

Supporting Information

MIL-101(Cr)/Aminoclay Nanocomposites for Conversion of CO₂ into Cyclic Carbonates

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PXRD pattern of AC

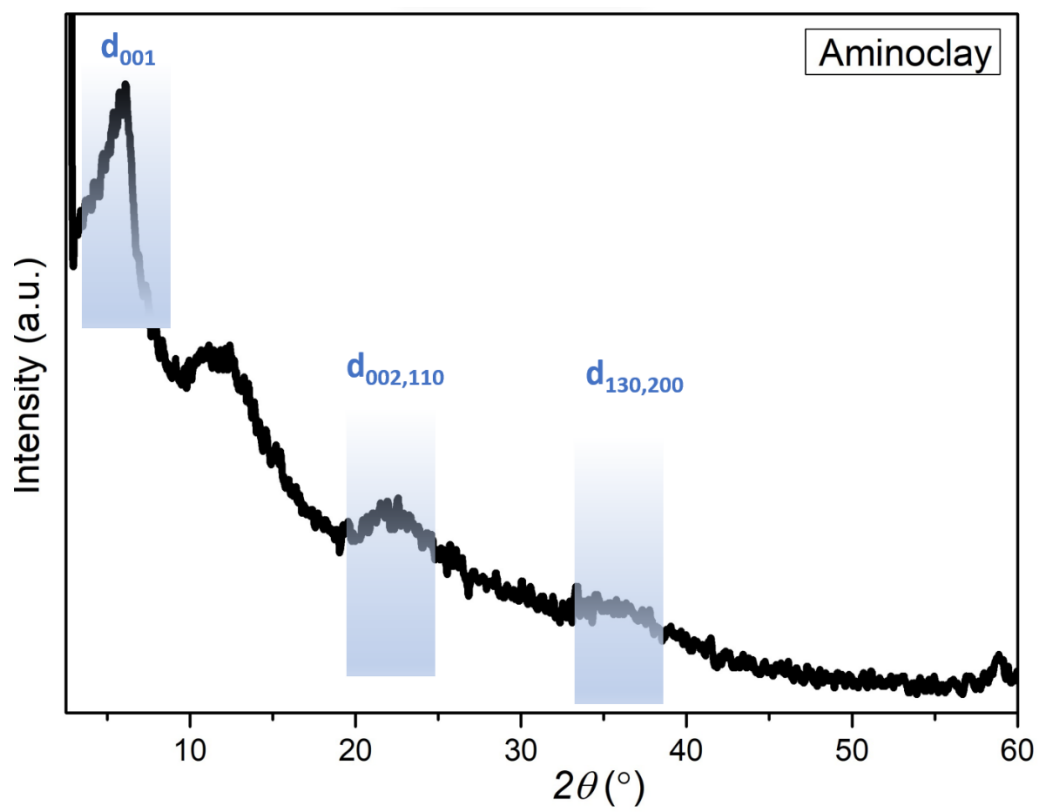


Fig. S1 PXRD pattern of AC. The d_{001} , d_{002} and d_{130} peaks are highlighted.

FT-IR spectra of AC, PMIL and MIL-101(Cr)/AC-1

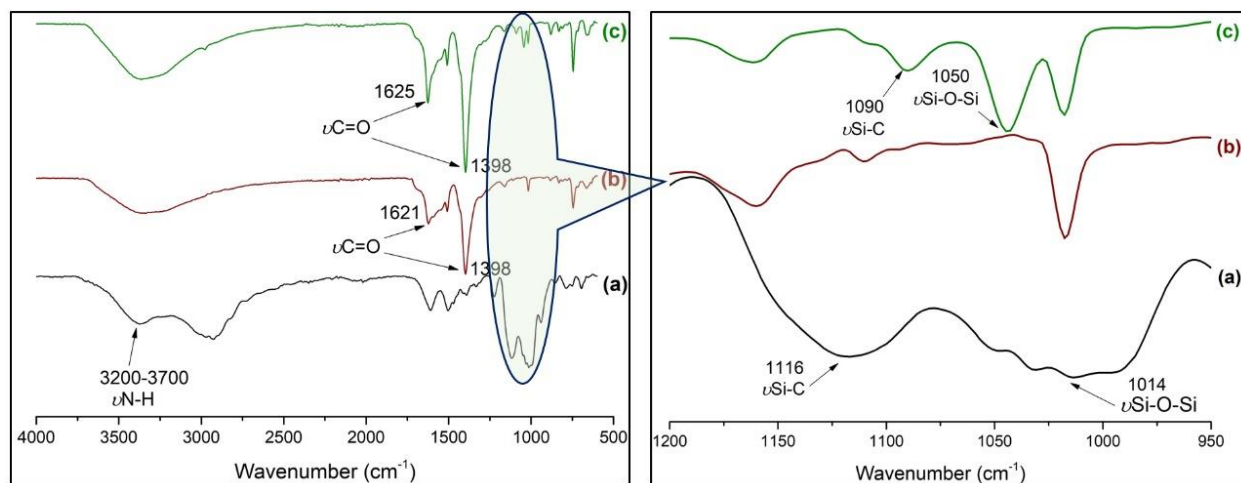


Fig. S2 FT-IR spectra of (a) AC, (b) PMIL and (c) MIL-101(Cr)/AC-1.

TGA profiles of synthesized materials

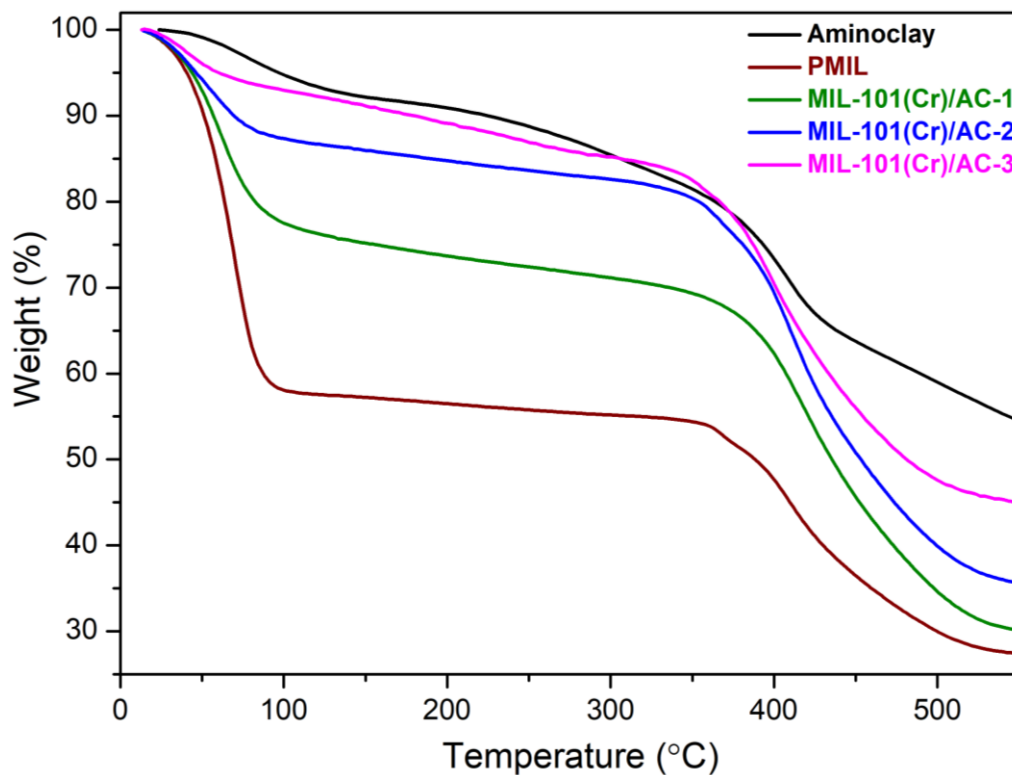


Fig. S3 TGA profiles of PMIL, AC, MIL-101(Cr)/AC-1, MIL-101(Cr)/AC-2 and MIL-101(Cr)/AC-3.

FESEM images and the particle size distribution histograms

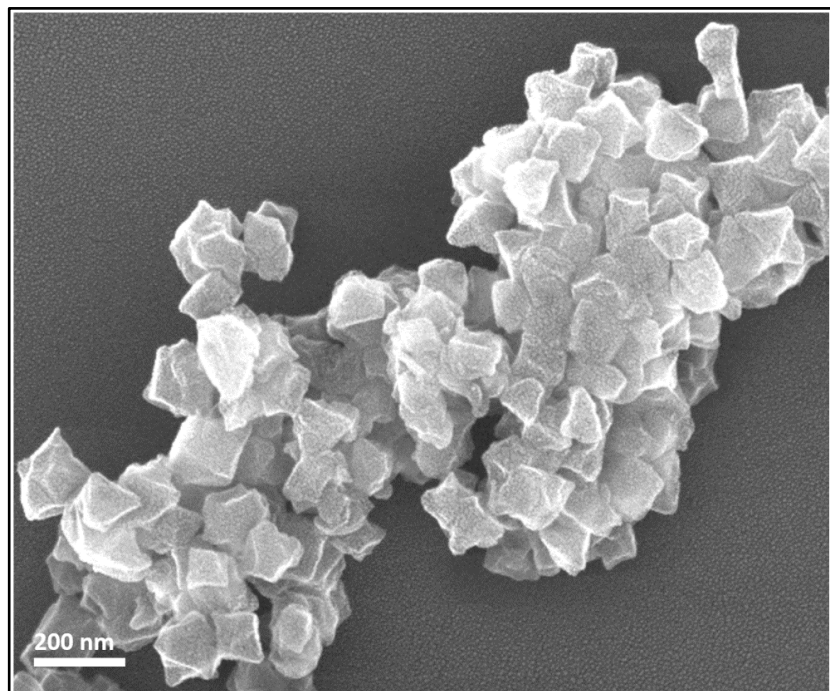


Fig. S4 FESEM image of **PMIL**.

