

# Electronic Supplementary Material

## Efficient hydrothermal deoxygenation of methyl palmitate to diesel-like hydrocarbons on carbon encapsulated Ni-Sn intermetallic compounds with methanol as hydrogen donor

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### *Synthesis of supported catalysts*

#### **(1) Active carbon (AC) supported Ni and Ni<sub>3</sub>Sn IMC**

Ni/AC and Ni<sub>3</sub>Sn<sub>2</sub> IMC/AC catalysts were prepared via the wetness impregnation method. The nominal loading of Ni was 15 wt.% and nominal Ni/Sn molar ratio was 3/1.8. The active carbon (>200 mesh) was first dried at 120 °C for 24 h. Then, it was impregnated with the Ni(NO<sub>3</sub>)<sub>2</sub> ethanol solution for preparing Ni/AC, or the Ni(NO<sub>3</sub>)<sub>2</sub> and dibutyltin dilaurate (C<sub>32</sub>H<sub>64</sub>O<sub>4</sub>Sn) isopropyl alcohol solution for preparing Ni<sub>3</sub>Sn<sub>2</sub> IMC/AC-1, or the Ni(NO<sub>3</sub>)<sub>2</sub> and SnCl<sub>2</sub> ethanol solution for preparing Ni<sub>3</sub>Sn<sub>2</sub> IMC/AC-2. The resulting slurry were placed at room temperature for 48 h, and further dried at 120 °C for 12 h. Then, the precursors were reduced at 500 °C in a 100 mL/min H<sub>2</sub> flow for 2 h with a ramping rate of 10 °C/min. After that, the reduced samples were passivated in a 320 mL/min 0.5 vol.% O<sub>2</sub>/N<sub>2</sub> flow for 4 h.

#### **(2) Al<sub>2</sub>O<sub>3</sub> supported Ni and Ni<sub>3</sub>Sn IMC**

Ni/Al<sub>2</sub>O<sub>3</sub> and Ni<sub>3</sub>Sn<sub>2</sub> IMC/Al<sub>2</sub>O<sub>3</sub> precursors were synthesized via the co-precipitation method. The nominal loading of Ni was 20 wt.% and nominal Ni/Sn molar ratio was 3/1.8. Solution A is composed of metal salts (Ni(NO<sub>3</sub>)<sub>2</sub> and Al(NO<sub>3</sub>)<sub>3</sub> for Ni/Al<sub>2</sub>O<sub>3</sub>; Ni(NO<sub>3</sub>)<sub>2</sub>, SnCl<sub>2</sub> and Al(NO<sub>3</sub>)<sub>3</sub> for Ni<sub>3</sub>Sn<sub>2</sub> IMC/Al<sub>2</sub>O<sub>3</sub>) with a total cationic concentration of 1 mol/L. Solution B is the alkaline solution with the NaOH concentration of 2 mol/L and the Na<sub>2</sub>CO<sub>3</sub> concentration of 1 mol/L. The solution A and solution B were dropped slowly into the deionized water under vigorous stirring at 30 °C and a pH value of 10±0.05. The resulting precipitate was aged at 65 °C for 12 h. After washing and drying at 120 °C for 12 h, the resulting samples were calcined at 500 °C for 5 h, followed by the reduction at a certain temperature (500 °C for Ni/Al<sub>2</sub>O<sub>3</sub>; 550 °C for Ni<sub>3</sub>Sn<sub>2</sub> IMC/Al<sub>2</sub>O<sub>3</sub>) for 2 h in a 100 mL/min H<sub>2</sub> flow with a ramping rate of 10 °C/min. After that, the reduced samples were passivated in a 320 mL/min 0.5 vol.% O<sub>2</sub>/N<sub>2</sub> flow for 4 h.

