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Synthesis, Characterization and Performance of Bifunctional Catalysts for the Synthesis of Menthol from Citronellal

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Appendix A

Conversion to rate data

Semi-batch reactor (constant hydrogen pressure) design equation:

$$\frac{dc_i}{dt} = -\left(\frac{W_{cat}}{V}\right) k \cdot c_i \quad \textbf{A.1}$$

$$\frac{dc_i}{c_i} = -\hat{c}_{cat} \cdot k \cdot dt \quad \textbf{A.2}$$

Separation of variables and integration:

$$ln\left(\frac{c_i}{c_{i0}}\right) = \ln\left(1 - x_i\right) = -\hat{c}_{cat} \cdot k \cdot t \quad \textbf{A.3}$$

$$\hat{c}_{cat} = \left(\frac{W_{cat}}{V}\right) \left[mg_{cat} mL^{-1}\right] \quad \textbf{A.4}$$

So for the first order rate constant, the initial rate and *TOF* we have, including dimensions:

$$k = -\frac{\ln\left(1 - x_i\right)}{\hat{c}_{cat} \cdot t} \left[mL \cdot mg_{cat}^{-1} \cdot s^{-1}\right] \quad \textbf{A.5}$$

$$r_0 = k \cdot c_{i0} \left[mmol \cdot mg_{cat}^{-1} \cdot s^{-1}\right] \text{ with } c_{i0} \text{ in } mmol \cdot mL^{-1} \quad \textbf{A.6}$$

$$TOF = \frac{r_0}{\hat{c}_{Pt}} \left[mmol \cdot mmol_{Pt}^{-1} \cdot s^{-1}\right] \text{ with } \hat{c}_{Pt} \text{ in } mmol_{Pt} \cdot mg_{cat}^{-1} \quad \textbf{A.7}$$

Where:

c_i concentration of component *i* $[mmol \cdot mL^{-1}]$
c_{i0} concentration of component *i* at *t* = 0 $[mmol \cdot mL^{-1}]$
W_{cat} catalyst mass $[mg]$
V reaction volume $[mL]$
$\hat{c}_{cat}$ catalyst on basis of concentration $\left[mg_{cat} mL^{-1}\right]$

k	rate constant $\left[mL \cdot mg_{cat}^{-1} \cdot s^{-1}\right]$
t	time $[s]$
x_i	conversion of component i $[-]$
r_0	initial rate $\left[mmol \cdot mg_{cat}^{-1} \cdot s^{-1}\right]$
TOF	turnover frequency $\left[mmol \cdot mmol_{Pt}^{-1} \cdot s^{-1}\right]$
$\hat{c}_{Pt}$	catalyst on basis of platinum concentration $\left[mmol_{Pt} \cdot mg_{cat}^{-1}\right]$

Appendix B

Mass transfer considerations utilising Carberry numbers and WW-criteria

Carberry number

The Carberry number is used to estimate extraparticle mass transfer, which can be neglected when Ca < 0.05.

$$Ca = \frac{r_{v,obs}}{a' k_f c_b} < \frac{0.05}{|n|}$$

Where:

Ca Carberry number $[-]$
$r_{v,obs}$ observed reaction rate per unit particle volume $[mol \cdot s^{-1} \cdot m_p^{-3}]$
a' specific external surface of the catalyst particle ($a' = 6/d_p$) $[m^2 \cdot m^{-3}]$
k_f mass transfer coefficient ($k_f = Sh \cdot D/d_p$) $[m \cdot s^{-1}]$
c_b concentration in the bulk $[mol \cdot m^{-3}]$
n reaction order $[-]$ – in these examples $n = 1$
d_p particle diameter $[m]$ – in these examples $d_p = 200 \mu m$
Sh Sherwood correlation $[m]$ – in these examples $Sh = 2$, which is valid for a sphere in a stagnant fluid
D diffusion coefficient of the reactant in the liquid phase ($D = D_{eff}/\sim 0.1$) $[m^2 \cdot s^{-1}]$ – D was taken from the thesis of Martijn Zieverink: $D = 1.8 \cdot 10^{-9}$ for the substrates and $D = 1.8 \cdot 10^{-8}$ for hydrogen

