Supplementary Information (ESI)

Spinel $CuMn_2O_4$ oxide as a superior catalyst for the aerobic oxidation of 5-hydroxymethylfurfural toward 2,5-furandicarboxylic acid in water solvent

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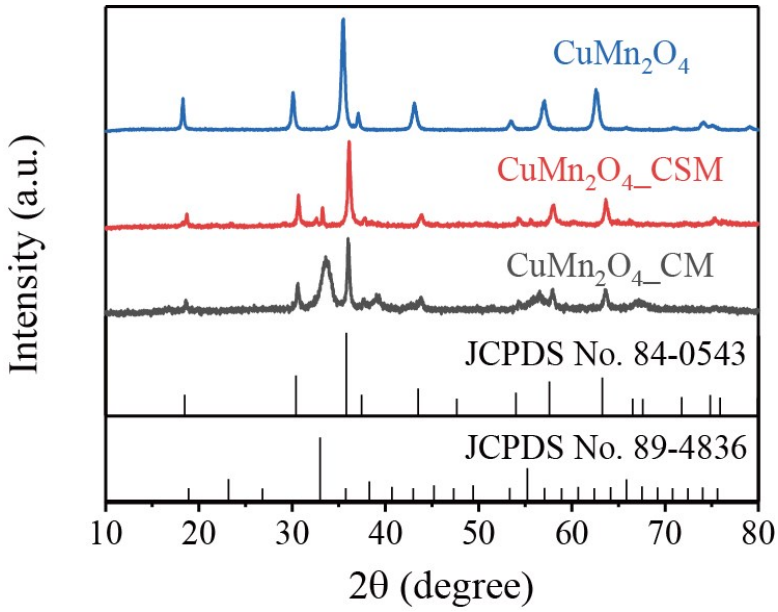

Figure S1. XRD patterns of $CuMn_2O_4$, $CuMn_2O_4$_CSM, and $CuMn_2O_4$_CM, respectively.

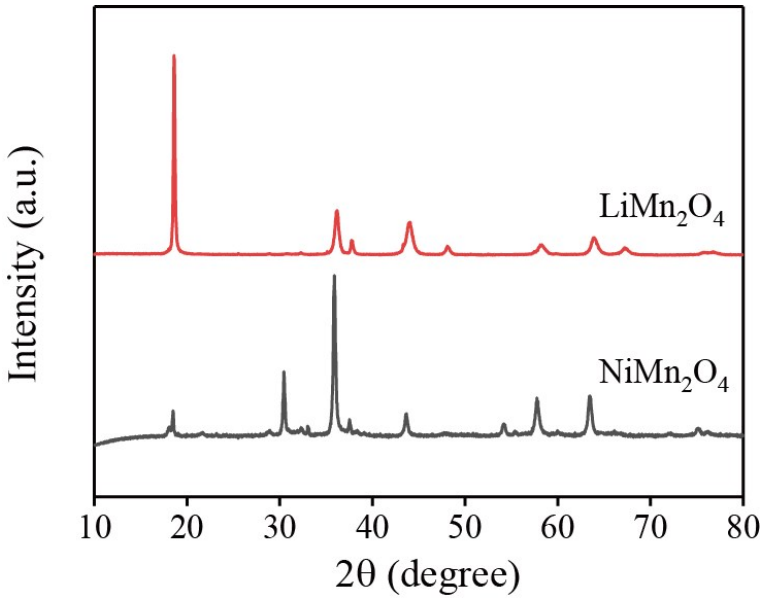

Figure S2. XRD patterns of $CuMn_2O_4$, $LiMn_2O_4$, and $NiMn_2O_4$, respectively.

