

Selective aerobic oxidation of biomass-derived HMF to 2,5-diformylfuran using a MOF-derived magnetic hollow Fe-Co nanocatalyst

Ruiqi Fang,^a Rafael Luque,^{b*} and Yingwei Li^{a*}

^a State Key Laboratory of Pulp and Paper Engineering, School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, China.

^b Departamento de Química Orgánica, Universidad de Córdoba, Edif. Marie Curie, Ctra Nnal IV_a, Km 396, E14014, Córdoba, Spain.

* Corresponding authors. Email: liyw@scut.edu.cn (Y. L.); q62alsor@uco.es (R. L.)

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Materials and methods

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1. Materials

All reagents were of analytical grade and were used without further purification.

2. Catalyst preparation

2.1 Synthesis of MIL-45b

$\text{CoCl}_2 \cdot 4\text{H}_2\text{O}$, fine Fe powder, trimesic acid (1,3,5-benzenetricarboxylate or BTC), and H_2O with the molar ratios of 1:1:1:80 (5 mL) were mixed. Then, 0.5 mL of KOH solution (10 mol L^{-1}) was added to adjust the pH value to ca. 5 to partly deprotonate the trimesic acid. The mixture was transferred into an autoclave to crystallize at 180°C for 3 days. The resulting red needle solid was filtered off and washed with demineralized water.

2.2 Synthesis of FeCo/C materials

The preparation procedure was as follow: MIL-45b (1.0 g) was heated at a certain temperature for 10 h with a heating rate of $1 \text{ }^\circ\text{C min}^{-1}$ from room temperature in argon atmosphere. The prepared material was denoted as FeCo/C(T), where T indicates the MOF pyrolysis temperature.

3. Catalyst characterization

Powder X-ray diffraction (PXRD) patterns of the samples were obtained on a Rigaku diffractometer (D/MAX-III A, 3kW) using Cu $K\alpha$ radiation (40 kV, 30 mA, λ

= 0.1543 nm). BET surface areas and pore sizes measurements were performed with N₂ adsorption/desorption isotherms at 77 K on a Micromeritics ASAP 2020M instrument. Before measurements, the samples were degassed at 100 °C for 12 h. The cobalt and iron contents in the samples were measured quantitatively by atomic absorption spectroscopy (AAS) on a HITACHI Z-2300 instrument. TGA was performed on a NETZSCH STA449C instrument loaded with 5 mg sample using a heating rate of 20 °C/min under nitrogen atmosphere.

The size and morphology of materials were studied by high-resolution scanning electron microscopy (HR-SEM) equipped with an energy dispersive X-ray spectroscopy (EDS). Transmission Electron Micrographs (TEM) were recorded on a JEOL JEM-2010HR instrument operated at 300 kV. Samples were suspended in ethanol and deposited straightaway on a copper grid prior to analysis.

XPS measurements were performed in a ultra-high vacuum (UHV) multipurpose surface analysis system (SpecsTM model Germany) operating at pressures <10⁻¹⁰ mbar using a conventional X-ray source (XR-50, Specs, Mg K_{alpha}, 1253.6 eV) in a “stop-and-go” mode to reduce potential damage due to sample irradiation. Detailed Fe/Co high-resolution spectra (pass energy 25 and 10 eV, step size 1 and 0.1 eV, respectively) were recorded with a Phoibos 150-MCD energy analyzer. Samples were deposited on a sample holder using double-sided adhesive tape and subsequently evacuated under vacuum (<10⁻⁶ Torr) overnight. Eventually, the sample holder containing the degassed sample was transferred to the analysis chamber for XPS studies. Binding energies were referenced to the C1s line at 284.6 eV from

adventitious carbon. Deconvolution curves for the XPS spectra were obtained using software supplied by the spectrometer manufacturer.

ATR-IR spectra were recorded on a Thermo Fisher iS10 equipped with a liquid nitrogen cooled MCT detector. The spectra were obtained by averaging 32 scans at a resolution of 1 cm^{-1} . The thin film of catalyst powder deposited on the ZnSe element for ATR-IR spectroscopic study was prepared as follow. A suspension of ca. 50 mg of catalyst powder and 0.1 mmol HMF in 2 mL of toluene was stirred overnight to eliminate any serious agglomeration in solution. Then, the slurry was dropped onto a ZnSe internal reflection element (IRE) for data collection. The IR spectrum for the catalyst in solvent was acquired as the reference background.

