Fast-Track Discovery of MOF-Derived M@NC Catalysts for HMF-to-FDCA Oxidation via DFT Prescreening and Box–Behnken Optimization

Zhan Chen,† [a] *Zhenzhi Xia*,† [a] *Zekun Hu*, [b] *Jing Liu*[*c] and *He Xie*[*b]

[a.] State Key Laboratory of Advanced Technology for Materials Synthesis and Processing Wuhan University of Technology Wuhan 430070, P. R. China

[b.] Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 117543, Singapore.

[c.] Co-Innovation Center of Efficient Processing and Utilization of Forest Resource, School of Materials Science and Engineering, Nanjing Forestry University, Nanjing, Jiangsu, 210037, China.

†These authors contributed equally to this work.

1. Experimental

1.1 Materials

All chemicals used in this study were purchased commercially and employed as received. Zinc acetylacetonate (≥97 %), iron(III) acetylacetonate (≥98 %), copper(II) acetylacetonate (≥97 %), nickel(II) acetylacetonate (≥95 %), and 2-methylimidazole (≥98 %) were obtained from Shanghai Aladdin Biochemical Technology Co., Ltd. Deuterium oxide (99.8 % D) was supplied by Energy Chemical.

1.2 Synthesis of Zn@NC

First, 2-methylimidazole (1.367 mmol) and zinc acetylacetonate (0.4 mmol) were thoroughly mixed and ground in an agate mortar for 10 min until a uniform, fine white powder was obtained.

An appropriate amount of the resulting mixture was then transferred to a porcelain boat and placed in a tube furnace. Under a 5 % H_2/Ar atmosphere, the sample was heated to 200 °C and held for 1 h, followed by further heating to 900 °C and maintained at this temperature for another 1 h. After natural cooling to room temperature, the obtained black powder was designated as Zn@NC.

1.3 Synthesis of M@NC (M = Ni/Cu/Fe)

M@NC (M = Ni, Cu, Fe) was synthesized by a route analogous to that used for Zn@NC. During the grinding step, 0.04 mmol of nickel (II) acetylacetonate, copper (II) acetylacetonate, or iron (III) acetylacetonate was introduced, yielding light-green, blue-gray, or pink mixed powders, respectively.

The resulting mixtures were then subjected to the identical pyrolysis protocol employed for Zn@NC. After cooling, the black products were collected and designated as the corresponding M@NC.

1.4 Material Characterization

Powder X-ray diffraction (XRD) patterns were collected on a Bruker D8 Advance diffractometer (Bruker AXS, Karlsruhe, Germany) using Cu Kα radiation (λ = 1.5406 Å). Raman spectra were acquired on a Renishaw in Via Raman microscope (Renishaw, UK). X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo Fisher Nexsa XPS system (Thermo Fisher Scientific, UK) to analyze the surface elemental composition and chemical states. The material morphologies were analyzed by scanning electron microscopy (SEM) analysis (Rigaku TG-DTA8122). Nuclear magnetic resonance (NMR) analyses were employed to calculate product yields using a Bruker Avance 500 spectrometer (^{1}H NMR at 500 MHz and ^{13}C NMR at 126 MHz), with D_2O serving as a deuterated solvent. Multiplicity in the spectra was denoted by the abbreviations: *s* = singlet, *d* = doublet, and *m* = multiplet. The properties related to surface area, gas adsorption, and porosity properties were assessed using N_2 as a probe gas on a Micromeritics ASAP 2020 instrument (Micromeritics, USA). Prior to the measurements, the samples were activated under vacuum at 70 °C for 3 h. The elemental contents and composition of the catalysts were determined via inductively coupled plasma optical emission spectroscopy (ICP-OES) utilizing a Prodigy 7 instrument (Hudson, NH, USA). The Micromeritics Brunauer–Emmet–Teller (BET) instrument was operated to measure samples. The degassing time and degassing temperature of the samples are 6 h and 120 °C, respectively. N2 sorption isotherms were performed at 77 K. The

specific surface area was calculated by the conventional BET method. The pore size distribution plot was recorded by the DFT model. The micropore volume was estimated by using the t-plot method.[1]

1.5 Standard Catalytic Process and Product Analysis

In keeping with the principles of green and sustainable synthesis, the catalytic process was performed under ambient air using only water as the solvent. The standard procedure was as follows: a 25 mL Schlenk tube was charged with the catalyst (70.0 mg), HMF (32.0 mg, 0.25 mmol), Na_2CO_3 (87.4 mg, 0.825 mmol, 1.65 equiv.), and deionized water (1 mL). Then heat the Schlenk tube at 100 °C under open air for 16 h. After completion, the reaction mixture was cooled room temperature and extracted with deionized water (3 × 3 mL). Acetonitrile (41 mg, 1.0 mmol) was then added as an internal standard for quantitative ^1H NMR analysis. An aliquot of the resulting solution (0.1 mL) was combined with D_2O (0.4 mL) in an NMR tube. HMF conversion and the yields of furan-derived products were determined by integration relative to the acetonitrile singlet at 2.06 ppm.

