Supplementary Material

Monolithic catalysts loaded with ZIF-derived Co$_3$O$_4$ on copper foam for the catalytic oxidation of toluene: The impact of synthetic methods

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1. Experimental

1.1. Chemicals and materials

The chemicals and materials used in this study are summarized in Table S1. All chemicals were analytical grade without further purification.

Table S1. List of chemicals and materials used in this study.

Chemicals or materials	Purity	Manufacturers
Cobalt nitrate hexahydrate	99%, AR	Shanghai Maclean Biochemical Technology Co., Ltd, China
2-Methylimidazole	98%, AR	Shanghai Maclean Biochemical Technology Co., Ltd, China
Ammonium fluoride	98%, AR	Shanghai Maclean Biochemical Technology Co., Ltd, China
Urea	99%, AR	Tianjin Kemiou Chemical Reagent Co., Ltd, China
Ethanol	99.7%, AR	Tianjin Fuyu Fine Chemical Co.
HCl solution	37%, AR	Tianjin Yuanli chemical Co., Ltd, China
Cu foam	99.7%, 110 ppi pore density and 1.8 mm thickness	Kunshan Longshengbao Electronic Material Co., Ltd, China
Toluene standard gas	1000 mg/m^3 toluene, 20 vol.% O_2 and N_2 (balance)	Jining Xieli Special Gases Co., Ltd, China

1.2. Catalyst preparation

1.2.1. Pretreatment of Cu foam

Cu foam (Φ=1.8 cm) was placed in a 0.1 mol/L HCl solution and ultrasonicated for 15 min, followed by washing with ethanol and deionized (DI) water several times. Finally, the pretreated Cu foam was dried at 60°C for 2 h.

1.2.2. Preparation of Co_3O_4@CF-E

Electrochemical deposition was carried out on an electrochemical workstation (Correst CS350M) using a three-electrode system. Cu foam, Ag/AgCl and graphite sheet were used as working, reference and counter electrodes, respectively. The electrochemical deposition was carried out by cyclic voltammetry (between -0.6 V and -1.60 V vs Ag/AgCl), and the deposition solution was 60 mL of 0.1 mol/L $Co(NO_3)_2$ solution with a scanning rate of 10 mV/s for four cycles. Subsequently, it was washed with DI water and dried at 80°C, and named as $Co(OH)_2$@CF.

$Co(OH)_2$@CF was immersed in 10 mL of DI water containing 2 mmol of dimethylimidazole for 12 h. Removed, washed with DI water and dried. ZIF-67@CF-E was obtained.

Co_3O_4@CF-E was obtained by calcining ZIF-67@CF-E in an air atmosphere with a temperature increase rate of 3°C/min to 350°C for 3 h.

1.2.3. Preparation of Co_3O_4@CF-H

2 mmol $Co(NO_3)_2 \cdot 6H_2O$, 8 mmol NH_4F, and 10 mmol urea were

dissolved in 15 mL of DI water. The mixed solution was transferred to a Teflon-lined autoclave containing a piece of Cu foam and placed in an oven at 120°C for 12 h. After cooling to room temperature, it was washed with DI water and dried at 80°C. Co-modified@CF was obtained.

The Co-modified@CF was pyrolyzed at 350°C for 1 h under N_2 atmosphere to obtain CoO@CF.

2 mmol dimethylimidazole was dissolved in a mixed solution of 5 mL DI water and 5 mL ethanol. Subsequently, CoO@CF was immersed in the above mixed solution for 12 h. It was removed, washed with DI water and dried at 80°C. ZIF-67@CF-H was obtained.

Co_3O_4@CF-H was obtained by calcining ZIF-67@CF-H in an air atmosphere with a temperature increase rate of 3°C/min to 350°C for 3 h.

1.2.4. Preparation of Co_3O_4/CuO@CF

CuO@CF was obtained by calcining Cu foam in an air atmosphere with a temperature increase rate of 3°C/min to 400°C for 4 h.

CuO@CF was immersed in 10 mL of DI water containing 8 mmol of dimethylimidazole for 1 h. Subsequently, 10 mL $Co(NO_3)_2$ solution (0.2 mol/L) was added to the above solution, and left to stand for 12 h. It was removed, washed with DI water, and dried at 80°C. ZIF-67/CuO@CF was obtained.

Co_3O_4/CuO@CF was obtained by calcining ZIF-67/CuO@CF in an air atmosphere with a temperature increase rate of 3°C/min to 350°C for 3

h.

