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## **Supporting Information**

### **Tailoring the catalytic activity of metal organic framework by tuning the metal centre and basic functional sites**

Poonam Rani and Rajendra Srivastava\*

*Department of Chemistry, Indian Institute of Technology Ropar, Rupnagar-140001, India*

\*E-mail: [rajendra@iitrpr.ac.in](mailto:rajendra@iitrpr.ac.in), Phone: +91-1881-242175; Fax: +91-1881-223395

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## **Experimental details**

### **Procedure for the catalytic reactions**

#### ***Condensation reactions***

Knoevenagel condensation was carried out in neat condition. A mixture of benzaldehyde (1.9 mmol) and catalyst (20 mg, activated at 100 °C for 12 h) was stirred at ambient condition for 5 min. Malononitrile (3.8 mmol) was added to the reaction mixture and the stirring was continued for a desired period of time at ambient condition. Progress of the reaction was monitored by gas chromatograph (GC) (Yonglin 6100; BP-5; 30 m × 0.25 mm × 0.25 μm). The product was confirmed using GC–MS (Schimadzu GCMS-QP 2010 Ultra; Rtx-5 Sil Ms; 30 m × 0.25 mm × 0.25 μm).

For the Aldol condensation, 15 mg of the activated catalyst (100 °C for 12 h) was taken in a reaction vessel. A mixture of heptanal (0.09 mmol) and benzaldehyde (1.32 mmol) was injected into the reaction vessel and the reaction mixture was stirred at 120 °C for 1h. The reaction mixture was analyzed by GC and the products were identified by GC-MS.

#### ***Cycloaddition reaction***

Cycloaddition reaction was carried out in a liquid phase pressure reactor (Parr reactor, USA). Catalyst was initially activated at 100 °C for 12 h. A mixture of epoxide and activated catalyst was fed into the reactor and the desired CO<sub>2</sub> pressure was maintained. The reaction mixture was stirred at 400 rpm at a desired temperature and pressure for stipulated time period. After the reaction, the reactor was cooled to ambient temperature and the reaction mixture was diluted with ethyl acetate. Catalyst was removed with the help of centrifuge machine, reaction mixture was analyzed by GC, and the products were identified by GC-MS.

### **Catalyst characterization**

X-ray diffraction (XRD) patterns were recorded in the 2θ range of 5–50° with a scan speed of 2°/min on a PANalytical X'PERT PRO diffractometer, using Cu Kα radiation (λ=0.1542 nm, 40 kV, 40 mA). Nitrogen adsorption measurements were performed at 77 K by Quantachrome Instruments, Autosorb-IQ volumetric adsorption analyzer. Sample was out-gassed at 150 °C for 3 h in the degas port of the adsorption apparatus. The specific surface area was

calculated from the adsorption branch using the Brunauer-Emmett-Teller (BET) equation. The pore diameter was estimated using non-local density functional theory (NLDFT) and Barret–Joyner–Halenda (BJH) method. Scanning electron microscopy measurements (SEM) and energy dispersive X-ray spectroscopy (EDS) were carried out on a JEOL JSM-6610LV to investigate the morphology and chemical composition of the MOF. Fourier transform infrared (FTIR) spectra were recorded on a Bruker spectrophotometer in the region 400–4000  $\text{cm}^{-1}$  (spectral resolution = 4  $\text{cm}^{-1}$ ; number of scans = 100). Diffused reflectance UV-visible (DRUV-visible) spectra were recorded on Shimadzu UV-2600 spectrophotometer.  $\text{BaSO}_4$  was used as reference material. Thermo gravimetric analysis (TGA) was performed in the range of 25–700  $^\circ\text{C}$  on a TGA/DSC 1 STAR<sup>c</sup> SYSTEM from Mettler Toledo, Switzerland, with temperature increments of 10  $^\circ\text{C}$  /min in  $\text{N}_2$  atmosphere.  $\text{NH}_3/\text{CO}_2$ -TPD was performed using CHEMBET<sup>TM</sup> TPR/TPD, Quntachrome, USA. In a typical TPD experiments, 100 mg of sample was placed in a U-shaped, flow through, quartz sample tube. The catalyst was pretreated in He (30 mL/min) at required temperature for 1 h. After cooling down to desired temp, ammonia (partial pressure 100 Torr)/ $\text{CO}_2$  was adsorbed on the samples for 1 h. The sample was subsequently flushed by He stream (30 mL/min) at desired temperature for 1 h to remove physisorbed ammonia/ $\text{CO}_2$ . The TPD experiments were carried out in the different range at a heating rate of 10 K/min. The ammonia/ $\text{CO}_2$  concentration in the effluent was monitored by using a gold-plated, filament thermal conductivity detector. X-ray photoelectron spectroscopy (XPS) was carried out in a XPS system PHI 5000 VersaProbeII (ULVAC–PHI, INC, Japan) with a micro focused (100  $\mu\text{m}$ , 25 W, 15KV) monochromatic Al-K $\alpha$  source ( $h\nu=1486.6$  eV), a hemispherical analyzer and a multichannel detector.

