Supporting Information

Fabrication of hierarchically porous MIL-88-NH_2(Fe): Highly efficient catalyst for the chemical fixation of CO_2 under ambient pressure

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Experimental Section

Chemicals

$FeCl_3.6H_2O$ (Alfa Aesar), NH_2-BDC (Sigma Aldrich), Cetyltrimethylammonium bromide (Sigma-Aldrich), DMF (Alfa Aesar), ECH, all epoxides (Sigma-Aldrich), toluene (Sigma-Aldrich) and dichloromethane (Sigma-Aldrich).

Synthesis of MIL-88-NH_2(Fe)

Typically, 0.25 g of NH_2-BDC and 0.374 g of $FeCl_3.6H_2O$ were dissolved in 30 mL of DMF and stirred vigorously for 2 h. Then, the mixed solution was transferred to a 50 mL Teflon-lined autoclave for the solvothermal treatment at 120 ˚C for 24 h. After being cooled to room temperature, the resultant brown precipitates were separated from the reaction mixture by centrifugation at 4000 rpm for 5 min, and washed thoroughly with DMF and ethanol to remove any unreacted starting materials.

Synthesis of HP-MIL-88-NH_2(Fe) (template-directed method)

Typically, 0.25 g of NH_2-BDC, 0.374 g of $FeCl_3.6H_2O$ and 0.1 g of CTAB (Cetyltrimethylammonium bromide) were dissolved in 30 mL of DMF and stirred vigorously for 2 h. Then, the mixed solution was transferred to a 50 mL Teflon-lined autoclave for the solvothermal treatment at 120 ˚C for 24 h. After being cooled to room temperature, the resultant brown precipitates were separated from the reaction mixture by centrifugation at 4000 rpm for 5 min, and washed thoroughly with DMF and ethanol to remove any unreacted starting materials.

CO_2-epoxide cycloaddition reactions

All the cycloaddition reactions were conducted in a 25 mL stainless steel autoclave reactor charged with the requisite amount of catalyst, epoxide, and cocatalyst and subjected to magnetic stirring at 500 rpm. The reactions were conducted under pre-decided CO_2 pressures at different temperatures. After finishing the reaction, the stirrer was turned off, the reactor was cooled to < 5 °C using an ice-bath, and the excess CO_2 was vented. The internal standards toluene and dichloromethane were added to the product mixture, which was then filtered. The yields were then determined using a gas chromatographer (Agilent technologies, HP 6890 A) fitted with a 30 m × 0.25 μm capillary column (HP-5) and a flame ionization detector.

Characterization

Powder X-ray diffraction (PXRD) patterns were obtained in XPERT-PRO diffractometer system using 40 kV CuKα radiation (30 mA) with minimum step size $2\theta = 0.001$ and scan step time of 0.9000 s. Elemental analysis (EA) was performed using a Vario-Micro cube system, Germany. 1.8 mg of catalyst was subjected to analysis at 1150 ˚C with benzoic acid (for Oxygen) and sulfanilic acid (for Carbon and Hydrogen) as the standards. The weight percentage of the metal in the catalyst were obtained from inductively coupled plasma atomic emission spectroscopy (ICP-OES) analysis using an Activa, JY Horiva (1.5 kW, 40.68 MHz, 130–800 mm) fitted with a monochromatic HDD and a polychromatic PMT detector. Thermogravimetric analysis (TGA) was conducted with SDT Q600 apparatus. 3.13 mg of sample was subjected to analysis at a heating rate of 10 ˚C/ min from 50 ˚C to 600 ˚C under a nitrogen flow of 100ml/ min. Fourier-transform infrared (FT-IR) spectra of the catalyst were recorded on an AVATAR 370 Thermo Nicolet spectrophotometer at a resolution of 4 cm^{-1}. Field emission scanning electron microscopy (FE-SEM, Zeiss supra 40 VP) images were observed using S-4200 field emission scanning electron microscope at 5.00 kV. The XPS analysis of the catalysts was carried out using theta probe AR-XPS system (Thermo Fisher Scientific (U.K)). The instrument used the X-ray source of monochromated Al Kα (hv= 1486.6 eV) having the energy of 150W. CO_2 and NH_3 TPD profiles were acquired with a chemisorption analyzer (BEL-CAT) as follows. Before the measurements, 0.053 g of the sample was activated in He (30 mL min^{-1}) at 280 °C for 1 h. The sample was subsequently exposed to the pulses of CO_2 or NH_3 in Heat 40 °C for 1 h. The sample was then flushed with He (30 mL min^{-1}) for 1 h. TPD measurements were carried out by raising the temperature from 40 to 280 °C at a heating rate of 5 °C min^{-1}. The textural properties of the catalyst were analyzed by recording an N_2 adsorption isotherm at 77 K with a BET apparatus (Micromeritics ASAP 2020). The specific surface area was determined using the BET model equation.

