

Supplementary Material

Ru/MgO-catalysed selective aerobic oxidation of 5-hydroxymethylfurfural to 2,5-furandicarboxylic acid

Priya Lokhande^{A,B,C}, Paresh L. Dhepe^{A,B,}, Karen Wilson^{D,*} and Adam F. Lee^{D,*}*

^ACatalysis and Inorganic Chemistry Division, Council of Scientific & Industrial Research–National Chemical Laboratory, Dr Homi Bhabha Road, Pune, 411008, India

^BAcademy of Scientific and Innovative Research (AcSIR), Ghaziabad, 201002, India

^CCatalysis, School of Science, RMIT University, Melbourne, Vic. 3001, Australia

^DCentre for Catalysis and Clean Energy, Griffith University, Gold Coast Campus, Southport, Qld 4222, Australia

*Correspondence to: Email: pl.dhepe@ncl.res.in, karen.wilson6@griffith.edu.au, adam.lee@griffith.edu.au

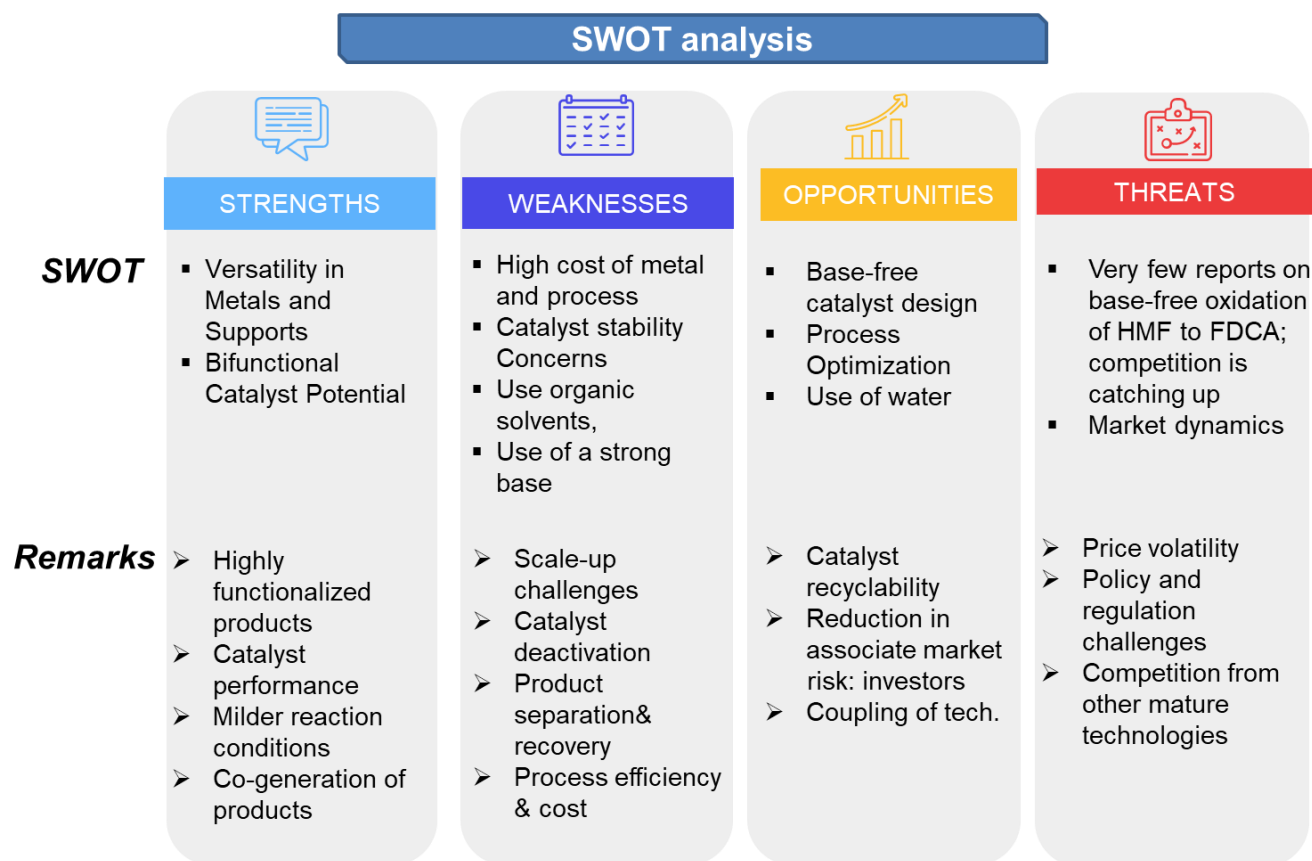


Figure S1. SWOT analysis for the oxidation of HMF to FDCA.

Catalyst characterisation

Powder X-ray diffractograms were recorded on Rigaku D MAX spectrometer using Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) between 5 and 90° at a scan rate of 2° min⁻¹. Transmission electron micrographs were obtained using a FEI TECNAI T20 microscope with an accelerating voltage of 200 kV; samples were dispersed in isopropyl alcohol by ultrasonication and drop cast on a carbon-coated copper grid. Textural properties were determined by N₂ physisorption at -196°C using a Quantachrome Autosorb iQ porosimeter; samples were degassed in vacuo at 150°C for 3 h, with specific surface areas determined by the BET method and mean pore diameters calculated by the BJH method applied to the desorption isotherms. Solid base properties were determined by temperature-programmed desorption of a saturated CO₂ adlayer using a Micromeritics Autochem-2920 instrument: samples were first annealed at 400°C under 40 mL min⁻¹ He for 1 h, then cooled to 50°C under He, prior to exposure to 30 mL min⁻¹ of 10 vol% CO₂ in He for 0.5 h; the sample was then heated to 100°C and flushed with flowing He at 100°C for 1 h to remove physisorbed CO₂; desorption of chemisorbed CO₂ was performed by annealing at 10°C min⁻¹ under 40 mL min⁻¹ He from 100 to 800°C with desorption monitored by a thermal conductivity detector.

