

## Unlocking the Potential of Lignocellulosic Biomass in Biodiesel Production: A Novel Co-Catalytic Strategy for One-Pot Hydrodeoxygenation and Esterification of Biomass-Derived Compounds

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### S1. Materials and methods

#### Chemicals

Zinc citrate (99%), 4-aminobenzenesulfonic acid (99.5%), Methanol (99.9%), N,N-Dimethylformamide (99.9%), ethanol (99.5%), Furfural, levulinic acid, Na<sub>2</sub>CO<sub>3</sub>, 5-Methyl furfural, cyclohexane, n-dodecane, Furfurylacrylic acid and 3-(5-methyl-2-furan)acrylic acid were purchased from Shanghai Meryer Biochemical Technology Co., Ltd (Shanghai, China). Isoamyl nitrite (95%) was purchased from Tokyo Chemical Industry (TCI). Pd/C (5 wt%), Pt/C (5 wt%) and Ru/C (5 wt%) were purchased from Sigma-Aldrich, Hydrochloric acid (37 wt%) and acetone (99.5%) were purchased from Sinopharm Chemical Reagent Company (Shanghai, China), All the chemicals were used without further purification.

**Preparation of ZCSH** : 20 g of Zinc citrate was carbonized in a tubular furnace under a nitrogen atmosphere. This process involved heating the Zinc citrate from room temperature to 1000 °C at a rate of 3 °C/min, followed by maintaining the temperature at 1000 °C for 60 minutes. The sample was then allowed to cool naturally to room temperature. Next, the carbonized precursor (Pre-ZC) was mixed with 2 mol/L hydrochloric acid and stirred for 6 hours, after which it was washed with deionized water at 60 °C until the conductivity (pH) of the filtrate reached neutral. Finally, the resulting sample was dried in an oven at 110 °C for 12 hours to obtain ZC. Subsequently, based on previous studies, ZC underwent sulfonation functionalization. ZC, p-aminobenzenesulfonic acid, and isopropyl nitrite were added to a 250 mL round-bottom flask containing 150 mL of deionized water in specific mass ratios (1:0.5:0.25, 1:1:0.5, 1:2:1, 1:3:1.5, or 1:4:2). The mixture was then magnetically stirred at 80 °C for 13 hours. After the solution cooled to room temperature, the resulting solid was filtered and subsequently washed with 200 mL DMF, 100 mL acetone, 200 mL ethanol, and 1000 mL deionized water in succession. The sample was then transferred to an oven and dried at 110 °C for 12 hours. The resulting catalyst was designated as ZCSH (ZCSH(1), ZCSH(2), ZCSH(3), ZCSH(4), or ZCSH(5)).

**Preparation of δ-furfurylidenelevulinic acid (FDLA, C<sub>10</sub> oxygenated compounds)** : 18.6 g LA was neutralized with 24.0 g Na<sub>2</sub>CO<sub>3</sub> at room temperature in 100 ml deionized water. The solution was heated to refluxed under stirring and then added with a mixture of 7.7 g furfural in 16 ml ethanol dropwise. It was cooled in ice water after no furfural was detected. The cooled solution was slowly poured into excessive diluted hydrochloric acid to collect the solid condensation products. FDLA

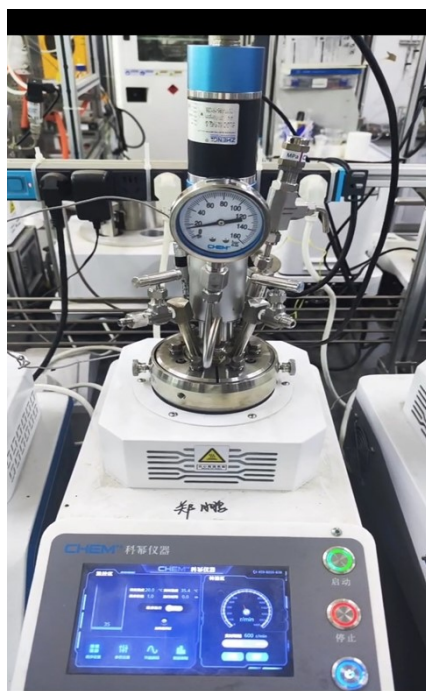
was obtained by recrystallization of the solid products from hot water.

