

Supporting Information

Catalytic Deoxygenation of Bio-Based 3-Hydroxydecanoic Acid to Secondary Alcohols and Alkanes

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Prolongation of the reaction time

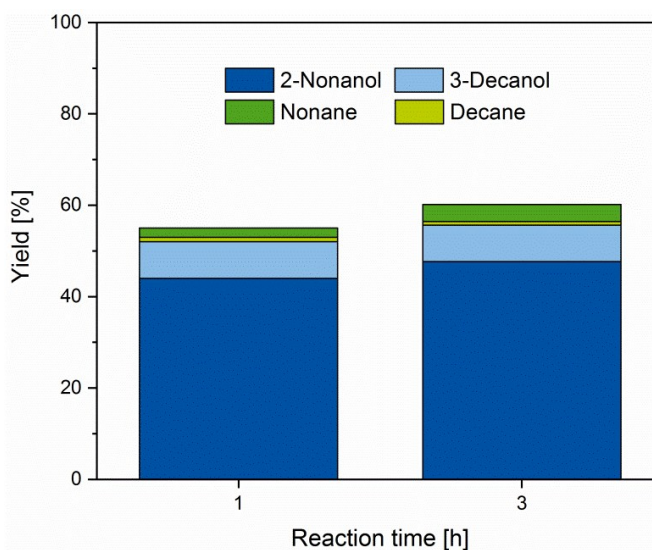


Fig. S1: Prolongation of reaction time from 1 to 3 h. Conditions: 25 mg 5 wt.% Ru/C, 250 mg 3-HDA, 5 ml water, 100 bar H₂, 200 °C.

N₂-Physisorption

N₂-physisorption was measured on a Quadrasorb SI (3P Instruments). Before the measurement, the samples were degassed in a FloVac degasser at 200 °C at reduced pressure overnight. The measurements were conducted at -196 °C and the data was evaluated using the software QuadraWin (3P Instruments). For the determination of the specific surface area S_{BET} , the BET model was applied ($0.05 \leq p/p_0 \leq 0.2$). The total pore volume V_{pore} was calculated from the highest relative pressure ($p/p_0 = 0.95\text{--}0.98$).

Table S1: Textural properties of the MFI-structured catalyst supports.

Support	Si:Al ratio	S _{BET} [m ² g ⁻¹]	V _{pore} [cm ³ g ⁻¹]
Silicalite	∞ ^{a)}	352	0.25
HZSM-5 (40)	40	436	0.25
HZSM-5 (15)	15	358	0.20

a) Does not contain any Al but only Si.

Initial pH of the catalytic systems (see also to Fig. 3 in the main article)

Table S2: Initial pH values of the reaction systems presented in Fig 3. Reaction conditions: 5 wt.% Ru-cat., 250 mg 3-HDA, 5 ml H₂O, 100 bar H₂, 200 °C, 1 h.

Entry	Catalyst	Brønsted acidic additive	pH ₀	Total yield [%]
1	-	-	3.44	-
2	50 mg Ru/C	-	4.11	91
3	50 mg Ru/C	2 wt.% H ₂ SO ₄	2.42	56
4	50 mg Ru/C	50 mg HZSM-5 (15)	3.30	78
5	50 mg Ru/HZSM-5 (15)	-	2.70	84

As depicted in Table S2 all of the discussed systems had an acidic pH₀ value ranging from 2.7 to 4.1 resulting from the deprotonation of the acid in the aqueous solvent. The highest activity (91%) was achieved at the highest pH₀ = 4.11 for neat Ru/C (entry 2), while the lowest (56%) was found for the lowest pH₀ of 2.42 for Ru/C + 2wt.% H₂SO₄ (entry 3). Both systems involving HZSM-5 (15) lie in between (entries 4 and 5). However, a small deviation from the general trend is found when comparing the latter two. The use of bifunctional Ru/HZSM-5 (15) despite its lower pH₀ results in slightly higher yields than Ru/C + HZSM-5 (15). This is believed to be rooted in the physical mixing of both solid catalysts in case of Ru/C + HZSM-5 (15), which effectively leads to slightly lower active surface areas *e.g.* when two different particles of each catalyst type agglomerate. In case of the bifunctional Ru/HZSM-5 (15), the reaction is expected to occur faster than over Ru/C + co-catalyst, since the decarbonylation, dehydration, and hydrogenation can all take place on one catalyst in close proximity and are thus less subjected to mass transfer effects.