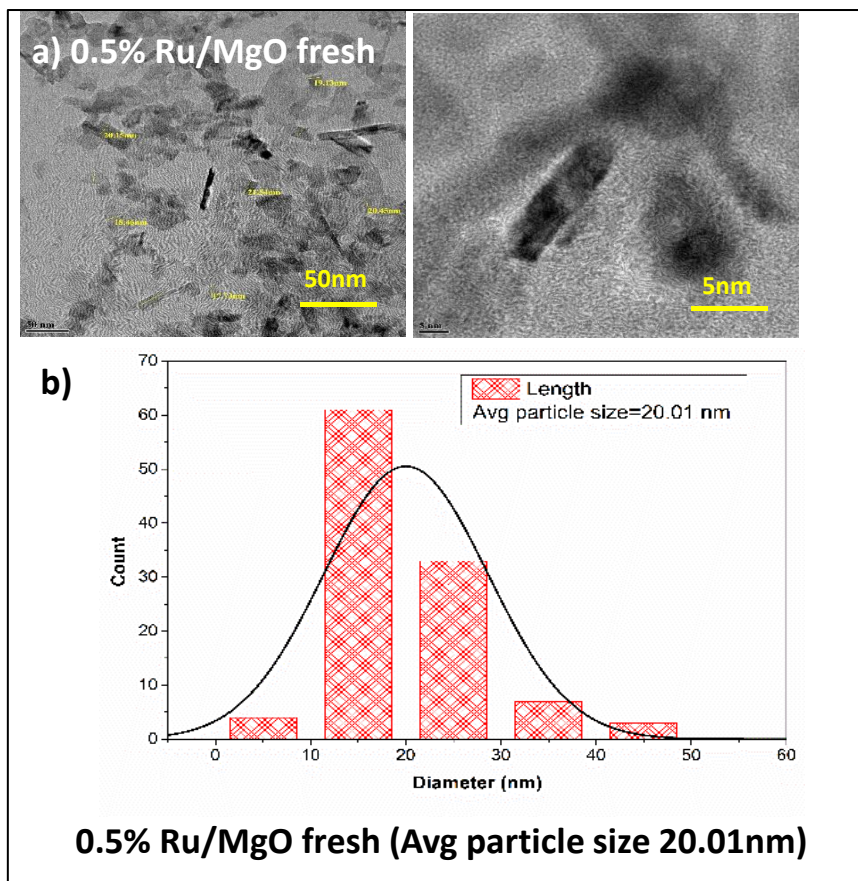


Figure S2. (a) TEM images of 0.5wt% Ru/MgO-300-2h and (b) corresponding Ru particle size distribution.

HMF oxidation

Table S1. Literature review of previous catalytic systems for the oxidation of HMF to FDCA.

Catalyst	Temperature (°C)	O ₂ pressure (bar)	Time (h)	HMF conversion (%)	FDCA yield (%)	References
Ru/MgO.La ₂ O ₃	140	2.5	6	99	96	[1]
2 wt% Ru/MgAlO	140	6	4	100	99	[2]
Au/CeO ₂ (w. NaOH)	130	5	3	100	88	[3]
Au/HT	95	10	7	99	98	[4]
10 wt% Au/HT	90	1	–	98	78	[5]
Pt/C-O-Mg	110	10	12	100	96	[6]
Pd/C@Fe ₃ O ₄	80	1	6	98	96	[7]
Homogeneous Co,Mn and K salts in acetic acid	180	30	0.5	90	90	[8]
Pt/γ-Al ₂ O ₃	140	10	24	96	96	[9]

Table S2. Impact of Ru metal loading (%) for the oxidation of HMF to FDCA.

Catalyst	HMF Conversion (%)	FDCA yield (%)	HMFCFA yield (%)	FFCA yield (%)	DFP yield (%)	Unidentified products (%)
0.1 wt% Ru/MgO 300°C 4 h	90	44	9	17	12	8
0.5 wt% Ru/MgO 300°C 4 h	96	68	4	9	10	5
1 wt% Ru/MgO 300°C 4 h	100	80	2	4	9	5
5 wt% Ru/MgO 300°C 4 h	100	88	2	1	4	5

Reaction conditions: 4 mmol of HMF, 15 bar O₂, Ru/MgO 300°C 4 h (substrate:metal molar ratio=120), 30 mL of deionised water, 160°C, 6.5 h.

Table S3. Controlled reactions for the oxidation of HMF to FDCA.

Control	HMF Conversion (%)	FDCA yield (%)	HMFCFA yield (%)	FFCA yield (%)	DFP yield (%)	Unidentified products (%)
No catalyst	25	12	2	4	–	7
No oxygen	16	7	1	3	–	5

Reaction conditions: 4 mmol HMF, 30 mL of deionised water, 160°C, 6.5 h. No catalyst: 15 bar O₂. No oxygen: Ru/MgO 300°C 4 h (substrate:metal molar ratio=120).

FDCA isolation and characterisation

The post-reaction mixture was centrifuged to remove the solid catalyst, and subsequently acidified to a pH of 2–3 using 0.1 M HCl. Ethyl acetate was then added to extract FDCA from the aqueous phase, and the ester subsequently evaporated to yielding solid FDCA. ¹H NMR (Figure S3), ¹³C NMR (Figure S4), HRMS (Figure S5) and FTIR (Figure S6) evidenced that the isolated FDCA was >99% pure.

