Supporting Information

One-pot hydrodeoxygenation of bioderived furans into octane at low temperatures *via* an octanediol route

Song Li, [ab] Qiaozhi Ma, [c] Wenxin Zhong, [c] Xuelai Zhao, [ad] Xiangqian Wei, [ad] Xinghua Zhang, [a] Qiying Liu, [a] Chenguang Wang, [a] Longlong Ma, [ad] Qi Zhang *[ad]

[a] Guangdong Provincial Key Laboratory of New and Renewable Energy Research and Development, CAS Key Laboratory of Renewable Energy, Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences, Guangzhou 510640, PR China. E-mail: zhangqi@ms.giec.ac.cn; Fax: +86 20 87057789; Tel: +86 20 87057789.
[b] University of Chinese Academy of Sciences, Beijing 100049, PR China.
[c] College of Materials and Energy, South China Agricultural University, Guangzhou 510642, China.
[d] Department of Thermal Science and Energy Engineering, University of Science and Technology of China, Hefei, 233022, China.

Contents page

Preparation details

Hydrogenation of FA:

100 mg of FA, 50 mg of 5 wt% Pd/C, 50 mg of HPW and 10 ml of cyclohexane were added into a Teflon tube. The sealed reactor was flushed with H_2 for four times and pressured to 1 MPa H_2. The hydrogenation was carried out at 30 ˚C for 4 h. **Figure S3**: ^{13}C-NMR (101 MHz, Chloroform-*d*) δ=208.7 , 78.3 , 67.6 , 40.4 , 31.3 , 29.9 , 29.5 , 26. 9 , 25.7.

Preparation of FHOH[1]:

100 mg of FA, 20 mg of 5 wt% Ru/C and 10 ml of cyclohexane were added into a Teflon tube. The sealed reactor was flushed with H_2 for four times and pressured to 8 MPa H_2. The autoclave was heated up to 50 ˚C and kept for 2 h with string at 400 rpm. After cooling down to room temperature, liquid products were collected by filtration through a 0.22 μm nylon membrane. FHOH was obtained after evaporation of solvent. **Figure S7**: ^{13}C-NMR (101 MHz, Chloroform-d) δ=79.7 , 79. 5 , 68.1 , 67.8 , 67.6 , 36.6 , 35.9 , 32.5 , 31.6 , 31.5 , 31.4 , 25.7 , 25.6 , 23.6 , 23.3.

Preparation of BTHF:

100 mg of 2-butylfuran, 50 mg of 5 wt% Pd/C, 50 mg of HPW and 10 ml of cyclohexane were added into a Teflon tube. The sealed reactor was flushed with H_2 for four times and pressured to 1 MPa H_2. The autoclave was heated up to 80 ˚C and kept for 4 h with string at 400 rpm. After cooling down to room temperature, liquid products were collected by filtration through a 0.22 μm nylon membrane. BTHF was obtained after evaporation of solvent. **Figure S8**: ^{13}C-NMR (101 MHz, Chloroform-*d*) δ=67.6, 35.4, 31.4, 28.6, 25.7, 22.8, 14.1.

D_2O isotope labelling experiment:

After Pd/C-HPW300 was pretreated in cyclohexane, 100 mg of FA and 400 μl of D_2O were added into the autoclave. The sealed reactor was flushed with H_2 for four times and pressured to 1 MPa H_2. It was firstly hydrogenated at 50 ˚C for 4 h, followed by hydrodeoxygenation at 130 ˚C for 4 h. Liquid organic products were collected by filtration through a 0.22 μm nylon membrane.

