Electronic Supporting Information

Pt-Re dehydrogenation catalysts synthesized via solvent deficient precipitation

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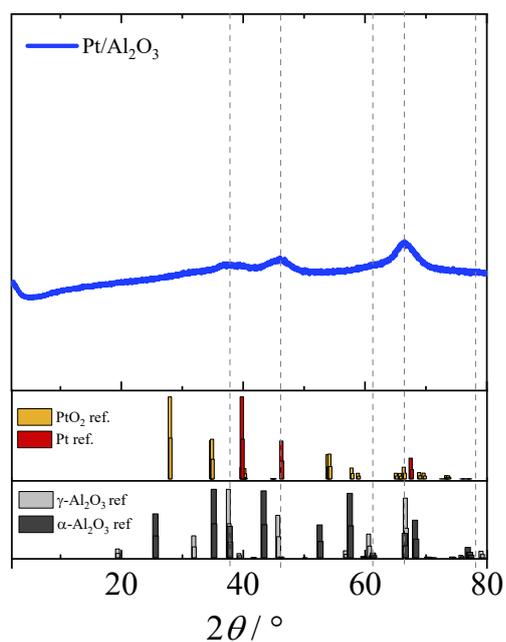
Textural properties

Figure A 1. Powder XRD patterns of a Pt/Al$_2$O$_3$ catalyst synthesised via the SDP method after calcination.
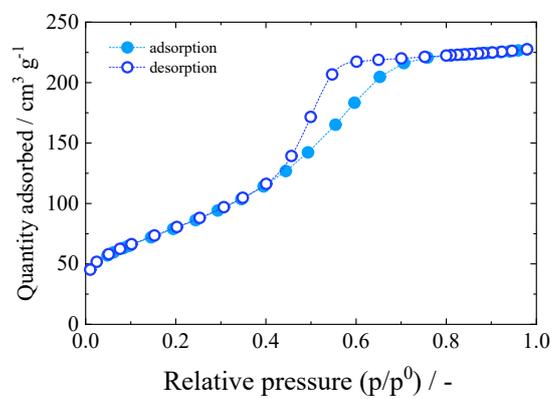*ref. = data obtained from Crystallography Open Database.

Figure A 2. N$_2$ physisorption isotherm of a Pt/Al$_2$O$_3$ catalysts synthesised via the SDP method with 0.3 wt% Pt. The hysteresis loop indicates a mesoporous structure.
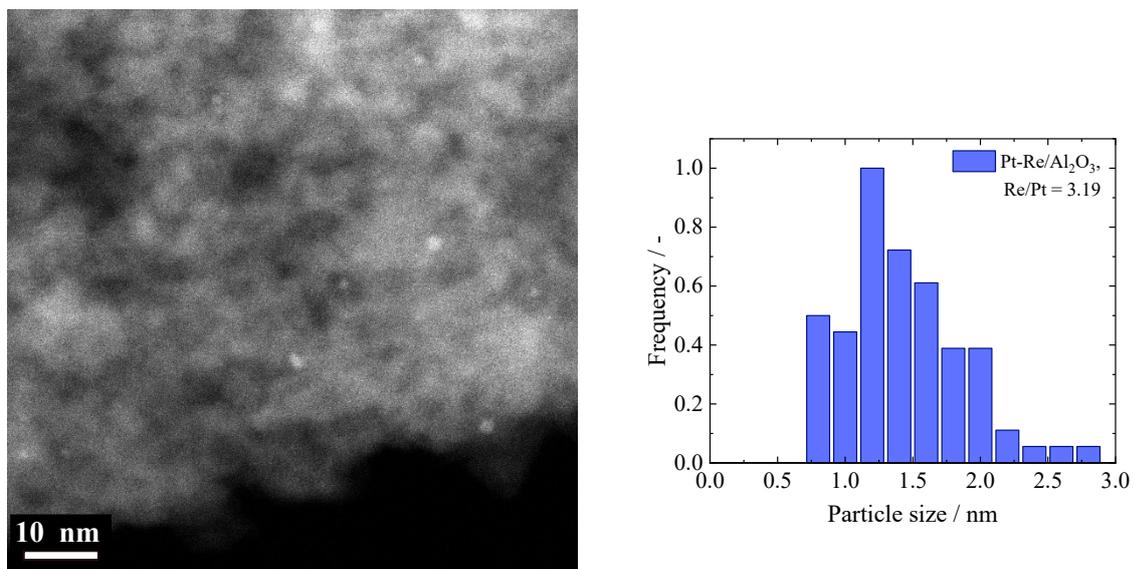
TEM analysis

