organic phase respectively, w_{org} is the width of the organic segment, $\underline{a}$ is the specific interfacial area of the organic-aqueous interface, C_{H_2sat} is the saturated concentration of dissolved hydrogen in the organic phase, and C_{hex} is the concentration of 1-hexene in the organic phase. From our experiments, we observe that w_{org} exhibits an approximately linear relationship with the inverse of flow speed *U* i.e $w_{org} = a/U + b$, where *a* and *b* are fitted from experimental measurements of w_{org} versus *U*.

A comparison between the reactor model, which uses equation (1) or (2) in the simple isothermal mass balance given in equation (3), and experimentally obtained 1-hexene conversions at different flow speeds is given in Fig. S4.

$$\frac{dC_{hex}}{d\tau} = -r \qquad (3)$$

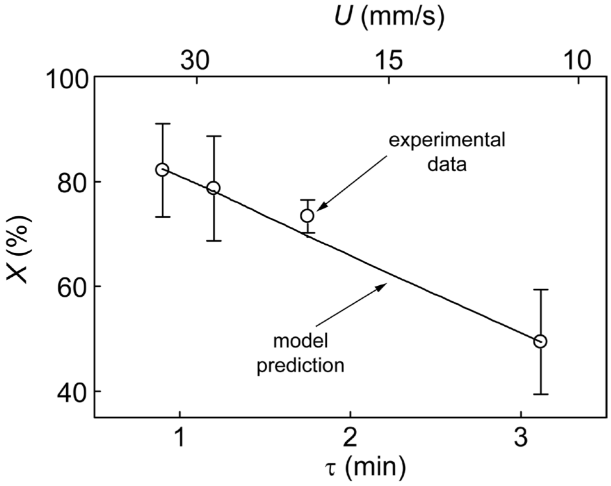


Fig. S4: Comparison between experimental data and model prediction of 1-hexene conversion, *x*, under different flow speed *U* and residence time τ. Our reactor model is able to capture the effect of increasing flow speeds on 1-hexene conversion despite the corresponding decrease in residence time.

From the experiments, it is observed that despite a decline in residence time at higher flow speeds, the conversion of 1-hexene in our 2 m millireactor continues to increase. A comparison of our reactor model above with the experimental data obtained shows that our model is able to capture this phenomenon completely (Fig. S4). Further details of the reactor model, including the rationale, derivation and application of equations (1) and (2) in the reactor model, will be published separately.

4. References

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