Electronic Supplementary Material (ESI) for Green Chemistry.

Insight into forced hydrogen re-arrangement and altered reaction pathways in a protocol for CO_2 catalytic processing of oleic acid into C_8-C_{15} alkanes

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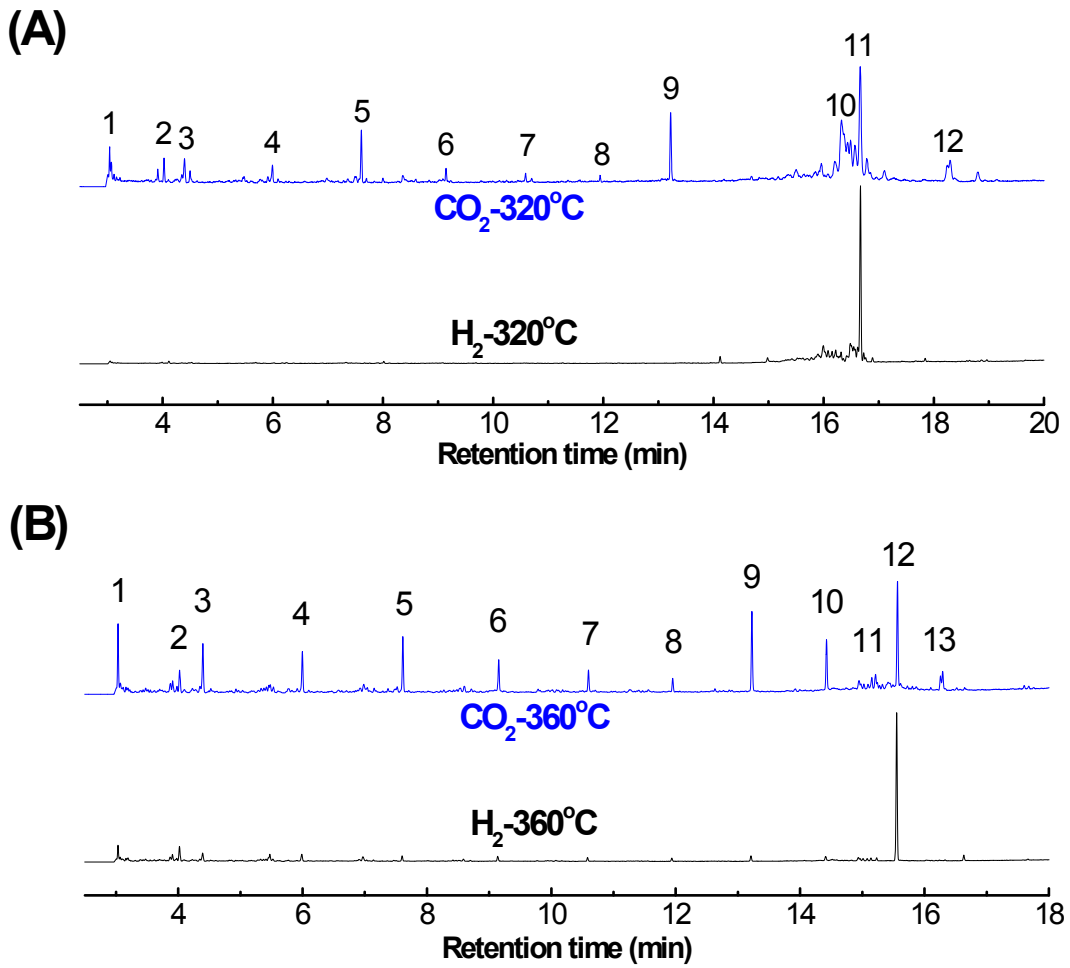

Figure S1. GC/MS spectra of the liquid products in CO_2 and H_2-processed oleic acid at 320℃ and 360℃.The main products as indexed are as follows: (1) 1,2,3-trimethyl-cyclopentene, (2) ethylbenezene, (3) σ-xylene, (4) nonane, (5) 1-ethyl-3-methyl-benzene, (6) decane, (7) 1-methyl-3-propyl-benzene, (8) undecane, (9) dodecane, (10) tridecane, (11) hexadecane, (12) heptadecane, (13) undecyl-cyclohexane.