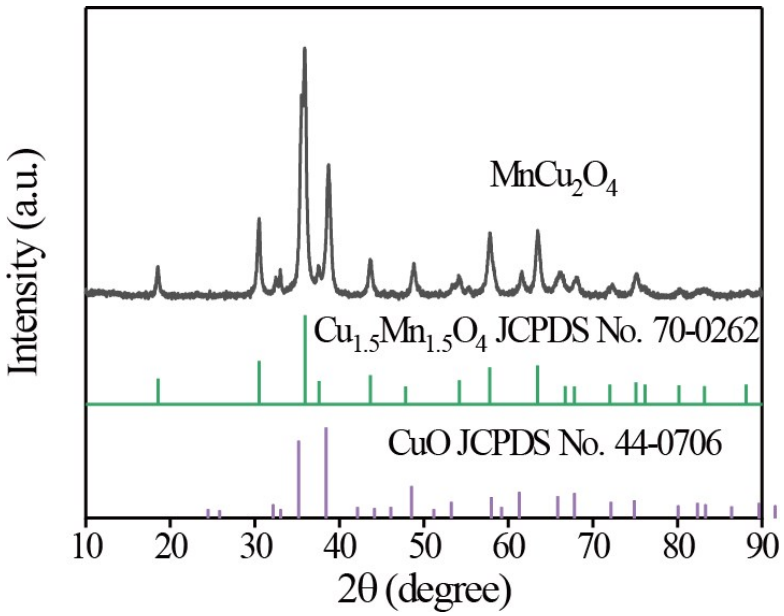

Figure S3. XRD patterns of $MnCu_2O_4$.

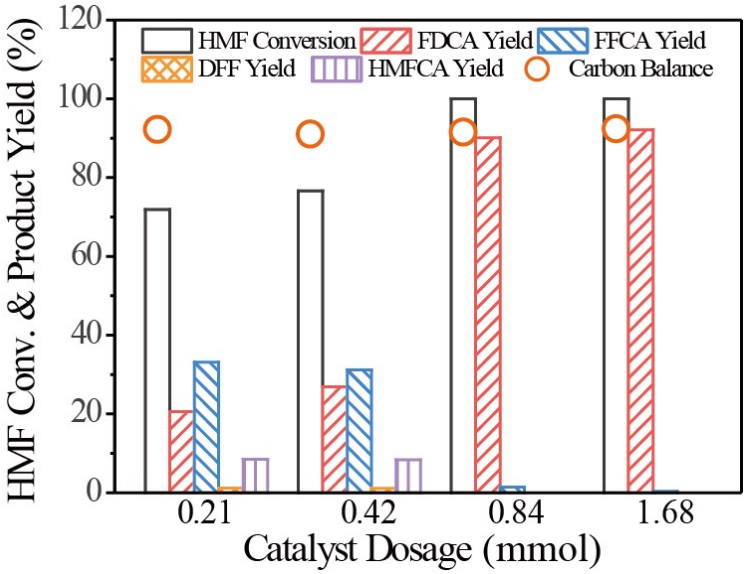

Figure S4 Effect of the catalyst dosage on the aerobic oxidation of HMF over $CuMn_2O_4$ spinel catalyst. Reaction conditions: 0.5 mmol HMF; O_2, 1 MPa; H_2O, 10 ml; temperature, 120 ^oC; reaction time, 18 h; $n(NaHCO_3)/n(HMF)=2$.

Table S1 Catalytic behavior with none oxide catalysts for aerobic oxidation of HMF.[a]

Conv. (%)	Yield[b] (%)				Carbon Balance[c] (%)	Others[d]
	DFF	FFCA	HMFCA	FDCA		
65.4	1.31	8.25	1.05	3.34	44.8	20.0

[a]Reaction conditions: 0.5 mmol HMF; none oxide catalyst; O_2, 1.0 MPa; H_2O, 10 ml; temperature, 120 ^oC; reaction time, 18 h; $NaHCO_3$/HMF=2. [b]DFF, HMFCA, FFCA, and FDCA denote 2,5-diformylfuran, 5-hydroxymethyl-2-furancarboxylic acid, 5-formyl-2-furan-carboxylicacid, and 2,5-furandicarboxylic acid, respectively. [c] Carbon Balance based on the detectable products including DFF, FFCA, HMFCA, FDCA, formic acid, levulinic acid, 2,5-furandimethanol (DHMF) and so on. [d] Others includes humin and other undetectable products by HPLC.

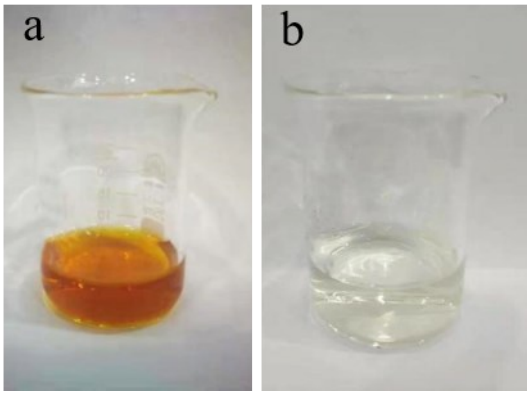

Figure S5 Photos of centrifugated liquid after reaction. Reaction conditions: (a) 0.5 mmol HMF; none oxide catalyst; O_2, 1.0 MPa; H_2O, 10 ml; temperature, 120 ^oC; reaction time, 18 h; $NaHCO_3$/HMF=2. (b) 0.5 mmol HMF; 0.84 mmol $CuMn_2O_4$ catalyst; O_2, 1.0 MPa; H_2O, 10 ml; temperature, 120 ^oC; reaction time, 18 h; $NaHCO_3$/HMF=2.

