Supporting Information

Jet-fuel range hydrocarbon production from propanal: Mechanistic insights into active site requirement of dual bed catalyst

*Isaac Yeboah[1†], Xiang Feng[1,3†], Gang Wang[4], Kumar Ranjan Rout[2], Zhenping Cai[1], Xuezhi Duan[4], Xinggui Zhou[4], and De Chen[1]**

[1] *Department of Chemical Engineering, Norwegian University of Science and Technology, Trondheim, Norway*

[2] *SINTEF Industry, Trondheim, Norway*

[3] *State Key Laboratory of Heavy Oil Processing, China University of Petroleum, Qingdao, China*

[4] *School of Chemical Engineering, East China University of Science and Technology, Shanghai, China.*

Email address of corresponding author (De Chen[*]): de.chen@ntnu.no

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† These authors contributed equally to this work.

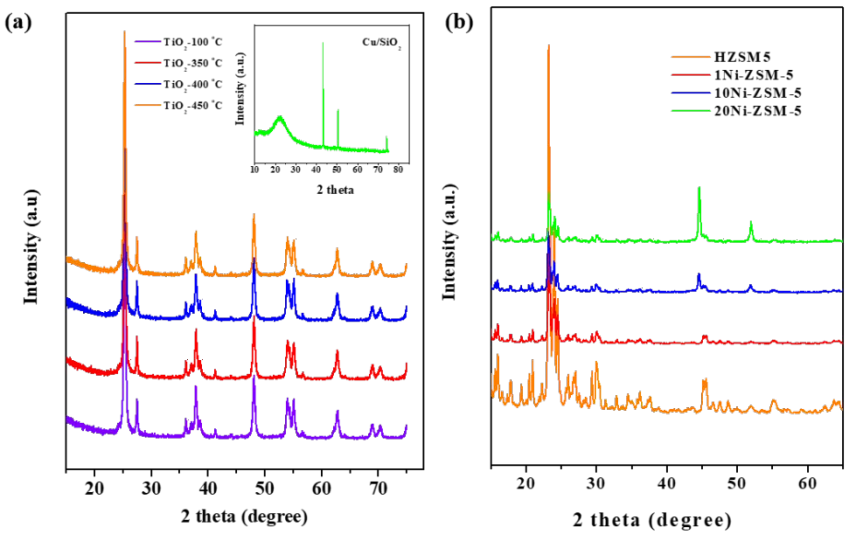

Figure S1. XRD patterns of (a) Cu/SiO_2 (inset) and TiO_2; (b) Ni/HZSM-5 catalysts.

