

Electronic Supplementary Information:

Significantly boosted activity for styrene oxidation through simultaneous regulation of porosity and copper sites in microporous metal-organic framework Cu-BTC

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Experimental Section:

Materials

$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (99%), d^6 -DMSO, 20% DCl and DMF were obtained from J&K Scientific Company. H_3BTC (98%), 5- NH_2 - H_2ip (98%), ethanol and 70% TBHP (tert-Butyl hydroperoxide) were purchased from Amethyst company. All the reagents are used directly without further purification.

Synthesis of parent Cu-BTC

$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (0.1285 g, 0.532 mmol) and H_3BTC (0.0740 g, 0.352 mmol) were added to a 25 mL teflon reactor with 6 mL DMF, 6 mL EtOH and 6 mL H_2O mixture. The loaded reactor was heated at 75°C for 24 h. And then it was cooled down to room temperature naturally. Subsequently, blue crystals were obtained in around 70% yield based on Cu. The pristine powder was washed by H_2O and ethanol several times. Finally the activation of sample was performed at 150°C for 6 hours under dynamic vacuum (around 10^{-1} mbar) condition in a quartz tube.

Synthesis of HP-DEMOF-1

$\text{Cu}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ (0.338 g, 1.40 mmol) was loaded into a 25 mL glass bottle followed by adding 5 mL DMF immediately, and then the mixture was stirred vigorously to completely dissolve all metal salts at room temperature for around 1 hour, yielding solution A. Ligand H_3BTC (0.177 g, 0.84 mmol) and 5- NH_2 - H_2ip (0.017g, 0.09 mmol) were dissolved in 7 mL DMF in another 25 mL glass bottle under vigorous stirring condition for around 1 hour to prepare solution B. Subsequently, solution B was added to the solution A under continuous stirring condition. After around 1.5 hour further stirring, the mixed solution in the glass bottle was sealed and placed into a preheated oven at 75 °C for 15 hours. Afterwards, the bottle was cooled down to room temperature naturally. The raw product was collected by centrifuge and then solvent exchanged by ethanol and H_2O for several times. Finally, the product was activated at 150°C for 6 hours under dynamic vacuum (around 10^{-1} mbar) condition in a quartz tube.

Synthesis of HP-DEMOF-2, HP-DEMOF-3, HP-DEMOF-4 and HP-DEMOF-5

All procedures were similar to the synthesis of HP-DEMOF-1 except for the amount of organic ligands, H_3BTC (0.157 g, 0.75 mmol) and 5- NH_2 - H_2ip (0.034 g, 0.19 mmol) for HP-DEMOF-2, H_3BTC (0.137 g, 0.65 mmol) and 5- NH_2 - H_2ip (0.051g, 0.28 mmol) for HP-DEMOF-3, H_3BTC (0.118 g, 0.56 mmol) and 5- NH_2 - H_2ip (0.068 g, 0.37 mmol) for HP-DEMOF-4, H_3BTC (0.098 g, 0.46 mmol) and 5- NH_2 - H_2ip (0.085 g, 0.45 mmol) for HP-DEMOF-5.

Powder X-Ray Diffraction (XRD)

The phase purity of samples was identified by reflection geometry with an Empyrean Theta-Theta diffractometer (Panalytical, Almelo) equipped with Cu anode and PIXcel-ld detector over the 2θ angle range 4 - 80°. Scan step is 0.01313°. 0.5° antiscatter slit was set for the incident beam. A Ni filter was used to suppress the K-beta emission.

Thermogravimetric Analysis (TG)

TG measurements were carried out on a NETZSCHSTA449F3 set-up. Heating ramp is 10 °C/min under N_2 atmosphere until final temperature 500 °C.

Nuclear magnetic resonance (¹H-NMR)

The incorporated amount of 5-NH₂-H₂ip in as-synthesized HP-DEMOFs was determined by liquid phase ¹H-NMR spectra on a Bruker Ascend 400 MHz NMR spectrometer using 0.1 mL 20% DCl and 0.5 mL DMSO-d₆ to digest the samples (3 mg).

Scanning electron microscope (SEM)

SEM and elemental mapping measurement were conducted by Regulus8220 setup with beam energy 200 kV. The Silicon Drift Detector (SDD) EDS collects X-rays at a solid angle of 0.98 steradians from a detection area of 100 mm². The effective area of detector is 200 mm².

