

Solid-state synthesis of CN encapsulated CoFe alloy catalysts for mild HMF oxidation to FDCA: Insights to the kinetics and mechanism

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Experimental

Materials

HMF (99%), DFF (98%), HMFCA (98%), FFCA (98%) and FDCA (98%) were purchased from Bide Pharmatech Co., Ltd. $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (99%) and HCl (99.5%) were purchased from Xilong Scientific Co., Ltd. $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (99.95%) was purchased from Shanghai Macklin Biochemical Co., Ltd. $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (99%) was purchased from Shanghai Aladdin Reagent Co., Ltd. 2-MeIM (98%) and ammonium formate (99%) were purchased from Shanghai Yien Chemical Technology Co., Ltd., Methanol (99%) and NaHCO_3 were purchased from Tianjin Yongda Chemical Reagent Co., Ltd. All chemicals were used as received without any further purification.

Catalyst preparation

The preparation of $\text{Co}_2\text{Fe}_1@\text{NC}$ involved the solid-phase milling-pyrolysis method. Firstly, 10 mmol $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 3.0 mmol $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 1.5 mmol $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, and 29 mmol 2-MeIM were mixed via solid-phase milling for 30 minutes. Subsequently, the foaming material was obtained by drying the mixture at 120 °C for 24 hours, then thoroughly ground and pyrolyzed at 800 °C for 2 hours under a nitrogen atmosphere with a heating rate of 5 °C/min. The material was treated with hydrochloric acid (1 mol/L) for 4 hours, followed by diafiltration and ultimately drying under vacuum at 60 °C overnight, which was labeled as $\text{Co}_2\text{Fe}_1@\text{NC}$.

Catalyst characterization

Powder X-ray diffraction (XRD) was performed on a Panalytic Empyrean diffractometer and analyzed using Cu $K\alpha$ radiation sources (45KV and 40mA) in the 2θ range of 10-80°. N_2 physisorption was carried out at -196 °C using the ASAP2460 auto-adsorption analyzer (Micromeritics). Before adsorption measurements were taken, the samples were degassed at 200 °C overnight. The total pore volume was determined from the aggregation of N_2 vapor adsorbed at a relative pressure of 0.99. The specific surface area was calculated using the B.E.T. method, and the pore size was estimated using BJH method from the desorption branch of the isotherms. X-ray photoelectron

spectroscopy (XPS) was conducted on a Kratos XSAM800 spectrometer, with all binding energies calibrated against the C1s peak at 284.6 eV. The contents of Co and Fe were determined by Thermo Scientific iCAP PRO X inductively coupled plasma - optical emission spectroscopy (ICP-OES). Transmission electron microscopy (TEM) images were obtained using an accelerating voltage of 200 kV on a JEOL-135 2010F Transmission Electron Microscope. Scanning TEM (STEM) images were recorded using the FEI Titan G260-300 Transmission Electron Microscope operated at 200 kV.

Chemisorption measurements were conducted using an Auto Chem II 2920 instrument (Micromeritics, USA) equipped with a thermal conductivity detector (TCD). For O₂-TPR, 100 mg of the catalyst was pretreated at 200 °C under an Ar atmosphere for 1 hour, followed by cooling to room temperature. The sample was then exposed to O₂ for 1 hour and swept with Ar for 1 hour. Subsequently, the sample was heated to 700 °C at a rate of 10 °C/min under an Ar atmosphere, and the desorbed O₂ signal was collected using a TCD detector.

Catalyst test

The HMF oxidation was conducted in a 50 mL stainless steel autoclave with a glass liner. Initially, HMF (0.25 mmol), NaHCO₃ (0.5 mmol), catalyst (60 mg), and H₂O (3 mL) were added. The reactor was purged with 0.1 MPa O₂ five times, and then pressurized to the specified pressure and heated to the desired reaction temperature. After the reaction, the reactor was rapidly cooled, 0.1 mL aliquots were collected and diluted 50 times. The filtrates were filtered and analyzed using high-performance liquid chromatography (Agilent Infinity Lab HPLC) at 30 °C with a C18 column and UV detector. The mobile phase consisted of a 5 mM ammonium formate aqueous solution and methanol (70:30, v/v), flowing at a rate of 1 mL/min. The UV detector was set to an absorption wavelength of 256 nm for HMFCFA and FDCA, 284 nm for HMF, and 290 nm for FFCA and DFF. The catalyst was recovered by diafiltration, washed with H₂O (500 mL), dried overnight in a vacuum at 60 °C, and then treated at 300 °C in H₂ flow for 1 h. The HMF conversion and product yields were determined based on the

external standard method.

