Supporting Information

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1.) Setup

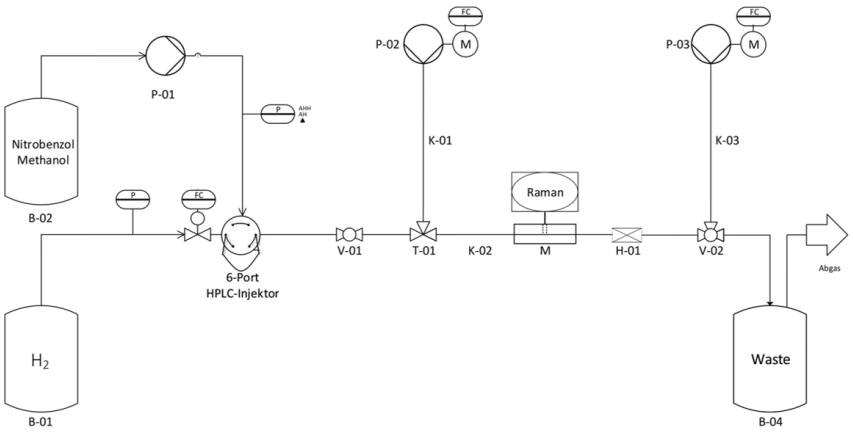

Figure S1: *Piping and instrumentation diagram of the oscillating droplet reactor.*

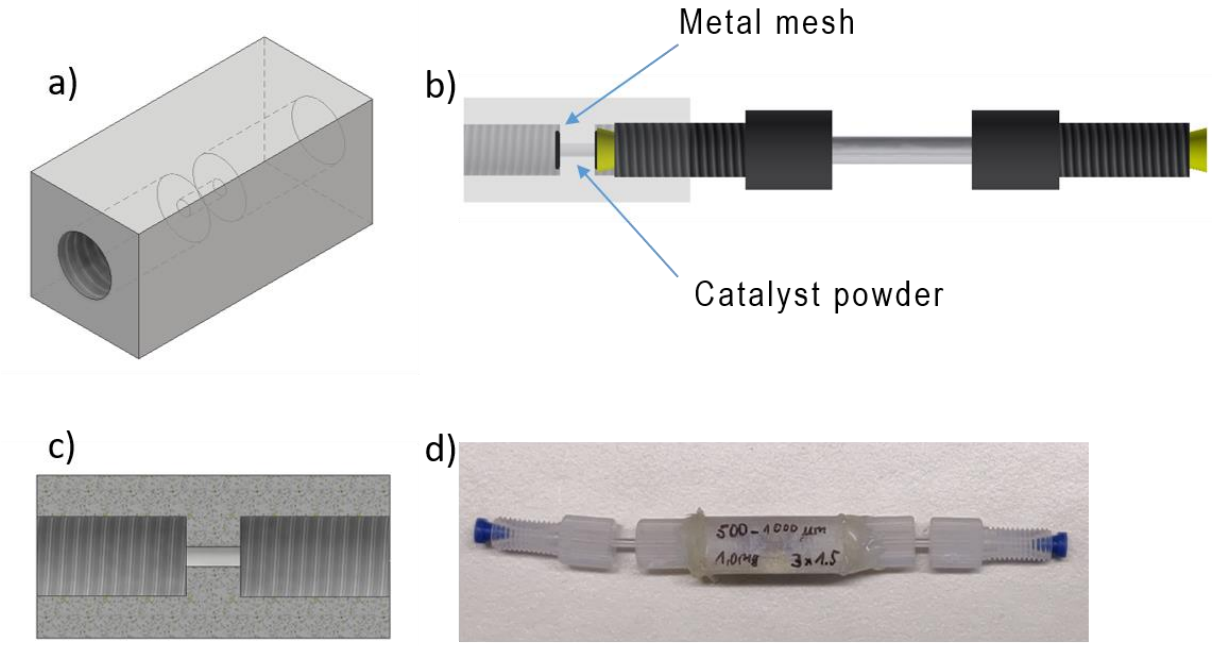

Figure S2: *Illustration of the catalyst carrier. a) CAD model of the holder for 3D printing. b) CAD representation of the built-in catalyst holder. c) Cross section of the holder. d) Photograph of the holder after installation and filling with catalyst. The unit can be prefabricated and efficiently exchanged for screening different catalysts.*

