

## Supporting Information

### **S, P modified CoFe-LDH derived CoFeS and CoFeP-400 catalysts efficiently catalyze the oxidation of HMF to FDCA**

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## Experimental

### Materials and reagents

5-(hydroxymethyl) furfural ( $C_6H_6O_3$ ,  $\geq 98\%$ ), 2,5-furandicarboxylic acid ( $C_6H_4O_5$ ,  $\geq 98\%$ ) and 2,5-furandicarboxaldehyde ( $C_6H_4O_3$ ,  $\geq 98\%$ ) were purchased from Shanghai Dibo Biotechnology Co. Ltd. 5-formyl-2-furancarboxylic acid ( $C_6H_4O_4$ ,  $\geq 98.0\%$ ) and 5-hydroxymethyl-2-furancarboxylic acid ( $C_6H_6O_4$ ,  $\geq 98\%$ ) were purchased from Aladdin Reagent Co. Ltd. (Shanghai, China). Thioacetamide ( $CH_3CSNH_2$ ,  $\geq 98.0\%$ ), sodium hypophosphite ( $NaH_2PO_2$ ,  $\geq 98\%$ ), sodium hydroxide ( $NaOH$ ,  $\geq 96\%$ ), ferric chloride hexahydrate ( $FeCl_3 \cdot 6H_2O$ ,  $\geq 98\%$ ), nickel nitrate hexahydrate ( $Co(NO_3)_2 \cdot 6H_2O$ ,  $\geq 98\%$ ), urea ( $CO(NH_2)_2$ ,  $\geq 99.0\%$ ) and absolute ethanol ( $CH_3CH_2OH$ ,  $\geq 99.7\%$ ) were purchased from Tianjin Kaitong Chemical Reagent Co. Ltd. Methanol ( $CH_3OH$ ,  $\geq 99.9\%$ ), hydrogen peroxide ( $H_2O_2$ , 30%) and acetonitrile ( $CH_3CN$ ,  $\geq 99.9\%$ ) were purchased from Tianjin Yongda Chemical Reagent Co. Ltd. Distilled deionized water was used in all experiments. Nitrogen gas (99.9%) and oxygen gas (99.9%) was obtained from Shandong Yingchun Gas Co. Ltd. All chemicals were of analytical grade and were used without further purification.

### Catalyst synthesis

#### Synthesis of CoFe-LDH

The CoFe-LDH used in this work was prepared by a hydrothermal method. Briefly, 0.02 mol of  $Co(NO_3)_2 \cdot 6H_2O$  and 0.01 mol of  $FeCl_3 \cdot 6H_2O$  were added to 60 mL of ionized water and stirred until the salts had fully dissolved. Next, 0.1 mol of urea was dissolved in 40 mL of water, with the resulting urea solution then added dropwise to the mixed metal nitrate solution under magnetic stirring. After stirring for 1 h at room temperature, the solution was then transferred to a teflon-lined autoclave and heated at 120 °C for 24 h. After natural cooling to room temperature, the solid CoFe-LDH product was collected by filtration and washed with deionized water until the pH of the filtrate was 7. Finally, the CoFe-LDH product was dried in an oven at 90 °C for 10 h.

#### Synthesis of the CoFeS Catalyst

The CoFeS catalyst was prepared as follows. CoFe-LDH (0.5 g) was dispersed in 60 mL of absolute ethanol under ultrasonication, after which 0.5 g of thioacetamide was

added under magnetic stirring. After stirring for 1 h at room temperature, the dispersion was then transferred to a Teflon-lined autoclave (volume 120 mL) and heated at 120 °C for 6 h. After natural cooling to room temperature, the solid product was collected by centrifugation, then washed three times with absolute ethanol and then deionized water. Finally, the product was dried at 50 °C under vacuum for 4 h. The obtained product is denoted herein as CoFeS.

### **Synthesis of the CoFeP Catalyst**

A series of CoFeP-x catalysts were prepared as follows. CoFe-LDH (0.5 g) and sodium hypophosphite (0.5 g) were placed in separate porcelain boats in the center of the tubular furnace. The porcelain boat containing the sodium hypophosphite was placed upstream of the boat containing CoFe-LDH, with the distance between boats around 7.5 cm. The tube furnace was then heated to a temperature (x) between 300 °C-500 °C at a heating rate of 2 °C/min under a N<sub>2</sub> gas flow. After heating at the specified temperature (x) for 2 h, the furnace was allowed to cool naturally to room temperature. The obtained P-doped samples were washed twice with ethanol and then water, then dried in an oven at 35 °C. The resulting catalysts are denoted here CoFeP-x (where x represents the temperature during the sodium hypophosphite treatment step).