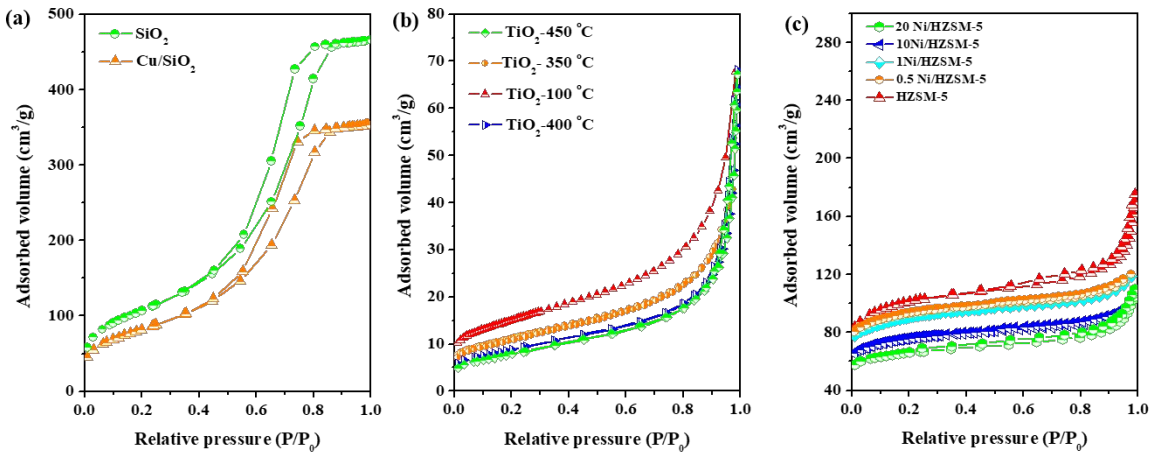

Figure S2. N_2 physisorption for (a) SiO_2, Cu/SiO_2, (b) TiO_2 with different calcination temperature, and (c) Ni/HZSM-5 with different Ni loadings.

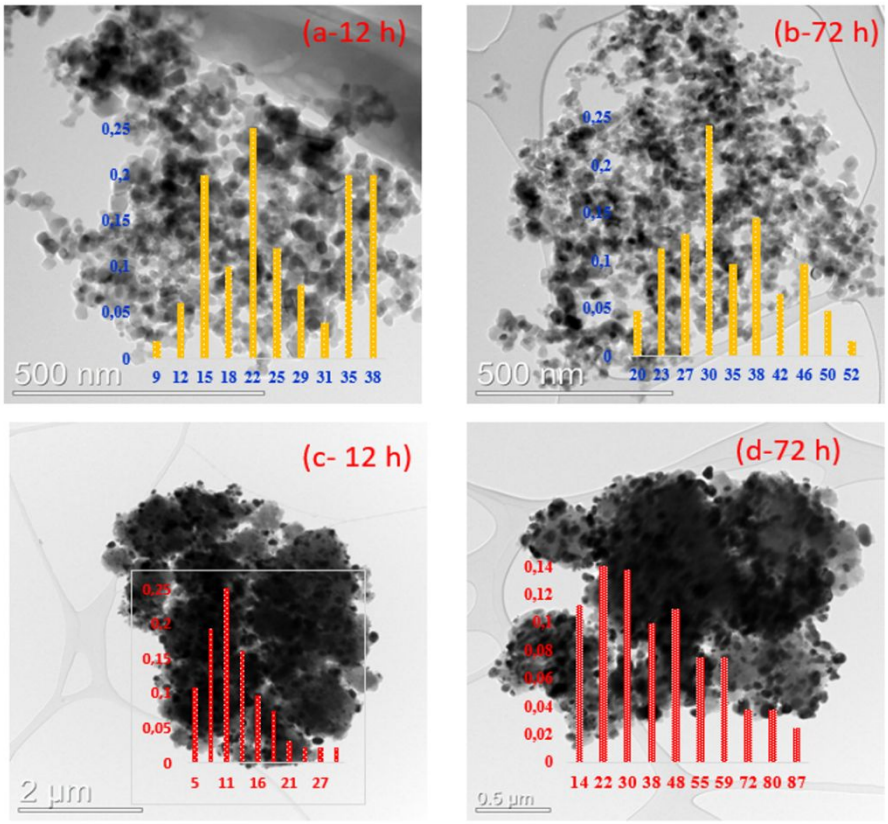

Figure S3. TEM image and particle size distribution (nm) of the upstream (a-b) and downstream catalyst (c-d) at 12 h (a- c) and 72 h (b-d) time on stream.

Table S1. Gas phase product distribution on Cu/SiO_2-TiO_2 || Ni/ZSM-5 catalyst with different Ni loadings. Reaction condition: 1/WHSV of 5.2 h; hydrogen pressure of 0.39 bar; propanal pressure of 0.21 bar; reaction temperature of 300 ^oC; total pressure of 1.0 bar; time-on-stream of 12 h.