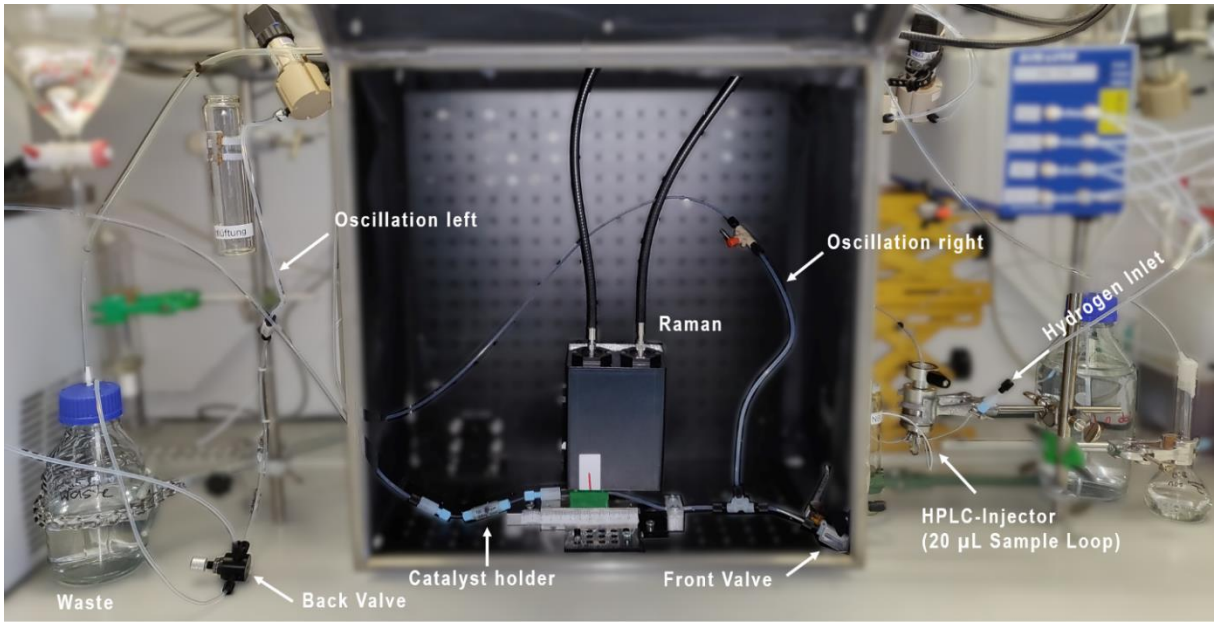

Figure S3: *Photography of the measuring set-up of the plant. All fluid carrying parts are highlighted.*

2.) Experimental details

The entire reaction system including the catalyst is flushed with hydrogen 2 mL/min for several minutes.

The substrate solution is supplied by syringe pumps into the loop injector, which contains a 20 µL loop.

To generate the slug, the loop is charged with hydrogen and the defined slug is pushed towards the measuring unit.

The slug is stopped about 2 cm before the measuring probe and the system is switched to oscillation.

The oscillation is realised by two syringe pumps, which always work in opposite directions and at both ends of the measuring capillary. This creates a uniform oscillating movement since an over- resp. under pressure is generated on both sides of the slugs.

After the reaction has been carried out, the slug is discharged by hydrogen and the plant is ready for the next experiment.

3.) Raman spectroscopy

The progress of the hydrogenation reactions was monitored using in-line contactless Raman spectroscopy. Therefore, the changes in the intensity of signals of the starting materials were followed over time. In order to obtain a maximum signal intensity, the focus of the laser should ideally be in the middle of the slug. Therefore, the capillary was fixated to guarantee a correct position. While the slug is passing the Raman probe, spectra are continuously gathered. The first and the last spectrum of one pass can be adversely affected by the edge of the slug. An apparently lower concentration would be measured here. To ensure at least one usable data point within one pass, the integration time of the CCD and the superficial velocity are set, to ensure a minimum of three spectra per slug passing the Raman probe.

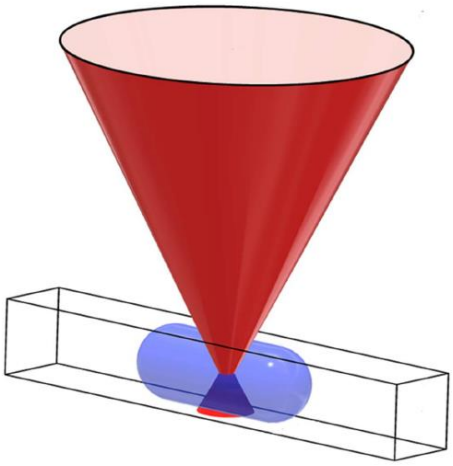

Figure S4: *Schematic representation of the focus of the laser in the droplet. Graphic adapted from Klement et. al.*[1]

For the evaluation of the reaction progress, the decrease of the starting material signals (nitrobenzene or cinnamaldehyde) was monitored, since in this case single signals could be detected easily without any overlays. From the raw data always the signal of the solvent and a blank spectrum of the FEP capillary are subtracted.