N₂ physisorption

BET surface area and pore size distribution were measured by N₂ physisorption/desorption at 77 K using Micromeritics ASAP 2460 machine from America. Cu-BTC and HP-DEMOF-1 to HP-DEMOF-4 samples were thermally activated at 150°C under dynamic vacuum condition before measurement.

High-resolution X-ray Photoelectron Spectroscopy (HR-XPS)

HR-XPS was performed using an ultra-high vacuum setup equipped with a high resolution Thermo Scientific K-Alpha. The spectra were obtained at pass energy 200 eV, base pressure around 3×10⁻¹⁰ mbar and analyser slit width 0.3 mm. Monochromatic Al Kα (1486.6 eV) was used as incident radiation. Energy resolution was better than 0.5 eV and flood gun was used to compensate for charging effects. All spectra were calibrated based on C 1s binding energy 284.5 eV. The analysis of the spectra was performed using CasaXPS software with mixed Gaussian-Lorentzian function and Shirley background subtraction.

Catalytic oxidation reaction

The oxidation of styrene was conducted in cylindrical glass bottle reactor (volume: 20 mL, height: 6 cm) with screw cap. In a typical run, the glass bottle reactor was loaded by magnetic stirring bar, 20 mg pre-activated catalyst, 40 mg styrene, 2.0 mL acetonitrile (MeCN) as solvent and 0.1 mL TBHP (70% in H₂O). And then the reactor was purged with 1 bar O₂ for three times, after which it was immediately sealed by screw cap with 1 bar O₂ inside. The oxidation reaction was carried out at 65°C with a stirring speed of 500 rpm. At corresponding time (1, 3, 5, 7, 11, 15h), the reaction was stopped and glass bottle reactor was cooled down to room temperature immediately by cooling water within 3 minutes. The resulting solution was centrifuged (9000 rpm) and then analyzed by gas chromatography (Agilent 7820A).

The obtained solution samples were analyzed by an Agilent 7820A gas chromatography equipped with a capillary column (HP-5, 30 m × 0.32 μm × 0.25 μm) and a flame ionization detector (FID). Temperatures of both injection port and FID detector were set at 260°C. The GC was calibrated using several mixed solution with different concentrations to obtain response factor for each product compound. The conversion of styrene as well as the selectivity of products was calculated based on normalization.

Table S1. Results of styrene oxidation reaction using 150°C activated HP-DEMOf-1 as catalyst.

Reaction time, hour	Conversion, %	Selectivity of benzaldehyde, %	Selectivity of styrene oxide, %
1	0.01	100	0
3	0.02	100	0
5	0.034	100	0
7	4.77	100	0
9	20.8	96.2	3.8

Table S2. Results of styrene oxidation reaction using 150°C activated HP-DEMOf-2 as catalyst.

Reaction time, hour	Conversion, %	Selectivity of benzaldehyde, %	Selectivity of styrene oxide, %
1	0.09	100	0
3	0.38	100	0
5	1.33	100	0
7	24.11	93.68	6.32
11	58	79.1	20.9

Table S3. Results of styrene oxidation reaction using 150°C activated HP-DEMOf-3 as catalyst.

Reaction time, hour	Conversion, %	Selectivity of benzaldehyde, %	Selectivity of styrene oxide, %
1	0.11	100	0
3	0.79	100	0
5	21.11	92.99	7.01
7	32.26	91.95	8.05
9	43.2	82.8	17.2
11	54.24	78.73	21.27

Table S4. Results of styrene oxidation reaction using 150°C activated HP-DEMOf-4 as catalyst.

Reaction time, hour	Conversion, %	Selectivity of benzaldehyde, %	Selectivity of styrene oxide, %
1	0.12	100	0
3	5.75	97.08	2.92
5	29.45	90.54	9.46
7	44.45	74.02	25.98
9	56.5	71.3	28.7
11	70.03	67.61	32.39
15	79.14	61.48	38.52

Table S5. Results of styrene oxidation reaction using 150°C activated HP-DEMOF-5 as catalyst.