Table S1 Elemental analysis and ICP-OES of parent MIL-88-NH_2 and hierarchical MIL-88-NH_2.

Catalyst	**C**	**H**	**N**	**O**	**Fe**
MIL-88-NH_2(Fe)	**39.45**	**5.51**	**10.55**	**34.33**	**10.14**
HP-MIL-88-NH_2(Fe)	**40.09**	**4.66**	**9.20**	**35.23**	**9.97**

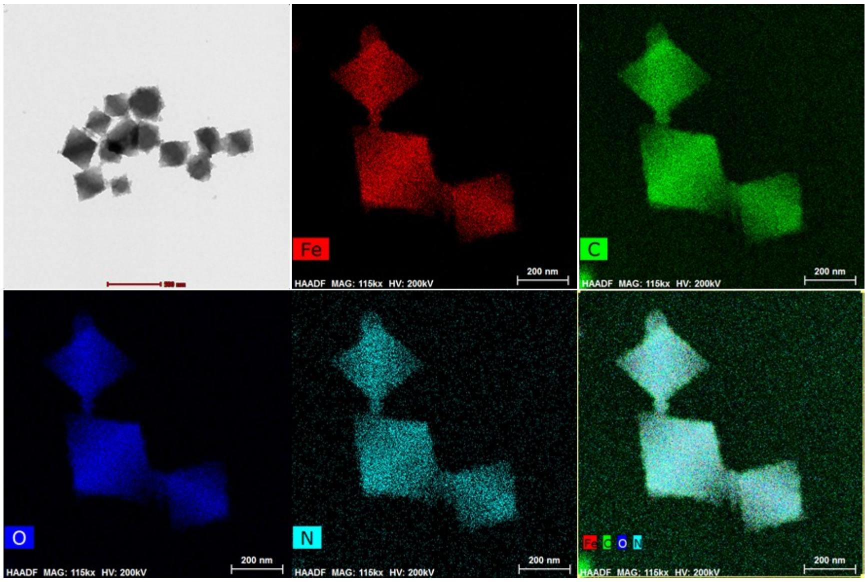


Fig. S1 TEM-EDX elemental mapping of MIL-88-NH_2(Fe).