**Equations**

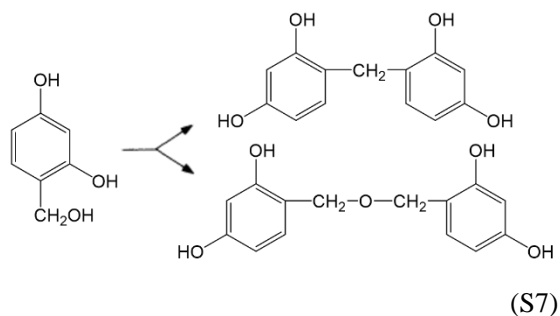
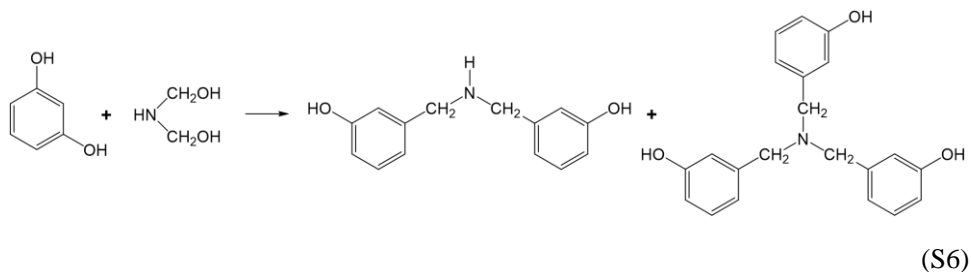
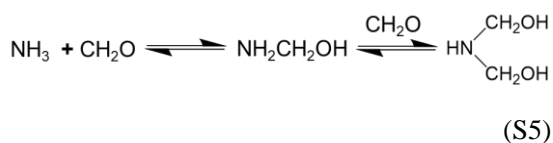
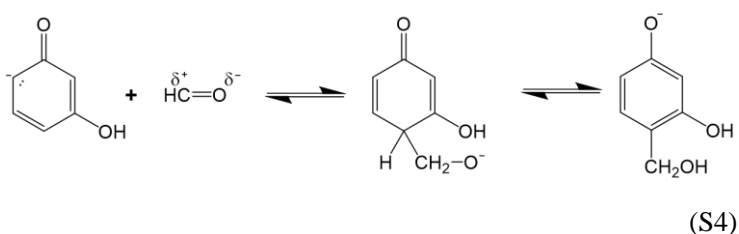
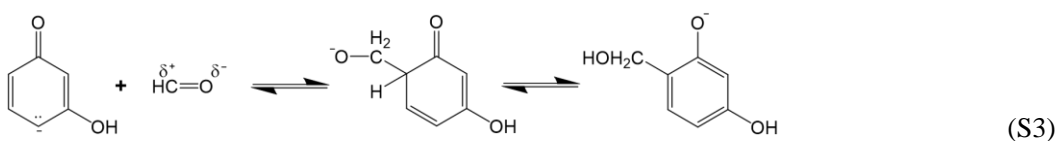
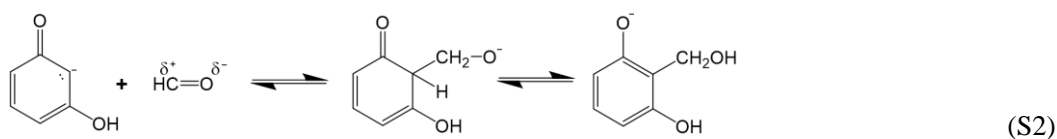
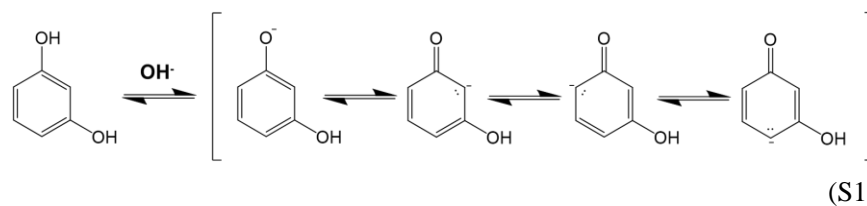


Table S1. Synthesis parameters of metal-doped RF resin precursors.

Precursors	Ni(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O/g	SnCl <sub>2</sub> ·2H <sub>2</sub> O/g
Ni@RF	3.268	0

Ni-Sn(3/1)@RF	3.268	0.846
Ni-Sn(3/1.7)@RF	3.268	1.437
Ni-Sn(3/1.8)@RF	3.268	1.521
Ni-Sn(3/2)@RF	3.268	1.691
Ni-Sn(1/1)@RF	3.268	2.537
Ni-Sn(3/4)@RF	3.268	3.382

Table S2. Summary of HTDO on Ni-based catalysts.

