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Supporting Information

Influence of the Nanoparticle Size on Hydrogen Release and Side Product Formation in Liquid Organic Hydrogen Carrier Systems with Supported Platinum Catalysts

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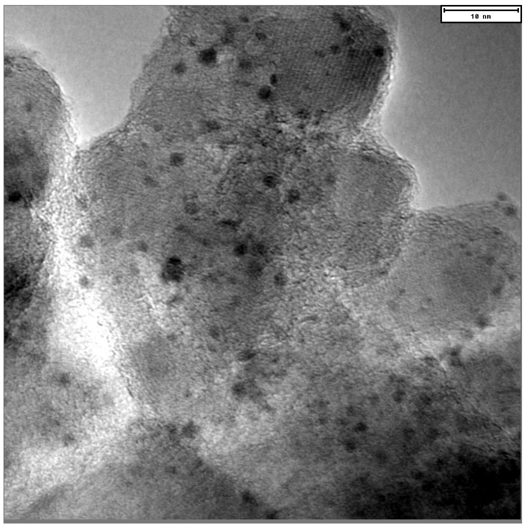
Synthesis parameter for catalysts with different platinum nanoparticle size

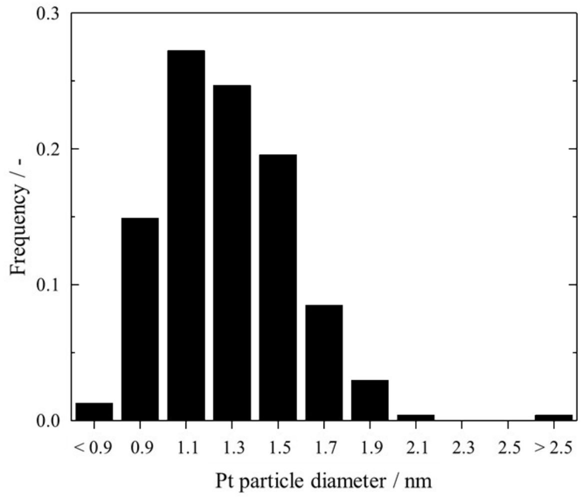
Nominal particle diameter d / nm	Synthesis method	Parameters
1.2	Production by Clariant	-
1.4	Production by Clariant	-
1.55	Wet impregnation	Reduction at 400 °C
1.75	Wet impregnation	Reduction at 500 °C
1.95	Wet impregnation	Reduction at 600 °C
2.7	Colloidal approach	n(Pt) : n(PVP) = 1:50
2.9	Production by Clariant	-
3.1	Colloidal approach	$c(H_2PtCl_6)$ = 1 mmol/l n(Pt) : n(PVP) = 1:40 V(EtOH) : $V(H_2O)$ = 1:9 T = 90 °C, t = 3 h
3.7	Colloidal approach	Seed mediated growth from 3.1 nm solution
3.9	Colloidal approach	$c(H_2PtCl_6)$ = 6 mmol/l
4.6	Colloidal approach	Seed mediated growth from 3.9 nm solution

For the colloidal approach the parameters for the synthesis of 3.1 nm particles serve as standard; deviations from these parameters to obtain other sizes of platinum particles are given in the above table.

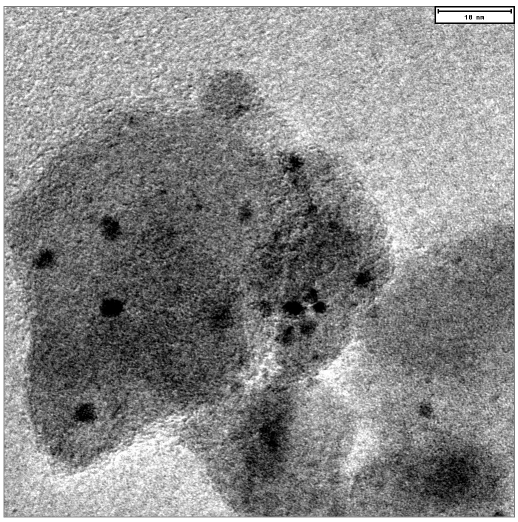
TEM images and platinum particle size distributions for remaining catalysts