The HDO of FA under different hydrogen pressure

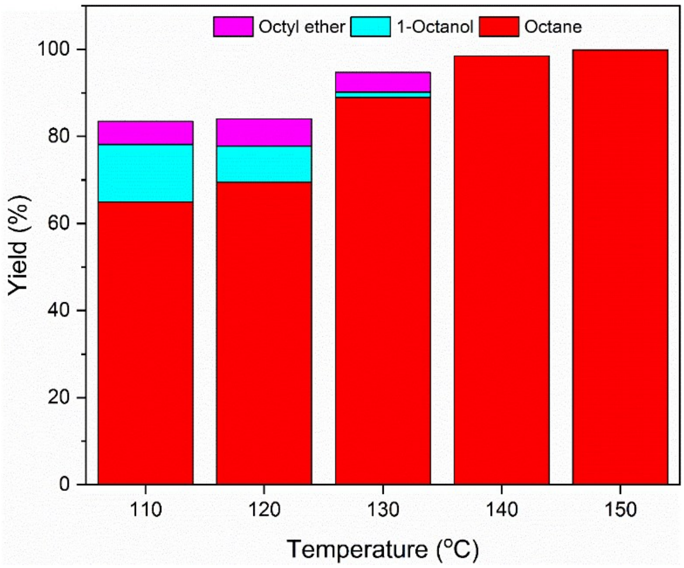


Figure S1 The HDO of FA over Pd/C-HPW catalysts under 3 MPa H_2 at different temperature. Reaction conditions: FA (100 mg), cyclohexane (10 mL), Pd/C (50 mg), HPW (50 mg), 400 rpm, 4 h.

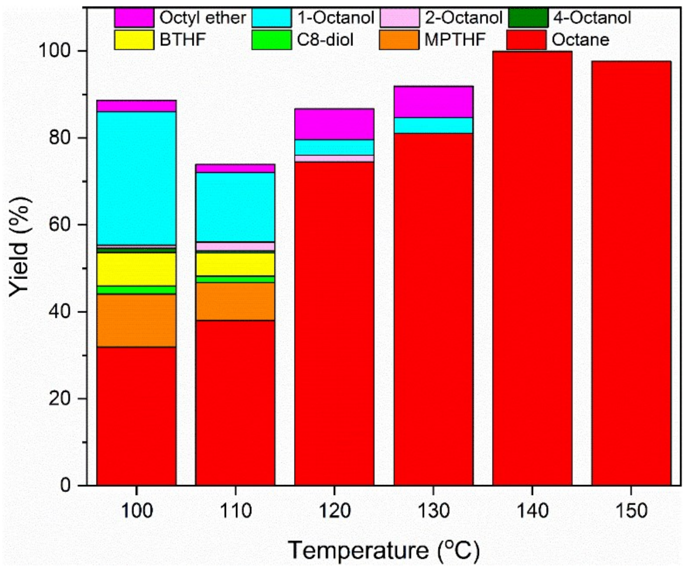


Figure S2 The HDO of FA over Pd/C-HPW catalysts under 5 MPa H_2 at different temperature. Reaction conditions: FA (100 mg), cyclohexane (10 mL), Pd/C (50 mg), HPW (50 mg), 400 rpm, 4 h.

