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# Supplementary Information

# Hydrodecarboxylation of Fatty Acids into Liquid Hydrocarbons over Commercial Ru/C Catalyst under Mild Conditions

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### *Materials*

Stearic acid (98%) was purchased from Shanghai Macklin Biochemical Co., Ltd. Heptadecane (99%), octadecane (99%) and Ru/C (5% Ru loading) catalyst were all purchased from Sigma-Aldrich, USA. Acetone (99.5%) was acquired from Sinopharm Chemical Reagent Co., Ltd. Dodecane was purchased from Aladdin Industrial Corporation, Shanghai, China. All chemicals were used without further purification.

### *Experimental procedure*

The hydrodeoxygenation of stearic acid was carried out in a stainless steel autoclave of ~8 mL capacity. Per the procedure, the reactor was simultaneously charged with calculated amount of the feedstock (stearic acid), catalyst and solvent and then purged thrice with $H_2$ before been pressurized to required pressure with the same gas. Thereafter, the sealed reactor was placed onto a pre-heated electric heating device. At the end of the reaction time, the reactor was immediately submerged into a cold-water bath to quench the reaction. Subsequently, the gaseous products were collected into an air bag in readiness for analysis. Similarly, the liquid products were dissolved in acetone in preparation for quantitative analysis.

### *Characterizations*

X-ray diffraction patterns of both fresh and used Ru/C catalysts were recorded on a PANalytical Empyrean 200895 instrument using Ni-filtered Cu Kα radiation (λ=0.154 nm) at 30 mA and 40 kV. The catalysts were scanned over a 2θ range of 5-90°. The thermogravimetric analysis (TGA) of the both catalysts were performed in TAQ500 instrument. The samples were heated from 50 °C up to 200 °C in air to obtain the relevant TGA profiles. The $N_2$ adsorption-desorption isotherms (BET) were performed via a Micromeritics 3Flex adsorption instrument. Prior to the measurements, the sample was degassed under $N_2$ for 12 h at 160 °C. Temperature programmed desorption (TPD) of CO was measured on a FineSorb-3010 equipped with a thermal

conductivity detector (TCD), Zhejiang FINETEC INSTRUMENTS co., LTD. Prior to test, the catalysts were preheated at 120 °C under Ar atmosphere, and then exposed to 5% CO/95% $N_2$ for 30 mins or 1 min. The reactor was heated to 800 °C with the argon flow of 20 sccm.

### *Analysis method*

The analyses of the liquid products were carried out on gas chromatograph (Agilent 7890B) equipped with an Agilent CP-FFAP column and flame ionization detector (FID). Identification of the products was performed on gas chromatography-mass spectrometry (Agilent 5977A MSD) system by matching the retention times of the unknowns to those of reference standards. The quantitative analysis was performed using external calibration curves for each compound. For the gaseous products, the quantification was done on gas chromatograph (SHIMADZU GC-2018) equipped with an Agilent PLOT 5A molecular sieve filled column and thermal conductivity detector (TCD). The conversion of stearic acid, yield and selectivity of products were calculated using the following equations. The reported data are average values of three repeated measurements. The error bars represent the standard deviation from three replicate experiments.

$$\text{Conversion}(\%) = 1 - \frac{\text{moles of remaining reactant}}{\text{moles of reactant added}} \times 100\%$$

$$\text{Yield}(\%) = \frac{\text{moles of product}}{\text{moles of reactant added}} \times 100\%$$