Feedstock	Reactor	Catalyst	Conditions	H <sub>2</sub> O:Feedstock:C atalyst/(g:g:g)	Conversi on	Yield	Referen ce
Methyl palmitate	Batch	15 wt% Ni-Sn@C Ni:Sn=3:1.8 (mole ratio)	330 °C;6 h methanol	80:20:3 0.6 g catalyst	99 C%	88.1 C% n-C <sub>15</sub> : 4.7 C% n-C <sub>16</sub>	<b>This work</b>
Methyl palmitate	Batch	15 wt% Ni-Co@C Ni:Co=1:1 (mole ratio)	330 °C;6 h methanol	40:10:1 0.4 g catalyst	100 C%	15.7 C% C <sub>6</sub> -C <sub>14</sub> 73.5 C% C <sub>15</sub>	[1]
Methyl palmitate	Batch	Ni/La <sub>2</sub> O <sub>3</sub> Ni:La=1:1 (mole ratio)	315 °C;2 h methanol	8:4:1 1 g catalyst	100 C%	25.6 C% C <sub>6</sub> -C <sub>14</sub> 45.5 C% C <sub>15</sub>	[2]
Oleic acid	Micro-b atch	40 wt% Ni-Cu/Al <sub>2</sub> O <sub>3</sub> Ni:Cu=2:1 (weight ratio)	330 °C;1 h methanol	100:10:3 15 mg catalyst	100 C%	92.7 C% C <sub>17</sub>	[3]
Oleic acid	Micro-b atch	20 wt% Ni-Cu/ZrO <sub>2</sub> Ni:Cu=2:1 (weight ratio)	370 °C;5 h methanol	100:10:3 15 mg catalyst	100 C%	92.5 C% C <sub>17</sub>	[4]
Canola Oil	Batch	Ni/C	315 °C; 12 h 1.95 MPa external H <sub>2</sub>	40:10:1 6.15 g catalyst	100 C%	51.9 wt% C <sub>17</sub>	[5]
Palmitate acid	Batch	10 wt% Ni/ZrO <sub>2</sub>	300 °C; 6 h 5.52 MPa external H <sub>2</sub>	9:1:1 0.5 g catalyst	100 C%	23.8 C% C <sub>15</sub> 30.8 C% C <sub>8</sub> -C <sub>14</sub> 18.2 C% CH <sub>4</sub>	[6]
Palmitate	Batch	10 wt%	300 °C; 6 h	9:1:1	63 C%	16.1 C% C <sub>15</sub>	[6]

acid		Ni/ZrO <sub>2</sub>	5.52 MPa N <sub>2</sub>	0.5 g catalyst		22.1 C% C <sub>8</sub> -C <sub>14</sub> 11 C% CH <sub>4</sub>	
Oleic acid	Micro-batch	6.66 wt% NiWC/Al-SB A-15 Ni:W=2:1(wei ght ratio)	400 °C; 4 h glycerol	321:22:5 10 mg catalyst	97.3%	5.2 mol% heptadecane 12 mol% heptadecene 73 mol% stearic acid	[7]
Oleic acid	Micro-batch	6.67 wt% NiNbC/Al-SB A-15 Ni:Nb=2:1(wei ght ratio)	400 °C; 4 h glycerol	321:22:5 10 mg catalyst	~80%	0.3 mol% heptadecane 43 mol% heptadecene 33 mol% stearic acid	[7]

Table S3. Conversion of methyl palmitate and hexadecanol on Ni-Sn(1/1)@C

Entry	Condition	Yield/%	Gas phase composition/mmol%
1	4 g methyl palmitate; 93.6 mmol methanol; 8 mL D.I. water; 0.4 g catalyst; 330 °C; 6 h	n-C <sub>15</sub> : 9.3 n-C <sub>16</sub> : 6.1 hexadecanol: 41.5	H <sub>2</sub> : 71.3 CO: 0.7 CO <sub>2</sub> : 26.8 CH <sub>4</sub> : 1.2
2	4 g methyl palmitate; 93.6 mmol methanol; 8 mL D.I. water; 0.4 g catalyst; 330 °C; 12 h	n-C <sub>15</sub> : 11.6 n-C <sub>16</sub> : 16.0 hexadecanol: 41.5	H <sub>2</sub> : 71.0 CO: 0.8 CO <sub>2</sub> : 27.0 CH <sub>4</sub> : 1.2
3	3.59 g hexadecanol; 8 mL cyclohexane; 0.4 g catalyst; 330 °C; 2 h	n-C <sub>15</sub> : 11.8 n-C <sub>16</sub> : 17.2 palmitic acid: 9.1	H <sub>2</sub> : 50 CO <sub>2</sub> : 50

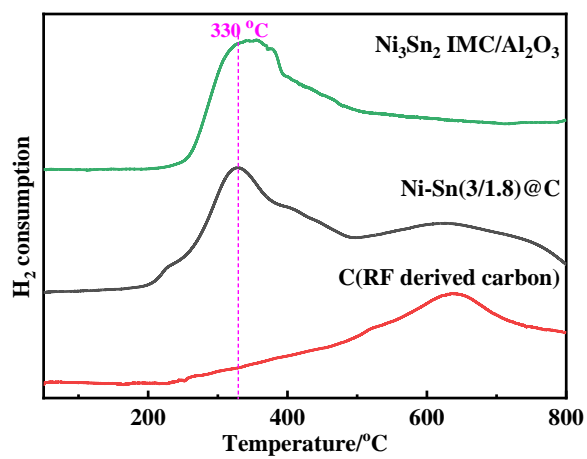


Fig. S1. H<sub>2</sub>-TPR profiles of passivated Ni-Sn(3/1.8)@C, passivated Ni<sub>3</sub>Sn<sub>2</sub> IMC/Al<sub>2</sub>O<sub>3</sub> and C.

