# Supporting Information

## Polymer Monomers Fabricated from Biomass Platform Molecules over Metal-free Catalysts

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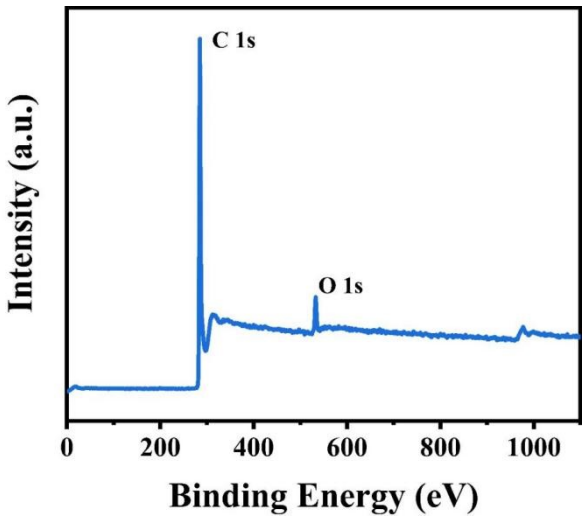



**Fig. S1.** The XPS survey scan of the MCC-800 catalyst.

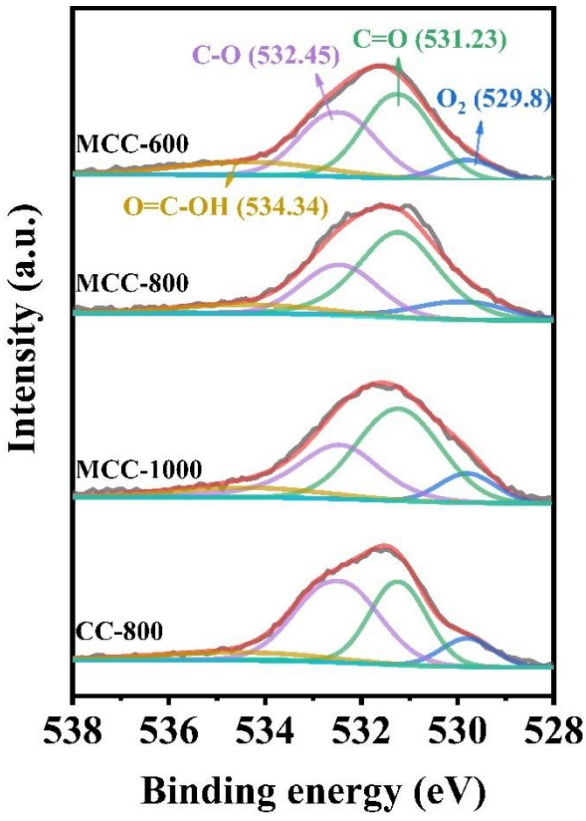



**Fig. S2.** O 1s XPS spectra of the as-prepared catalysts.

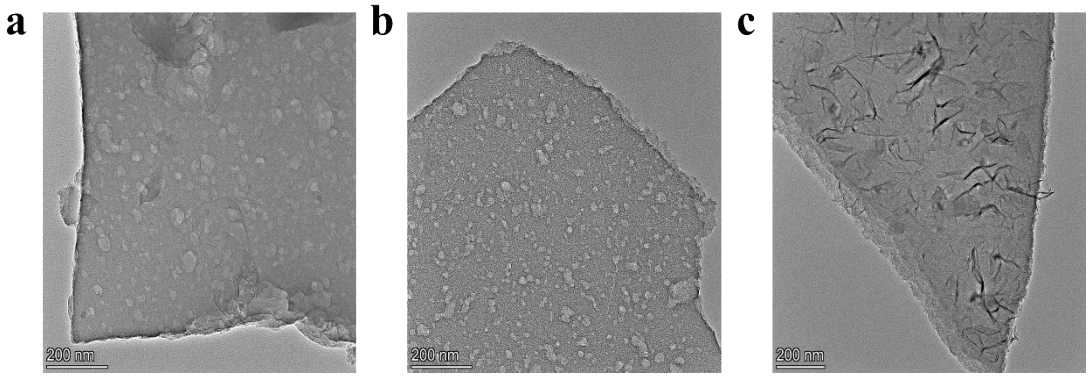



**Fig. S3.** TEM images of MCC-T catalysts. (a) MCC-600; (b) MCC-800; (c) MCC-1000

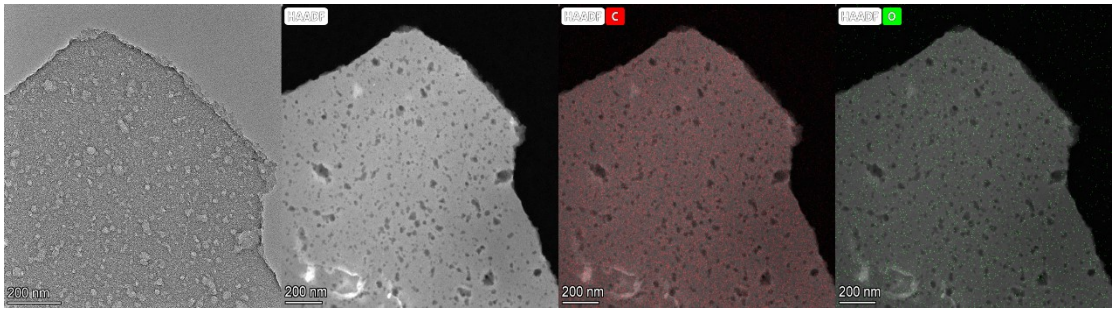



