Synthesis of menthol from citronellal over supported Ru- and Pt-catalysts in continuous flow

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Supporting information

1 Experimental

1.1 Synthesis of catalysts for batch reactor

Hexachloroplatinic acid, (H_2PtC_{l6}, Sigma-Aldrich) was used as a metal precursor to modify H-Beta-25 and H-Beta-300 using evaporation-impregnation method. The mixture was dried overnight at 100 °C in an oven and the resulting 2.5 wt.% Pt/H-Beta-25 and 1 wt.% Pt/ H-Beta-300 catalysts were calcined using a step calcination procedure in a muffle furnace (Table S2). Platinum modified catalysts were reduced at 350 °C for 2 h with a temperature ramp of 10 °C/min prior to each experiment.

Ruthenium(III) chloride trihydrate ($RuCl_3 \cdot 3H_2O$, technical, Sigma-Aldrich) was used as a metal precursor to modify H-Beta-300 using evaporation-impregnation method. The mixture was dried overnight at 100 °C in an oven and the resulting 2.5 wt.% Ru/H-Beta-300, which was calcined using a step calcination procedure in a muffle furnace (Table S2). Ruthenium modified catalyst was reduced at 350 °C for 2 h with a temperature ramp of 10 °C/min prior to each experiment.

1.2 One-pot synthesis of menthol in a batch reactor

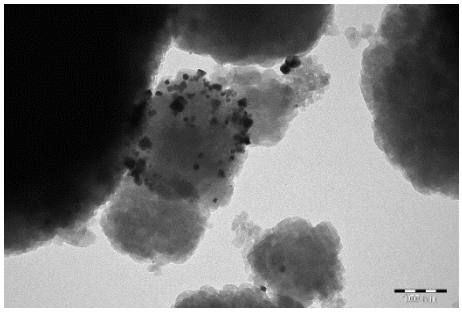
For each experiment the dried catalyst was weighted and prereduced ex-situ in a glass tube under hydrogen flow of 40 ml/min using the following temperature programme: 25 °C -10 °C/min-350 °C for 2 h. After reduction was completed, the temperature was lowered to the

ambient temperature, and 10 ml of cyclohexane (solvent) was added inside the glass tube and sealed to avoid oxidation.

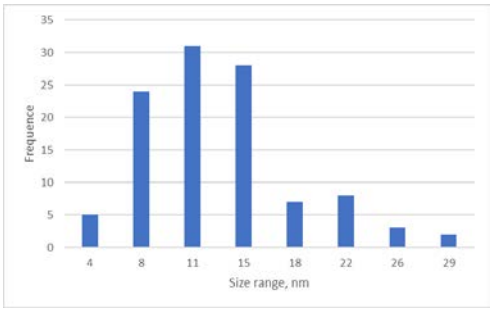
One-pot synthesis of menthol was performed in a batch reactor using 1 g of the pre-reduced catalyst and 1.2 g of citronellal dissolved in 90.2 ml of cyclohexane. After assembling, the reactor was flushed with an inert gas (≅95% N_2, ≅5% Ar, AGA) for 5-10 minutes. The reactor was then heated to 35 ˚C and pressurized with hydrogen (99.99%, AGA) to 10 bar. A stirring rate of 900 rpm was selected to avoid external mass transfer limitations during the reaction and the sieved catalyst particles below <63 µm were used to suppress the internal mass transfer limitations. The liquid phase samples were taken with a certain time internal and analyzed by GC.

2 Results

Supporting figures are shown here.



a)



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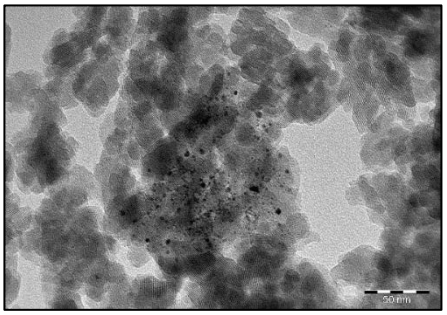

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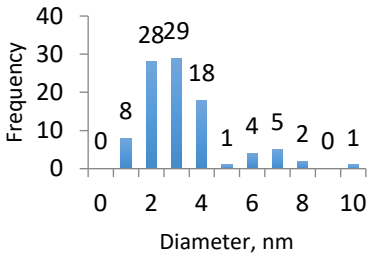

