



**Experiment title:**  
Impact of interfacial solvent restructuring onto catalytic behaviour – hydrogenation of styrene at Pd nanoparticles

**Experiment number:**  
CH 5509

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<b>Shifts:</b> 6	<b>Local contact(s):</b> Gavin Vaughan	

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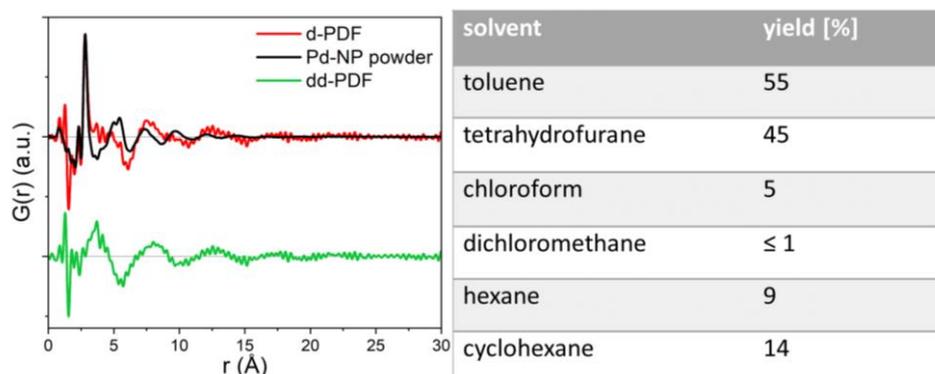
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## Report:

With this experiment we wanted to investigate the solvation shells of organic solvents around palladium (Pd) nanoparticles (NPs) with an average diameter of 3 nm. The overall sizes of the solvation shells, the molecular configurations of the solvent molecules at the particle-solvent interface and structural changes that occur during a catalytic reaction should be correlated with the catalytic activity of the NPs in the liquid-phase hydrogenation of styrene to ethylbenzene.

The proposed experiments were carried out using the 70 keV X-ray beam centered in the corner of the CdTe detector, the capillary holder provided by the beamline ID15-EH3 and an in-situ setup designed by our own.

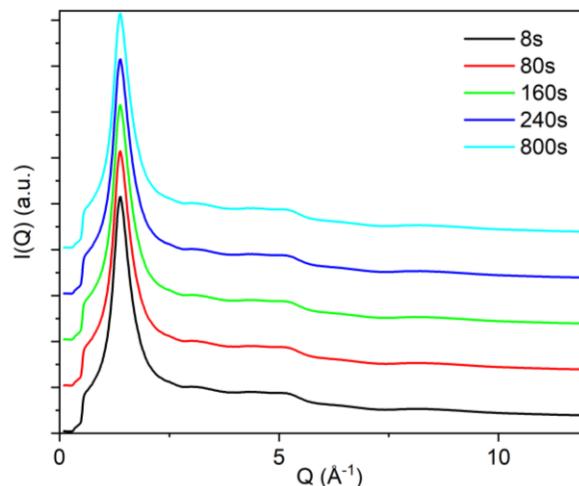
In preparation of the experiment Pd NPs stabilized by 1-hexanethiol and 1-dodecanethiol with a diameter of  $3.0 \pm 0.5$  nm were successfully synthesized. They were proven to be long term stable in dispersion in different organic solvents like tetrahydrofuran (THF), hexane, cyclohexane, toluene and chlorinated solvents like dichloromethane



*Fig. 1: left: Experimental difference-PDF (d-PDF) of colloidal Pd NPs in THF (solvent contribution already subtracted, black) with contribution of Pd NPs (red) and in offset the dd-PDF of the restructured solvent molecules (green); right: Results of the catalytic lab studies, yield given for ethyl benzene (selectivity  $\geq 99\%$ ); reaction conditions: 0.5 mmol styrene, rt, 1 bar  $H_2$ , 5 mol% catalyst (2.7 mg Pd, 0.025 mmol, 4 mg Pd NPs), 3 mL solvent, 2h.*

and chloroform. Preliminary ex-situ synchrotron experiments showed their amorphous structure and the evidence of restructured solvent molecules at the NP-solvent interface (*Fig. 1, left*). Catalytic tests of the Pd NPs in the hydrogenation of styrene under mild conditions (1 bar H<sub>2</sub>; room temperature) in different organic solvents showed exemplarily the solvent dependency of such liquid-phase catalysis (*Fig 1, right*).

For the experiment, the nanoparticles were first mixed with the organic solvent in a special gas tight Schlenk flask. Via connectors with valves, Swagelok fittings and perfluoralkoxy (PFA) hoses, the flask got connected to a 1.55 mm borosilicate capillary, which was mounted in a capillary holder and placed in the X-ray beam. The mixture was pumped through the circuit with a micro annular gear pump. Before purging the flask with 1 bar H<sub>2</sub> and adding styrene to start the reaction, a background measurement was recorded. We performed different catalysis with Pd NPs with different capping agents. Each catalysis was measured for 2 h with a readout time of 8 s, and the data was binned afterwards to enhance statistics. Unfortunately and against the expectations, the shape, position and intensity of the first sharp diffraction peak was entirely unaffected by the occurring catalysis for all NP-solvent mixtures (*Fig. 2*). This indicates that i) there is in principle no significant solvent restructuring around the Pd NPs or ii) there is at least no impact of the Pd NPs onto the interfacial solvent structure in the range where our dispersions showed catalytic activity and were colloidally stable.



*Fig. 2: Selected  $I(Q)$  datasets of the hydration of styrene in THF catalyzed by Pd-NPs after a specific time period.*

Besides the in-situ experiments, we performed ex-situ background measurements of the Pd NP powders, pure solvents and reactants. Additional, we brought oleic acid stabilized Fe<sub>x</sub>O<sub>y</sub> NP powders and dispersions in THF and cyclohexane to investigate the solvent restructuring at the NP-solvent interface. By subtraction of the bulk solvent and the Fe<sub>x</sub>O<sub>y</sub> powder signal, the double-difference PDF (dd-PDF) is gained. It contains the information of the restructured solvent molecules around the NPs, which was present over ca. 20 Å in this case as a sinusoidal oscillation. For comparison of the restructured solvent molecules 6 nm and 9 nm sized NPs were measured in the different solvents. Further analysis hereof is still ongoing. We expect submission of the paper in the start of fall 2019.