

Electronic Supplementary Information (ESI)

Structuring hybrid palladium nanoparticles in metallic monolithic reactors for continuous-flow three-phase alkyne hydrogenation

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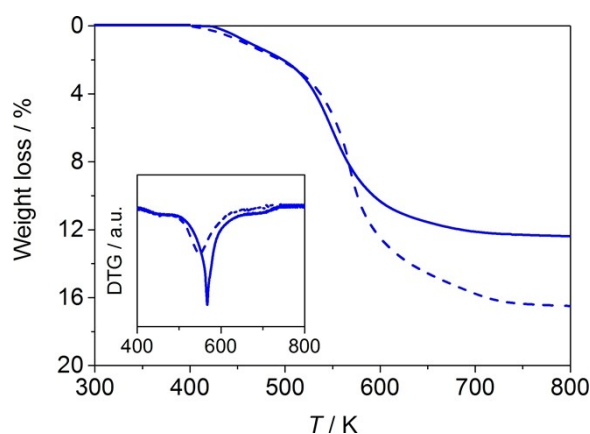


Fig. S1. Thermogravimetric profile in air of the Pd-HHDMA/Al₂O₃-p (dashed line) and NanoSelect (solid line) catalysts. The inset shows the first derivative curves of the gravimetric profiles.

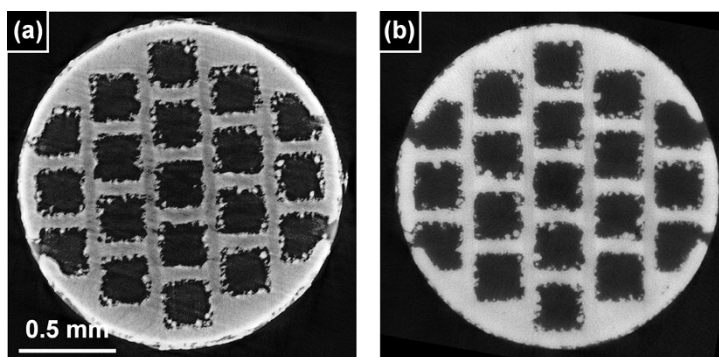


Fig. S2. Two-dimensional virtual slices of perpendicular cross-sections of the bare (a) and the washcoated (b) monoliths computed through micro-CT. In both cases, a similar surface roughness is observed in the microchannels.