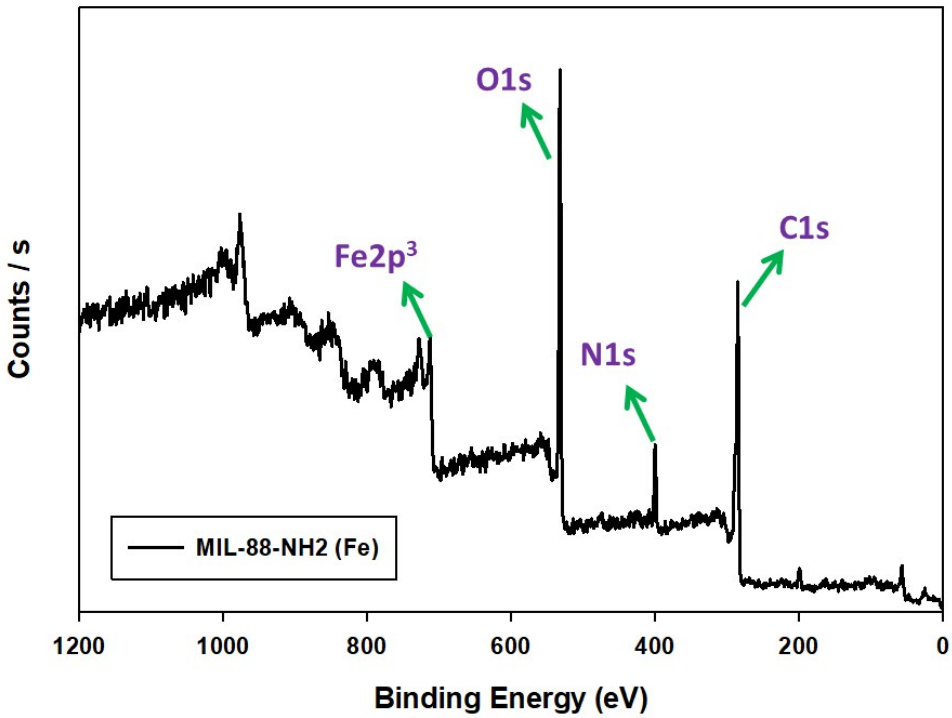
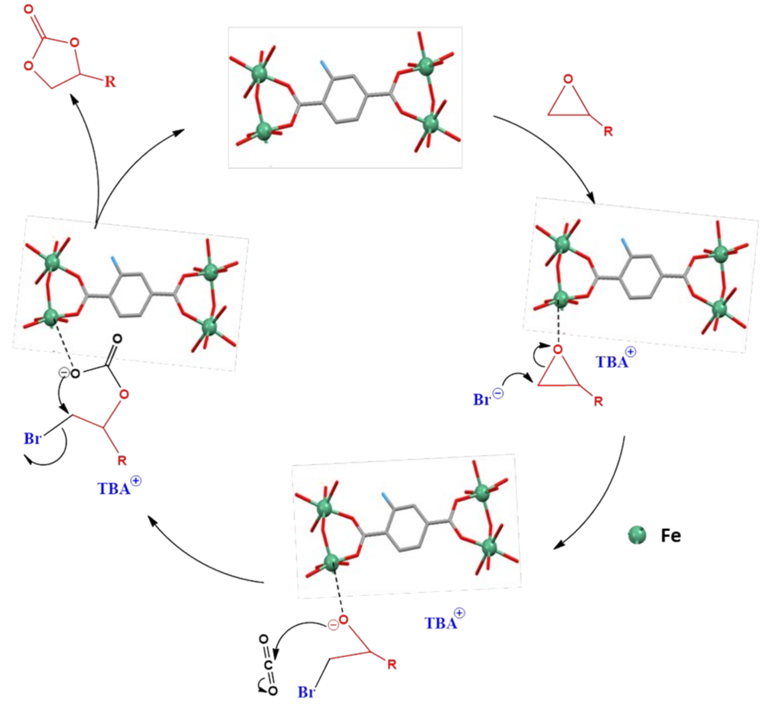


Fig. S2 XPS analysis of MIL-88-NH$_2$(Fe).

