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# Supporting Information

## Industrially oriented method for the aqueous phase oxidation of crude 5-hydroxymethyl furfural (HMF) to 2,5-furandicarboxylic acid (FDCA)

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**Table S1:** Summary on the non-noble metal catalysts for the oxidation of HMF to FDCA

| Entry | Name of the catalyst | Reaction Conditions | FDCA Yield (%) | HMF conversion (%) | References |
|---|---|---|---|---|---|
| 1 | Fe-POP | 10 bar $O_2$,100$^oC$,10h, | 79 | 100 | [1] |
| 2 | $Fe_3O_4$-$CoO_X$ | t-BuOOH,80$^oC$,12h | 68.6 | 97.2 | [2] |
| 3 | $Fe_{0.6}Zr_{0.4}O_2$ | (Bmim)Cl, 20 bar $O_2$,160$^oC$,24h, | 60.6 | 99.7 | [3] |
| 4 | $Ce_{0.5}Fe_{0.15}Zr_{0.35}O_2$ | (Bmim)Cl, 20 bar $O_2$,140$^oC$,24h | 44.2 | 99.9 | [4] |
| 5 | $MnO_2$ | $NaHCO_3$, 10 bar $O_2$,100$^oC$,24h | 91 | 99 | [5] |
| 6 | MOF-$Mn_2O_3$ | $NaHCO_3$, 14 bar $O_2$,100$^oC$,24h | 99.5 | 100 | [6] |
| 7 | $MnO_x$-$CeO_2$ | $KHCO_3$, 20 bar $O_2$,110$^oC$,15h | 91 | 98 | [7] |
| 8 | $MnCO_2O_4$ | $KHCO_3$, 20 bar $O_2$,100$^oC$,24h | 70.9 | 99.5 | [8] |
| 9 | $Co_3O_4$/$Mn_xCo$ | Base free, 14 bar $O_2$,140$^oC$,24h | 99 | 100 | [9] |
| 10 | NNC-1173 | $K_2CO_3$, 1 bar $O_2$,80$^oC$,48h | 80 | 100 | [10] |
| 11 | Co-$Mn_{0.25}$ | $NaHCO_3$,10 bar $O_2$,120$^oC$, 5h | 95 | 99 | [11] |
| 12 | Co/Mn/Br | 1/0.015/0.5 molar ratio of Co, Mn, and Br, 7% (v/v) water, 30 bar ($CO_2$/$O_2$ = 1/1, mol/mol), 180$^oC$,0.5h | 90 | 99 | [12] |
| 13 | $Mn_xFe_y$ | NaOH,8 bar $O_2$,90$^oC$, 24h | 30 | 93 | [13] |
| 14 | $Li_2CoMn_3O_8$ | NaOH, NaBr, Acetic acid, water, 55 bar $O_2$,150$^oC$, 8h | 85 | 100 | [14] |
| 15 | CuCl | t-BuOOH, MeCN, TEMPO, RT, 48h | 45 | 100 | [15] |

**Catalyst characterization**

**X-ray diffraction study (XRD)**

In Figure 1. traces of CuO were also detected in the XRD pattern. Peaks for MnOx, along with $Mn_3O_4$ also have some contribution.

$Mn_2O_3$ (Cubic),2θ = 18°,33.5°, 36°, 41°,54°

$MnO_2$ (00-050-0866) and $Mn_2O_3$ (00-001-1061)

CuO ( 00-045-0937 and 00-003-0884) $Cu_{1.5}Mn_{1.5}O_4$ (00-035-1171)

$Cu_2O$ plain 110 (30°),111 (36°),200 (43°),211 (53°),220 (61°), (JCPDS 01-071-3645 and 05-0667)