Table S1. Mole distribution of C_8-C_{17} products in H_2 atmosphere at 360℃.

Compounds	Retention time (min)	Formula	Reaction pressure (MPa) / (mol %)			
			1	2	3	4
Alkanes						
Octane	3.03	C_8H_{18}	9.8	10.6	10.2	13.3
Nonane	4.39	C_9H_{20}	6.0	4.8	3.7	5.9
Decane	5.99	$C_{10}H_{22}$	3.7	2.3	2.4	3.6
Undecane	7.61	$C_{11}H_{24}$	2.6	1.4	1.4	2.1
Dodecane	9.14	$C_{12}H_{26}$	2.4	0.9	0.9	1.6
Tridecane	10.59	$C_{13}H_{28}$	1.5	0.6	0.0	1.2
Tetradecane	11.94	$C_{14}H_{30}$	0.0	0.4	0.0	0.9
Pentadecane	13.22	$C_{15}H_{32}$	2.3	1.2	1.1	1.7
Hexadecane	14.42	$C_{16}H_{34}$	2.4	1.3	1.2	1.1
			0.7	9.8	5.5	3.8
Heptadecane	15.56	$C_{17}H_{36}$	52.5	56.2	57.9	43.9
undercyl-cyclohexane	16.28	$C_{17}H_{34}$	0.0	0.0	2.2	1.5
Total			**83.9**	**89.5**	**86.5**	**80.6**
Olefins						
8-Heptadecene	16.33, 16.45, 16.50, 16.59,17.11	$C_{17}H_{34}$	**0**	**0**	**0**	**0**
Aromatics						
Ethylbenzene	3.91	C_8H_{10}	3.7	3.1	2.4	3.5
1,3-dimethy-benzene	4.01	C_8H_{10}	6.4	3.9	6.5	9.3
1-Ethyl-3-methyl-benzene	5.45	C_9H_{12}	3.2	2.0	2.6	3.9
1-Methyl-2-propyl-benzene	6.98	$C_{10}H_{14}$	2.5	1.4	1.9	2.5
Total			**15.8**	**10.4**	**13.4**	**19.2**

Table S2. Mole distribution of the deoxygenated products in CO_2 atmosphere at 320℃.

Compounds	Retention time (min)	Formula	Reaction pressure (MPa) / (mol %)			
			1	2	3	4
Alkanes						
Nonane	4.39	C_9H_{20}	4.4	4.6	4.6	5.5
Decane	5.99	$C_{10}H_{22}$	2.8	3.1	3.4	4.1
Undecane	7.61	$C_{11}H_{24}$	7.2	7.5	7.8	7.7
Dodecane	9.15	$C_{12}H_{26}$	1.4	1.7	1.7	2.2
2,3,5,8-Tetramethyl-decane	10.60	$C_{14}H_{30}$	0.8	0.9	1.2	1.0
Pentadecane	13.23	$C_{15}H_{32}$	7.3	7.7	7.6	6.8
Heptadecane	16.68	$C_{17}H_{36}$	16.7	15.9	14.6	13.2
Undercyl-cyclohexane	18.32	$C_{17}H_{34}$	6.2	6.0	5.8	5.5
Total			**46.8**	**47.4**	**46.7**	**46.0**
Olefins						
1-Octene	3.03	C_8H_{16}	3.7	6.3	8.3	11.0
4-Octene,(E)-	3.07	C_8H_{16}	2.3	0.0	0.0	0.0
2-Octene	3.12	C_8H_{16}	1.2	1.1	1.0	1.5
Cis-4-nonene	4.35	C_9H_{18}	1.1	0.7	0.8	1.0
4-Decene	5.91	$C_{10}H_{20}$	0.7	0.9	1.2	1.4
8-Heptadecene	16.33, 16.45, 16.50, 16.59	$C_{17}H_{34}$	27.7	25.2	24.1	17.8
5-Octadecene,(E)-	16.80	$C_{18}H_{36}$	2.7	3.0	2.3	1.2
8-Heptadecene	17.11	$C_{17}H_{34}$	1.4	1.3	1.1	0.9
Total			**40.8**	**38.5**	**38.8**	**34.8**
Aromatics						
Ethylbenzene	3.91	C_8H_{10}	1.9	2.2	3.3	4.1
1,3-Dimethy-benzene	4.02	C_8H_{10}	4.6	5.0	5.2	7.3
1-Ethyl-3-methyl-benzene	5.48	C_9H_{12}	1.3	1.1	1.5	2.6
2-Methyl-naphthalene	10.71	$C_{11}H_{10}$	0.4	0.7	0.3	0.4
Total			**8.2**	**9.0**	**10.3**	**14.4**
Others						
Cyclohexanone	4.48	$C_6H_{10}O$	2.4	2.1	2.1	2.8
Phenylethyl alcohol	8.02	$C_8H_{10}O$	0.8	0.5	1.0	0.7
2-Dodecanone	11.95	$C_{12}H_{24}O$	0.6	0.8	0.6	0.7
Total			**3.8**	**3.4**	**3.7**	**4.2**