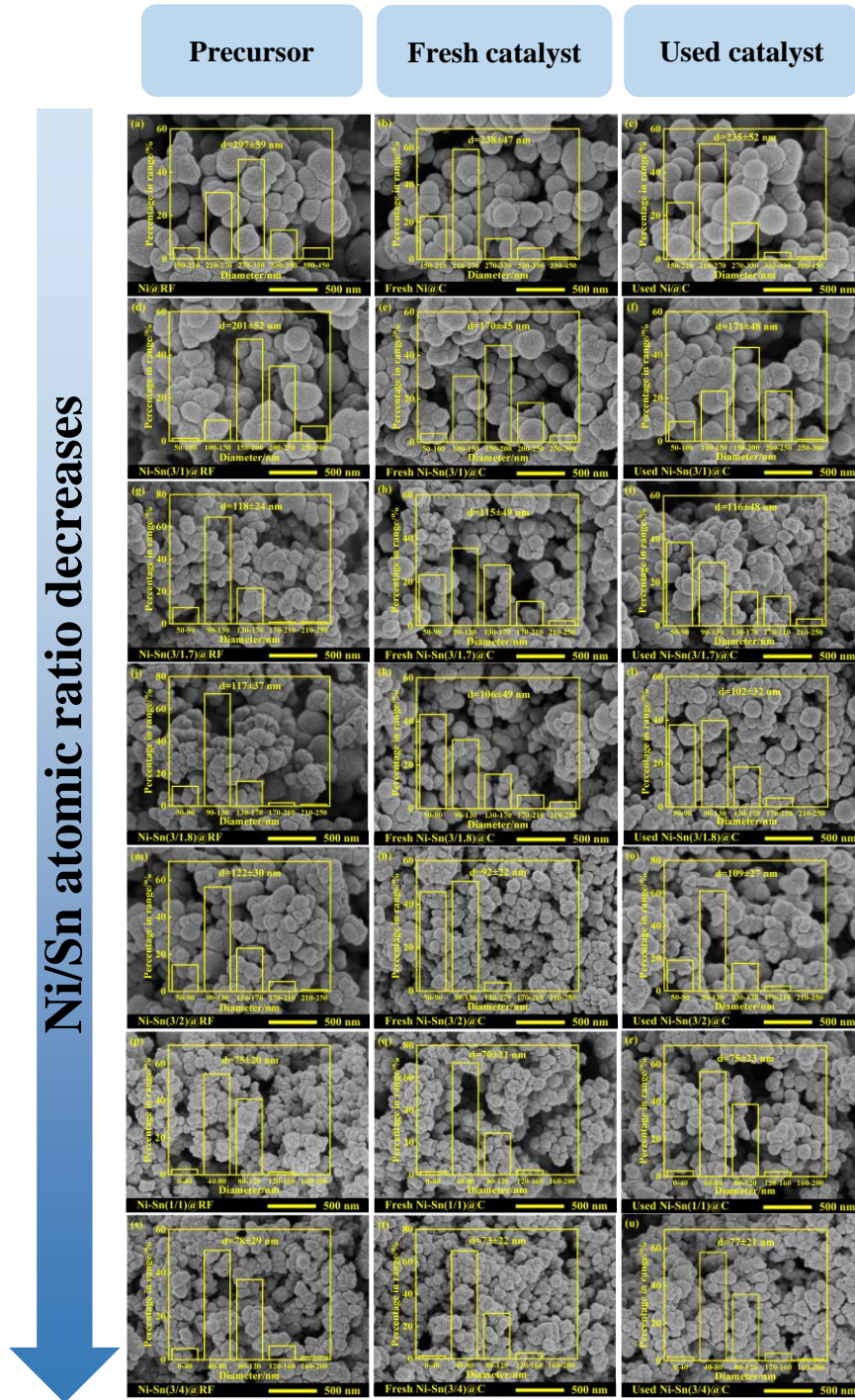


Fig. S2. SEM images of RF resin-based precursors and RF derived carbon-encapsulated Ni and Ni-Sn catalysts before and after in-situ HTDO at 330 °C for 6 h.

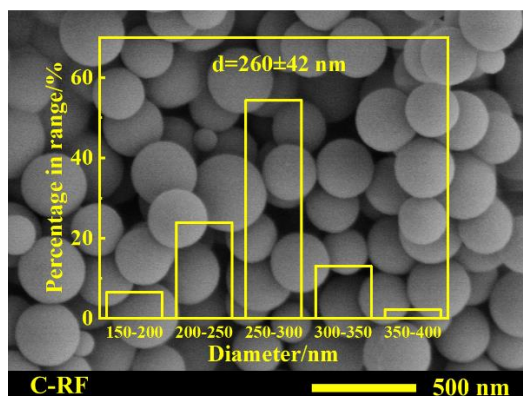


Fig. S3. SEM images of C-RF.