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

$$(2) \text{ Product yield (\%)} = \frac{\text{Moles of obtained products}}{\text{HMF mole before the reaction}} \times 100\%$$

$$(3) \text{ Product selectivity (\%)} = \frac{\text{Product yield}}{\text{HMF conversion}} \times 100\%$$

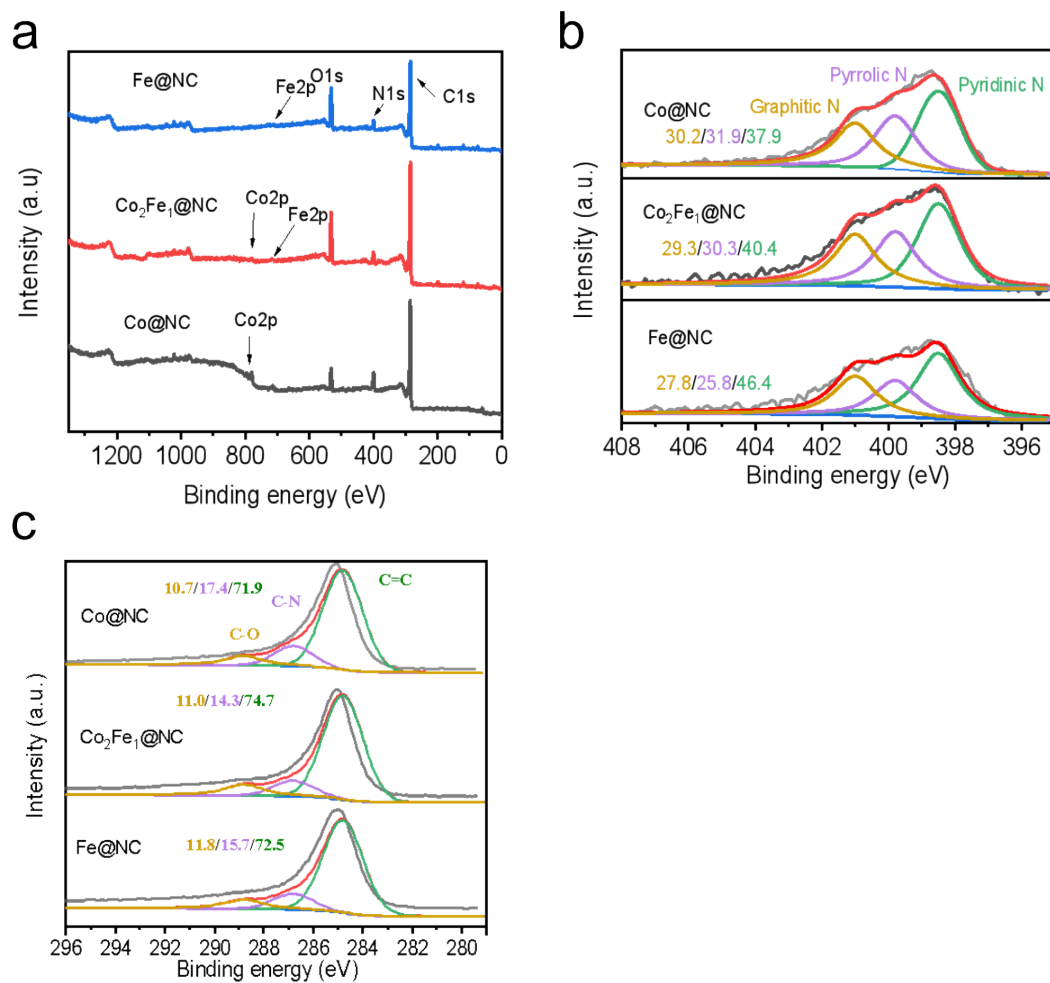


Fig. S1 XPS spectra of Co_xFe_y@NC catalyst: (a) full spectrum, (b) N 1s, and (c) O 1s.