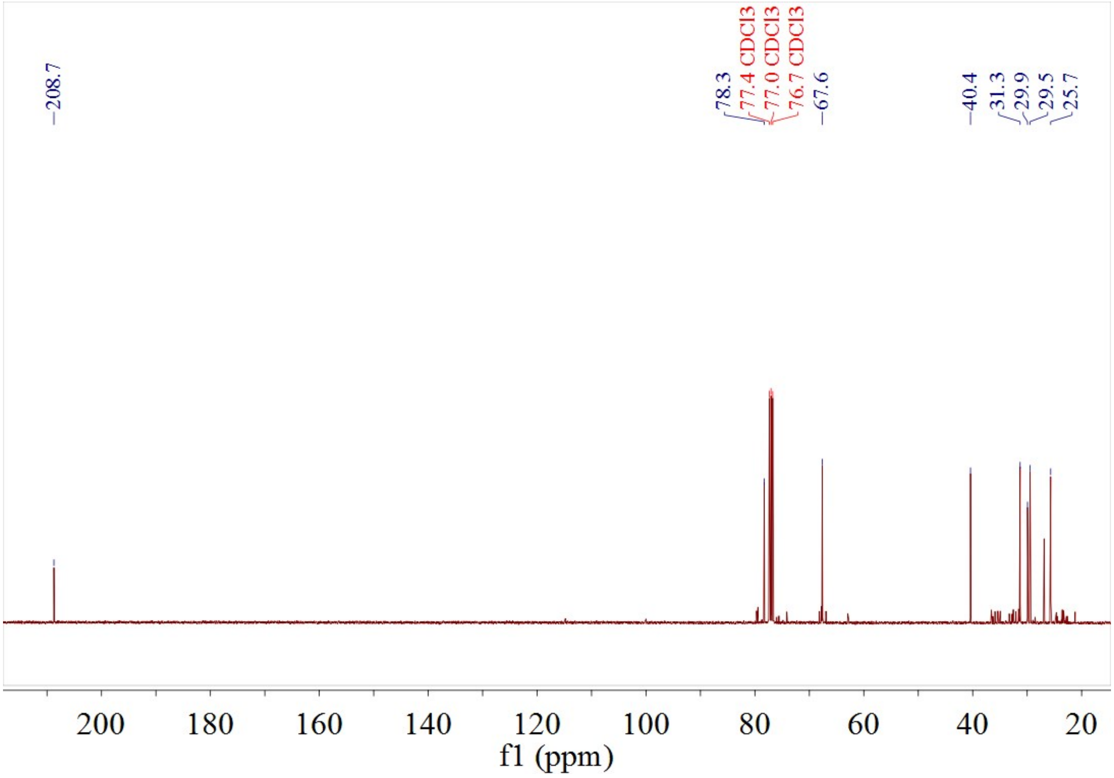


Figure S3 ^{13}C-NMR spectra of liquid products after hydrogenation of FA over Pd/C-HPW under 1 MPa H_2 at 30 °C for 4h.

^{13}C-NMR spectra of liquid products after hydrogenation of FA

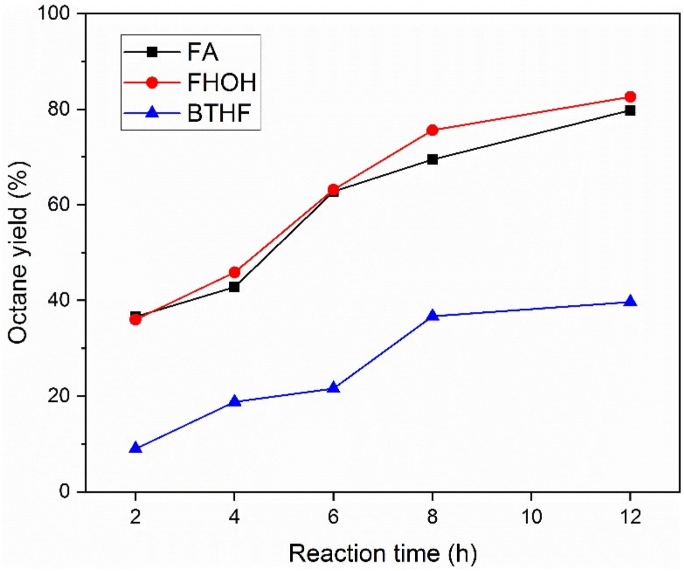


Figure S4 The HDO of FA, FHOH and BTHF at 100˚C for different reaction time. Reaction conditions: FA, FHOH or BTHF (0.73 mmol), cyclohexane (10 mL), Pd/C (50 mg), HPW (50 mg), 1 MPa H_2 at room temperature, 100 ˚C, 400 rpm.