**Fig. S4.** TEM image for MCC-800 catalyst, HADDF-STEM image and corresponding EDX elemental mapping images for MCC-800 catalyst.

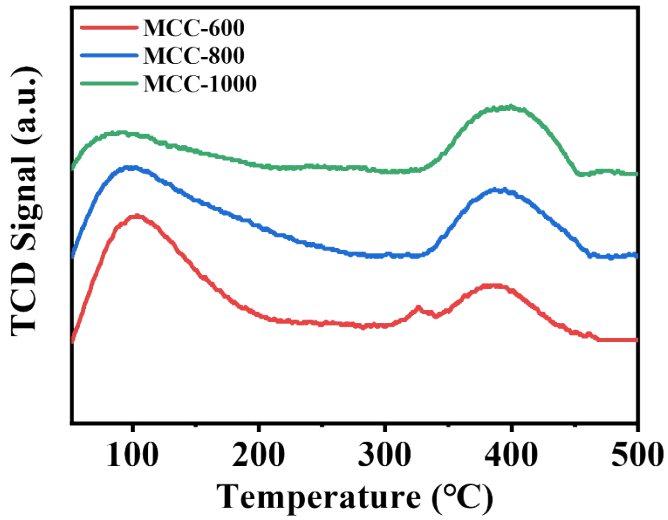



**Fig. S5.** NH3-TPD curves of as-prepared MCC-T and CC-800 catalysts.

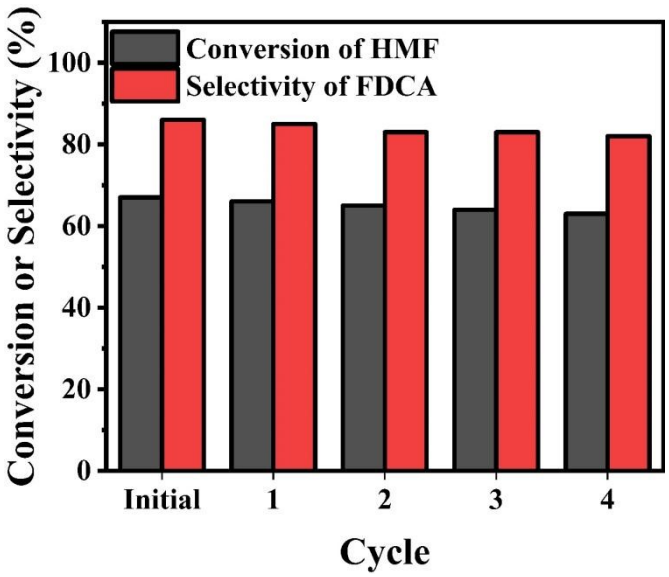



**Fig. S6.** Reuse of MCC-800 catalyst. Reaction conditions: HMF (1 mmol), $K_2CO_3$ (1 mmol), the MCC-800 catalyst (50 mg), Methanol (10 mL), 80 °C, 10 bar $O_2$ and 8 h.