Figure A 3. TEM image of an SDP Pt-Re/Al$_2$O$_3$ (0.29 wt% Pt, 0.87 wt% Re, Re/Pt = 3.19), showing the Pt nanoparticles distributed over the γ-Al$_2$O$_3$ and PSD based the measurement of 78 particles. Due to the low metal loadings, Pt and Re particles could not be distinguished.

0.28 wt% Pt + 0 wt% Re
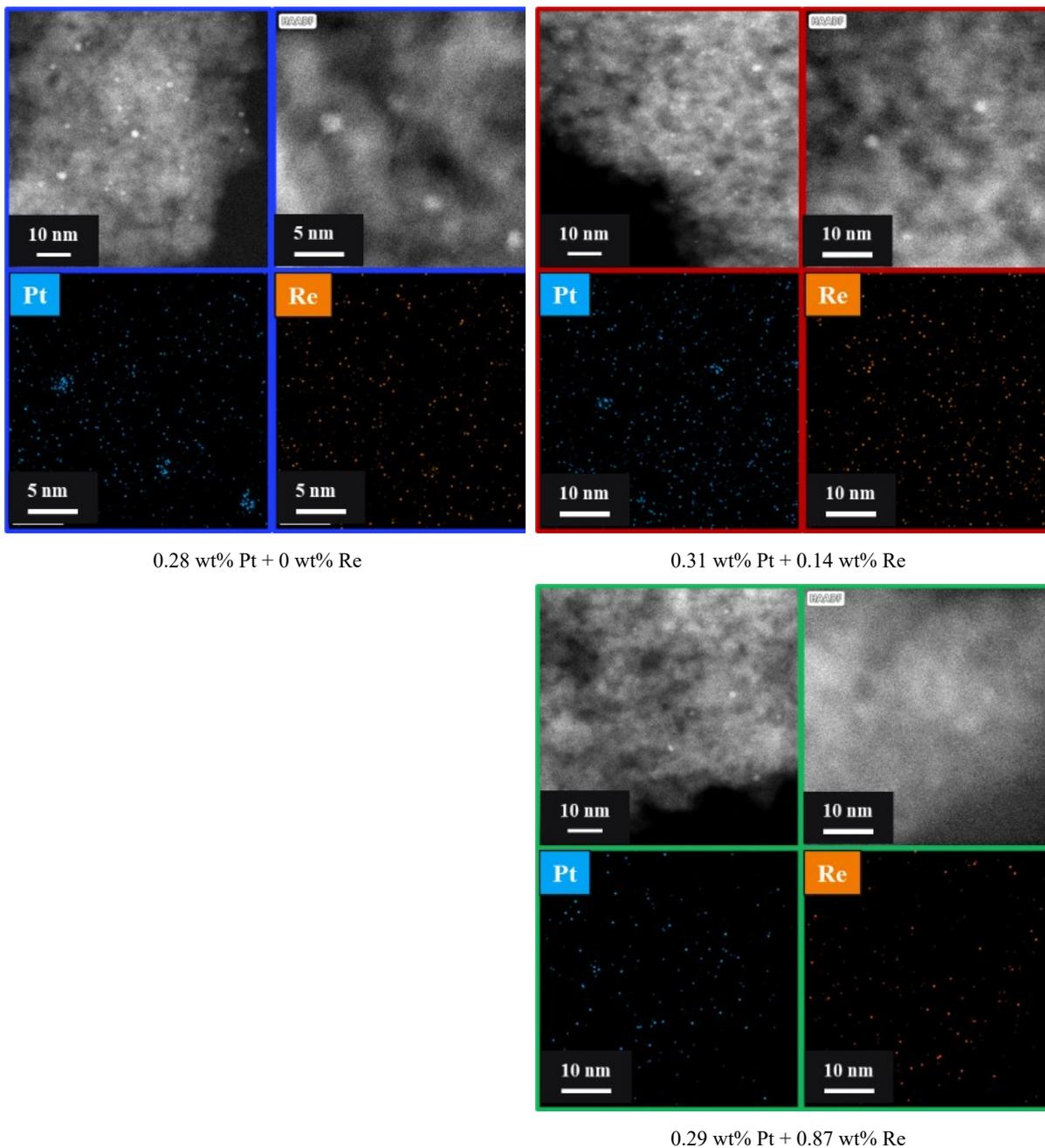
0.31 wt% Pt + 0.14 wt% Re