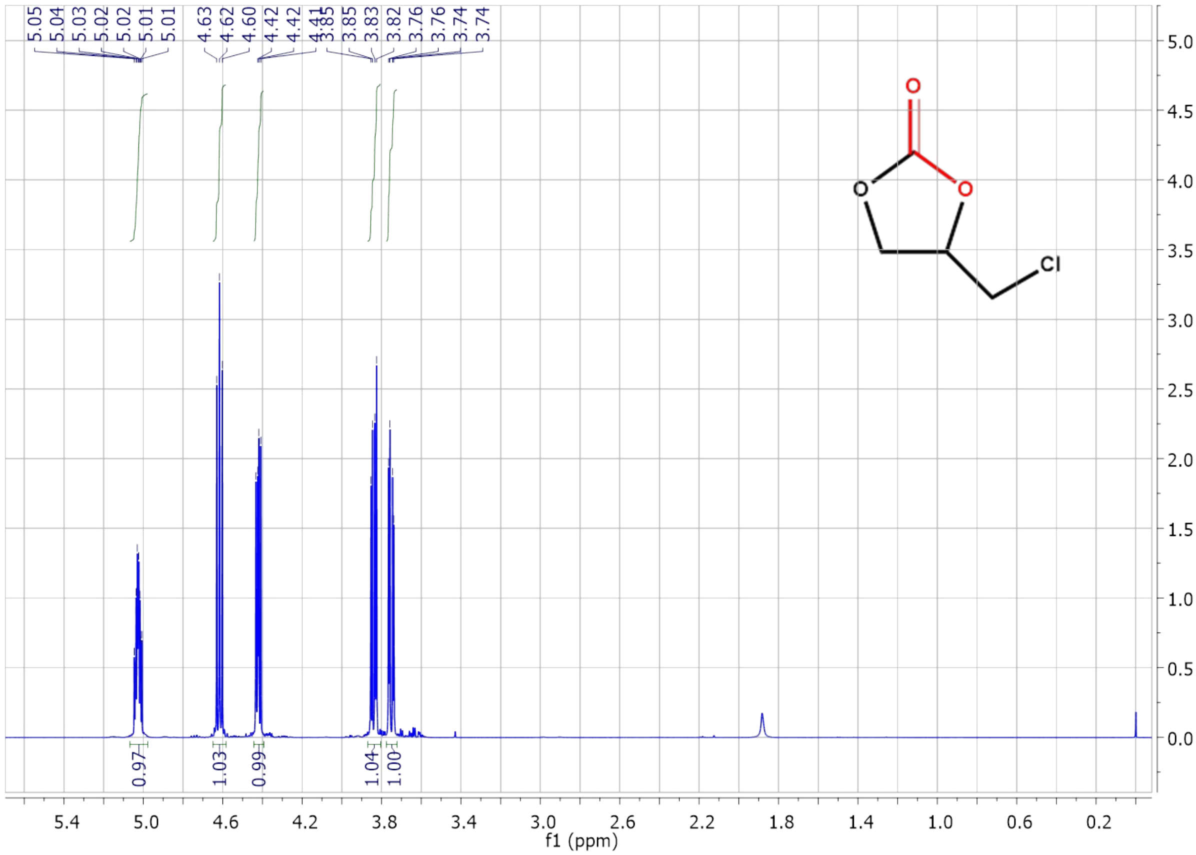


Scheme S1 Proposed mechanism for the cycloaddition of epoxide and CO$_2$ catalyzed by HP-MIL-88-NH$_2$(Fe)/TBAB.

^{1}H NMR Details of Cyclic Carbonates

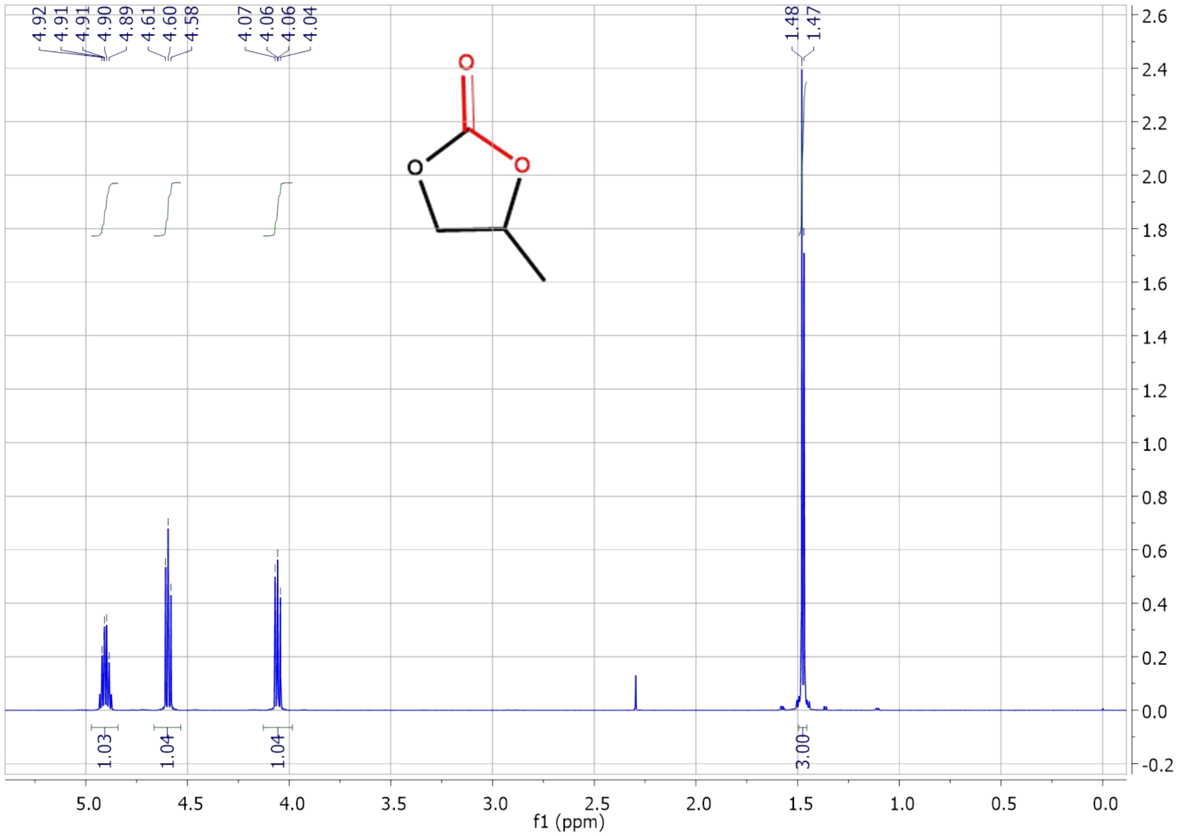
Epichlorohydrin Carbonates

(600 MHz, $CDCl_3$): δ 5.02 – 4.97 (m, 1H), 4.63 – 4.59 (m, 1H), 4.42 (dd, J = 8.6, 5.7 Hz, 1H), 3.83 – 3.79 (m, 1H), 3.74 (dd, J = 12.5, 3.5 Hz, 1H).