Octane production for the HDO at 100 ˚C

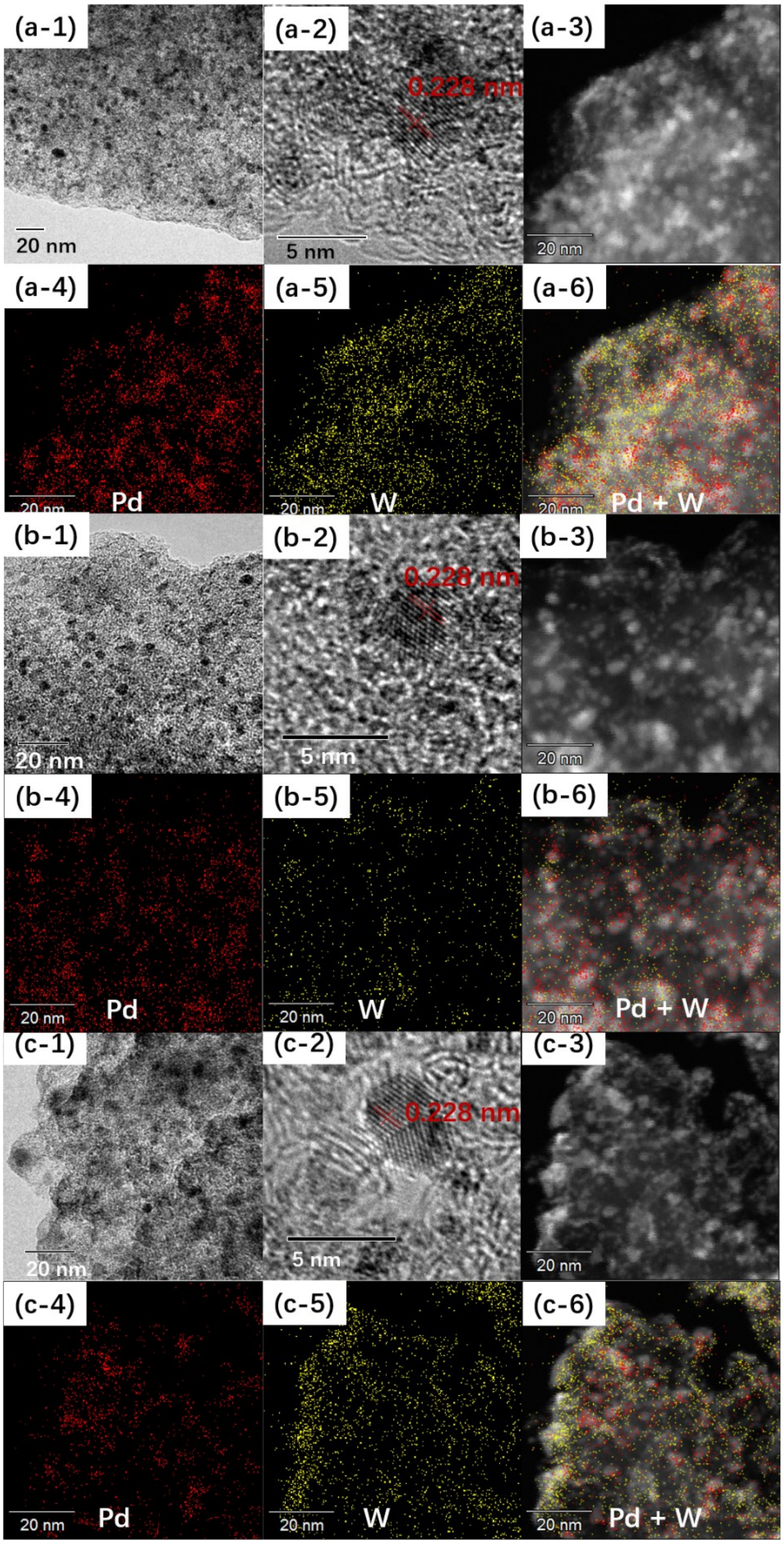


Figure S5 TEM micrographs of (a) Pd/C-HPW, (b) Pd/C-HPW300 and (c) Pd/C-HPW300 promoted by water

TEM micrographs of differernt catalysts

XRD and FT-IR patterns of used catalysts

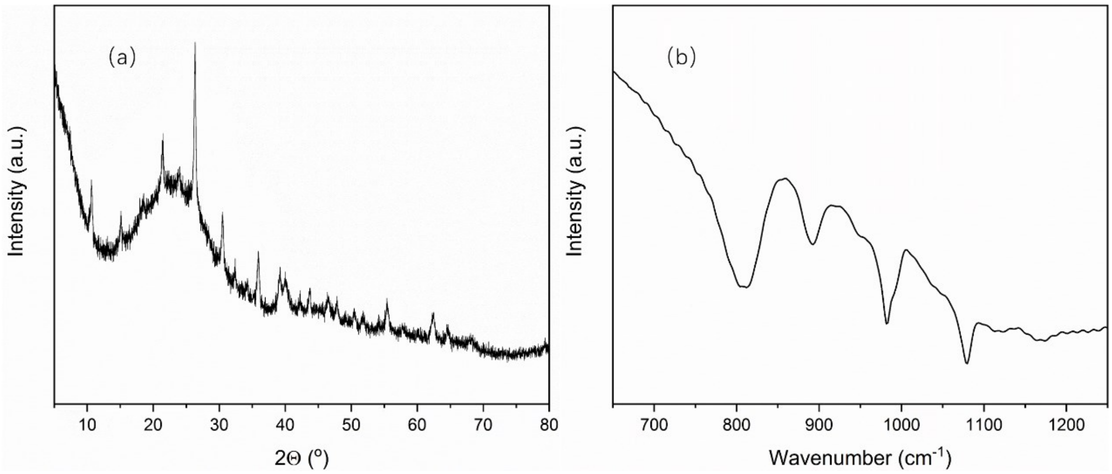


Figure S6 (a) XRD and (b) FT-IR patterns of used catalysts.