	Yield (C mol %)							
Ni loading (wt%)	methane	ethene	ethane	propene	propane	CO_2	Coke	total
0	1.39	0.00	0.50	3.00	3.04	2.02	6.68	16.99
0.5	0.37	0.00	0.52	3.01	3.34	1.21	5.80	14.25
1	0.44	0.00	0.22	3.37	3.24	1.15	5.02	13.42
10	0. 29	0.00	0.51	1.07	1.05	0.31	3.44	6.65
20	0.29	0.00	0.50	0.00	1.04	0.02	1.78	3.63
Physically mixed bed	2.70	0.50	5.05	2.50	7.98	1.62	7.06	27.40

Table S2. Gas phase product distribution on time scale analysis for 5 wt% Cu/SiO_2-TiO_2 || 20 wt% Ni-ZSM-5. Reaction condition: 1/WHSV of 5.2 h; hydrogen pressure of 0.39 bar; propanal pressure of 0.21 bar; temperature of 300 ^oC; total pressure of 1.0 bar.

	Yield (C mol %)							
TOS (h)	methane	ethene	ethane	propene	propane	CO_2	coke	total
12	0.57	0.00	0.72	0.01	0.34	0.21	1.78	3.63
24	0.76	0.00	1.28	0.02	2.38	0.37	2.02	5.84
36	1.19	0.00	1.60	0.00	2.79	0.45	3.86	7.93
48	1.54	0.00	2.02	0.00	2.74	0.73	5.72	12.75
60	1.70	0.07	2.18	0.44	3.98	0.90	6.38	15.65
72	1.81	0.07	2.19	0.46	3.66	1.10	9.07	17.36

Table S3. Major organic phase product distributions on **5wt%CuSiO$_2$-TiO$_2$ || HZSM-5** using propanal as feed. Reaction condition: feeding rate of 8 μm/min; 1/ WHSV of 5.2 h, hydrogen pressure of 0.39 bar; propanal pressure of 0.21 bar; reaction temperature of 300 ^{o}C; total pressure of 1.0 bar.

Product distribution	**Selectivity (%)**
Benzene	0.00
Toluene	7.50
2-Pentenal, 2-methyl-	0.00
Ethylbenzene	1.38
p-Xylene	11.33
o-Xylene	3.10
Benzene, 1-ethyl-3-methyl-	7.25
Benzene, 1,3,5-trimethyl-	0.90
Benzene, 1,2,3-trimethyl-	9.07
Cyclohexane, 1,3-dimethyl-, cis-	0.70
Benzene, 1,3-diethyl-	0.83
Benzene, 1,3-diethyl-	0.68
3-Cyclopenten-1-one, 2,2,5,5-tetramethyl-	0.59
Benzene, 1-methyl-3-(1-methylethyl)-	1.30
1,4-cyclohexadiene, 1,5 dimethyl	0.00
2-Cyclopenten-1-one, 2,3,4,5-tetramethyl-	29.98
Benzene, 1-ethenyl-4-ethyl-	0.52
Benzene, 1-methyl-4-(1-methylpropyl)-	0.55
Benzene, (2-methyl-1-butenyl)-	0.67
2,4-Hexadiene, 2,4-dimethyl-	4.38
Naphthalene, 2-methyl-	1.83
Benzene, 1-ethyl-3-methyl-	6.60
Benzene, 1-ethyl-2-methyl-	3.12
Naphthalene, 2,7-dimethyl-	3.30
Benzene, 1-ethyl-4-methyl-	2.03
1,3-Cyclopentadiene, 5,5-dimethyl-1,2-Dipropyl-	1.21
2-Propanone, 1-(3,5,5-trimethyl-2-cyclohexen-1-ylidene)-, (Z)-	0.34
Naphthalene, 2,3,6-trimethyl-	0.86

Table S4. Major organic phase product distributions on **physical mixture** (5wt%Cu/SiO_2-TiO_2 || 20wt%Ni/HZSM-5) using propanal as feed. Reaction condition: feeding rate of 8 μm/min; 1/ WHSV of 5.2 h, hydrogen pressure of 0.39 bar; propanal pressure of 0.21 bar; reaction temperature of 300 ^oC; total pressure of 1.0 bar.

