Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Tri-functional metal-organic framework heterogeneous catalyst for efficient conversion of CO_2 under mild and co-catalyst free conditions

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1. Materials and Instrumentation.

All reagents used in the syntheses were commercially available and used without further purification. Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet Impact 410 FT-IR spectrometer. Powder X-ray diffraction (PXRD) was performed with a Rigaku D/MAX2550 diffractometer. Scanning transmission electron microscopy (STEM) was performed on a FEI Tecnai G2 S-Twin with a field emission gun operating at 200 kV. Images were acquired digitally on a Gantan multiple CCD camera. Energy dispersive spectroscopy (EDS) spectra were obtained using a JEOL JSM-6300 at 5 kV. Gas adsorption experiments were carried out on a Micrometrics ASAP 2020M volumetric gas adsorption analyzer. X-ray photoelectron spectroscopy (XPS) measurements were performed on an ESCALAB 250 X-ray photoelectron spectroscopy, using Mg Kα X-ray as the excitation source. Elemental analysis was tested by ThermoFisher Flash 2000. GC-MS were tested by TRACE DSQ GC-MS (column type: TR-wax-ms, 30 m×0.25 mm×0.25 μm; injector temperature 250°C).

2. Experimental Details

2.1 Synthesis of MIL-101

A solution containing $Cr(NO_3)_3{\cdot}9H_2O$ (6.00 g), 1,4-benzene dicarboxylic acid (3.76 g), hydrofluoric acid (0.75 mL, 40 % in water) and H_2O (72 mL) was introduced in a 100 mL Teflon-liner. The mixture was heated to 220 ºC in an autoclave for 9 h. After cooling, the reaction mixture was doubly filtered to remove the free terephthalic acid. The resulting solid was soaked in 1 M of NH_4F solution at 80 ºC for 24 h and immediately filtered, washed three times by hot water. The solid was finally dried overnight at 150 ºC.

2.2 Synthesis of MIL-101-Br [1]

The starting materials $CrCl_3$ (198 mg, 1.25 mmol), 1,4-benzene dicarboxylic acid (104 mg, 0.625 mmol) and 2-Bromoterephthalic acid (153 mg, 0.625 mmol) were introduced into a 10 mL Teflon reactor. After the addition of 5 mL of demineralized water, the reactor was sealed and heated to 180 °C for 96 h. The green solid was centrifuged, and then washed with water and ethanol three times. The resulting green solid was dried in air at 70 °C.

2.3 Synthesis of MIL-IMAc-Br$^-$

100 mg MIL-101-Br was placed in a round bottomed three necked flask under a slow stream of N_2. 10 mL acetonitrile was added and slurry gently stirred. Then 30 mg of 1H-imidazole-1-acetic acid was added and the flask was heated to 80 ºC in an oil bath for three days with continuous stirring. The product was recovered by filtration and washed with acetonitrile, followed by methanol and ethyl ether. Then the resulting product was degassed at 80 ºC for 12 h.

MIL-IMOH-Br^- and MIL-IMPRO-Br^- are synthesized using same method with 2-(1H-imidazol-1-yl)ethanol and 1-propylimidazole.

2.4 Catalytic reactions

In a typical reaction, an autoclave was charged with MIL-IMAc-Br^- 50 mg and PO 30 mmol. After sealing, the assembled autoclave was purged of air three times with CO_2. After the CO_2 (0.5 MPa) was introduced, the reaction mixture was stirred at 60 ºC. After a certain time, the reactor was cooled in an ice bath, the unreacted CO_2 was slowly released, the catalyst was separated by centrifugation, and the products were analyzed by TRACE DSQ GC-MS (column type: TR-wax-ms, 30 m × 0.25 mm × 0.25 μm; injector temperature 250 ºC).

3. Characterization

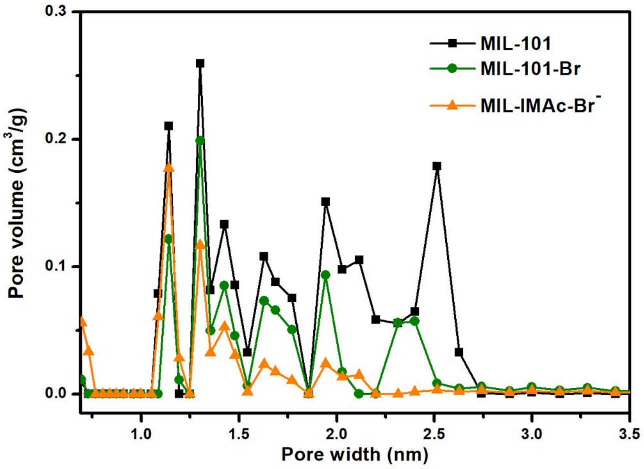


Figure S1. DFT pore-size distribution profiles of MIL-101, MIL-101-Br and MIL-IMAc-Br^-.