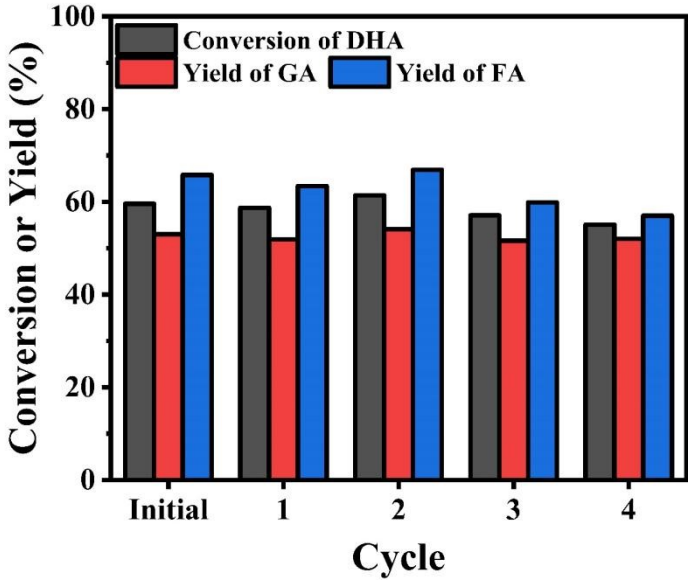



**Fig. S7.** Reuse of MCC-800 catalyst. Reaction conditions: DHA (1 mmol), $H_2O_2$ (4 mmol), the MCC-800 (20 mg), $H_2O$ (10 mL), 30 °C and 12 h