Weisz criterion

The Weisz modulus is used to estimate the influence of pore diffusion on reaction rates in heterogeneously catalysed reactions. pore diffusion limitations are insignificant if the modulus satisfies the criterion.

$$M_W = \eta \varphi^2 = \left(\frac{r_{v,obs} L^2}{D_{eff} c_s}\right)\left(\frac{n+1}{2}\right) < 0.15$$

Where:

M_W Weisz Modulus
φ Thiele modulus: $\varphi = L\sqrt{k_v / D_{eff}}$
k_v rate constant per unit volume $[s^{-1}]$
η effectiveness factor
D_{eff} effective diffusivity in particle $[m^2 \cdot s^{-1}]$ – D_{eff} was taken from the thesis of Martijn Zieverink: $D_{eff} = 1.8 \cdot 10^{-10}$ for the substrates and $D = 1.8 \cdot 10^{-9}$ for hydrogen
$r_{v,obs}$ observed reaction rate per unit particle volume $[mol \cdot s^{-1} \cdot m_p^{-3}]$
L characteristic catalyst dimension $L = d_p/6$ $[m]$
c_s concentration at the external particle surface $[mol \cdot m^{-3}]$
n reaction order $[-]$ – in these examples $n = 1$
d_p particle diameter $[m]$ – in these examples $d_p = 200 \mu m$

Table A1. Carberry numbers and WW-criteria for catalytic data Table 2 – isopulegol hydrogenation

	concentration bulk		rate constant	initial rate	observed reaction rate	Carberry number		WW-criterion	
	$Cb_{isopulegol}$ (mol·m^{-3})	Cb_{H2} (mol·m^{-3})	k (mL·mg$_{cat}^{-1}$·s^{-1})	r_o (mmol·mg$_{cat}^{-1}$·s^{-1})	$r_{v,obs}$ (mol·s^{-1}·m$_p^{-3}$)	$Ca_{isopulegol}$ -	Ca_{H2} -	$\Phi_{isopulegol}$ -	Φ_{H2} -
Pt/W-TUD-1$_{28}$	509.1	92.9	4.1E-06	2.1E-06	2.07	7.5E-03	4.0E-03	2.5E-02	1.4E-02
Pt/W-TUD-1$_{16}$	518.2	92.9	9.3E-08	4.8E-08	0.05	1.7E-04	9.6E-05	5.7E-04	3.2E-04
Pt/W-TUD-1$_{11}$	532.1	92.9	5.3E-07	2.8E-07	0.28	9.9E-04	5.7E-04	3.3E-03	1.9E-03
Pt/W-TUD-1$_{9}$	507.8	92.9	2.3E-06	1.2E-06	1.18	4.3E-03	2.3E-03	1.4E-02	7.8E-03
Pt/W-TUD-1$_{7}$	497.4	92.9	8.6E-07	4.3E-07	0.43	1.6E-03	8.6E-04	5.3E-03	2.9E-03
Pt/WO3/TUD-1$_{5}$	508.4	92.9	2.4E-07	1.2E-07	0.12	4.4E-04	2.4E-04	1.5E-03	8.0E-04
Pt/WO3/TUD-1$_{10}$	508.6	92.9	2.0E-07	1.0E-07	0.10	3.8E-04	2.1E-04	1.3E-03	6.8E-04
Pt/WO3/TUD-1$_{20}$	490.6	92.9	3.6E-07	1.8E-07	0.18	6.7E-04	3.5E-04	2.2E-03	1.2E-03

