

## *Supporting Information*

### *Heterogeneous Mesoporous Manganese/Cobalt Oxide Catalyst for Selective Oxidation of 5-hydroxymethylfurfural to 2,5-diformylfuran*<sup>†</sup>

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## Chemicals

Manganese (II) nitrate tetrahydrate ( $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ,  $\geq 97.0$ ), Cobalt (II) nitrate hexahydrate ( $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\geq 97.0$ ), 1-butanol (anhydrous, 99.8%), and poly (ethylene glycol)- block- Poly(propylene glycol)-block- Poly (ethylene glycol)  $\text{PEO}_{20}\text{PPO}_{70}\text{PEO}_{20}$  (Pluronic P123), hydroxymethylfurfural (HMF), toluene, water, acetonitrile, 1,4-dioxane, dimethylformamide (DMF), commercial  $\text{Mn}_2\text{O}_3$  were purchased from Sigma Aldrich. Concentrated nitric acid ( $\text{HNO}_3$ , 68-70 %) was purchased from J. T. Baker. All chemicals were used as received without further purification.

## Preparation of meso Mn/ CoOx

The catalyst was synthesized following the procedure described by Poyraz *et al.*<sup>1</sup> In a typical synthesis 0.02 mol of manganese nitrate tetrahydrate ( $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , 0.02 mol), required amounts of cobalt nitrate hexahydrate ( $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ), and 0.134 mol of 1-butanol were added into a 120 mL beaker. To this solution 0.0034 mol of poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (Pluronic P123,  $\text{PEO}_{20}\text{PPO}_{70}\text{PEO}_{20}$ , molar mass 5750 g  $\text{mol}^{-1}$ ) and 0.032 mol of concentrated nitric acid ( $\text{HNO}_3$ ) were added and stirred at room temperature until the solution became clear (light pink). The resulting clear solution was then kept in an oven at 120°C for 3 h. After reaction, the black product was washed with excess ethanol, centrifuged, and dried in a vacuum oven overnight. At the end, the dried black powders were subjected to a heating cycle. First they were heated at 150°C for 12 h and cooled down to room temperature followed by heating to 250°C for 4 h.

### **Reaction procedure of HMF oxidation**

In a typical reaction, a mixture of HMF (0.50 mmol), meso Mn/ CoO<sub>x</sub> (50 mg) and DMF (5 mL) was added in a 25 mL round bottom flask (two-necked flask was used for time dependent study) equipped with a condenser. The reaction mixture was heated to reflux under vigorous stirring (700 rpm) for the required time under air. After reaction, the mixture was cooled and the catalyst was removed by filtration. The product analysis was done using GC-MS (gas chromatography-mass spectrometry). The conversion was determined based on the concentration of HMF. Most reactions were repeated twice and the average values were used. The GC-MS analyses were performed with a 7820A GC system connected with a mass detector of 5975 series MSD from Agilent Technologies and a nonpolar cross-linked methyl siloxane column with dimensions of 12 in × 0.200 mm × 0.33 μm was used. The products were isolated by silica gel column chromatography (a mixed solvent of 5 % ethyl acetate in petroleum ether was used as an eluent). The <sup>1</sup>H NMR spectra were recorded on a Bruker AVANCE III- 400 MHz spectrometer at 400 MHz with chemical shift referenced to the residual peak in CDCl<sub>3</sub> (δ: H 7.26 ppm). Multiplicities are written as s (singlet), d (doublet), t (triplet), and m (multiplet).

### **Catalyst Characterization**

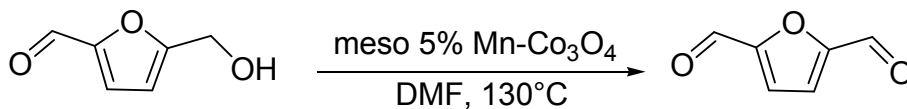
The powder X-Ray diffraction (PXRD) data were collected by a Rigaku Ultima IV diffractometer (Cu K $\alpha$  radiation,  $\lambda=1.5406 \text{ \AA}$ ) with an operating voltage of 40 kV and a current of 44 mA. The PXRD patterns were collected over a  $2\theta$  range of 5–75° with a continuous scan rate of 1.0° min<sup>-1</sup>. The Nitrogen adsorption desorption experiments were performed with a Quantachrome Autosorb-1-1C automated adsorption system. The samples were treated at 150°C for 6 h under helium prior

to measurement. X-ray photoelectron spectroscopy (XPS) was done on a PHI model 590 spectrometer with multiprobes ( $\Phi$ Physical Electronics Industries Inc.), using Al-K radiation ( $\lambda=1486.6$  eV) as the radiation source and was fitted using CasaXPS software (version 2.3.12). The powder samples were pressed on carbon tape mounted on adhesive copper tape stuck to a sample stage placed in the analysis chamber. For correction of surface charging, the C 1s photoelectron line at 284.6 eV was taken as a reference. A mixture of Gaussian (70%) and Lorentzian (30%) functions was used for the least-squares curve fitting procedure. Temperature-programmed reduction ( $H_2$ -TPR) analyses were conducted in a programmable tube furnace equipped with a gas analyzer MKS coupled with a quadruple mass selective detector. About 100 mg of materials were packed in a quartz tube reactor mounted into the tube furnace 5 %  $H_2$ / Ar flow was passed through the catalyst bed at a flow rate of 50 sccm, while the temperature was ramped from room temperature (RT) to 800 °C.