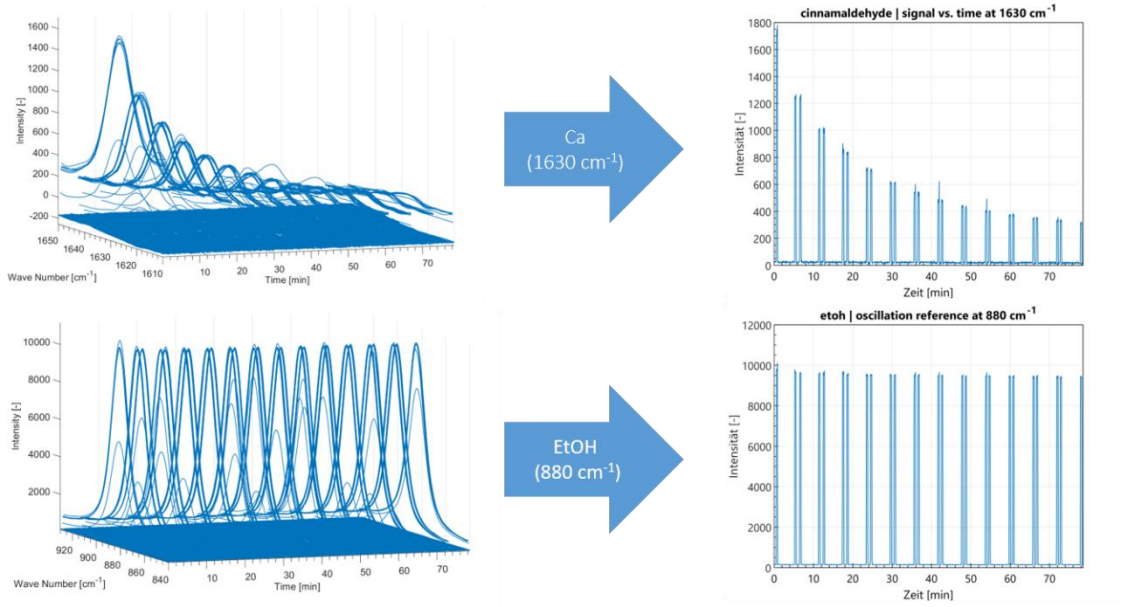

Figure S5: *Typical data acquisition during the hydrogenation of cinnamaldehyde. Shown above is the time course of the representation of the double bond. Below shown is a typical band of methanol to control the slugs over the total reaction time.*

The stability of the droplet was evaluated by monitoring the intensity of the characteristic Raman signal of methanol at 1035 cm^{-1} in the case of the hydrogenation of nitrobenzene or ethanol at 880 cm^{-1} in the case of the hydrogenation of cinnamaldehyde. Figure S6 shows exemplary the development of the methanol signal over a measurement time of 160 min. For all 34 oscillation cycles a constant intensity was observed.

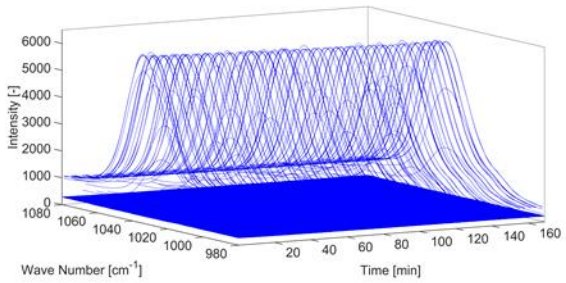

Figure S6: *Development of the characteristic Raman signal of methanol at 1035 cm^{-1} over time.*

Ensuring stable slugs throughout the reaction time is an important point of the measurement method. In addition to the Raman signal of the reactants, the slug length can be monitored via the Raman signal of methanol at 1035 cm^{-1}. Evaporation or disintegration of the slug can be detected by this. Typically, the velocity of the drop relative to the integration time of the Raman detector is chosen such that two measurements are taken at the edge of the slug and at least three spectra are taken inside the slug. Figure S14 shows an example of the same slug during an experiment at three different times.