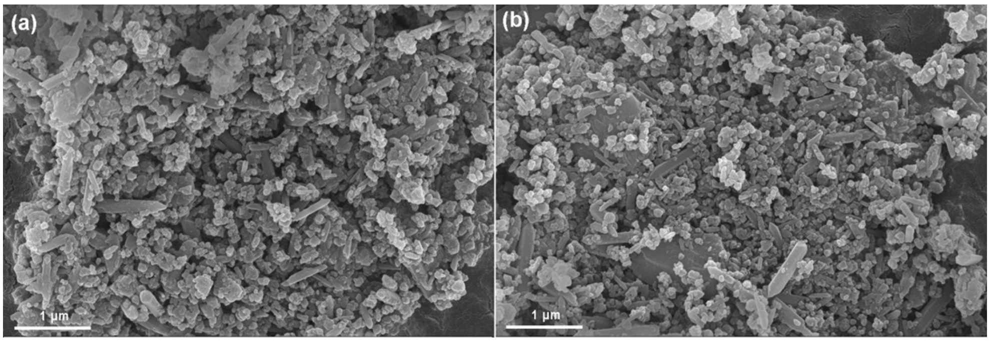


Figure S2. Comparison of SEM images of MIL-101-Br (a) and MIL-IMAc-Br$^-$ (b).

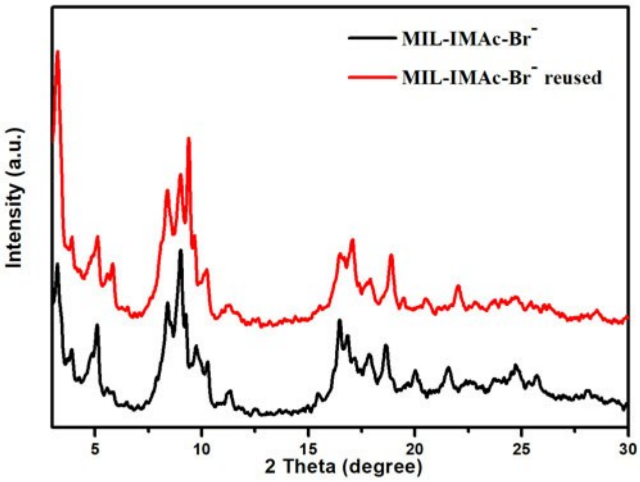


Figure S3. Comparison of PXRD patterns of the as-made sample MIL-IMAc-Br$^-$ and the MIL-IMAc-Br$^-$ after catalysis cycles.

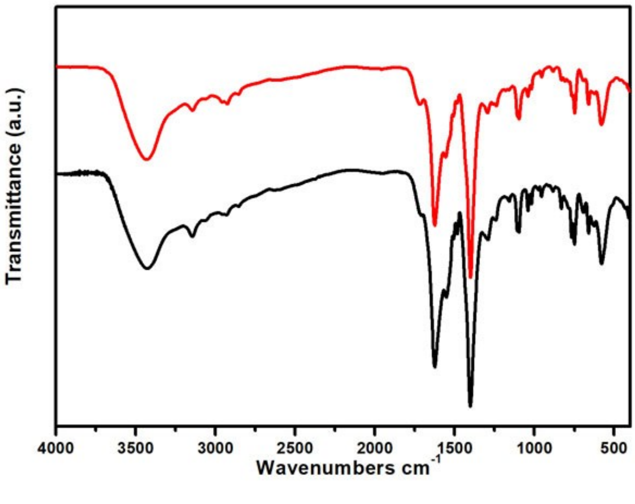


Figure S4. FT-IR of the as-made sample MIL-IMAc-Br- (black) and the MIL-IMAc-Br- after catalysis cycles (red).