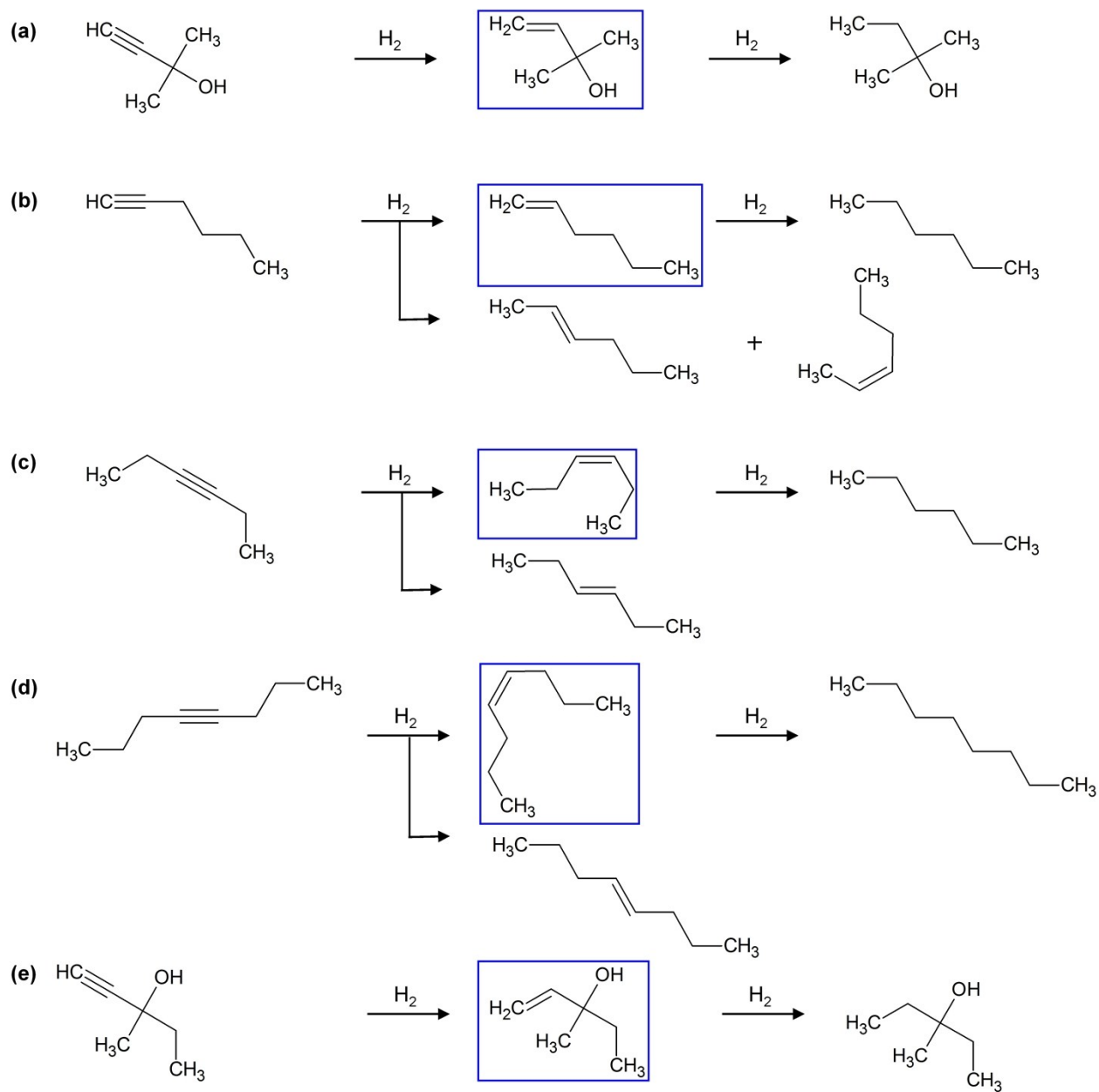


Fig. S3. Reaction schemes showing possible products upon hydrogenation of 2-methyl-3-butyn-2-ol (a), 1-hexyne (b), 3-hexyne (c), 4-octyne (d), and 3-methyl-1-pentyn-3-ol (e). The desired product is highlighted with a blue box.

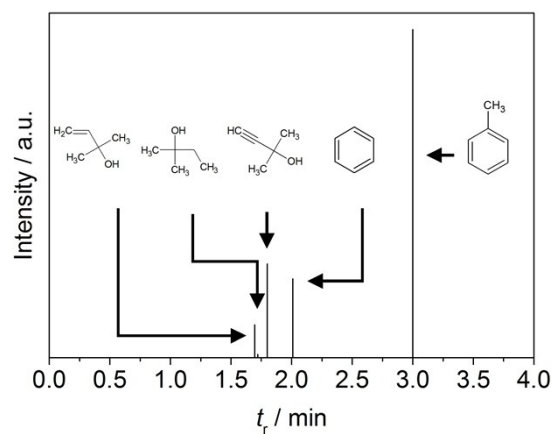


Fig. S4. Representative GC chromatogram confirming the product separation obtained during the hydrogenation of 2-methyl-3-butyn-2-ol. The chromatogram highlights the retention time of 2-methyl-3-buten-2-ol (1.70 min), 2-methyl-butan-2-ol (1.72 min), 2-methyl-3-butyn-2-ol (1.80 min), benzene (2.00 min) and toluene (2.90 min). The GC analysis was conducted using helium as a carrier gas (flow rate = 3 cm³ min⁻¹); the column was kept at an initial temperature of 323 K for 0.5 min, then the temperature was ramped from 323 to 473 K with a heating rate of 10 K min⁻¹.