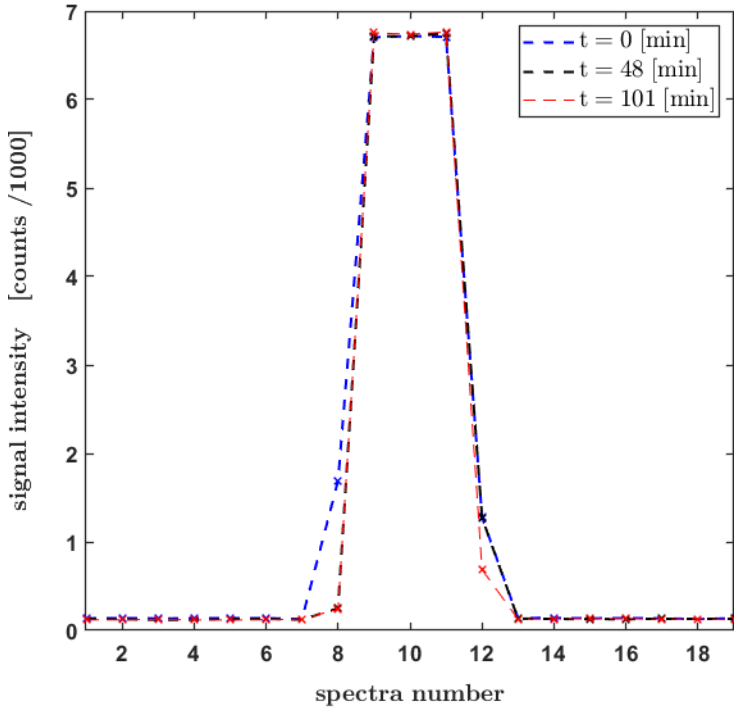

Figure S7: *Exemplary representation of the droplet at three time points of a measurement using the Raman signal of methanol at 1035 cm^{-1}.*

Note: The dashed lines are for orientation and do not describe the edges of the drop. There are three complete measurements inside the drop at each time and one at each edge.

4.) Catalyst synthesis and characterisation

Catalyst fibres

10 1 cm long carbon fibres (Goodfellow, diameter 0.5 mm) were added to a solution of 100 mL of deionised water. Subsequently, 5.5 µL of a 2,726 mol/L $Pd(NO_3)_2$ solution in water was added. The mixture was heated to 80°C and stirred for 30 mins. Afterwards, 5 µL formic acid in 5 mL deionised water were added dropwise at 80°C and the mixture was stirred for 3h at this temperature. After the solution was cooled to room temperature, a black precipitate was formed. The fibres were isolated and gently washed with deionised water and dried in a drying oven at 80°C for 10 mins. Blank samples without Pd were obtained using exactly the same synthetic procedure described before without the addition of $Pd(NO_3)_2$.

ICP-OES

Inductively coupled plasma atomic emission spectroscopy was utilised to determine the Pd content of the carbon fibres. 10 Fibres were analysed and Pd contents in the range of 19 – 42 mg/kg were obtained, with the average being 29.5 mg/kg. After the catalytic reaction, the fibre did not show any substantial loss of Pd, as the Pd content of 27 mg/kg showed.

Scanning Electron Microscopy

Scanning electron microscopic imaging was carried out on a Zeiss GeminiSEM 500. The backscattered electron analysis was carried out using a 4QBSD-detector at a 5 kV acceleration voltage. The palladium particles are appearing lighter in colour in comparison to the graphite. For the inlens pictures an inlens secondary electron detector was utilised.