Reaction time, hour	Conversion, %	Selectivity of benzaldehyde, %	Selectivity of styrene oxide, %
1	0.1	100	0
3	0.12	100	0
5	9	94.1	5.9
7	23.67	76.32	23.68
11	60.77	67.98	32.02

Table S6. Results of styrene oxidation reaction using 150°C activated Cu-BTC as catalyst.

Reaction time, hour	Conversion, %	Selectivity of benzaldehyde, %	Selectivity of styrene oxide, %
1	0	100	0
3	0	100	0
5	0.02	100	0
7	1.8	100	0

Table S7. Catalytic activities toward the styrene oxidation of some previously reported Cu-based MOFs.

Cu-based MOF catalysts	Conv. (%)	Selec. (%) of styrene oxide	Selec. (%) of benzaldehyde	Oxidant	Ref.
Cu(H ₂ btec)(bipy)	61	26	--	TBHP	1
(Cu ₄ (OH) ₂ (Hppdc) ₂ (H ₂ O) ₂)	78.3	60.7	--	TBHP	2
Cu ₄ (OH) ₂ (Hppdc) ₂ (H ₂ O) ₃ (DMF)	75.2	48.9	--	TBHP	2
nano-sized HKUST-1	99	6	--	TBHP	3
Cu-TCPP nanosheets	94	49.2	--	TBHP	4
HP-DEMOF-4	79.1	38.5	61.5	O ₂ +TBHP	This work

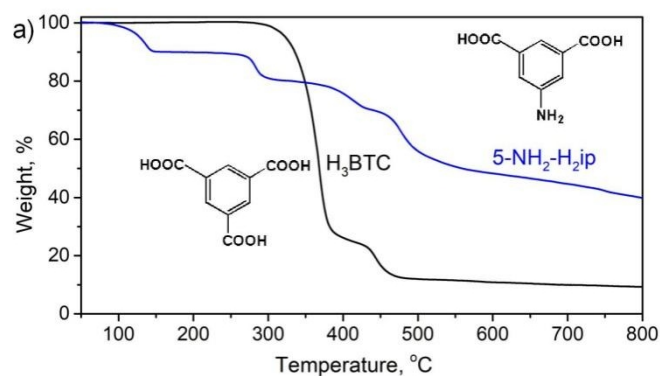
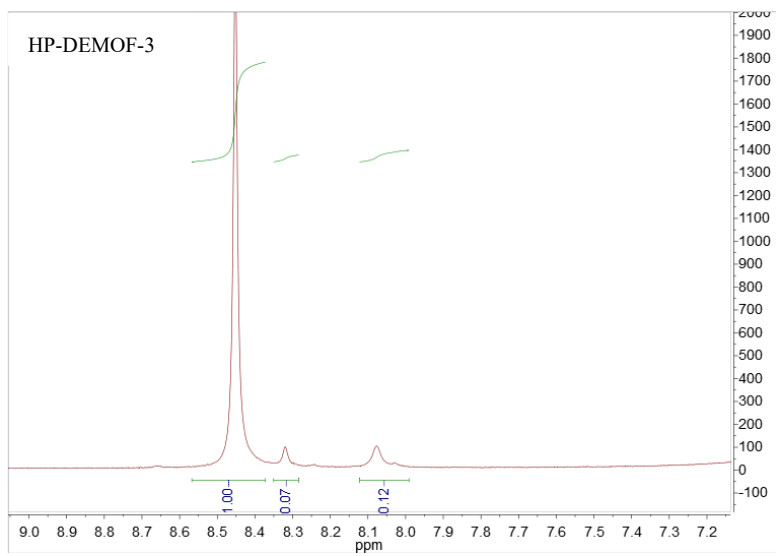
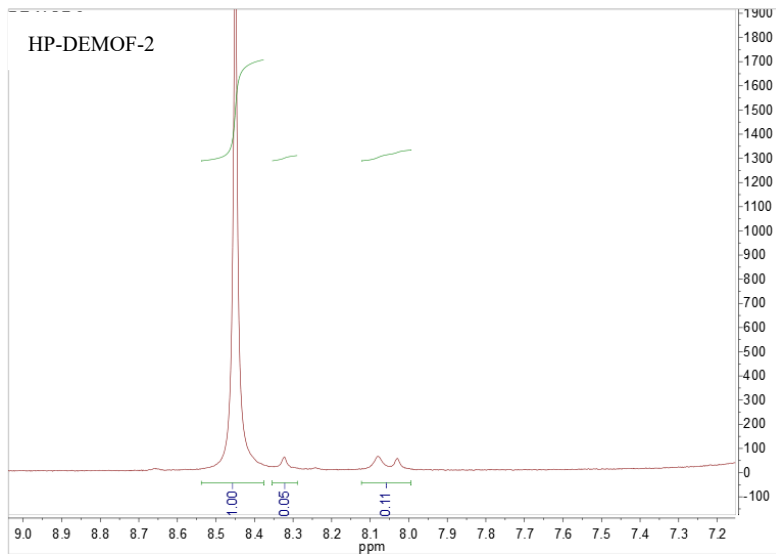
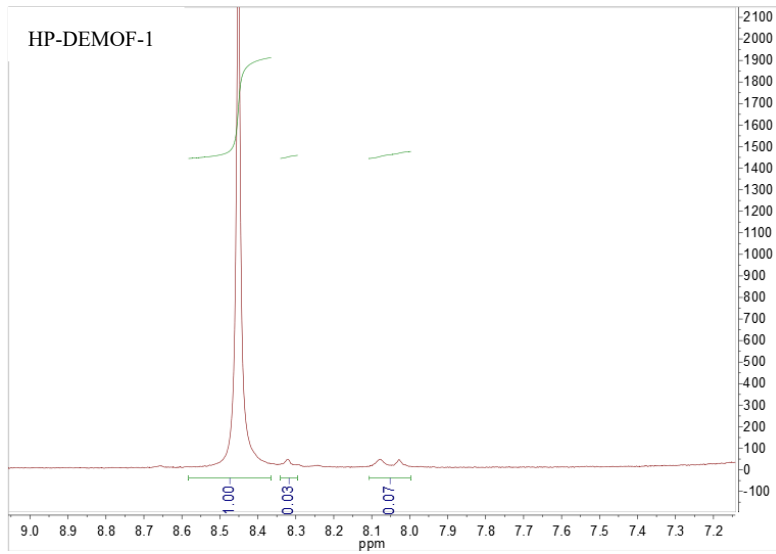


