Supplementary Information

Structure sensitivity of the low temperature dehydrogenation of perhydro (di)benzyltoluene on supported platinum nanoparticles

Yazan Mahayni[a,b], Lukas Maurer[a,b], Franziska Auer[a], Andreas Hutzler[a], Peter Wasserscheid[a,b], Moritz Wolf[c,*]

[a] Forschungszentrum Jülich GmbH, Helmholtz-Institute Erlangen-Nürnberg for Renewable Energy (IEK-11), Erlangen, Germany

[b] Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU), Lehrstuhl für Chemische Reaktionstechnik, Erlangen, Germany

[c] Karlsruhe Institute of Technology (KIT), Engler-Bunte-Institut & Institute of Catalysis Research and Technology, Karlsruhe, Germany

[*]Corresponding author. Address: Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany. E-Mail-address: moritz.wolf@kit.edu

1. Textural analysis of the Al_2O_3 catalyst support material

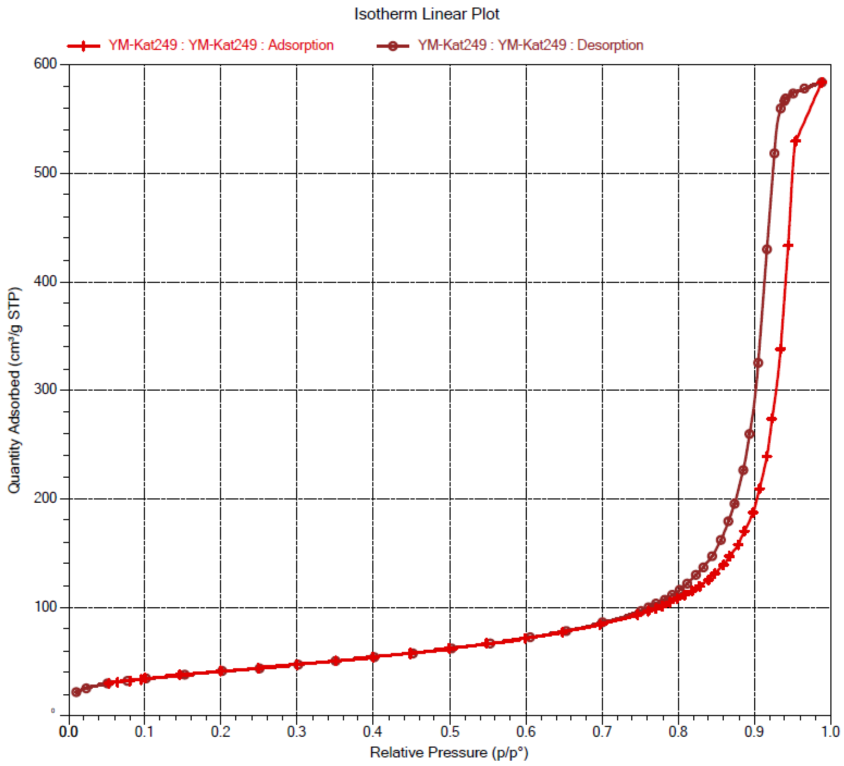


Figure S1: N_2 adsorption and desorption isotherm for the powdery Al_2O_3 support.