4. Catalytic oxidation of HMF

The selective oxidation of HMF was carried out in a stainless steel reactor equipped with a magnetic stirrer. In a typical run, HMF (1.0 mmol), catalyst (metal 20 mol% relative to HMF), Na_2CO_3 (1 mmol), and toluene (2 mL) were added in a stainless steel reactor. After purging the reactor several times with oxygen, the outlet valve was closed to maintain 1.0 MPa of oxygen pressure (ambient temperature). The reactor was conducted at $100\text{ }^\circ\text{C}$ for 10 h with a stirring speed of 900 rpm. After the reaction was halted, the reactor was cooled to room temperature. The catalyst was isolated from the solution by centrifugation. The liquid phase was decanted into a volumetric flask using toluene as diluent, and subsequently analyzed by GC-MS (Shimadzu GCMS-QP5050A equipped with a $0.25\text{ mm} \times 30\text{m}$ DB-WAX capillary

column).

The conversions and selectivities were evaluated on the basis of the amounts of HMF. The conversion of HMF (mol%), products yield (mol%), DFF selectivity (mol%) and carbon balance (mol%) were calculated using the following equations:

$$\text{HMF conversion} = \left(1 - \frac{\text{Moles of HMF}}{\text{Moles of HMF loaded}} \right) \times 100\%$$

$$\text{Product selectivity} = \frac{\text{Moles of product}}{\text{Moles of HMF converted}} \times 100\%$$

$$\text{DFF yield} = \frac{\text{Moles of DFF}}{\text{Moles of HMF loaded}} \times 100\%$$

$$\text{Carbon balance} = \frac{\text{Moles of products}}{\text{Moles of HMF converted}} \times 100\%$$

The recyclability of the FeCo/C catalysts was tested for HMF oxidation maintaining the same reaction condition as described above, except using the recovered catalyst. Each time, the catalyst was isolated from the reaction mixture by magnetic separation at the end of catalytic reaction, and then thoroughly washed with methanol.

5. Solvent effects on HMF oxidation

The reaction was carried out at 100 °C and 1 MPa O₂ using FeCo/C(500) as catalyst (metal 20 mol%) with 1 mmol HMF and 1 mmol Na₂CO₃ dissolved in 2 mL solvent. The reaction performed in 2 mL toluene afforded the highest DFF yield. It seemed that in this catalytic system, aromatic solvent like toluene was beneficial for HMF conversion.

Table S1. Effects of solvent on HMF oxidation.

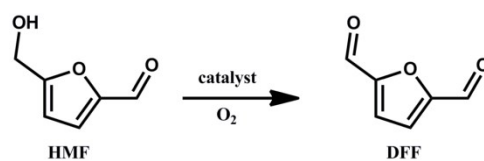
Entry	Solvent	HMF conversion (%)	DFF selectivity (%)
1	Water	71	65
2	DMSO	72	74
3	Cyclohexane	75	95
4	Toluene	>99	>99

6. Effect of base on HMF oxidation

The reaction was carried out at 100 °C and 1 MPa O₂ using FeCo/C(500) as catalyst (metal 20 mol%) using 1 mmol HMF but different Na₂O₃ amount dissolved in 2 mL toluene. Only traces of conversion of HMF was observed without the presence of Na₂O₃. The HMF conversion increased with the amount of Na₂O₃. When the molar ratio of base to HMF was enhanced to 1.0, a quantitative conversion of HMF to DFF was achieved.

Entry	Na ₂ CO ₃ /HMF molar ratio	HMF conversion (%)	DFF selectivity (%)
1	1.0	>99	>99
2	0.5	60	99
3	0	5	99

Table S2. Reaction results of HMF oxidation over the FeCo/C(T) catalysts^a



Entry	Catalyst	HMF conversion (%)	DFF selectivity (%)
1	FeCo/C(500)	>99	>99
2	FeCo/C(600)	37	>99
3	FeCo/C(700)	28	>99
4	FeCo/C(800)	20	>99

^a Reaction conditions: 1 mmol HMF, catalyst (metal 20 mol%), Na₂CO₃ 1 mmol, 2 mL toluene, 1 MPa O₂, 100 °C, 6 h.