**Table S1.** Influence of solvents in the Knoevenagel condensation reaction using DMAP-Zr-BDC-MOF

Catalyst	Solvent	Benzaldehyde conversion (%)
Zr-BDC-MOF	Toluene	10.4
DMAP-Zr-BDC-MOF	Toluene	32.2
DMAP-Zr-BDC-MOF	DMF	41.3
DMAP-Zr-BDC-MOF	Ethanol	96.8
DMAP-Zr-BDC-MOF	DMSO	90.3
DMAP-Zr-BDC-MOF	CH <sub>3</sub> CN	60.5
DMAP-Zr-BDC-MOF	CH <sub>2</sub> Cl <sub>2</sub>	27.3
DMAP-Zr-BDC-MOF	H <sub>2</sub> O	81.4
DMAP-Zr-BDC-MOF	None	95.4

**Reaction conditions:** Catalyst (20 mg), benzaldehyde (1.9 mmol), malononitrile (3.8 mmol), temperature (30 °C), time (10 min).

**Table S2.** Comparative catalytic activity of various MOF reported in literature with respect to catalyst reported in this study.

<b>Catalyst</b>	<b>Methylene compound</b>	<b>Reaction parameter</b>	<b>Product yield (%)</b>	<b>Ref.</b>
DMAP-Zr-BDC-MOF	Malononitrile	Aldehyde (1.9 mmol), methylene compound (3.8 mmol), catalyst (0.020 g), temp. (40 °C), time (30 min.).	98.9	This work
DMAP-Zr-BDC-MOF	Diethyl malonate	Aldehyde (1.9 mmol), methylene compound (3.8 mmol), catalyst (0.050 g), temp. (100 °C), time (16 h).	92.5	This work
UiO-66-NH <sub>2</sub>	Malononitrile	Aldehyde (5 mmol), methylene compound (10 mmol), DMF (5 ml), catalyst (0.144 g), temp. (40 °C), time (40 min.).	98	45
UiO-66-NH <sub>2</sub>	Ethyl cyanoacetate	Aldehyde (5 mmol), methylene compound (10 mmol), DMF (5 ml), catalyst (0.144 g), temp. (40 °C), time (120 min.).	92	45
UiO-66-NH <sub>2</sub>	Diethyl malonate	Aldehyde (5 mmol), methylene compound (10 mmol), DMF (5 ml), catalyst (0.144 g), temp. (40 °C), time (120 min.).	<2	45
ED-MIL-101	Ethyl cyanoacetate	Aldehyde (1 mmol), methylene compound (1 mmol), cyclohexane (5 ml), catalyst (20 mg), temp. (80 °C), time (19 h).	97.7	46
MIL-101	Ethyl	Aldehyde (1 mmol), methylene	31.5	46

		cyanoacetate compound (1 mmol), cyclohexane (5 ml), catalyst (20 mg), temp. (80 °C), time (19 h).		
Al-MIL-101-NH <sub>2</sub>	Malononitrile	Aldehyde (4 mmol), methylene compound (4 mmol), catalyst (70 mg), temp. (80 °C), time (30 min.).	61	47
Fe-MIL-101-NH <sub>2</sub>	Malononitrile	Aldehyde (4 mmol), methylene compound (4 mmol), catalyst (70 mg), temp. (80 °C), time (30 min.).	78	47
{Zn <sub>2</sub> (ptaH) <sub>2</sub> ·11H <sub>2</sub> O} <sub>n</sub>	Malononitrile	4-Nitrobenzaldehyde (10.4 mmol), methylene compound (10.4 mmol) dichloromethane (20 mL), catalyst (5 wt%), RT, time (180 min.).	80	48
{Zn <sub>2</sub> (ptaH) <sub>2</sub> ·11H <sub>2</sub> O} <sub>n</sub>	Ethyl cyanoacetate	4-Nitrobenzaldehyde (10.4 mmol), methylene compound (10.4 mmol) dichloromethane (20 mL), catalyst (5 wt%), RT, time (120 min.).	85	48
{Zn <sub>2</sub> (ptaH) <sub>2</sub> ·11H <sub>2</sub> O} <sub>n</sub>	Diethyl malonate	4-Nitrobenzaldehyde (10.4 mmol), methylene compound (10.4 mmol), dichloromethane (20 mL), catalyst (5 wt%), RT, time (120 min.)	0	48

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**Table S3.** Comparative catalytic activity of various MOF reported in literature with respect to catalyst reported in this study for the cycloaddition reaction of CO<sub>2</sub>.