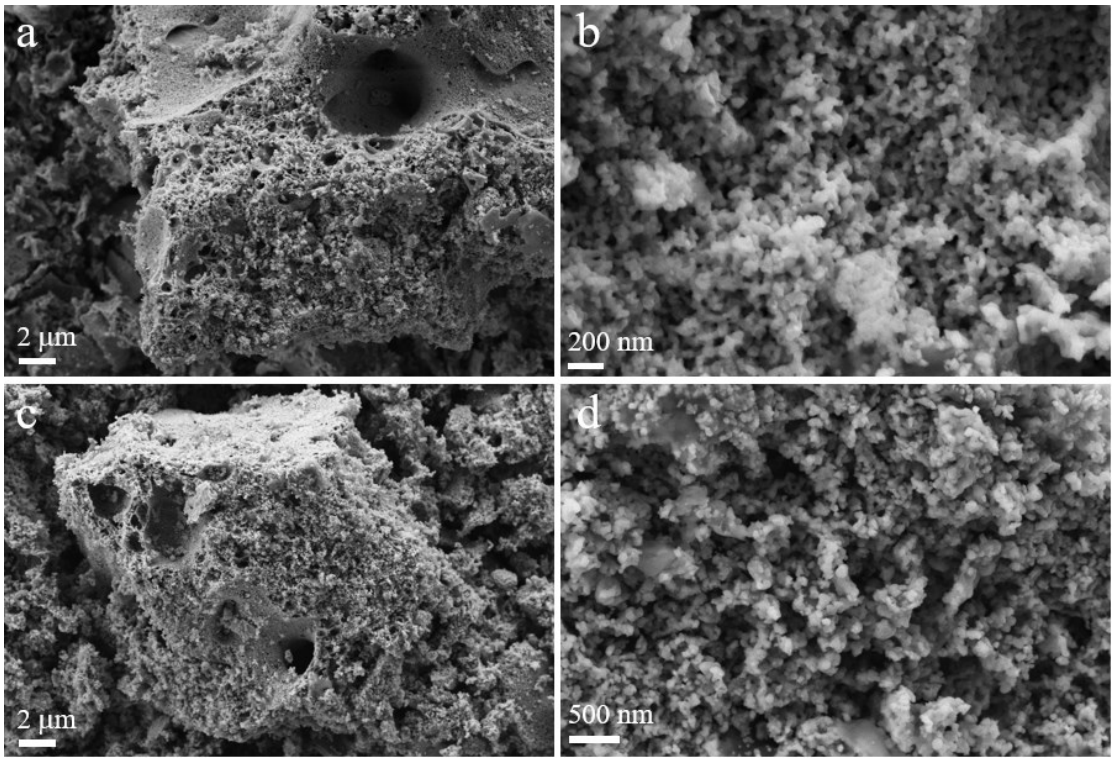

Figure S6 SEM images of (a, b) $CuMn_2O_4$ and (c, d) $CuMn_2O_4$ catalyst after the 6-time-repeatability by regeneration *via* calcination in air at 500 ^oC for 3 h.

