

Supporting information

**Integrated Production of Bio-Jet Fuel Containing Lignin-derived  
Arenes via Lipid Deoxygenation**

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## Experimental Section

**Chemicals.** The chemicals were received from commercial supplier and directly used without any pretreatments. Stearic acid (Sinopec Co., Ltd., AR), ethylbenzene (Aladdin, AR), nano-alumina (Micxy reagent), H $\beta$  (Nankai University, Si/Al ratio: 50), HUSY (Nankai University, Si/Al ratio: 50), HZSM-5 (Nankai University, Si/Al ratio: 100), PtCl<sub>4</sub> (J&K), IrCl<sub>4</sub> (J&K), NH<sub>4</sub>ReCl<sub>4</sub> (Sinopec Co., Ltd., GR), SnCl<sub>4</sub>·6H<sub>2</sub>O (Sinopec Co., Ltd., AR), Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Sinopec Co., Ltd., AR), Ru/C (Shaanxi Kaida Co., Ltd, 5wt%), Air, H<sub>2</sub>, and N<sub>2</sub> gases (99.999 vol.%) were supplied by Shanghai Pujiang Specialty Gases Co., Ltd.

**Preparation of bimetallic Pt-M catalysts by incipient wetness impregnation.** A typical Pt-Ir/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was synthesized as follows. First an H<sub>2</sub>PtCl<sub>6</sub> solution and an H<sub>2</sub>IrCl<sub>6</sub> solution were prepared, and mixed them with  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, with continuous stirring at ambient temperature overnight. Afterwards, the as-formed catalysts were filtered, dried at 80 °C overnight, calcined in flowing air (flowing rate: 100 mL/min) at 350 °C for 4 h, and finally reduced in flowing H<sub>2</sub> (flowing rate: 100 mL/min) at 350 °C for 240 min.

**Catalytic Measurements.** A typical experiment was carried out as follows: stearic acid (0.5 g), ethyl-cyclohexane (25 mL), and PtIr/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst (0.3 g) were charged into a batch autoclave (High temperature and pressure reactor, 50 mL). The reactor was first flushed with N<sub>2</sub> at ambient temperature three times, and was then heated up to 400 °C at a stirring speed of 600 rpm. Conversion = (weight of converted reactant/weight of the starting reactant)  $\times$  100%. Yield of liquid products (C %) = (C atoms in liquid products/C atoms in the starting reactant)  $\times$  100%. Selectivity (C %) = (C atoms of each product/C atoms in all the liquid products)  $\times$  100%.

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

### **Catalyst Characterization.**

The specific surface area and pore size distribution were performed by N<sub>2</sub> adsorption at 77 K on a BELSORP-MAX instrument after activating the samples under vacuum at 573 K for 10 h.

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 60 min before equilibration with pyridine at 423 K; then they were evacuated at 423 K for 60 min.

Powder X-ray diffraction (XRD) patterns were measured on Rigaku Ultima IV X-ray diffractometer utilizing Cu K $\alpha$  radiation ( $\lambda = 1.5405 \text{ \AA}$ ) operated at 35 kV and 25 mA.

Transmission electron microscopy (TEM) images were performed on a FEI Tecnai G<sup>2</sup>F30 microscope working at 300 kV.

The IR spectra of adsorbed CO were measured on a Nicolet Fourier transform infrared spectrometer (NEXUS 670). The samples were activated in H<sub>2</sub> at 673 K for 1 h, and then H<sub>2</sub> was removed by Vacuum pump. After the temperature was cooled to 313 K, the samples were exposed to CO until adsorption saturation. Subsequently the samples were evacuated at 313 K to remove the physically adsorbed CO. Afterwards, the IR spectra of adsorbed CO were recorded until no further changes in the spectra were observed.

### Computational methods.

DFT calculations were performed using Vienna *ab initio* Simulation Package (VASP). The projector augmented wave (PAW) method combined with cutoff energy of 400 eV were adopted to describe the core and valence electrons. The exchange-correlation effects were described within the generalized gradient approximation with the use of Perdew-burke-Ernzerhof (PBE) functional.

The Pt(111) and Ir(111) were modeled by 4-layer slabs separated by 10 Å vacuum space, with the top two layers relaxed. The  $p(2 \times 2)$  unit cells were chosen, which means a coverage of 0.25 monolayer for a single adsorbate on the surface. The Brillouin zone of the systems were sampled with a  $3 \times 3 \times 1$  Monkhorst-Pack grid.