**Table S2:** Summary of the results obtained by using different mixed metal oxides on crude HMF (80-90%) oxidation

| Sr. No. | Catalyst (M:M' mol ratio) | Temp. (°C) | Time (h) | Press.O2 (bar) | FDCA Sel. (%) | HMF Conv. (%) |
|---|---|---|---|---|---|---|
| 1 | Without catalyst | 120 | 6 | 10 | 4 | 90 |
| 2 | Co-Mn (1:4) | 120 | 4 | 10 | 65 | 100 |
| 3 | Co-Mn-Ce (1:4:1) | 120 | 4 | 10 | 30 | 78 |
| 4 | | | 6 | | 53 | 96 |
| 5 | | | 8 | | 52 | 98 |
| 6 | Co-Mn-Ce (1:4:0.25) | 120 | 4 | 10 | 67 | 95 |
| 7 | | | 6 | | 75 | 100 |
| 8 | | 140 | 6 | 6 | 80 | 100 |
| 9 | Co-Mn-Fe (1:4:1) | 120 | 4 | 10 | 68 | 95 |
| 10 | | | 8 | 15 | 78 | 98 |
| 11 | Co-Mn-Fe-Zr (1:4:0.5:0.5) | 120 | 4 | 10 | 62 | 95 |
| 12 | | | 8 | | 67 | 97 |
| 13 | Cu-Mn (1:4) | 120 | 4 | 10 | 75 | 92 |
| 14 | | | 8 | 15 | 90 | 100 |
| 15 | Co-Mn-Zr (1:4:1) | 120 | 8 | 10 | 68 | 100 |
| 16 | | 140 | 6 | 12 | 73 | 100 |

| | | | | | | |
|---|---|---|---|---|---|---|
| 17 | Mn-Fe-Cu (4:1:1) | 120 | 6 | 10 | 19 | 97 |
| 18 | Mn-Fe-Ce (4:1:0.25) | 140 | 6 | 6 | 54 | 96 |
| 19 | Co-Cu-Mn (1:1:4) | 120 | 10 | 10 | 42 | 100 |
| 20 | Co-Mn-V (1:4:1) | 120 | 6 | 10 | 2 | 53 |
| 21 | Co-Cu-Mn-Ce (1:1:4:0.25) | 120 | 6 | 10 | 60 | 92 |
| 22 | Co-Cu-Mn-Fe(1:1:4:1) | | | | 62 | 95 |
| 23 | Co-Mn/HT | | | | 52 | 92 |
| 24 | Co-Mn-Ce/HT | | | | 59 | 96 |
| 25 | Cu-Mn-Ce (1:4:0.25) | | | | 49 | 88 |
| 26 | Cu-Mn-Fe-Zr(1:4:1:1) | | | | 54 | 93 |
| 27 | Ru/Co-Mn (1:4) | 120 | 6 | 10 | 75 | 95 |
| 28 | Ru-Co-Mn-Ce (1:4:0.25) | | | | 85 | 100 |
| 29 | Ru-Cu-Mn (1:4) | | | | 83 | 100 |
| 30 | #Ru/Carbon | | 4 | | 93 | 100 |
| 31 | Ru-Co-Mn-Ce/C (1:4:0.25) | | | | 90 | 100 |
| 32 | Co/NG | 120 | 8 | | 35 | 98 |
| 33 | $CuO_x$/MC | 120 | 6 | | 45 | 100 |
| 34 | $MnO_x$-$CoO_x$/MC | 120 | 6 | | 35 | 100 |
| 35 | CuMn/NG | 120 | 8 | | 53 | 100 |

*Reaction condition: 0.5wt% Solution of crude HMF (Purity 80-90%), Catalyst (0.5 g), Water (30mL), Base ($Na_2CO_3$: 0.15 g). (MC= Mesoporous carbon, NG= Nitrogen-doped graphene) #0.25 g catalyst. *Note: When a solid base is used in the reaction, homogeneous base is not used*.