Table A2. Carberry numbers and WW-criteria for catalytic data figure 8 – isopulegol hydrogenation

	concentration bulk		rate constant	initial rate	observed reaction rate	Carberry number		WW-criterion	
	$Cb_{isopulegol}$ (mol·m^{-3})	Cb_{H2} (mol·m^{-3})	k (mL·mg$_{cat}^{-1}$·s^{-1})	r_o (mmol·mg$_{cat}^{-1}$·s^{-1})	$r_{v,obs}$ (mol·s^{-1}·m$_p^{-3}$)	$Ca_{isopulegol}$ -	Ca_{H2} -	$\Phi_{isopulegol}$ -	Φ_{H2} -
Pt/W-TUD-1$_{11}$	466.6	92.9	4.3E-06	2.0E-06	1.99	7.9E-03	4.0E-03	2.6E-02	1.3E-02

Table A3. Carberry numbers and WW-criteria for catalytic data table 4 – Prins cyclisation

	concentration bulk $Cb_{citronellal}$ mol·m^{-3}	rate constant k (mL·mg$_{cat}^{-1}$·s^{-1})	initial rate r (mmol·mg$_{cat}^{-1}$·s^{-1})	observed reaction rate $r_{v,obs}$ (mol·s^{-1}·m$_p^{-3}$)	Carberry number $Ca_{citronellal}$ -	WW-criterion $\Phi_{citronellal}$ -
Pt/W-TUD-1$_{28}$	468.7	8.4E-06	4.0E-06	3.95	1.6E-02	5.2E-02
Pt/W-TUD-1$_{16}$	515.1	1.0E-05	5.2E-06	5.18	1.9E-02	6.2E-02
Pt/W-TUD-1$_{11}$	525.0	2.3E-05	1.2E-05	11.98	**4.2E-02**	**1.4E-01**
Pt/W-TUD-1$_9$	493.0	1.2E-05	5.9E-06	5.92	2.2E-02	7.4E-02
Pt/W-TUD-1$_7$	516.2	1.2E-05	6.0E-06	5.95	2.1E-02	7.1E-02
Pt/WO3/TUD-1$_5$	497.2	1.6E-06	7.9E-07	0.79	2.9E-03	9.8E-03
Pt/WO3/TUD-1$_{10}$	527.1	1.3E-06	6.6E-07	0.66	2.3E-03	7.8E-03
Pt/WO3/TUD-1$_{20}$	511.5	1.2E-06	6.1E-07	0.61	2.2E-03	7.3E-03

Table A4. Carberry numbers and WW-criteria for catalytic data table 4 - hydrogenation

	concentration bulk		rate constant	initial rate	observed reaction rate	Carberry number		WW-criterion	
	$Cb_{isopulegol}$ (mol·m^{-3})	Cb_{H2} (mol·m^{-3})	k (mL·mg$_{cat}^{-1}$·s^{-1})	r (mmol·mg$_{cat}^{-1}$·s^{-1})	$r_{v,obs}$ (mol·s^{-1}·m$_p^{-3}$)	$Ca_{isopulegol}$ -	Ca_{H2} -	$\Phi_{isopulegol}$ -	Φ_{H2} -
Pt/W-TUD-1$_{28}$	399.3	92.9	5.3E-06	2.1E-06	2.10	9.7E-03	4.2E-03	3.2E-02	1.4E-02
Pt/W-TUD-1$_{16}$	466.8	92.9	2.2E-06	1.0E-06	1.04	4.1E-03	2.1E-03	1.4E-02	6.9E-03
Pt/W-TUD-1$_{11}$	522.5	92.9	4.6E-06	2.4E-06	2.41	8.5E-03	4.8E-03	2.8E-02	1.6E-02
Pt/W-TUD-1$_9$	461.4	92.9	4.9E-06	2.2E-06	2.25	9.0E-03	4.5E-03	3.0E-02	1.5E-02
Pt/W-TUD-1$_7$	482.4	92.9	5.0E-06	2.4E-06	2.41	9.3E-03	4.8E-03	3.1E-02	1.6E-02
Pt/WO3/TUD-1$_5$	152.3	92.9	5.9E-07	2.1E-07	0.21	2.5E-03	4.1E-04	8.3E-03	1.4E-03
Pt/WO3/TUD-1$_{10}$	129.1	92.9	7.7E-07	2.9E-07	0.29	4.1E-03	5.8E-04	1.4E-02	1.9E-03
Pt/WO3/TUD-1$_{20}$	122.6	92.9	1.0E-06	4.0E-07	0.40	6.0E-03	7.9E-04	2.0E-02	2.6E-03