TPD-analysis and peak deconvolution (see also Fig. 4 in the main article)

The analysis of the TPD-signals and interpretation was performed with the help of the Origin 2018 software. A baseline correction was performed and peak deconvolution was achieved using a Gaussian fit. The amount of weak or strong acid sites corresponds to the sum of their respective peak areas. In case a peak stretched over a broad range and thus into both the low and high-temperature regime, a separate integration of the deconvoluted peak was performed and the value was assigned to the respective acidity (*e.g.* integration from 370-600 °C and assignment to strong acid sites). In accordance with the literature, the low-temperature region corresponding to weak acidity was set to 100-370 °C, while the high-temperature region corresponding to strong acidity was set to 370-600 °C.

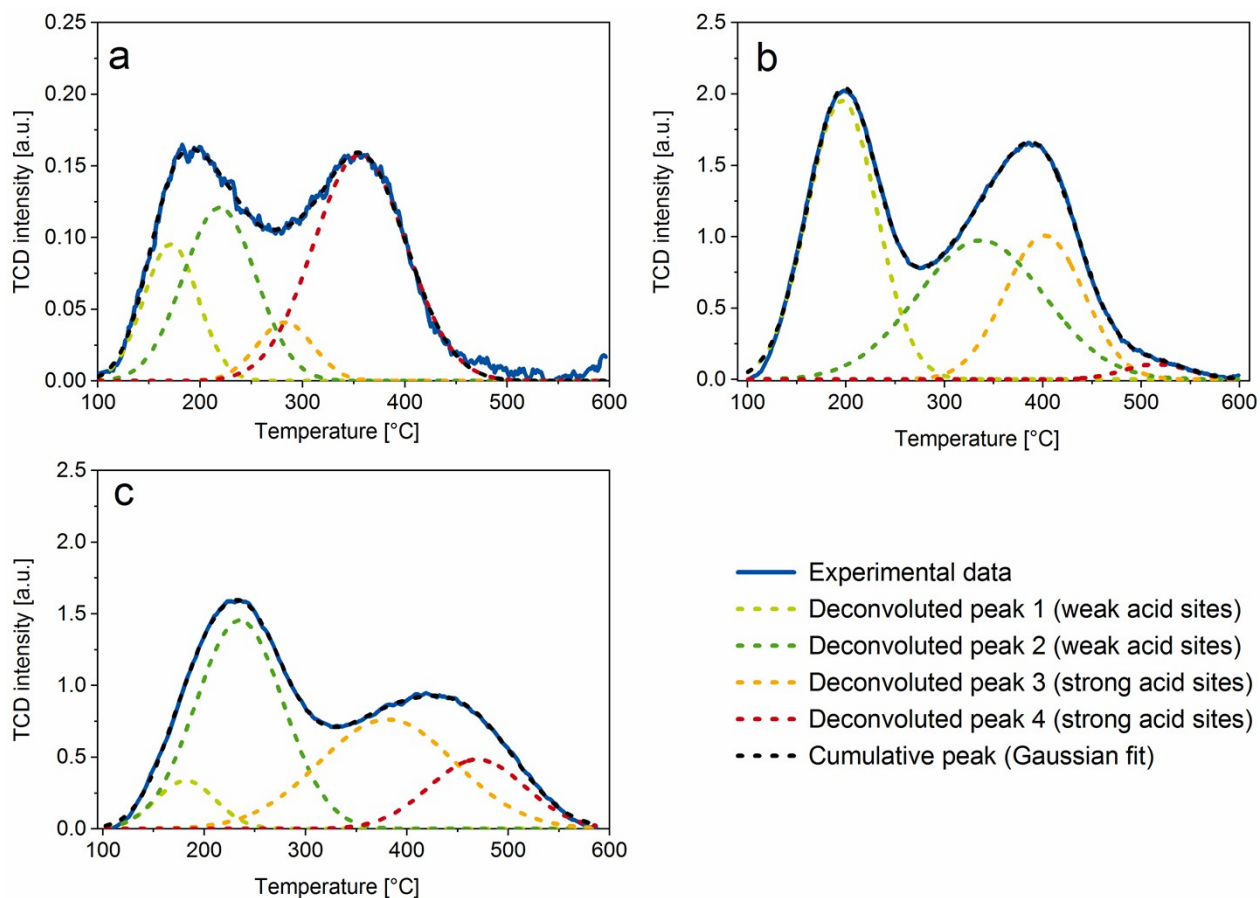


Fig. S2: Deconvoluted TPD-profiles for a) Silicalite, b) HZSM-5 (40), and HZSM-5 (15).

Variation of Si:Al ratio in the support of the bifunctional Ru-catalyst (see also Fig. 5 in the main article)

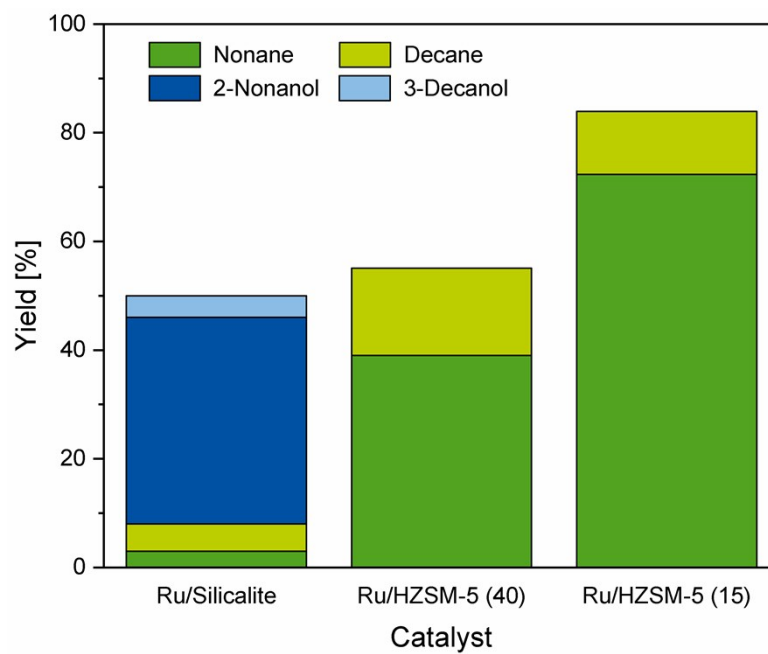