**Table S1.** Physicochemical properties of meso Mn/ CoOx

Catalyst	Surface Area $S_{BET}$ ( $m^2g^{-1}$ )	BJH ads. pore size (nm)	Pore volume ( $cc g^{-1}$ )
Meso-CoOX	139	7.5	0.37
1% Mn-CoOX	91	9.4	0.39
3% Mn-CoOX	113	17.0	0.36
5% Mn-CoOX	121	5.2	0.34

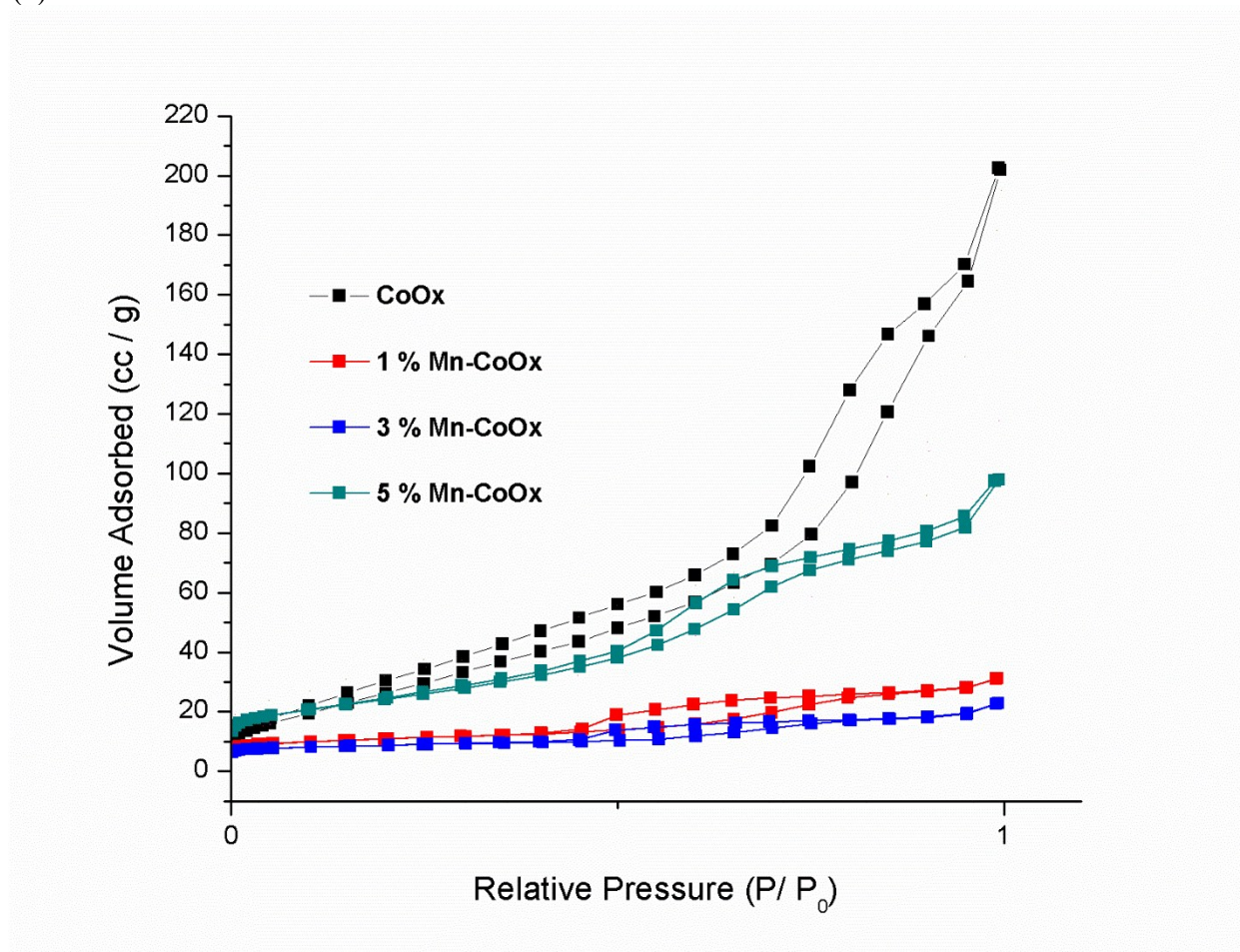
**Table S2.** Effect of oxidants in oxidation of HMF to DFF