0.29 wt% Pt + 0.87 wt% Re

Figure A 4. TEM-EDX characterisation of SDP-synthesised Pt and Pt-Re catalysts with Re loadings of 0, 0.14, and 0.87 wt%, showing the distribution of Pt and Re elements and corresponding metal particle sizes.
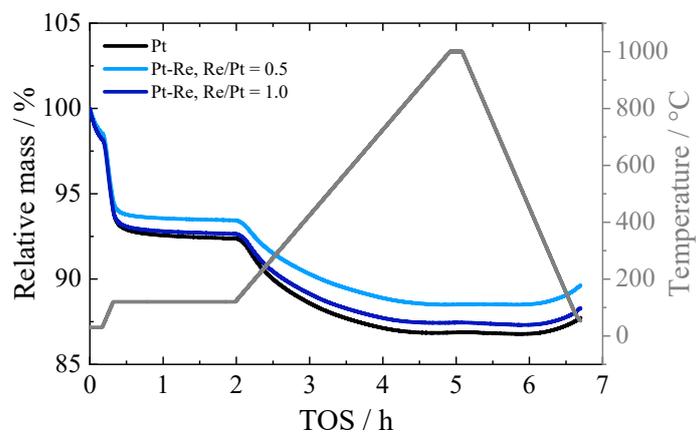
MCH dehydrogenation

Figure A 5. TGA during temperature-programmed oxidation of the spent SDP Pt and Pt-Re/Al$_2$O$_3$ catalysts with after usage in dehydrogenation of MCH.
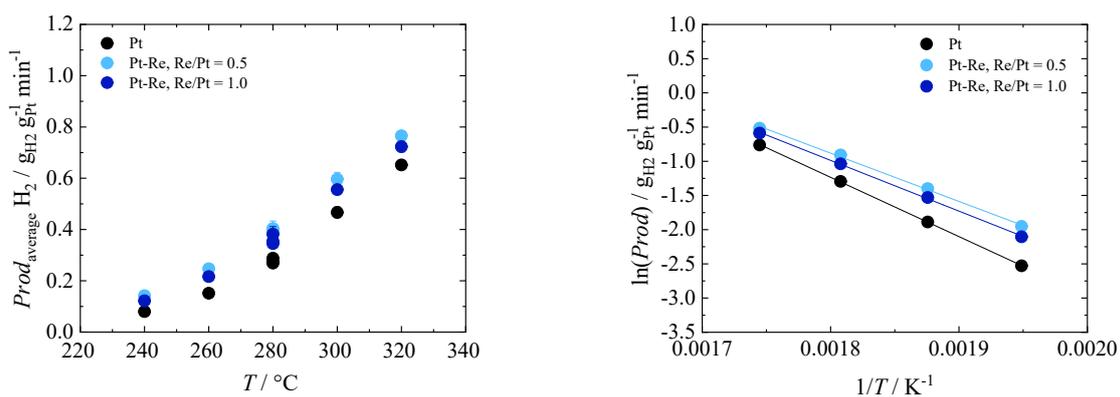

