

Electronic Supplementary Information

**A New Approach for Bio-Jet Fuel Generation from Palm Oil and Limonene
in absence of Hydrogen ****

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Materials and Methods

Palm oil was provided by China Grain Reserves Co.. The chemicals of D-limonene, stearic acid, nickel nitrate, copper nitrate, cobalt nitrate, ferric nitrate, zinc nitrate and hydrochloric acid were received from Sinopec Co., Ltd. with analytic grade. The chemicals of aluminum oxide, silicon dioxide, aluminium isopropoxide (AIP), Pd/C, palladium chloride, ruthenium trichloride, rhodium chloride and auric chloride acid were obtained from J&K Co. with analytic grade. The zeolite material including HBeta (Si/Al ratio = 26), HUSY (Si/Al ratio = 9 and 30) were purchased from Nankai University Plant in China. Air, H₂ and N₂ gases (99.999 vol.%) were supplied by Shanghai Pujiang Specialty Gases Co., Ltd..

Synthesis of HZSM-5

Firstly, AIP (0.1385 g) was dissolved in a mixture of TPAOH (20.34 g) and distilled water (11.75 g) with stirring at ambient temperature for 2 h until AIP was totally dissolved. Then TEOS (21.13 g) was added drop-wise into the mixed solution and kept stirring for 4 h before transferred into a Teflon-lined stainless steel autoclave. Crystallization was executed in an oven lasted 72 h at 170 °C. After cooled down to ambient temperature naturally, the solid product was washed by water, and sequentially centrifugated to remove supernatant liquid, and finally collected after drying at 110 °C overnight. Prior to use, it was calcined in flowing air (flowing rate: 100 mL·min⁻¹) at 550 °C for 6 h.

Synthesis of amorphous silica alumina

Firstly aqueous AlCl₃·6H₂O and Na₂SiO₃ solutions were prepared as respective aluminum and silicon precursors with a SiO₂/Al₂O₃ weight ratio of 45:55. NH₃·H₂O was added to the mixed precursors to adjust pH attaining 8.0, and then the co-gelification was performed at 80 °C under reflux. In order to realize full decationization, the as-received *co*-gelificated gel was ion-exchanged with CH₃COONH₄ for three times, and then dried at 100 °C for 24 h before calcination in flowing air (flowing rate: 100 mL·min⁻¹) at 550 °C for 4 h.

Synthesis of supported 1 wt. % Pd catalysts

The supported 1 wt. % Pd catalysts were prepared by incipient wetness impregnation. PdCl₂ was firstly dissolved in an HCl solution to afford a transparent H₂PdCl₄ solution (6.25 mM). Then aqueous H₂PdCl₄ solution (30.1 mL) was slowly dropped onto variety supports (1.98 g), and kept continuous stirring at ambient temperature overnight. Afterwards, the as-formed catalysts were filtered, dried at 80 °C overnight. Finally, it was calcined in flowing air (flowing rate: 100 mL/min) at 350 °C for 4 h, and reduced in flowing hydrogen (flowing rate: 100 mL·min⁻¹) at 350 °C for 4 h.

Synthesis of supported bimetallic Pd-M catalysts

A typical bimetallic Pd-Ni/HZSM-5 was synthesized as follows. Firstly an H₂PdCl₄ solution (0.05 M, 9.4 mL) was prepared, and Ni(NO₃)₂·6H₂O (0.495 g) was dissolved in distilled water (10 mL) to form a second solution. Then the Ni and Pd precursor solutions were mixed and

well-dropped onto HZSM-5 (0.85 g), which kept magnetic stirring at ambient temperature for 10 h. Subsequently the slurry was filtered, dried at 80 °C overnight, calcined in flowing air (flowing rate: 100 mL·min⁻¹) at 460 °C for 4 h, and finally reduced in flowing H₂ (flowing rate: 100 mL·min⁻¹) at 460 °C for 4 h. Synthesis of Pd-M catalysts (M refers to Cu, Co, Fe, Zn, Ru, Rh, Au) was similar to the procedure for Pd-Ni/HZSM-5 preparation, but with different temperatures for calcination and reduction.

Catalytic tests

A typical catalytic experiment using stearic acid (1.0 g), limonene (100 ml), and PdNi/HZSM-5 catalyst (0.2 g, using the *co*-impregnation method) was conducted in a batch autoclave reactor (Parr Instrument, 300 ml). The reactor was firstly flushed with N₂ at ambient temperature for three times, and was then heated up to 280 °C while N₂ (at 0.8 MPa pressure) was purged through, and the reaction started at a stirring speed of 600 rpm. The liquid products were in situ sampled during the catalytic runs.

Conversion = (weight of converted reactant/weight of the starting reactant) × 100%.