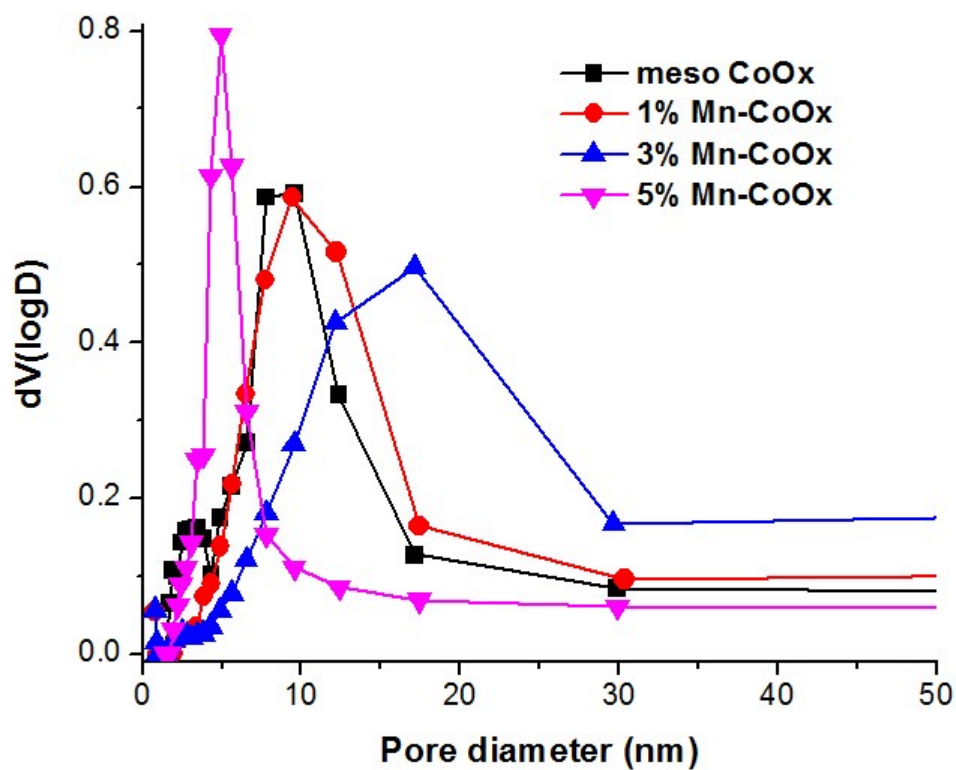


Entry	Oxidant	Additives	Conversion <sup>b</sup> (%)	Selectivity <sup>b</sup> (%)
1	Air	none	55	95
2 <sup>c</sup>	O <sub>2</sub>	none	59	95
3 <sup>c</sup>	N <sub>2</sub>	none	45	98
4 <sup>d</sup>	O <sub>2</sub> + Base	none	65	95

<sup>a</sup> **Reaction conditions:** HMF (0.50 mmol), Meso 5% Mn/CoO<sub>x</sub> (25 mg), DMF (3 mL), 130°C, 4 h. <sup>b</sup> Conversions and selectivity were determined by GC-MS. <sup>c</sup> O<sub>2</sub> and N<sub>2</sub> balloon were used. <sup>d</sup> 1 eqv. K<sub>2</sub>CO<sub>3</sub> was added.

(a)





**Figure S1.** (a) Nitrogen adsorption and (b) BJH adsorption pore size distribution of meso Mn/CoOx at different Mn/Co ratio. In Nitrogen adsorption isotherms a type IV adsorption isotherm followed by a type I hysteresis loop were observed for all the materials, which confirmed the mesoporous structure.

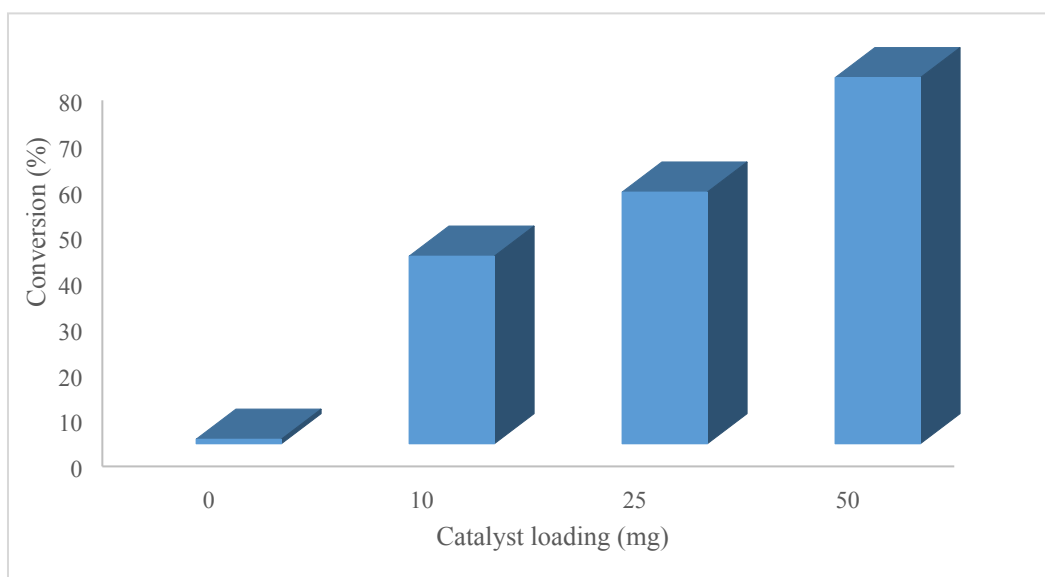
**Table S3.** a) Summary of Area Percentages of different elemental components, Obtained from the deconvoluted Co 2p<sub>3/2</sub>, Mn 2p<sub>3/2</sub> and O 1s XPS Spectra. b) area percentages of O1s spectra of meso 5%Mn\_CoOx before and after reaction in nitrogen

a)

Catalyst	Co <sup>3+</sup>	Co <sup>2+</sup>	Mn <sup>4+</sup>	Mn <sup>3+</sup>	O <sub>L</sub>	O <sub>OH</sub>	O <sub>MW</sub>
<b>Meso- CoOx</b>	43.17	23.50	-	-	60.3	30.5	9.2
<b>Meso- 1%Mn-CoOx</b>	21.39	45.37	28.59	38.08	37.75	20.73	41.52
<b>Meso- 3%Mn-CoOx</b>	19.58	47.23	28.09	38.65	41.88	46.82	11.30
<b>Meso- 5%Mn-CoOx</b>	19.32	47.44	21.12	45.62	70.56	22.61	6.82

