Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary Material

Mechanisms into Dehydroaromatization of Bio-derived Limonene to *p*-Cymene over Pd/HZSM-5 in presence and absence of H_2

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Table S1. Limonene dehydroaromatization over Pd/HZSM-5 at different H_2 pressure.[a]

Condition	Time (min)	Conv. (%)	Yield (%)				Pressure (bar)[b]
			Partial Hydrogenation	Full Hydrogenation	Dehydro-aromatization	Isomerization	
0 bar H_2	0	7	1	0	1	5	2
	30	19	1	0	3	15	
	60	19	1	0	2	16	
	90	17	1	0	2	14	
	120	21	1	0	3	17	
2 bar H_2	0	11	3	1	3	4	3
	30	24	6	1	7	11	
	60	37	10	1	13	13	
	90	46	12	1	19	14	
	120	54	15	1	24	14	
6 bar H_2	0	24	7	1	5	10	6
	30	42	13	1	12	16	
	60	62	21	2	24	15	
	90	72	28	2	30	12	
	120	78	33	3	35	7	
10 bar H_2	0	39	10	2	9	18	10
	30	59	18	2	19	20	
	60	71	25	2	27	17	
	90	83	34	4	33	11	
	120	83	34	4	34	10	
14 bar H_2	0	34	11	2	10	11	14
	30	64	24	4	25	11	
	60	86	38	8	36	3	
	90	92	41	12	38	1	
	120	95	40	17	36	1	

[a] General conditions: 10 mL limonene, 0.02g 1% Pd/HZSM-5(258), 80 mL *n*-dodecane, 260 ℃, stirring at 600 rpm.

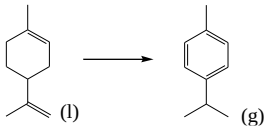
[b] This records the pressure for reactions lasting 2 h at working temperature.

Table S2. Equations for different systems with additional 6, 10, or 14 bar hydrogen.[a]

Condition	Equations
6 bar H_2	$\frac{dc_1}{dt} = -k_1 \times c_1$ $\frac{dc_2}{dt} = k_1 \times c_1 - k_2 \times c_2 - k_9 \times c_2$ $\frac{dc_3}{dt} = k_9 \times c_2 - k_6 \times c_3$ $\frac{dc_4}{dt} = k_6 \times c_3$ $\frac{dc_5}{dt} = k_2 \times c_2$
10 bar H_2	$\frac{dc_1}{dt} = -k_1 \times c_1 + k_8 \times c_2$ $\frac{dc_2}{dt} = k_1 \times c_1 - k_8 \times c_2 - k_2 \times c_2 - k_9 \times c_2$ $\frac{dc_3}{dt} = k_9 \times c_2 - k_6 \times c_3$ $\frac{dc_4}{dt} = k_6 \times c_3$ $\frac{dc_5}{dt} = k_2 \times c_2$
14 bar H_2	$\frac{dc_1}{dt} = -k_1 \times c_1$ $\frac{dc_2}{dt} = k_1 \times c_1 - k_2 \times c_2 - k_9 \times c_2$ $\frac{dc_3}{dt} = k_9 \times c_2 - k_6 \times c_3$ $\frac{dc_4}{dt} = k_6 \times c_3$ $\frac{dc_5}{dt} = k_2 \times c_2$

[a] c_X refers to the concentration of compound X, and X represent the labelling numbers in Scheme 3..

Calculation Methods:



$+ H_{2\,(g)}$ (1)

When the substrate limonene is 10 mL, and the density of limonene in atmosphere and room temperature was obtained as:

$n = \frac{D \times V}{M}$ (2)

Where D and V are density and volume of limonene, respectively.

Accordingly, *n* (limonene) = 59.19 *m*mol.

Theoretical yield was also calculated as well.

Thermodynamic parameters for limonene dehydroaromatization at 260 ℃ was gained from HSC software from Table 3, $K_{sp} = 2.26 \times 10^{10}$.

$$\frac{n_{(\text{p-cymene})}^{2}}{0.059\text{-}n_{(\text{p-cymene})}} = 2.26 \times 10^{10} \quad (3)$$

n (*p*-cymene) ≈ 0.059 mol.

The experimental yield was obtained: *n* (*p*-cymene) = 0.05919×74% = 0.0438 mol = 43.8 *m*mol.