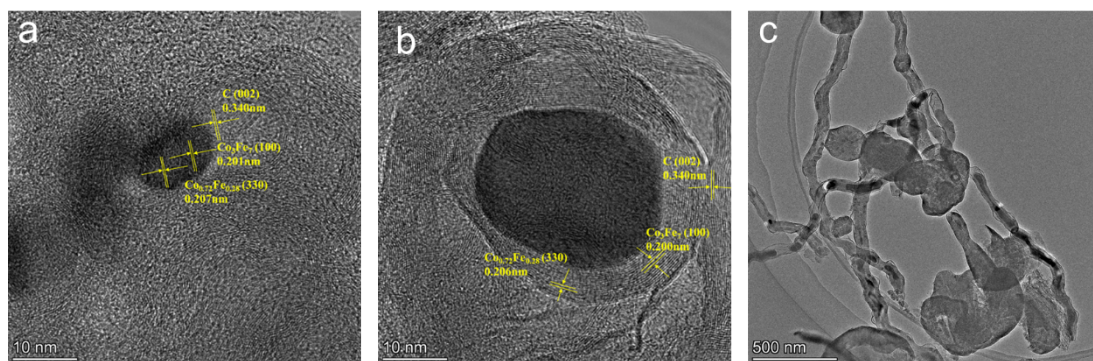


Fig. S2 (a-b)TEM images of (a-b) Co₂Fe₁@NC, (c) Fe@NC.

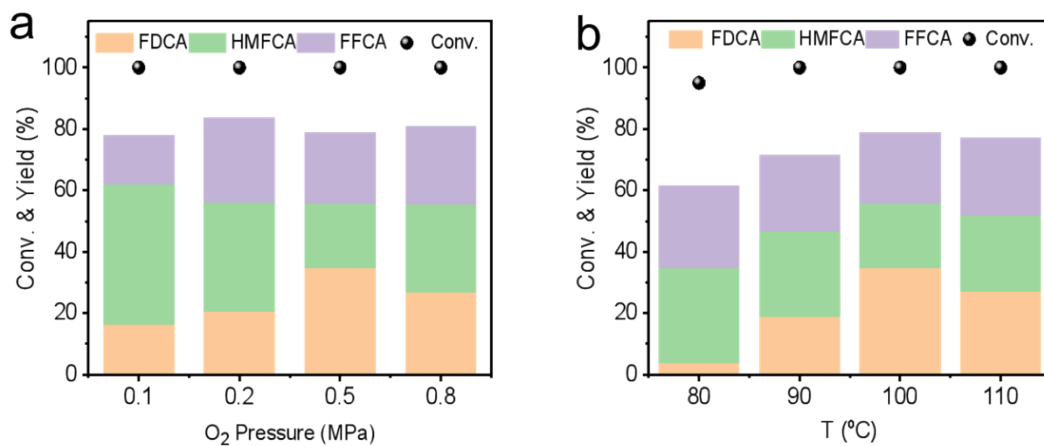


Fig. S3 Catalyst screening for HMF oxidation at 2 h over $\text{Co}_2\text{Fe}_1@\text{NC}$. The influences of (a) reaction temperature and (b) reaction pressure on HMF oxidation over $\text{Co}_2\text{Fe}_1@\text{NC}$ (Reaction conditions: HMF 0.25 mmol, $\text{Co}_2\text{Fe}_1@\text{NC}$ 60 mg, NaHCO_3 0.5 mmol, H_2O 3 mL; a: 100 °C; b: 0.5 MPa O_2).