### **Materials characterization**

X-ray diffraction (XRD) patterns were collected at room temperature on a Bruker D 8 Advance X-ray diffractometer equipped with a Cu K $\alpha$  radiation source (40 kV, 30 mA). Thermogravimetric analysis (TGA) data were collected on a SDT-Q600 simultaneous TGA/DSC thermal analyzer (TA Instruments, USA). Samples are heated from room temperature to 800 °C at 10 °C/min under a N<sub>2</sub> flow. Scanning electron microscopy (SEM) analyses were carried out on a NoVa Nano SEM 430 (FEI, USA) operating at electron acceleration voltage of 20 kV. Transmission electron microscopy analyses (TEM) were carried out on the Tecnai G20 (FEI, USA) instrument operating at an accelerating voltage of 200 kV. Nitrogen adsorption-desorption isotherms were collected at 77 K on ASAP 3020 (Micromeritics, USA). Specific surface area and pore volume are calculated by BET and BJH methods, respectively. XPS data were collected on a K-Alpha XPS system (ThermoFisher Scientific, USA) equipped with a

monochromated Al K  $\alpha$  X-ray source (1486.6 eV). CO<sub>2</sub>-TPD data were collected on a AutoChem II 2920 workstation. Samples were heated from room temperature to 800 °C at a heating rate of 10 °C/min, and then held at 800 °C for 30 min. Desorption products were analyzed by gas chromatography with a TCD detector (GC-TCD). The amount of CO<sub>2</sub> desorbed, expressed as mmol of CO<sub>2</sub> per gram of catalyst, was determined by the calibration curve method.

### Catalytic tests

HMF oxidation tests were carried out in a high pressure Teflon-lined reactor under vigorous stirring. Typical reaction conditions were as follows: 50 mg of HMF, 10 mL of acetonitrile (as solvent), oxidant (t-BuOOH (0.36 mL, 70 wt.% in water), H<sub>2</sub>O<sub>2</sub> (20 mL, 3 wt.%) or oxygen), 50 mg of catalyst, autogenic pressures, reaction temperatures ranging from 40 to 120 °C, and reaction times ranging from 1-12 h.

### Product Analysis

High performance liquid chromatography (HPLC, LC-20A) was used to determine the concentration of HMF and its oxidation products. The mobile phase was an acetonitrile-water mixture (5:95, v/v, flow rate 0.8 mL/min). A C-18-A (Diamosil, 5  $\mu$ m, 4.6 mm  $\times$  250 mm) column was used to separate HMF and its oxidation products. The column temperature was 30 °C. Under these conditions, the retention times for 2,5-furandicarboxylic acid (FDCA), 5-formyl-2-furanic acid (HMFCFA), 5-hydroxymethylfurfural (HMF) and 2,5-difuran (DFF) were 4.5, 7.0, 9.0 and 11.2 min respectively. The detection wavelength was 260 nm for these four compounds. The retention time of 5-formyl-2-furan carboxylic acid (FFCA) was 5.4 min (detection wavelength 290 nm).

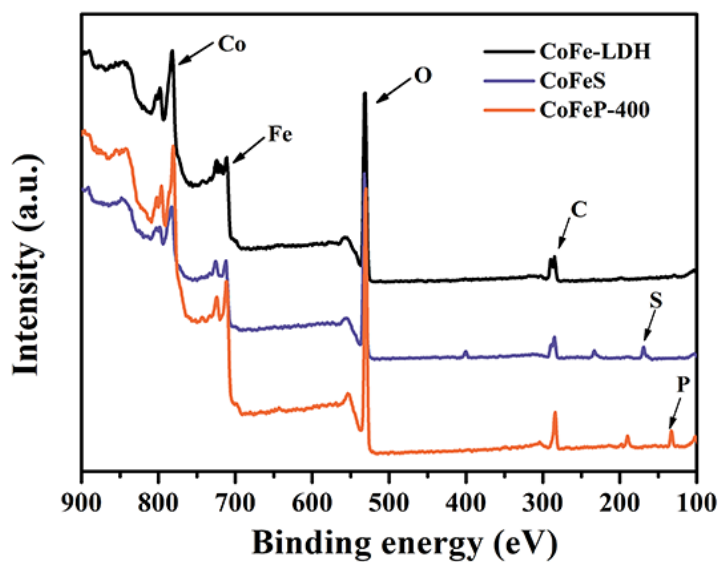
HMF conversion, product selectivities and product yields were calculated using equations 1, 2 and 3, respectively:

$$\text{HMF conversion} = \frac{\text{moles of HMF reacted}}{\text{moles of HMF initially added to reactor}} \times 100 \%$$