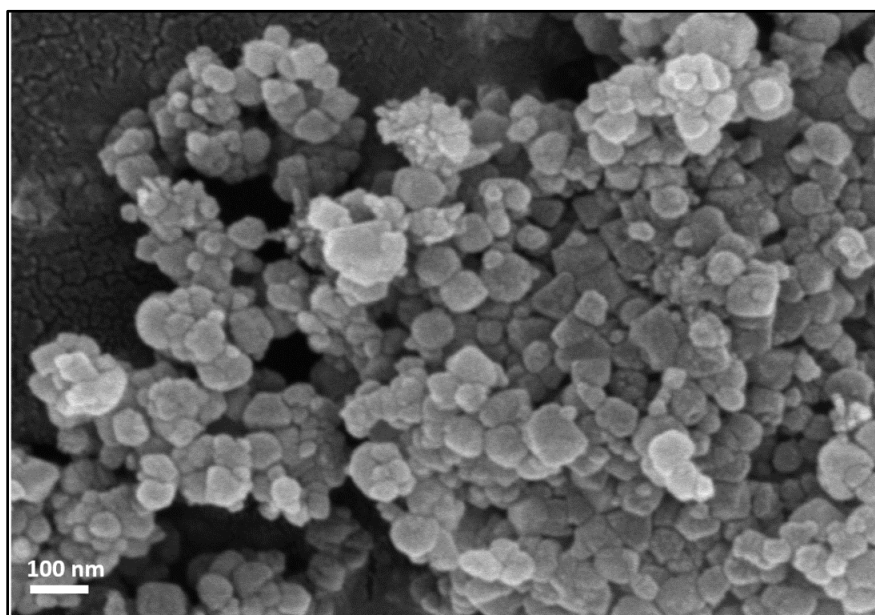


Fig. S5 FESEM image of **MIL-101(Cr)/AC-1**.

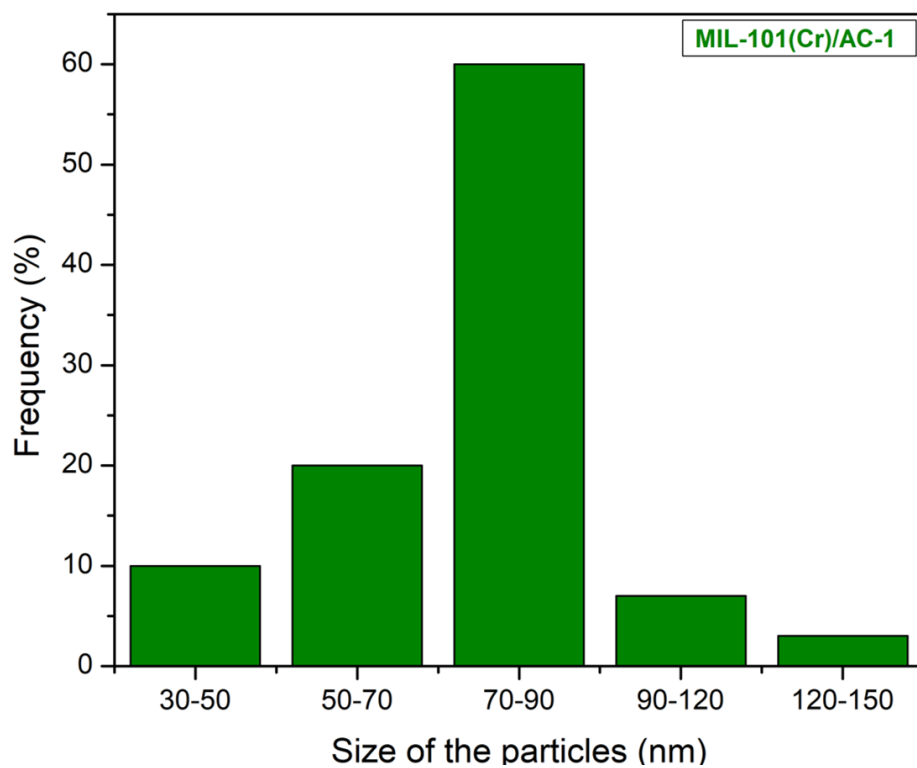


Fig. S6 The particle size distribution histogram plot of **MIL-101(Cr)/AC-1**.

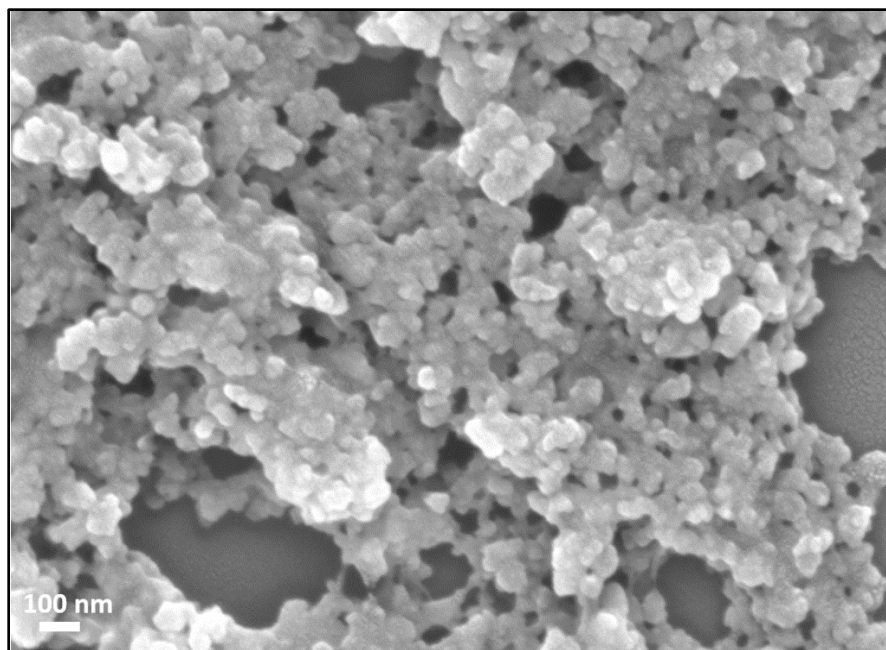


Fig. S7 FESEM image of **MIL-101(Cr)/AC-2**.

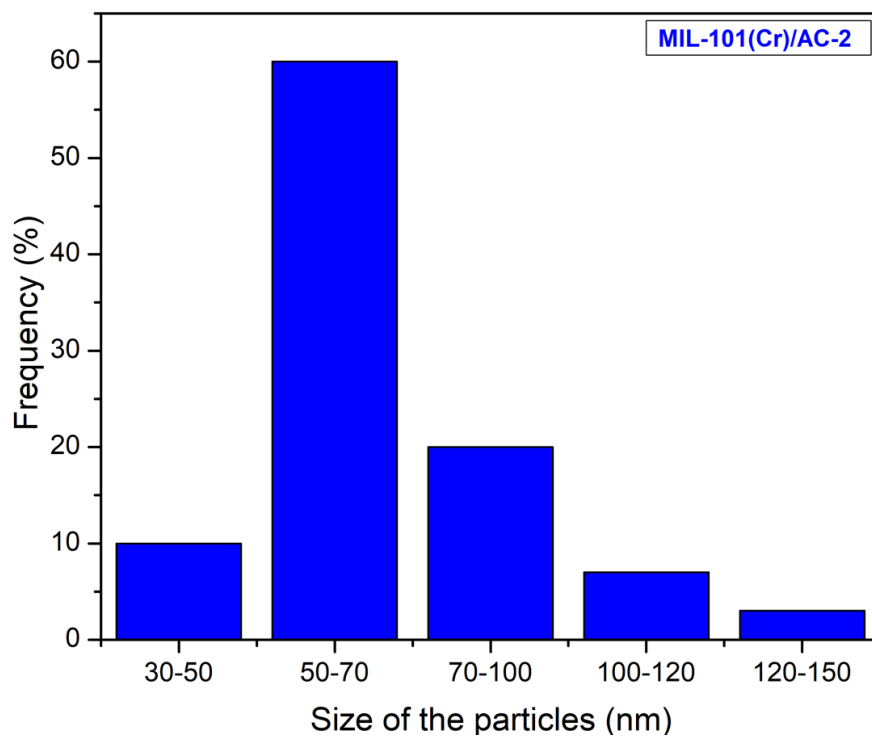


Fig. S8 The particle size distribution histogram plot of **MIL-101(Cr)/AC-2**.

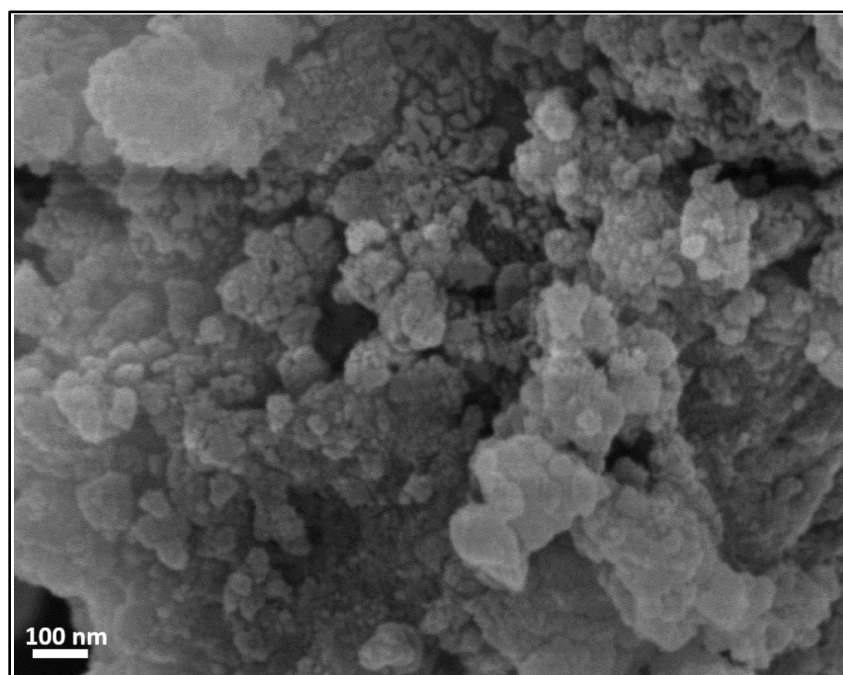


Fig. S9 FESEM images of **MIL-101(Cr)/AC-3**.