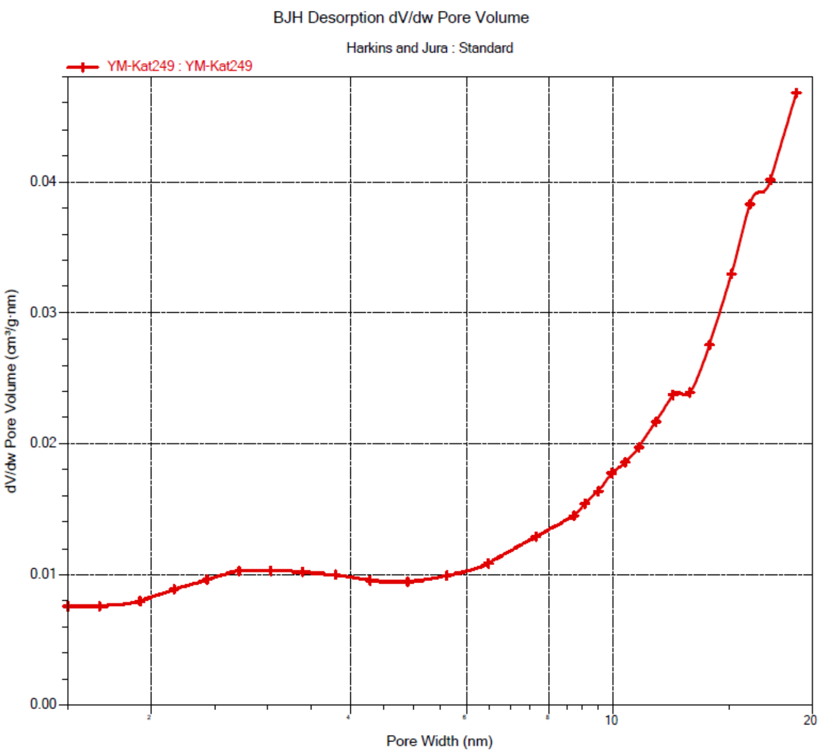
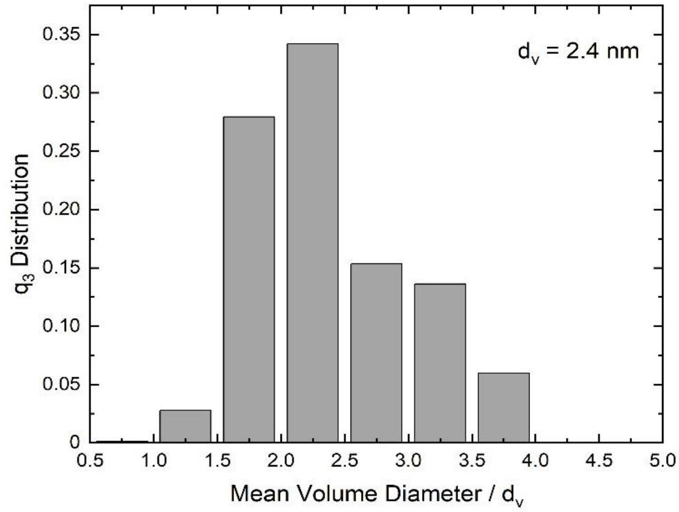
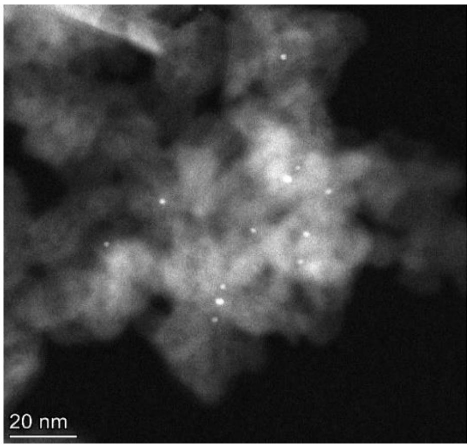


Figure S2: BJH analysis of the pore size distribution of the desorption isotherm of the powdery Al_2O_3 support.

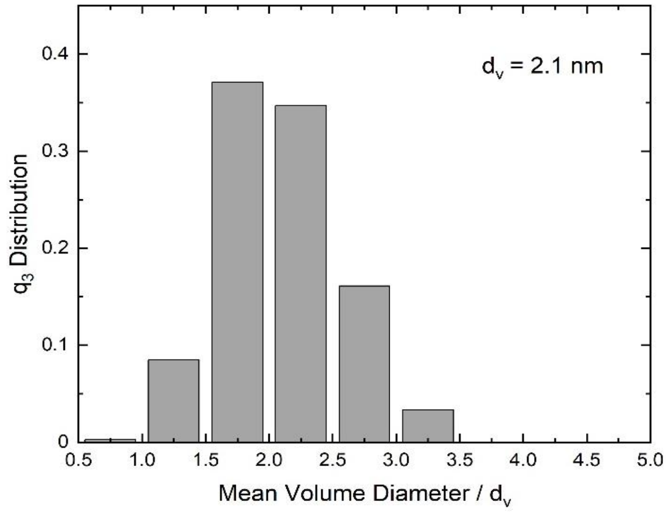
2. TEM images and Pt nanoparticle size distributions of catalysts