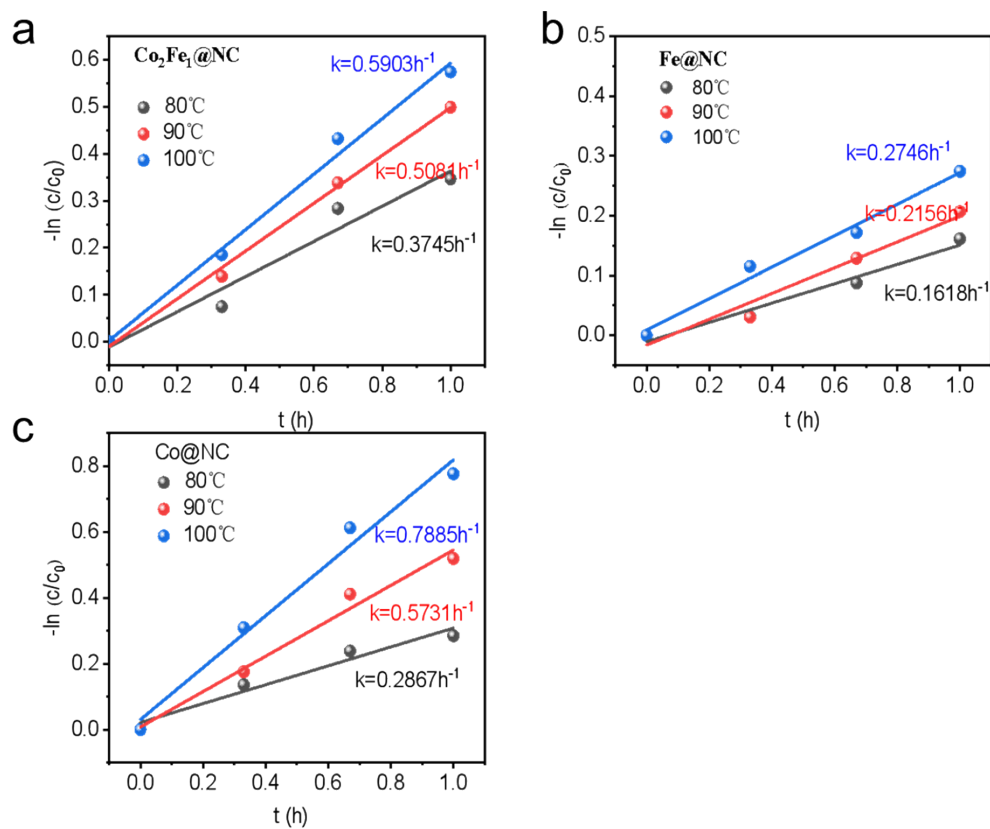


Fig. S4 Time–conversion plots of FFCA oxidation at various temperatures for $\text{Co}_2\text{Fe}_1@\text{NC}$, $\text{Fe}@\text{NC}$, and $\text{Co}@\text{NC}$ catalysts (Reaction conditions: FFCA 0.25 mmol, catalyst 60 mg, NaHCO_3 0.5 mmol, H_2O 3 mL, 0.5 MPa O_2).

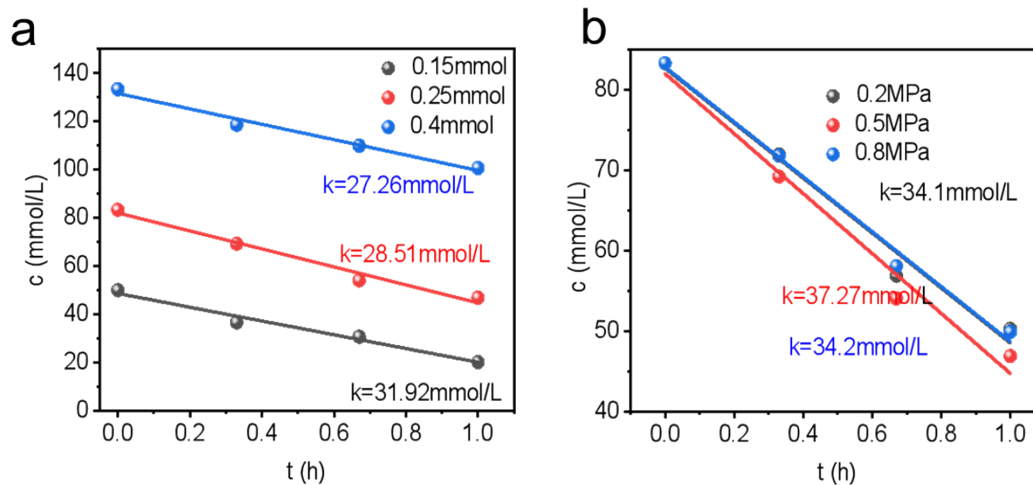


Fig. S5 Measurement of rate orders of (a) FFCA concentration and (b) O₂ pressure for the Co₂Fe₁@NC.