In this paper, the adsorption energy  $E_{ad}$  is defined as:

$$E_{ad} = E_{adsorbate/slab} - E_{slab} - E_{adsorbate}$$

Where  $E_{adsorbate/slab}$  is the total energy of interacting system of both slab and adsorbate after surface optimization.  $E_{slab}$  is the energy of the 4-layer slab with 10 Å vacuum space along z direction and  $E_{adsorbate}$  is the energy of adsorbate in vacuum.

**Table S1.** Conversion of ethyl-cyclohexane (ECH) and stearic acid (SA) with Pt-Ir/ $\gamma$ - $\text{Al}_2\text{O}_3$  catalyst in different temperatures or times.

Entry	T ( $^{\circ}\text{C}$ )	Time (h)	SA Amount(g)	ECH Conv.(%)	SA Conv.(%)
1	350	0	0	12	/
2	350	0	0.5	0.2	75
3	400	0	0	16	/
4	400	0	0.5	18	100
5	400	1	0	32	/
6	400	1	0.5	31	100
7	400	2	0	32	/
8	400	2	0.5	47	100

Reaction condition: 0.3 g Pt-Ir/ $\gamma$ - $\text{Al}_2\text{O}_3$ , 25 mL ethyl-cyclohexane, 0.1 MPa  $\text{N}_2$ , stirring at 600 rpm.

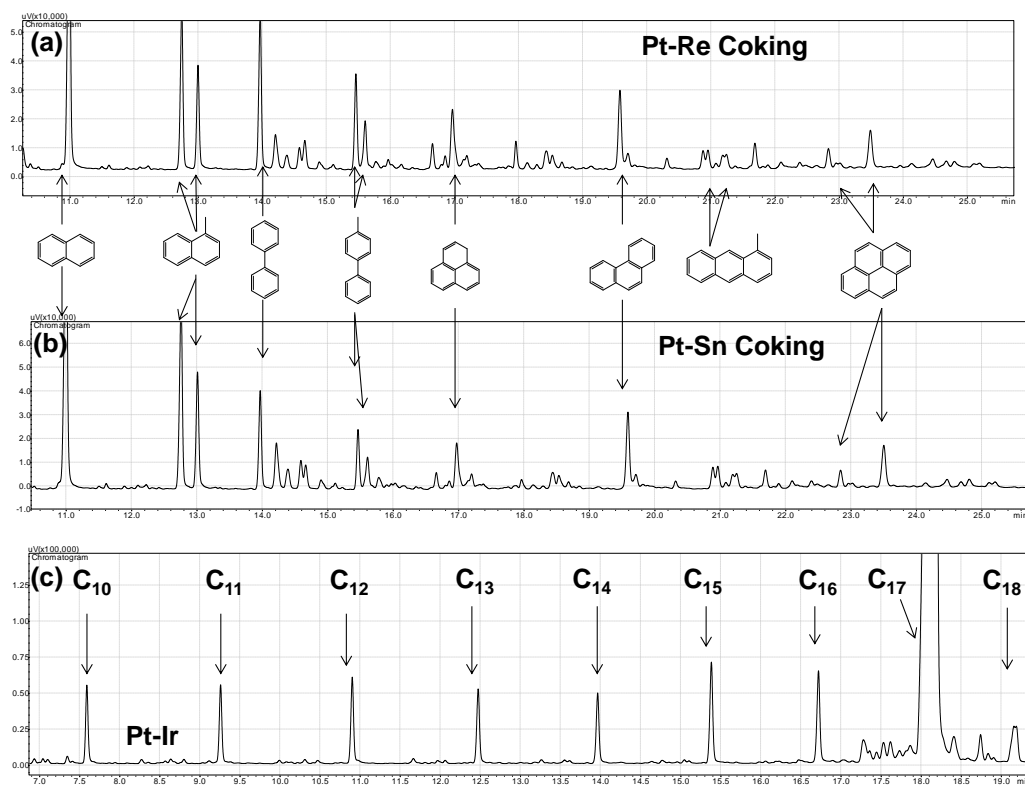
**Table S2.** The calculated acid concentrations of different supported Pt-Ir catalyst as calculated by IR spectra of adsorbed pyridine.

Entry	Catalyst	Acid <i>conc.</i> (mmol·g <sup>-1</sup> )	
		BAS	LAS
1	Pt-Ir/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	0	0.513
2	Pt-Ir/HZSM-5 (100)	0.044	0.365
3	Pt-Ir/H $\beta$ (50)	0.113	0.664
4	Pt-Ir/HUSY (50)	0.128	0.391

**Table S3.** Conversion of ethyl-cyclohexane (ECH) with 1.5%Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and 2.0%Ir/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst in N<sub>2</sub> and 10%CO (in N<sub>2</sub>) atmosphere.