EDX spectrum of MIL-101(Cr)/AC-2

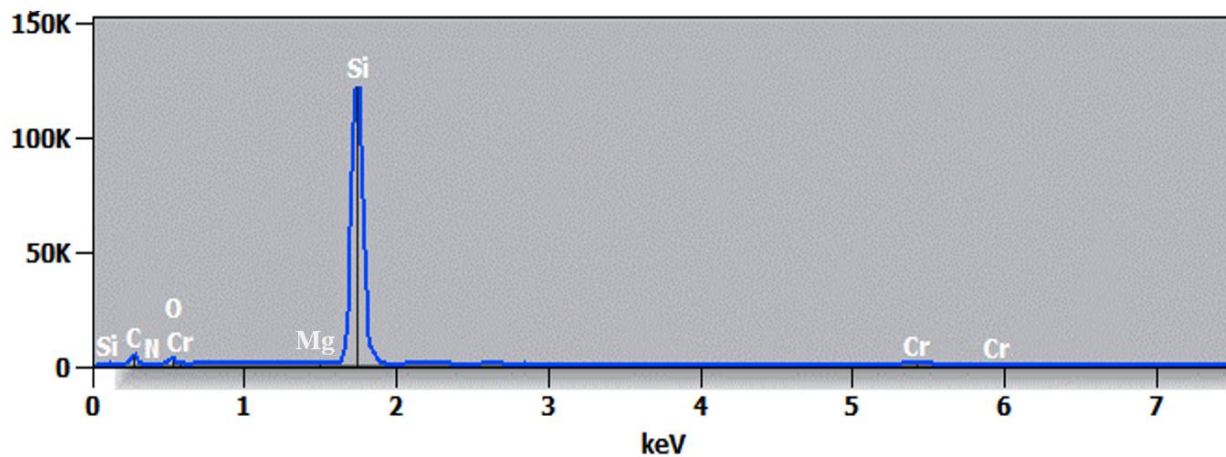


Fig. S10 EDX spectrum of MIL-101(Cr)/AC-2.

Dispersion test of PMIL and MIL-101(Cr)/AC-2



Fig. S11 Dispersion of samples in methanol (a) as-synthesized **PMIL** after 15 minutes and (b) **MIL-101(Cr)/AC-2** after 4 days.

Pore size distribution plots

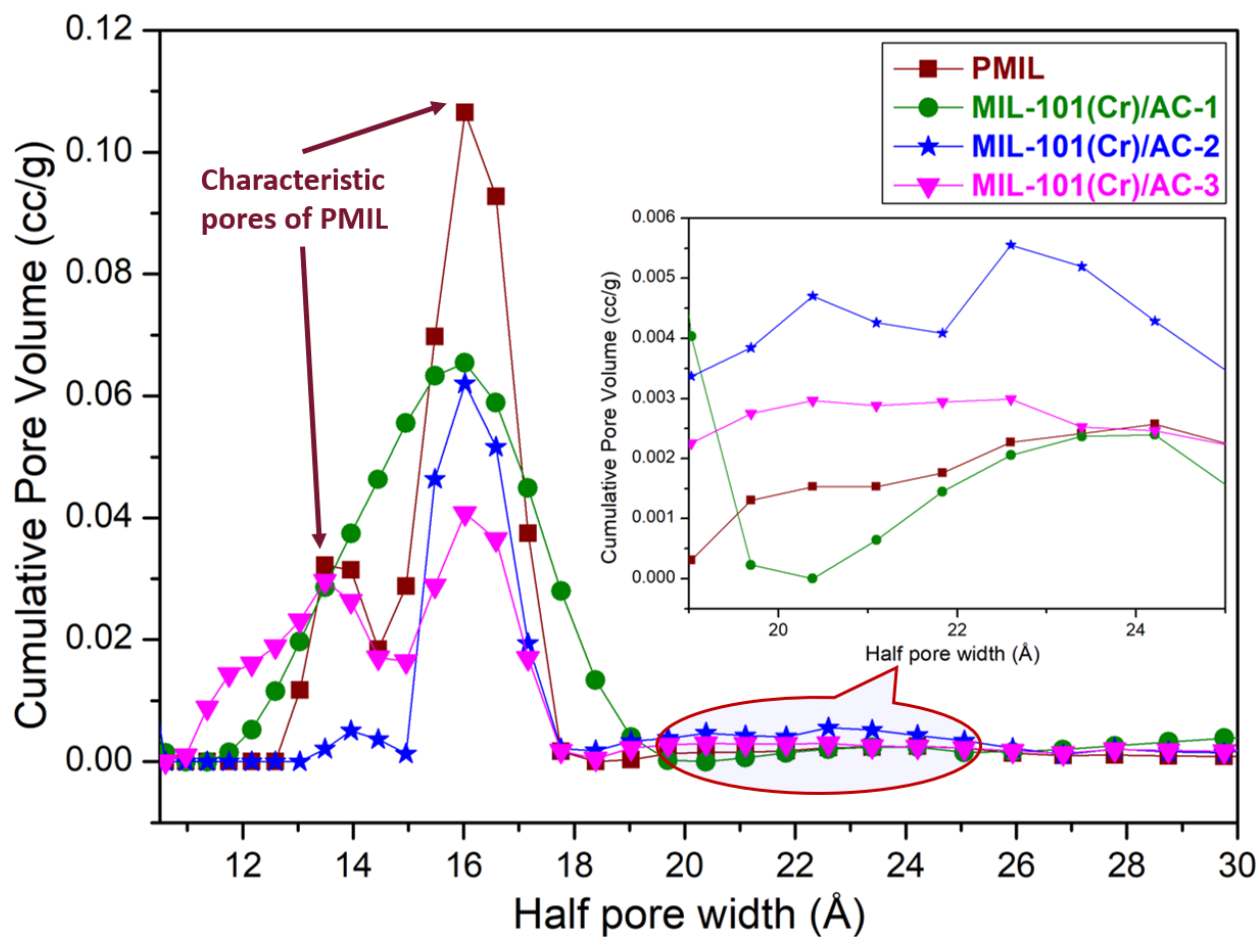


Fig. S12 Pore size distribution plots of PMIL, MIL-101(Cr)/AC-1, MIL-101(Cr)/AC-2 and MIL-101(Cr)/AC-3. Inset shows the presence of large pores at the MOF-clay interface in case of MIL-101(Cr)/AC-2 composite.

Temperature programmed desorption profiles of MIL-101(Cr)/AC-2

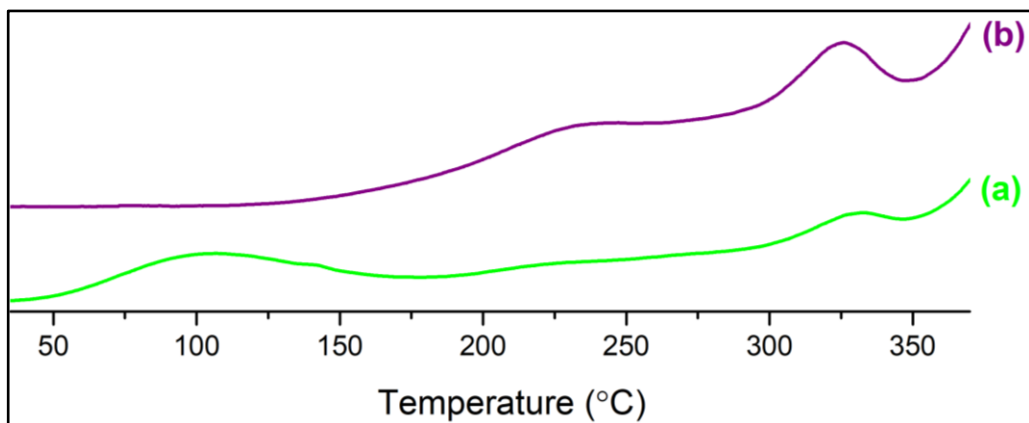


Fig. S13 Temperature programmed desorption profiles of **MIL-101(Cr)/AC-2** (a) NH_3 desorption and (b) CO_2 desorption.