Figure A 6. (left) H$_2$ average productivity for different operating temperatures for the continuous gas phase dehydrogenation of MCH with Pt-Re/Al$_2$O$_3$ catalysts, with Re varying 0, 0.14 and 0.27 wt%. (right) Arrhenius plots obtained.
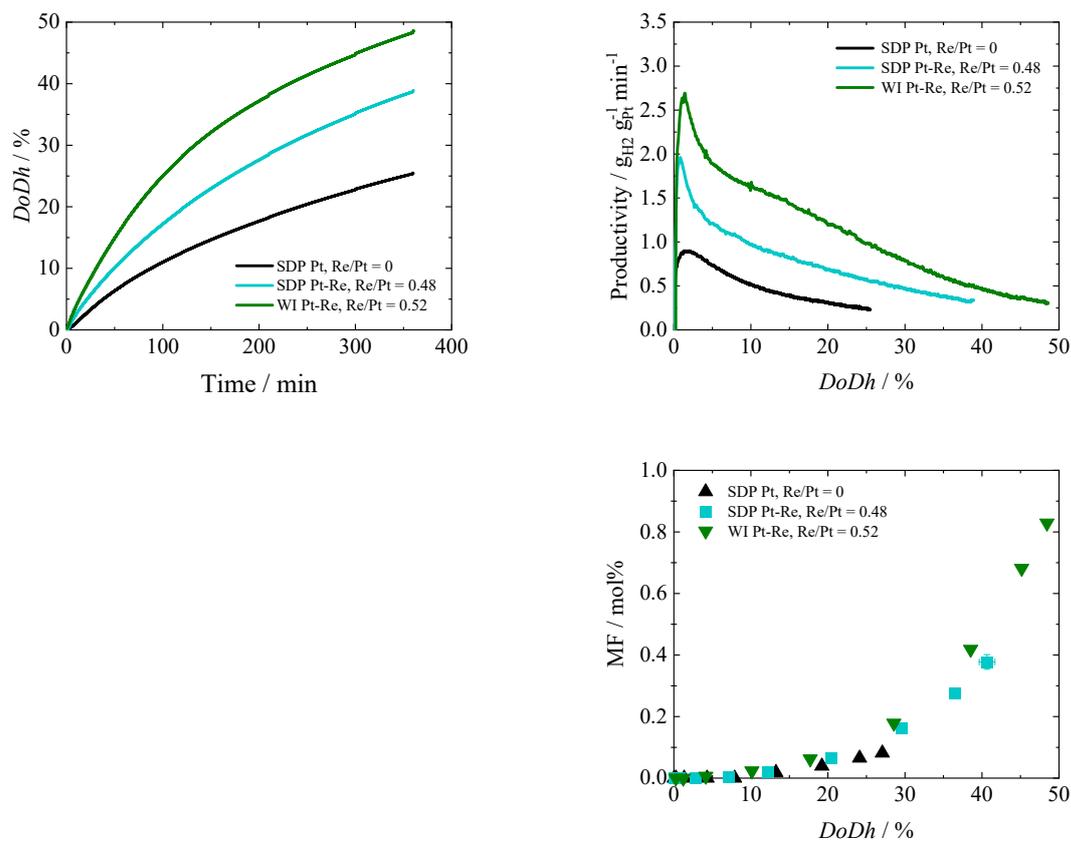
H12-BT dehydrogenation