Figure S1 TG plots of organic linkers H₃BTC and DL (5-NH₂-H₂ip).



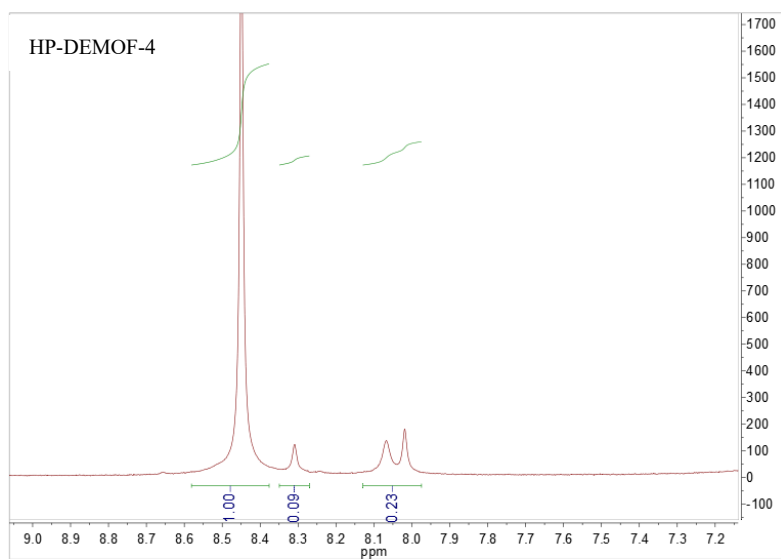
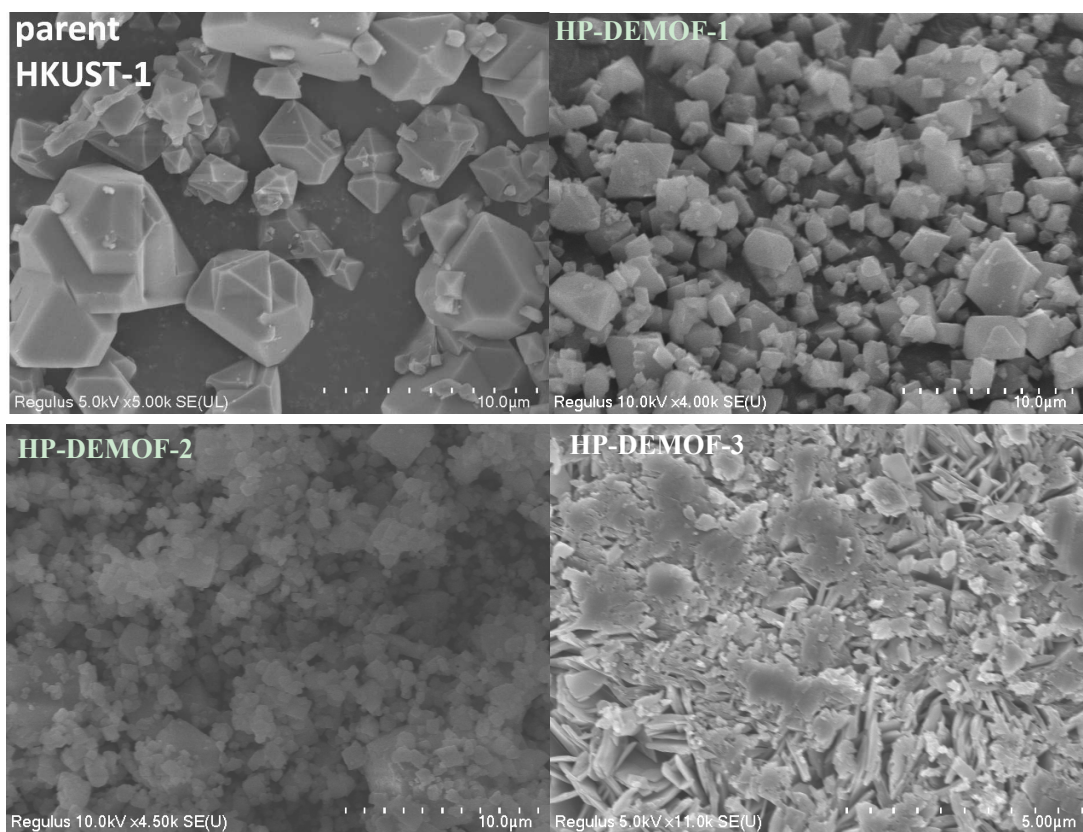


Figure S2 ^1H -NMR spectra of HP-DEMOF-1 to HP-DEMOF-4 samples (400 MHz, Solvent: $\text{DCI} + \text{DMSO-d}_6$).



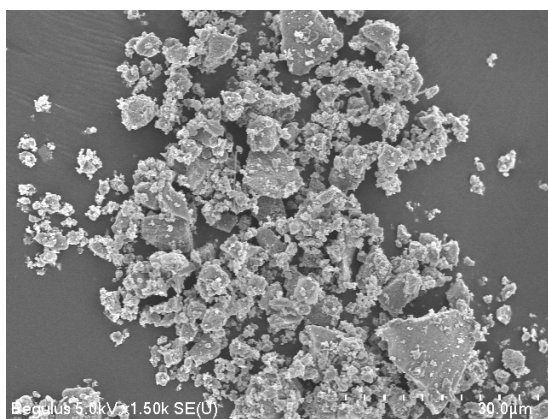


Figure S3 SEM images of as-synthesized Cu-BTC, HP-DEMOF-1 to HP-DEMOF-4 samples.