^1H NMR spectrum for the cycloaddition reaction using MIL-101(Cr)/AC-2 as a catalyst with epichlorohydrin

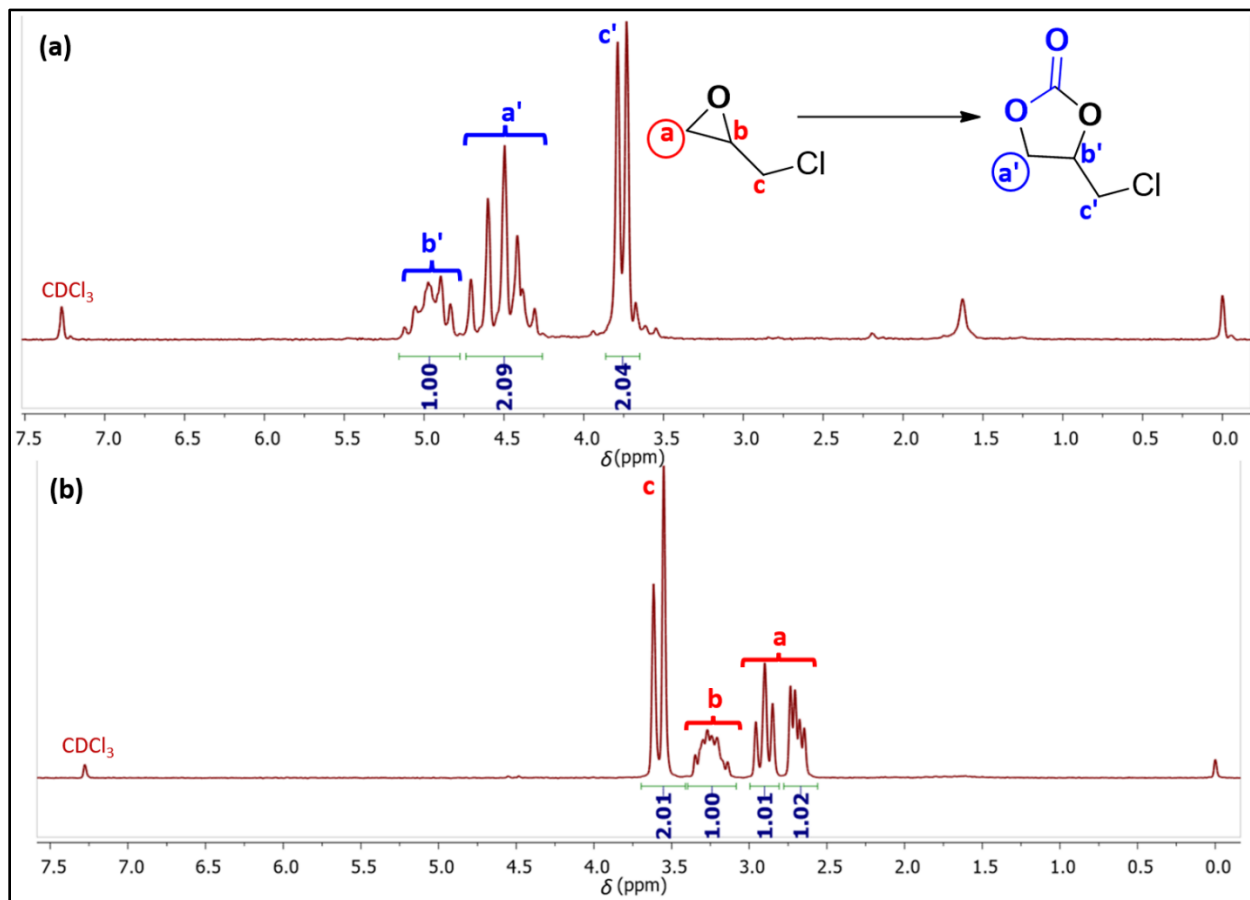


Fig. S14 The ^1H NMR spectra (in CDCl_3) (a) Purified product for the cycloaddition reaction of epichlorohydrin with CO_2 using MIL-101(Cr)/AC-2 as a catalyst. Reaction condition: 9.2 mmol of epichlorohydrin, 0.92 mmol of TBA^+Br^- (co-catalyst), 30 mg of catalyst, 30°C , 1 bar of CO_2 , 6 h. Conversion = 99.9% (b) Pure epichlorohydrin (reactant) before CO_2 cycloaddition reaction. Comparing both spectra (a and b) reveals that, in the purified product spectrum there is no traces of the reactant, indicating the completion of the reaction.

FT-IR spectra of EPH and reaction mixture of the product formed in the cycloaddition reaction with EPH using catalyst MIL-101(Cr)/AC-2

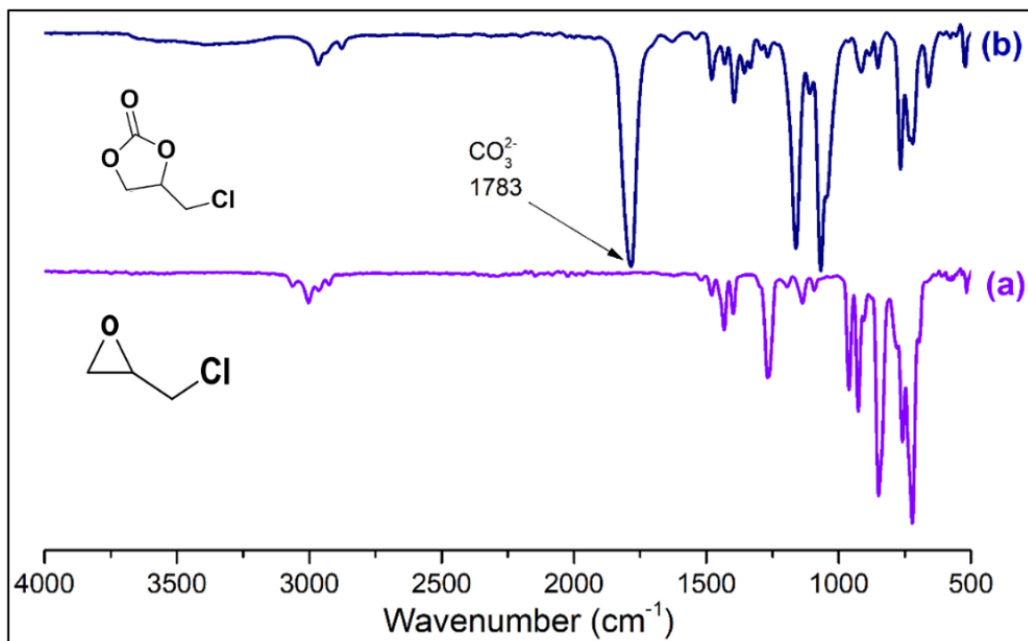
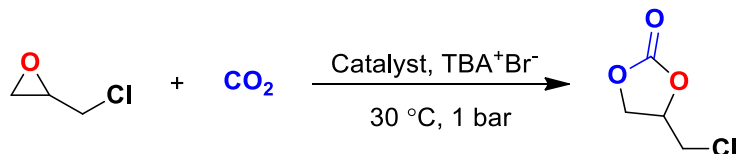


Fig. S15 FT-IR spectra of (a) EPH and (b) Reaction mixture of the product formed in the cycloaddition reaction with EPH using catalyst MIL-101(Cr)/AC-2.

Optimization table for cycloaddition of CO₂ to epichlorohydrin using different catalysts

Table S1 Cycloaddition of CO₂ with epichlorohydrin using as-synthesized **PMIL** and MIL-101(Cr)/AC composites as catalysts^a



Entry	Catalysts	Time (h)	Conversion (%)
1	AC	6	10
2	Cr(NO ₃) ₃ ·9H ₂ O	6	27
3	PMIL	3	18
4	PMIL	4	20
5	PMIL	5	26
6	PMIL	6	30
7	PMIL	12	80
8	PMIL	24	98
9	PMIL	26	99.9
10	MIL-101(Cr)/AC-1	3	17
11	MIL-101(Cr)/AC-1	4	30
12	MIL-101(Cr)/AC-1	5	35
13	MIL-101(Cr)/AC-1	6	44
14	MIL-101(Cr)/AC-1	12	78
15	MIL-101(Cr)/AC-1	24	99.9
16	MIL-101(Cr)/AC-2	3	63
17	MIL-101(Cr)/AC-2	4	69
18	MIL-101(Cr)/AC-2	5	92
19	MIL-101(Cr)/AC-2	6	99.9
20	MIL-101(Cr)/AC-3	3	6
21	MIL-101(Cr)/AC-3	4	22
22	MIL-101(Cr)/AC-3	5	31.5
23	MIL-101(Cr)/AC-3	6	42
24	MIL-101(Cr)/AC-3	12	79
25	MIL-101(Cr)/AC-3	16	99.9
26	PMIL+AC ^b	6	5
27	TBAB ^c	6	20
28	TBAB ^d	6	30
29	MIL-101(Cr)/AC-2^e	6	NIL

^aReaction conditions: 9.2 mmol (851 mg) epichlorohydrin, 30 mg catalyst and 0.92 mmol TBA⁺Br⁻ under 1 bar CO₂ and 30 °C. Conversion (%) were calculated from the ¹H NMR spectra by integration of epoxide peaks (a) versus cyclic carbonate peaks (a'). ^bPhysical mixture; ^cwithout catalyst; ^dwithout catalyst at 40 °C; ^ewithout co-catalyst

¹H NMR spectra for the cycloaddition reaction using different catalysts with epichlorohydrin