Figure A 7. Degree of dehydrogenation, H_2 productivity and methylfluorene (MF) formation during semi-batch dehydrogenation of perhydro benzyltoluene (H12-BT) with solvent deficient precipitation (SDP) and wet impregnated (WI) Pt-Re/Al$_2$O$_3$ catalysts. Experimental conditions: T = 250 °C, p = 1 bara, n_{LOHC} = 0.1 mol, w_{Pt} = 0.3 wt%, n_{Pt}/n_{LOHC} = 0.0001, t_R = 360 min, V_{Ar} = 300 mL$_N$ min^{-1}. *DoDh* and productivity data was obtained from TCD measurements, whereas product composition data were determined via the GC method.
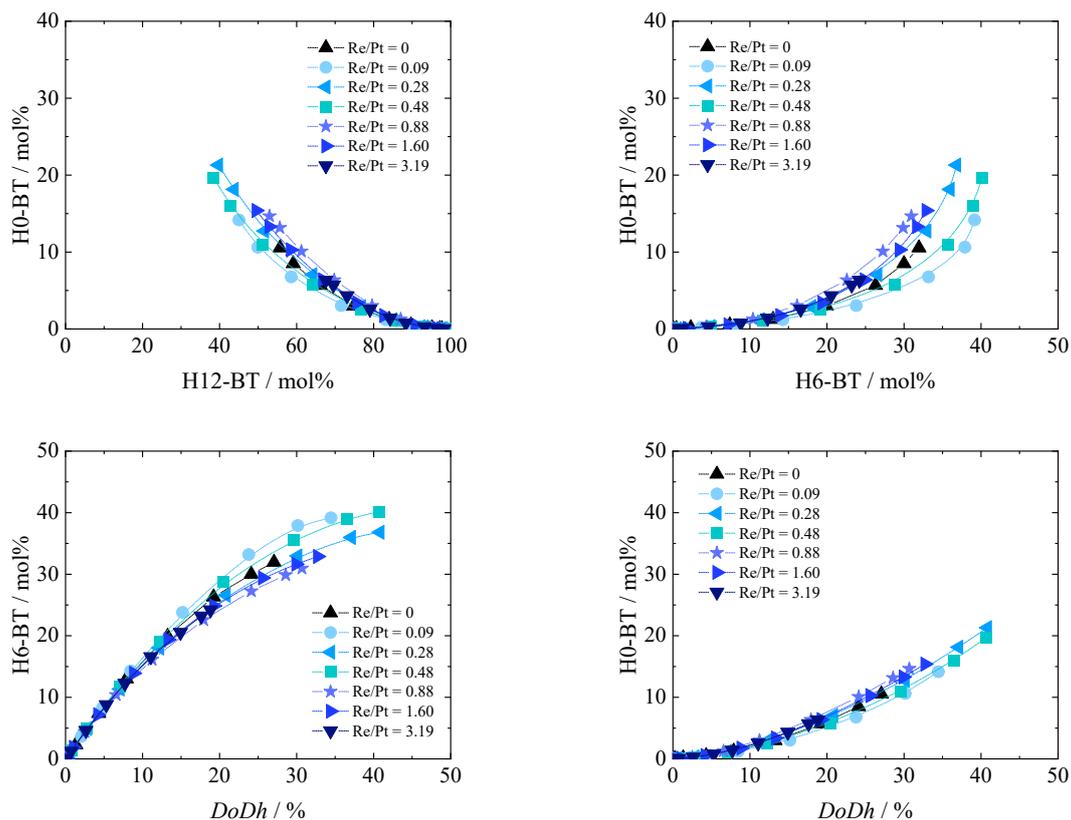
Figure A 8. Product composition (H12-BT, H6-BT, H0-BT) of the liquid samples taken during the dehydrogenation of H12-BT using Pt-Re/Al$_2$O$_3$ catalysts synthesised via the SDP method with various Re loadings.