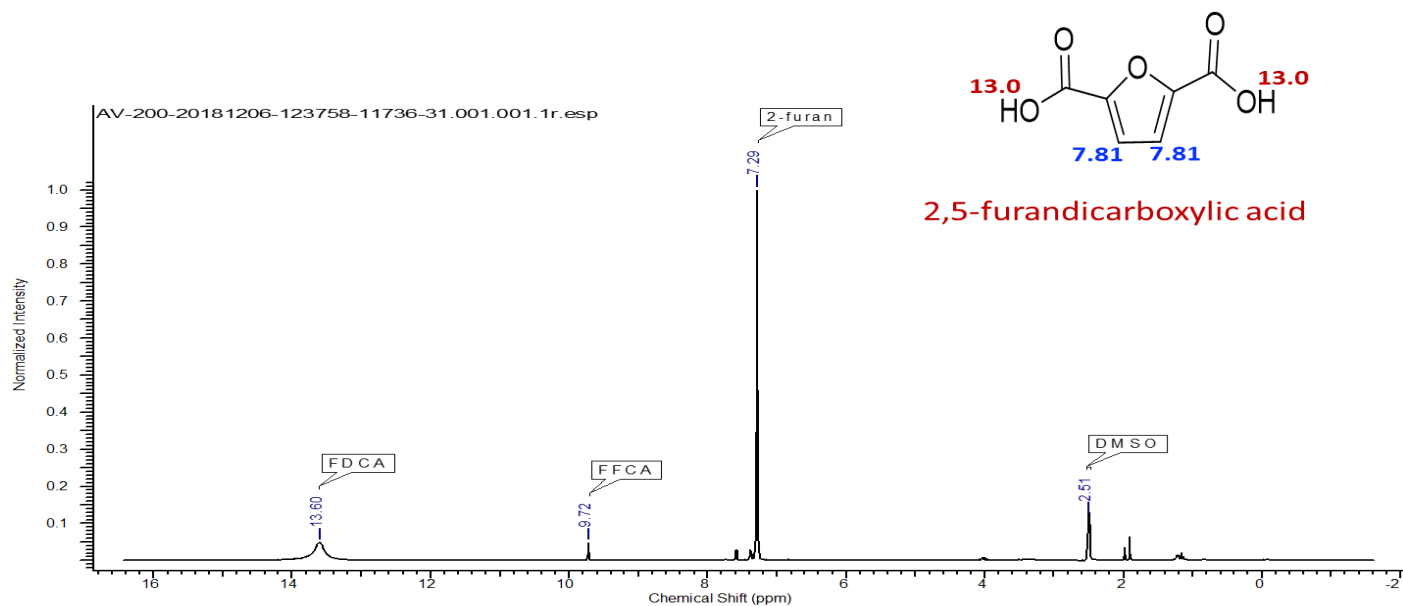


Figure S3. ^1H NMR spectrum of isolated FDCA obtained after the reaction. Solvent: DMSO.