Products	**Selectivity (%)**
Benzene	0.01
Toluene	15.52
2-Pentenal, 2-methyl-	1.18
Ethylbenzene	3.31
p-Xylene	23.83
o-Xylene	5.77
Benzene, 1-ethyl-3-methyl-	10.24
Benzene, 1,3,5-trimethyl-	0.96
Benzene, 1-ethyl-2-methyl-	0.25
Benzene, 1,2,3-trimethyl-	10.66
Cyclohexane, 1,3-dimethyl-, cis-	0.78
Benzene, 1,3-diethyl-	0.65
Benzene, 1,3-diethyl-	1.18
3-Cyclopenten-1-one, 2,2,5,5-tetramethyl-	0.72
Benzene, 1-methyl-3-(1-methylethyl)-	1.45
1,4-cyclohexadiene, 1,5 dimethyl	0.00
2-Cyclopenten-1-one, 2,3,4,5-tetramethyl-	12.16
Benzene, 1-ethenyl-4-ethyl-	0.43
Benzene, 1-methyl-4-(1-methylpropyl)-	0.75
Benzene, (2-methyl-1-butenyl)-	0.68
2,4-Hexadiene, 2,4-dimethyl-	1.48
Naphthalene, 2-methyl-	0.41
Benzene, 1-ethyl-3-methyl-	1.40
Benzene, 1-ethyl-2-methyl-	1.10
Naphthalene, 2-ethyl-	1.02
Naphthalene, 2,7-dimethyl-	1.47
Benzene, 1-ethyl-4-methyl-	0.18
1,3-Cyclopentadiene, 5,5-dimethyl-1,2-Dipropyl-	1.07
2-Propanone, 1-(3,5,5-trimethyl-2-cyclohexen-1-ylidene)-, (Z)-	0.76
Naphthalene, 2,3,6-trimethyl-	0.55

Table S5. Major organic phase product distributions on **5wt%Cu/SiO_2-TiO_2 || 0.5 wt% Ni/HZSM-5**, using propanal as feed. Reaction condition: feeding rate of 8 μm/min; 1/ WHSV of 5.2 h, hydrogen pressure of 0.39 bar; propanal pressure of 0.21 bar; reaction temperature of 300 °C; total pressure of 1.0 bar.

Products	**Selectivity (%)**
Benzene	0.01
Toluene	13.33
2-Pentenal, 2-methyl-	1.20
Ethylbenzene	2.92
p-Xylene	17.71
o-Xylene	4.76
Benzene, 1-ethyl-3-methyl-	9.89
Benzene, 1,3,5-trimethyl-	0.82
Benzene, 1-ethyl-2-methyl-	0.73
Benzene, 1,2,3-trimethyl-	6.69
3-Cyclopenten-1-one, 2,2,5,5-tetramethyl-	0.44
Benzene, 1-methyl-3-(1-methylethyl)-	1.62
2-Cyclopenten-1-one, 2,3,4,5-tetramethyl-	24.31
Benzene, 1-ethenyl-4-ethyl-	0.72
Benzene, 1-methyl-4-(1-methylpropyl)-	0.42
Benzene, (2-methyl-1-butenyl)-	0.83
2,4-Hexadiene, 2,4-dimethyl-	1.10
Naphthalene, 2-methyl-	2.78
Benzene, 1-ethyl-3-methyl-	0.59
Benzene, 1-ethyl-2-methyl-	1.12
Naphthalene, 2-ethyl-	1.12
Naphthalene, 2,7-dimethyl-	1.95
Benzene, 1-ethyl-4-methyl-	2.25
1,3-Cyclopentadiene, 5,5-dimethyl-1,2-Dipropyl-	0.89
2-Propanone, 1-(3,5,5-trimethyl-2-cyclohexen-1-ylidene)-, (Z)-	0.88
Naphthalene, 2,3,6-trimethyl-	0.94

Table S6. Major organic phase product distributions on **5wt%Cu/SiO_2-TiO_2||1.0 wt%Ni/HZSM-5**, using propanal as feed. Reaction condition: feeding rate of 8 μm/min; 1/ WHSV of 5.2 h, hydrogen pressure of 0.39 bar; propanal pressure of 0.21 bar; reaction temperature of 300 ^oC; total pressure of 1.0 bar.