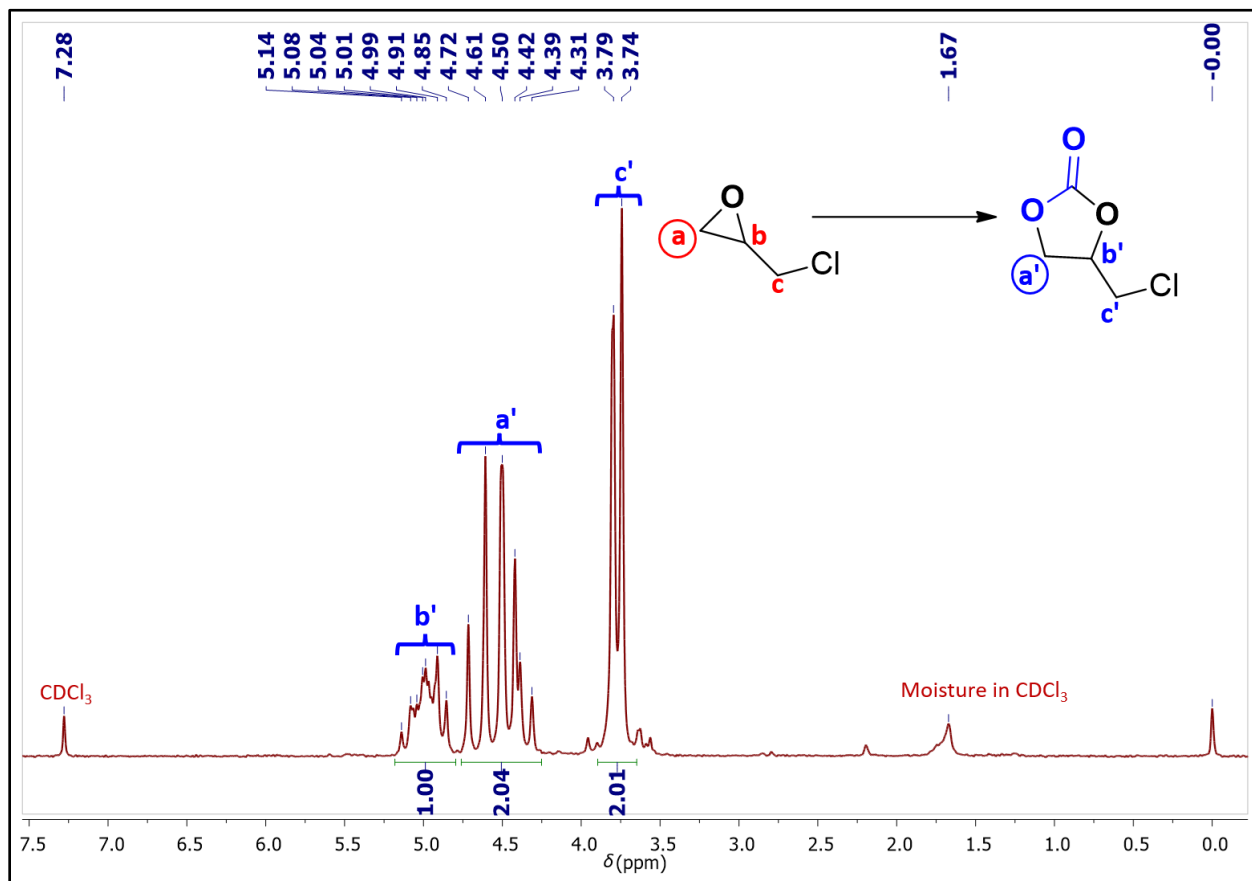


Fig. S16 The ¹H NMR spectrum (in CDCl₃) of the purified product for the cycloaddition reaction of epichlorohydrin with CO₂ using **MIL-101(Cr)/AC-1** as a catalyst. Reaction condition: 9.2 mmol of epichlorohydrin, 0.92 mmol of TBA⁺Br⁻ (co-catalyst), 30 mg of catalyst, 30 °C, 1 bar of CO₂, 24 h. Conversion = **99.9%**

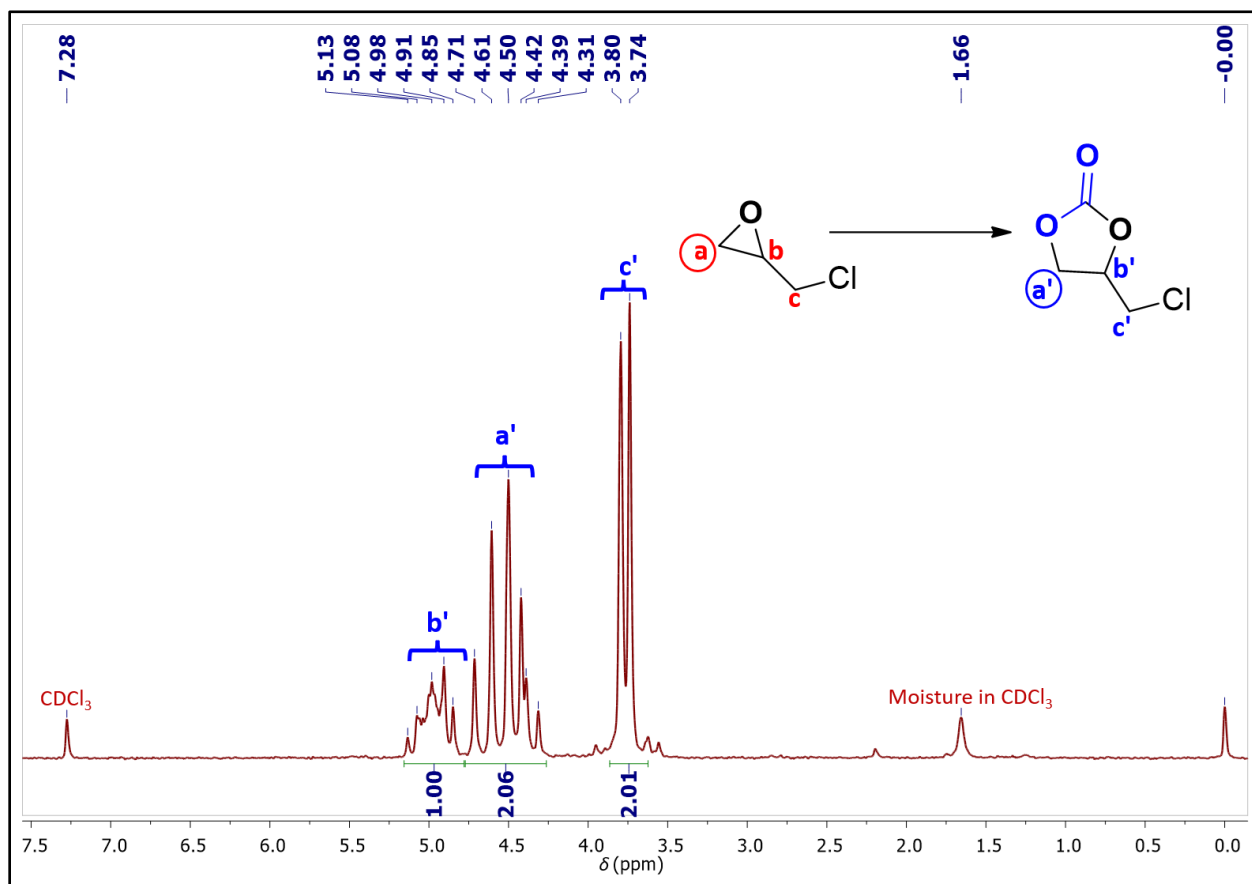


Fig. S17 The ^1H NMR spectrum (in CDCl₃) of the purified product for the cycloaddition reaction of epichlorohydrin with CO₂ using **MIL-101(Cr)/AC-3** as a catalyst. Reaction condition: 9.2 mmol of epichlorohydrin, 0.92 mmol of TBA⁺Br⁻ (co-catalyst), 30 mg of catalyst, 30 °C, 1 bar of CO₂, 16 h. Conversion = **99.9%**

PXRD patterns of MIL-101(Cr)/AC-2 before catalytic run and after 5th cycle of the catalysis

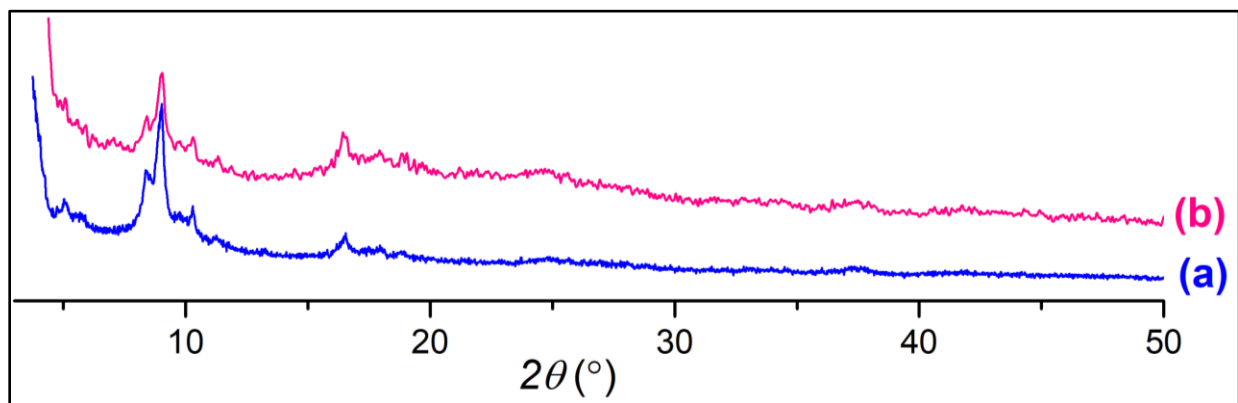


Fig. S18 PXRD patterns of (a) MIL-101(Cr)/AC-2 before catalytic run and (b) after 5th cycle of the catalysis.

FT-IR spectra of MIL-101(Cr)/AC-2 before catalytic run and after 5th cycle of the catalysis

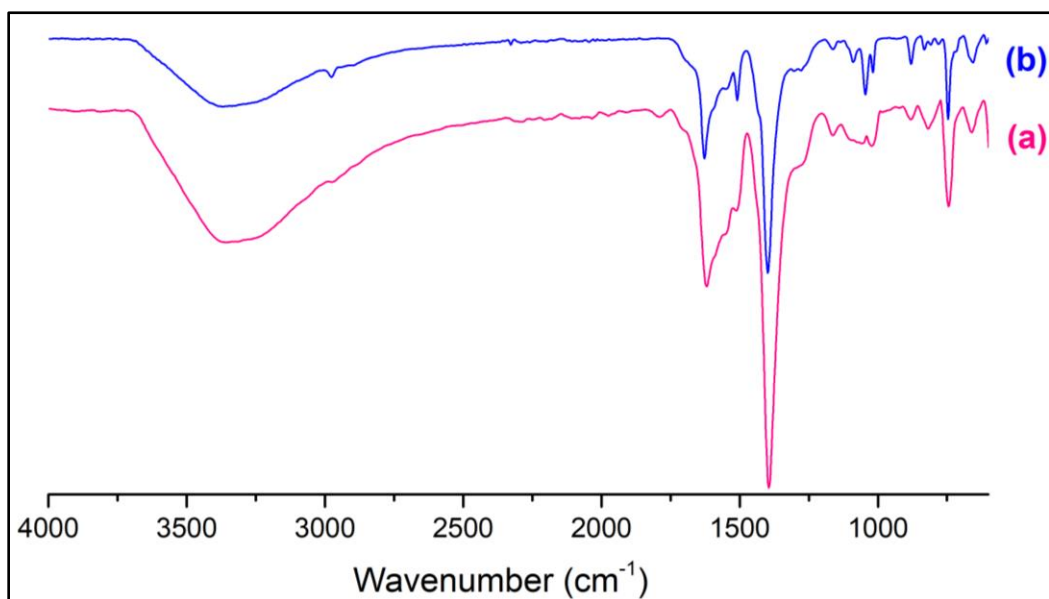
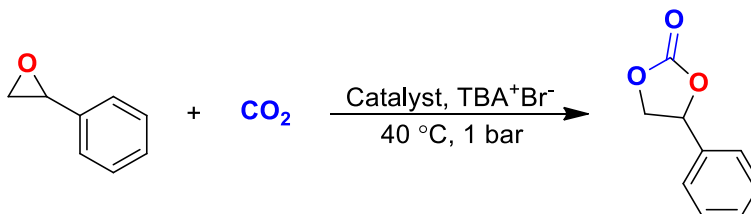


Fig. S19 FT-IR spectra of (a) after 5th cycle of the catalysis and (b) MIL-101(Cr)/AC-2 before catalytic run.