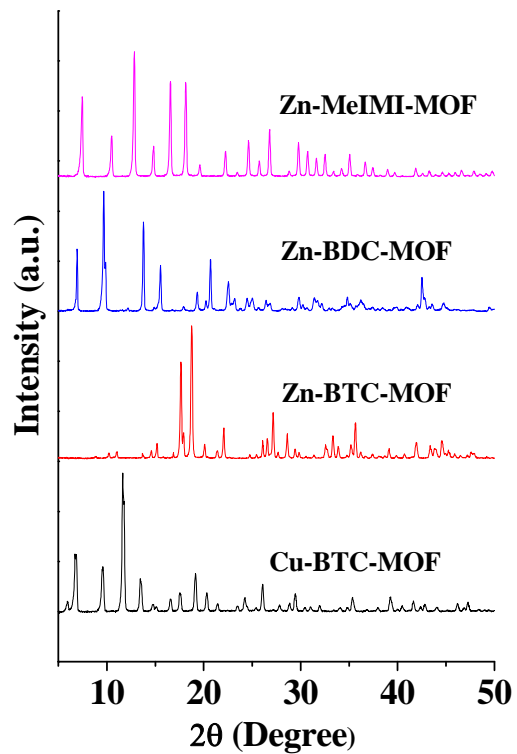
Catalyst	Co-catalyst	Reaction parameter	Product yield (%)	TOF(h <sup>-1</sup> )	Ref.
DMAP-Zr-BDC-MOF	-	Epichlorohydrin (38 mmol), catalyst (100 mg), CO <sub>2</sub> pressure (10 bar), temp. (100 °C), time (1 h).	79.6	593.1	This work
Zn-MOF-5	TBABr	Epichlorohydrin (20 mmol), TBABr (2.5 mol%), catalyst (100 mg), CO <sub>2</sub> pressure (1 bar), temp. (50 °C), time (12 h).	93	11.9	57
Mg-MOF-74	-	Styrene oxide (5 mmol), catalyst (20 mg), chlorobenzene (30 mL), CO <sub>2</sub> pressure (20 bar), temp. (100 °C), time (4h).	95	25.2	58
Meim-Uio- 66.	-	Epichlorohydrin (10 mmol), catalyst (0.052 mmol), CO <sub>2</sub> pressure (1 bar), temp. (120 °C), time (24 h).	100	8.0	59
Cu <sub>3</sub> BTC <sub>2</sub>	-	Epichlorohydrin (18 mmol), catalyst (100 mg), CO <sub>2</sub> pressure (7 bar), temp. (100 °C), time (4 h).	63.8	17.0	60
[Cu <sub>2</sub> L(H <sub>2</sub> O) <sub>2</sub> ] <sub>4</sub> H <sub>2</sub> O.2 DMF	TBABr	Epichlorohydrin (20 mmol), TBABr (0.3 mmol), catalyst (0.01mmol), CO <sub>2</sub> pressure (10 bar), temp. (373K), time (2h).	95.2	950.0	61

MIL-101-N(n-Bu) <sub>3</sub> Br	-	Propylene oxide (30 mmol), catalyst (0.27 mmol), CO <sub>2</sub> pressure (20 bar), temp. (80 °C), time (8 h).	99.1	13.7	62
MIL-101-NH <sub>2</sub>	TBABr	Propylene oxide (30 mmol), catalyst (0.27 mmol), CO <sub>2</sub> pressure (20 bar), temp. (80 °C), time (8 h).	98.4	13.6	62
MIXMOF (MOF-5)	TBABr	Propylene oxide (285 mmol), TBABr (0.1 mmol), catalyst (0.01mmol), CO <sub>2</sub> pressure (40 bar), temp. (140 °C), time (3 h).	63	494.6	63
Cr-MIL-101	TBABr	Propylene oxide (18 mmol), TBABr (0.62 mmol), catalyst (50 mg), CO <sub>2</sub> pressure (8.1 bar), temp. (25 °C), time (24 h).	91	16.2	64