Fig. S3: Catalytic performance over variation of the Si:Al ratio in the tested MFI-structured supports. Conditions: 50 mg cat. (5 wt.% Ru), 250 mg 3-HDA, 5 ml water, 100 bar H₂, 200 °C, 1 h.

Pyridine IR-spectroscopy (see also Table 1 in the main article)

The respective peak area was determined with Origin 2018 using a baseline fit and the built-in peak area integration function. The peak region corresponding to the Lewis acidity (L) was first deconvoluted using a Gaussian fit, to extract the sole contribution of the Lewis acidic species at around 1455 cm⁻¹. Equations (1)-(3), previously reported by Zhu *et al.*,¹ were employed to calculate the Brønsted and Lewis acidity, where a_{total} denotes the total acidity obtained *via* NH₃-TPD and $R_{L/B}$ the ratio of Lewis to Brønsted acidity determined from the peak areas after pyridine FT-IR. For the latter, the extinction coefficients reported by Emeis (1.67 cm μmol⁻¹ for the Brønsted acid sites at around 1545 cm⁻¹ and 2.22 cm μmol⁻¹ for the Lewis acid site at around 1455 cm⁻¹) were applied.²

$$R_{L/B} = \frac{a_L}{a_B} \quad [-] \quad (1)$$

$$a_B = \frac{a_{total}}{1 + R_{L/B}} \quad [\text{mmol g}^{-1}] \quad (2)$$

$$a_L = \frac{a_{total} * R_{L/B}}{1 + R_{L/B}} \quad [\text{mmol g}^{-1}] \quad (3)$$