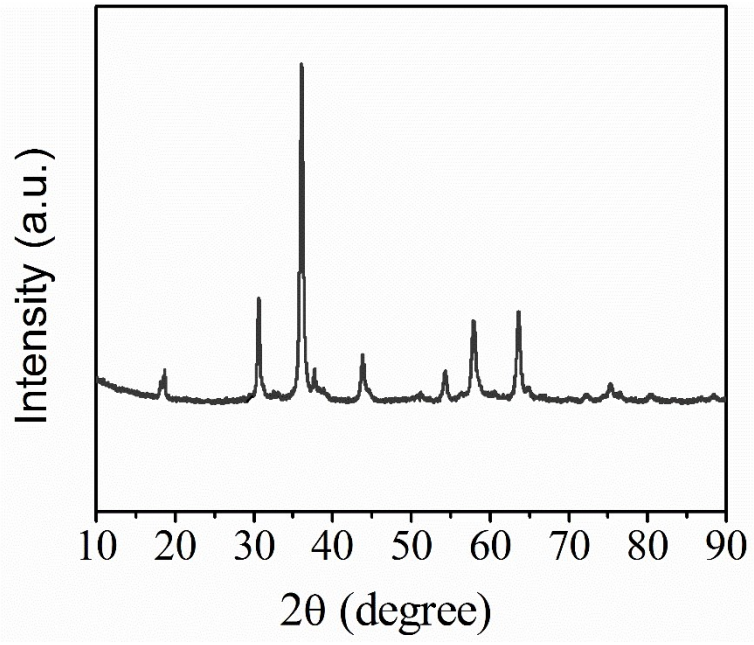

Figure S7 XRD of $CuMn_2O_4$ after the 6-time-repeatability by regeneration *via* calcination in air at 500 ^oC for 3 h.

Table S2 Catalytic behavior of different oxides catalysts for aerobic oxidation of HMF.[a]

Catalyst	Dosage (g)	Time (h)	HMF Conv. (%)	Select. (%)			
				DFF	FFCA	HMFCA	FDCA
$CuMn_2O_4$	0.2	0.5	13.0	19.2	57.2	19.2	4.5
$MnCu_2O_4$	0.2	1	24.2	23.3	70.9	0.0	5.8
CuO	0.2	1	19.0	30.9	25.4	0.0	28.6
Mn_2O_3	0.1	0.5	13.1	30.2	60.6	0.0	5.2

[a]Reaction conditions: 0.5 mmol HMF, 10 ml H_2O, 120 ^oC, 1.0 MPa O_2, 1.0 mmol $NaHCO_3$.

Table S3 Catalytic behavior of different oxides catalysts for aerobic oxidation of DFF.[a]

Catalyst	Dosage (g)	Time (h)	DFF Conv. (%)	Select. (%)	
				FFCA	FDCA
$CuMn_2O_4$	0.05	0.5	24.4	89.7	10.3
$MnCu_2O_4$ [b]	0.05	0.5	24.3	2.3	97.7
CuO	0.025	0.5	18.8	96.0	4.0
Mn_2O_3	0.02	0.5	25.6	1.6	98.4

[a]Reaction conditions: 2.0 mmol DFF, 10 ml H_2O, 120 ^oC, 1.0 MPa O_2, 1.0 mmol $NaHCO_3$.

[b]Reaction conditions: 1.0 mmol DFF, 10 ml H_2O, 120 ^oC, 1.0 MPa O_2, 1.0 mmol $NaHCO_3$.

Table S4 Catalytic behavior of different oxides catalysts for aerobic oxidation of FFCA[a]

Catalyst	Dosage (g)	Time (h)	FFCA Conv. (%)	Select. /% FDCA
$CuMn_2O_4$	0.3	1.0	12.8	100
$MnCu_2O_4$	0.3	1.5	12.7	100
CuO	0.3	24	14.0	100
Mn_2O_3	0.1	0.5	13.9	100

[a]Reaction conditions: 0.5 mmol FFCA, 10 ml H_2O, 120 ^oC, 1.0 MPa O_2, 1.0 mmol $NaHCO_3$.

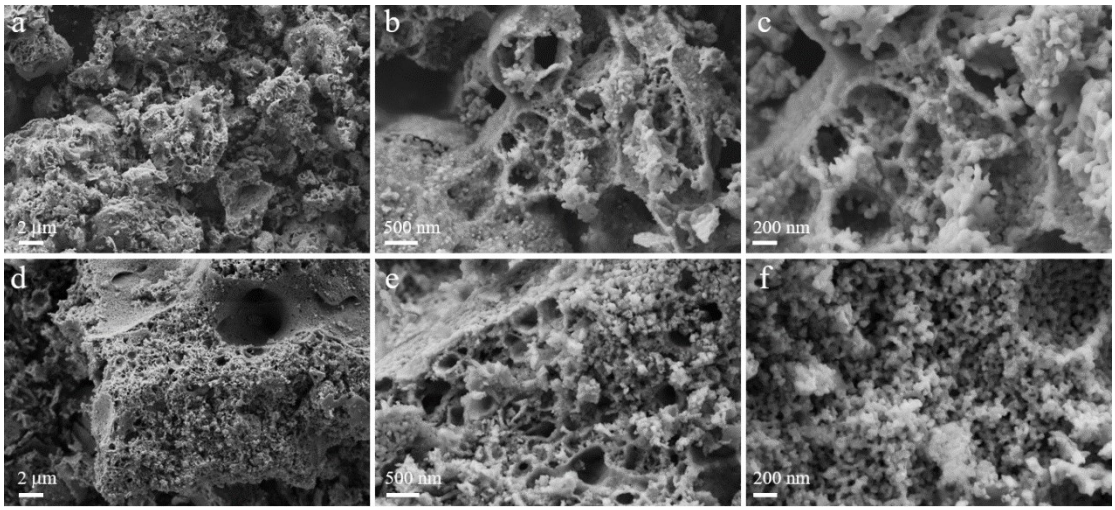

Figure S8 SEM images of (a, b, c) $MnCu_2O_4$ and (d, e, f) $CuMn_2O_4$.