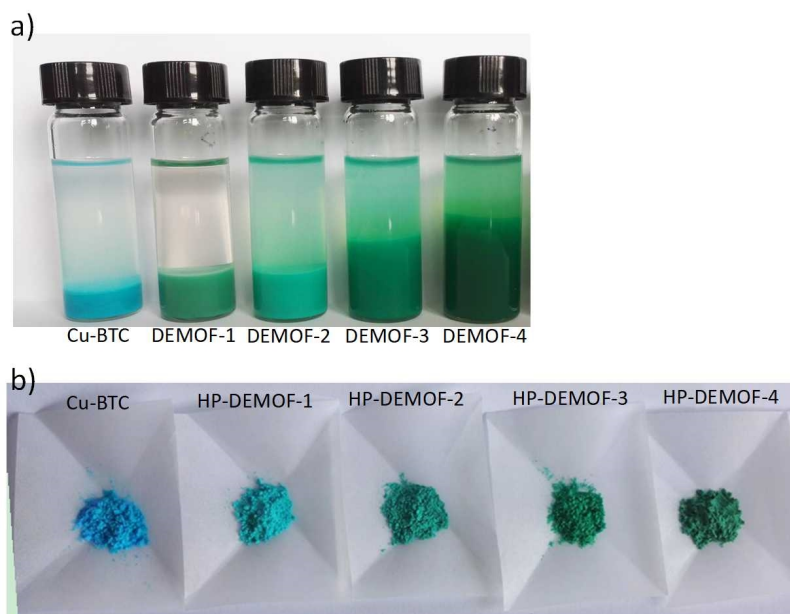


Figure S4 a) Suspension states of Cu-BTC and HP-DEMOFs samples from the same batch. b) Images of as-synthesized Cu-BTC and HP-DEMOFs samples after drying at room temperature.

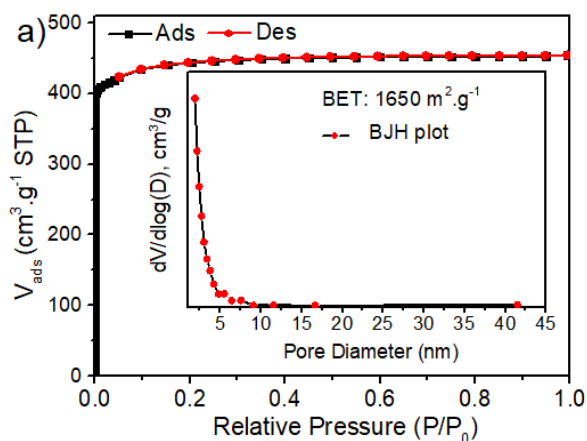


Figure S5 N_2 physisorption isotherms and pore size distributions (inset) for parent Cu-BTC activated at 150 °C for 6 hours.

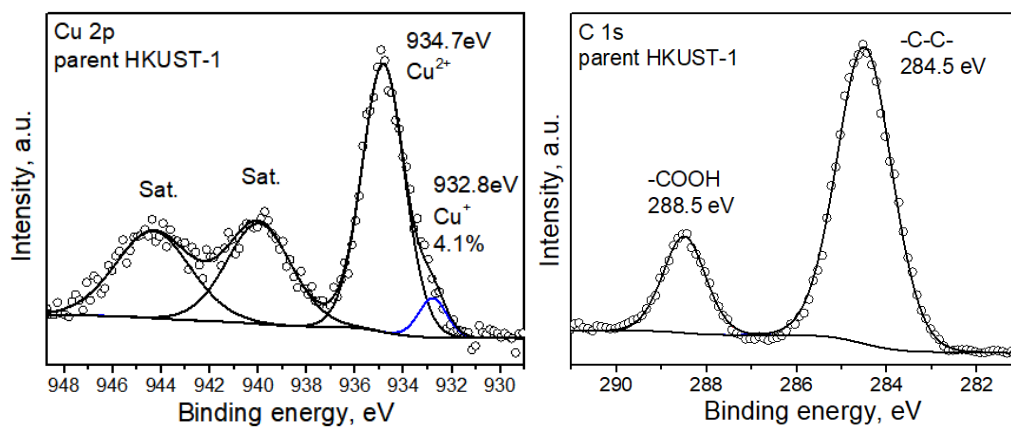
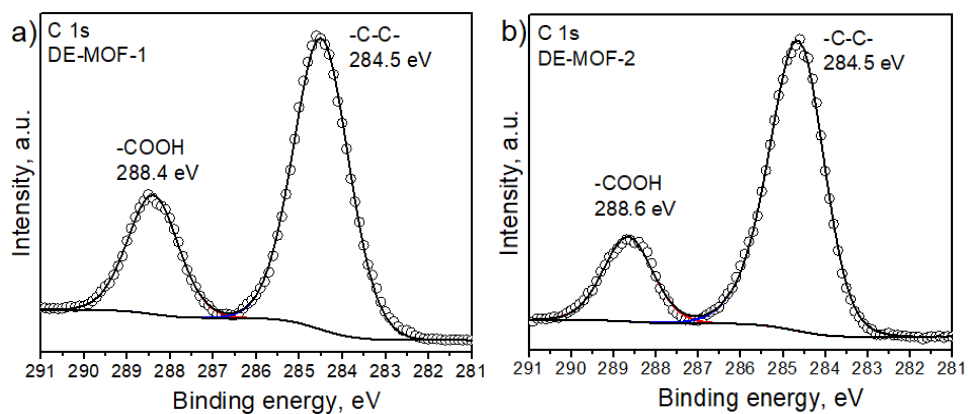