Products	**Selectivty (%)**
Benzene	0.00
Toluene	7.75
Ethylbenzene	1.25
p-Xylene	11.10
o-Xylene	2.46
Benzene, 1-ethyl-3-methyl-	6.94
Benzene, 1,3,5-trimethyl-	0.83
Benzene, 1,2,3-trimethyl-	6.43
Cyclohexane, 1,3-dimethyl-, cis-	0.48
Benzene, propyl	0.70
Benzene, 1,3-diethyl-	0.71
3-Cyclopenten-1-one, 2,2,5,5-tetramethyl-	0.99
Benzene, 1-methyl-3-(1-methylethyl)-	1.40
2-Cyclopenten-1-one, 2,3,4,5-tetramethyl-	20.38
Benzene, 1-ethenyl-4-ethyl-	0.28
Benzene, 1-methyl-4-(1-methylpropyl)-	1.17
Benzene, (2-methyl-1-butenyl)-	1.26
2,4-Hexadiene, 2,4-dimethyl-	3.89
Naphthalene, 2-methyl-	2.79
Benzene, 1-ethyl-3-methyl-	2.16
Benzene, 1-ethyl-2-methyl-	4.15
Naphthalene, 2-ethyl-	1.74
Naphthalene, 2,7-dimethyl-	3.33
Benzene, 1-ethyl-4-methyl-	1.07
1,3-Cyclopentadiene, 5,5-dimethyl-1,2-Dipropyl-	1.38
2-Propanone, 1-(3,5,5-trimethyl-2-cyclohexen-1-ylidene)-, (Z)-	1.08
Naphthalene, 2,3,6-trimethyl-	0.87

Table S7. Major organic phase product distributions on **5wt%Cu/SiO_2-TiO_2||10 wt%Ni/HZSM-5,** using propanal as feed. Reaction condition: feeding rate of 8 μm/min; 1/ WHSV of 5.2 h, hydrogen pressure of 0.39 bar; propanal pressure of 0.21 bar; reaction temperature of 300 ^oC; total pressure of 1.0 bar.

Products	**Selectivity (%)**
Benzene	0.00
Toluene	12.06
Ethylbenzene	1.84
p-Xylene	19.15
o-Xylene	7.28
Benzene, 1-ethyl-3-methyl-	7.61
Benzene, 1,3,5-trimethyl-	1.23
Benzene, 1,2,3-trimethyl-	13.47
Cyclohexane, 1,3-dimethyl-, cis-	0.59
Benzene, propyl	0.76
Benzene, 1,3-diethyl-	0.00
3-Cyclopenten-1-one, 2,2,5,5-tetramethyl-	0.42
Benzene, 1-methyl-3-(1-methylethyl)-	0.90
2-Cyclopenten-1-one, 2,3,4,5-tetramethyl-	14.28
Benzene, 1-ethenyl-4-ethyl-	1.00
Benzene, 1-methyl-4-(1-methylpropyl)-	0.45
Benzene, (2-methyl-1-butenyl)-	0.69
2,4-Hexadiene, 2,4-dimethyl-	1.01
Naphthalene, 2-methyl-	2.27
Benzene, 1-ethyl-3-methyl-	1.84
Benzene, 1-ethyl-2-methyl-	3.40
Naphthalene, 2-ethyl-	1.35
Naphthalene, 2,7-dimethyl-	2.51
Benzene, 1-ethyl-4-methyl-	1.72
1,3-Cyclopentadiene, 5,5-dimethyl-1,2-Dipropyl-	1.16
2-Propanone, 1-(3,5,5-trimethyl-2-cyclohexen-1-ylidene)-, (Z)-	1.63
Naphthalene, 2,3,6-trimethyl-	1.38