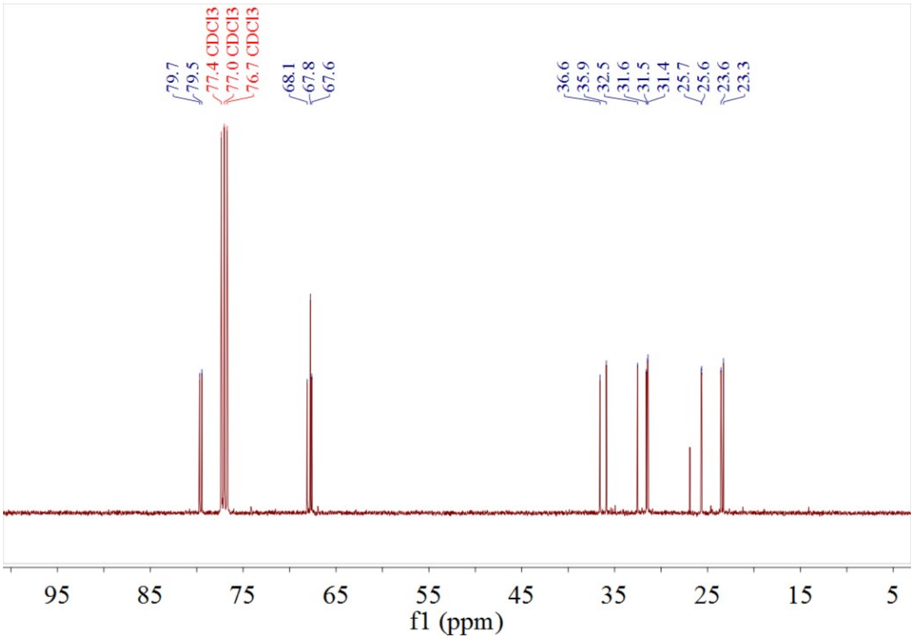


Figure S7 ^{13}C-NMR spectra of FHOH.

^{13}C-NMR spectra of FHOH

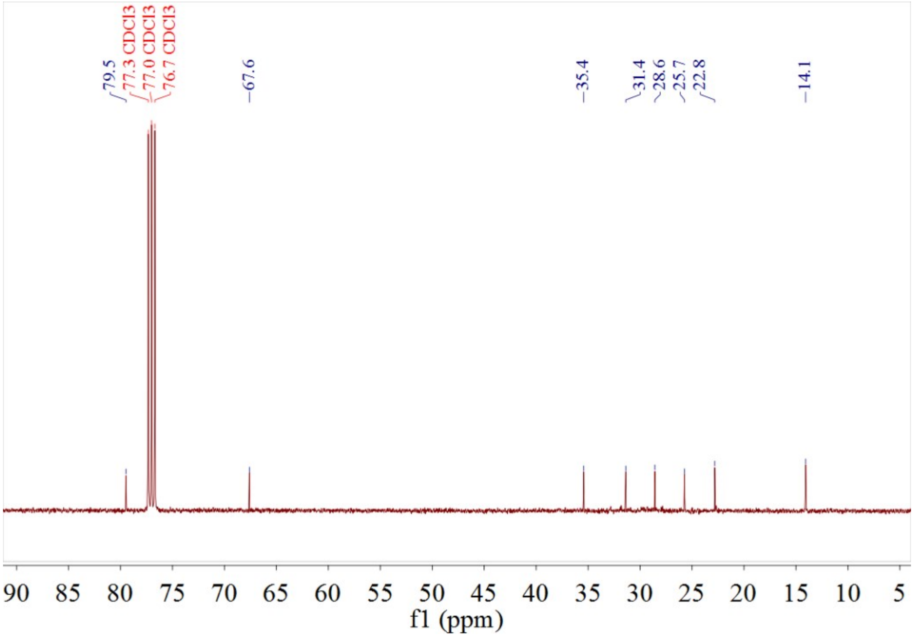
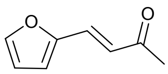
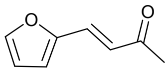
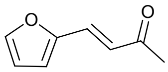
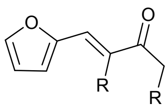
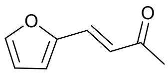
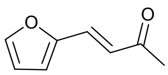
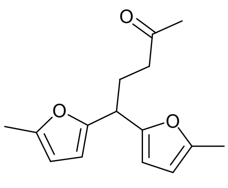
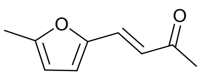
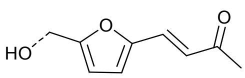
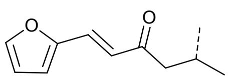
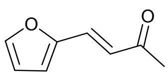
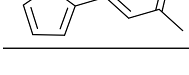