1.6 Catalyst recycling

After each run, the spent catalyst was recovered by vacuum filtration, rinsed successively with deionized water (3×10 mL) and absolute ethanol (3×10 mL), then dried at 90 °C under reduced pressure for 14 h to give a dark solid denoted R-M@NC. Then the recovered R-M@NC was heated at 600 °C under flowing argon for 1 h to reactivate the active sites. The thus-reactivated material was re-introduced into the standard reaction (1.65 eq Na_2CO_3, 1 mL H_2O, 70 mg catalyst, 100 °C, 16 h), and the entire recovery cycle was repeated for subsequent runs.

1.7 Theory calculations and simulations

The density functional theory (DFT) was implemented in the Vienna ab initio Simulation Package (VASP code 5.4.1). The interaction between ions and valence electrons was described using projector augmented wave (PAW) potentials, and the exchange-correlation between electrons was treated through using the generalized gradient approximation (GGA) in the Perdew-Burke-Ernzerhof (PBE) form. the DFT D3 method with Becke-Johnson damping function was employed to capture the effect of van der Waals (vdW) interaction. The cut-off energy was set to 400 eV. K point was 3×3×1. The ionic relaxations for all structures in the calculations were carried out under the conventional energy (2×10^{-5} eV) and force (0.05 eV/Å) convergence criteria. The iodinated single-atom models were built based on a graphene model. The appropriate vacuum layer of 15 Å were applied to all models. The adsorption energy E_{ads} was defined as $E_{ads} = E_{adsorbate/slab} - E_{slab} - E_{adsorbate}$, where $E_{adsorbate/slab}$, E_{slab}, and $E_{adsorbate}$ represented the total energies of the adsorbed system, the slab surface, and adsorbate molecule (HMF), respectively. Note that more negative Eads value means more heat release and much stronger adsorption.

2. Supplementary results

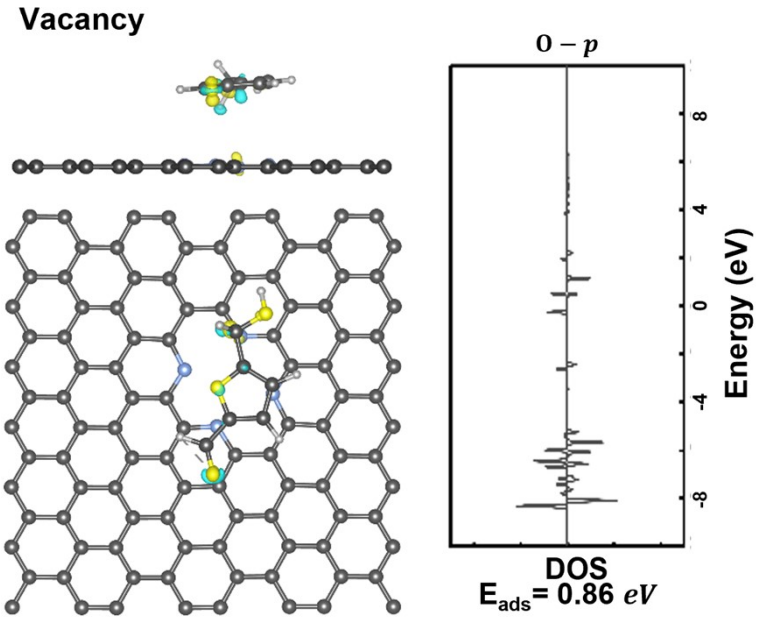


Figure S1 DFT model and electronic structure of the vacancy site. Left: optimized adsorption configuration of HMF on the vacancy-containing carbon surface (top: side view; bottom: top view). Right: projected density of states (pDOS, O–p) for the adsorbed intermediate on the vacancy site, with the calculated adsorption energy E_{ads}=0.86 eV.

