Supplementary information for "Catalytic hydrodenitrogenation of primary, secondary, and tertiary C12-alkyl amines over a platinum on zirconia catalyst"

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1. Details on the ICP-OES analysis

Approximately 100 mg of catalyst was first digested in aqua regia (7.5 ml HCl and 2.5 ml HNO₃) for 50 min at 200 °C, using a Speedwave XPERT Microwave Pressure Digestion System (Berghof, Analytic Jena). The liquid was then diluted with ultrapure (type 1) water, filtered and analyzed.

The ICP-OES analysis was performed using an Agilent 5900 SVDV ICP-OES spectrometer. The device was equipped with a CCD array detector (167 nm - 785 nm). The loop volume was 3.5 ml and the spray chamber was rinsed 30 times between measurements. The pump speed was set to 12 rpm and the rinse time was 15 s. The liquid sample was introduced by a AVS 6/7 autosampler system, with a uptake pump rate of 23 ml/min, an injection pump rate of 2 ml/min, a valve uptake delay of 26.4 s, a bubble injection time of 1.8 s and a preemptive rinse time of 2.4 s. The Pt 203.646 nm and Pt 214.424 nm lines were analyzed. Scandium (255.235 nm) was used as an internal standard, and the Scandium reference solution was automatically injected using the AVS 6/7 autosampler system.

An Agilent Seaspray borosilicate glass nebulizer was used for liquid sample introduction, together with a borosilicate glass spray chamber and an ICP quartz torch intended for analysis of aqueous samples. The plasma was analyzed in axial mode, with a read time of 10 s, a stabilization time of 10 s and the RF power set to 1.10 kW. The nebulizer flow was 0.70 L/min, the plasma flow 12.0 l/min, the auxiliary flow 1.00 L/min and the make-up flow 0.00 L/min. Four replicate measurements were collected per sample injection, and the results of these replicates were averaged. Two blank 5% HNO₃ samples were analyzed between each sample, to ensure no sample carryover occurred.

2. Details on the GC-FID analysis

Two methods were used for the product quantification, method 1 for the dodecylamine and *di*dodecylamine HDN experiments and method 2 for the HDN experiments with the heavier *tri*dodecylamine. For method 1 the injection volume was 2 μ L and the inlet split ratio was 5:1, the temperature of the inlet was 325°C. The FID and NPD detector temperatures were 325°C. The program started at 80 °C with a hold time of 3 min. Then the temperature was increased to 100 °C with a ramp of 20 °C/min and was held for 3 min. Next, the temperature was raised to 160 °C with a ramp of 10 °C/min. The final temperature of 325 °C was reached with a ramp of 20 °C/min and held for 20 min. For method 2 the injection volume was 1 μ L and the split ratio was 15:1, the temperature of the inlet was 325°C. The temperature of the FID and NPD detectors was 325°C. The program started at 100 °C. Then the temperature was raised to 110 °C with a ramp of 30 °C/min and held for 3 min. Next, the temperature went to 160 °C with a ramp of 20 °C/min. The final temperature of 325 °C was reached with a ramp of 30 °C/min and held for 15 min.

3. Experimental data

Reaction time	[min]	15	30	60	60	60	120	180	240	300
Batch residence time	[g _{cat} h/n _{N.re} _{actant}]	22.8	45.3	91.5	90.9	90.6	181.3	272.6	365.3	458.9
c(reactant), initial	[mmol/L]	6.26	6.28	6.70	6.96	6.79	6.94	6.92	6.99	6.30
c(dodecane)	[mmol/L]	0.37	1.23	2.45	3.01	2.66	4.42	5.31	5.90	5.85
c(dodecylamine)	[mmol/L]	4.75	3.83	2.55	2.58	2.04	1.29	0.74	0.49	0.39
c(dodecane-1-ol)	[mmol/L]	0.06	0.07	0.07	0.07	0.08	0.05	0.02	0.00	0.00
c(N- isopropyldodeca ne-1-amine + N- dodecylpropan-2- imine)	[mmol/L]	0.50	0.34	0.14	0.14	0.78	0.22	0.16	0.30	0.12
c(di- dodecylamine)	[mmol/L]	0.39	0.45	0.73	0.68	0.65	0.51	0.12	0.00	0.00
c(<i>tri-</i> dodecylamine)	[mmol/L]	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Conversion	[%]	26	40	63	65	70	83	90	94	93
Nitrogen removal	[%]	10	20	39	44	38	61	77	79	83
Carbon balance closure	[%]	100	101	100	103	99	98	93	96	101

Table S1: Experimental data of the HDN of dodecylamine over Pt/ZrO_2 . Experimental conditions: 300 °C, 80 bar H₂, 20 mg catalyst and 100 ppm initial nitrogen concentration.