$$\text{Selectivity}(\%) = \frac{\text{yield}}{\text{conversion}} \times 100\%$$

**Table S1**. The hydrodecarboxylation of stearic acid over different catalysts

| Catalysts | T/°C | t/h | $H_2$ pressure/MPa | Solvent | Conv./% | Yield of heptadecane/% | References |
|---|---|---|---|---|---|---|---|
| Ru/C | 160 | 9 | 3 | hexane | 100 | 90.1 | our work |
| Ru/C | 200 | 1.5 | 3 | hexane | 100 | 90.8 | our work |
| $Ru/La(OH)_3$ | 200 | 4 | 4 | hexane | 100 | 95.9 | [1] |
| $Ru/Mg(OH)_2$ | 200 | 4 | 4 | hexane | 91.5 | 78.5 | [1] |
| $Ru/SiO_2$ | 200 | 4 | 4 | hexane | 67.2 | 26.9 | [1] |
| $Ru/La(OH)_3$ | 200 | 4 | 4 | $H_2O$ | 93.4 | 83.6 | [1] |
| Ru/PON | 180 | 8 | 3 | $H_2O$ | 95.6 | 58.5 | [2] |
| Ru/C | 180 | 8 | 3 | $H_2O$ | 43.6 | 20.7 | [2] |
| $Ru/ZrO_2$ | 180 | 8 | 3 | $H_2O$ | 56.5 | 9.8 | [2] |
| Ru/HAP | 180 | 1 | 2 | $H_2O$ | 95.8 | 60 | [3] |
| Ni/HZSM-5 | 260 | 8 | 4 | dodecane | 100 | 9.2 | [4] |
| Ni/HBeta | 260 | 8 | 4 | dodecane | 100 | 14.8 | [4] |
| $NiO/Al_2O_3$ | 300 | 6 | 3 | dodecane | 31 | 26 | [5] |
| $Ni/Al_2O_3$ | 300 | 6 | 3 | dodecane | 99 | 96 | [5] |
| Pd/Al-SBA-15 (38) | 250 | 3 | 0.6 | dodecane | 72 | 59.7 | [6] |
| Pd/Al-SBA-15 (152) | 250 | 3 | 0.6 | dodecane | 48 | 43.2 | [6] |

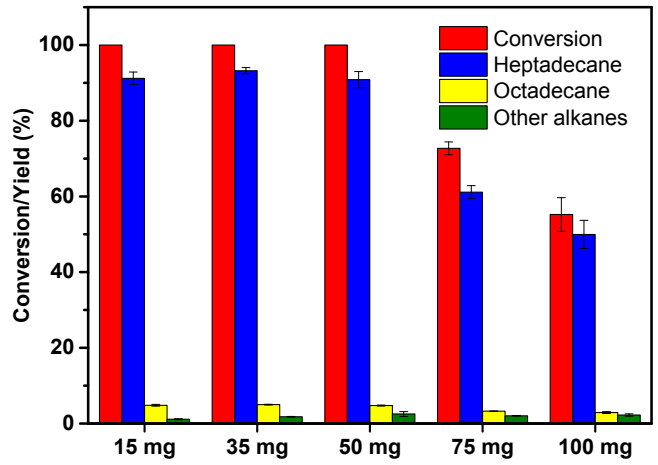
**Table S2**. Textural properties of fresh Ru/C (1st), Ru/C after 1st usage cycle (2nd) and Ru/C after 3rd usage cycle (4th) catalysts.

| Ru/C | Surface Area ($m^2/g$)[a] | Pore Volume ($cm^3/g$)[b] | Pore Size (nm)[c] |
|---|---|---|---|
| 1st | 934.3 | 0.53 | 6.9 |
| 2nd | 856.9 | 0.47 | 6.8 |
| 4th | 718.7 | 0.45 | 6.4 |