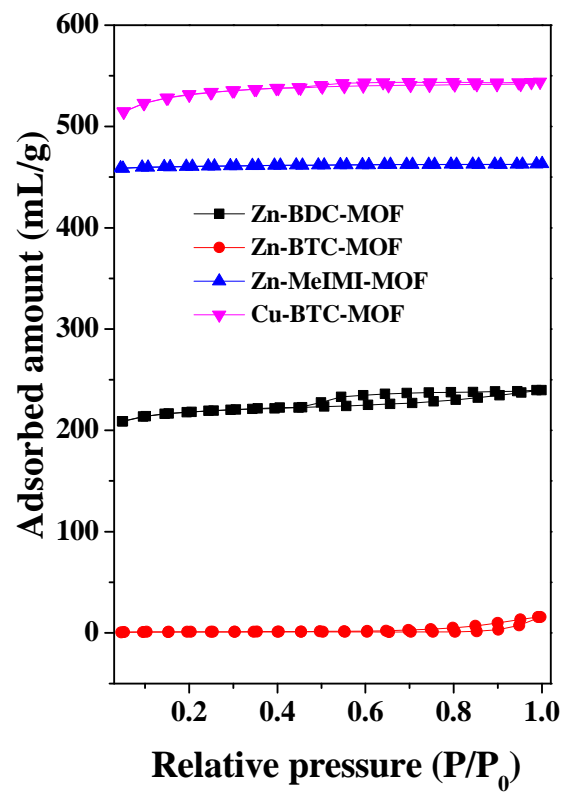
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TOF (h<sup>-1</sup>) = moles of epoxide converted per mole of active species per hour.