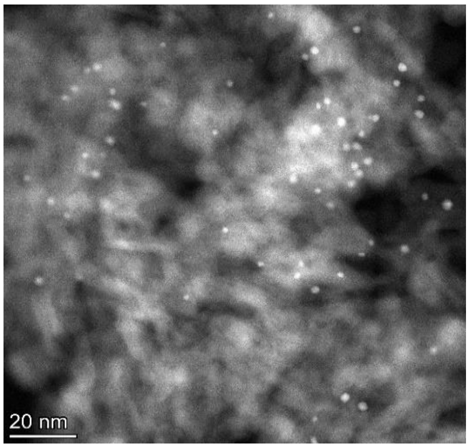
0.8 mL $NaBH_4$



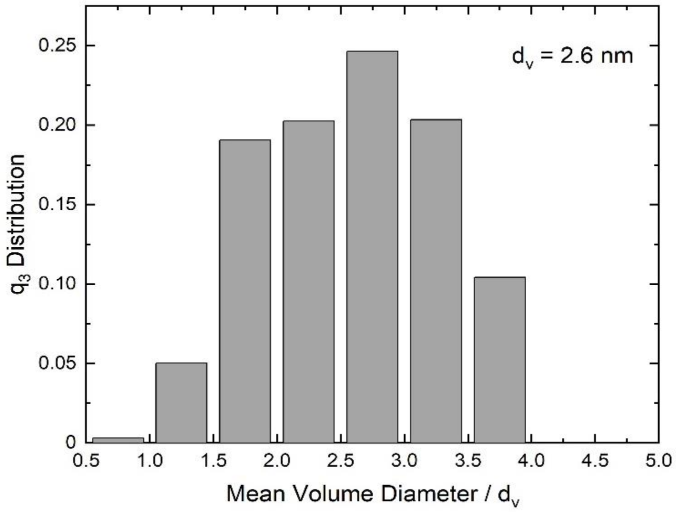


1.0 mL $NaBH_4$





1.2 mL $NaBH_4$



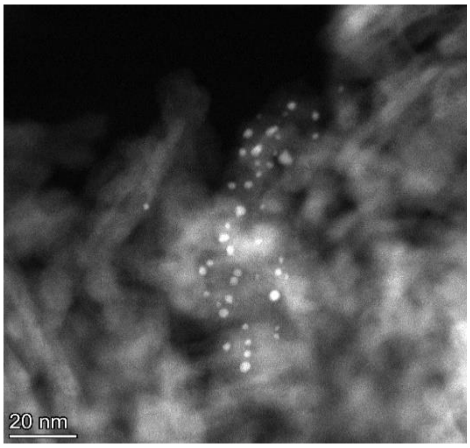
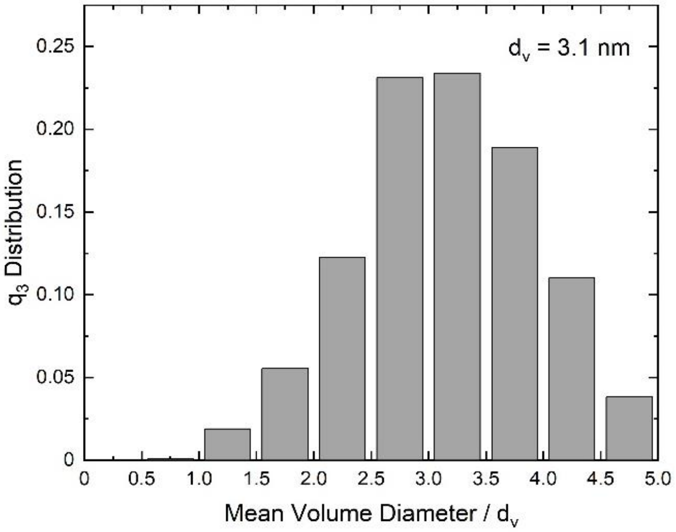
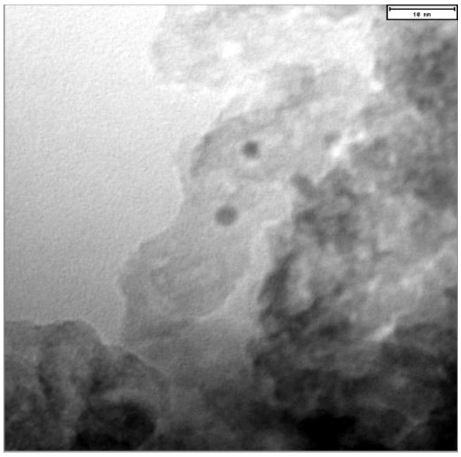


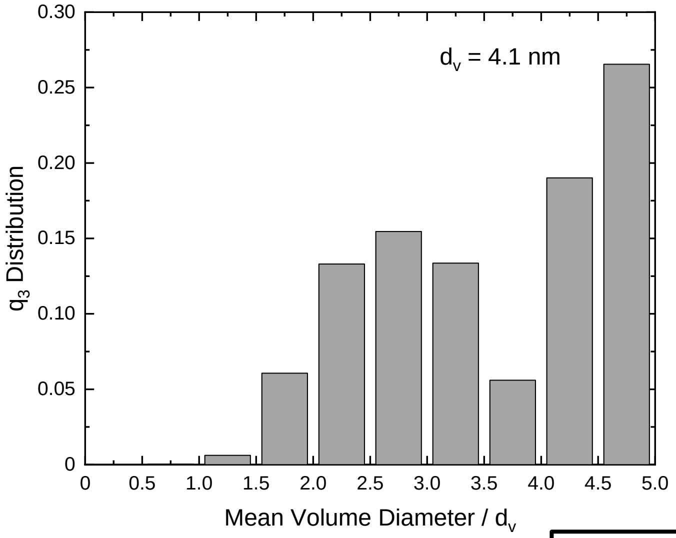
Figure S3: Nanoparticle size distributions of Pt/Al_2O_3 catalysts synthesized via 0.8, 1.0, and 1.2 mL aqueous $NaBH_4$.