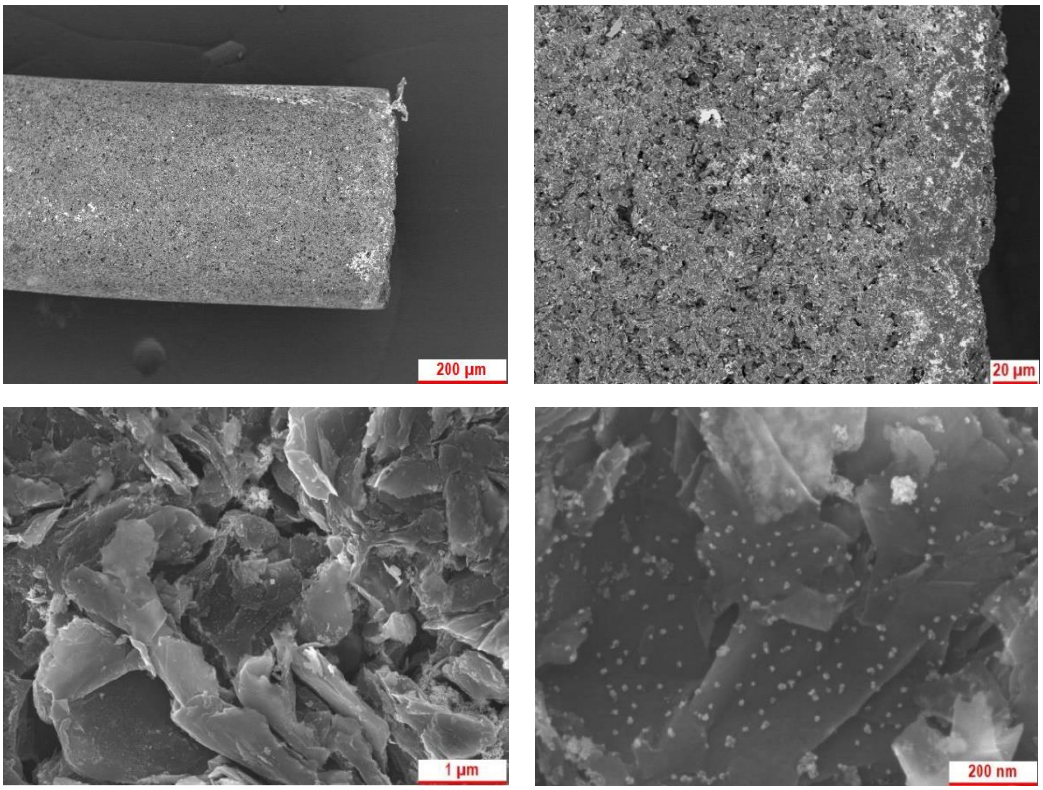

Figure S8: *SEM pictures of the edge of a Pd carbon fibre at different resolutions. Top: backscattered electron analysis, bottom: inlens pictures.*

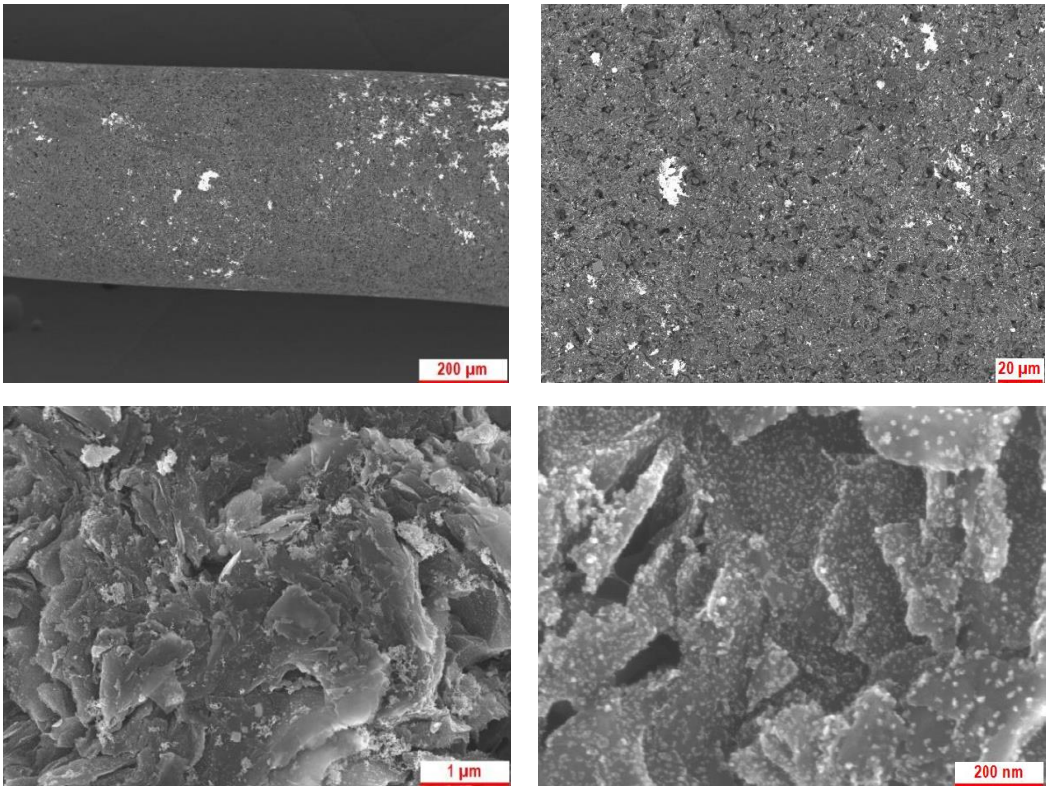

Figure S9: *SEM pictures of the middle of a Pd carbon fibre at different resolutions. Top: backscattered electron analysis, bottom: inlens pictures.*

Catalyst powders

Different grain sizes of the carbon material (125-160 µm, 160 – 250 µm, 315 – 500 µm, 500 – 1000 µm) were used. Whereas the smaller fractions were crushed and sieved, for the 500 – 1000 µm particle fraction charcoal extrudates (Norrit Rox 0.8) were sieved. The maximum water uptake of the different particle size fraction was determined through a slow water addition until saturation was achieved. For the experiments different palladium supported on carbon catalysts were prepared via incipient wetness impregnation. The desired amount of activate charcoal was impregnated with an aqueous solution of $Pd(NO_3)_2$ depending on the maximum water uptake. Afterwards the solid material was dried under air for a few hours and subsequently in a rotary kiln under nitrogen. In the next step, the catalysts were heated to 300°C at 5 K/min under forming gas (5% H_2 in N_2) and kept at this temperature for 2h. After this activation step, the cooling down was performed under nitrogen and later under air.