**Preparation of (E)-6-(5-methylfuran-2-yl)-4-oxohex-5-enoic acid** (C<sub>11</sub> oxygenated compounds) : 18.6 g LA was neutralized with 24.0 g Na<sub>2</sub>CO<sub>3</sub> at room temperature in 100 ml deionized water. The solution was heated to reflux under stirring and then added with a mixture of 7.7 g furfural in 16 ml ethanol dropwise. It was cooled in ice water after no furfural was detected. The cooled solution was slowly poured into excessive diluted hydrochloric acid to collect the solid condensation products. (E)-6-(5-methylfuran-2-yl)-4-oxohex-5-enoic acid was obtained by recrystallization of the solid products from hot water.

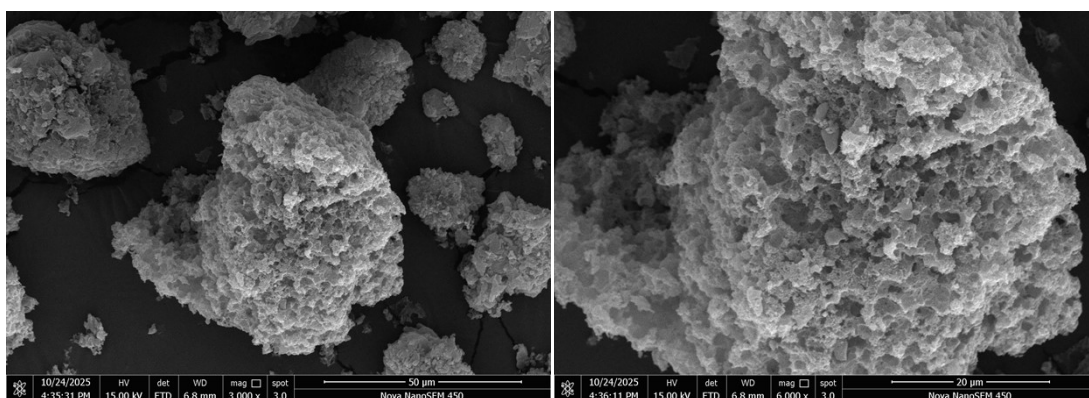
**Preparation of (3Z,5E)-6-(furan-2-yl)-3-(furan-2-ylmethylene)-4-oxohex-5-enoic acid** (C<sub>15</sub> oxygenated compounds): Aldol condensation was carried out in batch mode using pure furfural and ethyl levulinate as feedstock. Typically, furfural (2.0 g, 0.0208 mol), ethyl levulinate (1.5 g, 0.0104 mol), and aqueous NaOH solution (25 mL, 1.0 mol/L) were added into a 100 mL beaker, which was then placed in a water bath at 50°C during reaction. After reaction, the beaker was cooled down and neutralized with HCl solution; then the solid product was precipitated and separated by filtration, washed with warm water, and then dried at 50 °C overnight.

**HDOE catalytic test:** The HDOE catalytic test was performed in a stainless steel high temperature and high pressure reactor equipped with 50ml quartz tube (Anhui Kemi Machinery Technology Co., Ltd), as shown in Figure S1. Typically, 100 mg of FDLA, 100 mg of Pd/C, 50 mg of ZCSH, 10 ml of cyclohexane and 0.1 mL CH<sub>3</sub>OH were added into a quartz tube. The sealed reactor was flushed 3 times with H<sub>2</sub> and subjected to a pressure of 4 MPa H<sub>2</sub>. The autoclave was heated up to 200 °C and held for 2 h at a stirring speed of 600 rpm. Liquid products were collected by filtration through a 0.22 μm nylon membrane after cooling down to room temperature. Dodecane was used as an internal standard substance for quantitative calculations. Gas chromatography (GC- 2014C Shimadzu, Japan) and gas chromatography/mass spectrometry (GC-MS, Agilent 8860, USA) were used for product analysis. Nuclear magnetic resonance (NMR, Bruker AVANCE AV III 400) spectroscopy was performed to characterize the intermediates in chloroform-d solvent. The product yield was determined using the following equations:

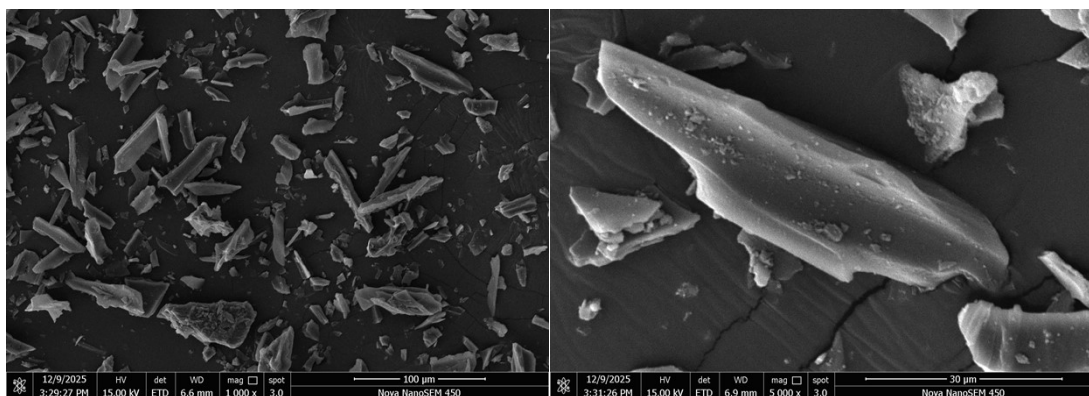
$$\text{Yield ( \% )} = \frac{\text{mol of methyl esters of fatty acids}}{\text{mol of long - chain oxygenated compounds}} \times 100\% \quad \text{Eq.1}$$



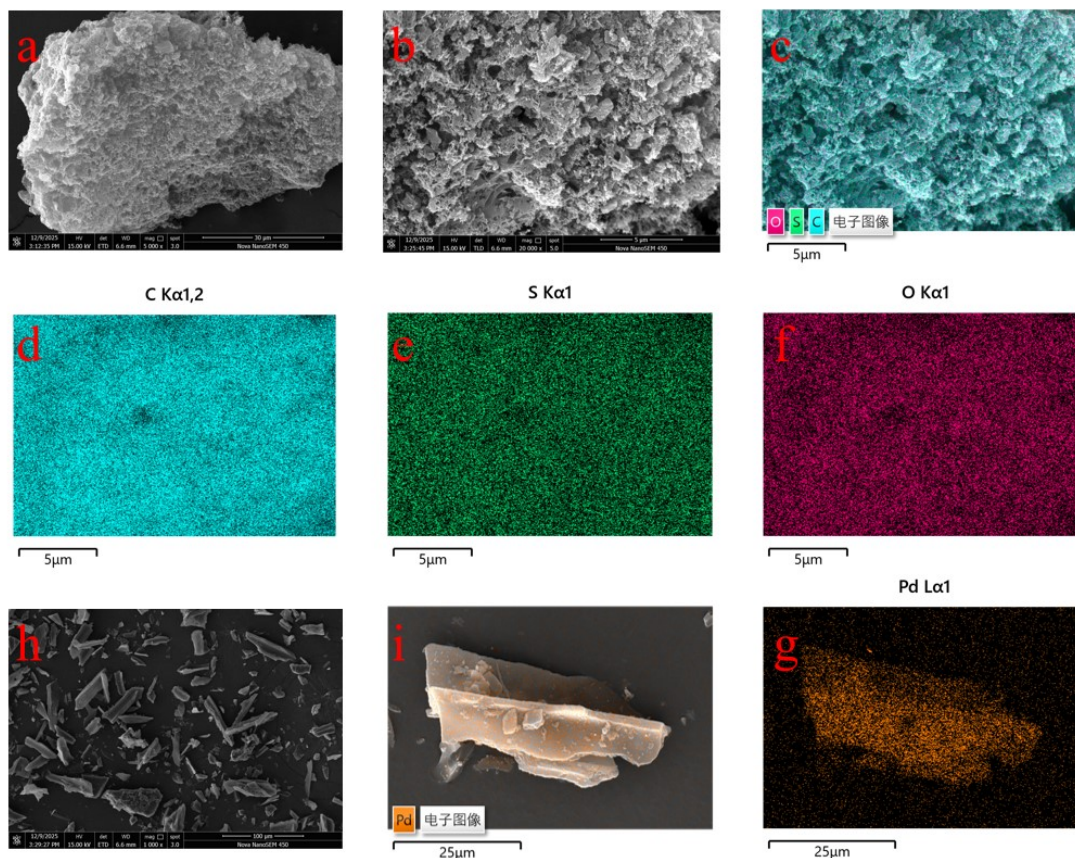
**Figure S1.** Images of the reaction generator (HDOE).