1.2.5. Preparation of Co₃O₄/CF

2 mmol $Co(NO_3)_2 \cdot 6H_2O$ was dissolved in 20 mL of DI water. Later, the Cu foam was impregnated in the above solution and left to stand for 12 h. It was removed, washed with DI water and dried at 80°C. Finally, Co_3O_4/CF was obtained by calcining it in an air atmosphere at a temperature increase rate of 3°C/min to 350°C for 3 h.

1.2.6. Preparation of contrast catalyst

CF was obtained by calcining pretreated Cu foam in an air atmosphere with a temperature increase rate of 3°C/min to 350°C for 3 h.

2. Characterization

Field emission scanning electron microscope (SEM) was characterized on FEI Quattro S and the EDS mapping were obtained by EDAX ELECT PIUS. Transmission electron microscopy (TEM) was characterized on FEI Tecnai 20.

Thermogravimetric analysis (TGA) was conducted on a NETZSCH TG209F3 apparatus at a heating rate of 10°C/min in air atmosphere with a flow rate of 100 mL/min.

X-ray diffraction (XRD) analysis was conducted to explore the crystal phase of samples, which was recorded on a Rigaku MiniFlex 600 X-ray diffractometer with Cu Kα radiation (λ = 1.5418 Å) and run in the range of 10-90° with 60 kV and 55 mA.

N_2 adsorption-desorption was conducted on a Micromeritics ASAP 2420 instrument, and the specific surface area of the sample was determined by nitrogen adsorption in accordance with the Brunauer Emmett and Teller (BET) method. Before measurements, the sample was degassed at 150°C for 6 h, and BET surface area determination was calculated through six measurements at relative pressures of N_2 in the range of 0.05-1.00.

H_2-Temperature program reduction (H_2-TPR) was performed on a TP-5080-B automatic multi-function adsorption apparatus. 50 mg sample was loaded into the reaction tube. Before test, the sample was heated from

50°C to 300°C in a N_2 gas stream (30 mL/min) at a heating rate of 10°C/min and held at 300°C for 30 min for pretreatment. After cooling, the sample was exposed to a 10 vol.% H_2 and 90 vol.% N_2 gas mixture at 30 mL/min and heated at a heating rate of 10°C/min from 50°C to 800°C.

O_2-Temperature program desorption (O_2-TPD) was performed on a TP-5080-B automatic multi-function adsorption apparatus. Firstly, 100 mg samples were putted into the quartz tube reactor, and then they were purged with pure He gas (30 mL/min) at 300°C for 1 h. After that, the mixture gas of 10 vol.% O_2 and 90 vol.% N_2 (30 mL/min) was introduced at 50°C for 1 h, and then the pure He gas (30 mL/min) was used to remove the unabsorbed O_2 molecules at 50°C for 1 h. Ultimately, the samples were heated from 50°C to 800°C.

X-ray photoelectron spectroscopy (XPS) was conducted on a Thermo Scientific™ K-Alpha™+ spectrometer equipped with a monochromatic Al Kα X-ray source (1486.6 eV) operating at 100 W. Samples were analyzed under vacuum ($P < 10^{-8}$ mbar) with a pass energy of 150 eV (survey scans) or 50 eV (high-resolution scans). All peaks would be calibrated with C1s peak binding energy at 284.8 eV for adventitious carbon.

Raman spectra were performed on a RENISHAW inVia Raman microscope (Renishaw, UK) with a 532 nm laser.

The actual Co content of the catalysts was determined by inductively coupled plasma emission spectrometry (ICP-OES) on a 5110 ICP-OES.

The electron paramagnetic resonance (EPR) spectra were attained on a Bruker A300 spectrometer at room temperature.

In situ diffuse reflectance infrared Fourier transform spectroscopy (In situ DRIFTS): In situ DRIFTS was carried out on TENSOR II (Bruker, German). The powder samples were degassed in N_2 gas with 50 mL/min gas volume at 300°C for 30 min. After that, the samples were cooled to room temperature. Accordingly, the spectra were collected with the sample as the background. A nitrogen-oxygen gas mixture (20 vol.% O_2/N_2) containing 1000 mg/m^3 toluene was introduced at a flow rate of 100 mL/min. Finally, the samples were further heated to 250°C and the spectra were collected for 1 min, 5 min, 10 min, 15 min, 30 min, 60 min, and 90 min, respectively. To examine the change with temperature, the samples were purged with N_2 at 300°C for 30 min and then reduced to room temperature. A nitrogen-oxygen gas mixture (20 vol.% O_2/N_2) containing 1000 mg/m3 toluene was introduced, and the gas flow rate was 100 mL/min. Spectra were collected at temperatures of 100°C, 115°C, 130°C, 145°C, 160°C, 175°C, 190°C, 205°C, 220°C, 235°C, 250°C, 265°C, and 270°C, respectively.