Powder X-ray diffraction

For the XRD measurements a Bruker D8 ADVANCED diffractometer with Bragg-Brentano geometry was utilised. Experiments were carried out with Cupper Kα radiation in a 2θ area between 10 and 90°. Due to the very low palladium loading and the very high surface area of the carbon support material, probably very small PD particles are formed, which cannot be resolved in the diffractograms of the catalysts. The diffractograms of the 315-500 µm particle fraction catalysts is shown exemplary in Figure S10 and only displays very broad reflexes, due the small Pd particles.

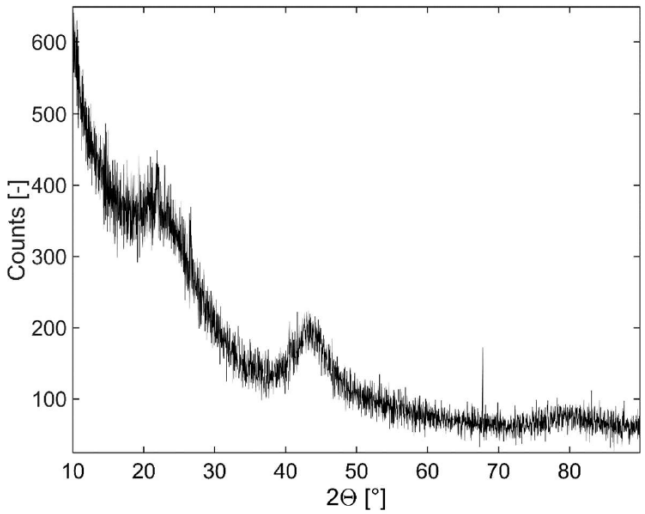

Figure S10: *PXRD of the 2 wt% Pd/C 315 – 500 µm catalyst.*

Nitrogen-sorption

The specific surface areas were determined via nitrogen physisorption measurements on a Micromeritics Tristar II 3020 apparatus.

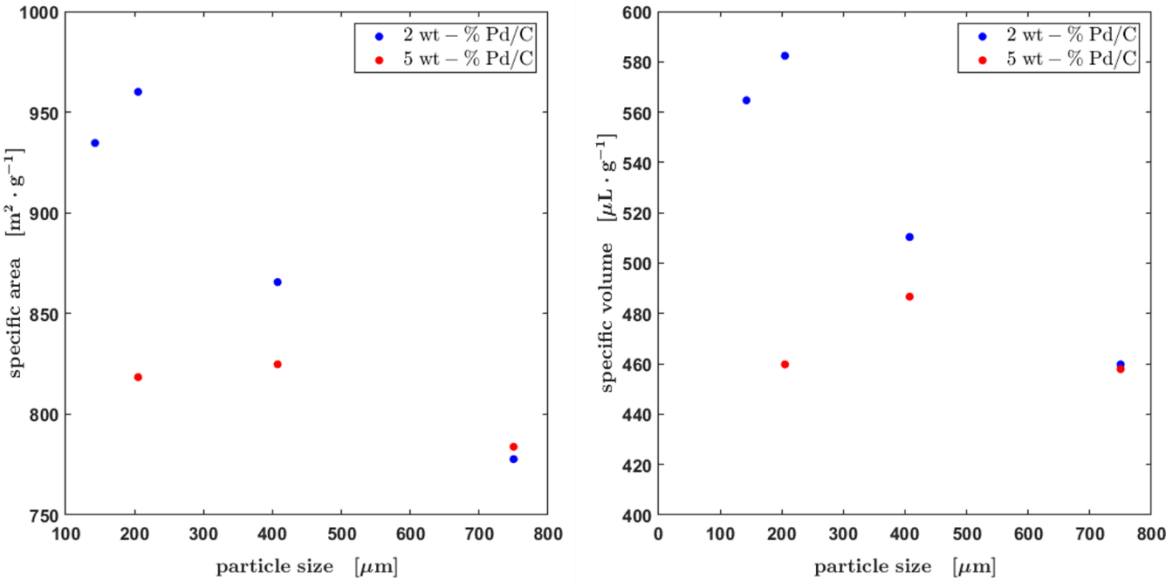

Figure S11: *Specific surface area and specific pore volume of the six different catalysts (three particle sizes with two weight fractions).*

Dispersion analysis

The palladium dispersion and the crystallite size of the 2wt% Pd/C catalyst (315 – 500 µm fraction) was determined via pulsed CO adsorption measurements. Using this method, a Pd dispersion of 14,75 % and a very small palladium crystallite size of 6.329 nm was determined.