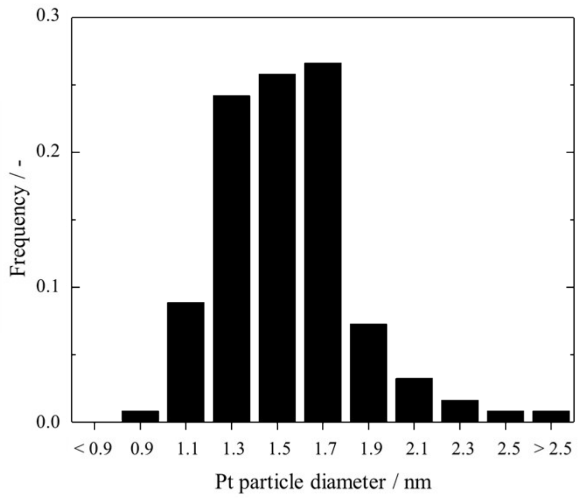
1.2 nm



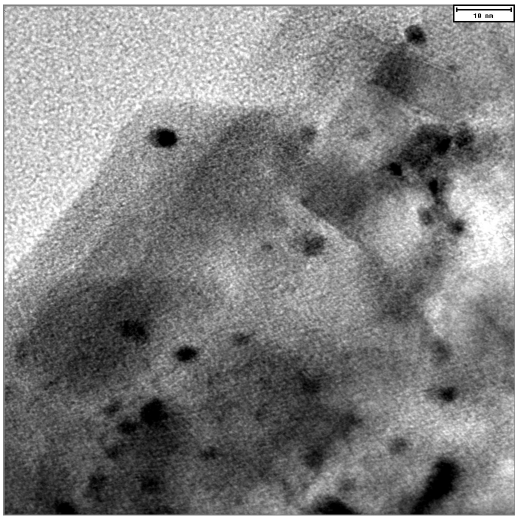


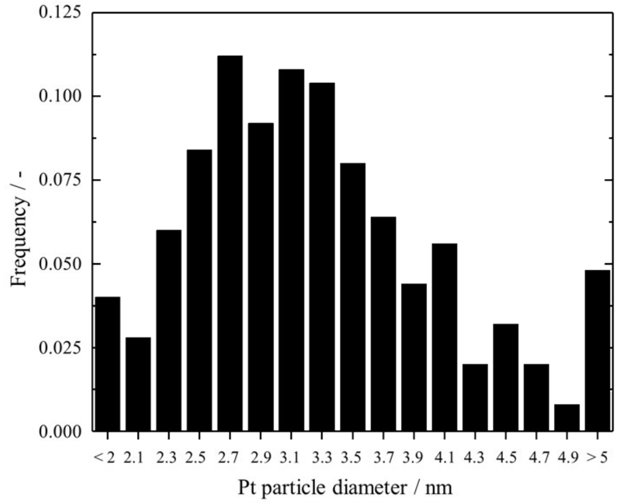
1.55 nm



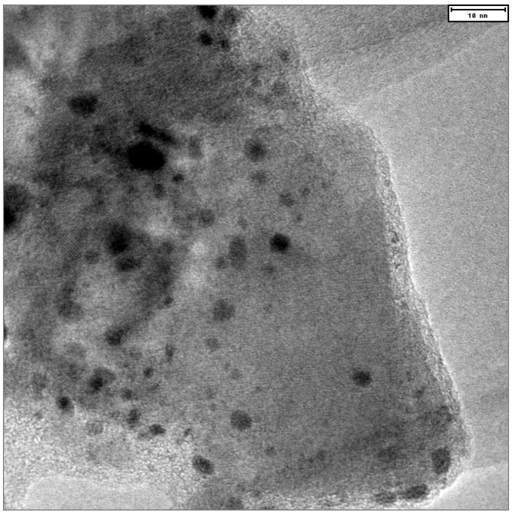


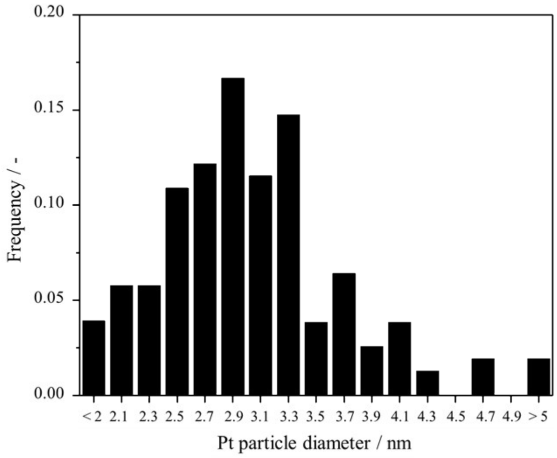
2.7 nm



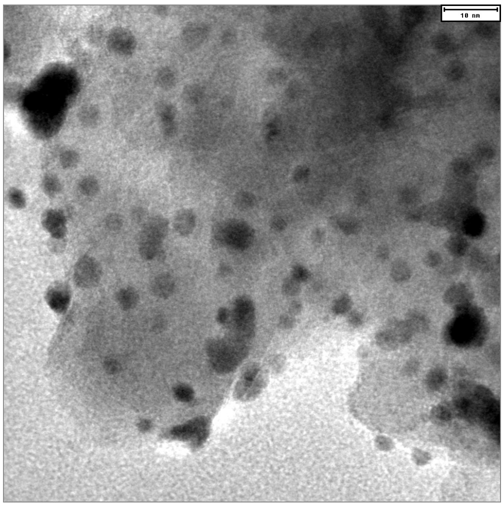


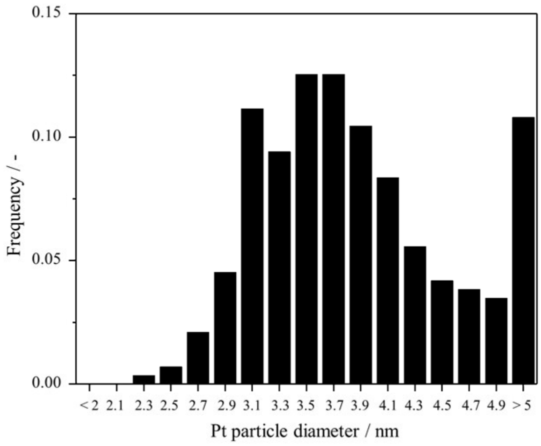
2.9 nm