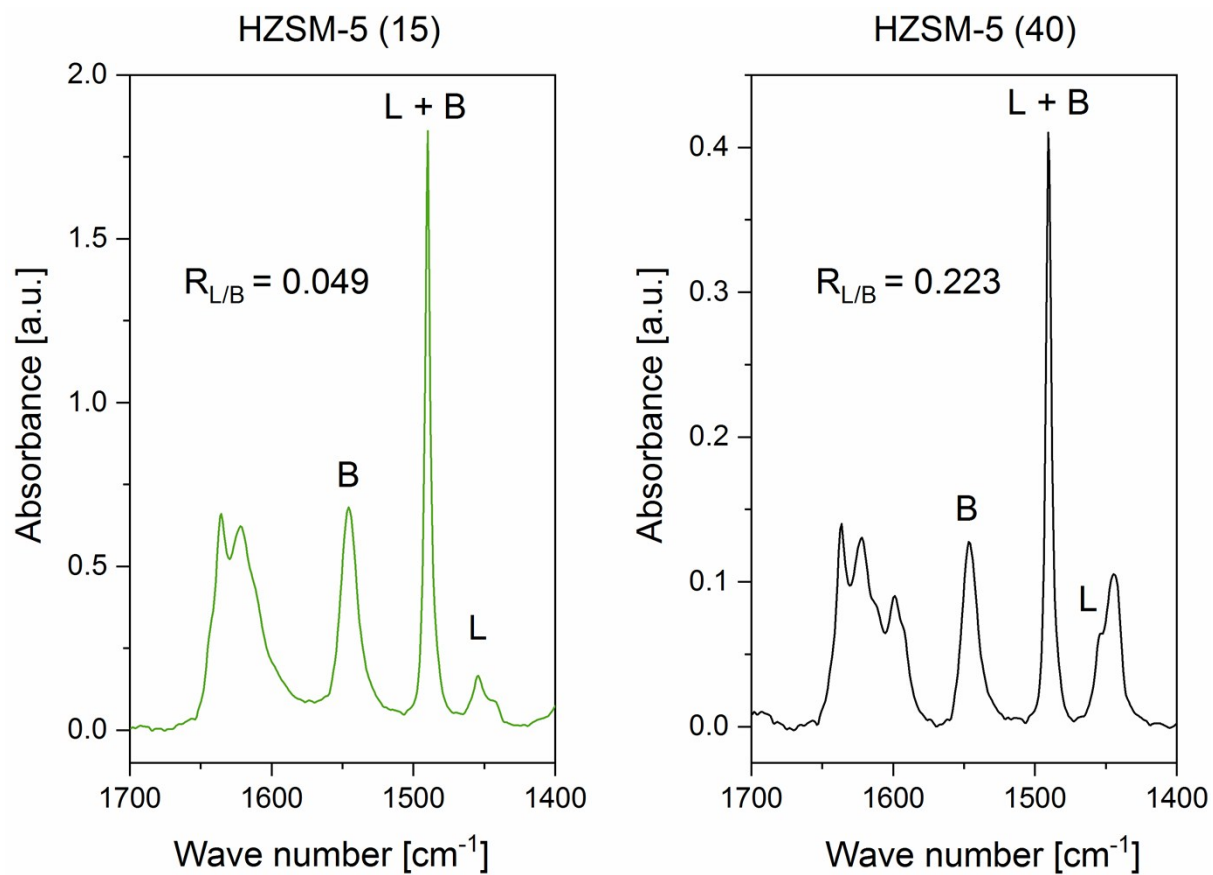


Fig. S4: FT-IR of adsorbed pyridine and respective $R_{L/B}$ values for HZSM-5 (15) and HZSM-5 (40).