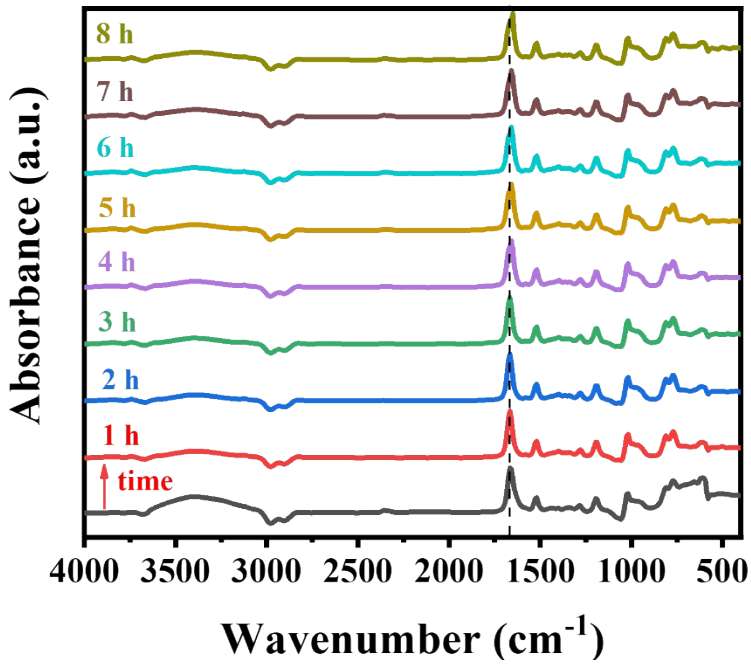



**Fig. S8.** Operando ATR-FTIR spectra during conversion of HMF

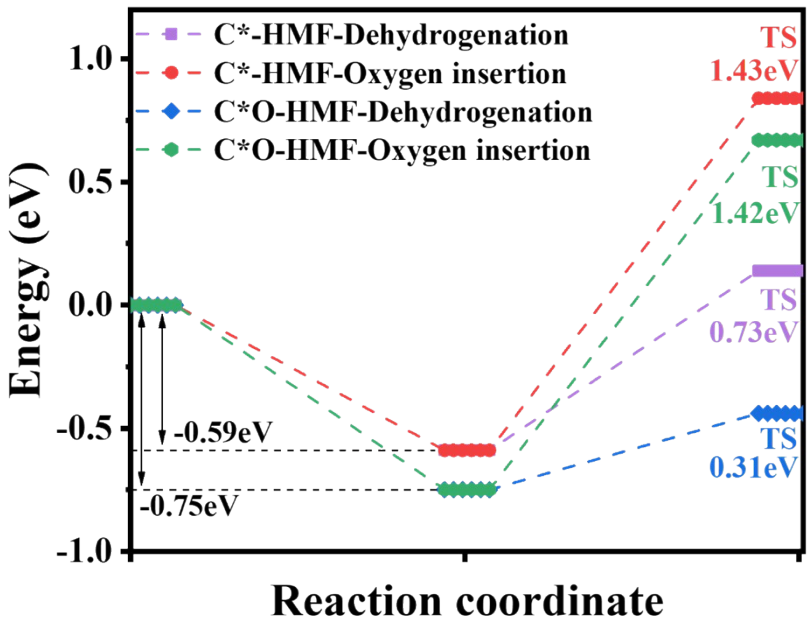



**Fig. S9.** DFT calculations for the HMF transformation.

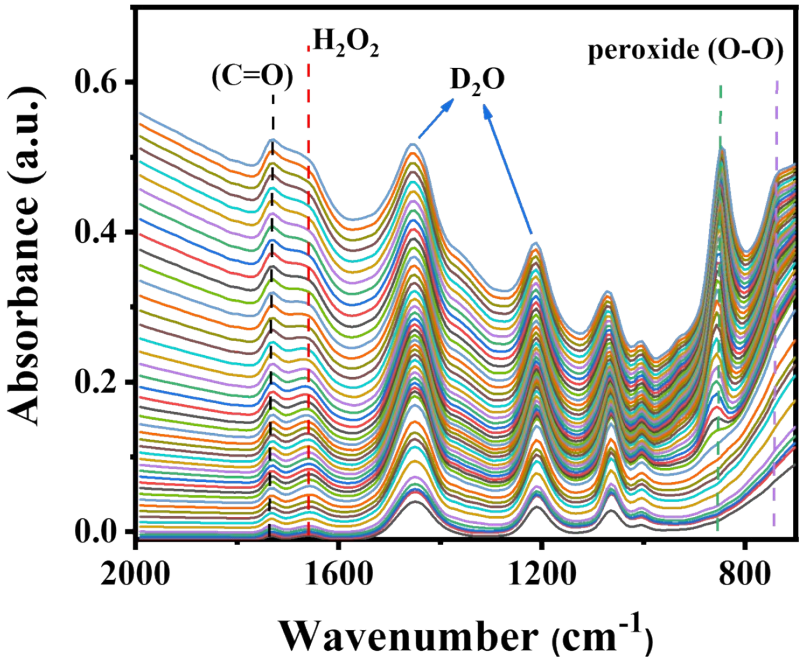



**Fig. S10.** Operando ATR-FTIR spectra during conversion of DHA

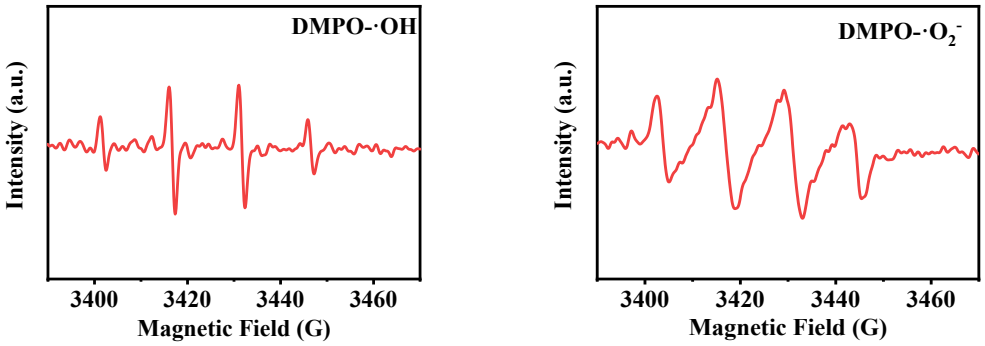



**Fig. S11.** EPR signals of ·OH and $\cdot O_2^-$.

# Tables

**Table S1.** Area-based peak proportions in the XPS C 1s spectra of as-prepared materials.

| Catalyst | C $sp^2$ (284.8 eV) (%) | C $sp^3$ (285.2 eV) (%) | O-C-O (287.5 eV) (%) | C=O (289.1 eV) (%) | $sp^3/sp^2$ area ratio |
|---|---|---|---|---|---|
| MCC-600 | 55.05 | 30.55 | 2.04 | 12.36 | 0.55 |
| MCC-800 | 47.09 | 34.03 | 3.76 | 15.12 | 0.72 |
| MCC-1000 | 57.42 | 20.52 | 9.55 | 2.85 | 0.35 |
| CC-800 | 48.77 | 33.34 | 3.34 | 14.55 | 0.68 |

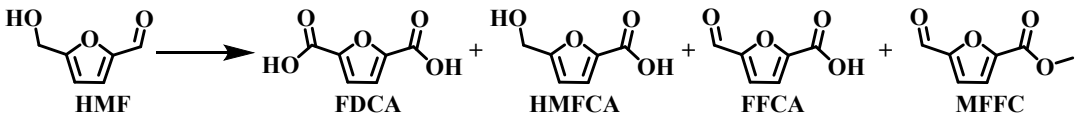
**Table S2.** Area-based peak proportions in the XPS O 1s spectra of as-prepared materials

| Catalyst | C=O (531.23 eV) (%) | C-O (532.45 eV) (%) | O=C-OH (534.34 eV) (%) | $O_2$ (529.8 eV) (%) |
|---|---|---|---|---|