Figure S8 ^{13}C-NMR spectra of BTHF.

^{13}C-NMR spectra of BTHF

Performance of different catalysts

Table S1 Performance of different catalysts in hydrodeoxygenation of bioderived furans to alkanes

Raw materials	Catalysts	Conditions	Alkanes	Yield(%)	Ref.
	Pd/Al_2O_3, 4wt%Pt/SiO_2-Al_2O_3	5.5 MPa H_2, 120 ˚C, 5.5-6 MPa H_2, 250-265˚C.	C_8	77.7	2
	Pd/$NbOPO_4$	2 MPa H_2, 170˚C, 24 h	C_8	94	3
	Pd/10%Nb_2O_5/SiO_2	2.5 MPa H_2, 170˚C, 24 h	C_8	99.5	4
 R:-$C_{10}H_{21}$	Ir-ReO_x/SiO_2	5 MPa H_2, 180˚C, 18 h.	C_{28}	73.6	5
	10% Ni 10% Cu/Nb_2O_5	4 MPa H_2, 250°C, 12 h.	C_8	86.5	6
	Pd/Al-MCM-41	14 MPa CO_2, 4 MPa H_2, 60˚C, 8 h,	C_8	99	7
	Ir−MoO_x/SiO_2(0.13)	5 MPa H_2, 180°C, 24 h.	C_{15}	85	8
	Pd/C-Hf$(OTf)_4$	6 MPa H_2, 60˚C, 8 h, 180˚C, 20 h.	C_9	93	9
	Pd/C, glacial acetic acid; Pd/C-La$(OTf)_3$	65˚C, 2 h, 100˚C, 3 h; 2.07 MPa H_2, 200˚C, 16 h	C_9	87	10
	5%Pd-2.5%FeO_x/SiO_2	1 atm H_2, 300-350˚C	C_{10}, C_{11}	87-94	11
	Pt/Co_2AlO_4, Pt/$NbOPO_4$	0.5-2 MPa, 130-150˚C, 20 h; 2.5 MPa, 175˚C.	C_8	76	12
	Pd/C-HPW	1 MPa H_2, 130°C, 4 h.	C_8	96.6	This work

Time-course experiments for the HDO at 100 ˚C

Table S2 The HDO of FA, FHOH and BTHF at 100˚C for different reaction time[a]