3. DFT calculation details

Spin-polarized DFT calculations were carried out using the Vienna Ab-initio Simulation Package (VASP) with the frozen-core all-electron projector-augment-wave (PAW) method [1-3]. The exchange and correlation energies for all systems were treated under the generalized gradient approximation (GGA) proposed by Perdew-Burke-Ernzerhof (PBE) [4]. The cut-off energy for plane wave was set to 450 eV. To include dispersion interactions, we used the Grimme's DFT-D3 method [5]. The dipole correction along Z-direction was included in the calculations. The convergence criteria for electronic and ionic relaxations were set to 10^{-5} eV and 0.03 eV/Å, respectively. To partially correct the strong electron-correlation properties of oxides, DFT+U calculations [6, 7] were performed with U = 2 eV for Co and U = 7 eV for Cu, with the U values taken from literature [8, 9].

The $p(2\times3)$ Co_3O_4 (220) and $p(2\times3)$ Co_3O_4 (311) supercells with two layers was used in this calculations, the bottom one layer were frozen to their bulk positions, and the remaining one layer was relaxed. A $p(3\times5)$ slab of CuO (-111) with three layers was used, and the top one layer of the slab were allowed to relax, whereas the bottom two layers were fixed. All supercell slabs were repeated periodically with a 19 Å vacuum layer between the images in the direction of the surface normal. A CuO cluster with a stoichiometric ratio of 1:1 was extracted from CuO (-111) slab, and

a Cu cluster was extracted from Cu (111) slab. To keep the structure unchanged, all of the atoms in two clusters were allowed to relax in the Z direction. The single gamma-point grid sampling was used for Brillouin zone integration. All molecules were relaxed in a $20 \times 20 \times 20$ Å^3 box. Adsorption energy (E_{ads}) was calculated by using the following definitions:

$$E_{ads} = E_{adsorbate+slab} - E_{slab} - E_{adsorbate}$$

Where $E_{adsorbate+slab}$ is the total electron energy of the adsorbed molecule and slab; E_{slab} is the electron energy of the clean slab; $E_{adsorbate}$ is the electron energy of isolated molecule.