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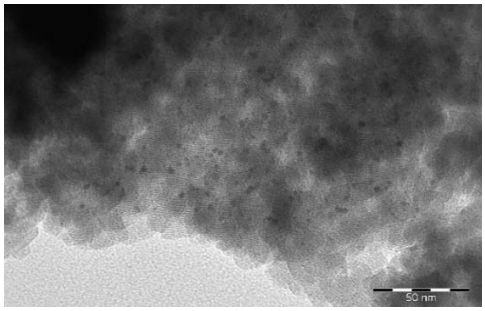

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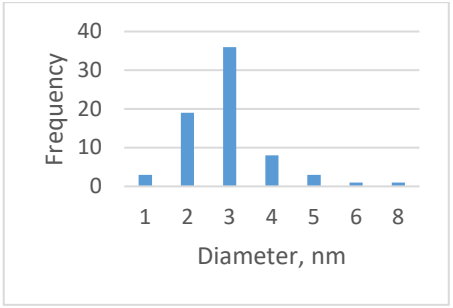


f)

Fig. S1 TEM image and metal particle size distribution for a, b) fresh 1 wt% Pt/H-Beta-300, c,d) fresh and e,f) spent 2.5 wt% Pt/H-Beta-25.

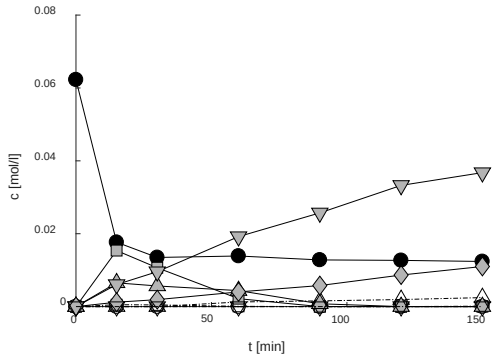
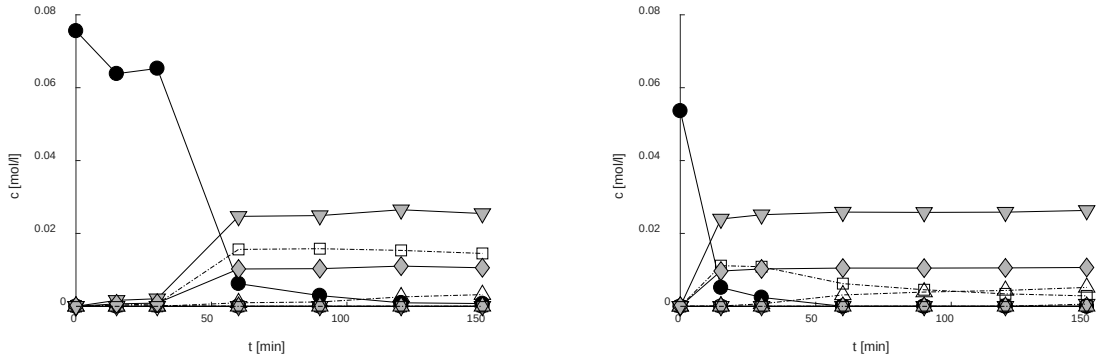


Fig. S2 Concentration of citronellal (●), citronellol (o), 3,7-dimethyloctanal (□), 3,7-dimethyloctanol (Δ), (-)-isopulegol (■), neoisopulegol (▲), menthol (▼), neomenthol (♦), dimeric ethers (∇) as a function of time in one-pot synthesis of menthols from citronellal at 35 °C under 10 bar over 2.5 wt% Ru/H-Beta-300.



a) b)

Fig. S3 Concentration of citronellal (●), citronellol (o), 3,7-dimethyloctanal (□), 3,7-dimethyloctanol (Δ), (-)-isopulegol (■), neoisopulegol (▲), menthol (▼), neomenthol (♦), dimeric ethers (∇) as a function of time in one-pot synthesis of menthols from citronellal at 35 °C under 10 bar total pressure in hydrogen over a) 1 wt% Pt/H-Beta-300, b) 2.5 wt% Pt/H-Beta-25.