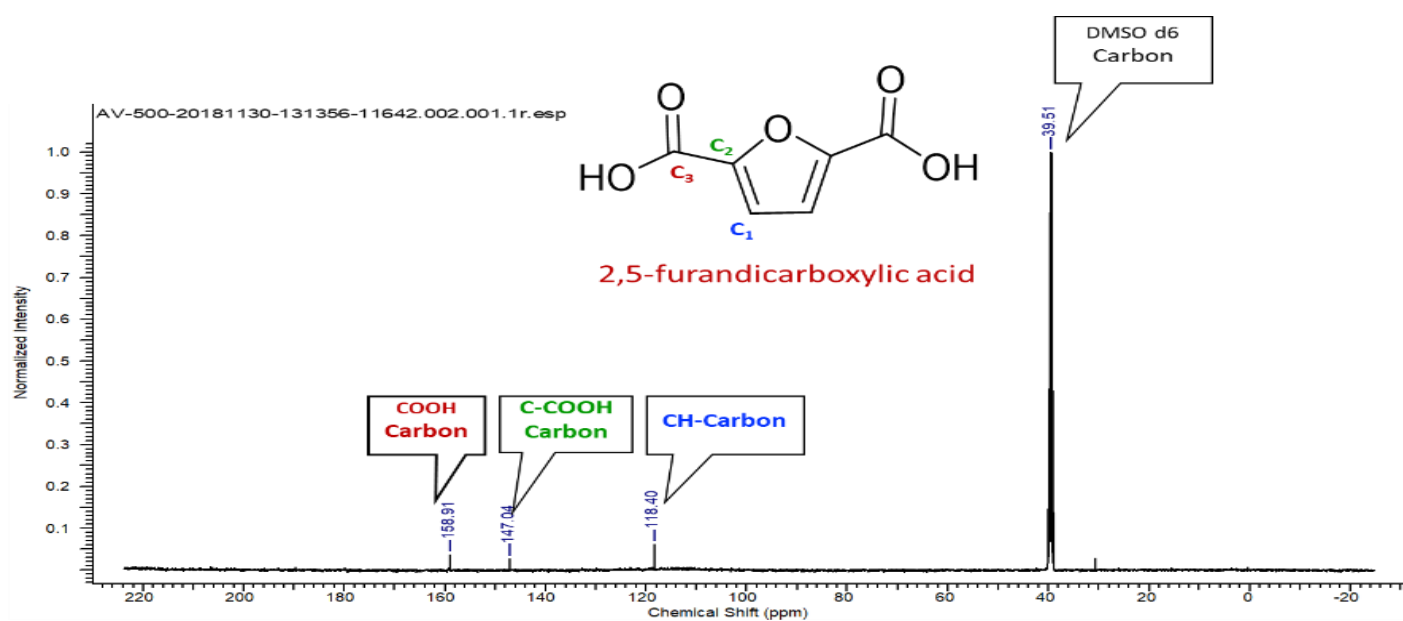


Figure S4. ^{13}C NMR spectrum of isolated FDCA obtained after the reaction. Solvent: DMSO.

c2 #521 RT: 2.32 AV: 1 NL: 7.65E7
T: FTMS + p ESI Full ms [100.0000-1500.0000]