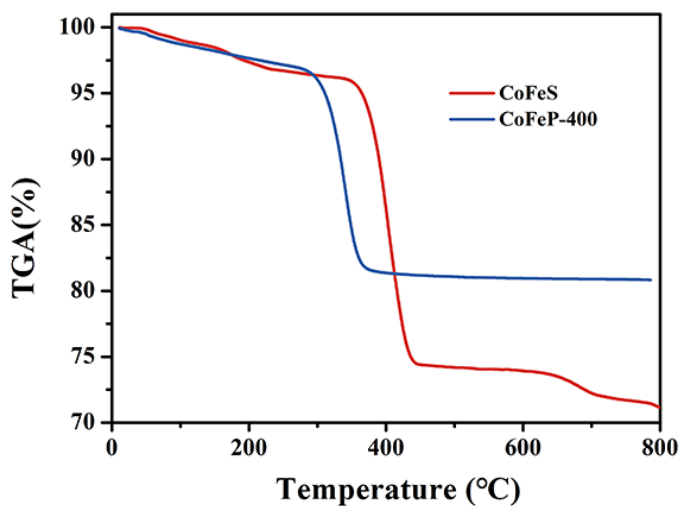
(1)

$$\text{HMFCFA, FFCA, or FDCA selectivity} = \frac{\text{moles of HMFCFA, FFCA, or FDCA}}{\text{moles of HMF reacted}} \times 100 \%$$
 (2)

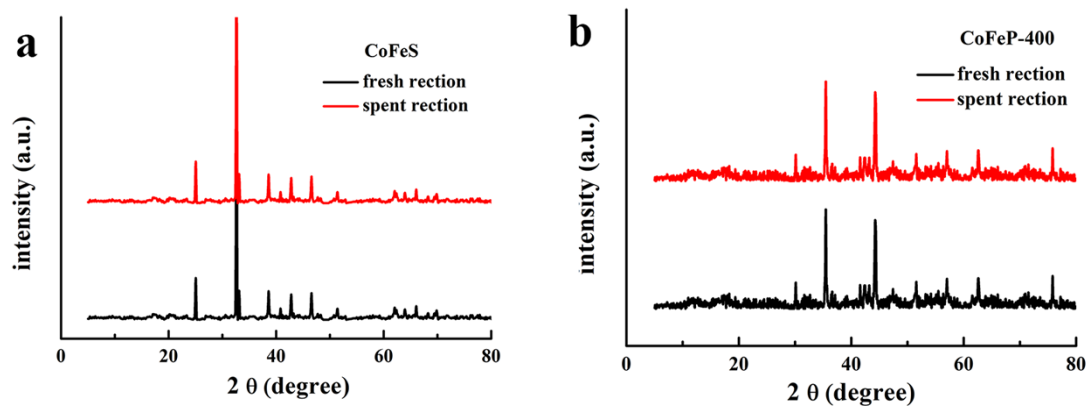
$$\text{HMFCA, FFCA, or FDCA yield} = \frac{\text{moles of HMFCA, FFCA, or FDCA}}{\text{moles of HMF initially added to reactor}} \times 100 \% \quad (3)$$



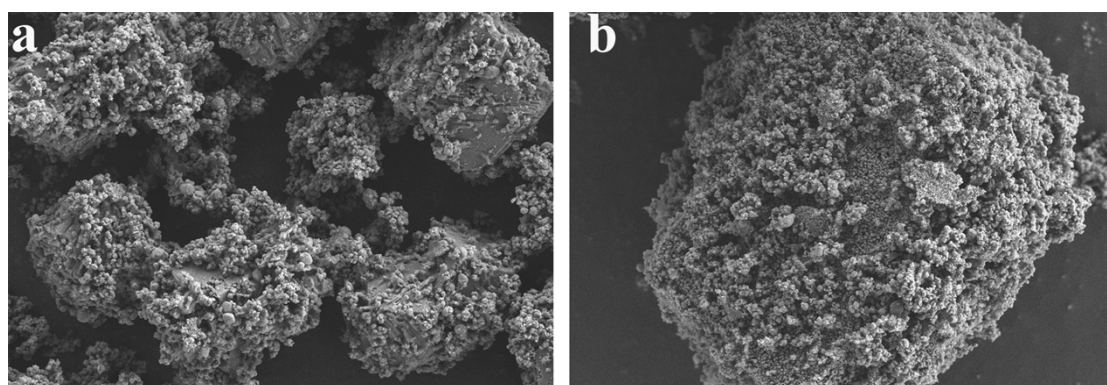
**Figure S1.** XPS survey spectra for CoFe-LDH, CoFeS and CoFeP-400.