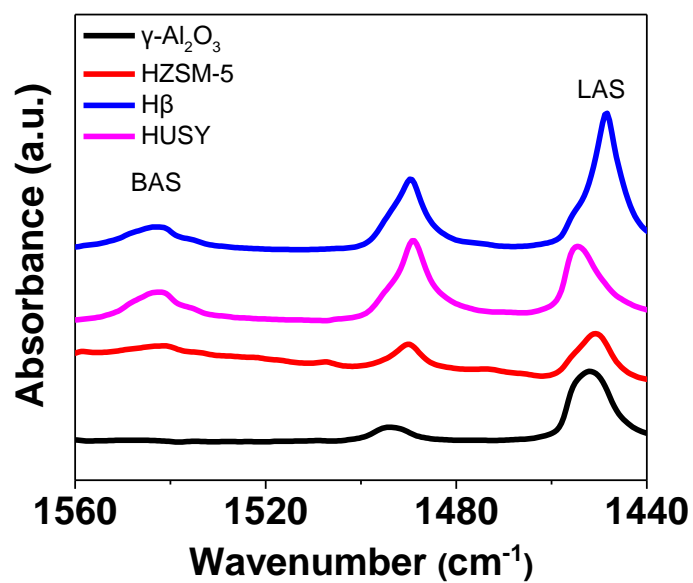
Entry	Catalyst	Gas atmosphere	ECH Conv. (%)	Arene yields (%)	Light alkane yields (%)
1	1.5%Pt	N <sub>2</sub>	26	10	16
2	1.5%Pt	10%CO in N <sub>2</sub>	15	9	6
3	2.0%Ir	N <sub>2</sub>	25	19	6
4	2.0%Ir	10%CO in N <sub>2</sub>	8	6	2

Reaction condition: 0.3 g catalyst, 25 mL ethyl-cyclohexane, N<sub>2</sub> or 10% CO in N<sub>2</sub> (0.1 MPa), stirring at 600 rpm.

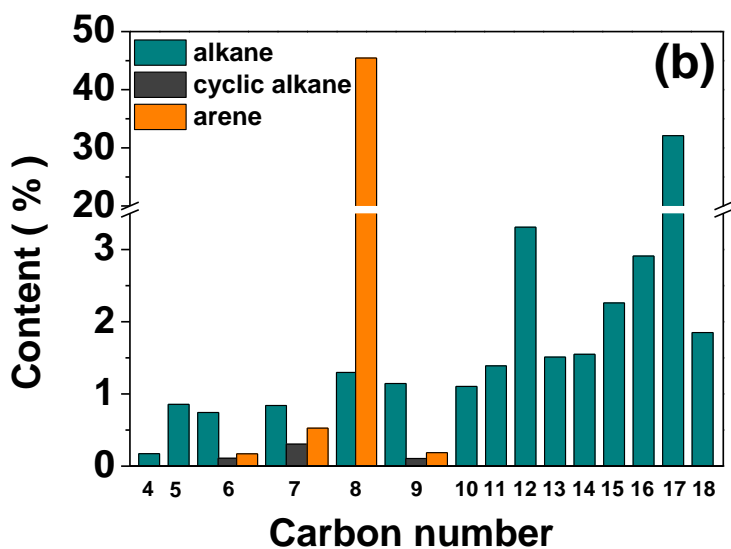
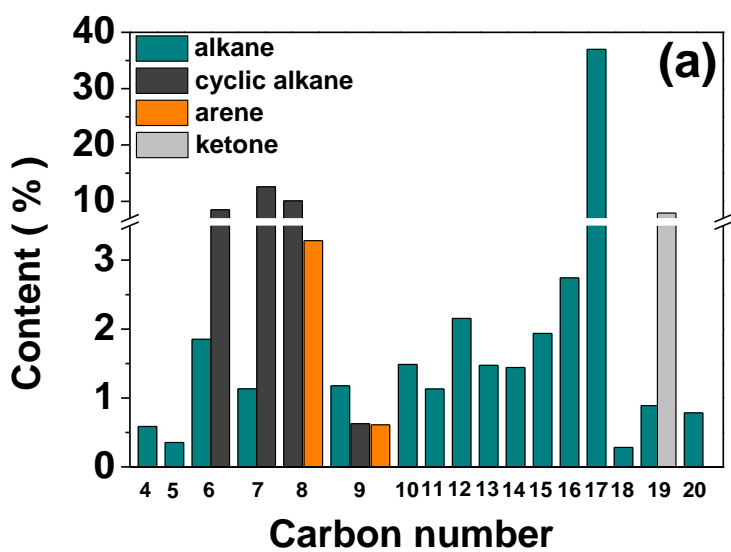