Additional plot for alkane yield over acid concentration (see also Fig. 5 in the main article)

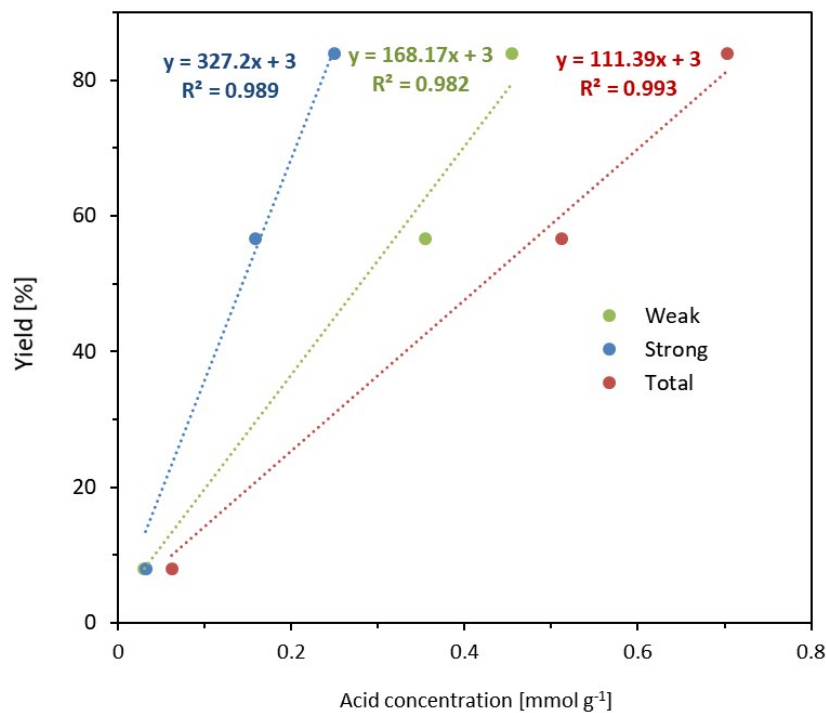
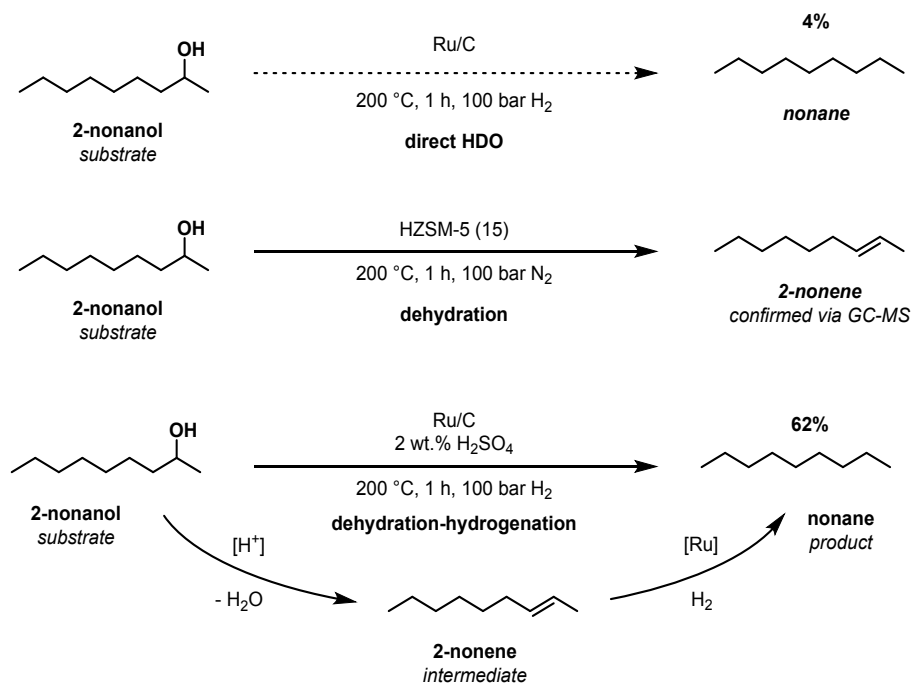