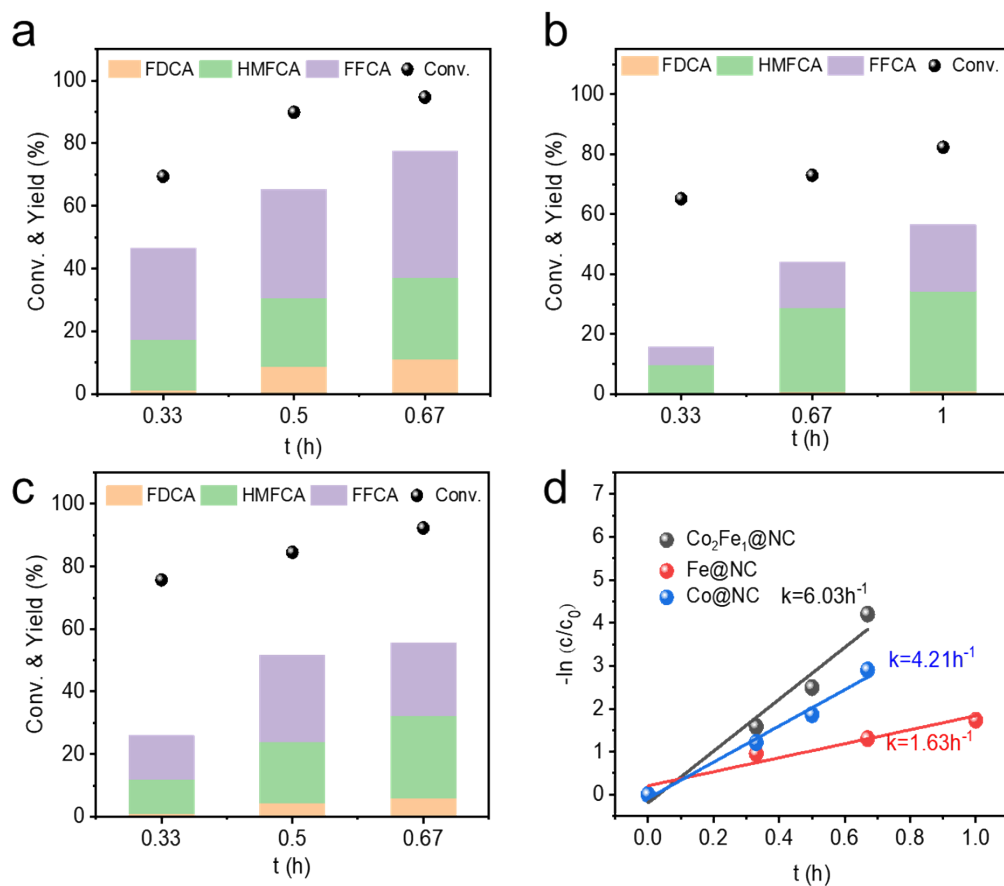


Fig. S6 The reaction time profiles of HMF on different catalysts: (a) Co₂Fe₁@NC, (b) Fe@NC, (c) Co@NC, and (d) Time–conversion plots of HMF oxidation for Co₂Fe₁@NC, Fe@NC, and Co@NC catalysts (Reaction conditions: HMF 0.25 mmol, catalyst 60 mg, NaHCO₃ 0.5 mmol, H₂O 3 mL, 0.5 MPa O₂, 100 °C).