**Product analysis and characterization**

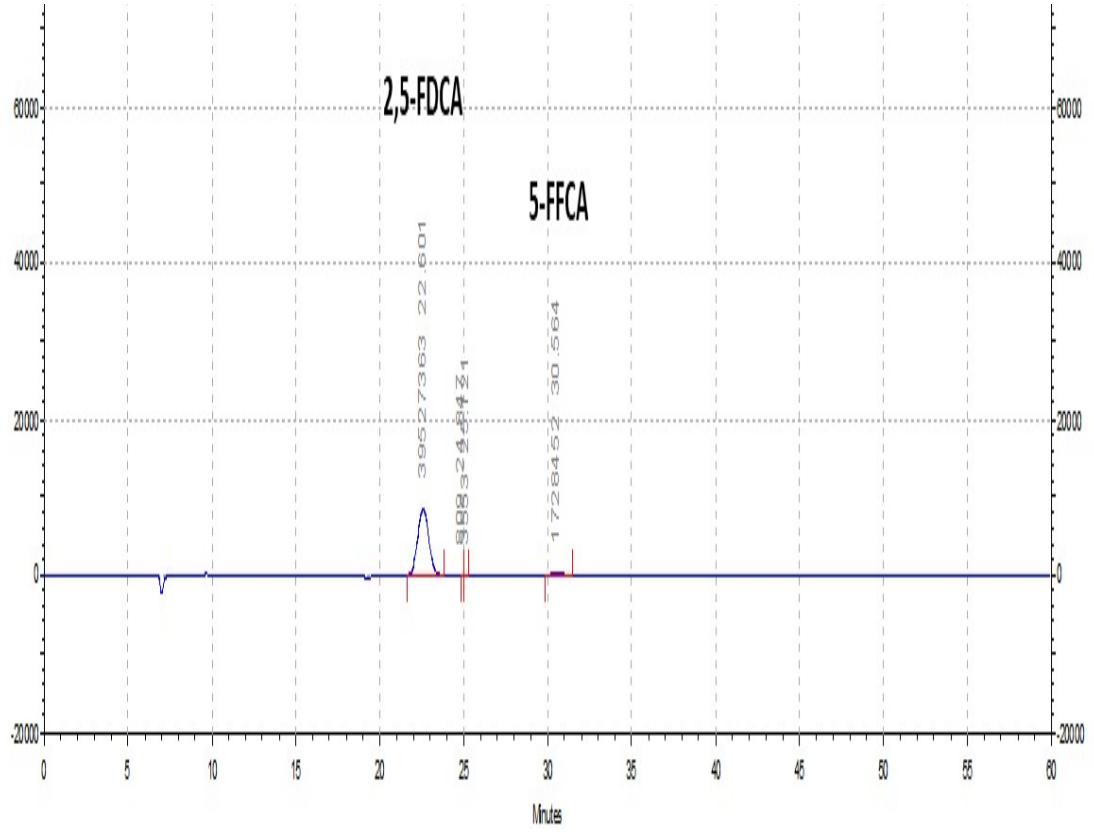


**Figure S1**. HPLC profile of the reaction mixture

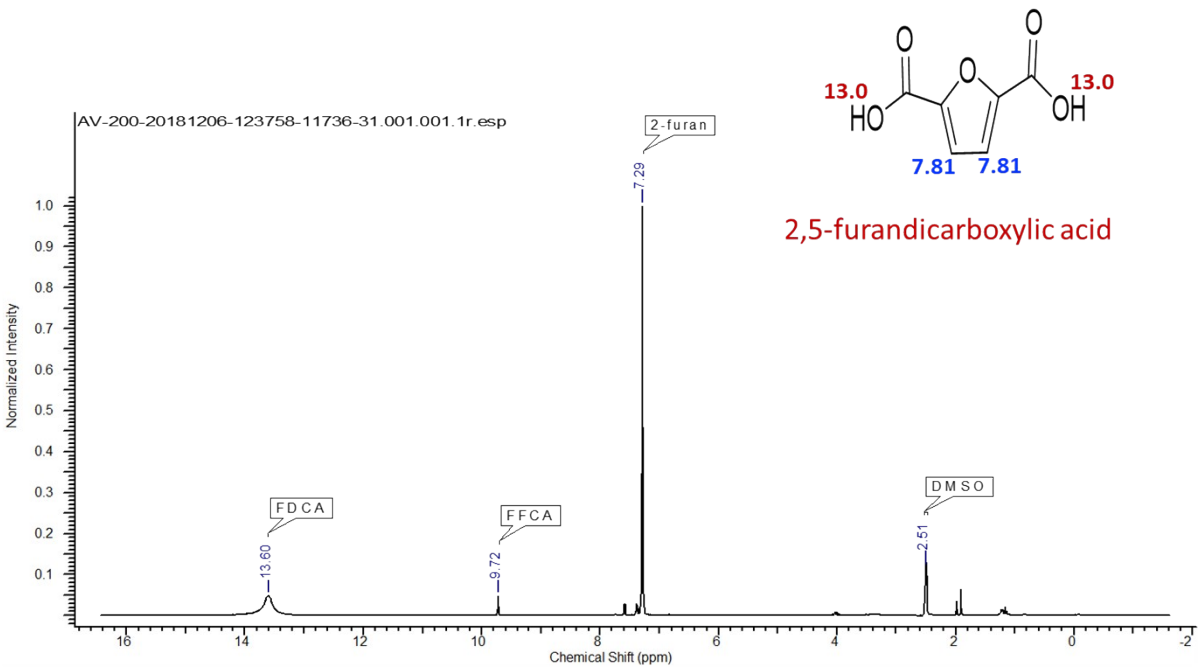