| MCC-600 | 42.80 | 35.14 | 13.48 | 8.57 |
| MCC-800 | 52.55 | 26.60 | 9.06 | 11.79 |
| MCC-1000 | 49.38 | 31.58 | 8.77 | 10.27 |
| CC-800 | 35.11 | 46.00 | 8.80 | 10.10 |

**Table S3.** The textural parameters of the MCC-T and CC-800 catalysts

| Catalyst | Surface area ($m^2/g$) | | Pore size (nm) | | Pore volume ($cm^3/g$) | |
|---|---|---|---|---|---|---|
| | Meso | Micro | Meso | Micro | Meso | Micro |
| MCC-600 | 62.3 | 123.2 | 13.51 | 0.60 | 0.086 | 0.042 |
| MCC-800 | 576.4 | 764.6 | 3.42 | 0.55 | 0.50 | 0.39 |
| MCC-1000 | 465.3 | 732.7 | 4.51 | 0.54 | 0.49 | 0.30 |
| CC-800 | 525.3 | 445.7 | 5.58 | 0.55 | 0.39 | 0.16 |

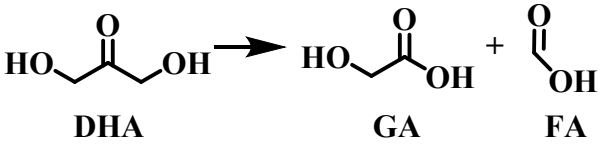
**Table S4.** HMF conversion and product distribution along witg reaction time over the MCC-800 catalyst




| Entry | Time (h) | Conversion (%) | Yield (%) | | | |
|---|---|---|---|---|---|---|
| | | | FDCA | HMFCA | FFCA | MFFC |
| 1 | 2 | 35 | 18 | 1 | 14 | 2 |
| 2 | 4 | 49 | 36 | 1 | 9 | 3 |
| 3 | 8 | 67 | 58 | 1 | 5 | 3 |
| 4 | 16 | 86 | 77 | 1 | 3 | 4 |
| 5 | 24 | 96 | 90 | 1 | 1 | 4 |

Reaction conditions: 80 ℃，1.0 mmol HMF, 50 mg MCC-800，1 eq. K2CO3，10 ml MeOH，1 MPa $O_2$.