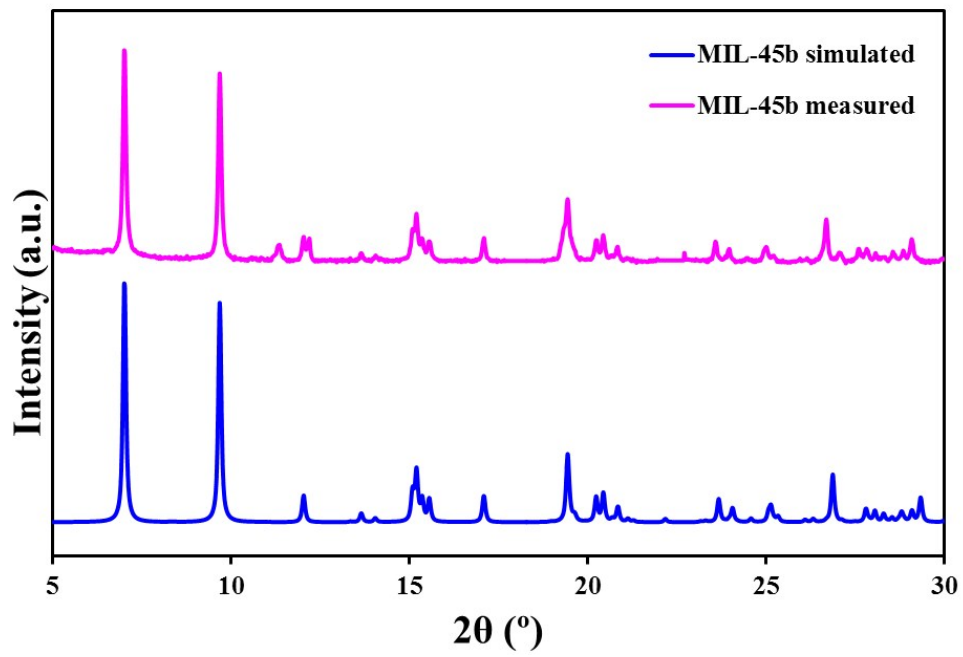


Figure S1. Powder X-ray diffraction patterns of MIL-45b.

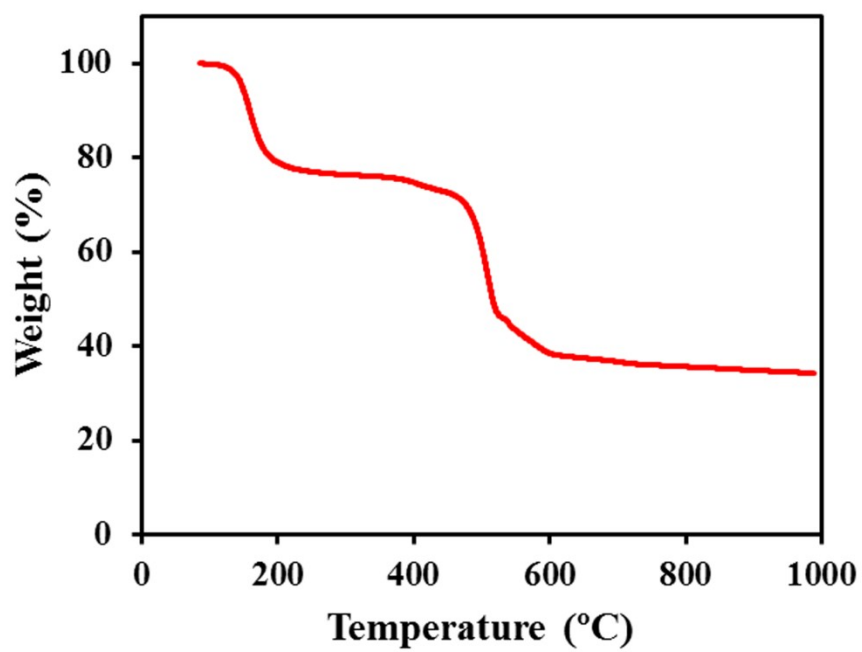


Figure S2. The thermogravimetric (TG) curve of MIL-45b.