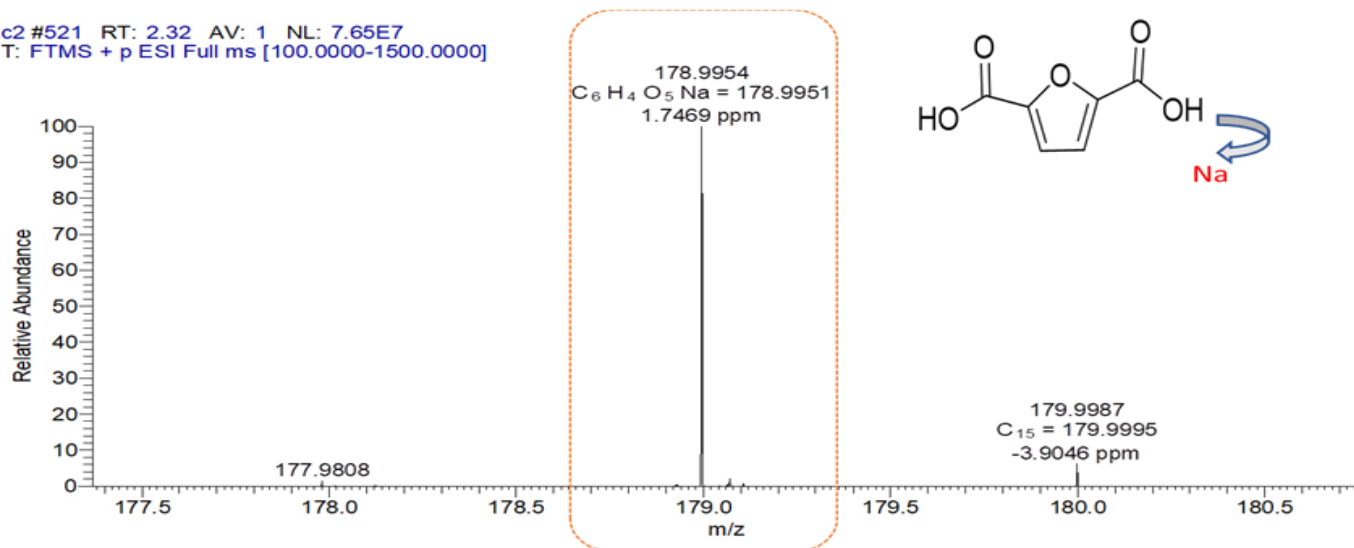
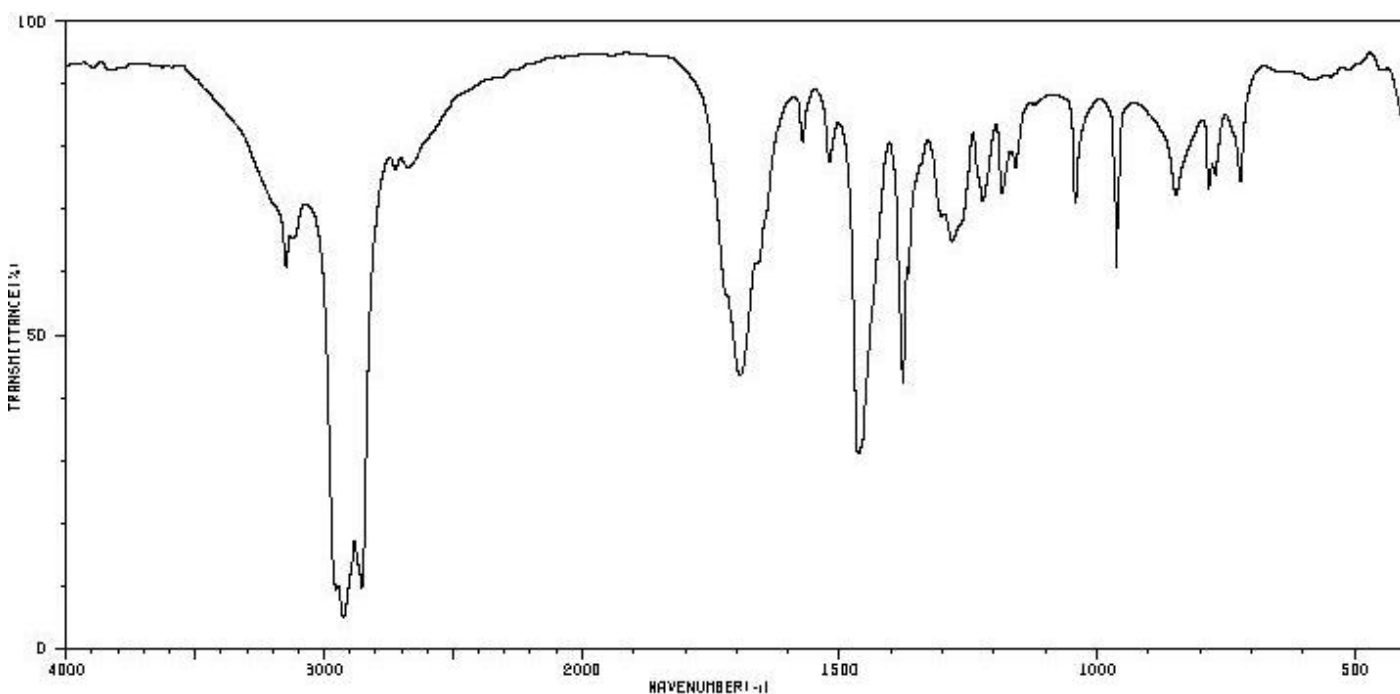
