Highly durable spray-coated plate catalyst for the dehydrogenation of perhydro benzyltoluene

Supporting information

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E.1 Catalytic plate reactor concept

The sketch below shows the catalytic plate reactor (CPR) concept. The CPR consists of at least two metal plates that are coated with a catalyst on one side and heated from the backside. Heating fluid or electrical heating elements can be used to reach the desired reaction temperature suitable for dehydrogenation.
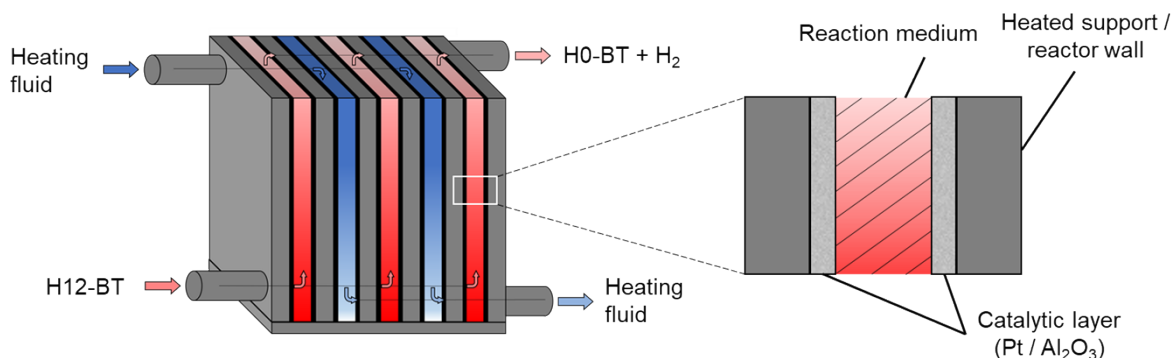

Figure ESI 1 Visualization of the CPR concept for LOHC dehydrogenation.

E.2 Dip coating as an alternative coating method

For all dip coating experiments, stainless steel plates measuring 20 x 50 mm were used. After cleaning the plates with soap water and acetone the following dip coating procedure was carried out:

1. Fully submerging the plates in dispersion
2. Withdrawal of the plates at 4 mm s^{-1} for 47 mm
3. Withdrawal of another 6 mm at 0,75 mm s^{-1} (3 mm extra to tear off the meniscus)
4. Drying of the plates in hot air stream (~80 °C)

This procedure was repeated up-to 5 times to reach the final coating load.

E.3 Post processing of SEM-EDX data

The noise of the EDX spectra was subtracted via the TrueLine function of the Aztec Software. Next, the EDX-line data was processed with an in-house Matlab script. The region of interest for each line spectra was determined, where the moving mean Fe-signal drops below (left edge, coming from the left) and the Al-signal raises above (right edge, coming from the right) a certain threshold of 500 counts per second (cps). After that, the platinum signal was reversed and the new origin was defined, where the Al signal rises above a threshold of 500 cps. A mean platinum signal for each catalyst loading was determined by averaging the three EDX-line scans of each measurement. The penetration depth of the platinum coating was determined as the interval where the moving average of the platinum signal exceeded and deseeded for the first time a threshold of 200 cps. This value was chosen as the threshold above the platinum signal noise in stainless steel and as the threshold to exclude small non representative Pt signals in deeper penetration depths especially for the 3.7 wt.% Pt plate. The threshold was chosen as a close value of the noise of the Platinum-signal. Therefore, the actual penetration depth of the deposition will be slightly underestimated.

E.4 Batch dehydrogenation setup

For the batch dehydrogenation, a three-neck flask (1) is connected to a reflux condenser (2) and a glass bridge with a catalyst addition mechanism (3). Feed is added into the flask and then the setup is heated to the reaction temperature of 250 °C with a heating jacket (4), while continuously stirred with a magnetic stirrer (5). The whole setup is flushed with Argon before use. When the operating temperature is reached, the stirrer and Argon supply are switched of and the catalyst is dropped in the reaction mixture, starting the dehydrogenation reaction. Liquid samples are taken with a glass syringe through a silicon septum (6) at several reaction times.

Figure 11	Coating layer / -	Pt-loading / wt.%	Catalyst mass / mg
a/b	15	3.7	326
a/b	15	2.7	320
a/b	15	1.9	345
a/b	15	1.0	324
c/d	15 (experiment 1)	3.7	326
c/d	15 (experiment 2)	4.0	328
c/d	10 (experiment 1)	3.9	270
c/d	10 (experiment 2)	4.1	246
c/d	5	3.6	101

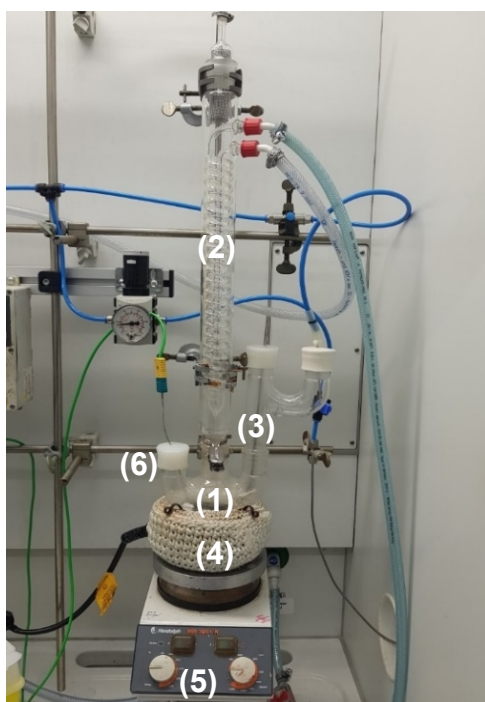*Table ESI 1 Properties of plates used in the batch dehydrogenation.*

Figure ESI 2 Batch dehydrogenation setup for hydrogen release from H12-BT.