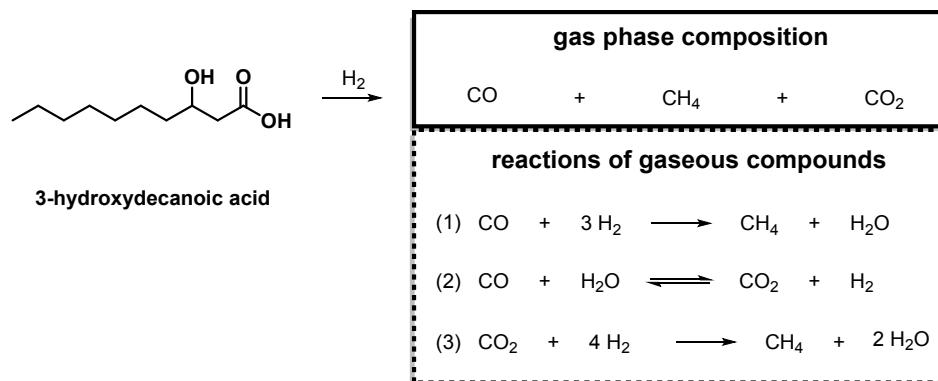
Fig. S5: Alkane yield over acid concentration of weak, strong, and total acid sites.

Testing of different substrates (see also Scheme 2b in the main article)

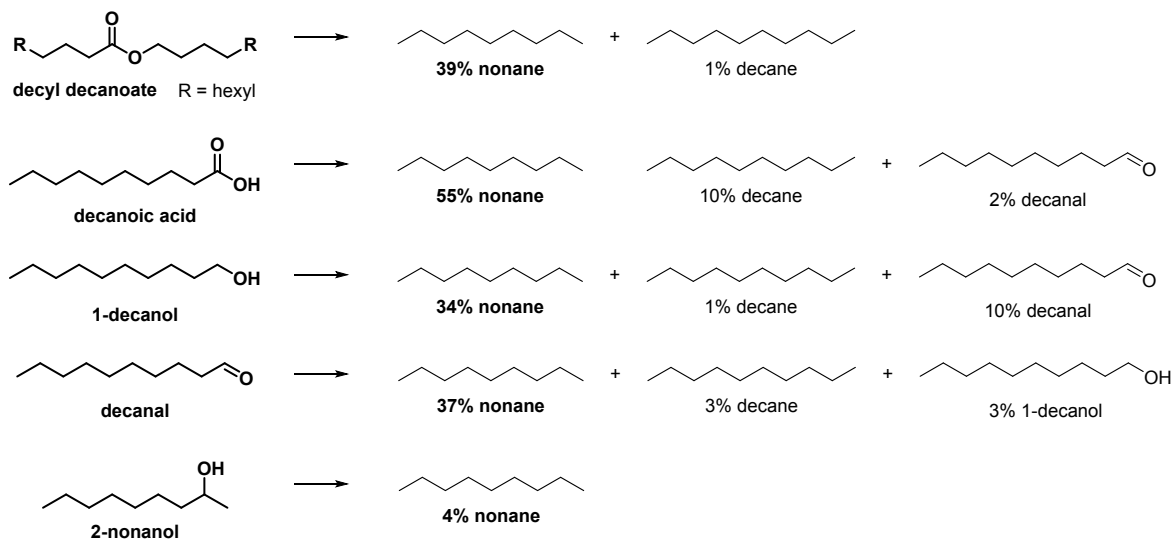


Scheme S1: Conversion of 2-nonanol over HZSM-5 (15) under N₂-atmosphere, and over Ru/C and H₂SO₄ under H₂-atmosphere.