Table A5. Carberry numbers and WW-criteria for catalytic data table 5 – Prins cyclisation

	concentration bulk	rate constant	initial rate	observed reaction rate	Carberry number	WW-criterion
	$Cb_{citronellal}$ mol·m^{-3}	k (mL·mg$_{cat}^{-1}$·s^{-1})	r (mmol·mg$_{cat}^{-1}$·s^{-1})	$r_{v,obs}$ (mol·s^{-1}·m$_p^{-3}$)	$Ca_{citronellal}$ -	$\Phi_{citronellal}$ -
Pt/W-TUD-1$_{28}$	694.0	5.9E-07	4.1E-07	0.41	1.1E-03	3.6E-03
Pt/W-TUD-1$_{16}$	576.8	8.6E-07	5.0E-07	0.50	1.6E-03	5.3E-03
Pt/W-TUD-1$_{11}$	551.8	6.7E-07	3.7E-07	0.37	1.2E-03	4.2E-03
Pt/W-TUD-1$_9$	-	-	-	-	-	-
Pt/W-TUD-1$_7$	551.1	1.7E-07	9.4E-08	0.09	3.2E-04	1.1E-03
Pt/WO3/TUD-1$_5$	553.6	1.9E-07	1.0E-07	0.10	3.5E-04	1.2E-03
Pt/WO3/TUD-1$_{10}$	523.1	1.8E-07	9.4E-08	0.09	3.3E-04	1.1E-03
Pt/WO3/TUD-1$_{20}$	532.0	1.9E-07	1.0E-07	0.10	3.6E-04	1.2E-03

Table A6. Carberry numbers and WW-criteria for catalytic data table 5 - hydrogenation

	concentration bulk		rate constant	initial rate	observed reaction rate	Carberry number		WW-criterion	
	$Cb_{isopulegol}$ (mol·m-3)	Cb_{H2} (mol·m-3)	k (mL·mg$_{cat}^{-1}$·s^{-1})	r (mmol·mg$_{cat}^{-1}$·s^{-1})	$r_{v,obs}$ (mol·s^{-1}·m$_p^{-3}$)	$Ca_{isopulegol}$ -	Ca_{H2} -	$\Phi_{isopulegol}$ -	Φ_{H2} -
Pt/W-TUD-1$_{28}$	562.2	92.9	8.8E-07	5.0E-07	0.50	1.6E-03	9.9E-04	5.4E-03	3.3E-03
Pt/W-TUD-1$_{16}$	455.5	92.9	5.3E-07	2.4E-07	0.24	9.7E-04	4.8E-04	3.2E-03	1.6E-03
Pt/W-TUD-1$_{11}$	462.3	92.9	1.0E-06	4.8E-07	0.48	1.9E-03	9.6E-04	6.4E-03	3.2E-03
Pt/W-TUD-1$_9$									
Pt/W-TUD-1$_7$	485.4	92.9	4.5E-05	2.2E-05	21.93	**8.4E-02**	**4.4E-02**	**2.8E-01**	**1.5E-01**
Pt/WO3/TUD-1$_5$	532.9	92.9	1.3E-07	6.8E-08	0.07	2.4E-04	1.4E-04	7.9E-04	4.5E-04
Pt/WO3/TUD-1$_{10}$	497.8	92.9	5.1E-07	2.5E-07	0.25	9.4E-04	5.0E-04	3.1E-03	1.7E-03
Pt/WO3/TUD-1$_{20}$	528.3	92.9	7.2E-07	3.8E-07	0.38	1.3E-03	7.5E-04	4.4E-03	2.5E-03

Reference

Martijn Zieverink, 2006, “A catalysis engineering approach to selective hydrogenation”, TU Delft, Delft, pp 1-166.