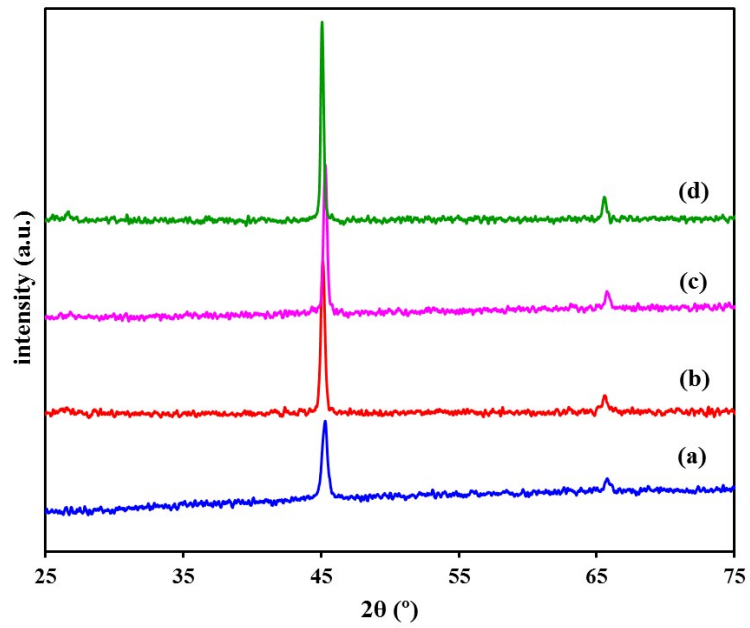


Figure S3. PXRD patterns of FeCo/C (T) materials: a) FeCo/C (500), b) FeCo/C (600), c) FeCo/C (700), and d) FeCo/C (800).

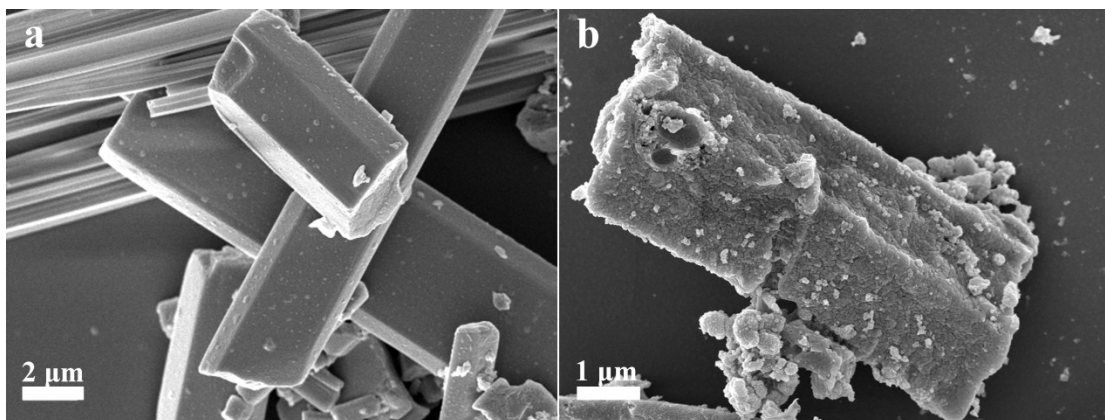


Figure S4. a) SEM image of MIL-45b; b) SEM image of FeCo/C (500).

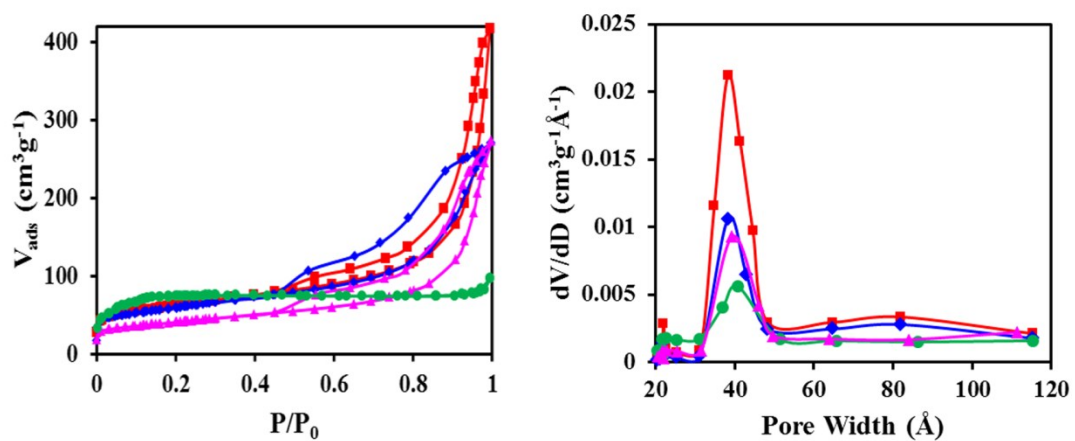


Figure S5. Nitrogen adsorption isotherms at 77 K (left) and corresponding pore-size distribution curves (right) of the calcined MIL-45b at 500 °C (■); 600 °C (◆); 700 °C (▲); 800 °C (●), respectively.