Cu foam	Co(OH)₂@CF	ZIF-67@CF-E	Co₃O₄@CF-E
Cu foam	Co-modified@CF	CoO@CF	ZIF-67@CF-H	Co₃O₄@CF-H
Cu foam	CuO@CF	2-MIM/CuO@CF	ZIF-67/CuO@CF	Co₃O₄/CuO@CF
Cu foam	Co(NO₃)/CF	Co₃O₄/CF
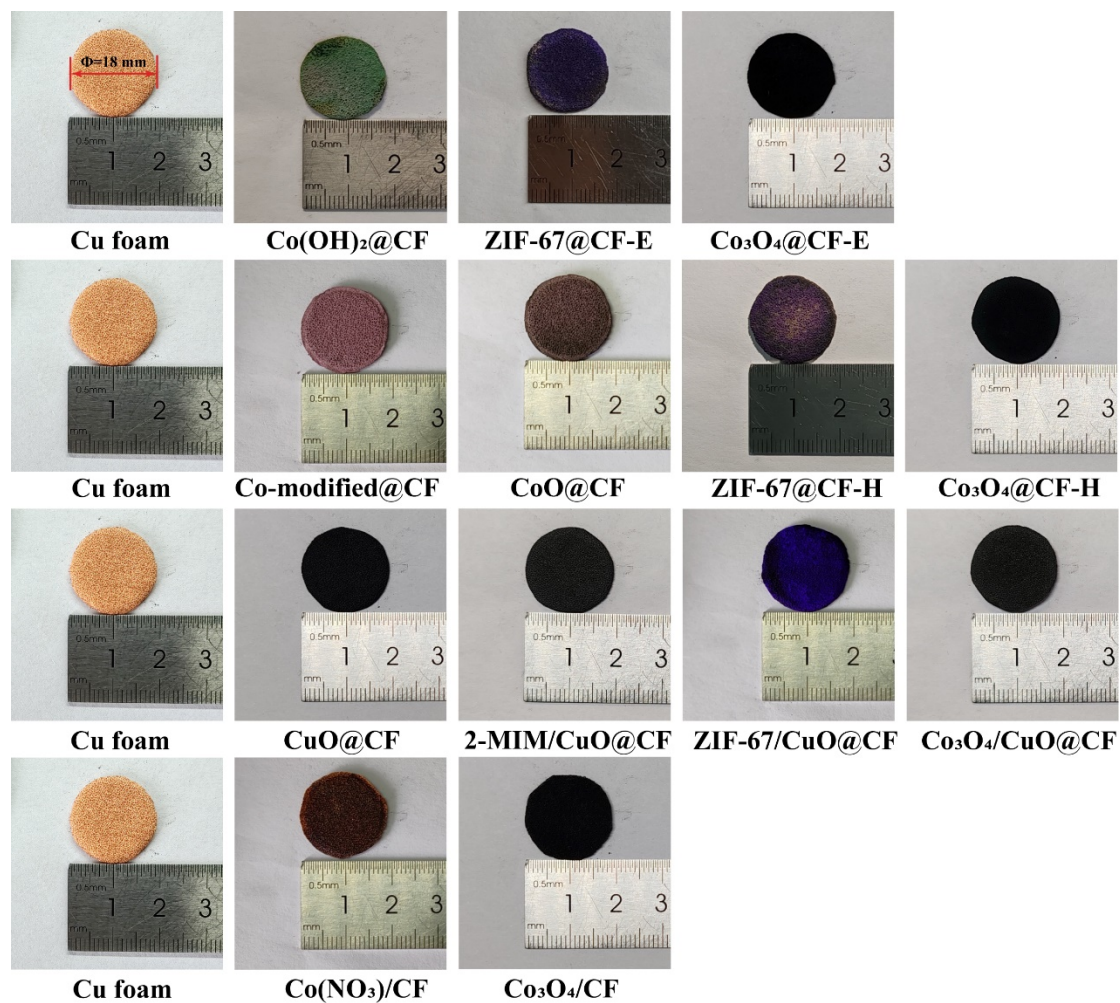
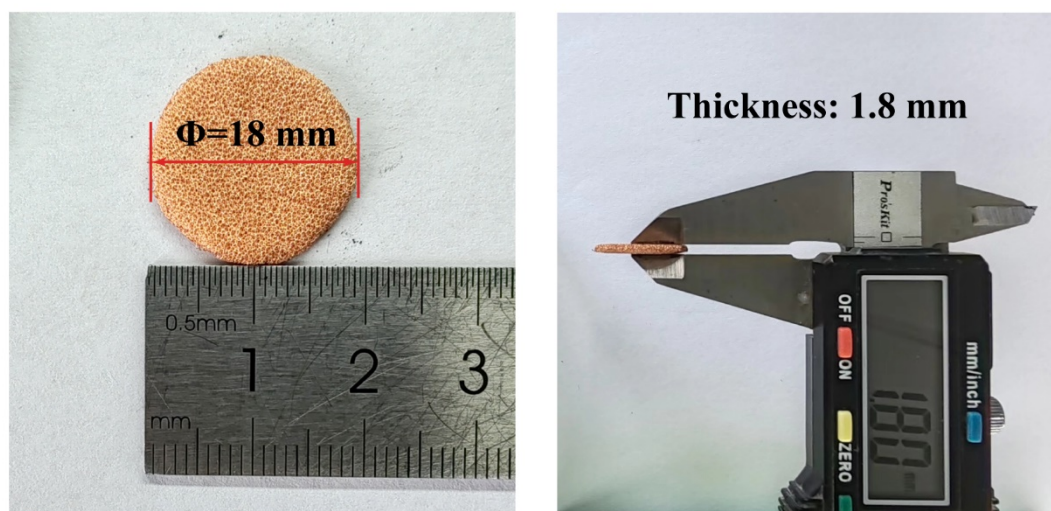**Figure S1.** Physical photos of all monolithic catalysts.

Figure S2. Copper foam round sheet size measurement results.