Yield of liquid products (C %) = (C atoms in liquid products/C atoms in the starting reactant) × 100%.

Selectivity (C %) = (C atoms of each product/C atoms in all the liquid products) × 100%.

Liquid products were analyzed on a gas chromatograph (GC) equipped with a mass spectrometer (GCxGC-MS, Shimadzu QP-2010 Ultra) with a Rtx-5Sil MS capillary column (30 m×0.25 mm×0.25 μm). Analysis for gaseous products was performed on a GC (Techcomp 7900) equipped with thermal conductivity detector (TCD) and columns (TDX-01: 30 cm×3 mm, TDX-01: 2 m×3 mm), as well as flame ionization detector (FID) and a HP-PLOT Q capillary column (50 m×0.53 mm×25 μm).

Catalyst characterization

The specific surface area and pore size distribution were performed by N₂ adsorption at 77 K on a BELSORP-MAX instrument after activating the samples under vacuum at 573 K for 10 h. Inductively coupled plasma atomic emission spectroscopy (ICP–AES) was performed on a Thermo IRIS Intrepid II XSP emission spectrometer after dissolving the catalyst in the HF solution. Powder X-ray diffraction (XRD) patterns were measured on Rigaku Ultima IV X-ray diffractometer utilizing Cu-Kα radiation (λ = 1.5405 Å) operated at 35 kV and 25 mA. Scanning electron microscopy (SEM) equipped with energy dispersive X-ray (EDX) analysis unit (Oxford, UK) was operated on a Hitachi S-4800 microscope to illuminate crystal morphology and size. Transmission electron microscopy (TEM) images were performed on a FEI Tecnai G² F30 microscope working at 300 kV. The IR spectra of adsorbed pyridine (IR-Py) were recorded with a Bruker VERTEX 70 spectrometer equipped with an in-situ IR cell. The samples were activated in vacuum at 673 K for 1 h before equilibrated with pyridine at 423 K, then evacuated at 423 K for 1 h.

Table S1. Dehydroaromatization of limonene with Pd based catalysts at 280 °C. ^a

Entry	Catalyst	Conv. (%)	Yield (%)				P (bar) ^b
			A	B	C	D	
1	Pd/C	100		19	79	16	
2	Pd/ASA	100	2	17	81	17	
3	Pd/SiO ₂	100	5	14	79	16	
4	Pd/Al ₂ O ₃	100	12	11	76	16	
5	Pd/HBeta	100	43		56	1	16
6	Pd/HY (9)	100	10	19	68		16
7	Pd/HY (30)	100	2	25	65		14
8	Pd/HZSM-5 (197)	100	2	11	67		18

^a Reaction condition: 10 mL limonene, 0.20 g 1 wt.% Pd catalysts, 80 mL *n*-dodecane, 0.8 MPa N₂, stirring at 650 rpm.

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

Table S2. Conversion of stearic acid in limonene with supported Pd-M catalysts.^a

Entry	Catalyst	Limonene Dehydrogenation				HDO of Stearic Acid			P ^c (bar)		
		Conv. (%)	Yield (C%) ^b				Conv. (%)	Yield (C%) ^b			
			A	B	C	D		C ₁₇		C ₁₈	Ester
1	Pd/HZSM-5	98	24	6	65	3	14	4		10	20
2	Pd-Ni/HZSM-5	98	12	11	72	3	100	84	8	8	26
3	Pd-Co/HZSM-5	100	20	2	71	4	4	2		2	24
4	Pd-Cu/HZSM-5	100	16		44	22	7			7	21
5	Pd-Fe/HZSM-5	80			28	47	21			21	20
7	Pd-Zn/HZSM-5	93			51	42	39			39	20
8	Pd-Ru/HZSM-5	100	23		73		53	46	5	2	30
9	Pd-Rh/HZSM-5	100	15	12	72		20	6		14	26
10	Pd-Au/HZSM-5	100	25	2	71		9	5		4	24

^a General conditions: 1.0 g stearic acid, 50 mL limonene, 0.20 g 5 wt.%Pd-10 wt.%M (Ni, Co, Cu, Fe, Zn, Ru, Rh, Au) catalysts, 280 °C, 0.8 MPa N₂, 2 h, stirring at 650 rpm.

^b A: Partial hydrogenation products, B: Full hydrogenation products, C: Dehydroaromatization products, D: Isomerization products. The residual products contain cyclic ring-opening and limonene condensation products.

^c This records the pressure for reactions lasting 2 h at working temperature.