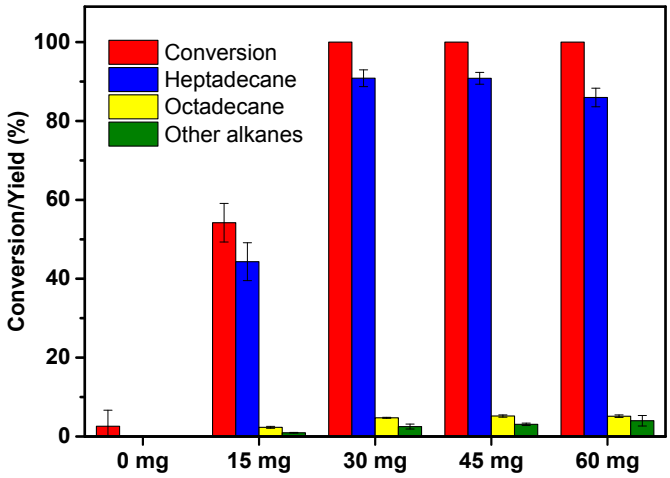
[a]Total surface area determined by Brunner–Emmet–Teller (BET) method.

[b]BJH adsorption cumulative volume of pores between 1.7000 nm and 300.0000 nm diameter.

[c]BJH adsorption average pore diameter(4V/A).




(a)




(b)

**Figure S1**. Conversion of stearic acid and yield of products with different (a) stearic and (b) catalyst addition. Reaction conditions: T = 200 °C, hexane = 3 mL, t = 90 min, stearic acid = 15 - 100 mg, Ru/C catalyst = 0 - 60 mg, 3 MPa $H_2$.