E.5 The design of experiments

The experienced plan of the d-optimal DoE with all combinations of the influencing factors used is listed in Table ESI 2.

Table ESI 2 Experienced plan of the D-optimal DoE for spray coated plates.

Nr.	B: F	Solid content/ wt.%	Acid content/ wt.%	Glycerine content/ wt.%	Aging time/ h	Particle size/ µm
1	1:9	18.2	1.79	0	4	7
2	1:7	28.3	1.79	0	4	30
3	1:9	28.3	3.58	2	6	30
4	1:7	28.3	2.69	5	4	7
5	1:9	18.2	2.69	5	16	30
6	1:7	18.2	1.79	5	4	7
7	1:9	18.2	3.58	0	16	30
8	1:3	28.3	1.79	0	4	7
9	1:3	28.3	1.79	0	6	30
10	1:7	28.3	1.79	5	16	7
11	1:9	28.3	3.58	5	4	7
12	1:7	38.4	1.79	0	16	7
13	1:3	28.3	3.58	5	16	7
14	1:3	28.3	3.58	0	16	7
15	1:7	18.2	3.58	5	16	7
16	1:7	18.2	2.69	2	4	30
17	1:3	28.3	1.79	5	16	30
18	1:3	28.3	3.58	5	4	30
19	1:3	18.2	2.69	5	6	7
20	1:7	38.4	1.79	0	4	30
21	1:7	18.2	3.58	0	6	7
22	1:7	18.2	1.79	0	6	7
23	1:7	18.2	3.58	5	6	30
24	1:7	28.3	3.58	2	16	30
25	1:7	28.3	1.79	5	4	30
26	1:7	28.3	3.58	0	4	7
27	1:7	28.3	2.69	0	4	30
28	1:9	18.2	1.79	2	16	30
29	1:7	18.2	3.58	5	4	7
30	1:7	38.4	3.58	5	16	7
31	1:7	18.2	1.79	0	4	30
32	1:9	18.2	1.79	0	4	7
33	1:9	18.2	1.79	0	4	7

E.6 Improvement of the mechanical stability and support mass

The improvement of the mechanical stability was carried out using the results of test of mechanical stability by means of ultrasound. Hereby we used the same DoE evaluation software (visual XSel 17) as for the optimization of the viscosity. The value for R^2_{adj} was calculated to be 0.816, which made the evaluation of the data difficult. Furthermore, the value of R^2_{adj} suggests that the data collected does not fit the regression model well. The evaluation gave negative effects of almost all influencing parameters, which experimentally could not be proven.

The same procedure was used to increase the support mass coated per layer. The R^2_{adj} value for was calculated to 0.776, which is even lower than that of the mechanical stability. The data used here was collected by weighing the catalyst plates after the spray coating (wet support mass) and after the calcination (dry support mass).

E.7 Chemical stability of the plate catalysts

To determine the chemical stability of the impregnated catalysts ICP-AES measurements of the coatings before and after a batch experiment have been carried out (see Table ESI 3). No significant change in platinum loading of the catalysts have been observed. Therefore, leaching of platinum during the dehydrogenation experiments can be excluded.

Table ESI 3 Platinum loading of selected plate catalyst measured via ICP-AES before and after batch dehydrogenation experiment; reaction conditions: 250 °C; 1 atm.; 15 g H12-BT, 6 h.

	before experiment	after experiment
Pt-loading / wt.%	3.10	3.11

E.8 By-product formation

Figure ESI 3 shows the methylfuorene content and DoDH of the remaining product after 6 h batch dehydrogenation. It can be noted that the by-product formation**.** As described by Rüde et al. methylfluorene is the main by-product formed during the dehydrogenation and it can act as precursor for further formation of high boiling species.[16] Therefore, methylfluorene was used as a key indicator for the selectivity of the catalysts. In general the by-product formation is low with the given catalyst, as to be expected from a selectively sulphur poisoned platinum catalyst similar to the one described by Auer et al.[12] Furthermore, the by-product formation mostly correlates to the DoDH of the samples rather than the platinum loading. This can be attributed to the formation mechanism of methylflourene. With increased DoDH more benzyltoluene is present in the system that can subsequently react to methylfluorene.
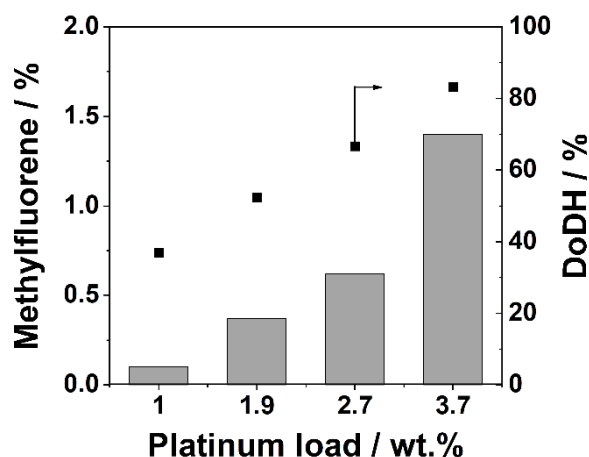

Figure ESI 3 Methylfluorene content and DoDH after 6 h batch-dehydrogenation measured via GC-FID.