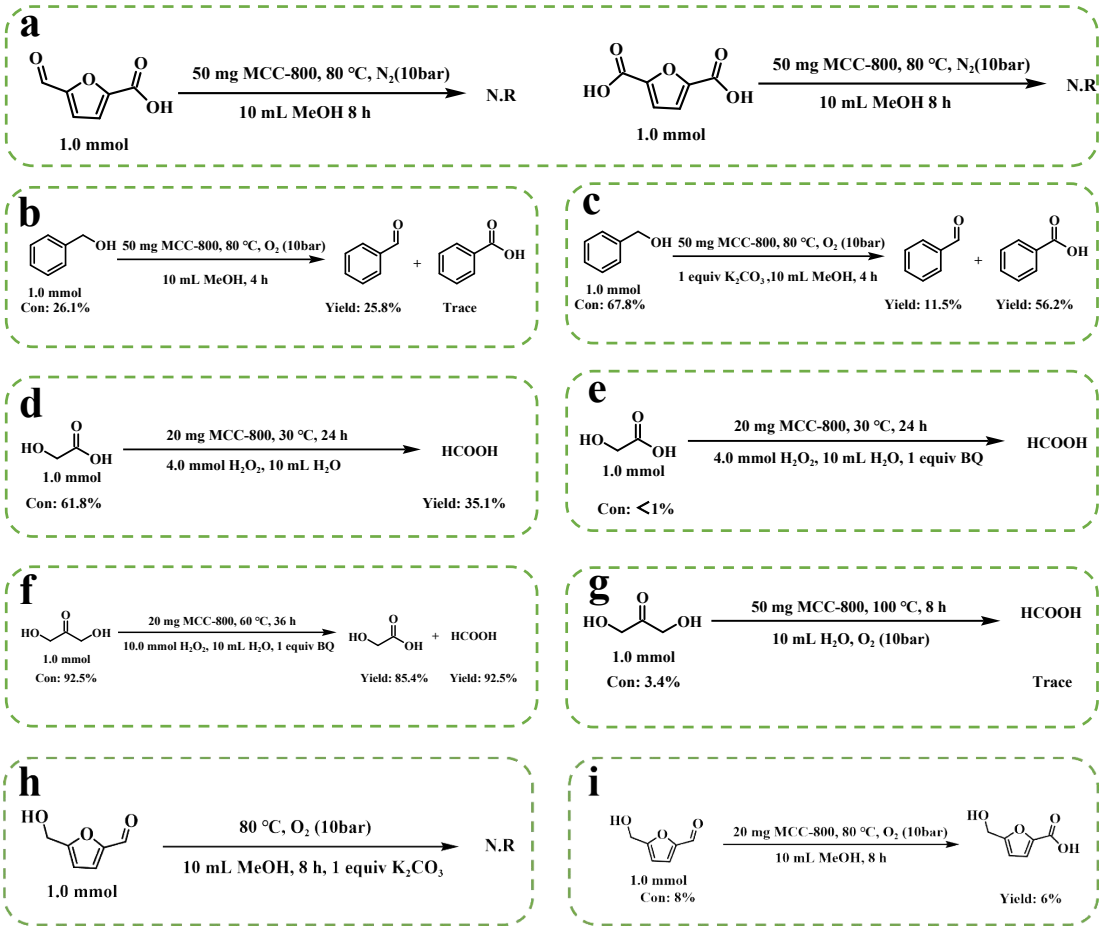
**Table S5.** DHA conversion and product distribution along witg reaction time over the MCC-800 catalyst




| Entry | Time (h) | Conversion (%) | Yield (%) | |
|---|---|---|---|---|
| | | | GA | FA |
| 1 | 2 | 12.0 | 12.0 | 12.0 |
| 2 | 4 | 20.7 | 20.7 | 20.7 |
| 3 | 6 | 32.9 | 32.9 | 32.9 |
| 4 | 8 | 41.0 | 41.0 | 41.0 |
| 5 | 12 | 59.6 | 53.0 | 65.8 |
| 6 | 16 | 66.5 | 54.7 | 74.0 |
| 7 | 20 | 74.8 | 54.8 | 78.0 |
| 8 | 24 | 87.9 | 53.1 | 85.3 |

Reaction conditions: 1.0 mmol DHA, 20mg MCC-800，4 mmol $H_2O_2$, 10 ml $H_2O$.

# Scheme




**Scheme S1.** Control experiments.