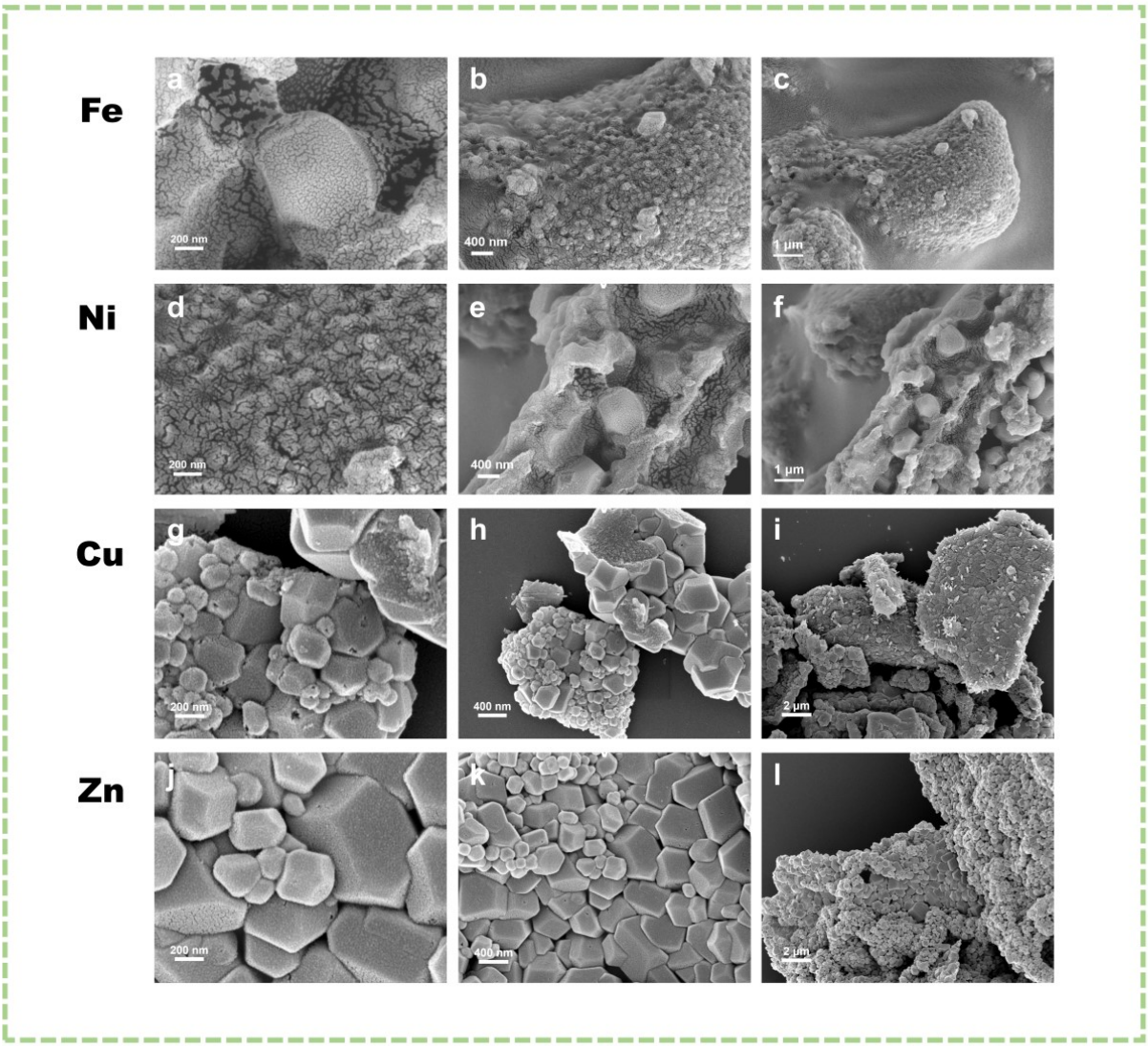


Figure S2 SEM images of (a-c) Fe@NC; (d-f) Ni@NC; (g-i) Cu@NC; (j-l) Zn@NC.

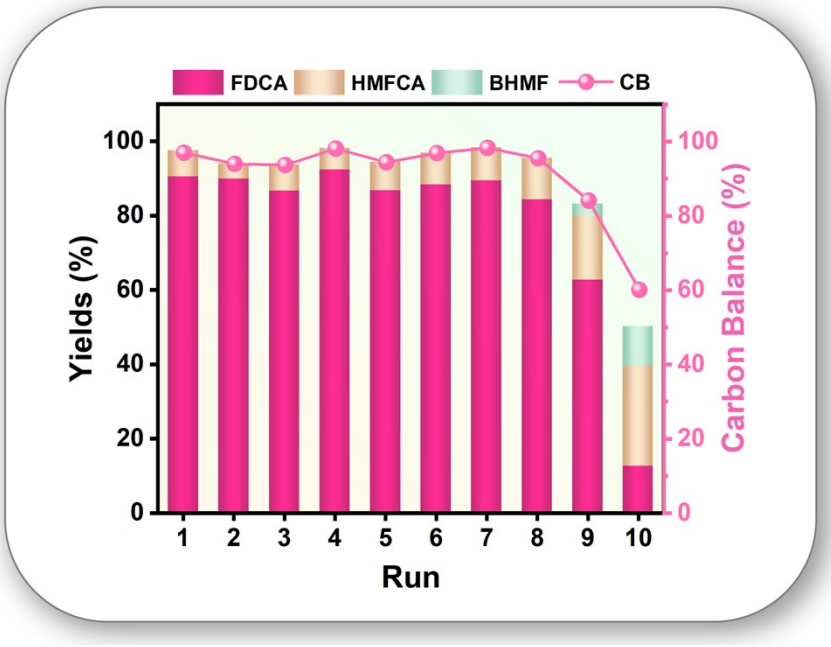


Figure S3 Reusability Experiment of Fe@NC. (After each run, the catalyst was recovered by filtration, washed with water/ethanol, vacuum-dried at 90 °C for 14 h, and reactivated at 600 °C under Ar for 1 h before reuse).

Table S1 Variables and their levels in the Box-Behnken design.

Factor	Time (h)	Temp. (℃)	Na^+ (eq.)
Low	12	80	2.2
Mid	16	100	3.3
High	20	120	4.4

Table S2 Box-Behnken experimental design.

No.	Time (h)	Temp. (℃)	Na^+ (eq.)	FDCA (%)
1	16	100	3.3	90.5
2	16	80	2.2	62.8
3	12	120	3.3	42
4	20	100	2.2	85.8
5	20	100	4.4	92.2
6	16	80	4.4	65.4
7	12	100	2.2	50.1
8	16	120	2.2	40.7
9	12	80	3.3	51.2
10	16	120	4.4	45.4
11	16	100	3.3	91.2
12	20	80	3.3	63.1
13	20	120	3.3	56.2
14	16	100	3.3	91.3
15	12	100	4.4	59.3

Table S3. The BET surface area, pore volume, and pore size of the M@NC catalysts.