Table S5 The ICP results of $CuMn_2O_4$ and $MnCu_2O_4$.

Catalyst	Concentration (mg/L)		Cu: Mn Ratio	Mother Liquor Concentration in Prepareration
	Cu	Mn		
$CuMn_2O_4$	8.77	15.1	1: 1.99	1:2
$MnCu_2O_4$	16.075	6.92	1.99: 1	2:1

Composition analysis of the powders by ICP

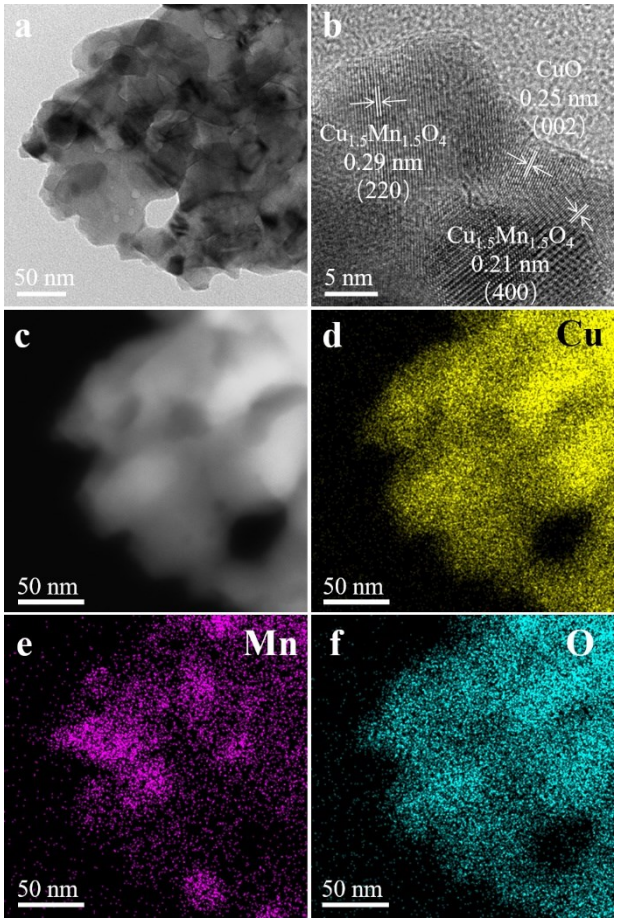

Figure S9. The TEM (a), HRTEM (b), HAADF-STEM (c) images and corresponding EDS mapping of Cu (d), Mn (e) and O (f) elements, respectively, of $MnCu_2O_4$ catalysts.