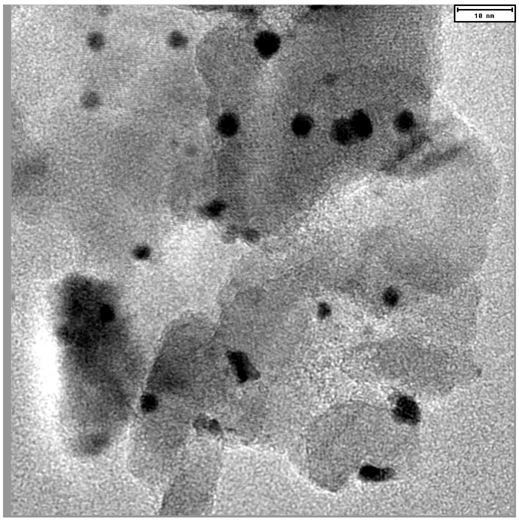


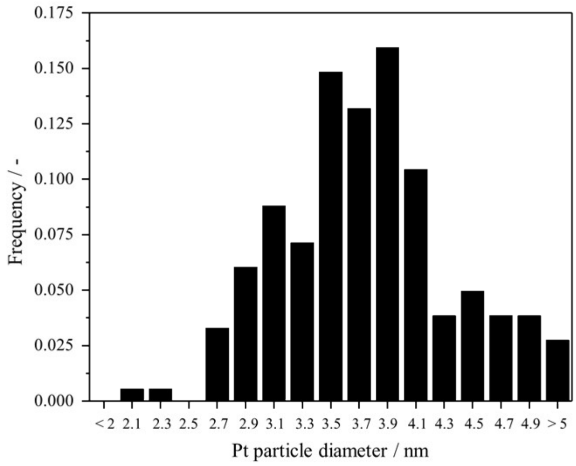
3.7 nm



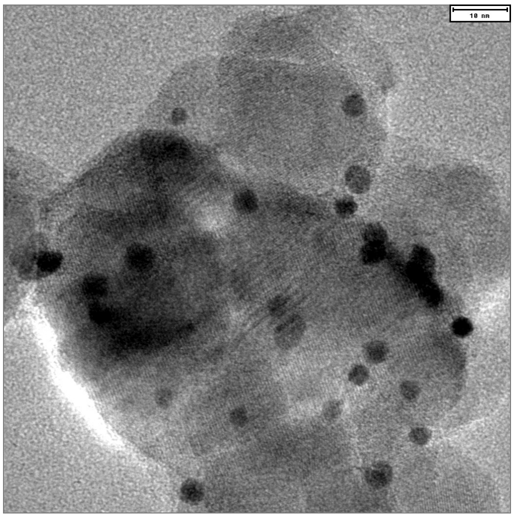


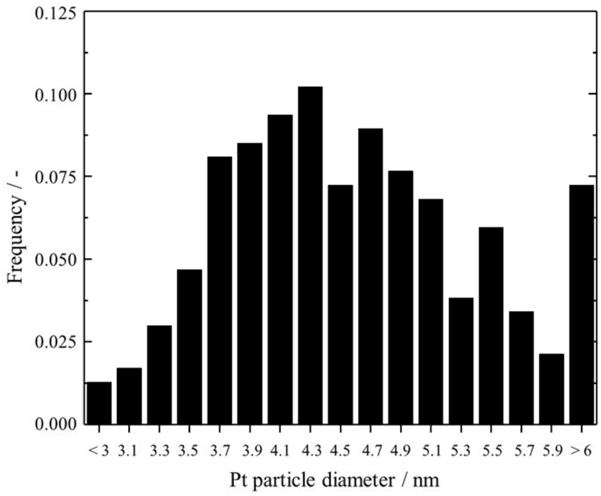
3.9 nm


10 nm


0.175
0.150
0.125
0.100
0.075
0.050
0.025
0.000
Frequency / -
< 2 2.1 2.3 2.5 2.7 2.9 3.1 3.3 3.5 3.7 3.9 4.1 4.3 4.5 4.7 4.9 > 5
Pt particle diameter / nm