Table S3. Liquid and gas phase product distributions on stearic acid conversion in limonene. ^a

Liquid Phase Product		Liquid Phase Product		Gas Phase Product	
(C %)		(C %)		(ppm)	
C ₄ H ₁₀	0.21	<i>p</i> -Cymene	63.3	H ₂	998032
C ₅ H ₁₂	0.05	C ₁₀ H ₁₄ (arene)	0.75	CH ₄	38534
C ₆ H ₁₄	0.06	limonene	4.53	C ₂ H ₄	2314
Cyclic C ₆ H ₁₂	0.05	C ₁₀ H ₁₆ (arene)	0.02	C ₂ H ₆	596
C ₇ H ₁₆	0.19	C ₁₂ H ₂₆	0.02	C ₃ H ₈	39712
Cyclic C ₇ H ₁₄	0.16	C ₁₅ H ₂₀ (arene)	0.28	<i>i</i> -C ₄ H ₁₀	422
Toluene	1.85	C ₁₇ H ₃₆	1.3	<i>n</i> -C ₄ H ₁₀	357
C ₈ H ₁₈	0.16	C ₁₈ H ₃₈	0.17	<i>i</i> -C ₅ H ₁₂	20
C ₉ H ₂₀	0.18	Limonene condensation products	1.34	<i>n</i> -C ₅ H ₁₂	20
C ₁₀ H ₂₂	0.13			CO	175942
C ₁₀ H ₁₈ (arene)	15.65			CO ₂	781
Menthane	9.51				

^a Conditions: 1.0 g stearic acid, 50 mL limonene, 0.2 g 5 wt.%Pd-10 wt.%Ni/HZSM-5, 280 °C, 0.8 MPa N₂, 2 h, stirring at 650 rpm.

Table S4. Physicochemical and acidic properties of parent and metal supported HZSM-5 catalysts.

Catalyst	S _{BET}	Pore volume	BAS	LAS
	/m ² g ⁻¹ ^a	/cm ³ g ⁻¹ ^a	/mmol·g ⁻¹ ^b	/mmol·g ⁻¹ ^b
HZSM-5	473	0.66	66	95
Pd/HZSM-5	446	0.64	105	61
Pd-Ni/HZSM-5	371	0.51	92	208

^a Determined by N₂ sorption.

^b Analyzed by IR spectra of adsorbed pyridine.

Table S5. Fatty acid composition in the used palm oil.^a

Palm Oil	C _{13:0} ^a	C _{14:0}	C _{15:0}	C _{16:1}	C _{16:0}	C _{17:1}	C _{17:0}	C _{18:1}	C _{18:2}	C _{18:0}	C _{20:1}	C _{20:0}	C _{22:0}	C _{24:0}
	0.17	0.88	0.03	0.21	35.96	0.02	0.06	28.76	21.14	12.23	0.14	0.29	0.04	0.05

^a The composition is analyzed by transesterification with methanol. The nomenclature shows the number of carbon atoms and the number of C=C double bonds.

Table S6. Liquid and gas phase product distributions on palm oil conversion in limonene.

Liquid Phase Product (C %)		Liquid Phase Product (C %)		Gas Phase Product (C %)	
C ₄ H ₁₀ (<i>i-, n-A</i>) ^a	0.24	<i>p</i> -Cymene (Are.)	70.15	H ₂	82.35
C ₆ H ₁₄ (<i>i-, n-A</i>)	0.06	C ₁₀ H ₁₆ (<i>c-O</i>)	0.78	CH ₄	2.41
C ₆ H ₁₂ (<i>c-A</i>) ^b	0.02	C ₁₅ H ₂₀ (<i>d-Are.</i>) ^f	0.03	C ₂ H ₄	0.11
C ₇ H ₁₆ (<i>i-, n-A</i>)	0.14	C ₁₅ H ₃₂ (<i>i-, n-A</i>)	1.12	C ₂ H ₆	0.21
C ₆ H ₁₂ O (K) ^c	0.38	C ₁₆ H ₃₄ (<i>i-, n-A</i>)	0.19	C ₃ H ₈	1.74
Toluene (Are.) ^d	0.28	C ₁₇ H ₃₆ (<i>i-, n-A</i>)	1.47	<i>i</i> -C ₄ H ₁₀	0.06
C ₈ H ₁₈ (<i>i-, n-A</i>)	0.13	C ₁₈ H ₃₈ (<i>i-, n-A</i>)	0.24	<i>n</i> -C ₄ H ₁₀	0.003
C ₉ H ₂₀ (<i>i-, n-A</i>)	0.18	Limonene		<i>i</i> -C ₅ H ₁₂	0.090
C ₁₀ H ₂₂ (<i>i-, n-A</i>)	0.39	condensation	2.76	<i>n</i> -C ₅ H ₁₂	0.001
C ₁₀ H ₁₈ (<i>c-O</i>) ^e	8.62	products (<i>c-O</i>)		CO	12.87
Menthane (<i>c-A</i>)	12.82			CO ₂	0.16

Conditions: 1.0 g palm oil, 50 mL limonene, 0.2 g Pd-Ni/HZSM-5, 280 °C, 0.8 MPa N₂, 2 h, stirring at 650 rpm.