Experimental conditions: T = 250 °C, p = 1 bara, n_{LOHC} = 0.1 mol, w_{Pt} = 0.3 wt%, n_{Pt}/n_{LOHC} = 0.0001, t = 360 min, V_{Ar} = 300 mL min^{-1}. *DoDh* and productivity data were obtained from TCD measurements, while product composition was determined via GC analysis. Data represent average values.
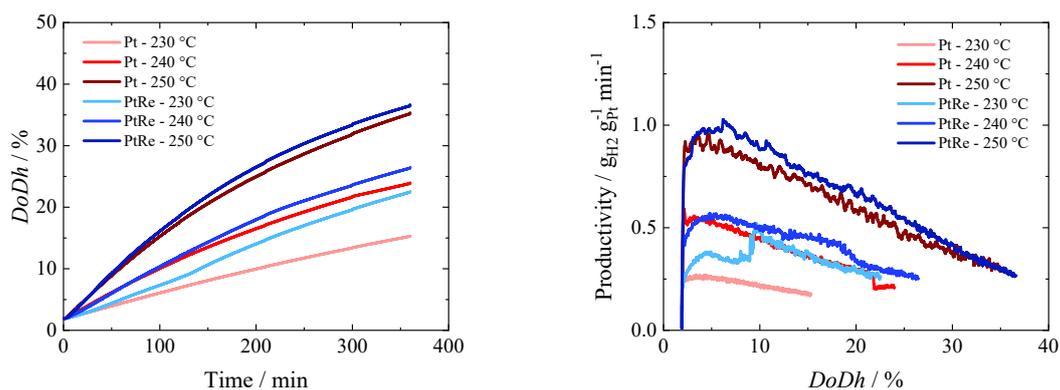

Figure A 9. Progression of *DoDh* over time (left), corresponding H$_2$ productivity (right) during the dehydrogenation of H12-BT at various temperatures (230, 240, and 250 °C) using Pt/Al$_2$O$_3$ and Pt-Re/Al$_2$O$_3$ (Re/Pt = 0.5) catalysts synthesised via the SDP method. Data were employed in Arrhenius analysis.

Experimental conditions: T = 230, 240, and 250 °C, p = 1 bara, n_{LOHC} = 0.1 mol, w_{Pt} = 0.3 wt%, n_{Pt}/n_{LOHC} = 0.0001, t = 360 min, V_{Ar} = 300 mL min^{-1}. *DoDh* and productivity data were obtained from TCD measurements.
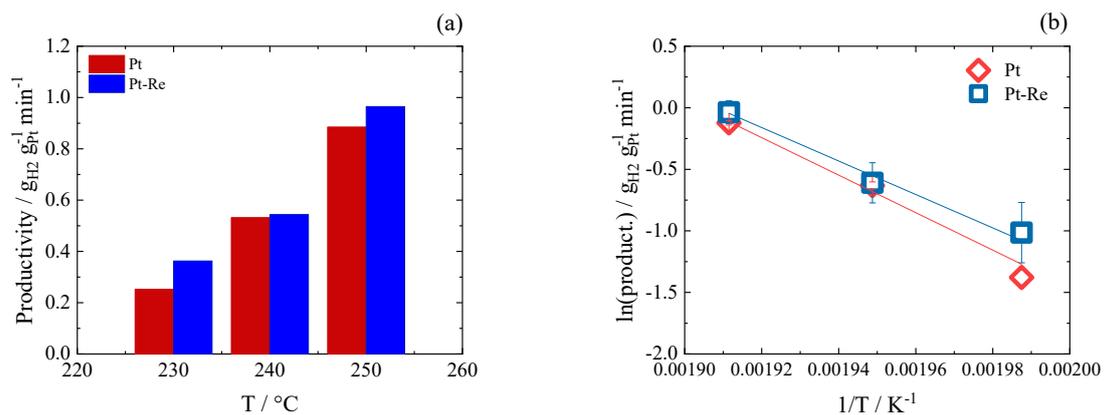
Figure A 10. (a) Average H_2 productivity (2-25% *DoDh*) during dehydrogenation of H12-BT at three different temperatures (230, 240 and 250 °C) using Pt and Pt-Re-based catalyst systems synthesised via the SDP method. (b) Corresponding Arrhenius plot.
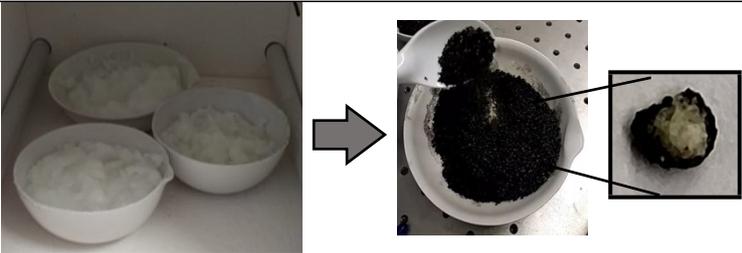
Table A 1. Values obtained from the linear regression of the Arrhenius plot, included the calculated effective activation energy and pre-exponential factor k_0.