Entry	Raw Materials	Time (h)	Conversion (%)	Yield (%)							
				Octane	MPTHF	C8-diols	BTHF	2-Octanol	1-Octanol	Octyl ether	Sum
1	FA	2	100.0	36.6	11.3	0.5	7.7	0.4	24.4	2.3	83.2
2	FA	4	100.0	42.8	/	8.4	4.4	/	21.7	3.4	80.6
3	FA	6	100.0	62.8	/	/	/	/	13.4	7.6	83.7
4	FA	8	100.0	69.5	/	/	/	/	2.6	9.6	81.7
5	FA	12	100.0	79.8	/	/	/	/	1.3	10.1	91.3
6	FHOH	2	100.0	36.0	12.8	2.3	7.2	/	26.5	1.8	86.6
7	FHOH	4	100.0	45.9	8.1	/	3.5	/	23.1	3.3	83.9
8	FHOH	6	100.0	63.2	/	/	/	/	15.4	6.5	85.1
9	FHOH	8	100.0	75.6	/	/	/	/	2.4	6.6	84.7
10	FHOH	12	100.0	82.6	/	/	/	/	3.8	5.6	92.0
11	BTHF	2	17.7	9.0	/	/	/	2.0	1.9	4.7	17.6
12	BTHF	4	28.3	18.8	/	/	/	/	6.9	/	25.7
13	BTHF	6	51.6	21.6	/	/	/	1.1	4.8	4.4	32.0
14	BTHF	8	73.6	36.7	/	/	/	/	10.6	4.5	51.8
15	BTHF	12	80.2	39.7	/	/	/	/	10.0	4.2	53.9

[a]Reaction conditions: FA, FHOH or BTHF (0.73 mmol), cyclohexane (10 mL), Pd/C (50 mg), HPW (50 mg), 1 MPa H_2 at room temperature, 100 ˚C, 400 rpm.

Molecular fragments in mass spectra

Table S3 The possible molecular fragments of octane

Octane (Figure 8, a)		Labeled octane (Figure 8, b)	
m/z	Molecular fragments	m/z	Molecular fragments
29	C_2H_5	31	$C_2H_3D_2$
43	C_3H_7	46	$C_3H_4D_3$
57	C_4H_9	60	$C_4H_6D_3$
71	C_5H_{11}	75	$C_5H_7D_4$
85	C_6H_{13}	90	$C_6H_{10}D_4$
114	C_8H_{18}	118	$C_8H_{14}D_4$
/	/	119	$C_8H_{13}D_5$
/	/	120	$C_8H_{12}D_6$
/	/	121	$C_8H_{11}D_7$
/	/	122	$C_8H_{10}D_8$
/	/	123	$C_8H_9D_9$
/	/	124	$C_8H_8D_{10}$

References

1. M. Strohmann, A. Bordet, A. J. Vorholt and W. Leitner, *Green Chemistry*, 2019, **21**, 6299-6306.
2. G. W. Huber, J. N. Chheda, C. J. Barrett and J. A. , *Science*, 2005, **308**, 1446.
3. X. Qi-Neng, C. Qian, L. Xiao-Hui, G. Xue-Qing, L. Guan-Zhong and W. Yan-Qin, *Angewandte Chemie International Edition*, 2014, **53**, 9755-9760.
4. Y. Shao, Q. Xia, X. Liu, G. Lu and Y. Wang, *ChemSusChem*, 2015, **8**, 1761-1767.
5. A. M. Norton, S. Liu, B. Saha and D. G. Vlachos, *ChemSusChem*, 2019, **12**, 4780-4785.
6. P. Wang, Y. Jing, Y. Guo, Y. Cui, S. Dai, X. Liu and Y. Wang, *Catalysis Science & Technology*, 2020, **10**, 4256-4263.
7. M. Chatterjee, K. Matsushima, Y. Ikushima, M. Sato, T. Yokoyama, H. Kawanami and T. Suzuki, *Green Chemistry*, 2010, **12**, 779-782.
8. S. Liu, W. Zheng, J. Fu, K. Alexopoulos, B. Saha and D. G. Vlachos, *ACS Catalysis*, 2019, **9**, 7679-7689.
9. H.-J. Song, J. Deng, M.-S. Cui, X.-L. Li, X.-X. Liu, R. Zhu, W.-P. Wu and Y. Fu, *ChemSusChem*, 2015, **8**, 4250-4255.
10. A. D. Sutton, F. D. Waldie, R. Wu, M. Schlaf, L. A. 'Pete' Silks Iii and J. C. Gordon, *Nature Chemistry*, 2013, **5**, 428.
11. S. Zhu, X. Gao, Y. Zhu, Y. Zhu, X. Xiang, C. Hu and Y. Li, *Applied Catalysis B: Environmental*, 2013, **140-141**, 60-67.
12. W. J. Xu, Q. N. Xia, Y. Zhang, Y. Guo, Y. Q. Wang and G. Z. Lu, *ChemsusChem*, 2011, **4**, 1758-1761.