^a *i-A*, isomerized alkanes; *n-A*, normal alkanes; ^b *c-A*, cyclic alkanes; ^c K, ketone; ^d Are., arene; ^e *c-O*, cyclic olefins; ^f *d-Are.*, arene derivatives.

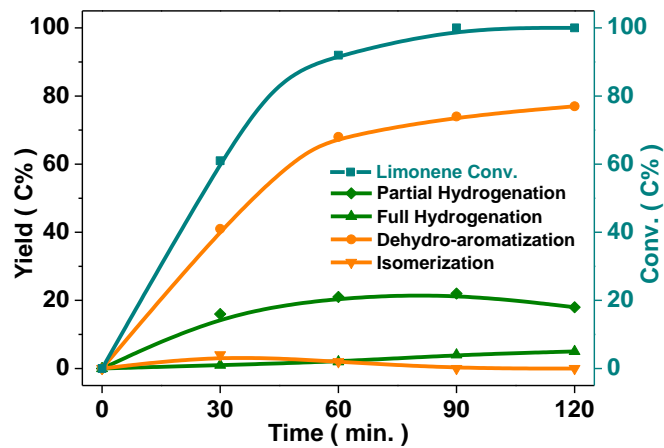


Figure S1. Kinetic curve of limonene conversion with Pd/HZSM-5 catalyst as a function of time. General conditions: 10 mL limonene, 0.020 g 1 wt.% Pd/HZSM-5, 80 mL *n*-dodecane, 280 °C, 0.8 MPa N₂, stirring at 650 rpm.

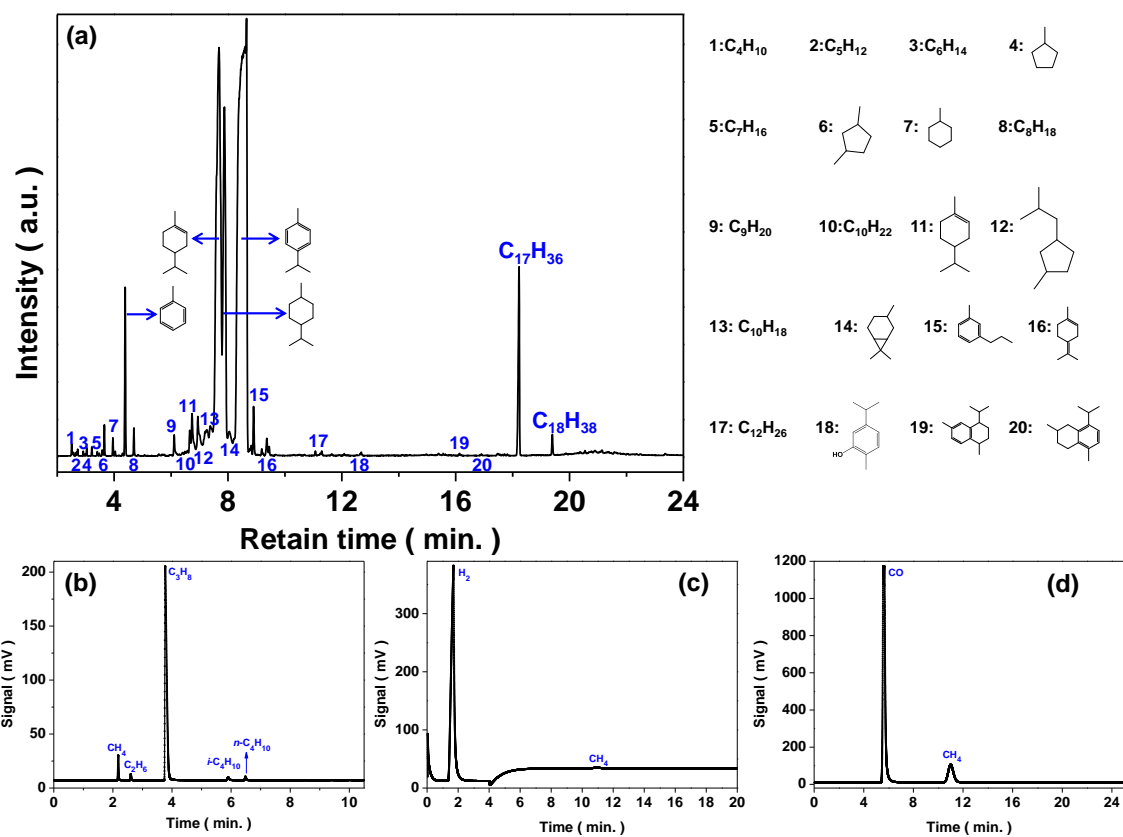


Figure S2. GC spectra of (a) liquid phase and (b-d) gas phase products for catalytic conversion of stearic acid in limonene. General conditions: 1.0 g stearic acid, 50 mL limonene, 0.2 g Pd-Ni/HZSM-5, 280 °C, 0.8 MPa N_2 , 2 h, stirring at 650 rpm.