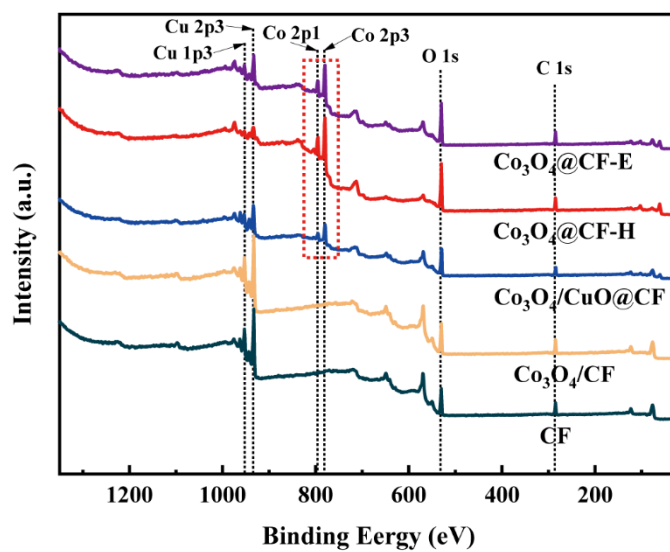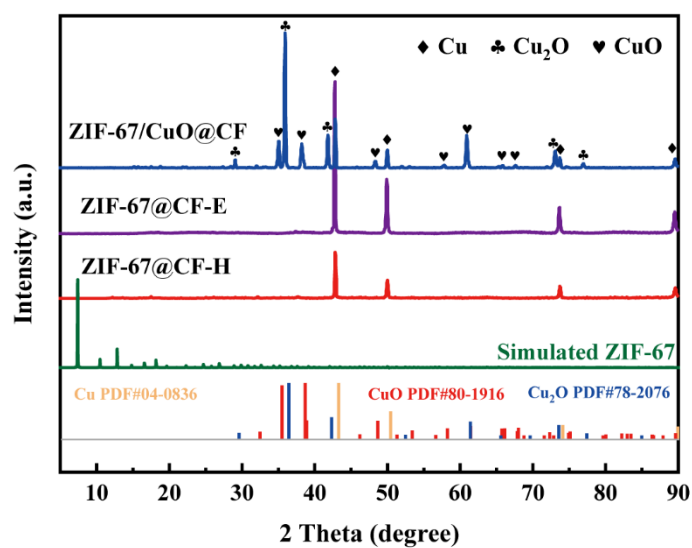**Figure S3.** XPS full spectrum of monolithic catalysts.

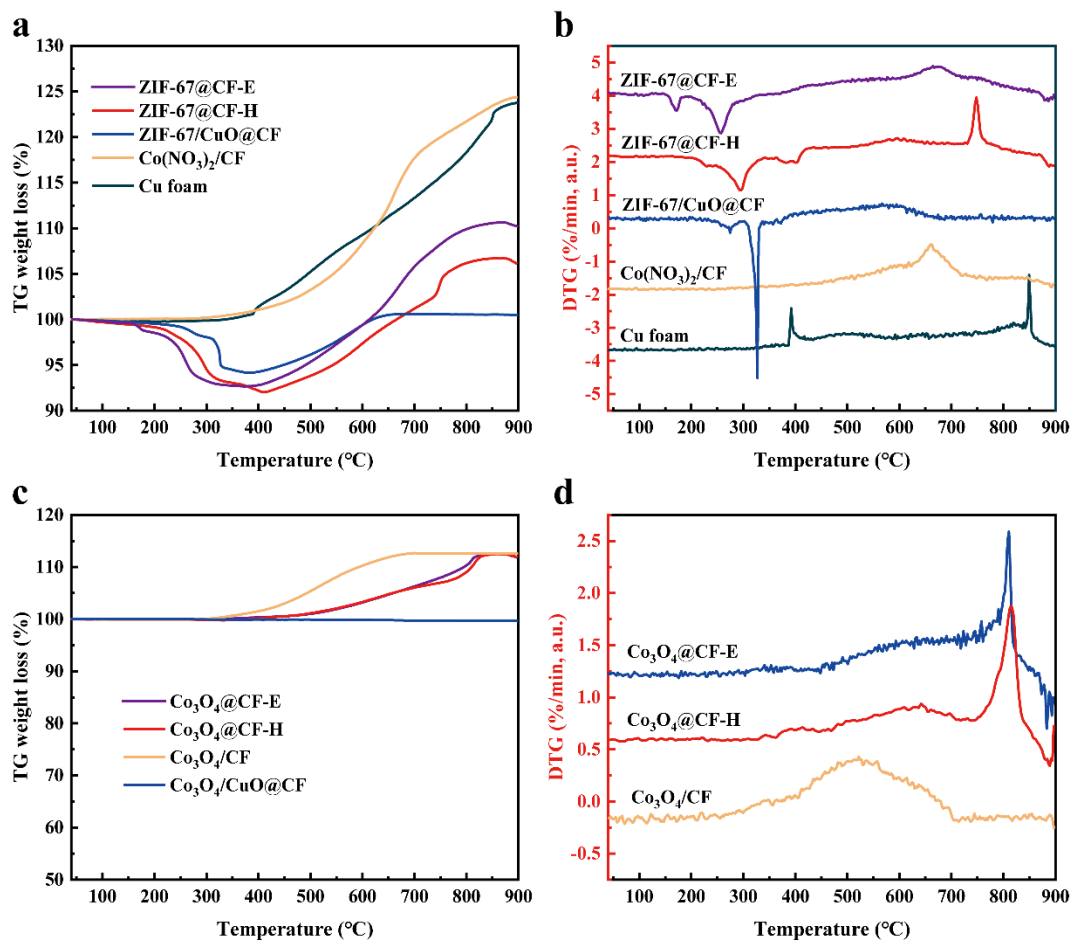**Figure S4.** XRD patterns of ZIF-67@CuO/CF, ZIF-67@CF-E and ZIF-67@CF-H samples.