System	Slope A	$E_{A,eff}$ / kJ mol^{-1} K^{-1}
Pt	-15229.4 ± 1646.5	126.6 ± 13.7
Pt-Re	-13592.0 ± 1381.3	113.0 ± 11.5

Details on Scale up process

First, to prepare γ-Al$_2$O$_3$ ball milling with 30 g of starting material was investigated. Although the process performed apparently well towards a wet solid within 15 min, product isolation from the milling balls was time consuming, significant contamination of the product with residual material from abrasion of the milling balls was observed and the BET surface area was reduced to 197 ± 1 m^2/g. As second attempt, a three-neck round-bottom flask equipped with a Teflon agitator powered by an electrical motor (KPG mixer) was used. The preparation of the 3 g small batch size (36 g of starting material) took 3 h 30 min to proceed over all expected steps from liquefaction, bubbling and precipitation of a wet solid. Fortunately, scaling of the synthesis was successful and a batch size increased by a factor of 10 completed in 4 h. Product isolation was straightforward and after calcination, a quantitative yield with a BET surface area of 265 ± 1 m^2/g was achieved, which is in agreement of the results from the small-scale synthesis. A maximal batch size of 85 g, corresponding to approx. 1 kg of starting material, was realized in a 2 L round-bottom flask. The calcination step was observed to scale not as straightforward as the SDP synthesis (see **Table A 2**). To suppress the mobility of the heavy metal ions, and to optimise the inhomogeneous drying process, a freeze-drying step was included. Freeze-drying of the aqueous paste was readily possible on the 85 g scale, and fortunately, the BET surface area was not affected by the freeze-drying step (265 ± 1 m^2/g). The stepwise process allowed to roughly correlate the mass loss during the SDP synthesis with the reaction steps of CO$_2$ release during mixing, removal of water of hydration during freeze-drying and decomposition of NH$_4$NO$_3$ as well as condensation of Al(OH)$_3$ during calcination. Following this procedure, larger batches of Pt und Pt-Re catalysts have been prepared.

Table A 2. Overview of scale-up of SDP synthesis of Pt/Al$_2$O$_3$ catalysts and description of approaches used to overcome calcination limitations.

Scaled-up SDP synthesis	Calcination
Without freeze-drying (85 g of Pt/Al$_2$O$_3$ catalyst with 3.0 wt% Pt)	 • During calcination, large amounts of water formed and spectator ions present in the wet mass migrated towards the outer surface, driving Pt particles alongside, which resulted in a "core-shell"-like material structure with inhomogeneities • Calcination led to extensive release of NO$_x$ and HNO$_3$ gases, as a result of NH$_4$NO$_3$ thermal decomposition
With freeze-drying (40 g of Pt/Al$_2$O$_3$ catalyst with 0.3 wt% Pt)	 • In order to suppress extensive mobility of Pt particles during calcination, a freeze drying step was added before (12 h freezing at 55 °C, 84 h drying at -30 °C and 0.3 mbar, 12 h post-drying at -45°C and 0.08 mbar) • Dried material showed a reduction of 133 g (water loss) • Final calcined material did not indicate any inhomogeneities