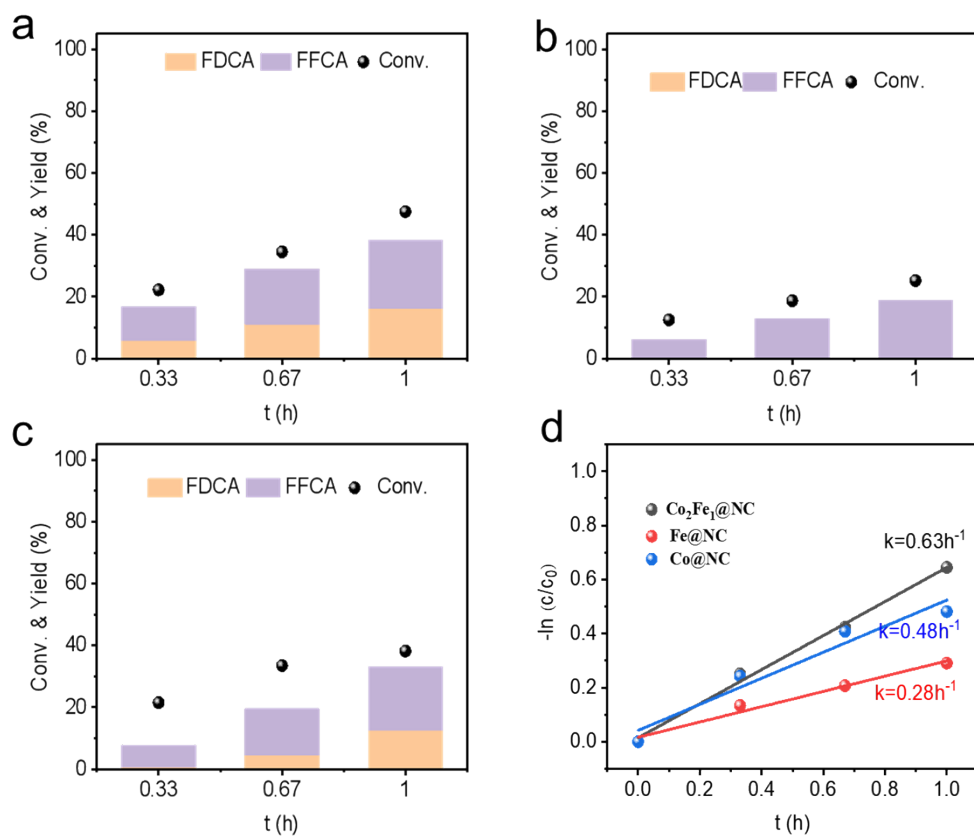


Fig. S7 The reaction time profiles of HMFCFA on different catalysts: (a) $\text{Co}_2\text{Fe}_1@\text{NC}$, (b) $\text{Fe}@\text{NC}$, (c) $\text{Co}@\text{NC}$, and (d) Time-conversion plots of HMFCFA oxidation for $\text{Co}_2\text{Fe}_1@\text{NC}$, $\text{Fe}@\text{NC}$, and $\text{Co}@\text{NC}$ catalysts (Reaction conditions: HMFCFA 0.25 mmol, catalyst 60 mg, NaHCO_3 0.5 mmol, H_2O 3 mL, 0.5 MPa O_2 , 100 °C).