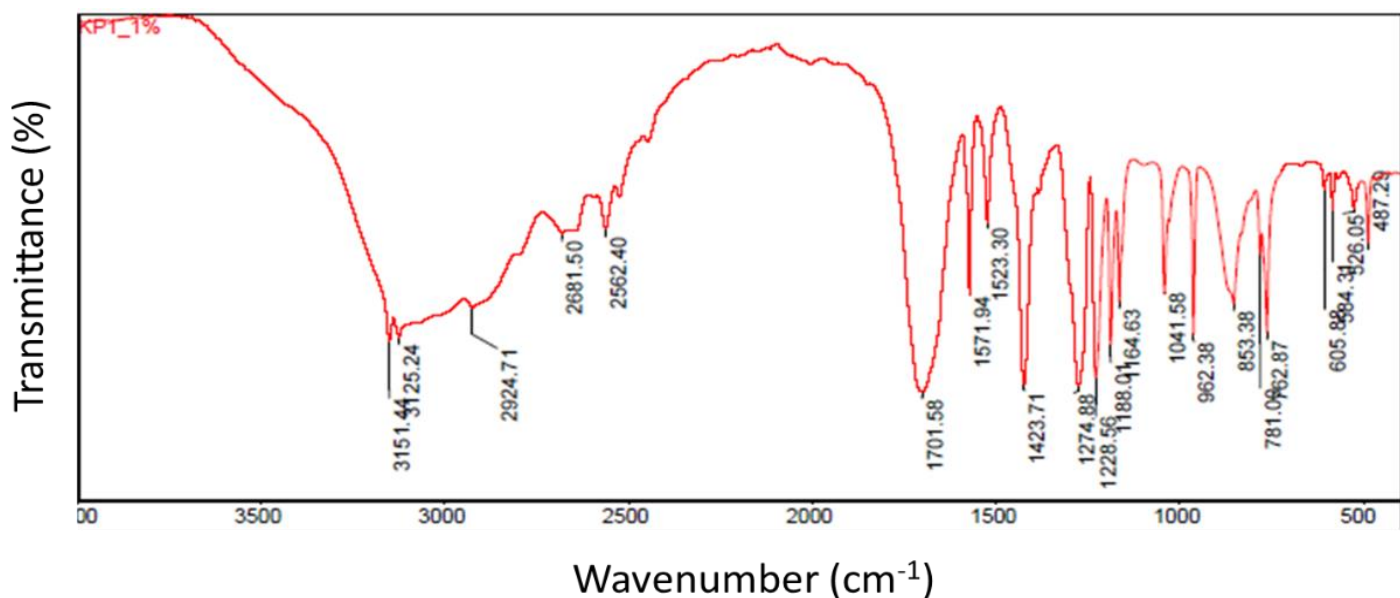