**Figure S2**. $^{1}$H NMR spectrum of isolated FDCA obtained after the reaction. Solvent: DMSO

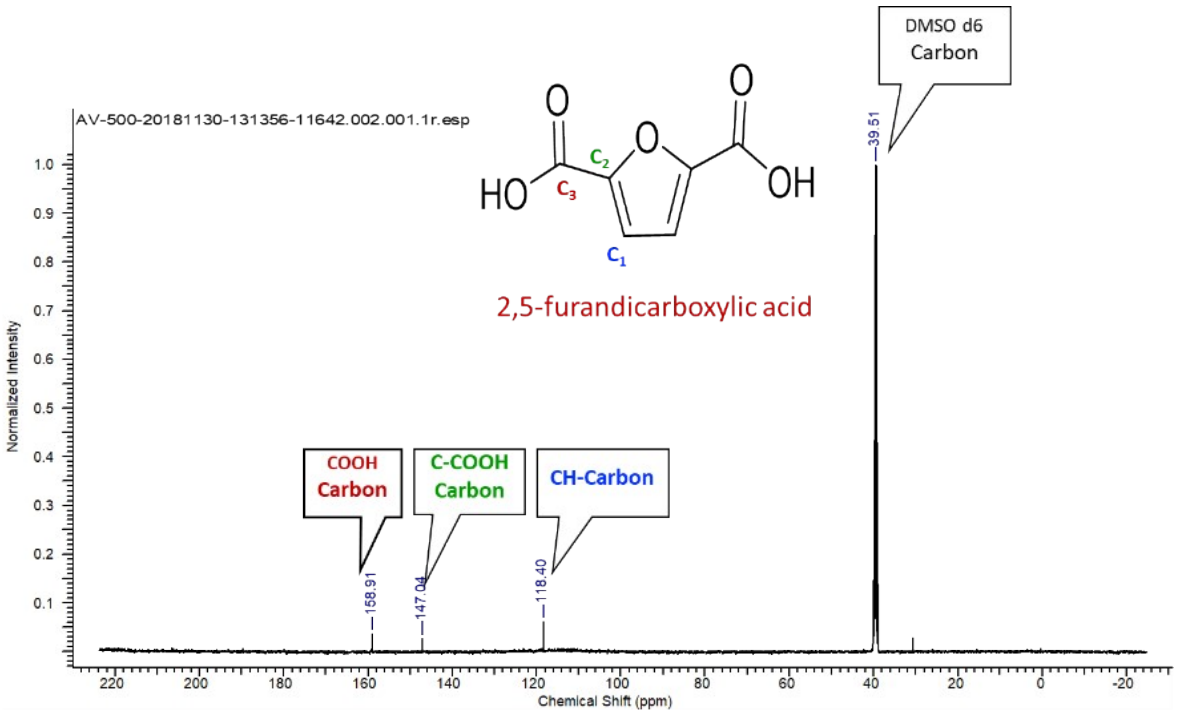


**Figure S3**. $^{13}C$ NMR spectrum of isolated FDCA obtained after the reaction. Solvent: DMSO