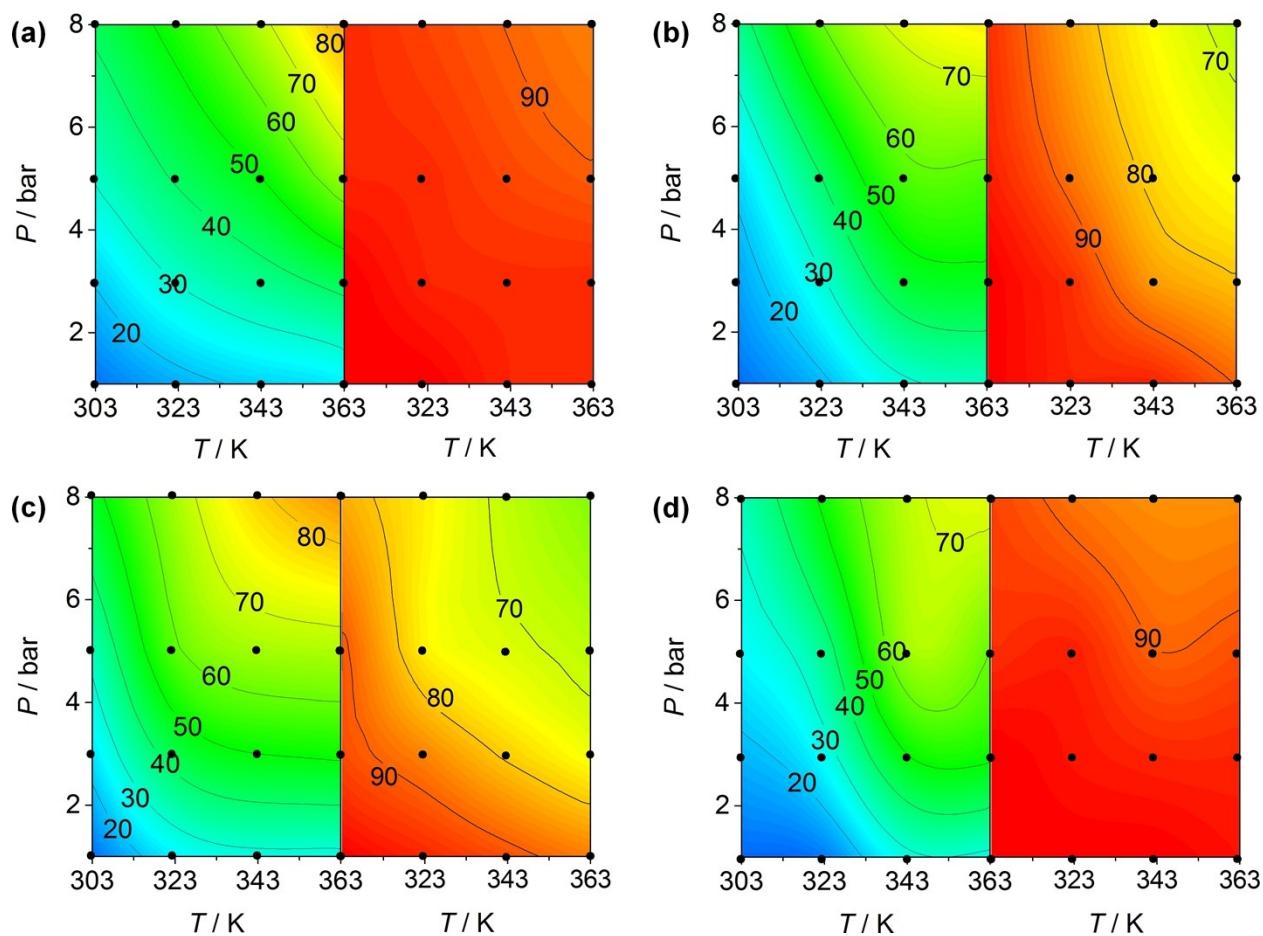


Fig. S5. Conversion (in %, left) and selectivity to 1-hexene (in %, right) in the hydrogenation of 1-hexyne over (a) Pd-HHDMA/ Al_2O_3 -m, (b) Pd-HHDMA/ Al_2O_3 -p diluted with Al_2O_3 , (c) NanoSelect, and (d) Pd-HHDMA/ Al_2O_3 -p diluted with SiC. Conditions: $W_{\text{cat}} = 0.1$ g, $F_{\text{L}}(1\text{-hexyne+toluene}) = 1$ cm^3 min^{-1} , and $F_{\text{G}}(\text{H}_2) = 36$. The contour maps were obtained through spline interpolation of 16 experimental points.