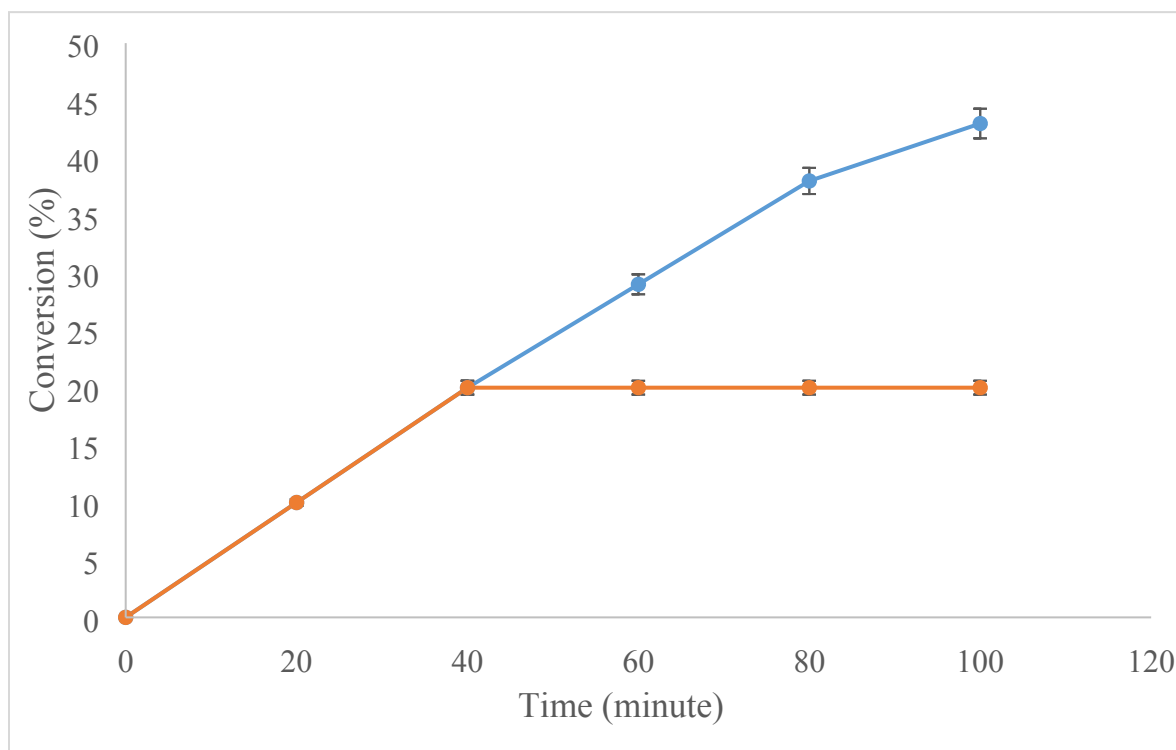
b)

Catalyst ( <b>Meso- 5%Mn-CoOx</b> )	O <sub>L</sub>	O <sub>OH</sub>	O <sub>MW</sub>
Before reaction	70.56	22.61	6.82
Reaction under N <sub>2</sub>	49.94	31.68	18.38



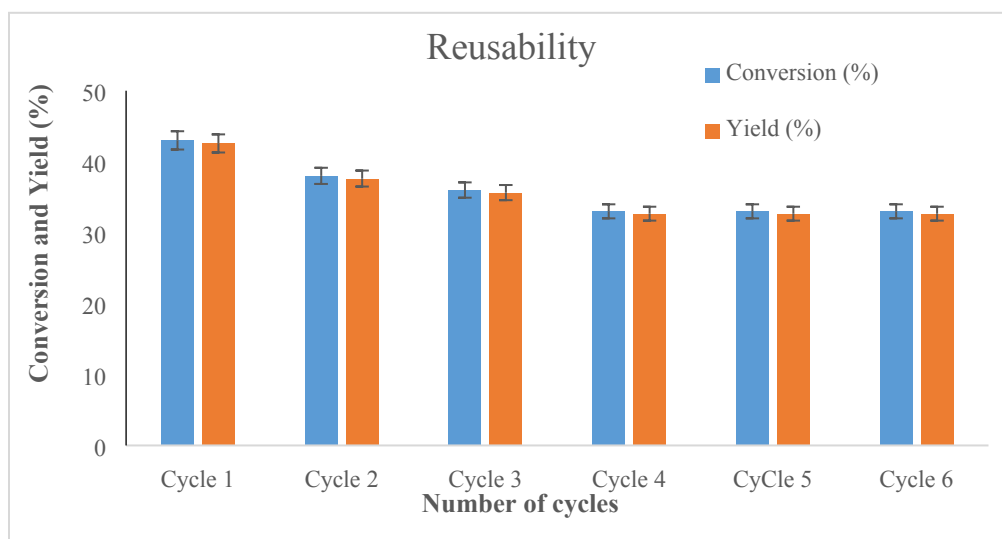
**Figure S2.** Effect of increasing amounts of catalyst loading. Reaction condition: HMF (0.50 mmol), Meso 5% Mn/CoO<sub>x</sub> (0-50 mg), DMF (3 mL) at 130°C, 4 hours.