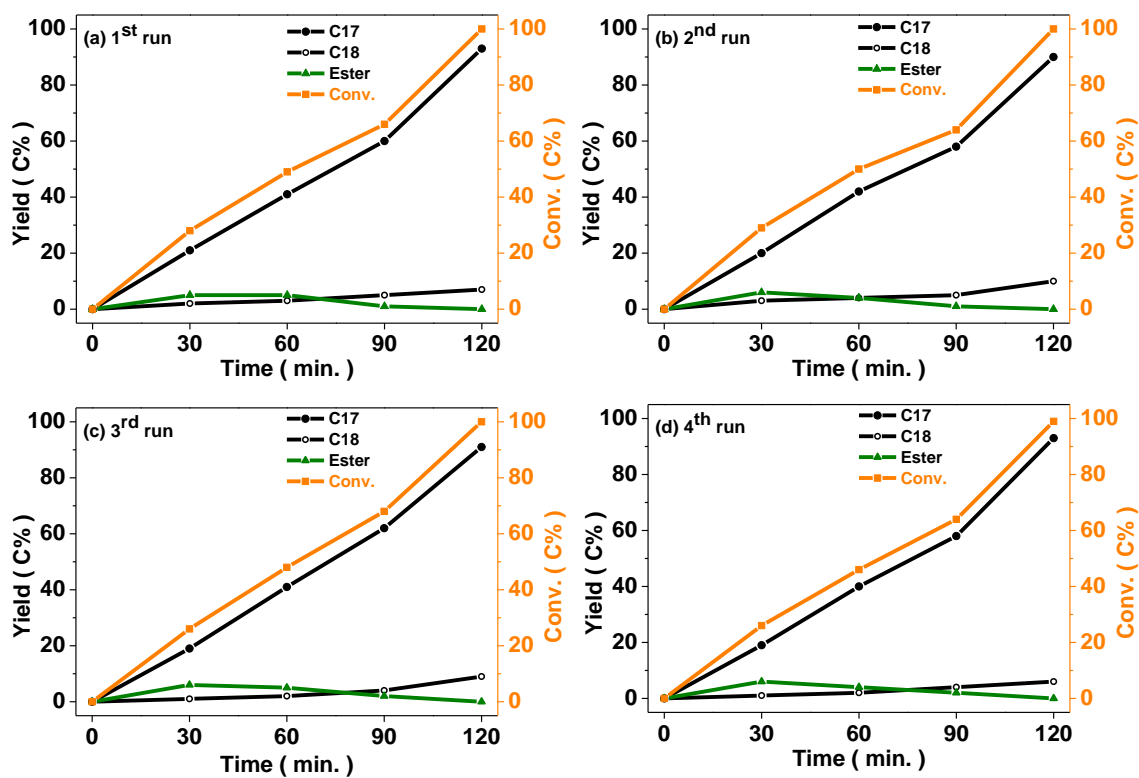


Figure S3. Recycling tests of Pd-Ni/HZSM-5 catalyst for stearic acid conversion in limonene. General conditions: 1.0 g stearic acid, 50 mL limonene, 0.2 g Pd-Ni/HZSM-5, 280 °C, 0.8 MPa N₂, 2 h, stirring at 650 rpm.