Figure S5. TG (a) and DTG (b) curves of catalyst precursor decomposition in air atmosphere before roasting; TG (c) and DTG (d) curves of catalyst decomposition in air atmosphere after roasting.
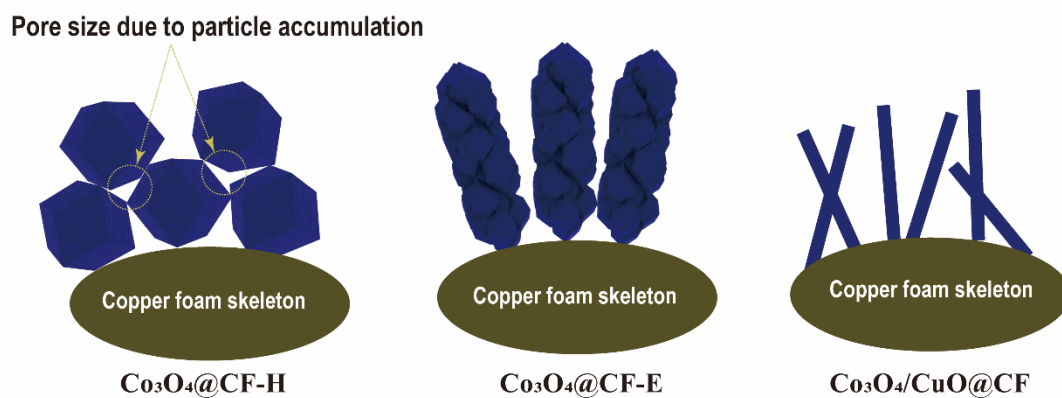
Figure S6. Schematic structure of $Co_3O_4@CF-H$, $Co_3O_4@CF-E$, and $Co_3O_4/CuO@CF$ samples (cross-section).