Entry	Catalyst	BET Surface Area(m^2g^{-1})	Pore Volume (cm^3g^{-1})	Pore Size (nm)
1	Fe	1086.4	0.52	1.16
2	Ni	1474.80	0.74	1.20
3	Cu	1160.70	0.59	1.17
4	Zn	4.63	0.021	2.78

Table S4. ICP-mass bulk composition of different samples for the determination of the metal content.

Sample name	Fe (w%)	Ni (w%)	Cu (w%)	Zn (w%)
1	/	/	/	5.4550%
2	0.5390%	/	/	3.0015%
3	/	0.3131%	/	4.4428%
4	/	/	0.2978%	3.6114%

3. BBD process

The Box–Behnken design (BBD) is a response surface methodology commonly used to construct quadratic models for multivariable optimization.[2] In BBD, experiments are arranged at the midpoints of the edges of the factor space together with replicated center points, which avoids extreme corner combinations and reduces the total number of runs while enabling reliable estimation of linear, interaction, and quadratic effects. Accordingly, the FDCA yield (Y) was fitted using a second-order polynomial model:

$$Y=-860.41250+22.36563x_1+13.48x_2+53.76136x_3+7.18750\times10^{-3}x_1x_2$$
$$-0.15909x_1x_3+0.023864x_2x_3-0.61250x_1^2-0.070187x_2^2-7.72727x_3^2$$

where x_1 x_2 and x_3 represent the reaction time, temperature, and Na_2CO_3 dosage, respectively.

4. ^{1}H and ^{13}C NMR data for the furan-based compounds

5-Hydroxymethyl-2-furancarboxylic acid (HMFCA) ^{1}H NMR (500 MHz, DMSO) δ 7.14 (d, *J* = 3.4 Hz, 1H), 6.44 (d, *J* = 3.4 Hz, 1H), 4.45 (s, 2H). ^{13}C NMR (126 MHz, DMSO) δ 160.2, 159.9, 144.5, 119.1, 109.5, 56.4.

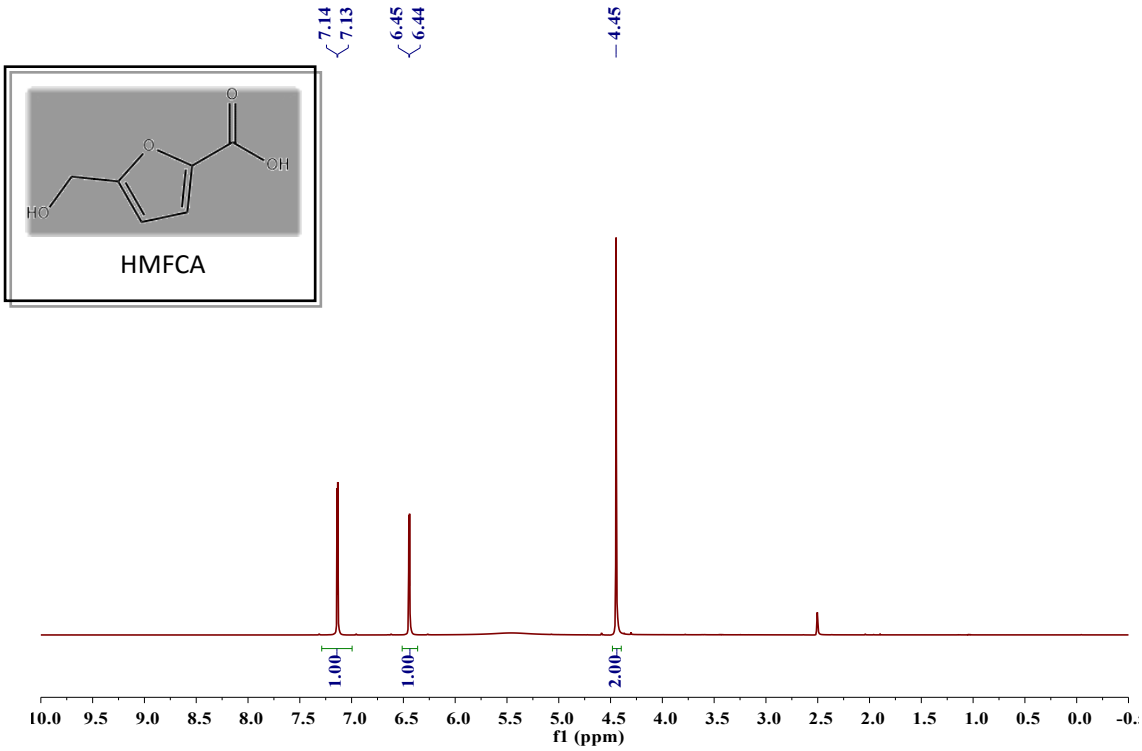
2,5-Furandicarboxylic acid (FDCA) ^{1}H NMR (500 MHz, DMSO) δ 7.42 – 7.14 (m, 1H). ^{13}C NMR (126 MHz, DMSO) δ 159.2, 147.3, 118.7.

5-Hydroxymethylfurfural (HMF) ^{1}H NMR (500 MHz, DMSO) δ 9.54 (s, 1H), 7.48 (d, *J* = 3.5 Hz, 1H), 6.59 (d, *J* = 3.5 Hz, 1H), 5.58 (s, 1H), 4.50 (s, 2H), 3.41 (s, 1H). ^{13}C NMR (126 MHz, DMSO) δ 178.0, 162.2, 151.8, 124.4, 109.7, 56.0.