Reaction time	[min]	15	30	60	120	180	240	300
Batch residence time	[g _{cat} h/n _{N.reactant}]	22.7	45.8	91.7	181.1	277.1	364.5	451.1
c(reactant), initial	[mmol/L]	7.20	7.11	7.03	6.82	7.10	6.93	7.33
c(dodecane)	[mmol/L]	1.12	2.75	5.14	8.21	9.70	11.34	12.34
c(dodecylamine)	[mmol/L]	0.37	0.74	0.97	0.82	0.74	0.63	0.49
c(dodecane-1-ol)	[mmol/L]	0.06	0.15	0.00	0.09	0.08	0.05	0.05
c(N-isopropyldodecane- 1-amine + N- dodecylpropan-2- imine)	[mmol/L]	0.07	0.05	0.31	0.10	0.23	0.00	0.00
c(di-dodecylamine)	[mmol/L]	6.27	5.13	3.62	2.23	1.40	0.69	0.75
c(<i>tri-</i> dodecylamine)	[mmol/L]	0.02	0.02	0.01	0.00	0.00	0.00	0.00
Conversion	[%]	13	28	49	67	80	90	90
Nitrogen removal	[%]	2	9	21	41	52	69	70
Carbon balance closure	[%]	99	100	98	101	94	97	92

Table S2: Experimental data of the HDN of *di*-dodecylamine over Pt/ZrO_2 . Experimental conditions: 300 °C, 80 bar H₂, 20 mg catalyst and 100 ppm initial nitrogen concentration.

Table S3: Experimental data of the HDN of *tri*-dodecylamine over Pt/ZrO_2 . Experimental conditions: 300 °C, 80 bar H₂, 20 mg catalyst and 100 ppm initial nitrogen concentration.

Reaction time	[min]	15	30	60	120	180	240	300
Batch residence time	$[g_{cat}h/n_{N.reactant}]$	22.6	45.3	91.3	182.3	272.5	362.3	423.3
c(reactant), initial	[mmol/L]	6.30	6.19	7.19	6.36	7.30	8.07	7.31
c(dodecane)	[mmol/L]	1.35	3.17	6.78	10.31	12.52	17.09	17.12
c(dodecylamine)	[mmol/L]	0.09	0.28	0.41	0.77	0.52	0.31	0.29
c(dodecane-1-ol)	[mmol/L]	0.13	0.10	0.12	0.08	0.08	0.00	0.08
c(N- isopropyldodecane-1- amine + N- dodecylpropan-2- imine)	[mmol/L]	0.09	0.39	0.38	0.31	0.10	0.20	0.17
c(di-dodecylamine)	[mmol/L]	0.72	1.33	1.64	1.27	0.72	0.36	0.41
c(<i>tri</i> -dodecylamine)	[mmol/L]	5.25	4.37	3.29	1.75	1.94	1.41	1.44
Conversion	[%]	17	29	54	73	73	82	80
Nitrogen removal	[%]	0	1	8	30	40	63	60
Carbon balance closure	[%]	100	104	96	100	94	93	104

Table S4: Experimental data of the HDN of dodecylamine, *di*-dodecylamine, and *tri*-dodecylamine (without a catalyst, thermal activity) at 60 min reaction time. Experimental conditions: 300 °C, 80 bar H₂, 100 ppm initial nitrogen concentration.

Reactant	-	dodecylamine	di-dodecylamine	tri-dodecylamine
c(reactant), initial	[mmol/L]	6.67	7.07	7.71
c(dodecane)	[mmol/L]	0.00	0.19	0.00
c(dodecylamine)	[mmol/L]	6.37	0.00	0.00
c(dodecane-1-ol)	[mmol/L]	0.00	0.00	0.00
c(N- isopropyldodecane-1- amine + N- dodecylpropan-2- imine)	[mmol/L]	0.00	0.00	0.04
c(di-dodecylamine)	[mmol/L]	0.00	6.65	0.26
c(<i>tri-</i> dodecylamine)	[mmol/L]	0.00	0.00	7.78
Conversion	[%]	5	6	-1
Nitrogen removal	[%]	-2	-3	0
Carbon balance closure	[%]	95	94	103

Table S5: Experimental data of the HDN of dodecylamine, *di*-dodecylamine, and *tri*-dodecylamine over ZrO₂ 60 min reaction time. Experimental conditions: 300 °C, 80 bar H₂, 20 mg ZrO₂ and 100 ppm initial nitrogen concentration.