Pressure drop calculation

For the **packed bed**, the pressure drop in the liquid and gas phase can be estimated independently applying the Blake-Kozeny equation [1,2]:

$$\frac{\Delta P_l}{L} = \frac{(1-\varepsilon)}{\varepsilon^3} 150 u_l \frac{\eta_l}{d_p^2} \quad [1]$$

$$\frac{\Delta P_g}{L} = \frac{(1-\varepsilon)}{\varepsilon^3} 150 u_g \frac{\eta_g}{d_p^2} \quad [2]$$

where ΔP_l and ΔP_g are the pressure drop (Pa) for the liquid and gas phase, respectively, L is the bed length (m), ε is the bed porosity, u_l and u_g are the velocity (m s^{-1}) of the liquid and gas phase, respectively, η_l and η_g are the dynamic viscosities ($\text{kg m}^{-1} \text{s}^{-1}$) of the liquid and gas phase, respectively, and d_p is the particle diameter (m). The total pressure drop, ΔP_{lg} (Pa), is calculated employing the Lockhart-Martinelli equation¹ [3]:

$$\log_{10} \frac{\Delta P_g}{\Delta P_l + \Delta P_g} = \frac{0.416}{\left(\log_{10} \frac{\Delta P_l}{\Delta P_g} \right)^2 + 0.686} \quad [3]$$

For the **monolith**, the pressure drop in the liquid and gas phase are estimated using the Hagen-Poiseuille equation [3]:

$$\Delta P_l = 32\varphi \frac{\eta_l u_l}{d_H^2} L \quad [4]$$

$$\Delta P_g = 32\varphi \frac{\eta_g u_g}{d_H^2} L \quad [5]$$

The total pressure drop, ΔP_{lg} (Pa), is calculated employing also in this case the Lockhart-Martinelli equation:

$$\log_{10} \frac{\Delta P_g}{\Delta P_l + \Delta P_g} = \frac{0.416}{\left(\log_{10} \frac{\Delta P_l}{\Delta P_g} \right)^2 + 0.686} \quad [6]$$

where φ is a parameter depending on the channel geometry (equal to 0.89 for square channels), and d_H is the aspect ratio of the channel ($4A_c/O_c$, where A_c is cross-sectional area of the monolith channel and O_c is the total periphery of channel cross-sections within the monolith). The obtained results are summarised in **Table S1**.

Table S1. Calculated pressure drops in the packed-bed and monolithic reactors.

Configuration	ΔP_l (mbar)	ΔP_g (mbar)	ΔP_{lg} (mbar)
Packed bed	0.2	1	3.54
Monolith	0.03	0.02	0.2

Residence time calculation

The residence time, that is the time a fluid element spend into the reactor, was calculated as the inverse of the liquid hourly space velocity [7]:

$$\tau = \frac{1}{LHSV} \quad [7]$$

In fact, in a three-phase operation, such as the hydrogenation of a liquid hydrocarbon over a solid surface, the reaction occurs in the liquid film surrounding the catalyst particles, where part of the gaseous hydrogen is solubilized².

For the **packed bed**, the liquid hourly space velocity, $LHSV$ (s^{-1}), has been calculated using the following equation² [8]:

$$LHSV = \frac{F_L}{V_r \varepsilon} \quad [8]$$

In particular, F_L is the total liquid flow rate ($0.017 \text{ cm}^3 \text{ s}^{-1}$), V_r is the total reactor volume (0.225 cm^3) calculated using the formula $V_r = \pi r^2 L$, where r is the radius of the reactor (0.0175 cm) and L is its length (2.34 cm); ε (0.35) is the bed porosity, calculated using the expression³ [9]:

$$\varepsilon = \frac{1}{\left(\frac{D}{d_p}\right)^2} + 0.375 \quad [9]$$

where D is the reactor diameter (0.35 cm) and d_p is the average diameter of the catalyst particle (0.03 cm).

For the **monolith**, the liquid hourly space velocity has been calculated using the following equation^{4,5} [10]:

$$LHSV = \frac{F_L}{V_{c,tot}} \quad [10]$$

where $V_{c,tot}$ is the total volume of all channels (0.060 cm³), calculated multiplying the volume of a single channel by the number of channels in the monolith (19). The former, in particular, is the volume of a parallelepiped of length L and base s [11]. Thus, we have:

$$V_{c,tot} = 19V_c = 19s^2L \quad [11]$$

The calculated values of $LHSV$ and τ for the two reactor configurations are shown in **Table S2**.

Table S2. Liquid hourly space velocity and residence time in the reactor configurations studied.

Configuration	$LHSV$ (s⁻¹)	τ (s)
Packed bed	0.21	4.7
Monolith	0.23	4.2

References

- [1] C. Satterfield, *AIChE J.* 1975, **21**, 209.
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