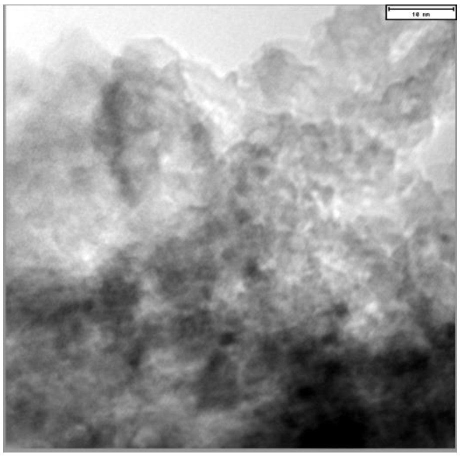
1.4 mL $NaBH_4$



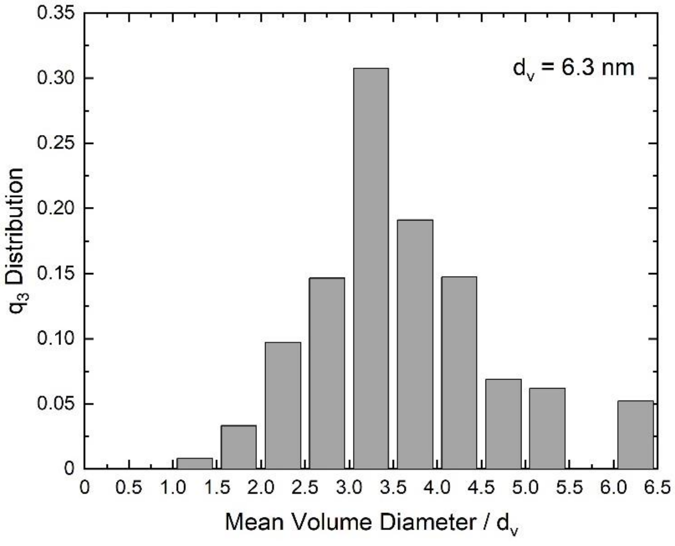


1.6 mL $NaBH_4$





1.8 mL $NaBH_4$



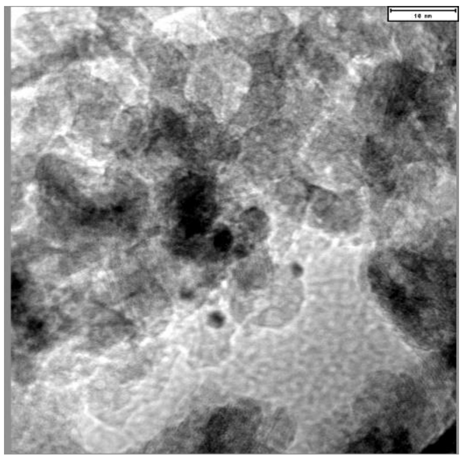


Figure S4: Nanoparticle size distributions of Pt/Al_2O_3 catalysts synthesized via 1.4, 1.6, and 1.8 mL aqueous $NaBH_4$.