Table S8. Major organic phase product distributions on **5wt%Cu/SiO_2-TiO_2||20wt% Ni/HZSM-5**, using propanal as feed. Reaction condition: feeding rate of 8 μm/min; 1/ WHSV of 5.2 h, hydrogen pressure of 0.39 bar; propanal pressure of 0.21 bar; reaction temperature of 300 ^oC; total pressure of 1.0 bar.

Products	**Selectivity (%)**
Benzene	0.00
Toluene	11.11
Ethylbenzene	2.06
p-Xylene	18.92
o-Xylene	5.32
Benzene, 1-ethyl-3-methyl-	8.41
Benzene, 1,3,5-trimethyl-	1.36
Benzene, 1,2,3-trimethyl-	15.14
Cyclohexane, 1,3-dimethyl-, cis-	0.95
Benzene, 1,3-diethyl-	1.02
3-Cyclopenten-1-one, 2,2,5,5-tetramethyl-	0.51
Benzene, 1-methyl-3-(1-methylethyl)-	1.05
2-Cyclopenten-1-one, 2,3,4,5-tetramethyl-	13.39
Benzene, 1-ethenyl-4-ethyl-	0.61
Benzene, 1-methyl-4-(1-methylpropyl)-	0.67
Benzene, (2-methyl-1-butenyl)-	0.78
2,4-Hexadiene, 2,4-dimethyl-	1.71
Naphthalene, 2-methyl-	2.67
Benzene, 1-ethyl-3-methyl-	1.45
Benzene, 1-ethyl-2-methyl-	1.39
Naphthalene, 2-ethyl-	2.22
Naphthalene, 2,7-dimethyl-	3.14
Benzene, 1-ethyl-4-methyl-	2.28
1,3-Cyclopentadiene, 5,5-dimethyl-1,2-Dipropyl-	1.71
2-Propanone, 1-(3,5,5-trimethyl-2-cyclohexen-1-ylidene)-, (Z)-	1.34
Naphthalene, 2,3,6-trimethyl-	0.77

Table S9. BET investigation of spent catalyst: upstream bed (Cu/SiO_2-TiO_2) and downstream bed (20wt% Ni/HZSM-5). Reaction condition: 1/WHSV of 5.2 h, hydrogen pressure of 0.39 bar; propanal pressure of 0.21 bar; reaction temperature of 300 ^oC; total pressure of 1.0 bar.) temperature of 300 ^oC and total pressure of 1.5 bar.

Catalyst	BET (m^2/g)	Pore volume (cm^3/g)	Mass loss (%)	Particle size from XRD	Particle size from TEM
upstream 12 h	228.21	0.430	0.11	20.98 [a]	21.50 [a]
upstream 72 h	108.62	0.194	3.73	27.15 [a]	33.50 [a]
downstream 12 h	224.09	0.146	1.68	-	12.98 [b]
downstream 72 h	83.46	0.067	9.24	-	26.6 [b]

[a] Cu and [b] Ni

Table S10 Catalytic performance of catalysts for propanal conversion.

1/WHSV (h)	Catalyst	Temp. (°C)	Aromatic yield (%)	Ref.
5.2	Cu/SiO_2-TiO_2||Ni/HZSM-5	300	81.7[a] (77.5)	This work
4.0	Desilicalited HZSM-5	400	50	J. Catal. 2010, 271, 88-98
0.2	$Ce_{0.25}Zr_{0.75}O_2$	400	<1	Appl. Catal. A. 2010; 385: 80-91
0.04	ZrO_2	400	<1	Appl. Catal. A. 2010; 385: 80-91

[a] Jet fuel range hydrocarbon yield (%).