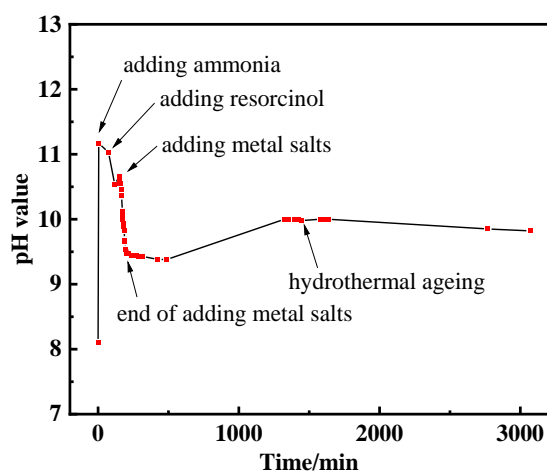


Fig. S4. pH value during preparing Ni-Sn(3/1.8)@RF microspheres via one-pot extended Stöber method.

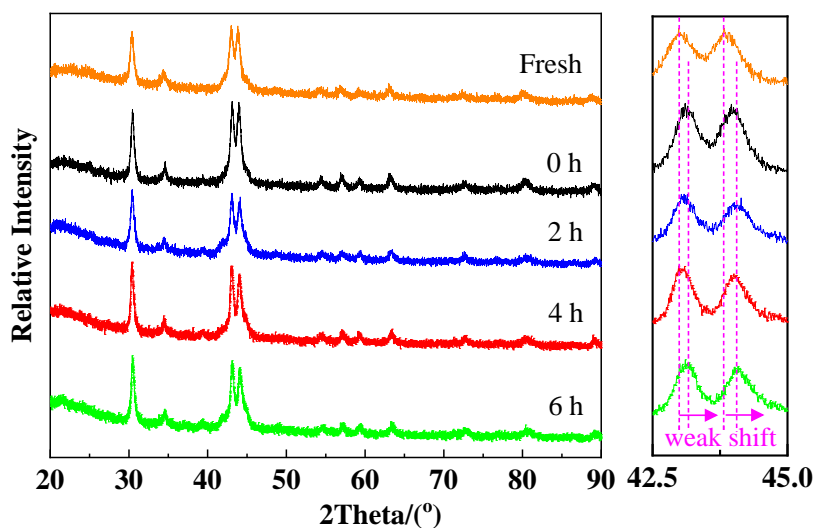


Fig. S5. XRD patterns of fresh and used Ni-Sn(3/1.8)@C at varied reaction time. Reaction condition: 330 °C, 4 g methyl palmitate, 3 g methanol, 8 g water, 0.4 g catalyst

