Supplementary Information

Decarbonylation of Fatty Acids to Alkenes over Co-N-C Catalysts Derived from Co Complexes

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Experimental procedures and analytical methods

Deoxygenation of long-chain fatty acids (C12, C14 and C18) was carried out in a 1.67 mL micro-batch reactor (Swagelok, USA). In each experiment, 50 mg of reactant and 10 mg of catalyst were loaded into the reactor without hydrogen or solvents. Subsequently, the sealed reactor was heated in a preheated fluidized sand bath (Techne SBL-2) at the desired temperatures (320, 350 or 380 °C) for 30, 60 or 90 min. When the predetermined reaction time elapsed, the micro-batch reactor was immediately cooled down with cold water and left overnight. The mixture in the reactor was rinsed out with ethanol, transferred to a 25 mL volumetric flask, and the volume was made up to the mark with ethanol. The filtrate would be used for the analysis of the product.

The quantification and identification of the products were performed with an Agilent 7890B gas chromatograph (GC) equipped with a flame ionization detector (FID) and Agilent-CP-FFAP-CB capillary column. Quantitative analysis of the samples was carried out using calibration curves for each compound. Identification analysis was performed by matching the gas chromatographic retention times against known standards. The results are the average of the values obtained from three independent measurements. The molar conversion was calculated as the ratio of the moles of fatty acids consumed to the moles of fatty acids initially added to the reactor. Selectivity was calculated by dividing the mole of the product obtained by the mole of fatty acid consumed. The product yield was calculated by multiplying the conversion efficiency and selectivity. Also, the olefin selectivity in this work is derived from both 1-alkenes and internal alkenes, and we did not measure the percentage of 1-alkene.

Characterizations

The crystal structure was evaluated by X-ray diffraction (XRD) analysis on MiniFlex 600 diffractometer with a Cu Kα source at 40 kV and 30 mA. The catalysts were scanned between 5~80°. Raman spectra were obtained at a HORIBA HR Evolution Raman Spectrometer. The excitation wavelength was 532 nm. Co contents were determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES) on a PerkinElmer Optima 8300. The samples were dissolved in concentrated nitric acid prior to analysis. N_2 adsorption–desorption isotherms were collected using N_2 at 77 K by a Micromeritics ASAP2020 apparatus. Before analysis, samples were degassed at 200 °C for 12 h. Surface area was determined based on the Brunauer–Emmett–Teller (BET) equation. The TEM and EDS-mapping images of the samples were achieved using JEM-2100F and Titan ChemiSTEM instrument with the acceleration voltage of 200 KV. AC HADDF-STEM images were recorded by Titan cubed Themis G2 300 microscope. Infrared (IR) spectra were recorded by a Nicolet-iS-50 Fourier–transform infrared (FTIR) spectrometer. X-ray photoelectron spectroscopy (XPS) analysis was performed on ESCALAB 250 Xi X-ray photoelectron spectrometer with Al Kα radiation. In situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) with propionic acid as the probe molecule was carried out on a Thermo Scientific IS-50R Fourier transform infrared spectrometer equipped with an MCT/A detector. 5 mg CoPc was diluted in 40 mg KBr and loaded into the IR chamber. The samples were first pretreated in N_2 at 350 °C and maintained 2 h. Then a background spectrum was collected as a reference. After that, propionic acid was introduced into the high-temperature in situ cell via bubbling at a N_2 flow rate of 120 $mL \cdot min^{-1}$ and the spectra were collected for a period of time. Then, the inlet and outlet of the in-situ cell were sealed, ceasing the introduction of propionic acid, and spectra were continuously collected for a period of time.