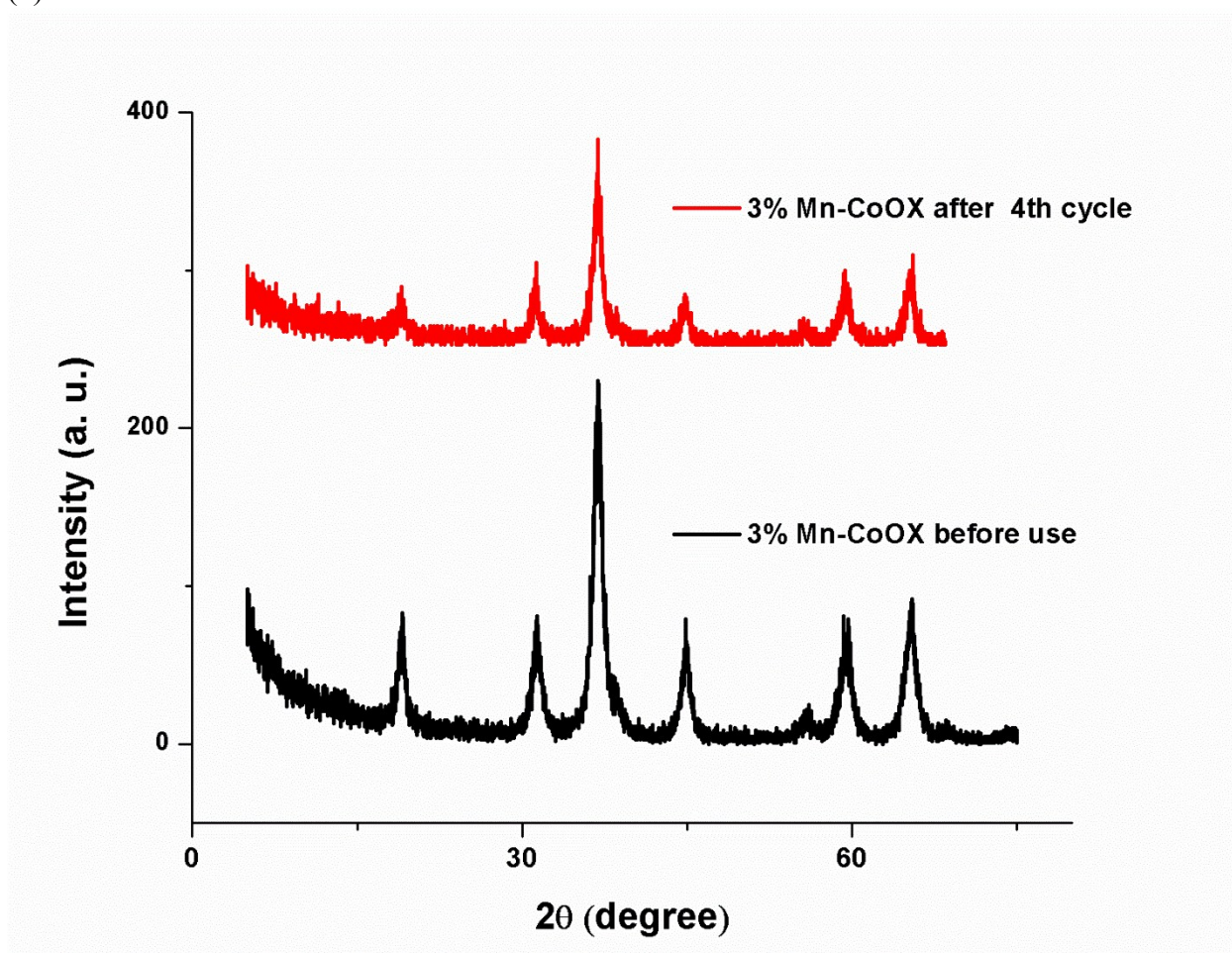


**Figure S3.** Effect of removal of the catalyst during the reaction (Hot filtration test). Reaction conditions were the same as mentioned in Figure S6. After 40 minutes of the reaction, catalyst was removed by filtration (at about 20% conversion) and let the filtrate run under similar condition for another 60 minutes.

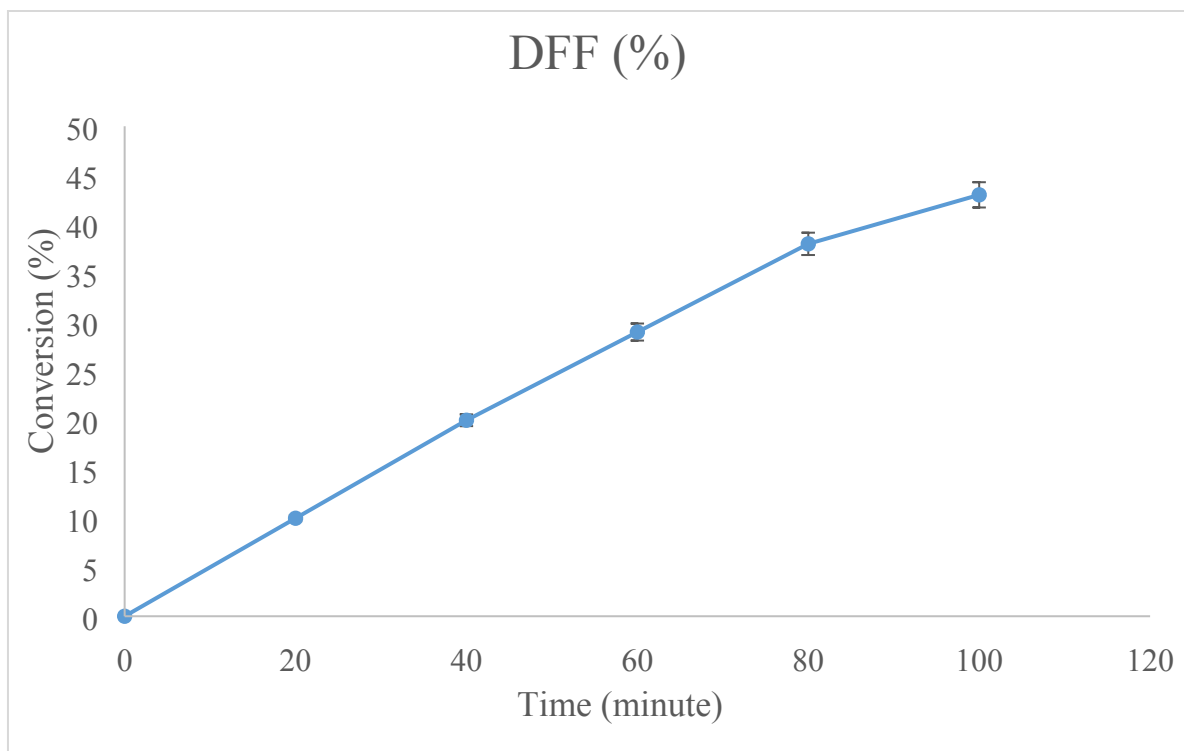
(a)