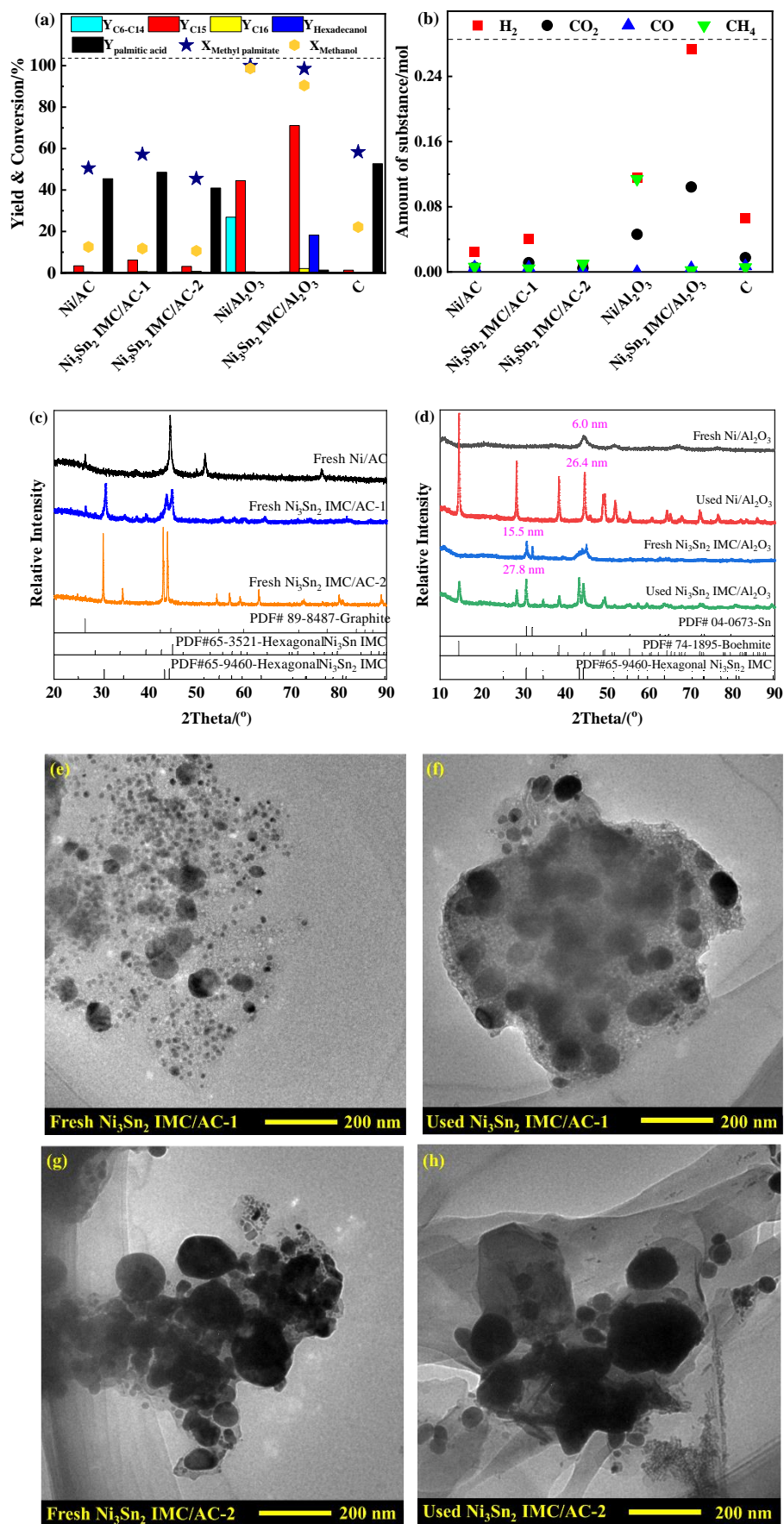


Fig. S6. (a, b) *In-situ* HTDO performance of phenolic resin derived carbon (C), carbon supported



and Al<sub>2</sub>O<sub>3</sub> supported Ni and Ni<sub>3</sub>Sn<sub>2</sub> IMC catalysts; (c, d) XRD patterns of carbon supported and Al<sub>2</sub>O<sub>3</sub> supported Ni and Ni<sub>3</sub>Sn<sub>2</sub> IMC catalysts; (e, f, g, h) TEM images of fresh and used carbon supported Ni<sub>3</sub>Sn<sub>2</sub> IMC catalysts

Reaction condition: 330 °C, 4 g methyl palmitate, 3 g methanol, 8 g water, 0.4 g catalyst, 6 h

The average particle sizes of Ni<sub>3</sub>Sn<sub>2</sub> IMC in fresh and used Ni<sub>3</sub>Sn<sub>2</sub> IMC/AC-1 are 27.8 nm and 59.4 nm, respectively, and these in fresh and used Ni<sub>3</sub>Sn<sub>2</sub> IMC/AC-2 are 71.9 nm and 92.8 nm, respectively. Clearly, compared with those in Ni<sub>3</sub>Sn<sub>2</sub>@C, the carbon supported Ni<sub>3</sub>Sn<sub>2</sub> IMC particles are very larger, and their sintering is more serious during *in-situ* hydrothermal deoxygenation.

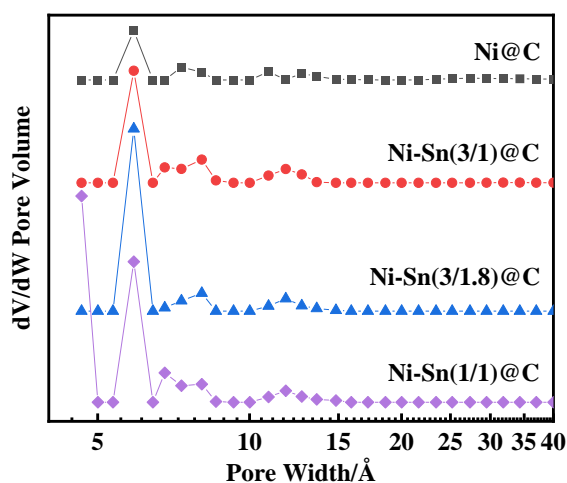


Fig. S7. Pore size distributions of Ni@C and Ni-Sn(x/y)@C.