Supplementary Figures

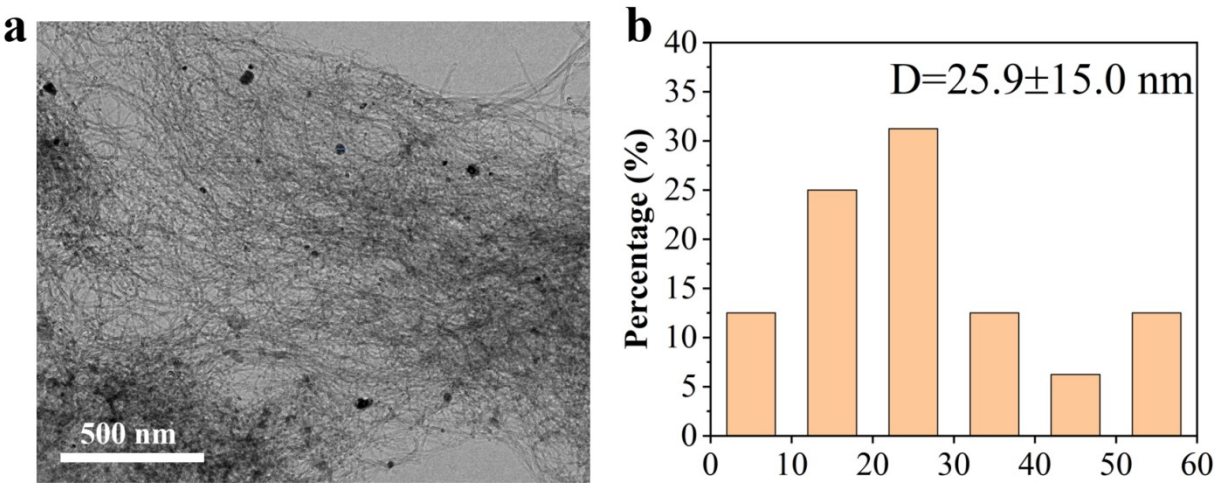

Figure S1. (a) TEM image of CoPhPhen/MWCNT-IM-900 prepared by solvent impregnation method using 4,7-diphenyl-1,10-phenanthroline (PhPhen) as ligand, (b) particle size distribution histogram of CoPhPhen/MWCNT-IM-900.

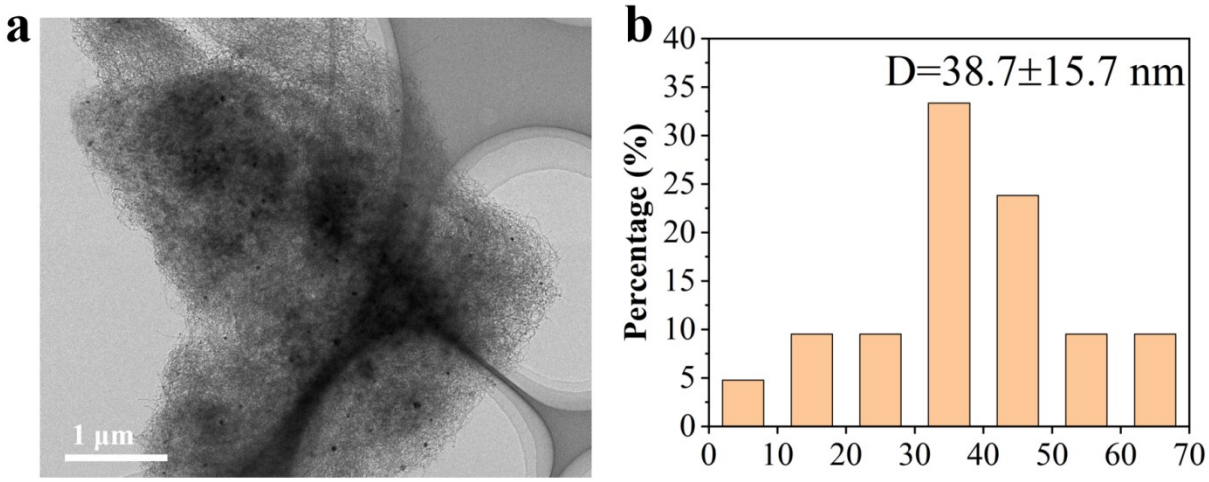

Figure S2. (a) TEM image of CoPhen/MWCNT-IM-900 prepared by solvent impregnation method using 1,10-phenanthroline (Phen) as ligand, (b) particle size distribution histogram of CoPhen/MWCNT-IM-900.