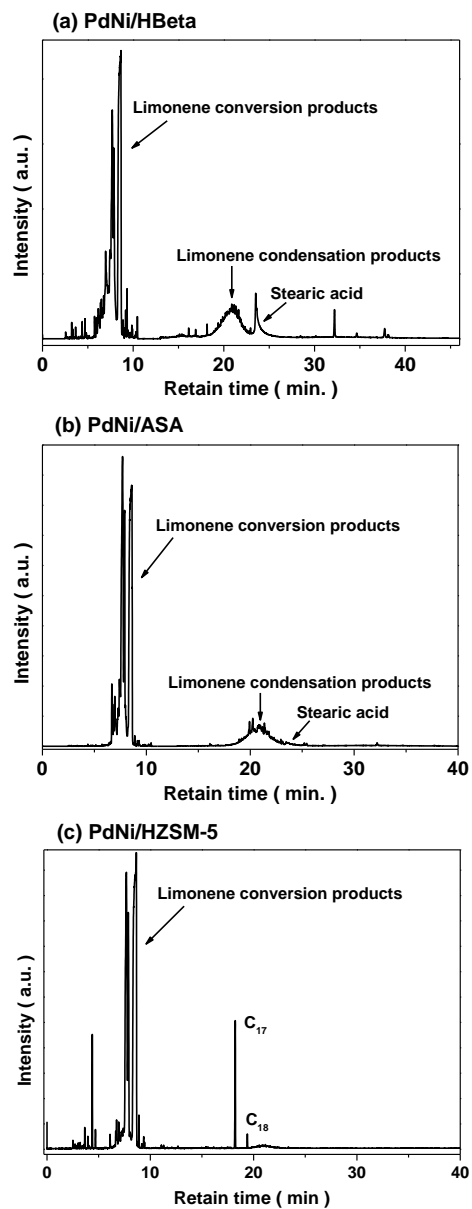
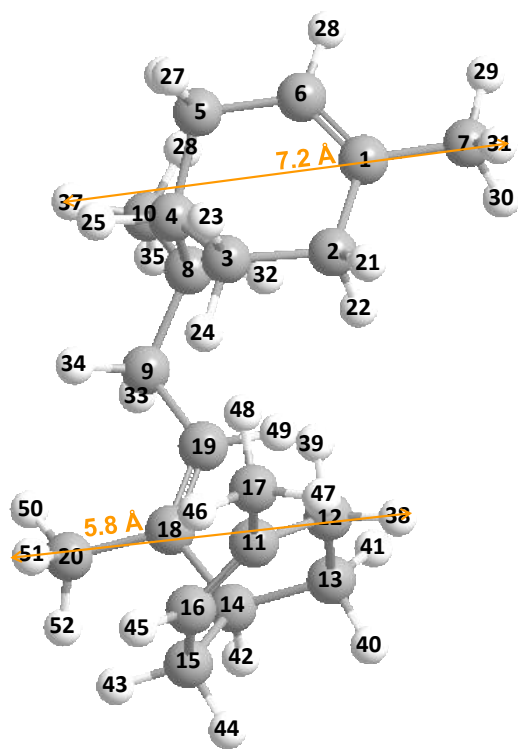


Figure S4. GC spectra of liquid phase products for conversion of stearic acid in limonene with (a) PdNi/HBeta, (b) PdNi/ASA, (c) PdNi/HZSM-5.



(1)

Figure S5. The 3D structure for the representative product from limonene condensation

The width diameter of this molecular can be estimated by the distances between H (38) and H (51) as well as H (31) and H (37) according to the coordinate of each atom.

$$D = \sqrt{(x_1 - x_2)^2 + (y_1 - y_2)^2 + (z_1 - z_2)^2} ,$$

D refers to diameter of molecular (1).

Space coordinate in ChemOffice 3D: H (38) (-1.3071, -0.8018, 2.0007)

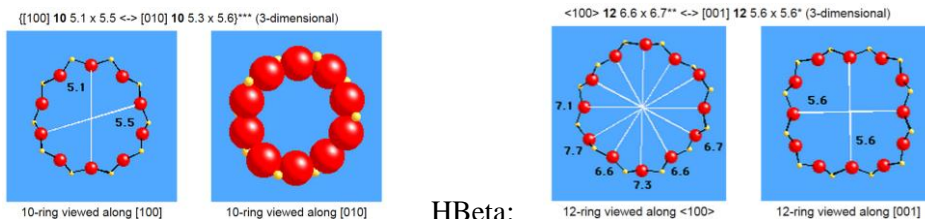
H (51) (-5.6030, -3.4265, -0.8037)

Therefore, $D = 5.8 \text{ \AA}$.

With the similar method, we can calculate that:

H(31) – H(37) 7.2 \AA

As for zeolite structures of HZSM-5 and HBeta, pore sizes in channels of **HZSM-5** were around $5.1\text{-}5.5 \text{ \AA}$ viewed along [100] and [010], while that of **HBeta** was $6.6\text{-}7.7 \text{ \AA}$ viewed along [100].



Therefore, it is concluded that, d (pore size of HZSM-5) $< d$ (limonene condensation product) $< d$ (pore size of HBeta).