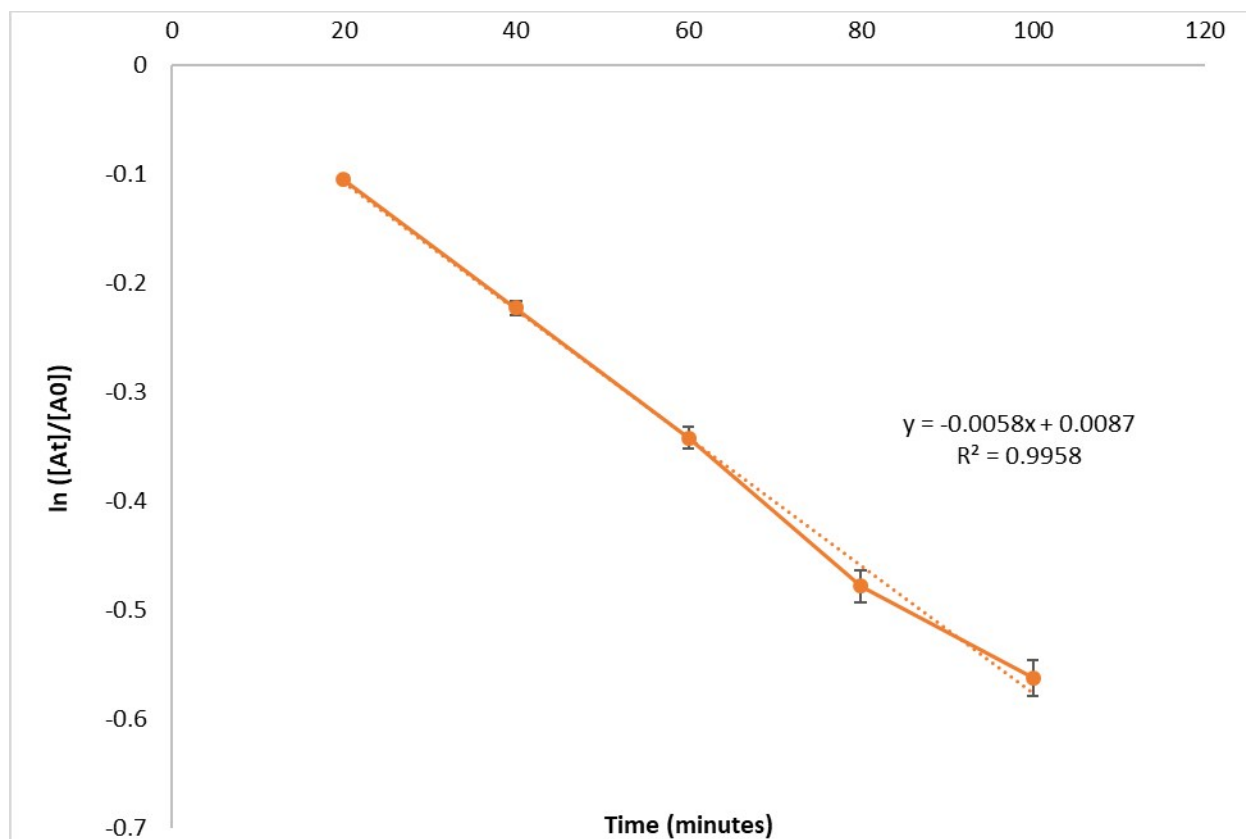
(b)



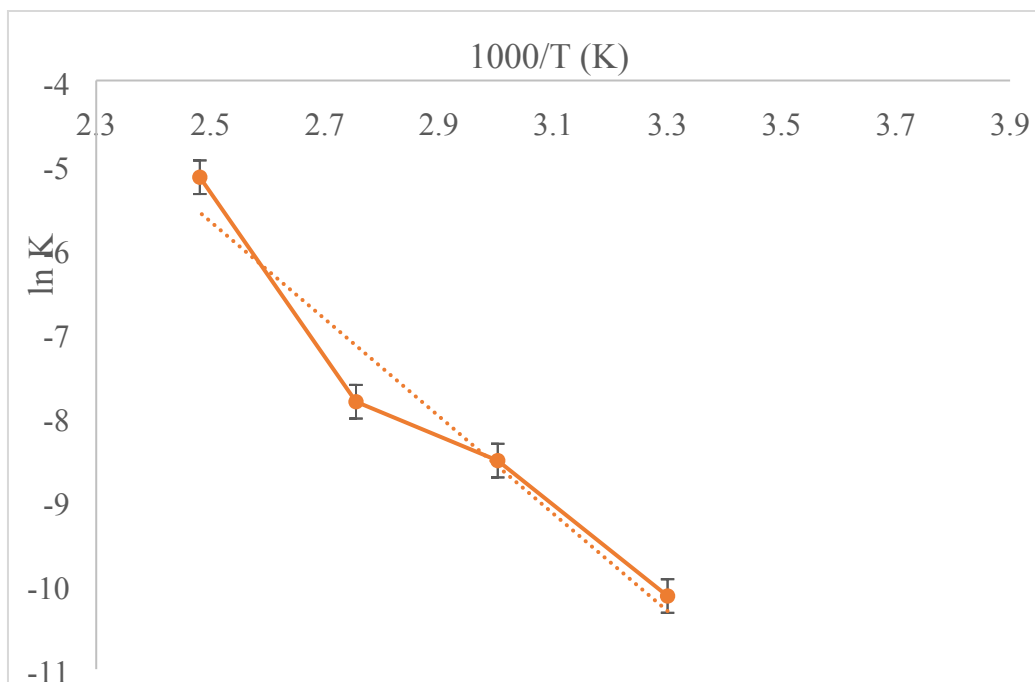
**Figure S4.** (a) Reusability test. Reaction condition: as mentioned in Figure S6. (b) PXRD before and after fourth reuse.