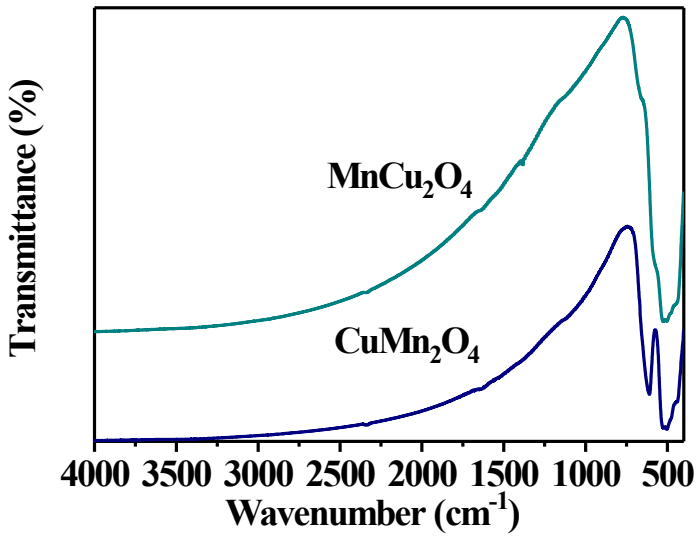

Figure S10 The FT- IR spectra of $CuMn_2O_4$ and $MnCu_2O_4$ samples

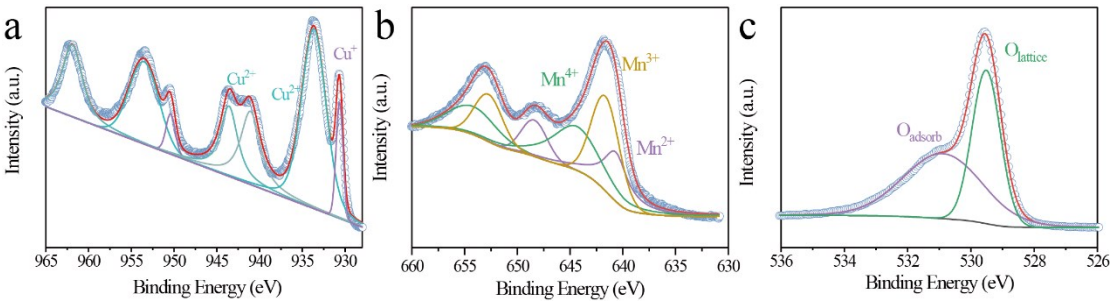

Figure S11 Deconvoluted XPS spectra of Cu 2p, Mn 2p, O 1s orbital levels from the $MnCu_2O_4$catalysts.

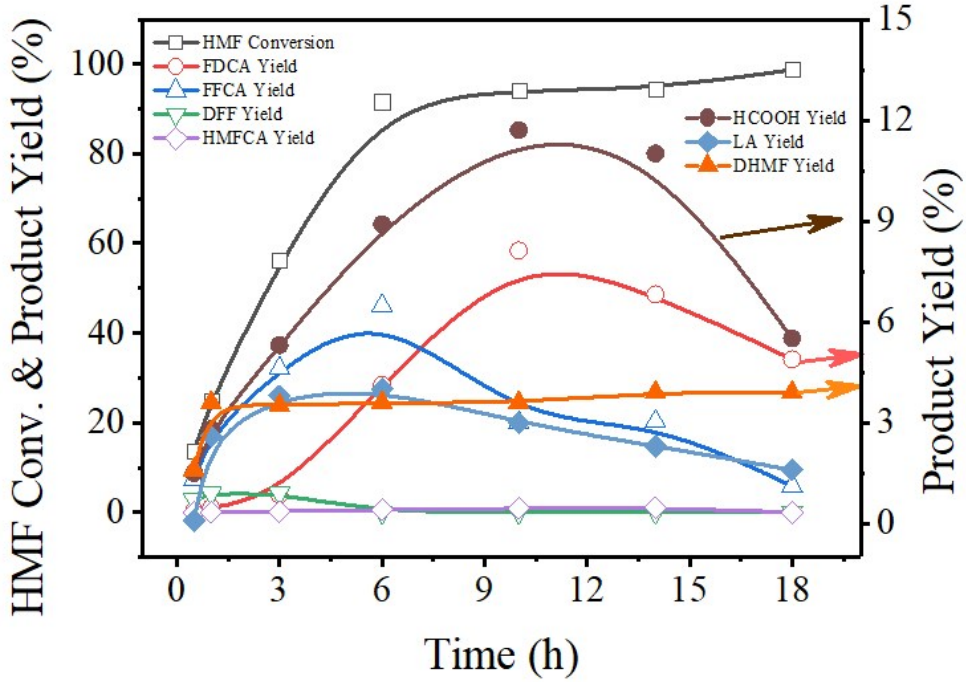

Figure S12 Time course of the aerobic oxidation of HMF over Mn_2O_3 catalyst. Reaction conditions: 0.5 mmol HMF, 1.64 mmol Mn_2O_3 ctalyst, 10 ml H_2O, 120 ^oC, 1.0 MPa O_2, n($NaHCO_3$)/n(HMF)=2.

Table S6 The anaerobic experiments of $CuMn_2O_4$ spinel catalyst in the oxidation of HMF.

Time	Conv. (%)	Yield (%)				Amount of
(h)	HMF	DFF	FFCA	HMFCA	FDCA	O_{ins} (μmol)
3	8.4	2.7	2.16	1.6	1.7	34.3
4	9.4	2.0	2.0	1.0	2.5	36.2
8	14.6	4.4	3.8	0.8	2.7	52.3

Reaction conditions：0.25 mmol HMF, 0.84 mmol catalyst, 20 ml H_2O, 120 ^oC, N_2：1 MPa