Figure S5. High resolution mass spectra of isolated FDCA post-reaction. The peak at m/z 179 [M+Na] in the HR-MS profile confirmed the formation of Na salt of FDCA.



3147	68	1692	42	1222	68	784	70
3128	62	1572	77	1185	70	777	74
3118	82	1520	74	1170	77	771	72
2924	4	1464	30	1158	74	722	72
2854	9	1378	41	1042	68		
2725	72	1367	57	962	58		
2673	74	1282	62	847	70		

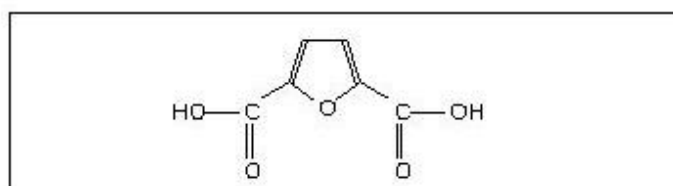


Figure S6. (top) FTIR spectrum of isolated FDCA obtained post-reaction: (ν cm^{-1}) 3151, 3125 ($-\text{OH}$); 1701 ($\text{C}=\text{O}$); 1571, 1423 (furan Ring $-\text{C}=\text{C}-$); 1274 (ester $-\text{C}-\text{O}-$), 1228 (furan ring $-\text{C}-\text{O}$); 962, 853, 762 ($=\text{CH}$). (bottom) reference spectra from Chemical Book (https://www.chemicalbook.com/SpectrumEN_3238-40-2_IR2.htm) on non-linear wavenumber scale.

References

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