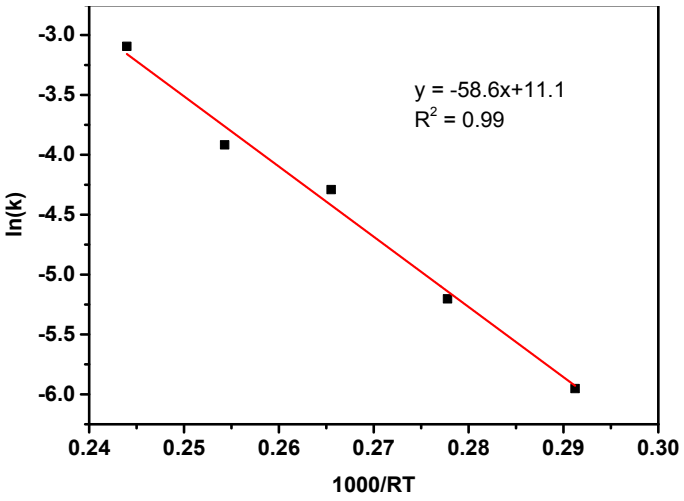



**Figure S2**. Arrhenius plot for data obtained from different temperature at 140, 160, 180, 200 and 220 °C.

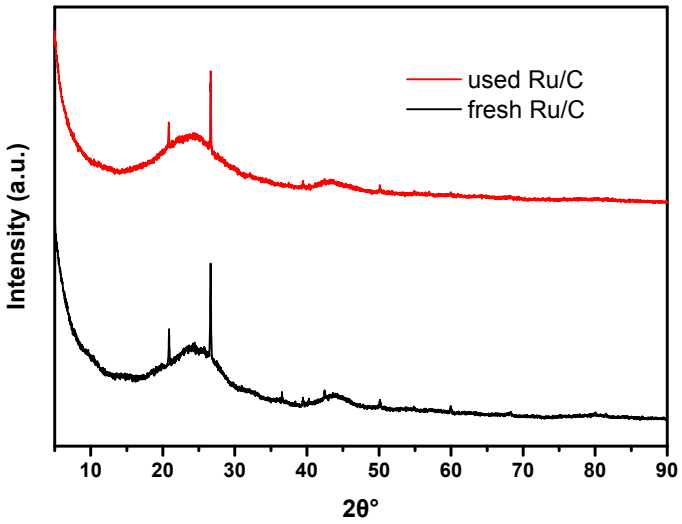
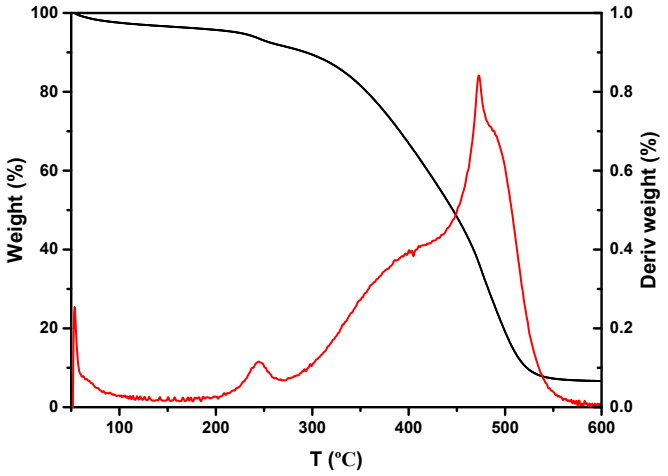
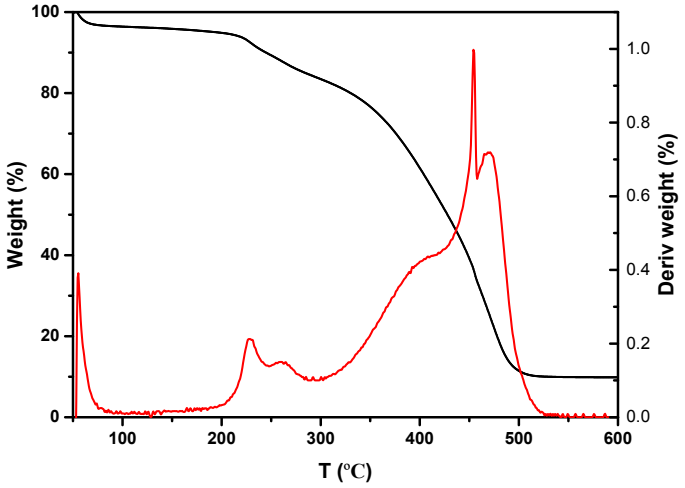



**Figure S3**. XRD patterns of fresh and used Ru/C catalysts

Based on the previous reports, the narrow diffraction peaks at around 20.9° and 26.5° in Figure S3 should be attributed to the graphitized carbon.[7,8]




(a)




(b)

**Figure S4**. TGA patterns of (a) fresh and (b) used Ru/C catalysts

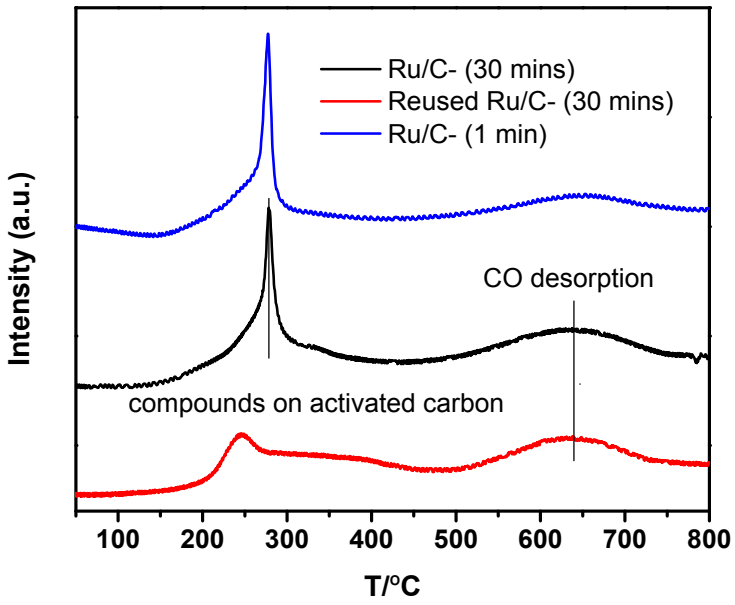



**Figure S5**. CO-TPD results of fresh and reused Ru/C catalysts; 30 mins and 1 min replace the adsorption time of gaseous CO.

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