Figure S6 XPS Cu 2p region of parent Cu-BTC activated at 170°C for 6 hours.



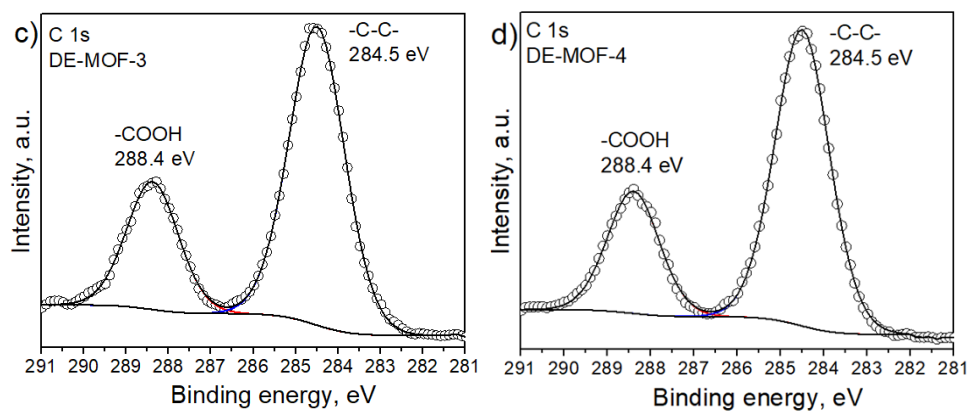


Figure S7 XPS C 1s region of HP-DEMOFs samples after activation at 150°C.

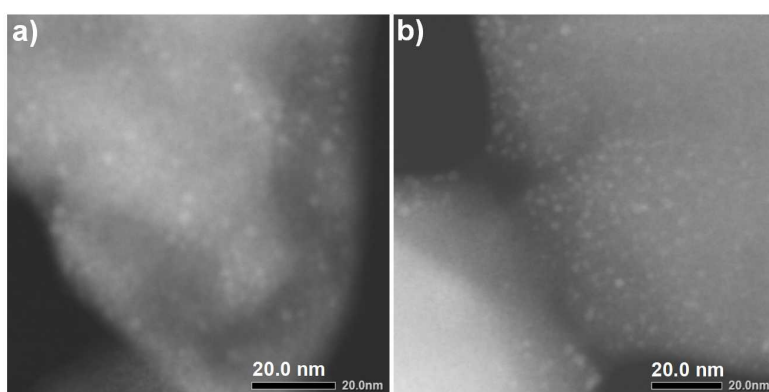


Figure S8 HAADF-STEM images for a) HP-DEMOF-2@150 and b) HP-DEMOF-3@150.

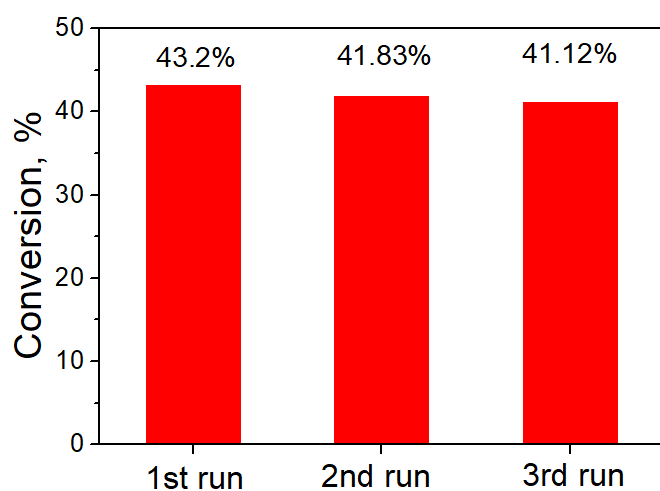


Figure S9 Recycling of HP-DEMOF-4@150 catalyst for styrene oxidation after 7 h reaction.