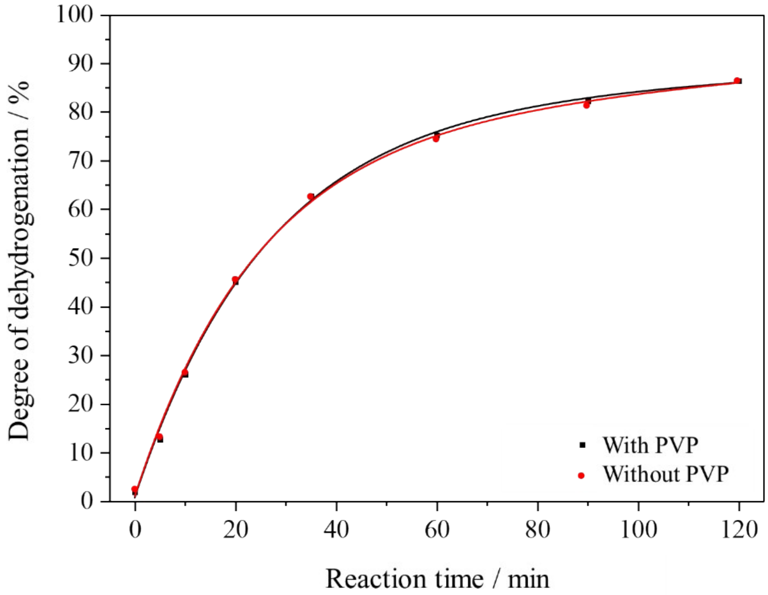
4.6 nm


10 nm


0.125
0.100
0.075
0.050
0.025
0.000
Frequency / -
< 3 3.1 3.3 3.5 3.7 3.9 4.1 4.3 4.5 4.7 4.9 5.1 5.3 5.5 5.7 5.9 > 6
Pt particle diameter / nm

Removal of PVP stabilizing agent

To show that there are no remaining residues of the stabilizing polymer PVP after calcination and therefore the catalyst activity is not influenced by the synthesis procedure, an impregnated catalyst was subsequently treated with PVP solution, followed by a calcination and reduction procedure as it is applied for the colloidal approach. The resulting catalyst was tested in a standard LOHC dehydrogenation experiment in comparison to its untreated counterpart.



Course of the degree of dehydrogenation over reaction time for a catalyst produced without PVP and a catalyst produced in the same batch, subsequently impregnated with PVP and calcined. Experimental conditions: T = 310 °C, p = 0.1 MPa, n_{LOHC} = 0.1 mol, n_{Pt}/n_{LOHC} = 0.001, t_V = 120 min, Ar atmosphere. Lines are guide to the eye.

From the graph there can be seen no activity difference between the catalyst produced without PVP and the catalyst subsequently impregnated with PVP. This indicates that the preparation method involving the stabilizing agent PVP does not influence the catalyst performance. Furthermore, the results suggest a complete removal of the polymer through the applied calcination procedure by oxidation of the organic compound.

Calculation of catalyst productivities

The productivity P of a catalyst indicates the mass of hydrogen released per mass of active component in a given time interval. It is calculated from the experimental data as follows:

$$P = \frac{m_{H_2}}{m_{Pt} \cdot t} = \frac{\Delta DoDH \cdot n_{H18-DBT} \cdot n_{H_2} \cdot M_{H_2}}{\Delta t \cdot m_{catalyst} \cdot B}$$

DoDH: degree of dehydrogenation, B: catalyst loading (0.3 wt%)

The initial productivity refers to the linear initial section of the DoDH vs. time curve. The overall productivity considers the full range of DoDH of the untreated catalysts. The latter thereby is especially helpful to compare sulphur modified catalysts as the effect of the treatment is more pronounced if a high share of dehydrogenated LOHC material (high DoDH) is present, i. e. at the end of the dehydrogenation experiment.

To obtain a better comparison, especially in the context of different sizes of active platinum particles, the productivity is related to the active platinum mass on the surface of the particles, calculated via the dispersion D of the catalysts:

$$P_{active} = \frac{P}{D} = \frac{m_{H_2}}{m_{Pt,\ active} \cdot t}$$