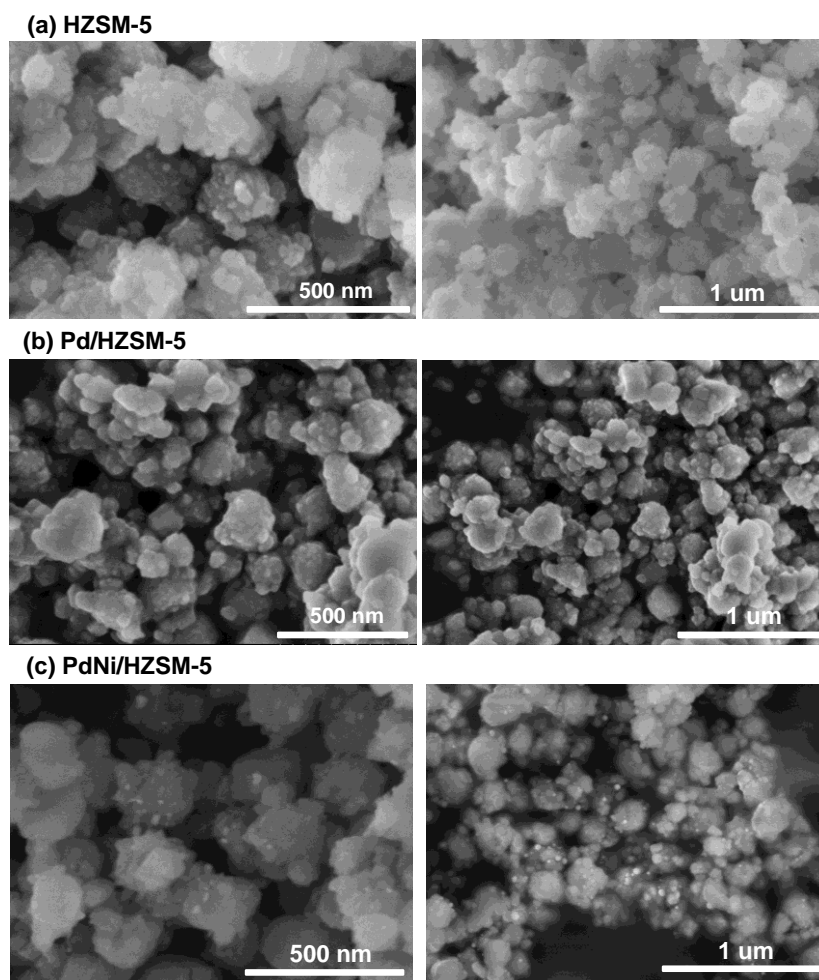


Figure S6. SEM images of (a) HZSM-5, (b) Pd/HZSM-5, (c) PdNi/HZSM-5 catalysts.