**Figure S1.** The GC-MS diagram with (a) Pt-Re/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, (b) Pt-Sn/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, (c) Pt-Ir/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. Reaction condition: 0.5 g stearic acid, 25 mL ethyl-cyclohexane, 0.3 g catalyst, 400 °C, 0.1 MPa N<sub>2</sub>, 2 h, stirring at 600 rpm.

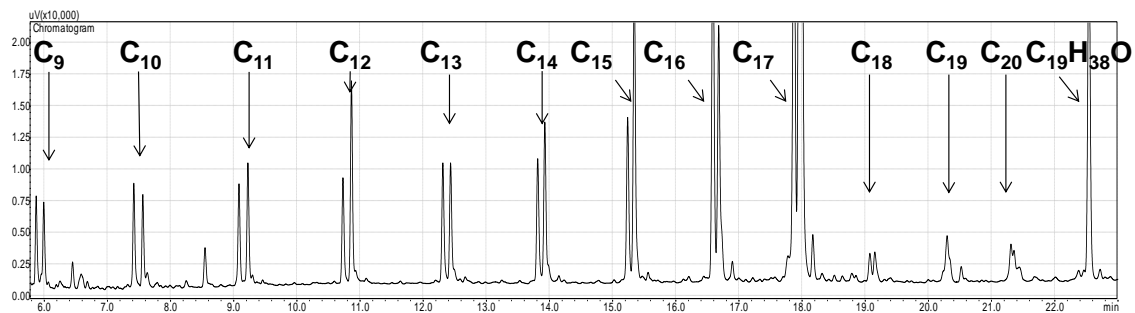
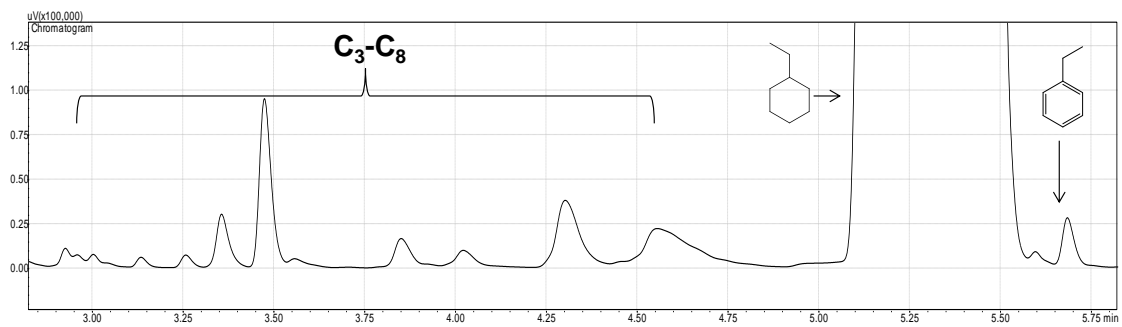




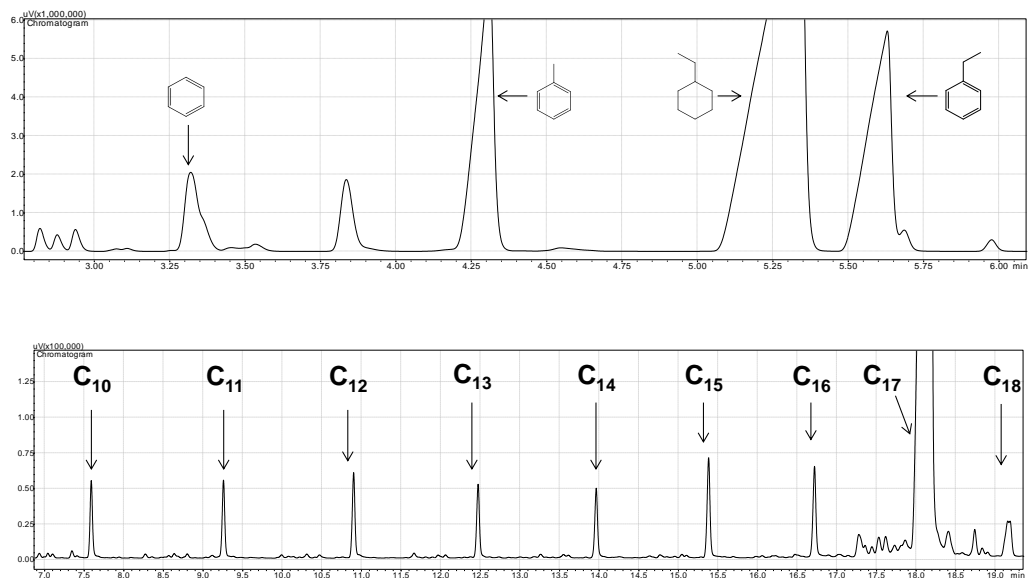
**Figure S2.** IR spectra of adsorbed pyridine on Pt-Ir/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, Pt-Ir/HZSM-5, Pt-Ir/H $\beta$ , and Pt-Ir/HUSY catalysts.