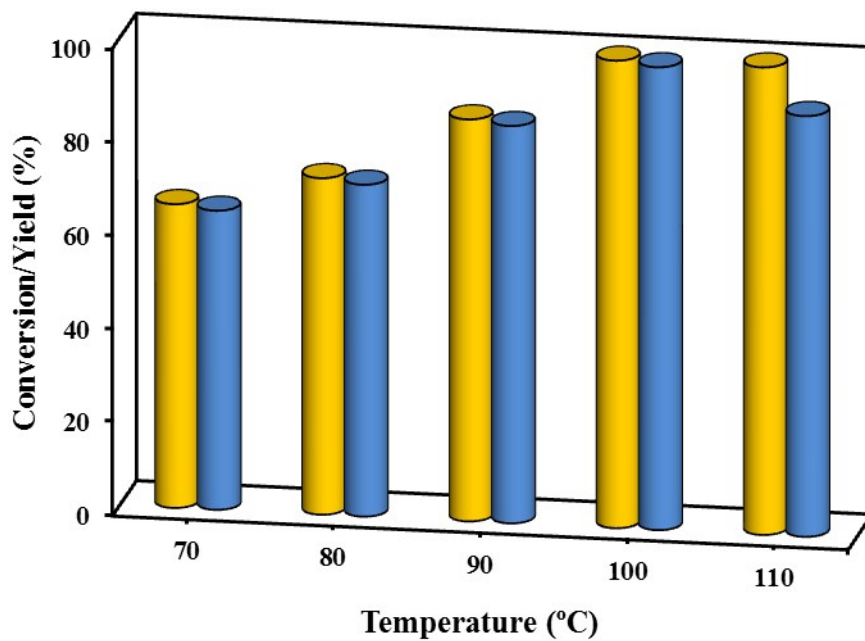


Figure S6. Effect of reaction temperature on the HMF transformation. Reaction conditions: 1 mmol HMF, catalyst (metal 20 mol%), Na₂CO₃ 1 mmol, 2 mL toluene, 1 MPa O₂, 6 h.

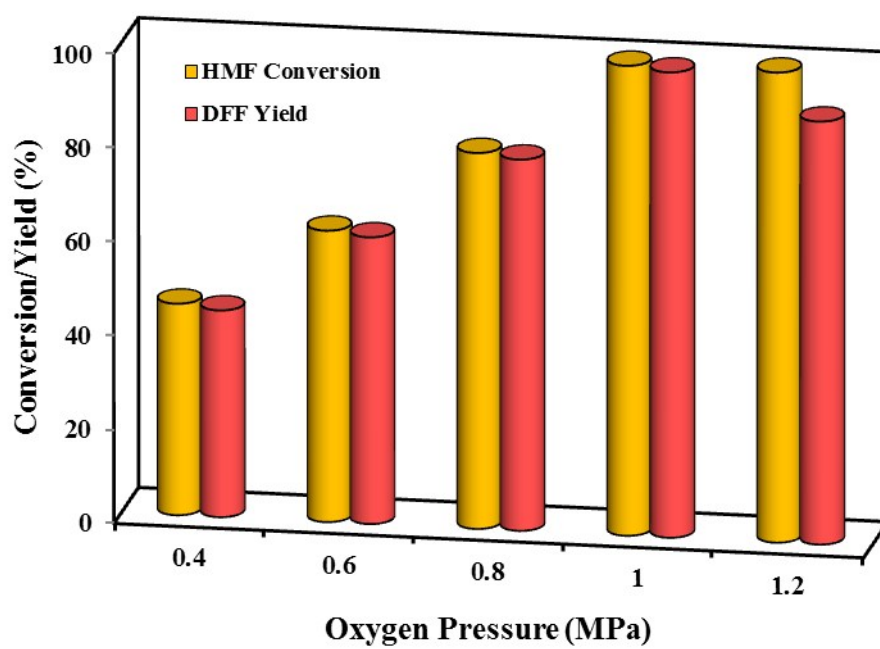


Figure S7. Effect of oxygen pressure on the HMF transformation. Reaction conditions: 1 mmol HMF, catalyst (metal 20 mol%), Na₂CO₃ 1 mmol, 2 mL toluene, 100 °C, 6 h.