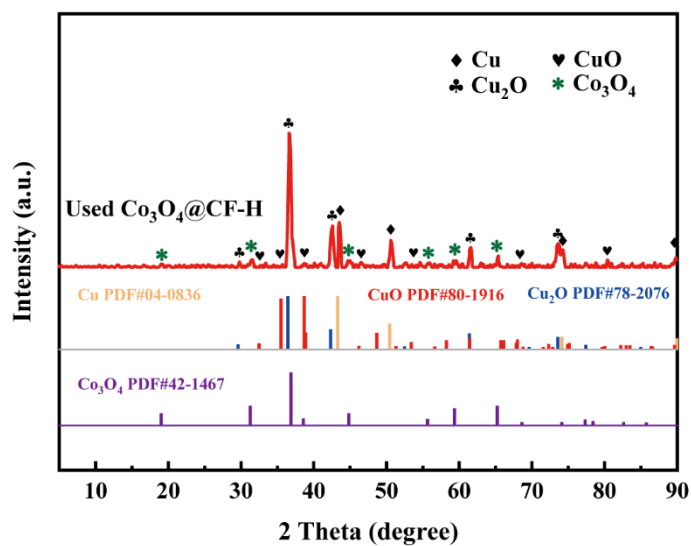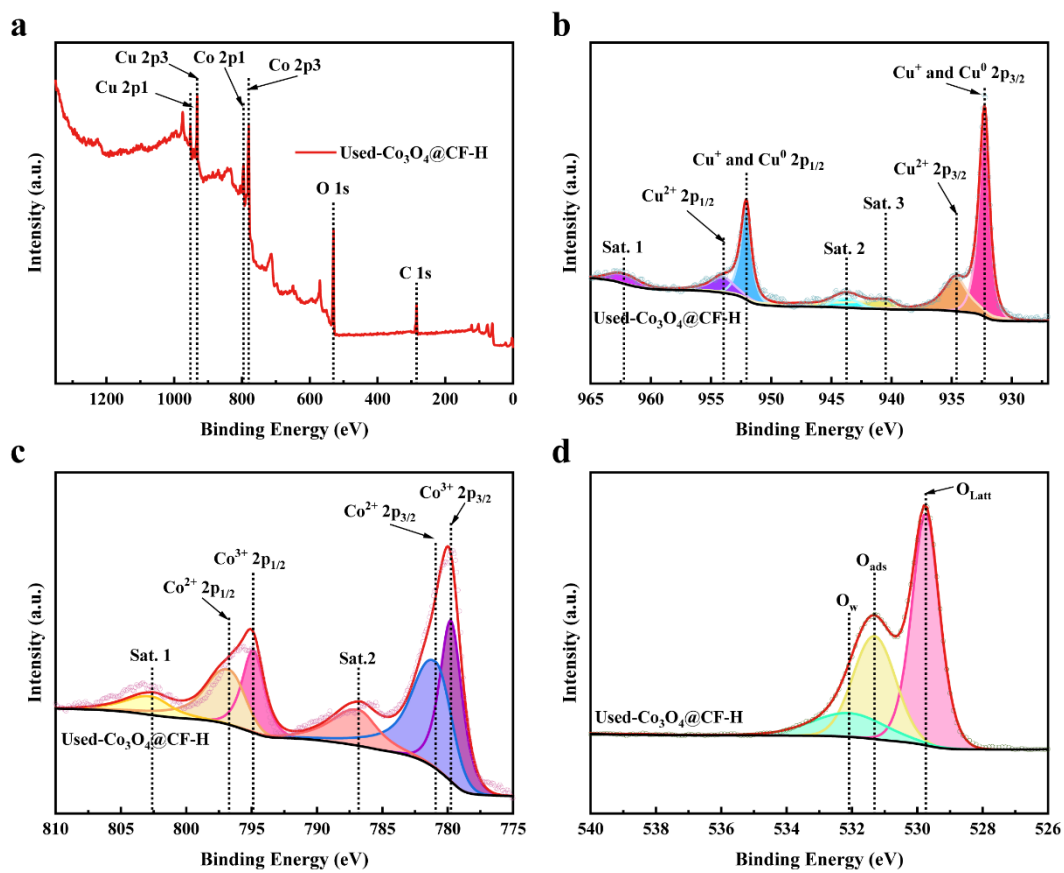**Figure S7.** XRD pattern of Used-$Co_3O_4@CF-H$ monolithic catalyst.

Figure S8. XPS energy spectra of Used-Co₃O₄@CF-H monolithic catalyst
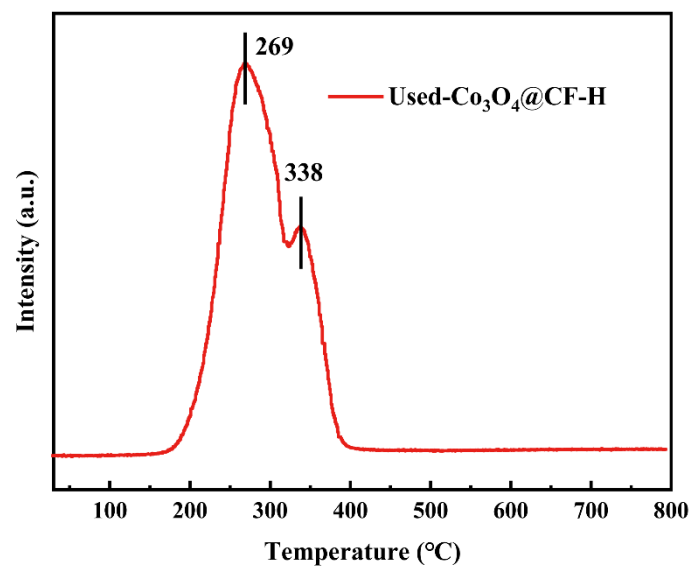
(a) full spectrum, (b) Cu 2p, (c) Co 2p, (d) O 1s.