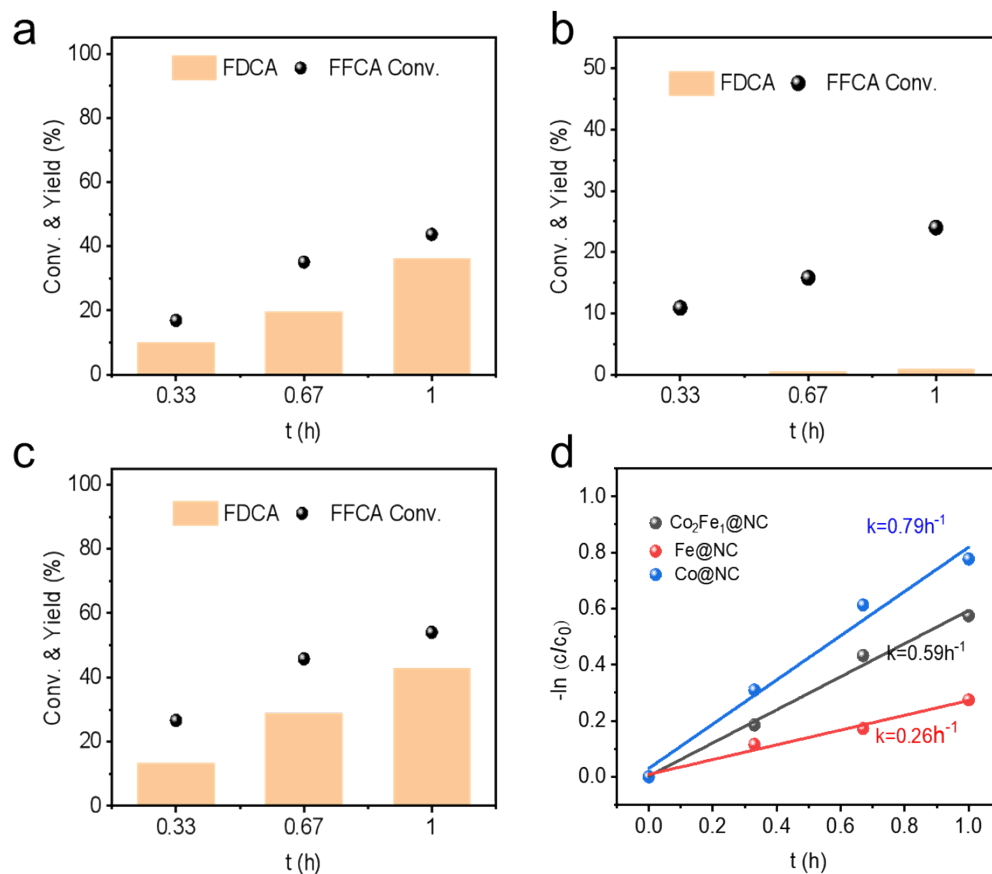


Fig. S8 The reaction time profiles of FFCA on different catalysts: (a) $\text{Co}_2\text{Fe}_1@\text{NC}$, (b) $\text{Fe}@\text{NC}$, (c) $\text{Co}@\text{NC}$, and (d) Time–conversion plots of FFCA oxidation for $\text{Co}_2\text{Fe}_1@\text{NC}$, $\text{Fe}@\text{NC}$, and $\text{Co}@\text{NC}$ catalysts (Reaction conditions: FFCA 0.25 mmol, catalyst 60 mg, NaHCO_3 0.5 mmol, H_2O 3 mL, 0.5 MPa O_2 , 100 °C).