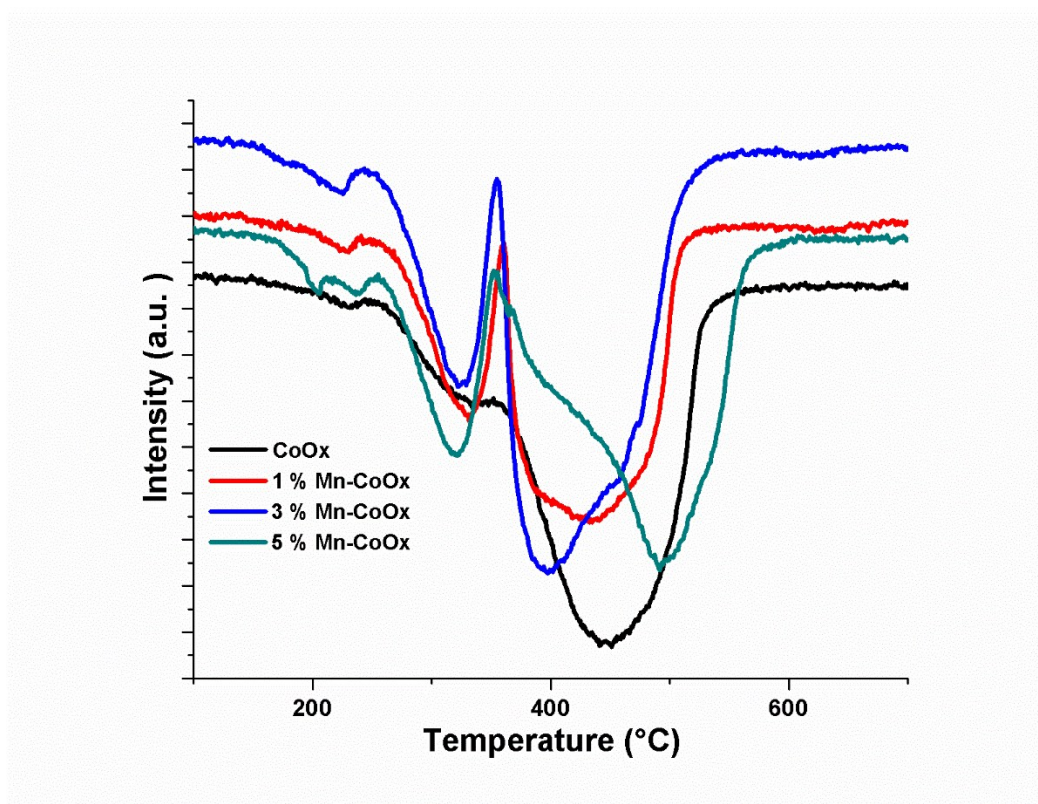
**Figure S5.** Time dependent study. Reaction condition: HMF (0.50 mmol), Meso 5% Mn/CoO<sub>x</sub> (50 mg), DMF (3 mL) at 130°C, 100 minutes.



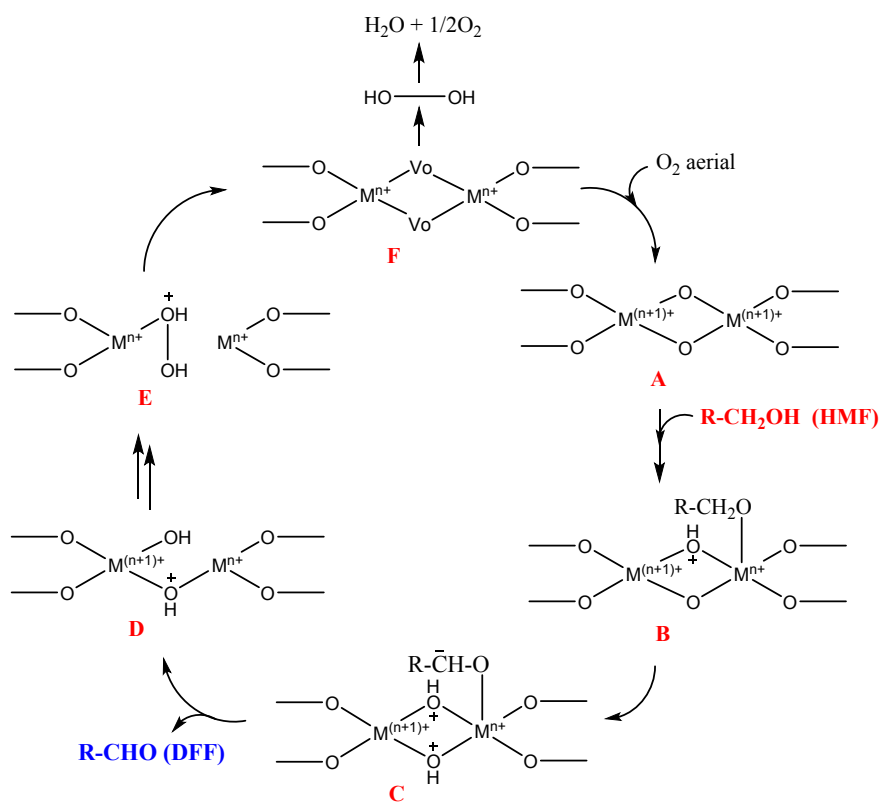
**Figure S6.** Kinetic study. Reaction condition: Reaction condition: HMF (0.50 mmol), Meso 5% Mn/CoO<sub>x</sub> (50 mg), DMF (3 mL) at 130°C, 100 minutes.



**Figure S7.** Arrhenius plot for oxidation of hydroxymethylfurfural by meso Co doped  $Mn_2O_3$ : The apparent activation energy was estimated as  $5.79 \text{ KJmol}^{-1}$ . Reaction conditions: HMF (0.5 mmol), Meso 5% Mn/CoO<sub>x</sub> (50 mg), DMF (3 mL), air balloon. K: rate constant.