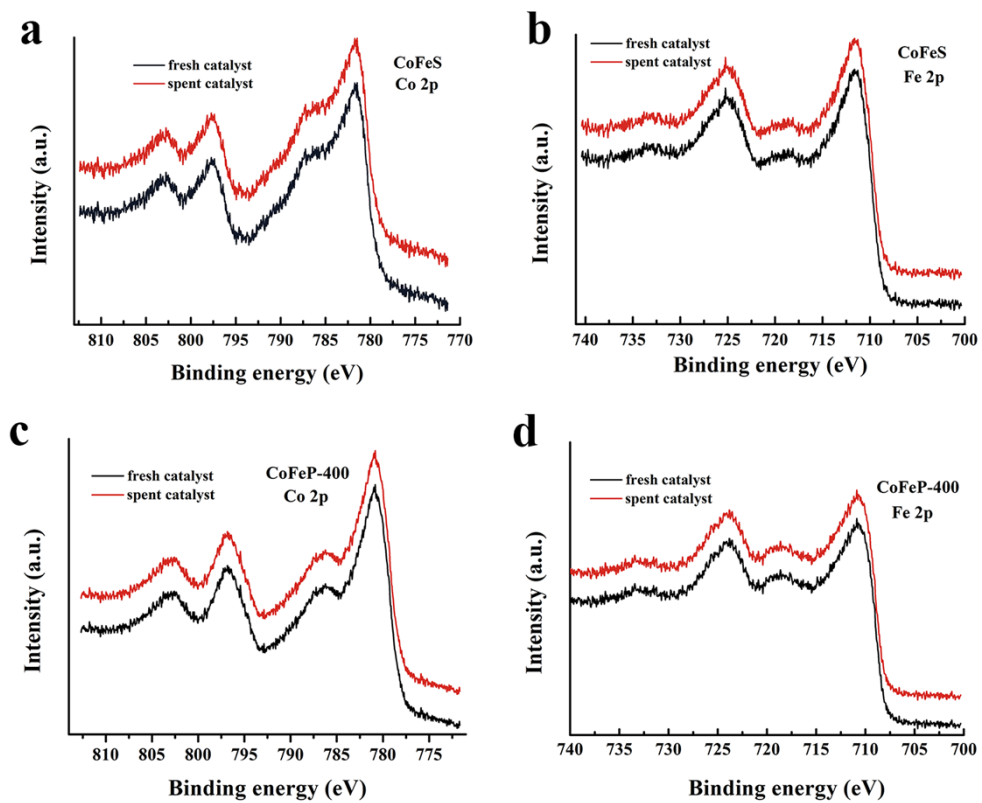
**Figure S2.** TGA curves for the CoFeS and CoFeP-400 catalysts with heating at 10 °C/min in N<sub>2</sub>.



**Figure S3.** Powder XRD patterns for different catalysts before and after the HMF oxidation reaction tests: (a) CoFeS and (b) CoFeP-400.



**Figure S4.** SEM images of different catalysts after the HMF oxidation reaction: (a) CoFeS after reaction and (b) CoFeP-400 after reaction.



**Figure S5.** Core level XPS spectra of different catalysts before and after the HMF oxidation reaction:

(a) Co 2p region and (b) Fe 2p region for CoFeS, (c) Co 2p region and (d) Fe 2p region for CoFeP-400.

Table S1. Summary for HMF Conversion and FDCA Yield Using Different Catalysts.

Entry	Catalyst	oxidant	Alkaline additive	HMF Con. (%)	FDCA Yield (%)	Ref.
1	CoFeS/CoFeP-400	t-BuOOH	--	100	89.5	This work
2	Fe <sub>3</sub> O <sub>4</sub> -CoOx	t-BuOOH	--	100	68.6	1
3	CuCl	t-BuOOH	--	100	45	2
4	Ru(OH) <sub>x</sub> /Fe <sub>3</sub> O <sub>4</sub>	O <sub>2</sub>	--	100	50	3
5	Mn-Co-O	O <sub>2</sub>	KHCO <sub>3</sub>	99.5	70.9	4
6	Pd-NOs/Pd-NCs	O <sub>2</sub>	NaHCO <sub>3</sub>	92.6	60	5
7	Au/graphitized C	H <sub>2</sub> O <sub>2</sub>	NaHCO <sub>3</sub>	99	75	6



## References

1. S. Wang, Z. Zhang and B. Liu, *ACS Sustainable Chemistry & Engineering*, 2015, **3**, 406-412.
2. T. S. Hansen, I. Sádaba, E. J. García-Suárez and A. Riisager, *Applied Catalysis A: General*, 2013, **456**, 44-50.
3. Y. Y. Gorbanev, S. Kegnæs and A. Riisager, *Topics in Catalysis*, 2011, **54**, 1318-1324.
4. S. Zhang, X. Sun, Z. Zheng and L. Zhang, *Catalysis Communications*, 2018, **113**, 19-22.
5. D. Lei, K. Yu, M.-R. Li, Y. Wang, Q. Wang, T. Liu, P. Liu, L.-L. Lou, G. Wang and S. Liu, *ACS Catalysis*, 2017, **7**, 421-432.
6. B. Donoeva, N. Masoud and P. E. de Jongh, *ACS Catal*, 2017, **7**, 4581-4591.