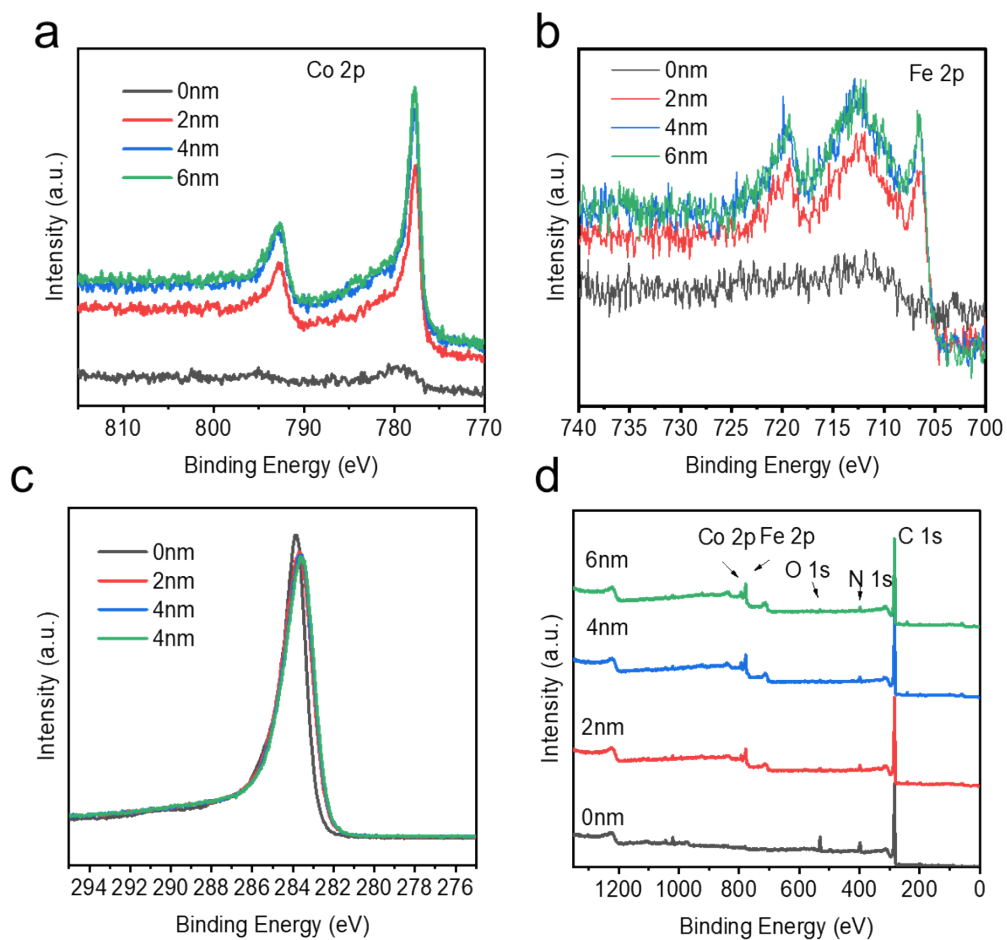


Fig. S9. Ar ion sputtering profile of the $\text{Co}_2\text{Fe}_1@\text{NC}$.

Table S1. Physical property data of Co and Fe-based catalysts.

Catalyst	S _{BET} (m ² /g)	V _{total} (cm ³ /g)	Pore size (nm)
Co@NC	328	0.126	6.5
Co ₃ Fe ₁ @NC	330	0.182	7.2
Co ₂ Fe ₁ @NC	372	0.141	4.9
Co ₁ Fe ₂ @NC	386	0.089	3.4
Fe@NC	510	0.131	3.8

Table S2. Metal content of Co and Fe based catalysts.

Catalyst	Metal loading (wt%)	
	Co	Fe
Co@NC	38.8	0
Co ₂ Fe ₁ @NC	14.2	5.67
Fe@NC	0	8.7

Table S3. The element content obtained from XPS analysis in the catalysts.

Catalyst	Content/at%				
	Co	Fe	N	C	O
Co@NC	1.35	0	10.95	79.94	7.75
Co ₂ Fe ₁ @NC	0.51	0.20	6.58	79.15	13.55
Fe@NC	0	0.57	7.29	76.37	16.08

Table S4. The crystallite sizes of nanoparticles in different $\text{Co}_x\text{Fe}_y\text{@NC}$ catalysts

Catalysts	Sizes of nanoparticles (nm)
$\text{Co}_1\text{Fe}_2\text{@NC}$	21.0
$\text{Co}_1\text{Fe}_1\text{@NC}$	18.9
$\text{Co}_2\text{Fe}_1\text{@NC}$	19.3
$\text{Co}_3\text{Fe}_1\text{@NC}$	19.9

Table S5. Comparison of oxidation performances for HMF of reported catalysts.

Catalyst	T (°C)	O ₂ pressure	Yield (%)	Ref.
Fe _{0.6} Zr _{0.4} O ₂	160	2 MPa	60.6	1
Pd/CC	140	1 MPa	85	2
Ag _{1.5} Pd _{1.5} /CeO ₂	20	0.1 MPa	93	3
Ru/C	140	4 MPa	98	4
CoCe-0.15	130	0.6 MPa	86.3	5
(Co ₁ →Co _p)/N-CNTs	100	0.1 MPa	96	6
Mn ₃ Co ₂ O _x -0.3VC	130	1.5 MPa Air	96	7
Co ₂ Fe ₁ @NC	100	0.5 MPa	96.1	This work

Table S6 Different methods of treating Co₂Fe₁@NC catalyst

Entry	Conv. (%)	Yield (%)			
		FDCA	HMFCFA	FFCA	DFC
Fresh	100	70.4	11.9	15.8	0
Run 2 ^a	100	62.2	13.0	14.6	0
Run 2 ^b	100	61.8	12.1	17.6	0
Run 2 ^c	100	68.2	12.9	7.9	0

^aTreated with water and NaHCO₃ at 100 °C, ^b Without treatment of water and NaHCO₃ at 100 °C, ^c Treated with hydrogen at 300 °C.

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