Macro pore volume via centrifugation

The macro pore volume was determined by centrifugation. The catalyst was impregnated with water and weighed. The water from the particle interstices and macro pores was separated by centrifugation and the catalyst was weighed again. From the difference in weight the macro pore volume can be calculated.

Pore diffusion and mass transport limitation

The free diffusion coefficient of nitrobenzene in methanol was determined by Lu *et. al.* [1] at $2.28 \cdot 10^{-9}$ $m^2 \cdot s^{-1}$. For hydrogen in methanol a diffusion coefficient of $1.65 \cdot 10^{-8}$ $m^2 \cdot s^{-1}$.was found by Sporka et al. [2] Assuming that the effective diffusion coefficient corresponds to one tenth of the free diffusion coefficient, the following diffusion times of nitrobenzene can be calculated using the following equation.

$$t_{pore} = \frac{r_p^2}{D_{eff}}$$

Table 1: *Diffusion time as a function of particle radius.*

Particle radius [µm]	Time[s] nitrobenzene	Time[s] hydrogen
70	21.3	3.0
100	43.5	6.1
200	173.9	24.2
375	611.4	85.2

Therefor especially for the larger catalyst particles a mass transfer limitation for nitrobenzene can be expected.

[1] J. G. Lu, R. Kong, T. C. Chan, *The Journal of Chemical Physics* **1999**, *110* (6), 3003–3008. DOI: 10.1063/1.477895

[2] J. G. Lu, R. Kong, T. C. Chan, *Collection of Czechoslovak Chemical Communications* **1969**, *34*, 3145–3148. DOI: 10.11.35/cccc19693145

5.) Interpolation of concentration including the holdup reaction

Procedure

The slug moves through the capillary with the concentration known from the Raman measurement $c_{n,1}$ and the volume of $V_{droplet}$.

The index n of each concentration indicates the n-th oscillation through the bed.

When the slug reaches the catalyst bed, the liquid droplet mixes with the liquid catalyst hold-up of the catalyst bed, which has an unknown concentration.

The catalyst hold-up volume is assumed to be the sum of the inter particle volume and the macro-pore volume.

The concentration after leaving the bed, which is indicated by the index 2 can be calculated by linear interpolation with the knowledge of all oscillation lengths and both measured concentrations after c_n and c_{n+1}.

$$c_{n,2} = c_{n+1,1} + \left(c_{n,1} - c_{n+1,1}\right) * \frac{t_2}{t_1 + t_2}$$