**Figure S8.** H<sub>2</sub>-TPR of meso- Mn/ CoO<sub>x</sub> with different percentages of Mn doping.

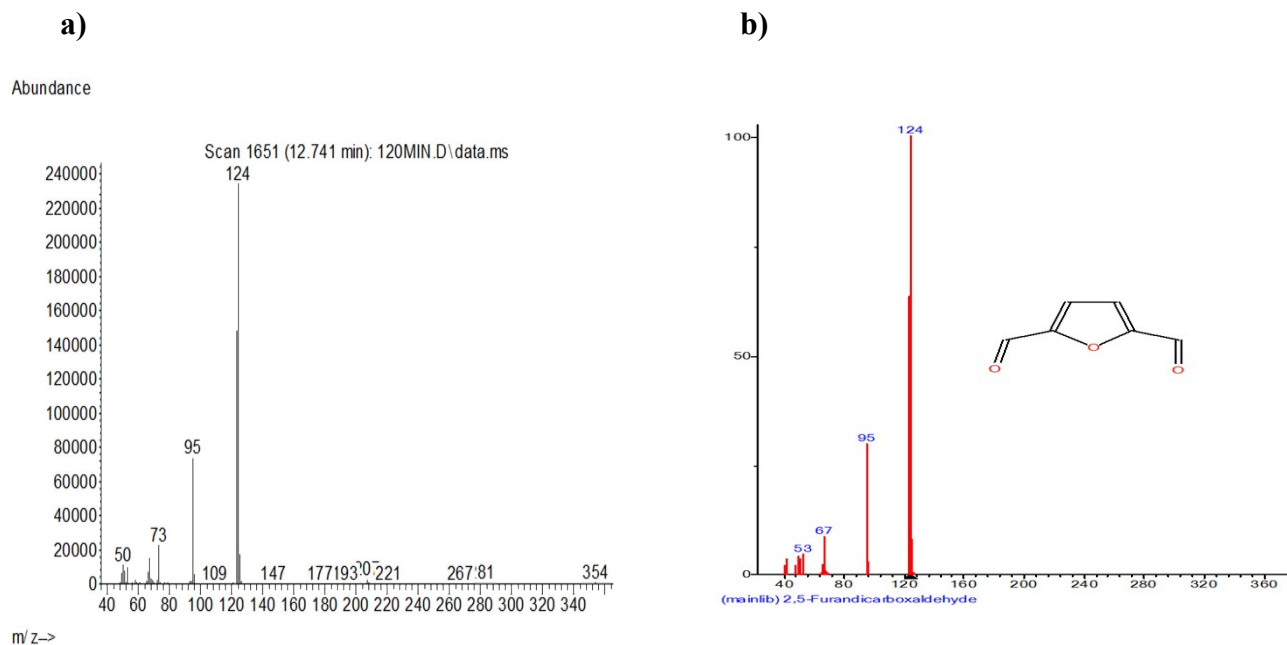


**Scheme S1.** Overall mechanism for the oxidation of HMF.

## Spectral Characterization of product (diformyl furan)

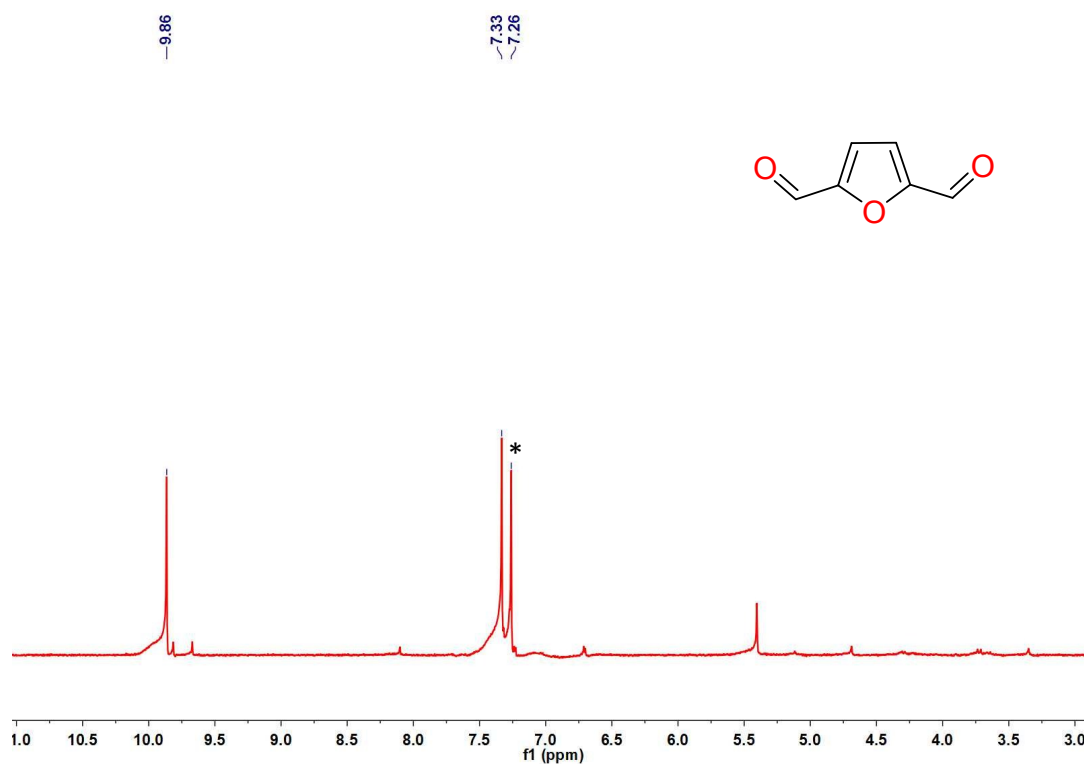
Appearance: Yellow powder

$^1\text{H NMR}$  (300 MHz, Chloroform-*d*):  $\delta$  9.88 (s, 2H), 7.28 (s, 2H).



m/z-->

**Figure S9.** **a)** Obtained mass spectra of DFF from GC-MS, **b)** Software predicted mass spectra of DFF.



**Figure S10.** <sup>1</sup>H NMR of DFF in CDCl<sub>3</sub> (\* denoted peak corresponds to solvent)

**References:**

1. A. S. Poyraz, C.-H. Kuo, S. Biswas, C. K. King'onde and S. L. Suib, *Nat. Commun.*, 2013, **4**, 1–10.