Optimization table for cycloaddition of CO₂ to styrene oxide using PMIL and MIL-101(Cr)/AC-2 as catalysts

Table S2 Cycloaddition of CO₂ to styrene oxide using as-synthesized **PMIL** and **MIL-101(Cr)/AC-2** as heterogeneous catalysts^a


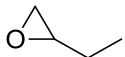
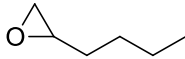
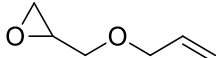
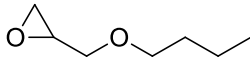


Entry	Catalysts	Time (h)	Conversion (%)
1	PMIL	6	NIL
2	PMIL	12	NIL
3	PMIL	24	5
4	PMIL	42	12
5	PMIL	48	15
6	MIL-101(Cr)/AC-2	6	36.7
7	MIL-101(Cr)/AC-2	12	60
8	MIL-101(Cr)/AC-2	24	71.4
9	MIL-101(Cr)/AC-2	42	92.5
10	MIL-101(Cr)/AC-2	48	99.9

^aReaction conditions: 9.2 mmol (1105 mg) styrene oxide, 30 mg activated catalyst and 0.92 mmol (296 mg) TBA⁺ Br⁻ under 1.0 bar CO₂ and 40 °C. Conversion (%) were calculated from the ¹H NMR spectra by integration of epoxide peaks (a) versus cyclic carbonate peaks (a').

Different substrates and their dimensions

Table S3 Different substrates and their dimensions¹

Substrates	Dimensions
 1,2-epoxy propane	4.34 X 3.41 Å ²
 1,2-epoxy butane	5.648 X 3.39 Å ²
 1,2-epoxy hexane	8.198 X 3.39 Å ²
 Allyl glycidyl ether	~8.901 X 3.140 Å ²
 Butyl glycidyl ether	~10.46 X 3.14 Å ²

^1H NMR spectra for the cycloaddition reaction using MIL-101(Cr)/AC-2 as a catalyst with different substrates

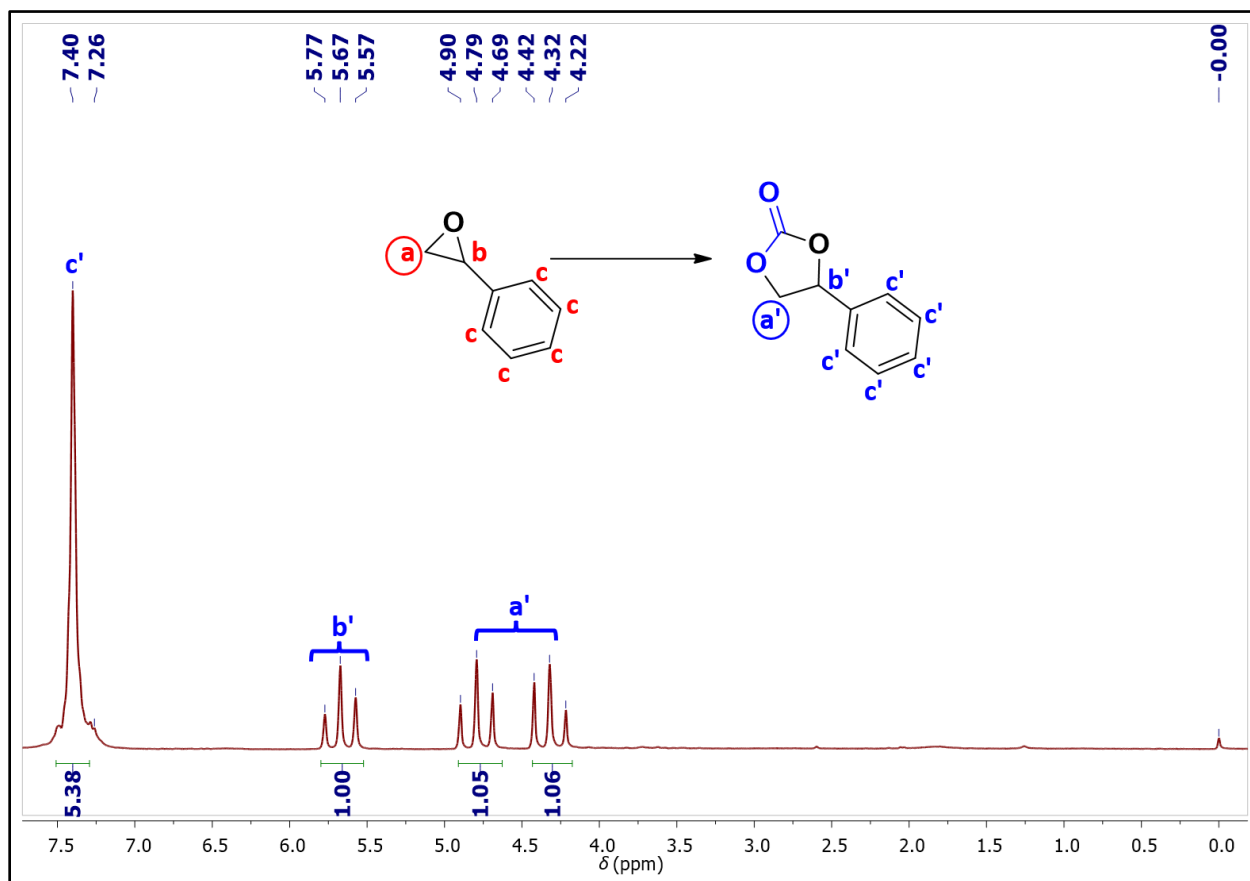


Fig. S20 The ^1H NMR spectrum (in CDCl_3) of the purified product for the cycloaddition reaction of styrene oxide with CO_2 using **MIL-101(Cr)/AC-2** as a catalyst. Reaction condition: 9.2 mmol of epichlorohydrin, 0.92 mmol of TBA^+Br^- (co-catalyst), 30 mg of catalyst, 40 $^\circ\text{C}$, 1 bar of CO_2 , 48 h. Conversion = **99.9%**

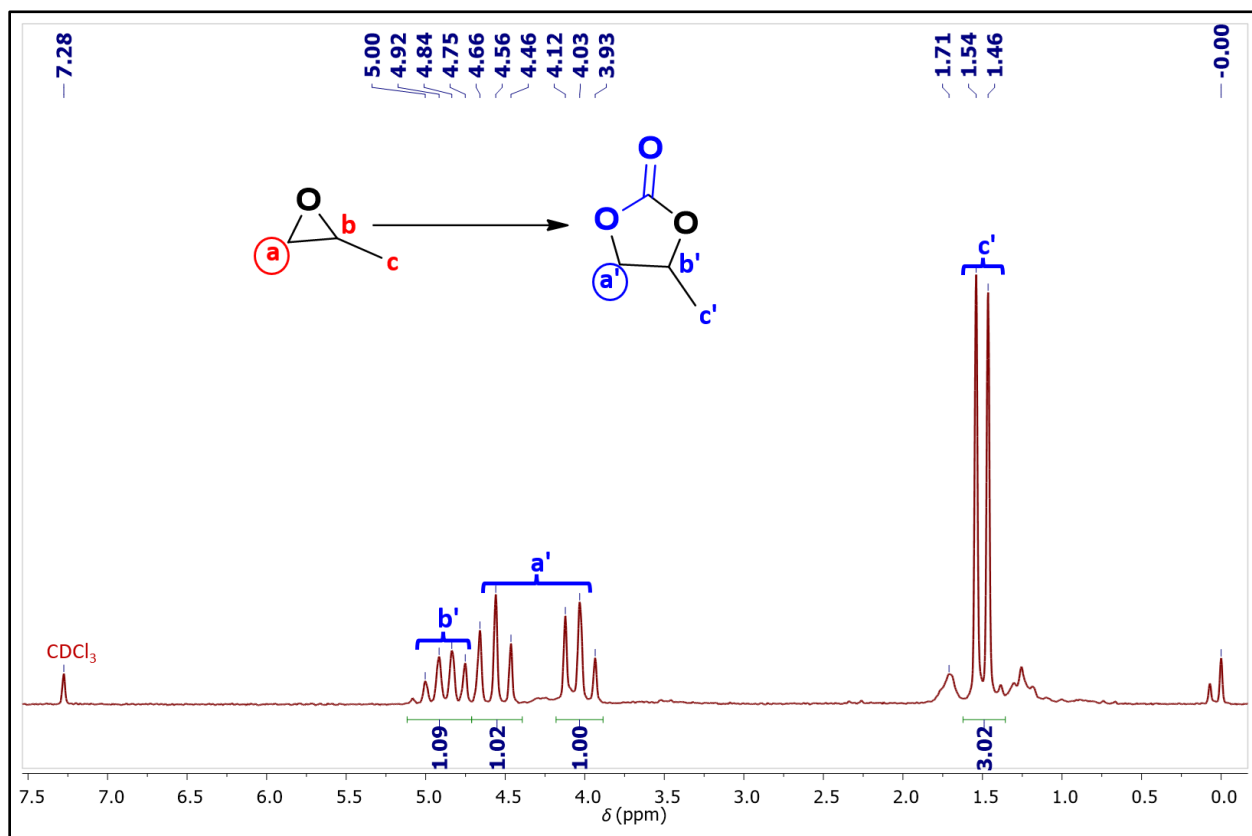


Fig. S21 The ¹H NMR spectrum (in CDCl₃) of the purified product for the cycloaddition reaction of propylene oxide with CO₂ using **MIL-101(Cr)/AC-2** as a catalyst. Reaction condition: 9.2 mmol of epichlorohydrin, 0.92 mmol of TBA⁺Br⁻ (co-catalyst), 30 mg of catalyst, 30 °C, 1 bar of CO₂, 6 h. Conversion = **99.9%**