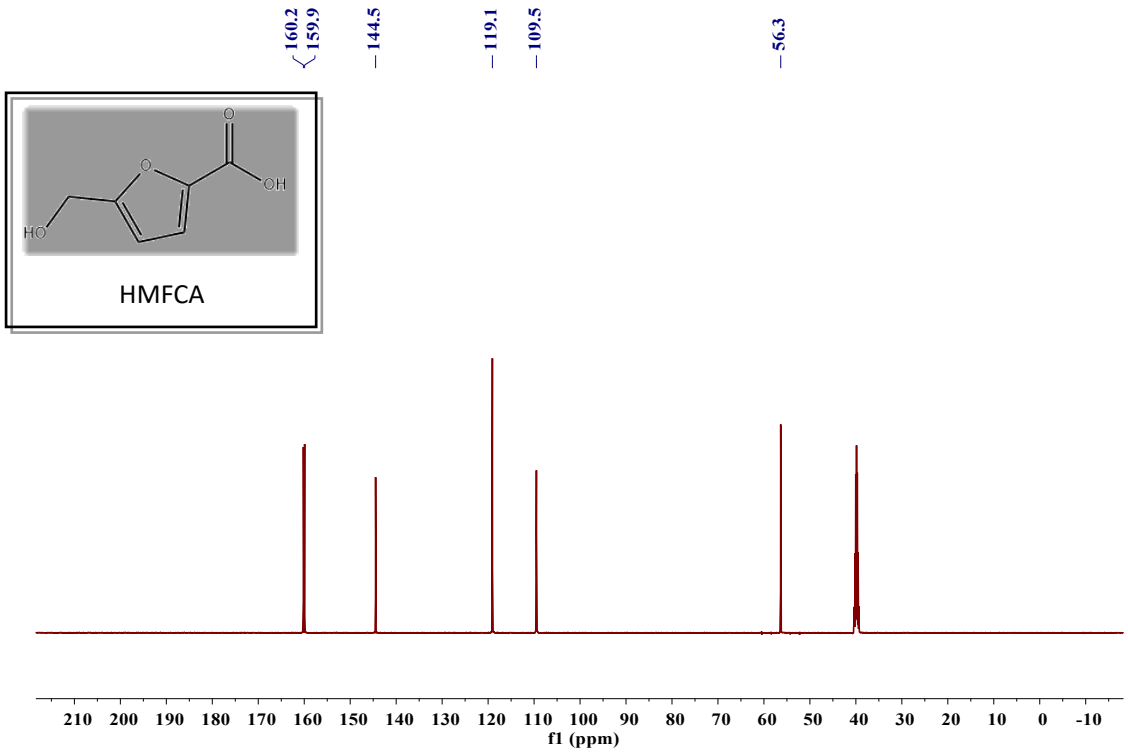
2,5-Furandimethanol (FDM) ^{1}H NMR (500 MHz, DMSO) δ 6.18 (s, 1H), 5.18 (s, 1H), 4.35 (s, 2H). ^{13}C NMR (126 MHz, DMSO) δ 154.7, 107.4, 55.8.