Reactant	-	dodecylamine	<i>di</i> -dodecylamine	tri-dodecylamine
Batch residence time	$[g_{cat}h/n_{N.reactant}]$	91.3	91.2	92.2
c(reactant), initial	[mmol/L]	6.79	7.59	6.37
c(dodecane)	[mmol/L]	0.02	0.00	0.00
c(dodecylamine)	[mmol/L]	5.52	0.00	0.00
c(dodecane-1-ol)	[mmol/L]	0.02	0.00	0.00
c(N-isopropyldodecane- 1-amine + N- dodecylpropan-2-imine)	[mmol/L]	0.66	0.00	0.00
c(di-dodecylamine)	[mmol/L]	0.08	6.78	0.33
c(<i>tri</i> -dodecylamine)	[mmol/L]	0.00	0.05	6.80
Conversion	[%]	19	11	-7
Nitrogen removal	[%]	4	-2	-2
Carbon balance closure	[%]	89	90	103

4. X-ray driffraction results



Figure S1. X-ray diffractograms of ZrO_2 and Pt/ZrO_2 as well as the m- ZrO_2 database reference (ICDD 00-065-0687)

5. Kinetic Simulation Supplementary information



Figure S2: Parity plot with the predicted concentration [mmol/L] vs the experimental concentration [mmol/L] for (a) the dodecylamine experiments, (b) the *di*-dodecylamine experiments, and (c) the *tri*-dodecylamine experiments. Experimental conditions: 300 °C, 80 bar H₂, 20 mg catalyst and 100 ppm initial nitrogen concentration. Modeling conditions: Power Law model, *least squares* solver, including reaction rate r_4 .

Table S6 Reactions of the HDN reaction network and their simulated reaction constants k _i . Simulation conditions
Power Law model, <i>least squares</i> solver, without reaction rate r_4 .

Reactions	Simulated reaction constants				
HDN (1)	k_1 [mmol/L min]	0.012691			
Condensation (2)	$k_2 [\text{mmol}^2 / \text{L}^2 \text{min}]$	0.002110			
Hydrogenolysis (3)	k ₃ [mmol/L min]	0.012452			
Hydrogenolysis (5)	k ₅ [mmol/L min]	0.013987			



Figure S3: Experimental (exp.) data and simulated fit as concentration [mmol/L] vs. reaction time [min] for (a) the dodecylamine experiments, (b) the *di*-dodecylamine experiments, and (c) the *tri*-dodecylamine experiments. Experimental conditions: 300 °C, 80 bar H₂, 20 mg catalyst and 100 ppm initial nitrogen concentration. Simulation conditions: Power Law model, *least squares* solver, without reaction rate r_4 .



Figure S4: On the right axis reaction rates r_1 , r_2 , r_3 , r_5 , r_6 and nitrogen removal rate [mmol/Lmin] vs reaction time [min] and on the left axis experimental nitrogen removal [%] (from the GC-FID/NPD) and simulated nitrogen removal [%] for the (a) dodecylamine HDN experiments, (b) *di*-dodecylamine HDN experiments, and (c) the *tri*-dodecylamine experiments. Experimental conditions: 300 °C, 80 bar H₂, 20 mg catalyst and 100 ppm initial nitrogen concentration. Simulation conditions: Power Law model, *least squares* solver, without reaction rate r_4 .



Figure S5: Parity plot with the predicted concentration [mmol/L] vs the experimental concentration [mmol/L] for (a) the dodecylamine experiments, (b) the *di*-dodecylamine experiments, and (c) the *tri*-dodecylamine experiments. Experimental conditions: 300 °C, 80 bar H₂, 20 mg catalyst and 100 ppm initial nitrogen concentration. Simulation conditions: Power Law model, *least squares* solver, without reaction rate r_4 .



Figure S6: Predicted nitrogen removal with and without the condensation reactions (**2**,**4**,**6**) [%] vs time for (a) the dodecylamine experiments, (b) the *di*-dodecylamine experiments, and (c) the *tri*-dodecylamine experiments. Experimental conditions: 300 °C, 80 bar H₂, 20 mg catalyst and 100 ppm initial nitrogen concentration. Simulation conditions: Power Law model, *least squares* solver.

6. Tridodecylamine calibration curve



Figure S7: GC-FID calibration curve for tridodecylamine, showing the relationship between the amine peak area, divided by the internal standard peak are, and the amine weight fraction, divided by the internal standard weight fraction. The slope of the line is the relative response factor (RRF).



7. CHNS analysis of the spent catalyst from the secondary amine experiments

Figure S8: Carbon content analysis results for spent catalysts used for didodecylamine (secondary amine) hydrotreating. Vertical bars show the standard deviation for repeated measurements. Note that the standard deviation is very low (< 0.1 C wt-%) for the samples with a batch residence time over 350 g(cat)h/mol(N).