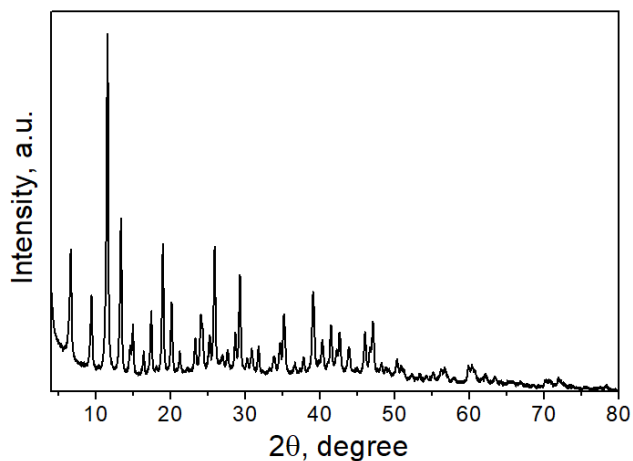
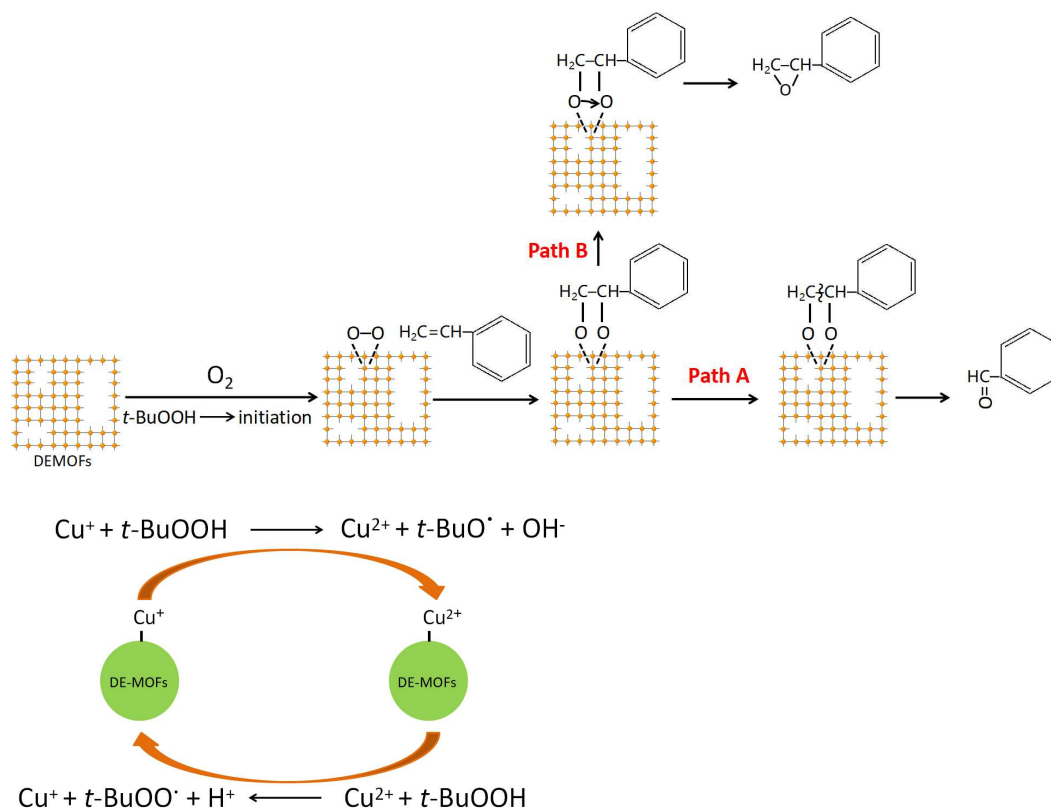


Figure S10 Powder XRD patterns of HP-DEMOF-4@150 catalyst after three recycles.



Scheme S1. Suggested reaction mechanism.

Notes and references

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