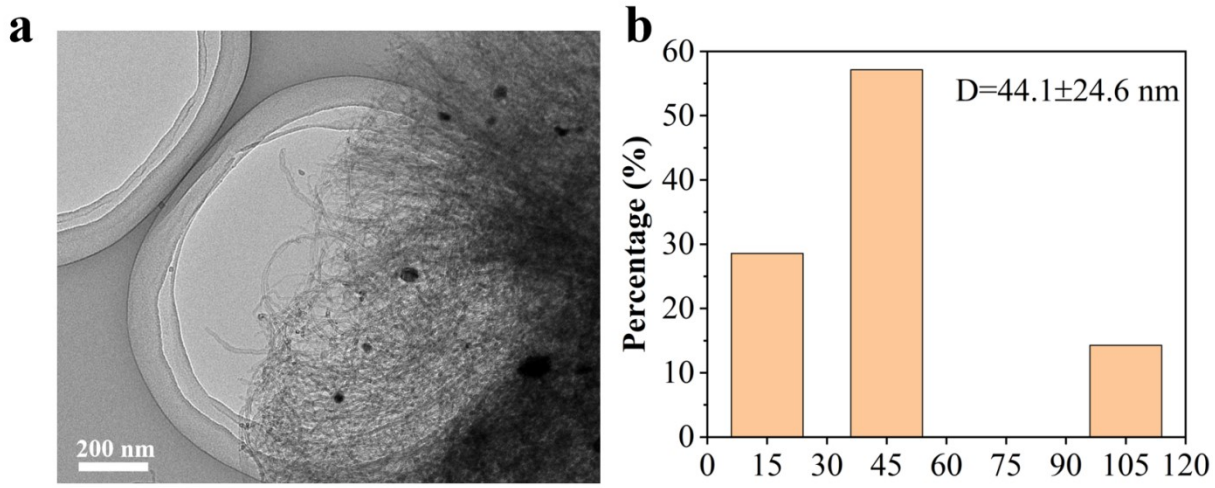

Figure S3. (a) TEM image of CoPc/MWCNT-IM-900 prepared by solvent impregnation method using Cobalt phthalocyanine (CoPc), (b) particle size distribution histogram of CoPc/MWCNT-IM-900.

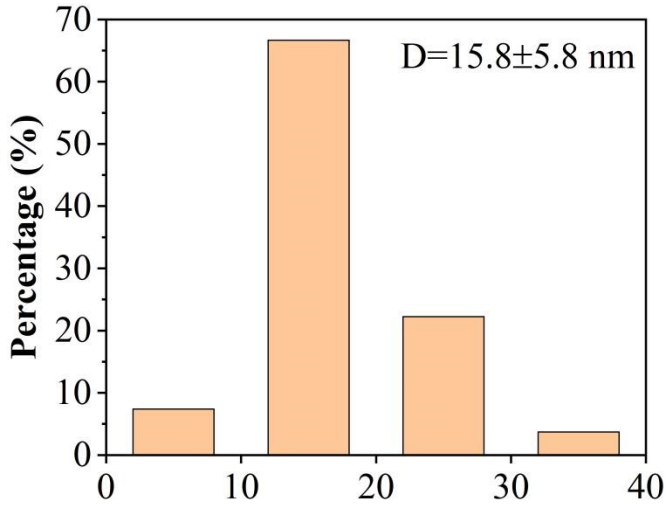

Figure S4. Particle size distribution histogram of CoPhPhen/MWCNT-900.

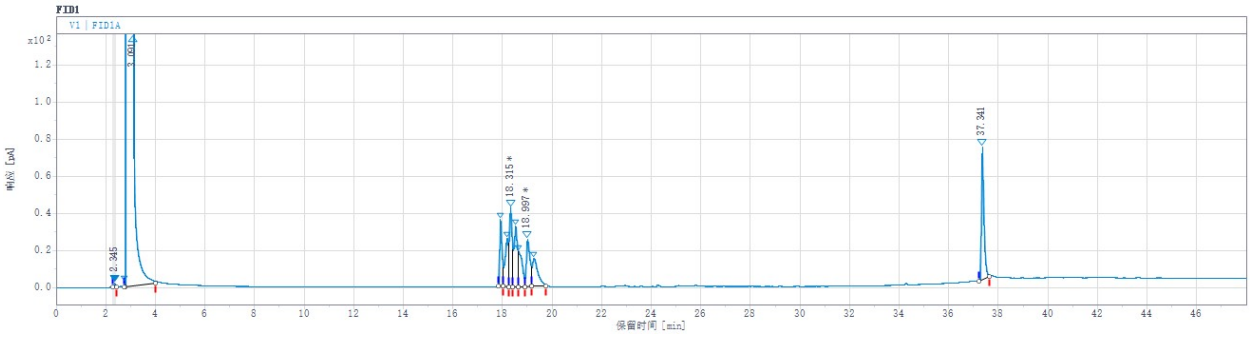

Figure S5. GC results of the deoxygenation of stearic acid over CoPhPhen/MWCNT-900. Retention time: heptadecane (17.8-18.0 min), internal heptadecene (18.0-19.0 min), α-heptadecene (19.0-19.5 min) and stearic acid (37.3 min).

Supplementary Tables

Table S1. Co content measured by ICP-OES.