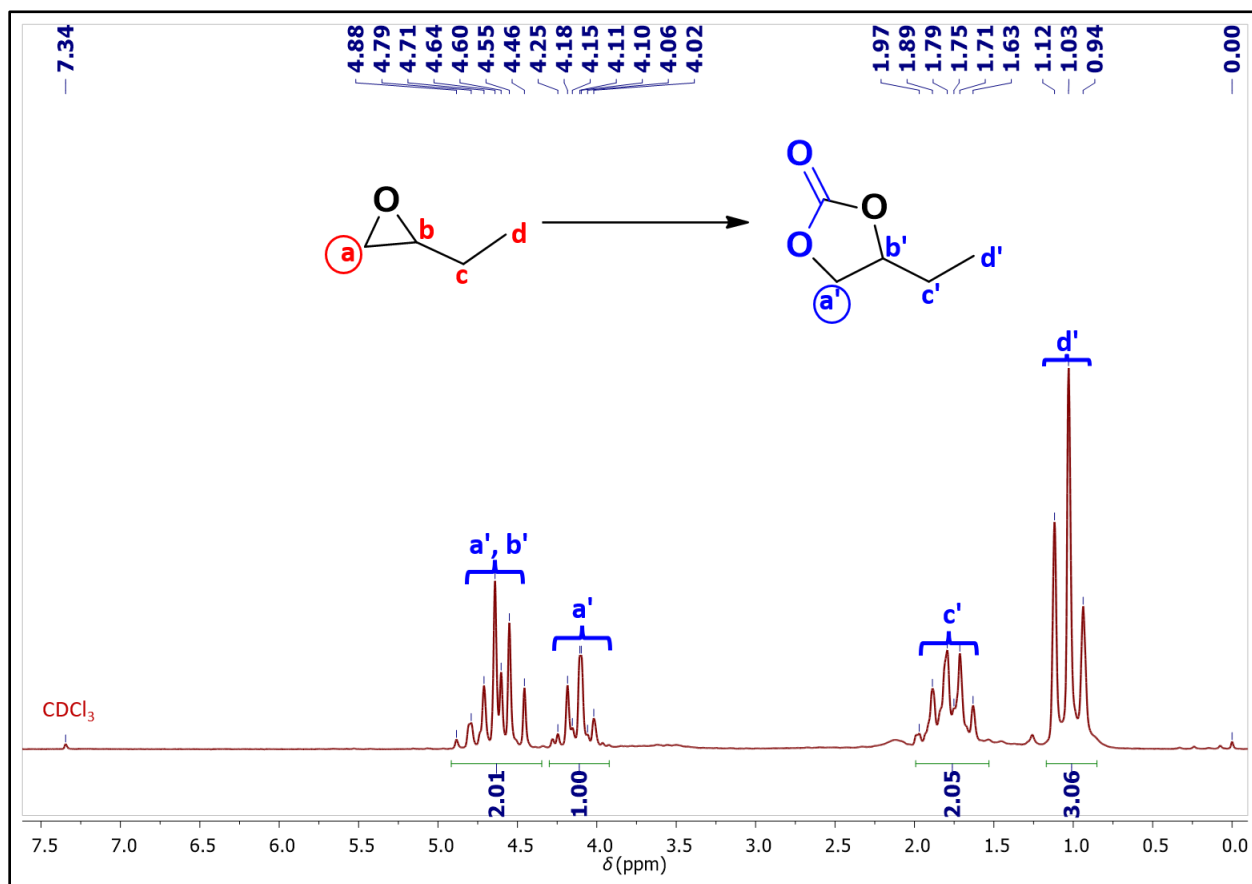


Fig. S22 The ^1H NMR spectrum (in CDCl_3) of the purified product for the cycloaddition reaction of 1,2-epoxybutane with CO_2 using **MIL-101(Cr)/AC-2** as a catalyst. Reaction condition: 9.2 mmol of epichlorohydrin, 0.92 mmol of TBA^+Br^- (co-catalyst), 30 mg of catalyst, 40 $^\circ\text{C}$, 1 bar of CO_2 , 6 h. Conversion = **99.9%**

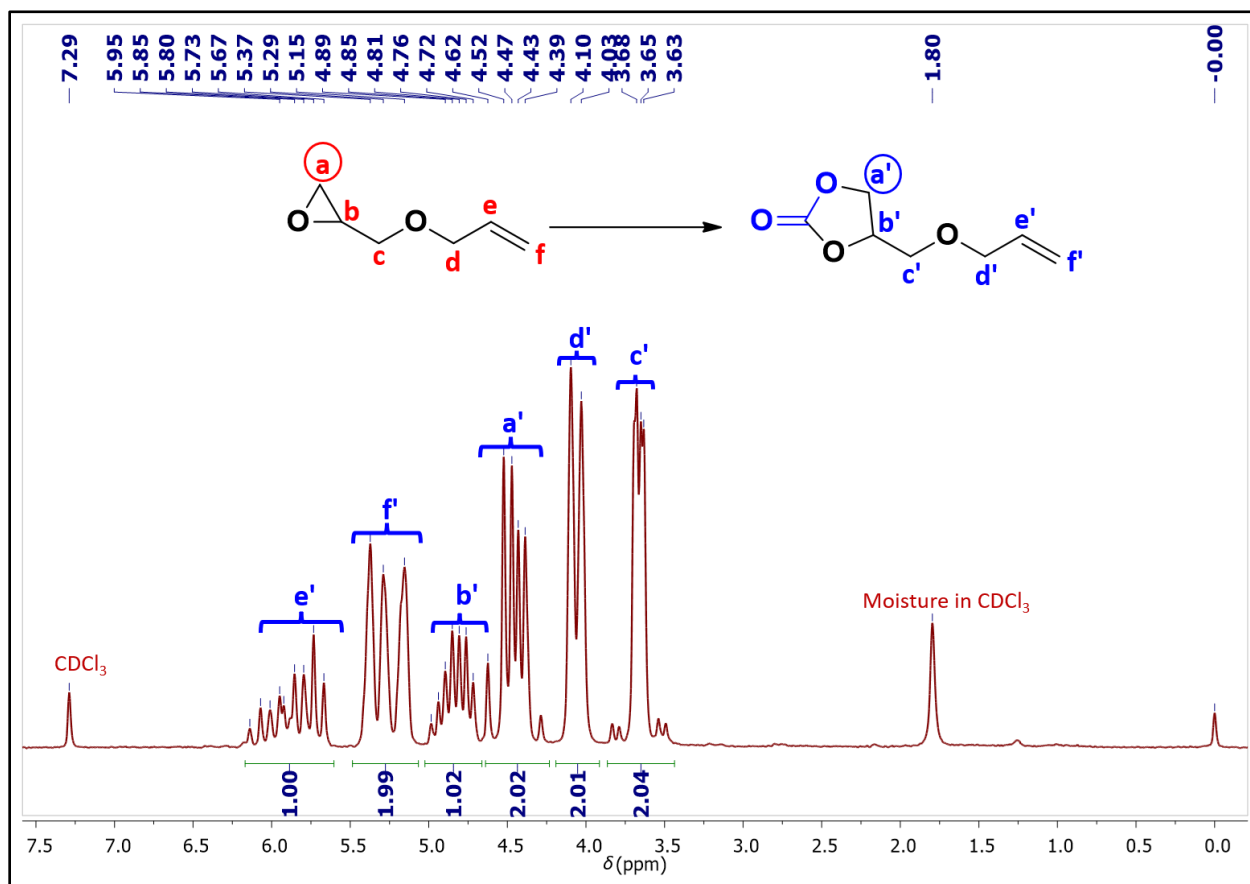


Fig. S23 The ^1H NMR spectrum (in CDCl_3) of the purified product for cycloaddition reaction of allyl glycidyl ether with CO_2 using **MIL-101(Cr)/AC-2** as a catalyst. Reaction condition: 9.2 mmol of epichlorohydrin, 0.92 mmol of TBA^+Br^- (co-catalyst), 30 mg of catalyst, 40°C , 1 bar of CO_2 , 12 h. Conversion = 99.9%