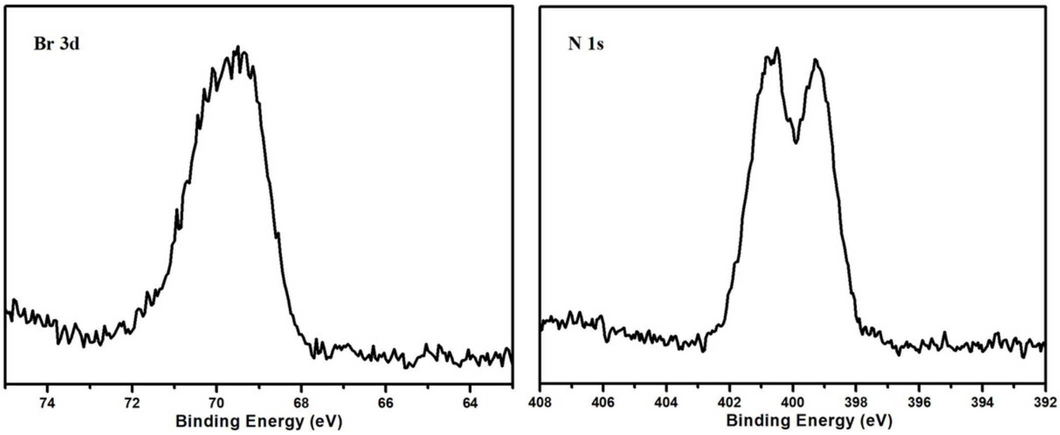


Figure S5. Br 3d and N 1s XPS spectra for MIL-IMOH-Br⁻.

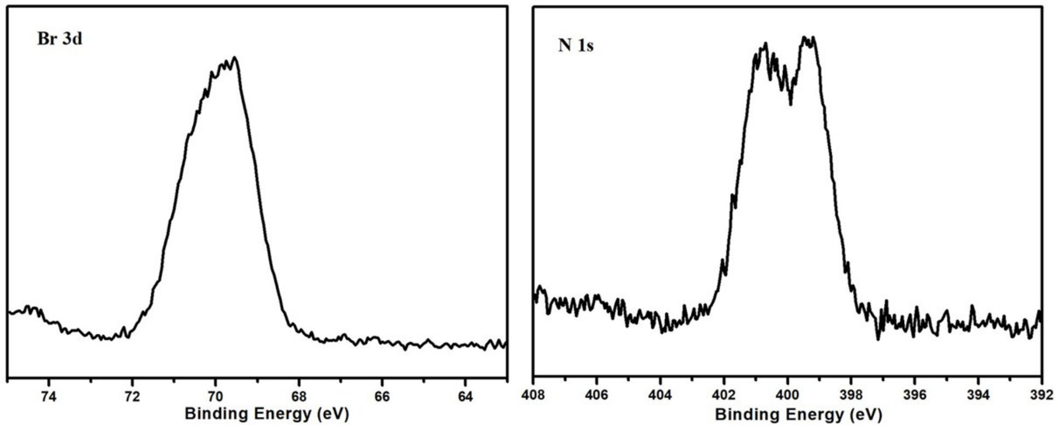
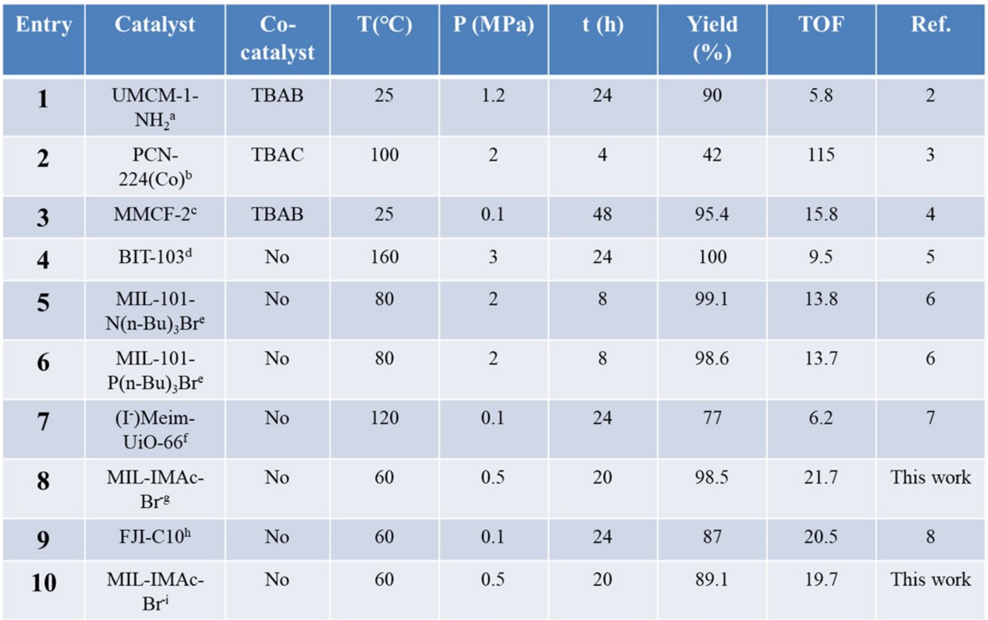


Figure S6. Br 3d and N 1s XPS spectra for MIL- IMPRO -Br⁻.