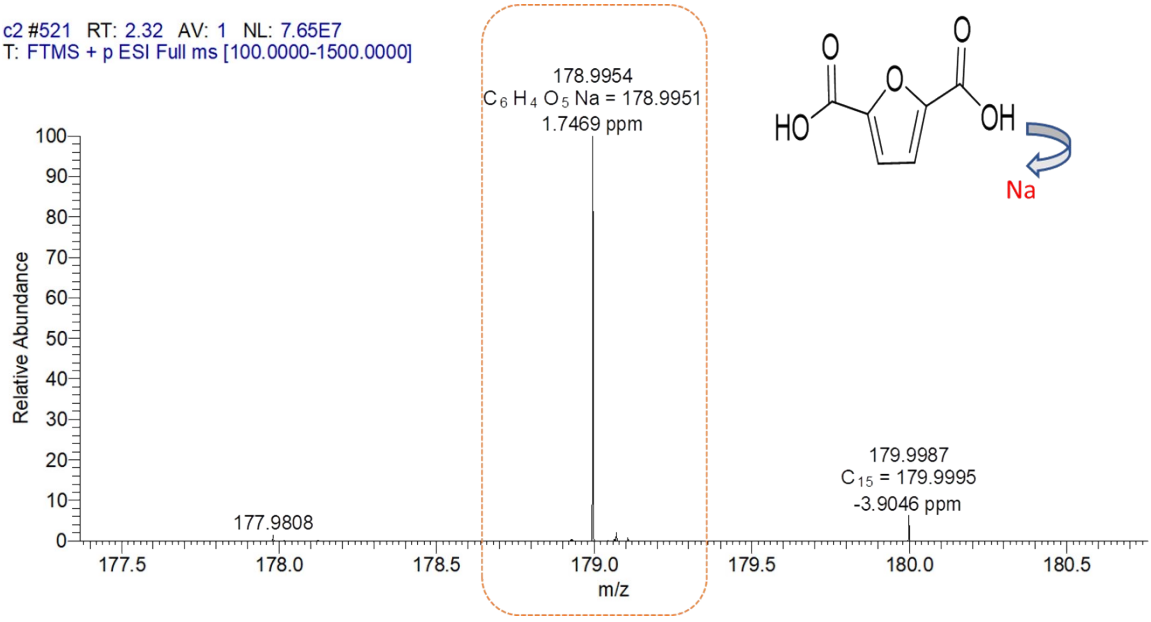


**Figure S4**. HRMS spectra of isolated FDCA obtained after the reaction.

The peak at M/Z of 179 [M+Na] in the HR-MS profile confirmed the formation of Na salt of FDCA.