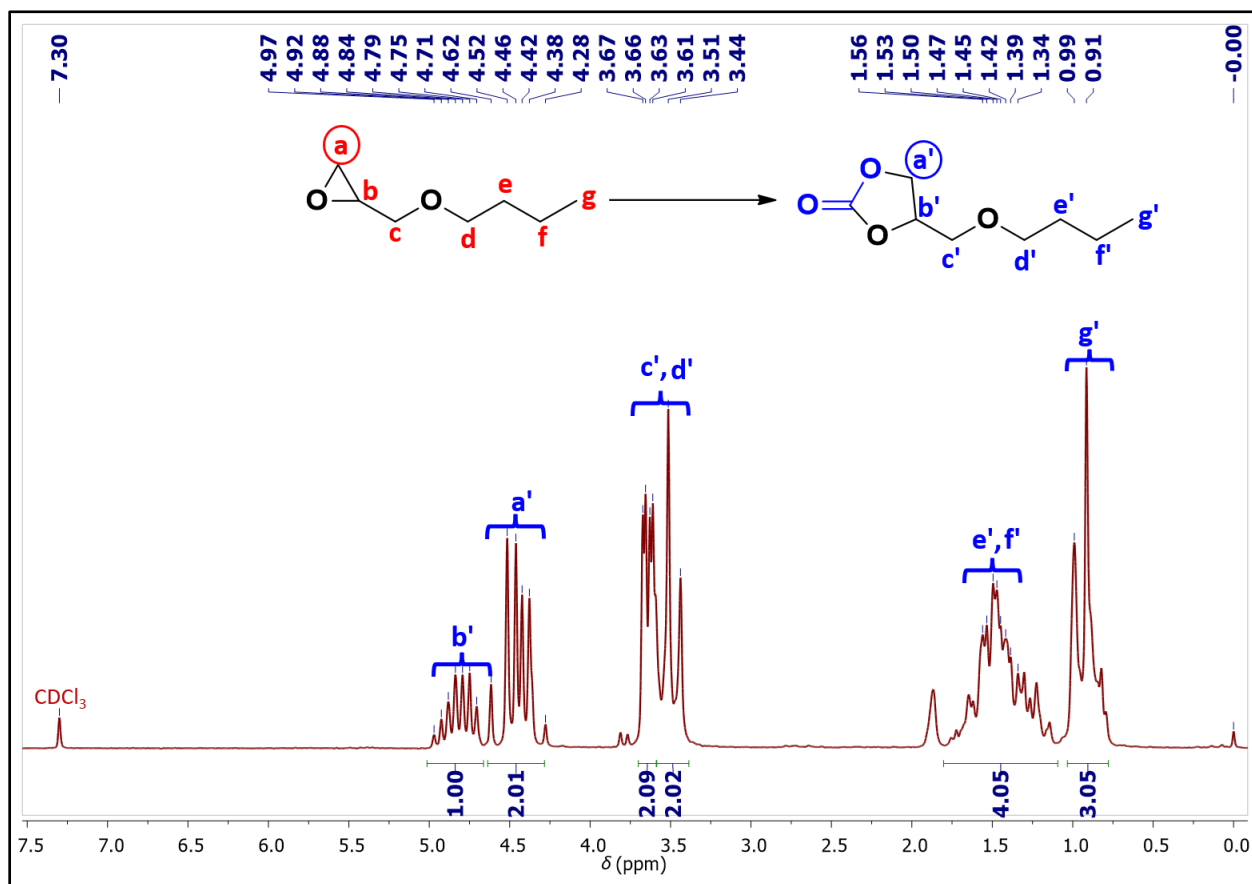


Fig. S24 The ^1H NMR spectrum (in CDCl_3) of the purified product for cycloaddition reaction of butyl glycidyl ether with CO_2 using **MIL-101(Cr)/AC-2** as a catalyst. Reaction condition: 9.2 mmol of epichlorohydrin, 0.92 mmol of TBA^+Br^- (co-catalyst), 30 mg of catalyst, 40°C , 1 bar of CO_2 , 15 h. Conversion = **99.9%**

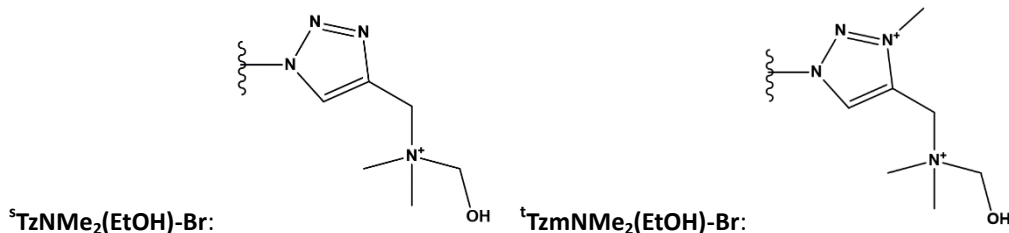
A comparison of the catalytic activity of different MIL-101(Cr)-based MOF catalysts with MIL-101(Cr)/AC-2

Table S4 A comparison of the catalytic activity of different MIL-101(Cr)-based MOF catalysts with **MIL-101(Cr)/AC-2** towards the cycloaddition of CO₂ with EPH, PO and SO

Entry	Catalysts	Substrates ^a	Temperature (°C)	Pressure (bar)	Time (h)	Conversion (%)	Ref.
1	MIL-101(Cr)	EPH	80	10	2.5	11	2
2	MIL-101(Cr)	PO	100	10	2.5	15.5	3
3	MIL-101(Cr)	PO	80	8	4	77.2	4
4	MIL-101(Cr)	PO	25	8	24	91	5
		SO	25	8	48	98	
5	MIL-101(Cr)	SO	90	5	3	41.2	6
6	MIL-101(Cr)	EPH	50	1	68	32	7
7	MIL-101-NH ₂	PO	80	20	8	23.4	8
8	MIL-101-Br	PO	80	20	8	25.1	
9	MIL-101-NH ₂	EPH	90	10	2	17	9
10	MIL-101-CH ₂ Cl	PO	80	8	4	90.8	4
11	MIL-101-N(n-Bu) ₃ Br ^b	PO	80	20	8	99.1	8
12	Co-POM@MIL-101 ^c	EPH	90	20	2	94	10
		SO	90	20	2	88	
13	MIL-101-TSIL ^d	SO	110	20	6	93.1	11
		EPH	110	20	2	81	
14	Cr-MIL-101-[BuPh ₃ P]Br ^e	EPH	120	20	2	98.3	12
		PO	120	20	2	97.8	
		SO	120	20	2	68.5	
15	MIL-101(Cr)-DABCO IL ^f	EPH	100	15	0.67	98.8	13
		PO	100	15	0.67	97	
		SO	100	15	0.67	44.5	
16	MIL-101-tzmOH-Br ^g	EPH	120	10	2	97	14
		PO	80	10	10	92	
		SO	80	10	10	57	
17	MIL-101-H/pmtzm-Br ^h	SO	80	10	10	73	9
		PO	80	10	2	94	
		EPH	80	10	2	95	
18	MIL-101-IL(BuBr) ⁱ	EPH	110	10	6	92	15
		PO	110	10	6	80	
19	Mim-6@MIL-101 ^j	EPH	100	10	2.5	95.5	3
		PO	100	10	2.5	92.5	
		SO	100	10	2.5	53.4	
20	MIL-101-tz-TMA-Br ^k	EPH	80	10	4	99	16
21	PIL-COOH@MIL-101 ^l	EPH	70	10	2.5	92.7	2
		PO	70	10	2.5	88	

		SO	90	10	2.5	80	
22	MIL-101-IMBr-6 ^m	EPH	80	8	4	92.3	4
		PO	80	8	4	95.8	
		SO	80	8	4	54.7	
23	MIL-101-IM ⁿ	PO	80	8	4	94.3	
24	IL@MIL-101-SO ₃ H ^o	EPH	90	1	24	98	17
25	polyILs@MIL-101 ^p	EPH	70	1	24	94	18
26	MIL-101-IP ^q	EPH	50	1	68	32	7
27	MIL-101-ImEtOH ^r	SO	90	5	3	95.6	6
28	MIL-101-TzNMe ₂ (EtOH)-Br ^s	EPH	80	10	2	99	19
29	MIL-101-TzmNMe ₂ (EtOH)-Br ^t	PO	80	10	1	99	
30	MIL-101(Cr)/AC-2	EPH	30	1	6	99.9	This work
		PO	30	1	6	99.9	
		SO	40	1	48	99.9	

^a**Substrates:** EPH (Epichlorohydrin), PO (Propylene Oxide), SO (Styrene Oxide); ^b**N(n-Bu)₃Br:** tributylammonium bromide; ^c**Co-POM:** Co-Polyoxometalates; ^d**TSIL:** 1-methylene-3-(4-carboxylbenzyl) imidazolium bromide; ^e**[BuPh₃P]Br:** n-butyltriphenylphosphonium bromide; ^f**DABCO:** 1,4-Diazabicyclo[2.2.2]octane, **IL:** 2-Bromoethanol; ^g**tzmOH-Br:** hydroxyl-functionalized 1,2,3-triazolium bromide; ^h**pmtzm:** 4(methylpyridinium)-1,2,3-triazolium; ⁱ**IL:** pyridine-based ionic liquids, BuBr: 1-bromobutene; ^j**Mim:** 1,1'-(Hexane-1,6-diyl)-bis(3-methylimidazolium) Dibromide; ^k**tz-TMA-Br:** N,N,N-trimethyl-1H-1,2,3-triazol-4-aminium bromide; ^l**PIL:** Hydrogen bond donor functionalized poly(ionic liquids); ^m**IMBr:** Imidazolium bromide, ⁿ**IM:** imidazole; ^o**IL:** 1-methyl-3-(2-aminoethyl)imidazolium bromide; ^p**polyILs:** imidazolium-based poly(ionic liquids); ^q**IP:** Ionic polymer; ^r**ImEtOH:** 2-(1-imidazol-1-yl) ethanol;



Entries 1-6 in **Table S4** indicates the catalytic activity of pristine MIL-101(Cr) which exhibits either poor catalytic activity or need higher temperature and high pressure to complete the reactions. Although, it's effectiveness could be improved by the modification in catalyst i.e., by changing substitution in ligand (**Entry 9, Table S4**) or the post-modification in the framework of MIL-101 (in respect of bdc linker) using different groups i.e., NH₂, Br and CH₂Cl (**Entries 7, 8, 10 & 11, Table S4**), inclusion of polyoxometalates and ionic liquids inside the porous framework (**Entries 12-29, Table S4**). However, these approaches still require either relatively high temperature and pressure or longer reaction time or the combination of the all the parameters to exhibit a decent catalytic conversion.

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