Figure S8. Magnetic separation of the catalyst after reaction.

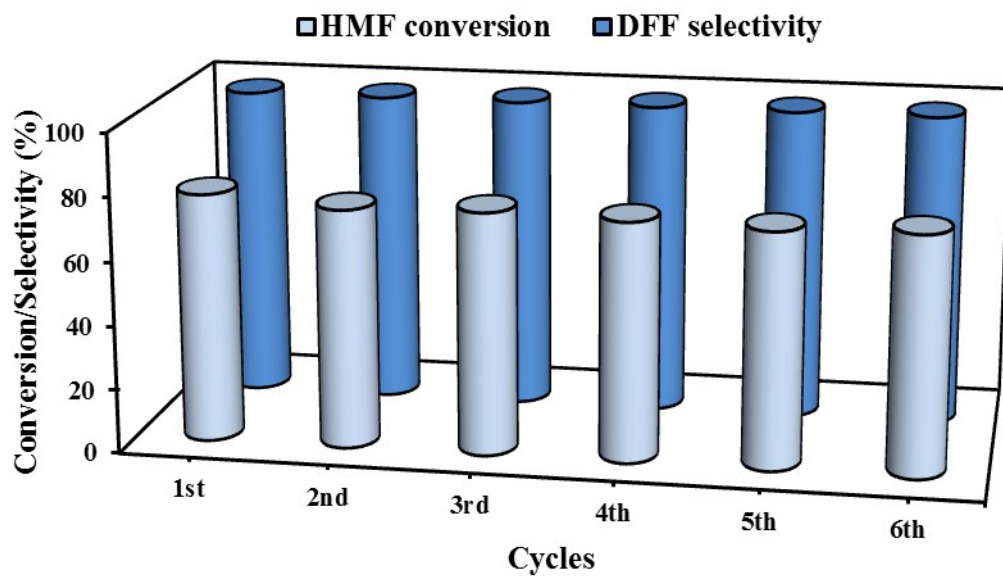


Figure S9. Reuses of the FeCo/C(500) catalyst for HMF oxidation. Reaction conditions: 1 mmol HMF, catalyst (metal 20 mol%), Na₂CO₃ 1 mmol, 1 MPa O₂, 100 °C, 3 h.

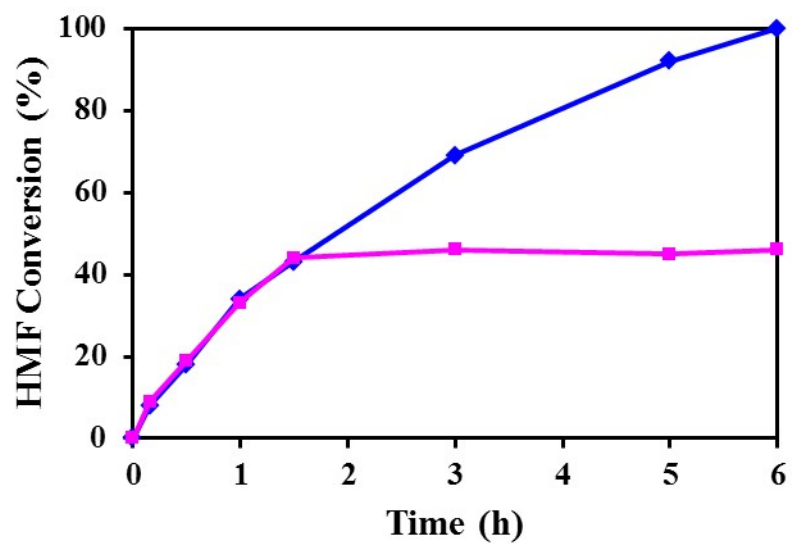


Figure S10. Activity profile for HMF oxidation. Reaction conditions: 1 mmol HMF, catalyst (metal 20 mol%), Na₂CO₃ 1 mmol, 1 MPa O₂, 100 °C, 6 h.