Testing of different substrates and gas phase analysis (see also Scheme 2 and 3 in the main article)



Scheme S2: Qualitative analysis of the gaseous phase and possible reactions of gaseous compounds, *i.e.* Sabatier reaction (1) and (3) besides water-gas-shift reaction (2).



Scheme S3: Ru/C-catalyzed conversion of different substrates for the proposed reaction network under H₂-pressure.

Table S3: Comparison of solid Ru/C and Ru/HZSM-5 (10) to a soluble RuCl₃-catalyst. Reaction conditions: 4.7 mol% Ru, 250 mg 3-HDA, 5 ml H₂O, 100 bar H₂, 200 °C, 1 h.

Catalyst	Product yields [%]				
	2-Nonanol	1-Decanal	3-Decanal	Nonane	Decane
RuCl ₃	23	1	3	10	2
Ru/C	79	-	6	7	1
Ru/HZSM-5 (15)	-	-	-	72	12

Circulation experiments

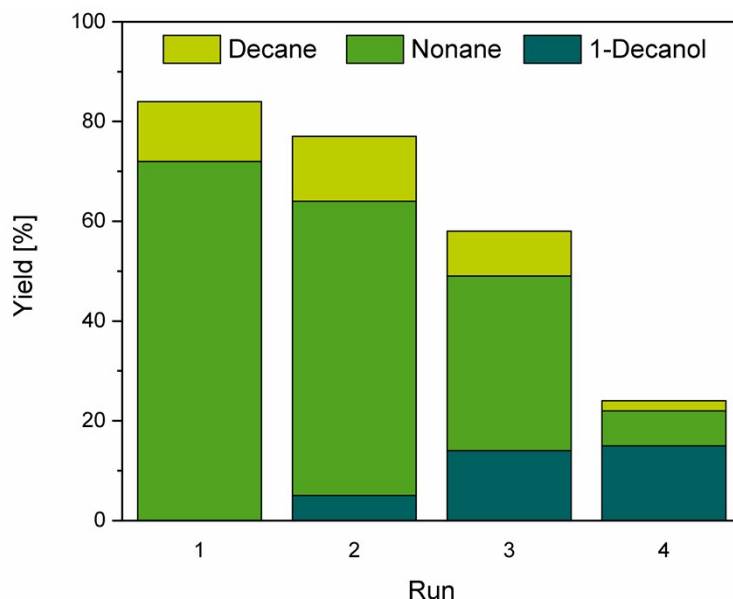


Fig S6: Circulation experiments for Ru/HZSM-5 (15). Conditions: Initially 50 mg cat. (5 wt.% Ru), 250 mg 3-HDA, 5 ml H₂O, 100 bar H₂, 200 °C, 1 h. The substrate to catalyst ratio was adjusted after each run to account for the material loss during recycling procedure.

To generate further insights on the catalyst stability of Ru/HZSM-5 (15), a recycling study was performed, in which the same batch of the catalyst was subjected to four subsequent deoxygenation reactions. After each run, the catalyst was separated from the organic phase *via* centrifugation, then carefully washed with water and isopropanol and finally dried at 60 °C in air overnight. The subsequent recycling runs were scaled down so that the substrate to catalyst ratio stayed constant over all experiments. A significant decrease of the total yields was observed over the course of four catalytic cycles with the most pronounced decline occurring after the third run. Moreover, a shift in the selectivity to primary alcohols, *i.e.* 1-decanol was found. The results show that further investigations are necessary to improve the long-term performance of the catalyst regarding its activity and selectivity.

References

- 1 H. Zhu, A. Ramanathan, J.-F. Wu and B. Subramaniam, *ACS Catal.*, 2018, **8**, 4848–4859.
- 2 C. A. Emeis, *J. Catal.*, 1993, **141**, 347–354.