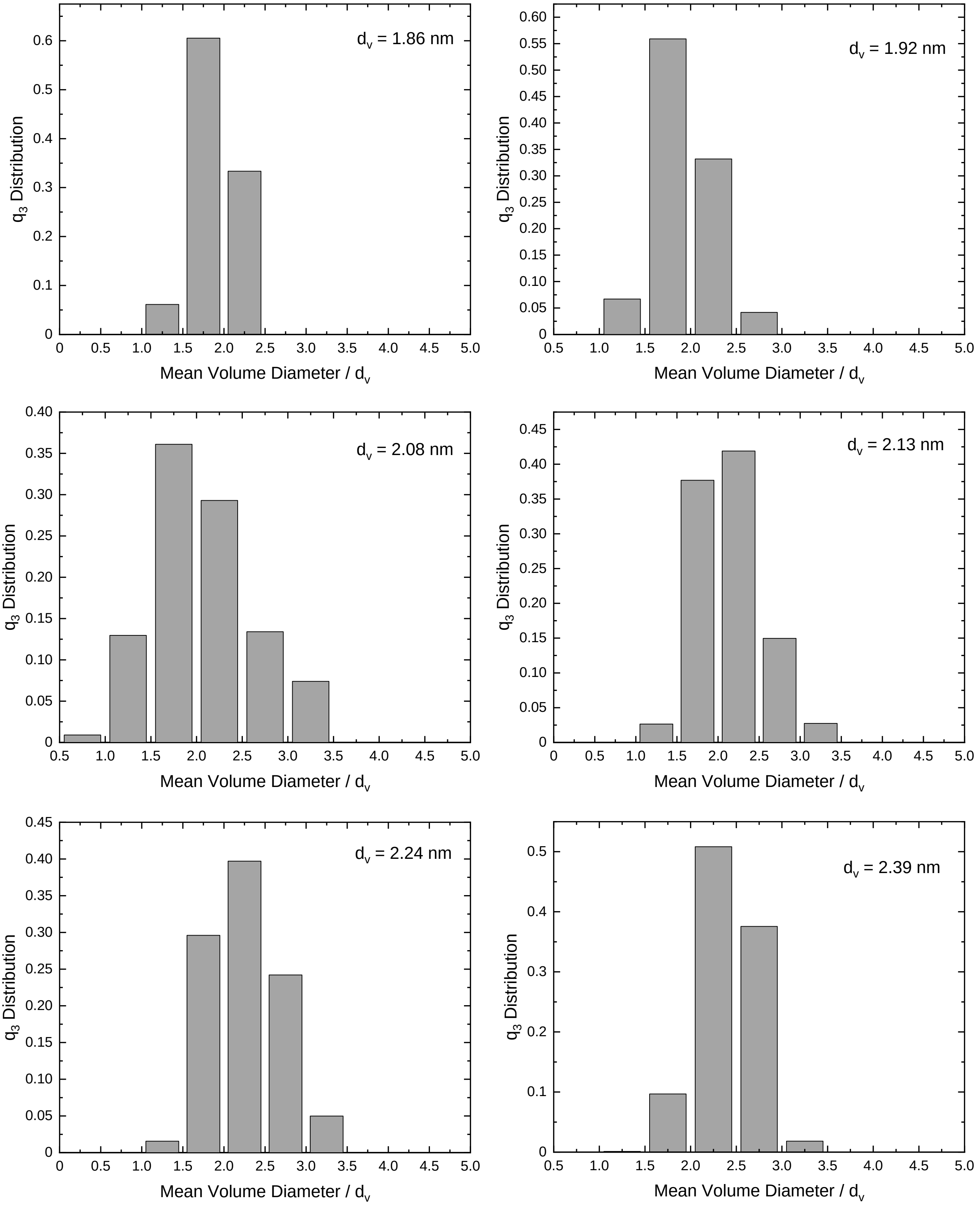


Figure S5: Nanoparticle size distributions of Pt/Al_2O_3 catalysts with platinum particle sizes 1.8-2.4 nm synthesized via basic $NaBH_4$.

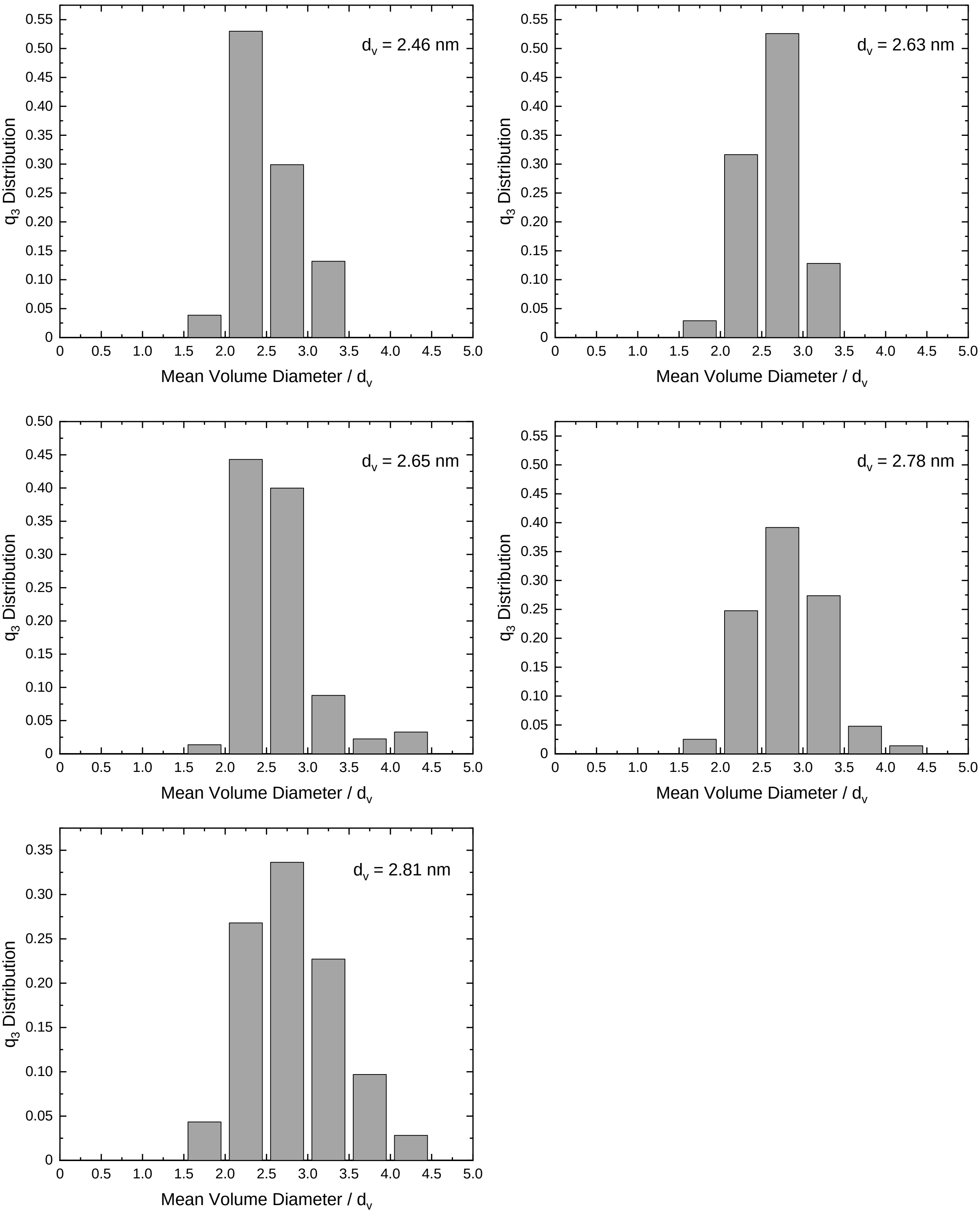


Figure S6: Nanoparticle size distributions of Pt/Al_2O_3 catalysts with platinum particle sizes 2.5-2.8 nm synthesized via basic $NaBH_4$.