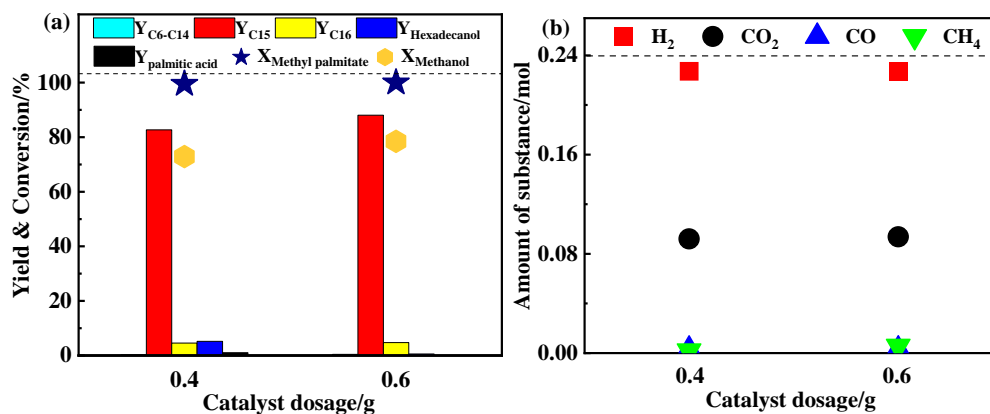


Fig. S8. *In-situ* HTDO performance of methyl palmitate over Ni-Sn(3/1.8)@C with varied catalyst dosage. (a) Conversions of methanol and methyl palmitate, yields of products and carbon balance; (b) Moles of gas phase products.

Reaction conditions: 330 °C, 4 g methyl palmitate, 3 g methanol, 8 g water, 0.4/0.6 g catalyst, 6 h

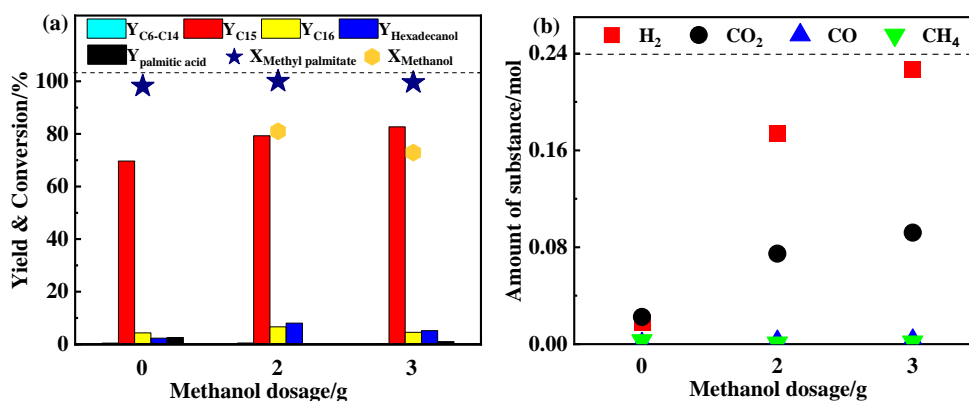


Fig. S9. *In-situ* HTDO performance of methyl palmitate over Ni-Sn (3/1.8) @C with varied methanol dosage. (a) Conversions of methanol and methyl palmitate, yields of products and carbon balance; (b) Moles of gas phase products.

Reaction conditions: 330 °C, 4 g methyl palmitate, 0~3 g methanol, 8 g water, 0.4 g catalyst, 6 h

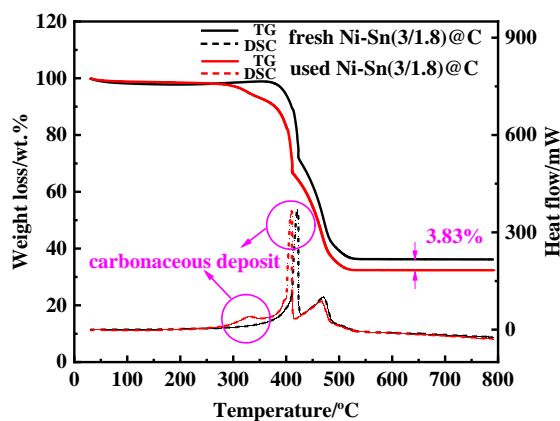


Fig. S10. TG-DSC curves of fresh and used Ni-Sn(3/1.8)@C catalysts.

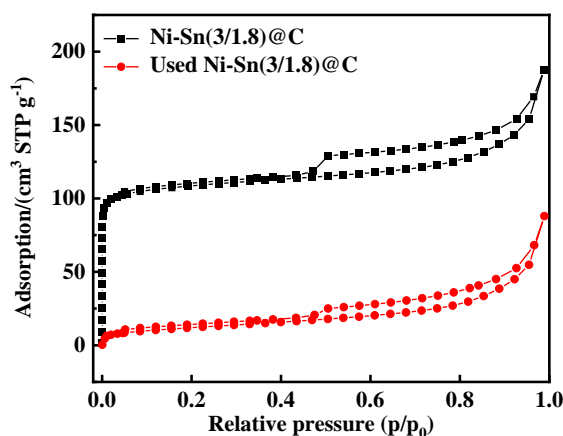


Fig. S11.  $N_2$  adsorption-desorption isotherms of fresh and used Ni-Sn(3/1.8)@C.