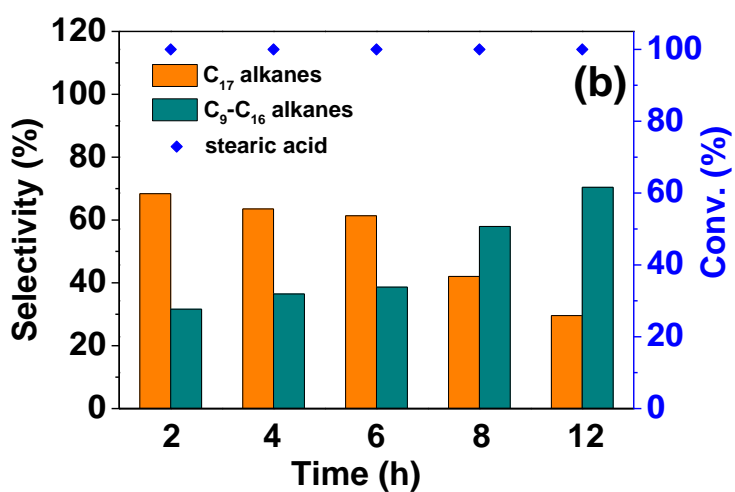
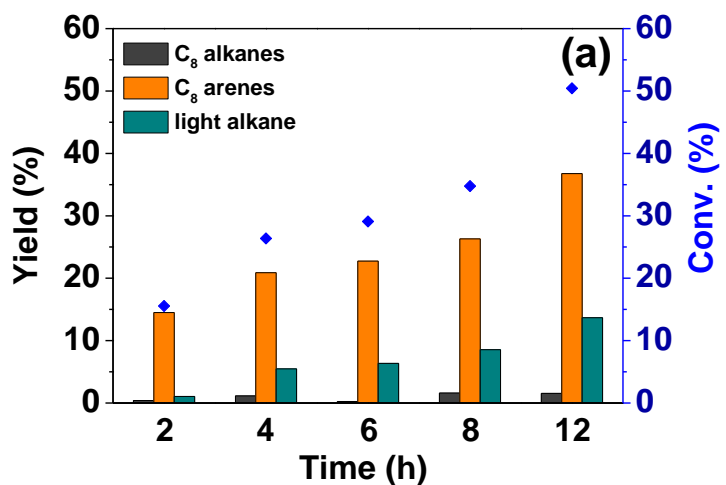
**Figure S3.** Product distribution (a) without catalyst, (b) 0.3g Pt-Ir/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst from co-conversion of stearic acid and ethyl-cyclohexane. Reaction condition: 25 mL ethyl-cyclohexane, 0.5 g stearic acid, 400 °C, 0.1 MPa N<sub>2</sub>, 2 h, stirring at 600 rpm.