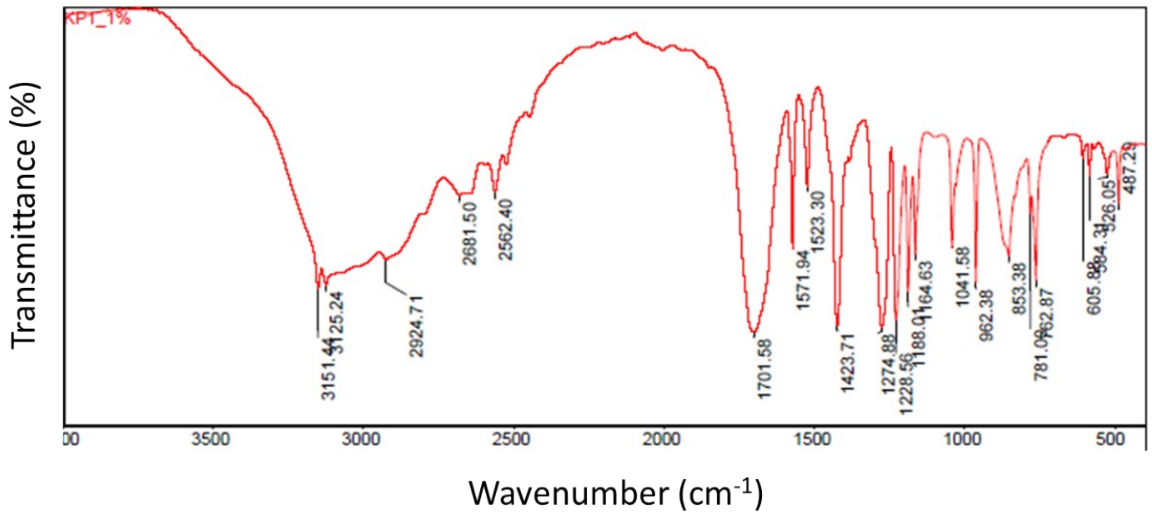


**Figure S5**. FTIR spectrum of isolated FDCA obtained after the reaction.

FTIR (ν $cm^{-1}$) 3151, 3125 (-OH); 1701 (C=O); 1571, 1423 (Furan Ring -C=C-); 1274 (ester-C-O-), 1228 (furan ring -C-O); 962, 853, 762 (=CH).

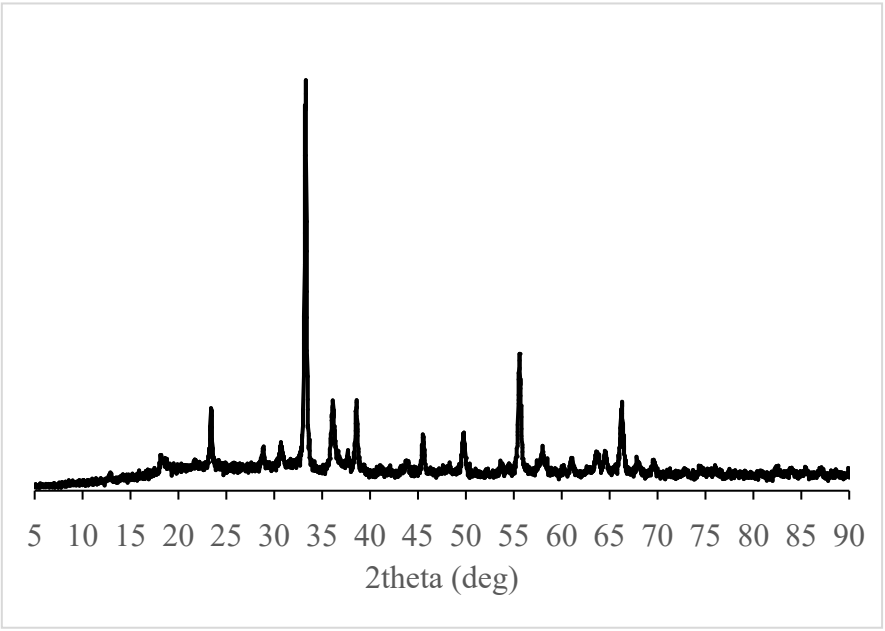


**Figure S6**. XRD of spent Cu-Mn Catalyst

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