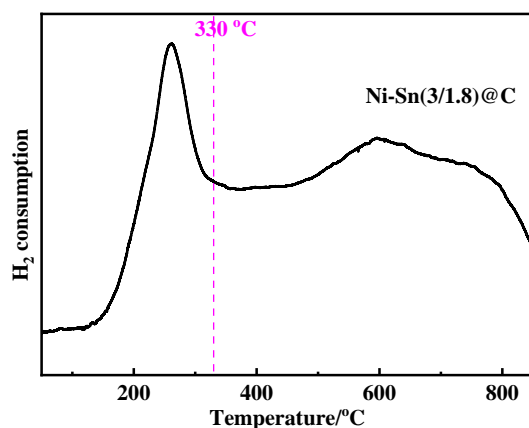


Fig. S12. H<sub>2</sub>-TPR profiles of Ni-Sn(3/1.8) @C after treated with 0.4 vol.% H<sub>2</sub>O/H<sub>2</sub> at 330 °C

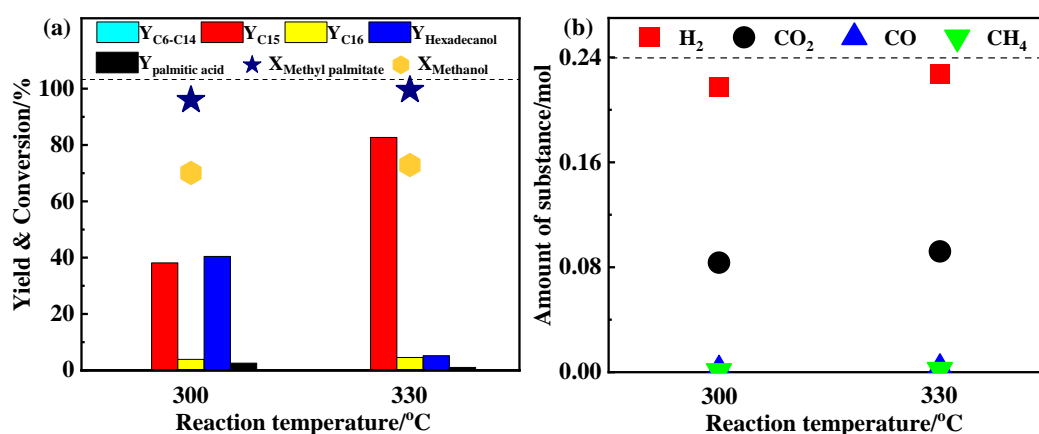


Fig. S13. *In-situ* HTDO performance of methyl palmitate over Ni-Sn (3/1.8) @C at varied temperature. (a) Conversions of methanol and methyl palmitate, yields of products and carbon balance; (b) Moles of gas phase products.

Reaction conditions: 300/330 °C, 4 g methyl palmitate, 3 g methanol, 8 g water, 0.4 g catalyst, 6 h

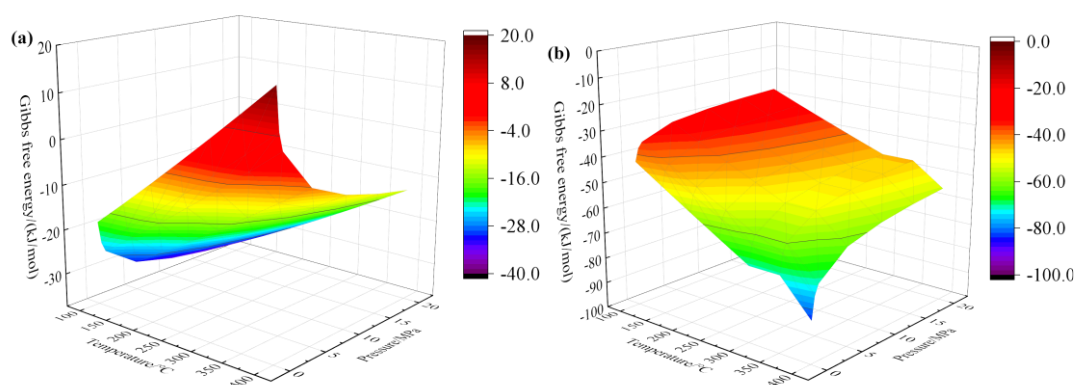


Fig. S14. Gibbs free energy change with temperature and pressure.

(a) hydrogenation of hexadecanal to hexadecanol and (b) decarbonylation of hexadecanal to n-pentadecane

## Reference

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