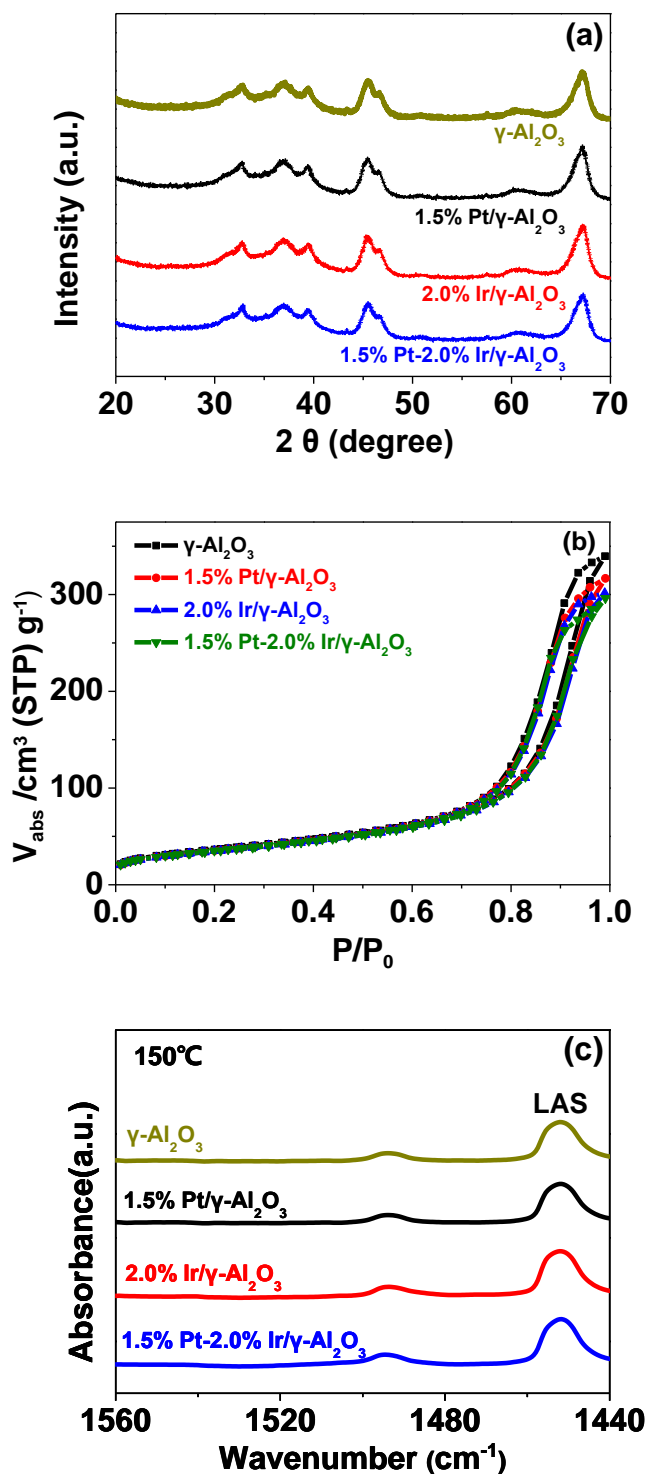
**Figure S4.** GC diagram of product with conversion of ethyl-cyclohexane and stearic acid without catalyst. Reaction condition: 25 mL ethyl-cyclohexane, 0.5 g stearic acid, 400 °C, 0.1 MPa  $N_2$ , 2 h, stirring at 600 rpm.



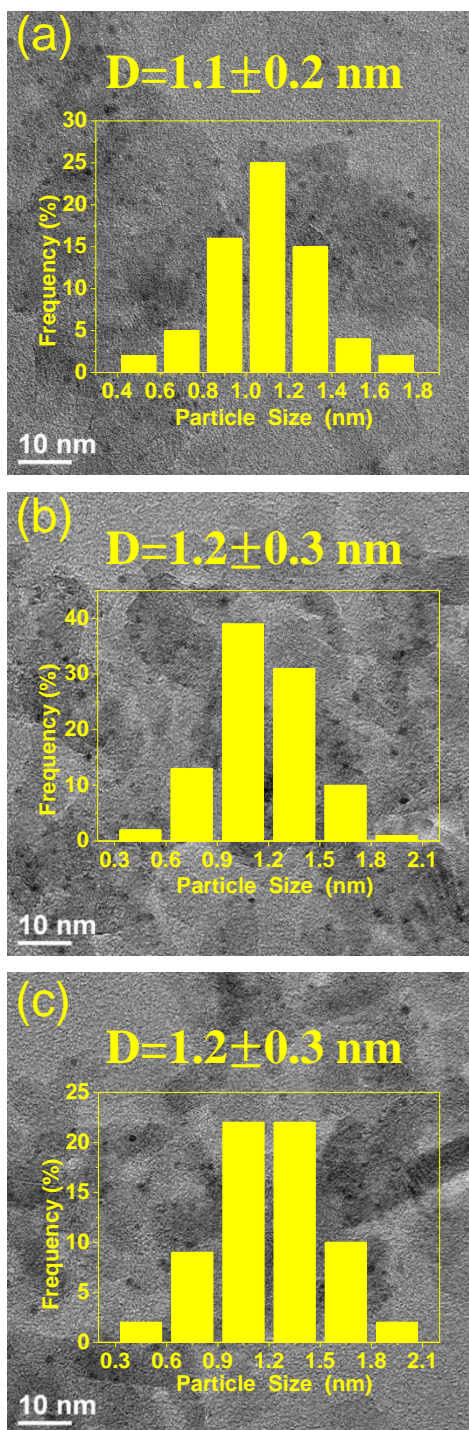
**Figure S5.** GC diagram of product with conversion of ethyl-cyclohexane and stearic acid with 0.3g Pt-Ir/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst. Reaction condition: 25 mL ethyl-cyclohexane, 0.5 g stearic acid, 400 °C, 0.1 MPa N<sub>2</sub>, 2 h, stirring at 600 rpm.