5. Original ^{1}H and ^{13}C NMR spectra for the furan-based compounds

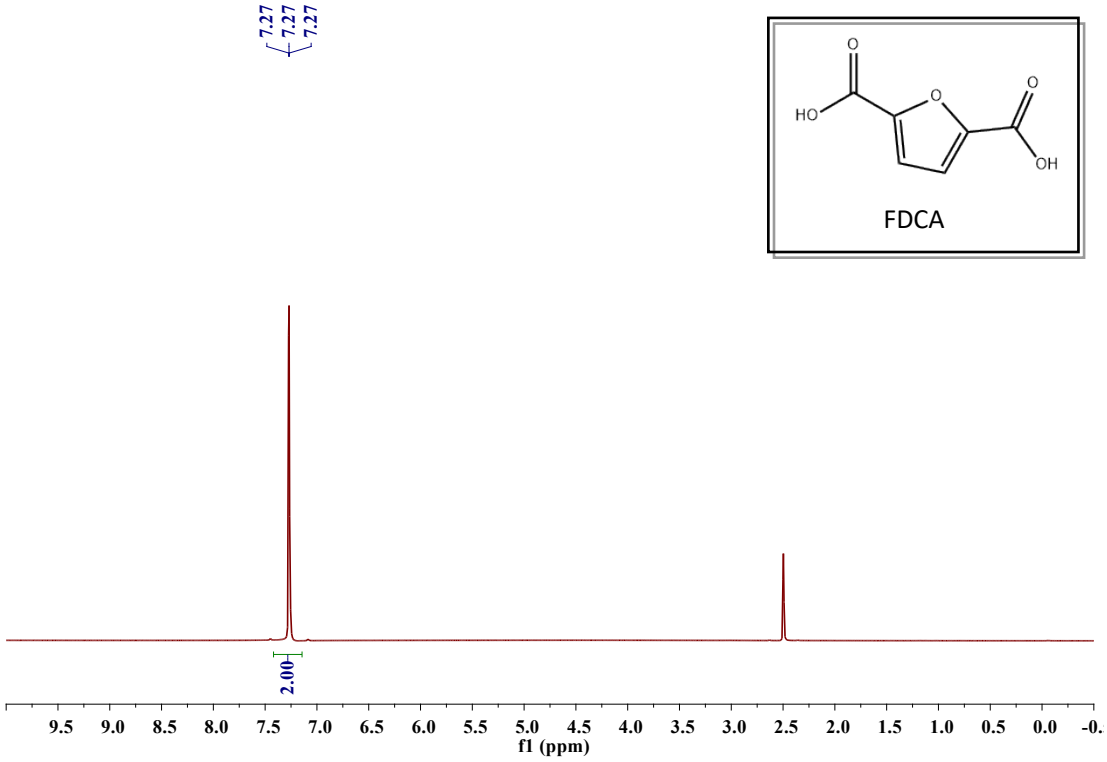
- ^{1}H spectra for **HMFCA**



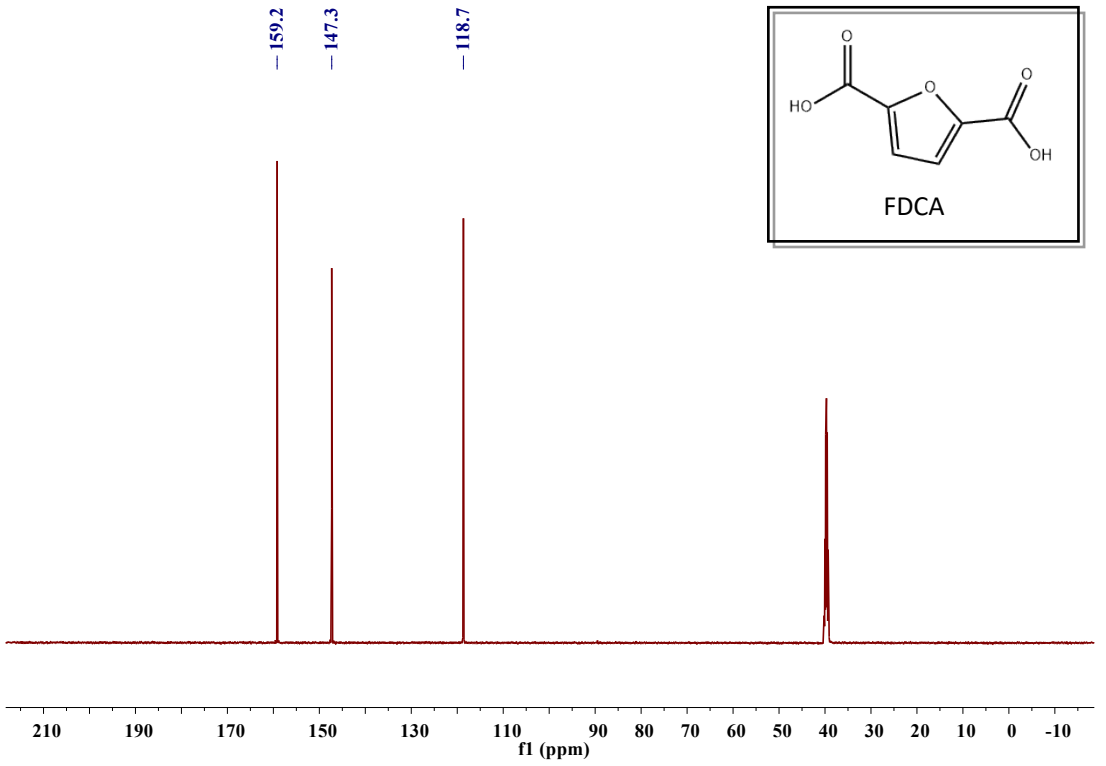
- ^{13}C spectra for **HMFCA**



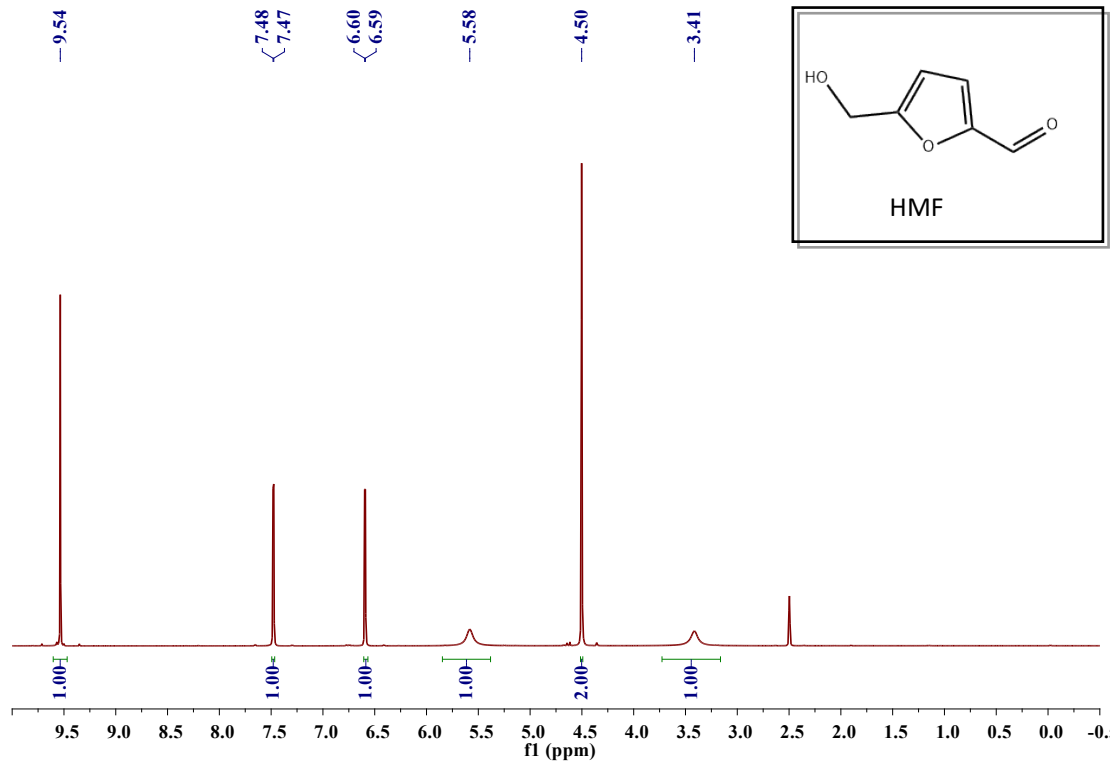
➢ ^{1}H spectra for **FDCA**



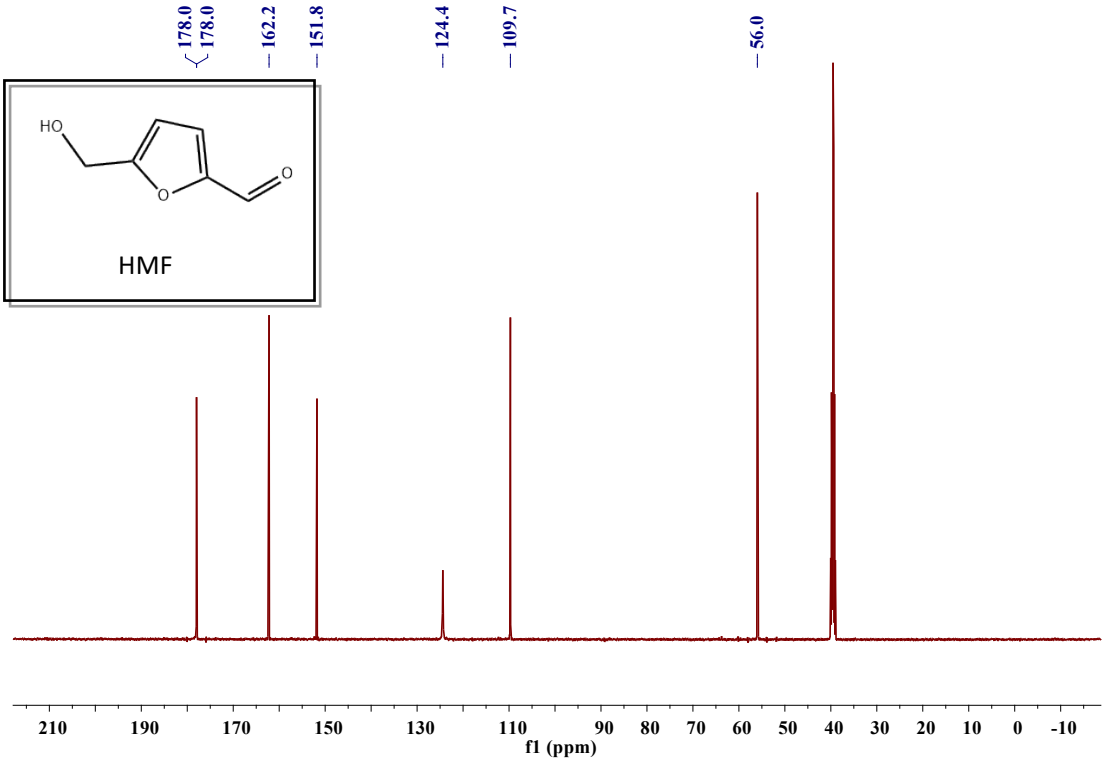