The XRD pattern of the prepared catalyst (Figure S2 (A)) shows three evident peaks at 37.22°, 43.33° and 62.89° indexing as NiO (111), NiO (200) and NiO (220), respectively, indicating that NiO is successfully loaded on HZSM-5. After H_2 reduction, all the NiO peaks disappear, whereas another three new peaks at 44.49°, 51.88° and 76.37° come out, corresponding to the formed Ni lattice plane. The XPS survey spectra are shown in Figure S2 (B) containing O1s and Ni2p detection. The O1s spectra (see Figure S2 (C)) indicate that there is only hydroxyl group at the binding energy of 532.78 eV on the HZSM-5 support. When loaded with NiO, a new peak at 529.78 eV occurs, associating to the lattice oxygen in NiO. After H_2 reduction, such new peak fades away, indicating the oxygen removal of NiO. The result of O1s spectra is consistent with that of Ni2p spectra (see Figure S2 (D)).

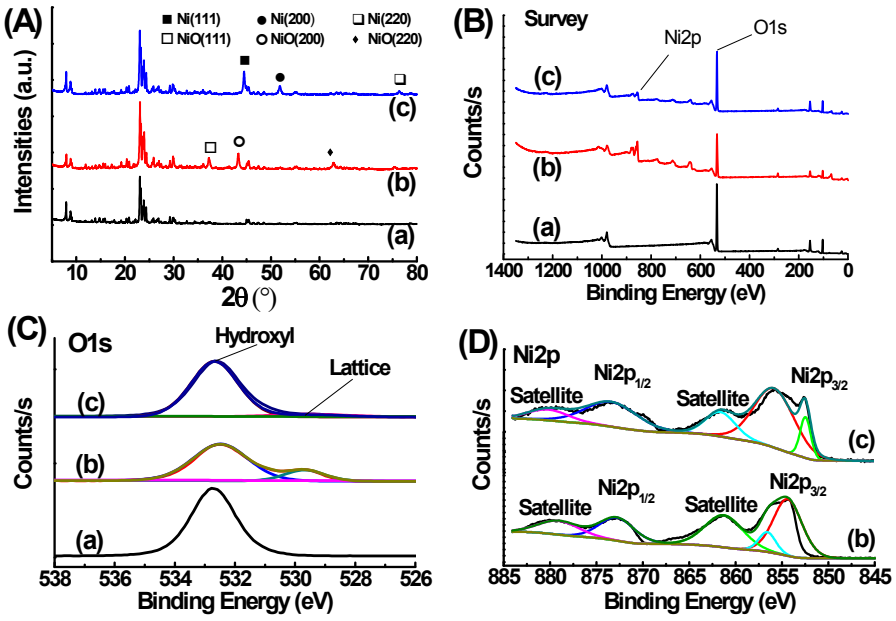

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Figure S2. XRD pattern (A) and XPS survey spectra (B), O1s (C) and Ni2p (D) for the catalyst of (a) HZSM-5, (b) 10 wt% NiO/HZSM-5 and (c) 10 wt% Ni/HZSM-5.