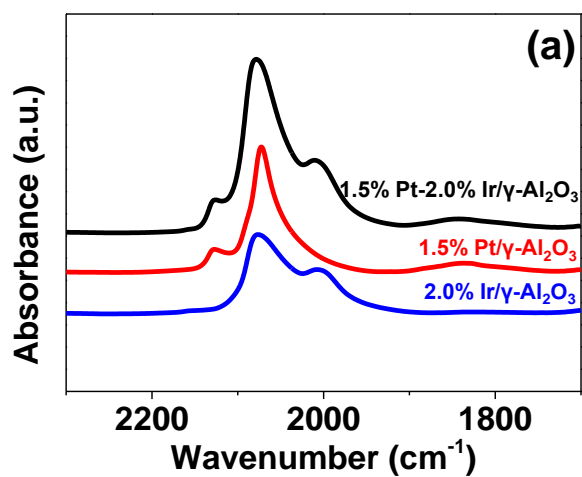
**Figure S6.** Conversion of ethyl-cyclohexane and stearic acid with Pt-Ir/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst at different reaction times. Reaction condition: 0.3 g 2.0% Ir-1.5%Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, 5 g stearic acid, 25 mL ethyl-cyclohexane, 0.1 MPa N<sub>2</sub>, 400 °C, stirring at 600 rpm.



**Figure S7.** (a) XRD patterns, (b)  $\text{N}_2$  adsorption and desorption isotherms, and (c) IR spectra of adsorbed pyridine on  $\gamma\text{-Al}_2\text{O}_3$ , 1.5%Pt/ $\gamma\text{-Al}_2\text{O}_3$ , 2.0%Ir/ $\gamma\text{-Al}_2\text{O}_3$  and 1.5%Pt-2.0%Ir/ $\gamma\text{-Al}_2\text{O}_3$ .

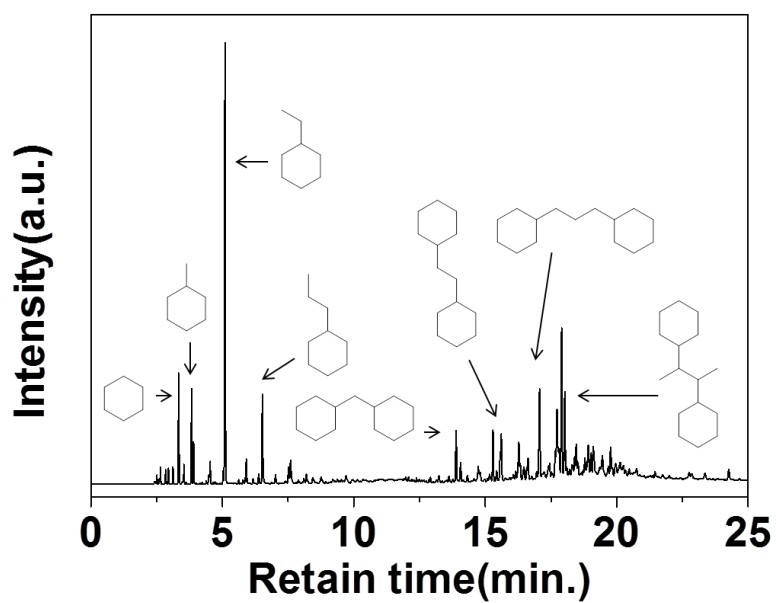


**Figure S8.** TEM images and particle size distribution of (a) 1.5%Pt-2.0%Ir/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, (b) 1.5%Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, (c) 2.0%Ir/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