Graphical description

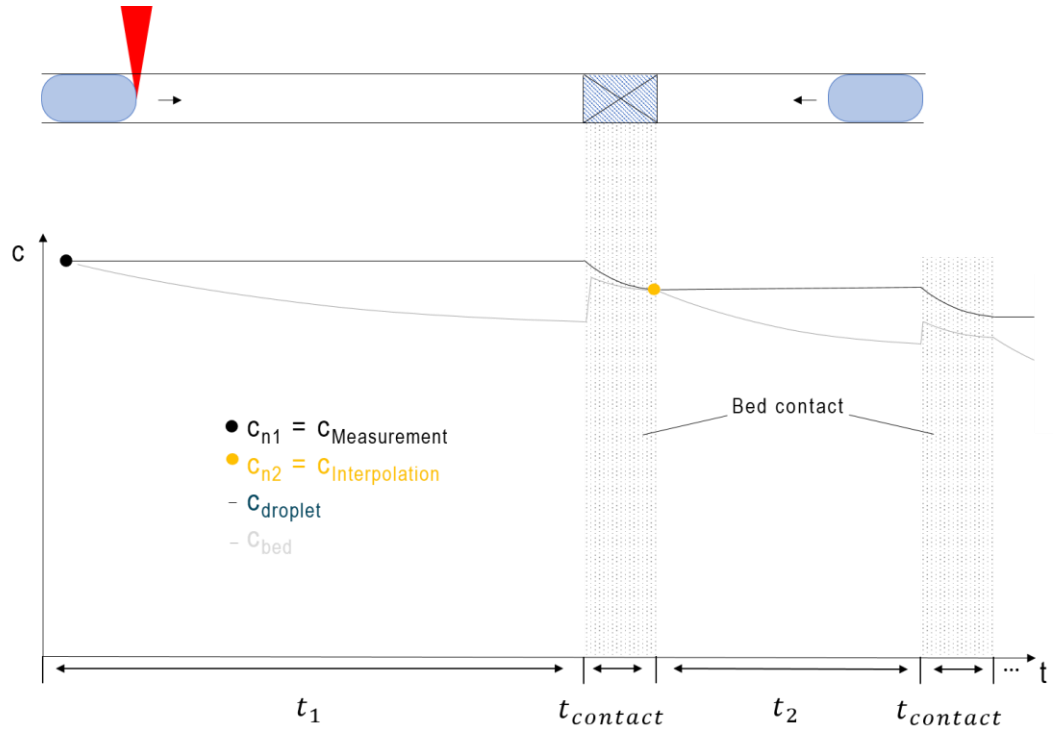

Figure S12: *Graphical representation of the interpolated concentration values.*

6.) Results and kinetic interpretation

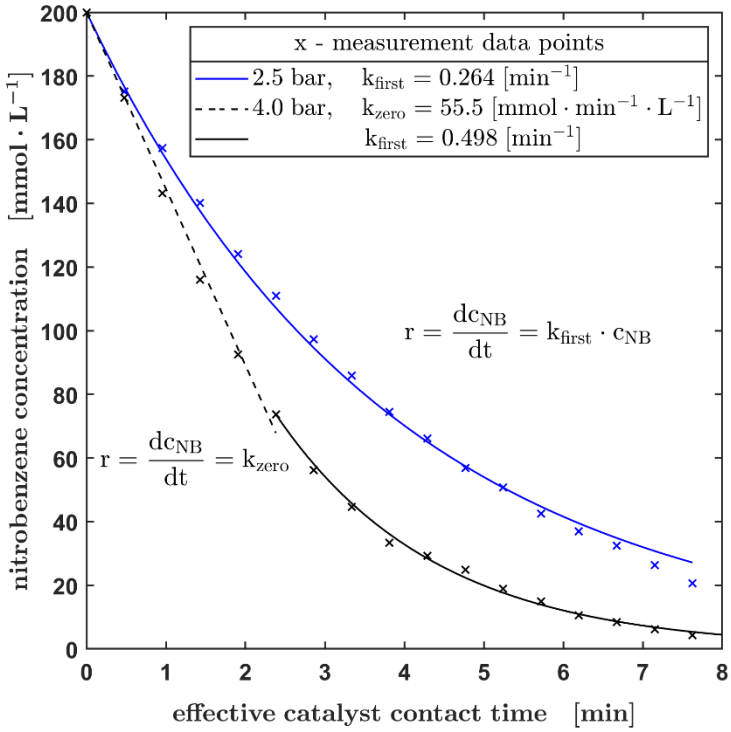

Figure S13: *Zero-order to first-order concentration profile of the hydrogenation of nitrobenzene at the Pd graphite fibres at different pressures.*

7.) Batch reaction

A batch experiment was carried out in a Buechi reactor. The reactor has a total volume of 300 mL and uses a Rushton turbine for mixing and gas injection.

The reaction volume in the experiment was 70 mL methanolic solution with 100 mmol/L nitrobenzene. Pure hydrogen was used. During the reaction, the hydrogen pressure was kept at 1.5 bar by replenishing. The conversion was determined by measuring the dosed hydrogen.

332 mg Pd catalyst (2 w%) with a grain size of 315-500 µm was used.

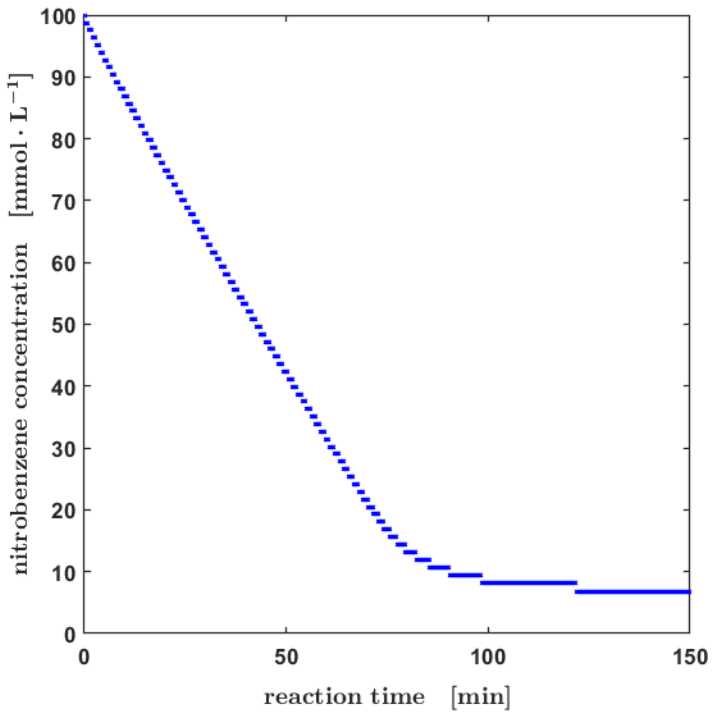

Figure S14: *Calculated nitrobenzene concentration over the reaction time.*

As shown in Figure S13 the majority of the concentration profile can be described as a linear decrease, which indicates a mass transport limitation.