Figure S9. H_2-TPR curve of Used-Co_3O_4@CF-H monolithic catalyst.

Table S2. Catalytic activity of Co_3O_4@CF-H catalyst for toluene at different WHSV.

WHSV (mL $g^{-1}h^{-1}$)	T_{20} (°C)	T_{50} (°C)	T_{90} (°C)
15,000	194	208	218
30,000	200	211	223
45,000	207	215	232
60,000	209	220	234

Table S3. XPS results for fresh and used monolithic catalysts.

Catalysts	Surface element composition (At.%)				$Cu^{2+}/(Cu^{+}+Cu^{0})$	Co^{3+}/Co^{2+}	O_{Latt}/O_{ads}
	Co	Cu	O	C			
Co_3O_4@CF-H	26.9	4.6	42.3	26.2	2.90	0.67	3.27
Used-Co_3O_4@CF-H	21.3	8.6	34.6	35.5	2.20	0.82	1.56

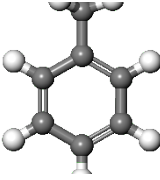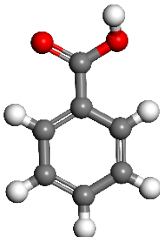**Table S4.** IR bands attributed in the *in-situ* DRIFTS tests.
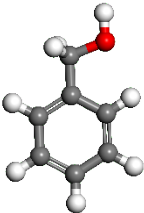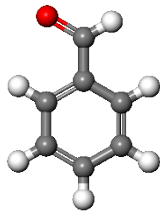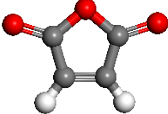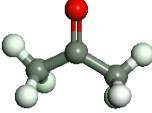
FT-IR spectra position (cm⁻¹)	Assignment	Structural formula	Corresponding species	Ref.
1040, 1079, 1177, 1471, 1520	The ν(C-O) stretching vibration of alcohols		Benzyl alcohol	10, 11
1447	The ν(C-C) skeleton vibrations of the aromatic ring			
1734	The ν(C=O) mode of an aldehyde group		Benzaldehyde	12, 13
1572	The ν(C=C) skeleton vibrations of the aromatic ring			
1246, 1494, 1603	the aromatic ring's in plane skeletal vibration		Toluene	14, 15
1380, 1548, 1557	The asymmetric stretching vibration of -COO-			
1541	The ν_s(C=O) stretching vibration of benzoate		Benzoic acid	10, 11, 16
1418	The C-O symmetric stretching vibration			
1458	The ν(C=C) skeleton vibrations of the aromatic ring			
1304, 1311, 1506, 1827, 1853, 1941	The vibrational peak of maleic anhydride		Maleic anhydride	10, 12, 16-18
1339	The symmetrical deformation vibration of $\delta_s CH_3$		Acetone	12, 19
1401	The symmetric vibrations of C=O			

Table S5. DFT calculated energies for simulated catalysts' surface (O_2).

/eV	$E_{adsorbate,O_2}$	E_{slab}	$E_{adsorbate+slab}$	E_{ads,O_2}
CuO (-111) slab	-9.86	-708.43	-718.43	-0.14
Co$_3$O$_4$ (220) slab	-9.86	-1020.17	-1030.32	-0.30
Co$_3$O$_4$ (311) slab	-9.86	-1017.52	-1027.87	-0.50
Cu@Co$_3$O$_4$ (220) slab	-9.86	-1105.17	-1117.14	-2.12

Table S6. DFT calculated energies for simulated catalysts' surface (toluene).

/eV	$E_{adsorbate,toluene}$	E_{slab}	$E_{adsorbate+slab}$	$E_{ads,toluene}$
CuO (-111) slab	-92.77	-708.43	-802.12	-0.92
Co$_3$O$_4$ (220) slab	-92.77	-1020.17	-1113.84	-0.90
Co$_3$O$_4$ (311) slab	-92.77	-1015.52	-1111.48	-1.19
Cu@Co$_3$O$_4$ (220) slab	-92.77	-1105.17	-1201.57	-3.64

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