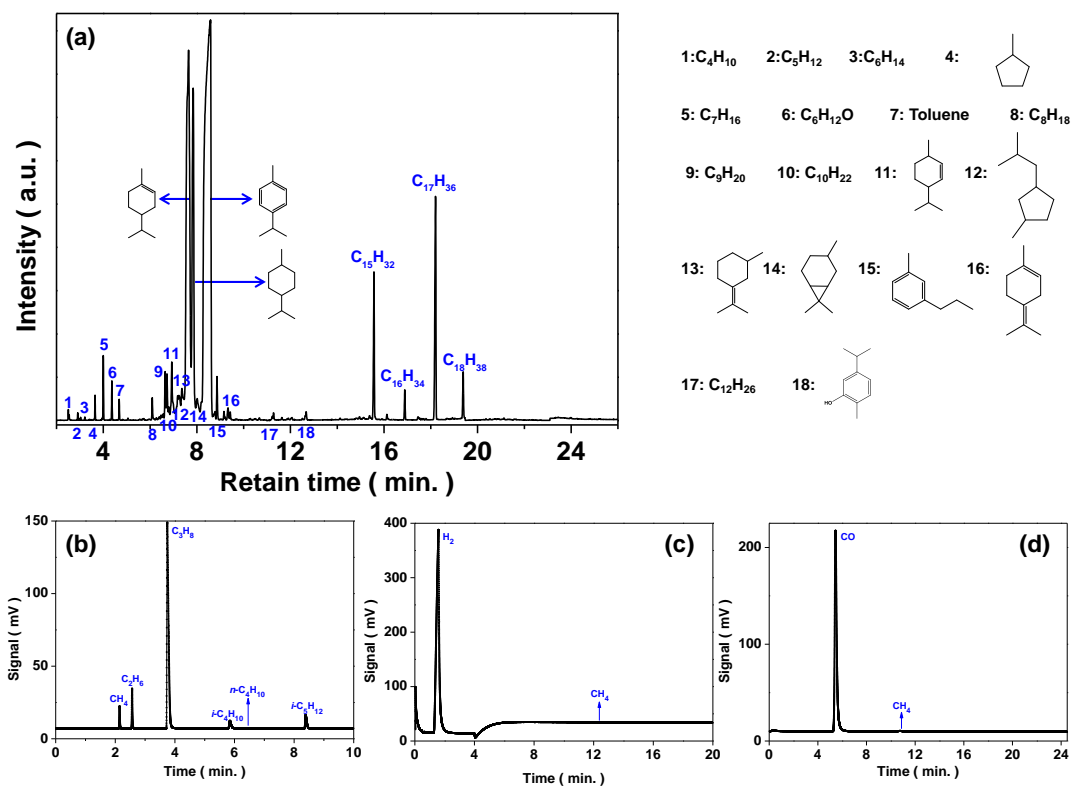


Figure S7. GC spectra of (a) liquid phase and (b) gas phase products for catalytic conversion of palm oil in limonene. Conditions: 1.0 g palm oil, 50 mL limonene, 0.20 g Pd-Ni/HZSM-5, 280 °C, 0.8 MPa N_2 , 2 h, stirring at 650 rpm.

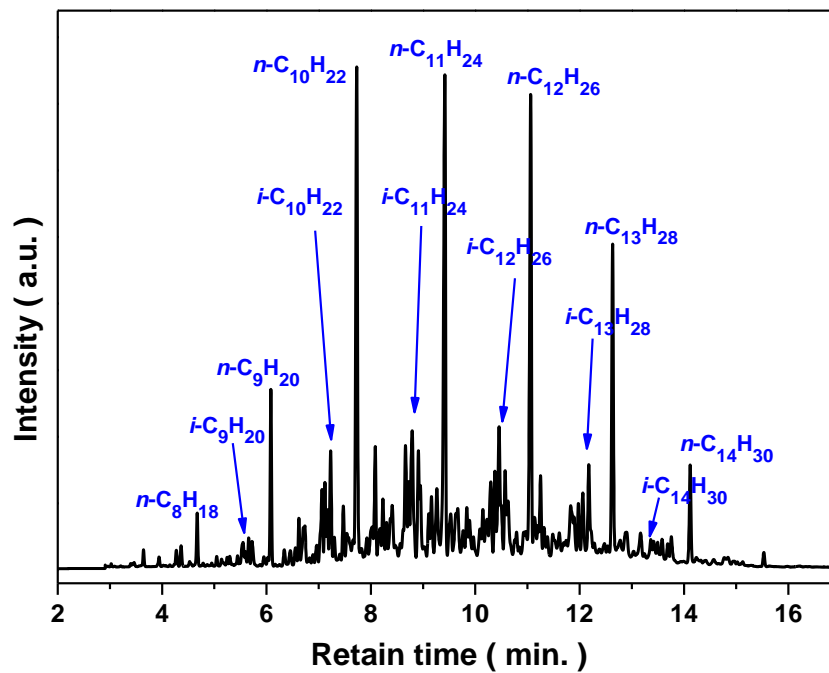


Figure S8. GC-MS spectrum of commercial 3# jet fuel (purchased from SINOPEC).

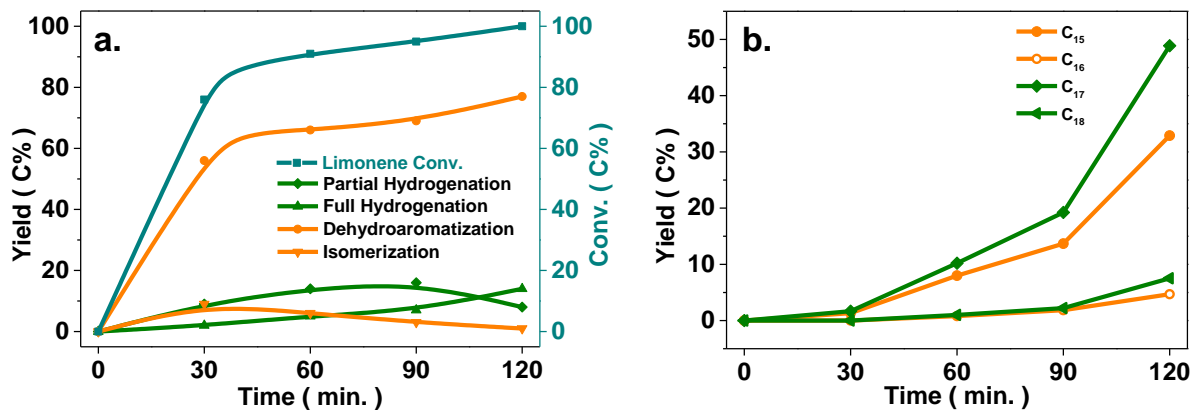


Figure S9. (a) Limonene conversion and (b) palm oil conversion for palm oil hydrodeoxygenation in limonene as a function of time. Conditions: 1.0 g palm oil, 50 mL limonene, 1.0 g 5%Pd-10%Ni/HZSM-5, 280 °C, 0.8 MPa N₂, 2 h, stirring at 650 rpm.