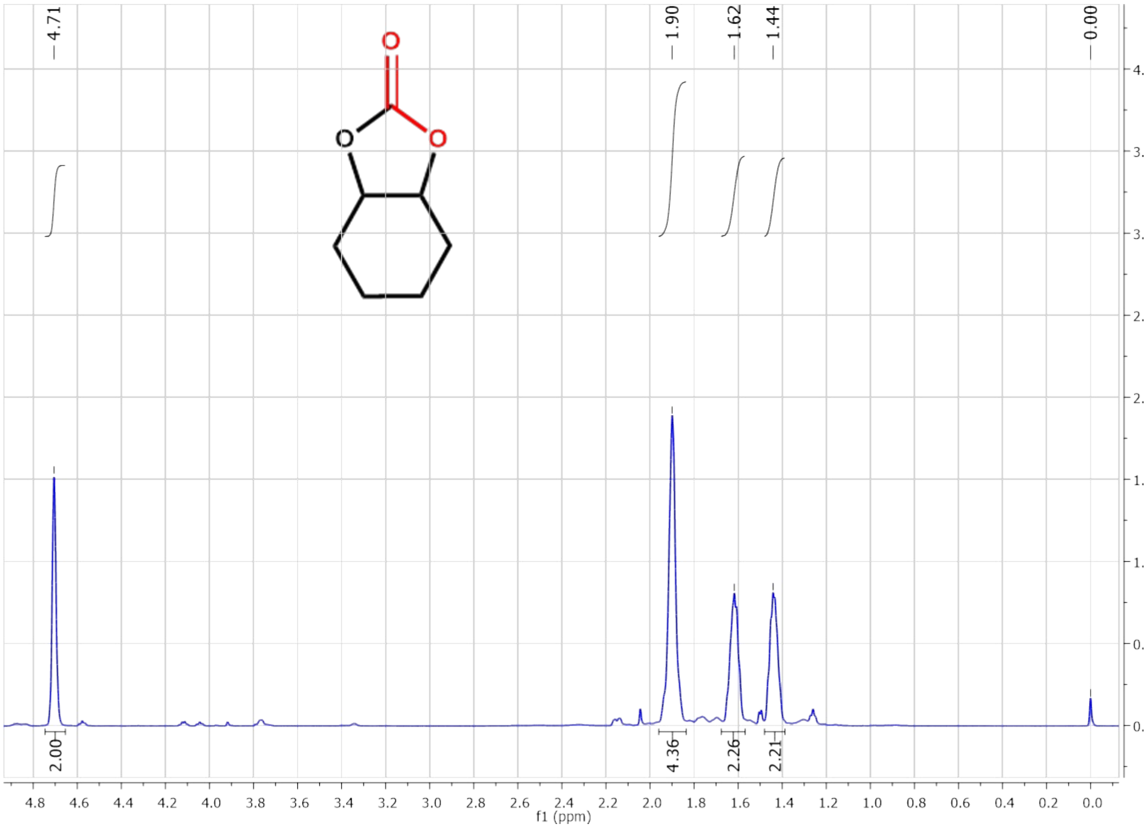
Propylene Carbonates

(600 MHz, $CDCl_3$): δ 4.94 – 4.87 (m, 1H), 4.64 – 4.55 (m, 1H), 4.06 (dd, J = 8.5, 7.2 Hz, 1H), 1.47 (d, J = 6.5 Hz, 3H).



Cyclohexene Carbonate

(600 MHz, $CDCl_3$): δ = 1.47 (m, 2H), 1.64 (m, 2H), 1.91 (m, 4H), 4.72 (m, 2H)



Styrene Carbonate

(600 MHz, $CDCl_3$): δ 7.40 (dd, 5H), 5.67 (t, J = 8.0 Hz, 1H), 4.80 (t, J = 8.5 Hz, 1H), 4.34 (t, J = 8.1 Hz, 1H).