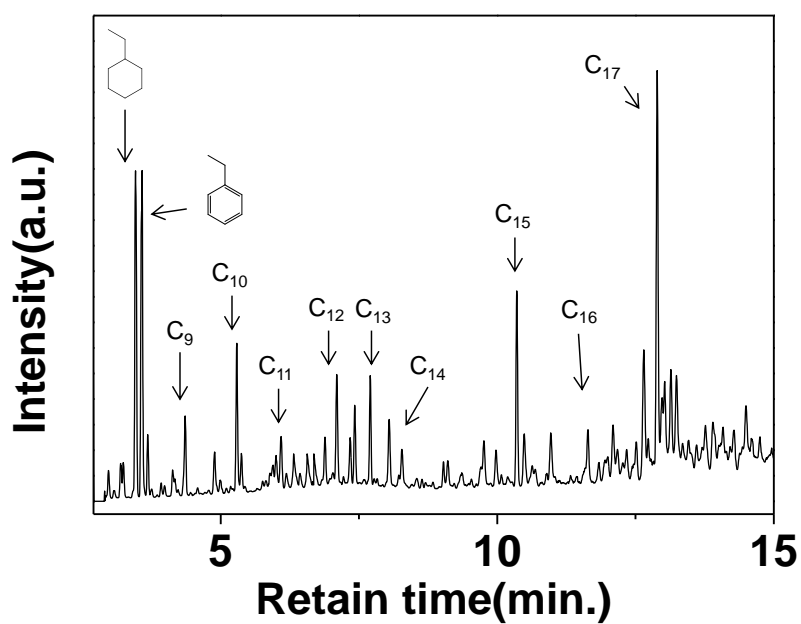


**Figure S9.** (a) IR spectra of CO adsorption at ambient temperatures on 1.5%Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, 2.0%Ir/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, and 1.5%Pt-2.0%Ir/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst.

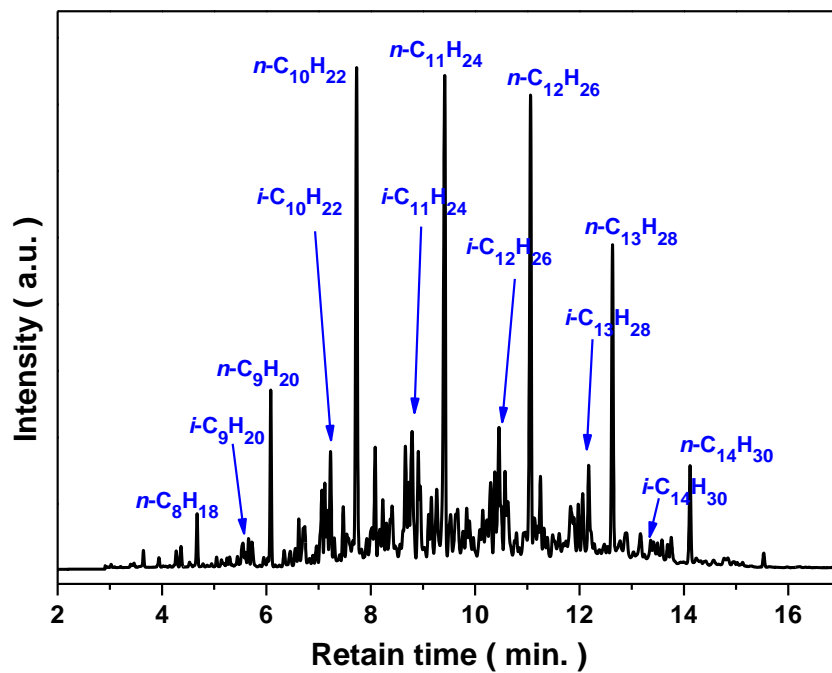




**Figure S10.** GC-MS spectrum of cycloalkanes mixture products derived lignin hydrogenation. Reaction conditions: 4 g lignin, 2 g Ni/ASA catalyst, dodecane solvent (80 mL), 300 °C, 5 MPa H<sub>2</sub>, 4 h, stirring at 600 rpm.



**Figure S11.** GC-MS spectrum of hydrocarbon mixture converted from palm oil and cycloalkanes derived lignin. Reaction condition: 15 mL cycloalkanes derived from lignin, 10 g palm oil, 0.3 g 1.5Pt-2.0Ir/Al<sub>2</sub>O<sub>3</sub>, 400 °C, 0.1 MPa N<sub>2</sub>, 12 h, stirring at 600 rpm.



**Figure S12.** GC-MS spectrum of commercial 3# jet fuel (purchased from SINOPEC).