**Figure S2.** Images of ZCSH(4).



**Figure S3.** Images of Pd/C.



**Figure S4.** (a,b,c,d,e,f): SEM and EDS image of ZCSH(4), (h,i,g): SEM and EDS image of Pd/C.

**Table S1.** The elemental analysis of ZC and ZCSH(4)

	N(%)	C(%)	H(%)	S(%)	<sup>a</sup> O(%)
ZC	0.31	94.07	0.69	0	4.93
ZCSH(4)	0.35	69.05	3.85	7.75	19

<sup>a</sup>The CHNS model was adopted for the analysis of elements, while the oxygen content was estimated.

#### **$\delta$ -furfurylidenelevulinic acid**

<sup>1</sup>H NMR (600 MHz, Chloroform-d) : $\delta$ 7.50 (d, J = 1.8 Hz, 1H), 7.35 (d, J = 15.8 Hz, 1H), 6.68–6.64 (m, 2H), 6.49 (dd, J = 3.4, 1.8 Hz, 1H), 2.95 (t, J = 6.6 Hz, 2H), 2.72 (t, J = 6.7 Hz, 2H). <sup>13</sup>C NMR (151 MHz, Chloroform-d)  $\delta$ 197.54, 178.60, 151.07, 145.25, 129.32, 122.90, 116.21, 112.73, 35.56, 28.13.

#### **(E)-6-(5-methylfuran-2-yl)-4-oxohex-5-enoic acid**

<sup>1</sup>H NMR (600 MHz, Chloroform-d)  $\delta$ 7.28 (d, J = 15.8 Hz, 1H), 6.59–6.56 (m, 2H), 6.09 (d, J = 3.2 Hz, 1H), 2.93 (t, J = 6.7 Hz, 2H), 2.71 (t, J = 6.7 Hz, 2H), 2.35 (s, 3H). <sup>13</sup>C NMR (151 MHz, Chloroform-d)  $\delta$ 197.61, 178.76, 156.19, 149.66, 129.44, 121.17, 118.18, 109.40, 35.48, 28.26, 14.06.

**(3Z,5E)-6-(furan-2-yl)-3-(furan-2-ylmethylene)-4-oxohex-5-enoic acid**

$^1\text{H}$  NMR (600 MHz, Chloroform-d)  $\delta$  7.63 (d,  $J = 1.7$  Hz, 1H), 7.54–7.49 (m, 3H), 7.31 (d,  $J = 15.2$  Hz, 1H), 6.91 (d,  $J = 3.5$  Hz, 1H), 6.71 (d,  $J = 3.4$  Hz, 1H), 6.56 (dd,  $J = 3.6, 1.8$  Hz, 1H), 6.51 (dd,  $J = 3.5, 1.8$  Hz, 1H), 3.90 (s, 2H).  $^{13}\text{C}$  NMR (151 MHz, Chloroform-d)  $\delta$  191.41, 174.63, 151.72, 150.64, 146.08, 145.17, 130.99, 130.22, 128.41, 118.13, 117.81, 116.62, 112.91, 33.85.