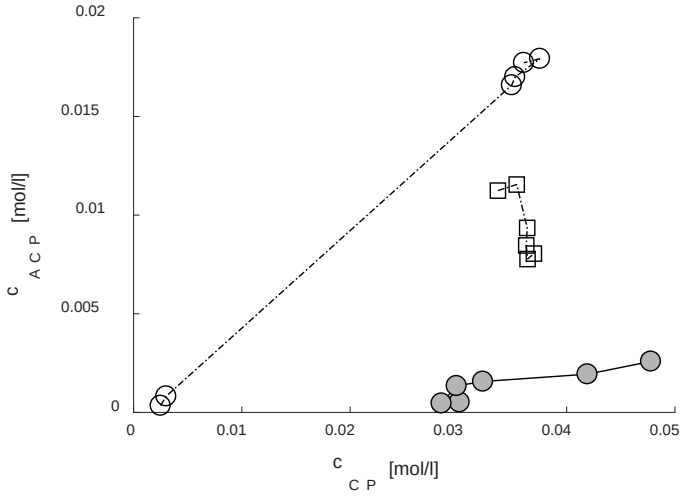


Fig. S4 Concentrations of sum of hydrogenation products (ACP) vs concentration of the sum of cyclization products (CP) in one-pot synthesis of menthol in a batch reactor at 35 °C under 10 bar total pressure in the presence of hydrogen. Symbols: 2.5 wt% Ru/H-Beta-300 (●), 1 wt% Pt/H-Beta-300 (o) and 2.5 wt% Pt/H-Beta-25 (□).

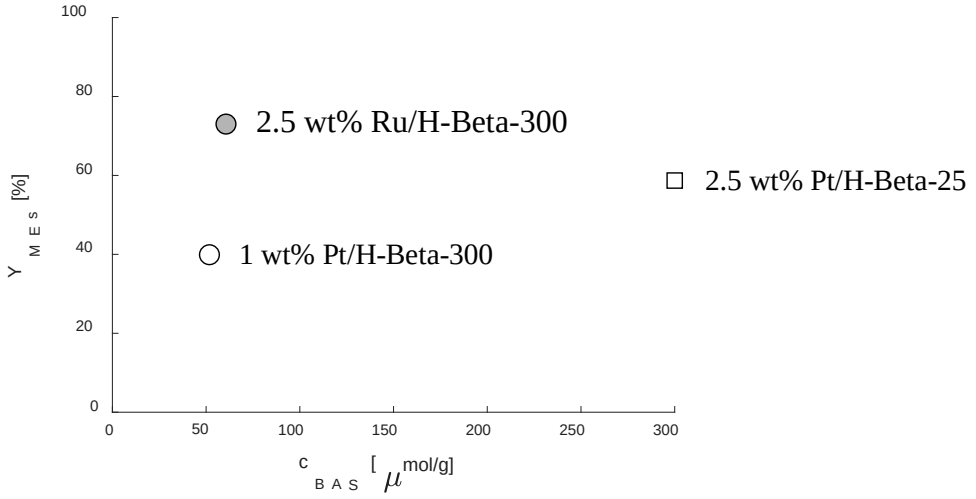


Fig. S5 The yield of menthols at 80% conversion in a batch reactor in one-pot synthesis of menthol from citronellal at 35 °C under 10 bar total pressure in H_2 pressure (if not otherwise stated) over different powder catalysts as a function of Brønsted acid site concentration.

Table S1

Step calcination program for NH_4-Beta-25

Steps	Time, min	Temperature, ˚C
Ramp	65	200
Dwell	50	200
Ramp	75	500
Dwell	240	500
	100	25

Table S2

Step calcination programs for Ru and Pt catalysts

Catalyst	Steps	Time, min	Temperature, ˚C
Ru-catalysts	Ramp	65	200
	Dwell	50	200
	Ramp	45	400
	Dwell	180	400
		100	25
Pt-catalysts	Ramp	75	250
	Dwell	50	250
	Ramp	65	400
	Dwell	180	400
		100	25

Table S3

Specific surface areaand popre volume of the catalysts

Catalyst (powder)	Specific Surface Area (m^2/g_{cat})	Pore Volume (cm^3/g_{cat})	Ref
H-Beta-25	681	0.69	[1]
H-Beta-300	629	0.43	
2.5 wt.% Ru/H-Beta-300	548 (214)	0.19 (0.29)	
1.0 wt.% Pt/H-Beta-300	592	0.21	CW
2.5 wt.% Pt/H-Beta-25	686	0.24	