3. Measured Pt loadings of the studied catalysts

Table S1: ICP loadings of Pt/Al_2O_3 catalysts .

Volume $NaBH_4$ / mL	Particle size / nm	Theoretical	ICP
0.8	**2.90**	0.20 wt.% Pt	0.19±0.002 wt.% Pt
1.0	**2.30**	0.20 wt.% Pt	0.18±0.003 wt.% Pt
1.2	**2.60**	0.20 wt.% Pt	0.19±0.002 wt.% Pt
1.4	**3.20**	0.20 wt.% Pt	0.17±0.01 wt.% Pt
1.6	**4.00**	0.20 wt.% Pt	0.18±0.004 wt.% Pt
1.8	**5.50**	0.20 wt.% Pt	0.17±0.004 wt.% Pt

4. Temperature stability @ 250 °C under N_2-atmosphere:

The thermal stability of supported Pt nanoparticles was analyzed by annealing under a continuous flow of N_2 in a muffle furnace at a temperature of 250 °C, with a ramp of 5 K/min and a total duration of four hours.

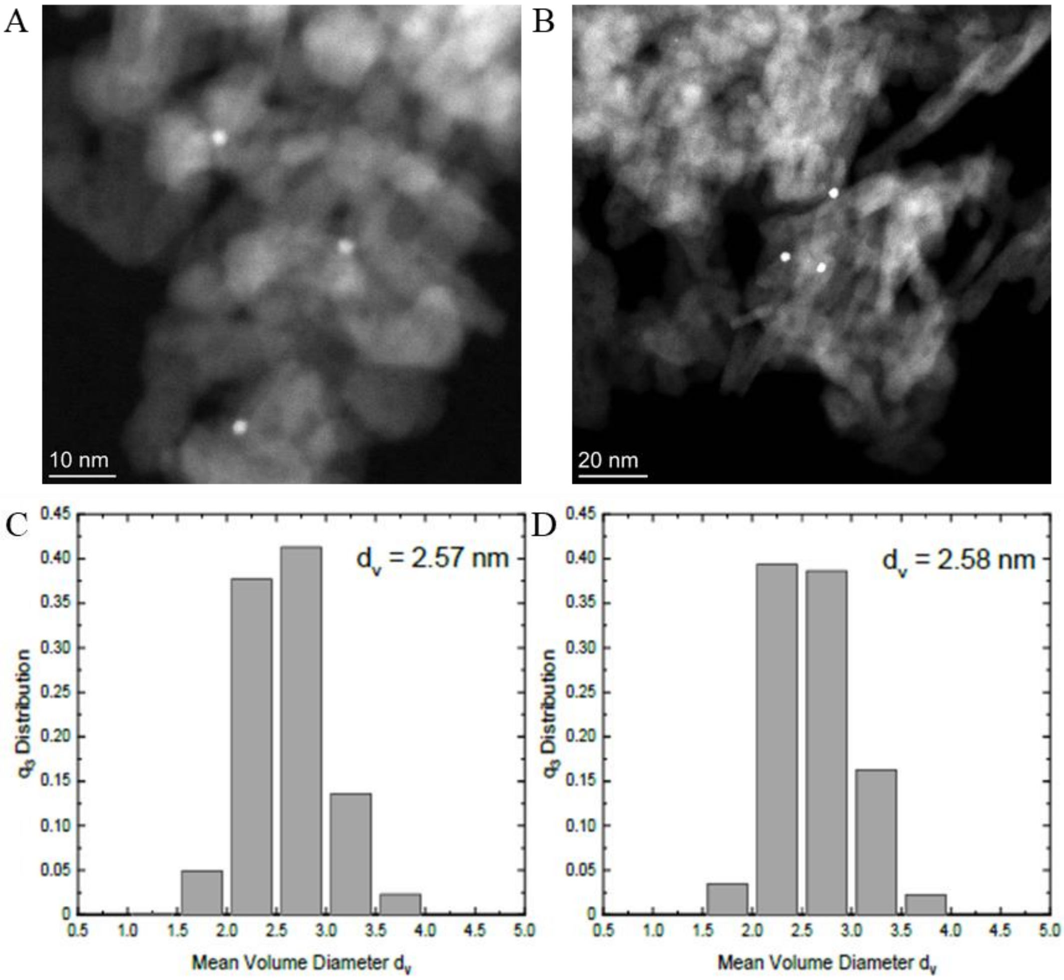


Figure S7: HRSTEM micrographs of Pt/Al_2O_3 catalysts before (A) and after (B) exposure to elevated temperatures of 250 °C under N_2 atmosphere with (C) and (D) corresponding Pt nanoparticle size distributions.