Entry	Catalyst	Co wt%
1	CoPhPhen/MWCNT[a]	0.371
2	CoPhPhen/MWCNT[b]	1.1-1.15
3	CoPhPhen/MWCNT-700[a]	1.197
4	CoPhPhen/MWCNT-800[a]	1.201
5	CoPhPhen/MWCNT-900[a]	1.272
6	CoPhPhen/MWCNT-900 Used4[a]	0.500
7	CoPc/MWCNT-IM-900[a]	0.967

[a] The obtained Co content of CoPhPhen/MWCNT by ICP-OES was significantly lower than the theoretical value, could be due to the excessive uncoordinated ligands inhibit the leaching of cobalt ions in the acidic digestion solution and decreased the Co content in the solution to be tested. [b] This cobalt content was obtained indirectly by calculating the mass change of the catalyst before and after pyrolysis.

Table S2. The deoxygenation of stearic acid over a series of Co-based catalysts.

Entry	Catalyst	Temperature (°C)	Time (h)	Conversion of acid (%)	Alkane yield (%)	Alkene yield (%)
1	[a]CoPhPhen/MWCNT-900	350	1	81.6±0.9	9.1±0.3	58.3±0.6
2	[a]CoPhPhen/MWCNT-900 Use2	350	1	61.1±1.2	7.2±0.7	39.5±2.5
3	[a]CoPhPhen/MWCNT-900 Use3	350	1	53.7±4.5	6.3±0.1	29.2±0.2
4	[a]CoPhPhen/MWCNT-900 Use4	350	1	52.9±1.7	6.2±0.1	21.3±0.7
5	[a]CoPhPhen/MWCNT-900	320	1	42.6±3.0	2.3±0.1	31.1±1.0
6	[a]CoPhPhen/MWCNT-900	380	1	96.5±0.9	32.7±2.2	32.5±0.7
7	[a]CoPhPhen/MWCNT-900	350	0.33	47.4±1.2	2.9±0.1	37.3±1.4
8	[a]CoPhen/MWCNT-900	350	0.33	45.7±3.8	3.2±0.3	33.6±2.8
9	[a]CoPc/MWCNT-IM-900	350	0.33	46.3±2.7	3.1±0.3	33.4±1.4
10	[b]CoPhPhen/MWCNT-900	350	1	69.2±3.0	4.9±0.2	43.4±1.9
11	[c]CoPhPhen/MWCNT-900	350	1	70.7±3.6	8.0±0.4	55.2±2.6
12	[a]CoPhPhen/MWCNT-700-H_2	350	1	56.2±1.3	8.9±0.2	32.3±0.8
13	[a]CoPhPhen-2%Co/MWCNT-700-H_2	350	1	59.4±1.8	10.3±0.3	34.8±2.2
14	[a]CoPhPhen-4%Co/MWCNT-700-H_2	350	1	60.9±2.0	11.2±0.2	35.0±1.2

15	[a]Co^{2+}/N-MWCNT	350	1	49.5±5.3	6.7±0.3	20.3±1.3

[a] Stearic acid as substrate, [b] lauric acid as substrate, [c] myristic acid as substrate. Standard deviations were calculated by the results of three repeated experiments.

Table S3. Performance comparison of catalysts from various studies with the state of the art.

Catalyst	Reaction condition	solvent	Yield of alkenes	Selectivity of alkenes	Stability of catalysts
This work	350 ℃, 1 h	without	58.3%	71.4%	4th (58.3% to 21.3%)
CoZn/NC (2024)[1]	350 ℃, 1 h	without	42.2%	70.8%	4th (42.2% to 33.0%)
CoNC-MWCNT (2025)[2]	350 ℃, 1 h	without	47.4%	57.8%	4th (47.4% to 21.2%)
Pt−WO_x (2025)[3]	350℃,1.5h	dodecane	43.8%	64.7%	7th (43.8% to 35.2%)
CoNC (2024)[4]	350 ℃, 1 h	without	39.5%	43..5%	3th (39.5% to 23.0%)
PtZn/NC (2022)[5]	360℃,0.5h	without	34.8%	67.1%	3th (34.8% to 22.5%)

References

1. *ACS Sustain. Chem. Eng.*, 2024, **12**, 1320-1332.

2. *Energy Fuels*, 2025, **39**, 15320-15329.

3. *ACS Catal.*, 2025, **15**, 15211-15223.

4. *Fuel*, 2024, **362**, 130721.

5. *Angew. Chem., Int. Edit.*, 2022, **61**, e202202017.