Table S3. Total carbon numbers calculation of the liquid products.

Reaction conditions	CO_2 atmosphere		H_2 atmosphere	
	320 ℃	360 ℃	320 ℃	360 ℃
1 MPa	1392	1257	1700	1360
2 MPa	1373	1207	1700	1441
3 MPa	1339	1203	1700	1431
4 MPa	1255	1212	1700	1310

The value was calculated according to the following method:

$$Carbon = \sum n_i * C_i$$

where i is the specific component of the liquid product, n is the mole value and C means the carbon numbers.

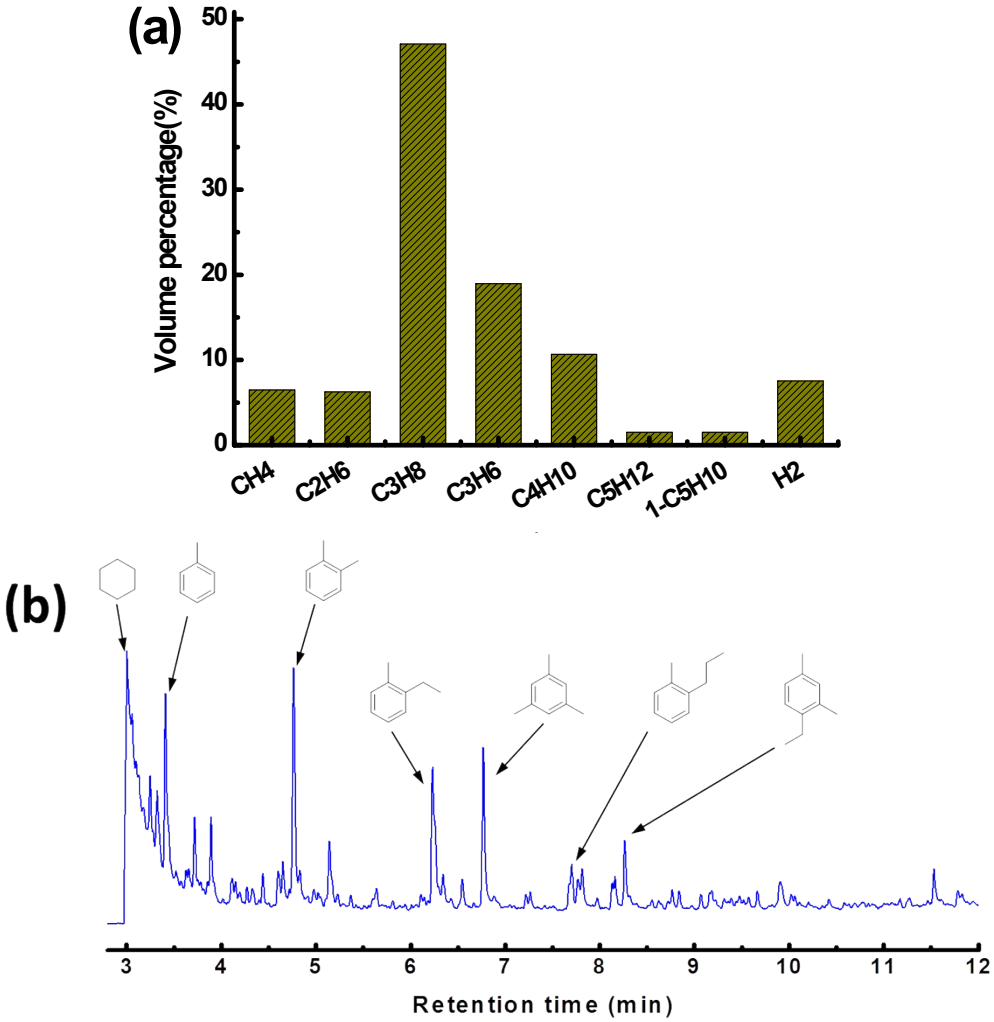

Figure S3 Distributions of gas (a) and liquid products (b) in the conversion of C_3H_6 using HZSM-5. Reaction conditions: 360℃, 0.8 MPa C_3H_6, 0.7 g HZSM-5, 5 h.