5. Observed initial normalized productivities in LOHC dehydrogenation

Table S2: Initial normalized productivities for the dehydrogenation of H18-DBT over the investigated Pt particle sizes and reaction temperatures

250 °C		280 °C	
Pt particle size / nm	**$P_{2-10\%}$ / g_{H2} $g_{Pt,surf}^{-1}$ min^{-1}**	**Pt particle size / nm**	**$P_{2-10\%}$ / g_{H2} $g_{Pt,surf}^{-1}$ min^{-1}**
1.94	0.1138	**2.02**	0.31797
2.12	0.08989	**2.33**	0.30975
2.26	0.12986	**2.56**	0.34034
2.37	0.18773	**2.79**	0.39555
2.59	0.07876	**3.37**	0.20784
2.93	0.05883	**3.99**	0.14191
3.13	0.06681		
3.44	0.03501		

Table S3: Initial normalized productivities for the dehydrogenation of H12-BT over the investigated Pt nanoparticle sizes and reaction temperatures

220 °C		230 °C		240 °C	
Pt particle size / nm	$P_{2\text{-}10\%}$ / g_{H2} $g_{Pt,surf}^{-1}$ min^{-1}	**Pt particle size / nm**	$P_{2\text{-}10\%}$ / g_{H2} $g_{Pt,surf}^{-1}$ min^{-1}	**Pt particle size / nm**	$P_{2\text{-}10\%}$ / g_{H2} $g_{Pt,surf}^{-1}$ min^{-1}
1.92	0.1138	**1.93**	0.31797	**1.86**	0.48483
2.08	0.08989	**2.09**	0.30975	**1.92**	0.48533
2.20	0.12986	**2.13**	0.34034	**2.08**	0.50259
2.33	0.18773	**2.35**	0.39555	**2.13**	0.45251
2.56	0.07876	**2.60**	0.20784	**2.24**	0.42948
2.78	0.05883	**2.85**	0.14191	**2.39**	0.52505
3.37	0.06681	**3.38**	0.11361	**2.40**	0.50973
4.03	0.03501	**4.11**	0.11818	**2.41**	0.54563
				2.65	0.70186
				2.95	0.71221
				3.37	0.71069
				3.99	0.77386

6. Arrhenius plot for the consideration of possible mass transport limitations

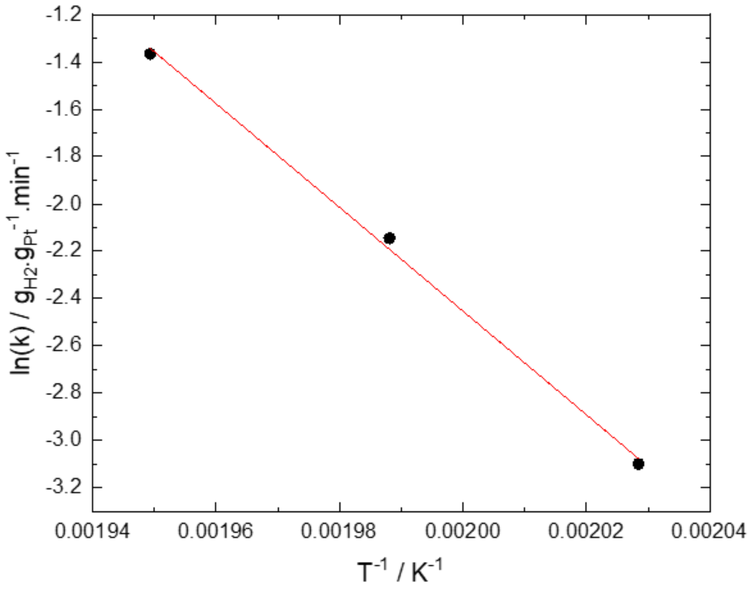


Figure S8: Arrhenius plot for the dehydrogenation of H12-BT at 220-240 °C for catalysts with 2.3 nm platinum nanoparticles, according to Arrhenius equation.

7. Continuous testing in H12-BT dehydrogenation at 250 °C

The reaction chamber of the dehydrogenation plant is a 120 mm long stainless-steel tube with an inner diameter of 10 mm, of which about 80 mm can be used as the active reaction chamber for catalyst. The feed is supplied using the MZR-2505 micro gear pump (HNP Mikrosysteme), calibrated for a mass flow rate of 0.1 to 4 g min^{-1}. The preheated H12-BT is fed at the bottom of the reaction chamber, allowing the reactor to operate exclusively in an upstream process. Both the feed preheating unit and the reactor are temperature-controlled using DAK 40D electric heating jackets (Ihne & Tesch), regulated by a fitron 4 TP temperature controller (Fiege electronic GmbH). The temperatures of the feed preheater and the reactor are regulated by Type-K thermocouples, while the temperature of the catalyst bed is measured in the middle of the reaction chamber.

A side overflow at the reactor head allows the liquid product of dehydrogenated/partially dehydrogenated species to flow into a product container. The gas phase, mainly consisting of hydrogen, flows through the reactor head into an intensive cooler at 5 °C, condensing any entrained LOHC. Finally, the hydrogen is filtered through an activated carbon cartridge before being mixed with an argon stream for dilution, and its concentration is measured by the FTC 300 thermal conductivity detector (Messkonzept GmbH).