CW – current work

Table S4

Brønsted and Lewis acid sites determined by pyridine adsorption desorption with FTIR. Notation: 250 ˚C = sum of weak (w) +medium (m) +strong (s) acid sites, 350 ˚C = m + s, 450 ˚C = s

Catalyst (powder)	Brønsted acidity, µmol/g			Lewis acidity, µmol/g			Ref
	250 ˚C	350 ˚C	450 ˚C	250 ˚C	350 ˚C	450 ˚C	
H-Beta-25	261	203	181	54	24	13	[1]
H-Beta-300	66	50	23	11	5	3	
2.5 wt.% Ru/H-Beta-300	61	2	0	6	0	0	
1.0 wt% Pt/H-Beta-300	52	0	0	3	0	0	CW
2.5 wt% Pt/H-Beta-25	300	16	0	88	2	0	

CW – current work

Table S5

Results from EDX analysis from the bifunctional catalysts and bifunctional extrudates as a function of weight percent (wt.%)

Catalyst (powder)	O	Al	Si	Other elements	Si/Al	Si/Pt, Si/Ru
2.5 wt.% Ru/H-Beta-300	74.54	0.5	23.29	Ru= 1.67	46.6	13.9
2.5 wt% Pt/H-Beta-25	51.5	3.4	42.6	Pt= 2.5	12.5	17

Table S6

Average metal particle size determined by TEM

Catalyst (powder)	Avg. particle size (nm)	Dispersion*, (%)
2.5 wt.% Ru/H-Beta-300	17 (13)	6 (7.7)
2.5 wt.% Pt/H-Beta-25	3.3 (3)	30 (35)
1.0 wt% Pt/H-Beta-300	13	8

*calculated by 100/average particle size

Table S7

Table S7

Results from one pot synthesis of menthol from citronellal in a batch reactor at 35 °C at 10 bar total pressure in H_2 (if not else state) in cyclohexane. Conversion of citronellal (X) and liquid phase mass balance (GCLPA) are given at 150 min of time. Yields (Y) of different products, stereoselectivity (SS), reaction rate (r) and TOF_{80} are given at 80% conversion. Conditions: amount of catalyst 1 g, the initial citronellal concentration 0.086 M

Catalyst (powder)	Initial TOF s^{-1}	X	GCLPA	Y_{Ps} %	Y_{MEs}	Y_{ACS}	Y_{DM}	Y_{CS}/Y_{ACS} -	SS_{IP}	SS_{ME} %	r mol/s·g	TOF_{80} s^{-1}	Δt min
2.5 wt% Ru/H-Beta-300	0.45	80.1	100	0.0	72.9	3.9	0.0	18.8	0.0	71.3 (83.1)*	$4.95\cdot10^{-7}$ ($4.26\cdot10^{-6}$)*	0.05 (0.43)*	15 (8.4)*
1.0 wt% Pt/H-Beta-300	0.54	99.0	76.6	0.0	39.8	18.6	0.0	2.1	0.0	70.2	$1.72\cdot10^{-6}$	0.43	55.5
2.5 wt% Pt/H-Beta-25	0.54	100	89.2	0.0	58.7	25.4	0.0	2.3	0.0	71.2	$4.49\cdot10^{-6}$	0.11	13.3

*at 40% conversion, Ps – pulegols = isopulegol (IP) + neoisopulegol (NIP) + isoisopulegol (IIP) + neoisopulegol (NIIP), MEs – menthols: menthol (ME) + neomenthol (NME) , CS – cyclic products: pulegols + menthols, ACS – acyclic monomeric products: citronellol (CLOL) + 3,7-dimethyloctanal (DMA) + 3,7-dimethyloctanol (DMO) + nerol (NRL) + geraniol (GRN), DM – dimeric ethers, SS_{IP} – stereoselectivity of isopulegol = IP/∑Ps, SS_{ME} – stereoselectivity of menthol = ME/∑MEs, Δt – time interval for reaction rate calculation.

3 References

1 Z. Vajglová, N. Kumar, M. Peurla, J. Peltonen, I. Heinmaa and D.Yu. Murzin, *Catal. Sci. Technol.*, 2018, **8**, 6150-6162.