Table S1. Elemental Analysis

MOFs	C%	H%	N%
MIL-IMAc-Br⁻	36.11	2.97	3.84
MIL-IMOH-Br⁻	37.13	3.29	3.75
MIL-IMPRO-Br⁻	37.22	3.37	3.33

Table S2. Cycloaddition reaction of CO_2 catalyzed by different MOF-based systems



Entry	Catalyst	Co-catalyst	T(°C)	P (MPa)	t (h)	Yield (%)	TOF	Ref.
1	UMCM-1-NH_2[a]	TBAB	25	1.2	24	90	5.8	2
2	PCN-224(Co)[b]	TBAC	100	2	4	42	115	3
3	MMCF-2[c]	TBAB	25	0.1	48	95.4	15.8	4
4	BIT-103[d]	No	160	3	24	100	9.5	5
5	MIL-101-$N(n\text{-}Bu)_3Br$[e]	No	80	2	8	99.1	13.8	6
6	MIL-101-$P(n\text{-}Bu)_3Br$[e]	No	80	2	8	98.6	13.7	6
7	(I^-)Meim-UiO-66[f]	No	120	0.1	24	77	6.2	7
8	MIL-IMAc-Br[g]	No	60	0.5	20	98.5	21.7	This work
9	FJI-C10[h]	No	60	0.1	24	87	20.5	8
10	MIL-IMAc-Br[i]	No	60	0.5	20	89.1	19.7	This work

Reaction condition: [a] propylene oxide (42.8 mmol) with catalyst 0.64 mol%, TBAB 0.64 mol%; [b] propylene oxide (35.7 mmol) with catalyst 32.1μmol, TBAC 71.6 μmol; [c] propylene oxide (25 mmol) with catalyst (0.125 mol% per paddlewheel units), TBAB 0.58 g; [d] propylene oxide (20 mmol) with catalyst 3.76 μmol; [e] propylene oxide (30 mmol) with catalyst 0.27 mmol; [f] propylene oxide (10 mmol) with catalyst 0.052 mmol; [g] propylene oxide (30 mmol) with catalyst 0.068 mmol; [h] epichlorohydrin (5 mmol) with catalyst 0.25 mol%; [i] epichlorohydrin (30 mmol) with catalyst 0.068 mmol.

Table S3. Conversion of propylene epoxide into propylene carbonate with CO_2 catalyzed by different MOF catalysts

Entry	**Catalyst**	**Yield (%) [a]**	**Yield (%) [b]**
1	MIL-IMAc-Br^-	98.5	78.6
2	MIL-IMOH-Br^-	92.7	65.3
3	MIL-IMPRO-Br^-	89.1	41.8

Reaction condition: [a] epoxide (30 mmol), catalyst (0.068 mmol based on imidazole), CO_2 pressure (0.5 MPa), reaction temperature (60 °C), reaction time (24 h), with high temperature pre-treatment. [b] epoxide (30 mmol), catalyst (0.068 mmol based on imidazole), CO_2 pressure (0.5 MPa), reaction temperature (60 °C), reaction time (24 h), without high temperature pre-treatment.

Notes and references

1. M. Lammert, S. Bernt, F. Vermoortele, D. E. D. Vos and N. Stock, *Inorg. Chem.,* 2013, **52**, 8521-8528.

2. R. Babu, A. C. Kathalikkattil, R. Roshan, J. Tharun, D. W. Kim and D. W. Park, *Green Chem.*,

2016, **18**, 232-242.

3. D. Feng, W. Chung, Z. Wei, Z. Gu, H. Jiang, Y. Chen, D. J. Darensbourg and H. Zhou, *J. Am. Chem. Soc.*, 2013, **135**, 17105-17110.

4. W. Gao, Y. Chen, Y. Niu, K. Willians, L. Cash, P. J. Perez, L. Wojtas, J. Cai, Y. Chen and S. Ma, *Angew. Chem. Int. Ed.*, 2014, **53**, 2615-2619.

5. X. Huang, Y. Chen, Z. Lin, X. Ren, Y. Song, Z. Xu, X. Dong, X. Li, C. Hu and B. Wang, *Chem. Commun.*, 2014, **50**, 2624-2627.

6. D. Ma, B. Li, K. Liu, X. Zhang, W. Zou, Y. Yang, G. Li, Z. Shi and S. Feng, *J. Mater. Chem. A*, 2015, **3**, 23136-23142.

7. J. Liang, R. Chen, X. Wang, T. Liu, X. Wang, Y. Huang and R. Cao, *Chem. Sci.*, 2017, **8**, 1570-1575.

8. J. Liang, Y. Q. Xie, X. S. Wang, Q. Wang, T. T. Liu, Y. B. Huang and R. Cao, *Chem. Commun.*, 2018, **54**, 342-345