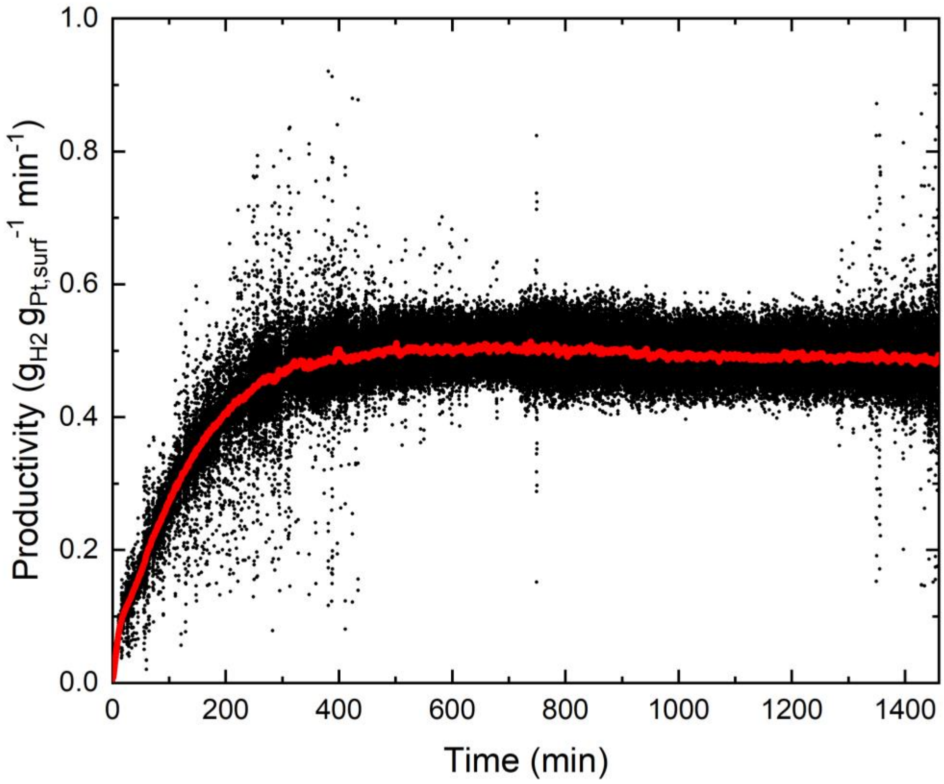


Figure S9: Continuous dehydrogenation of H12-BT at 250 °C for catalyst of this study with 2.3 nm platinum nanoparticles. Black dots are single measurements of H_2 release (frequency: 1 Hz), red line is smoothed using FFT filter over measurement points.

8. Side products analysis during H12-BT semi-batch dehydrogenation at 250 °C

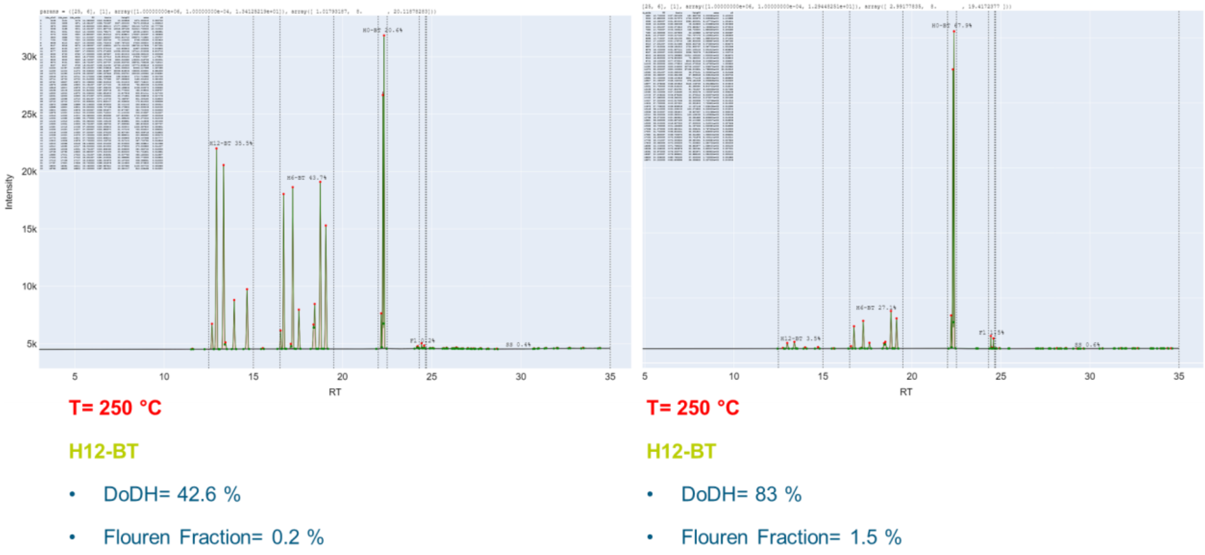


Figure S10: GC-spectrum after two hour dehydrogenation of H12-BT at 250 °C for catalyst of this study with 2.3 nm platinum nanoparticles.