➢ ^{13}C spectra for **FDCA**



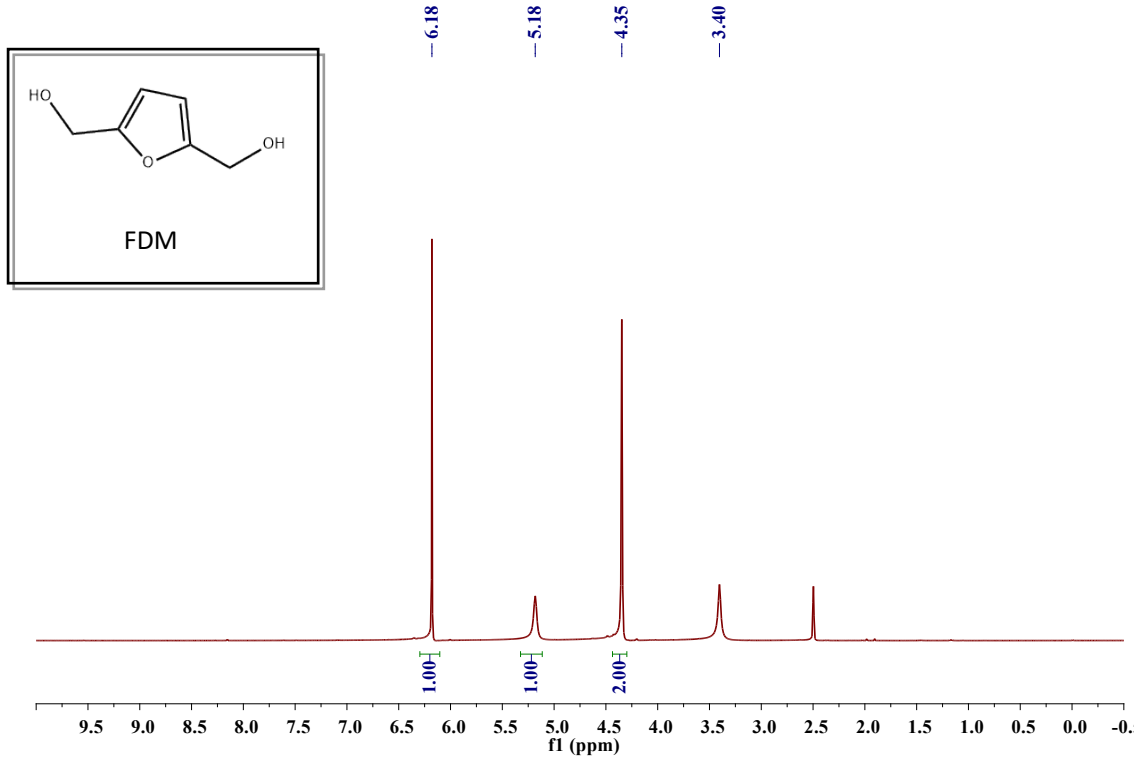
➢ ^{1}H spectra for **HMF**



➢ ^{13}C spectra for **HMF**



➢ ^{1}H spectra for **FDM**



➢ ^{13}C spectra for **FDM**

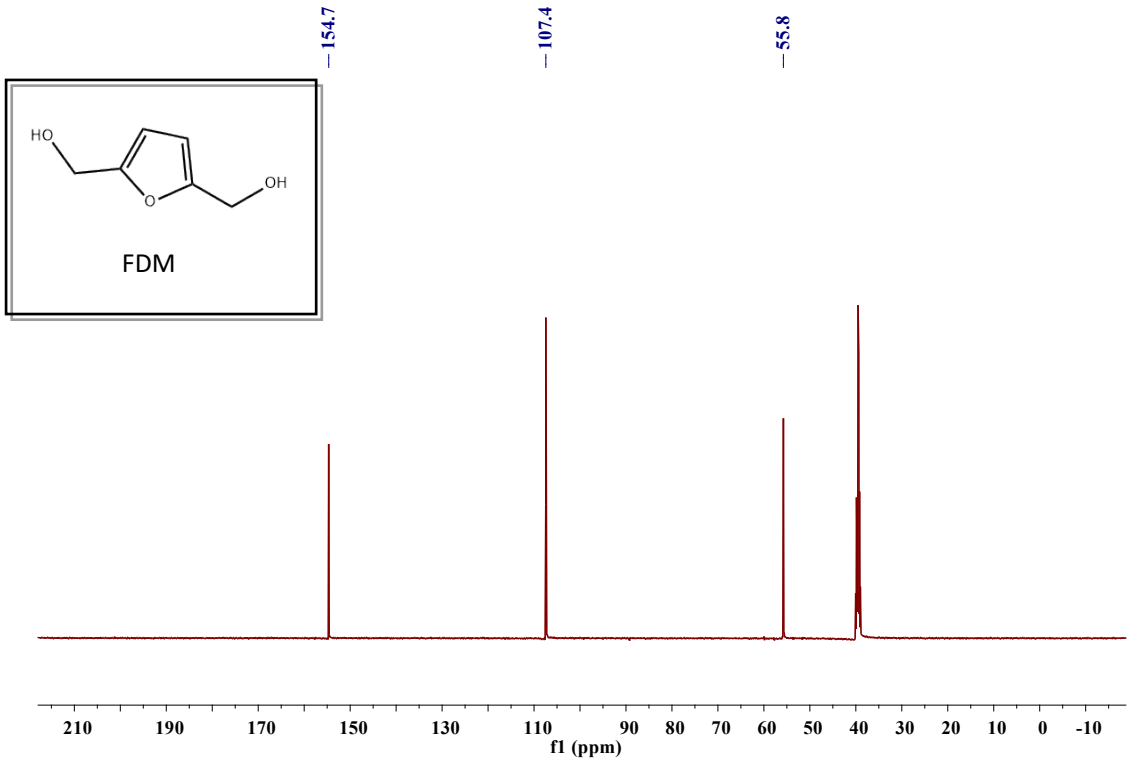


Figure S10 ^{13}C NMR (126 MHz, DMSO) δ 154.7, 107.4, 55.8.

Reference

[1] Ambroz F, Macdonald T J, Martis V, et al. Evaluation of the BET Theory for the Characterization of Meso and Microporous MOFs. Small methods, 2018, 2(11): 1800173.

[2] Guo L, Zhang Y, Chen W, et al. Catalytic Ethylene Oligomerization over Imine-Linked Covalent-Organic Frameworks with Coordinative Ni (II) and Cr (III). ACS Sustainable Chemistry & Engineering, 2025, 13(20): 7520-7531.