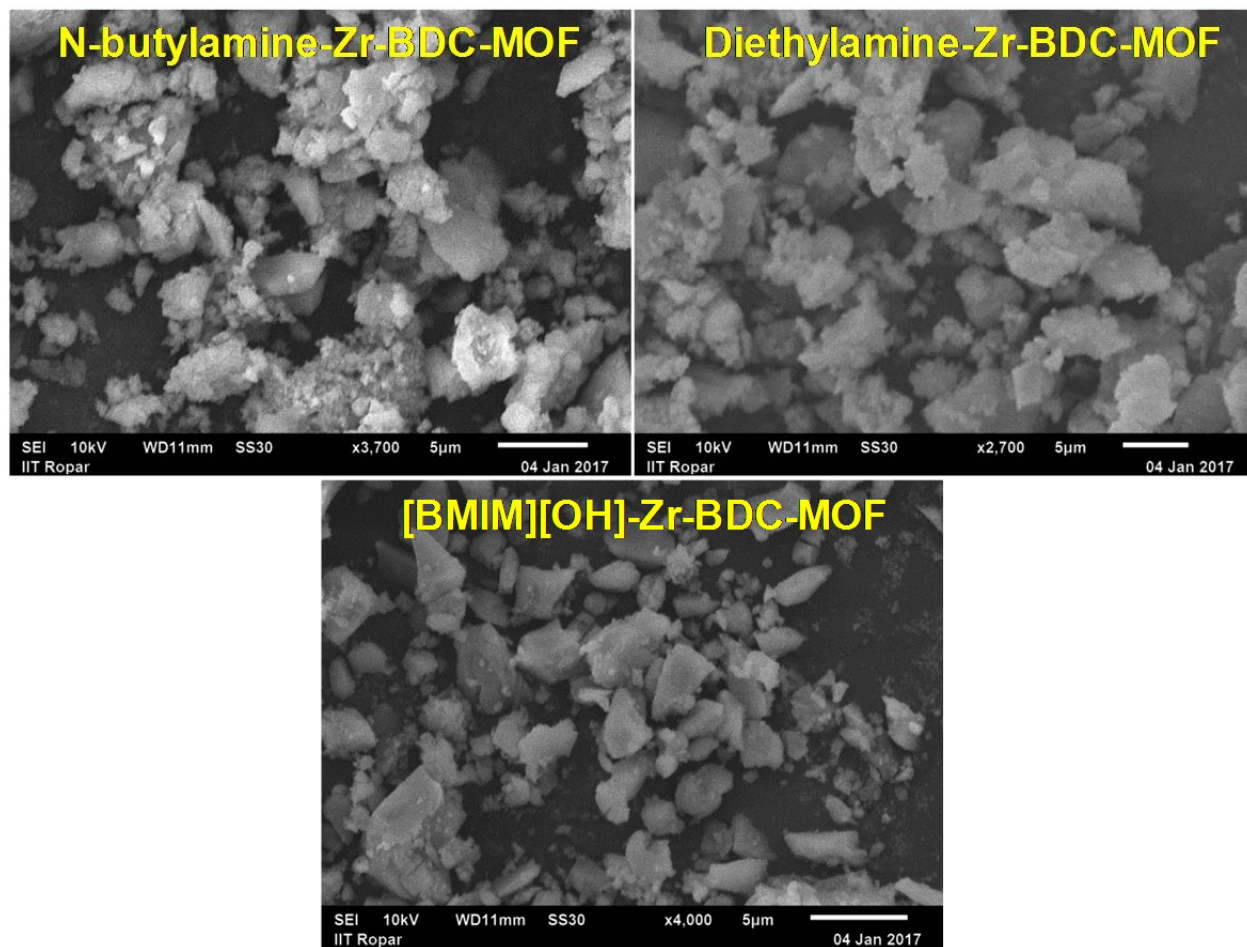




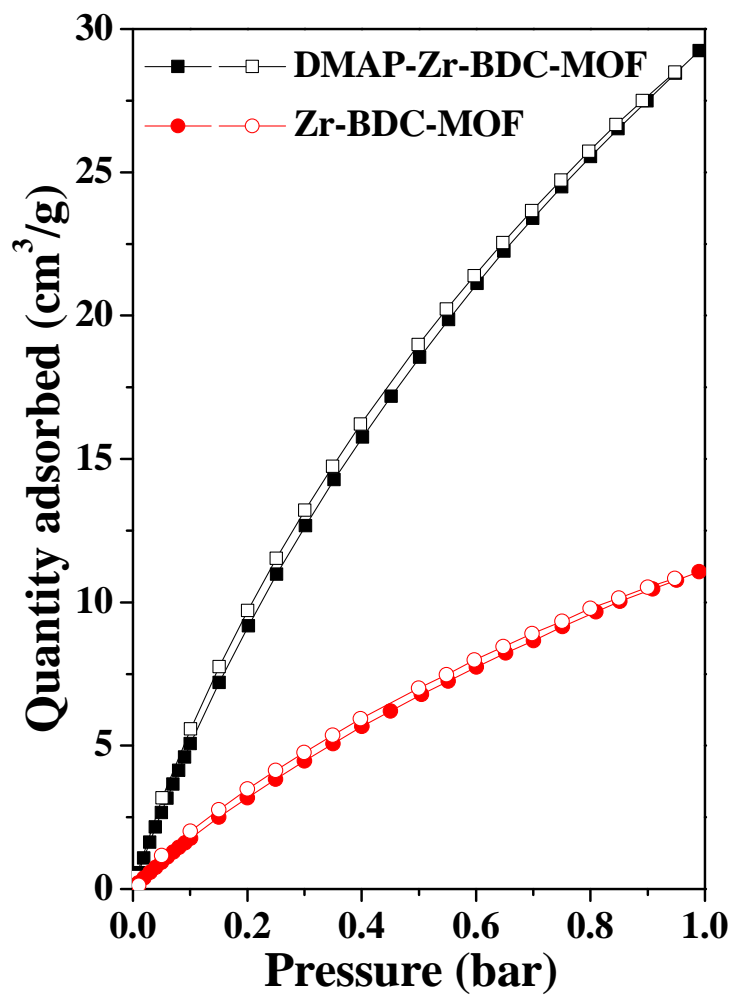
**Fig. S1.** Powder X-ray diffraction patterns of Zn and Cu based metal organic frameworks prepared in this study.



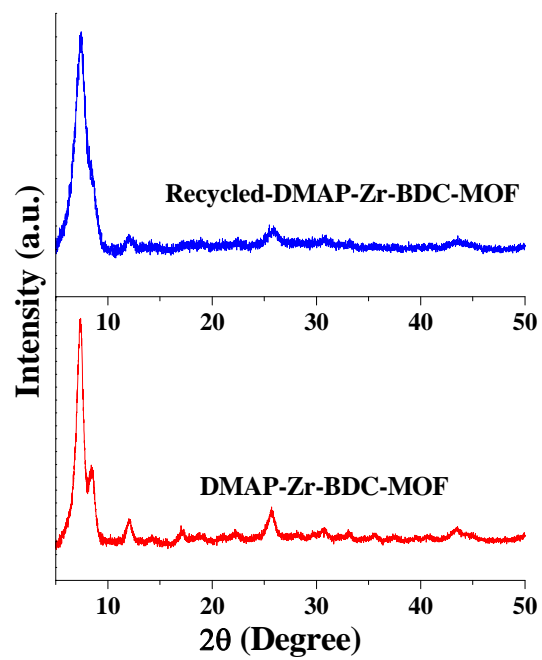
**Fig. S2.** N<sub>2</sub>-adsorption isotherms of different Zn and Cu based metal organic framework prepared in this study.



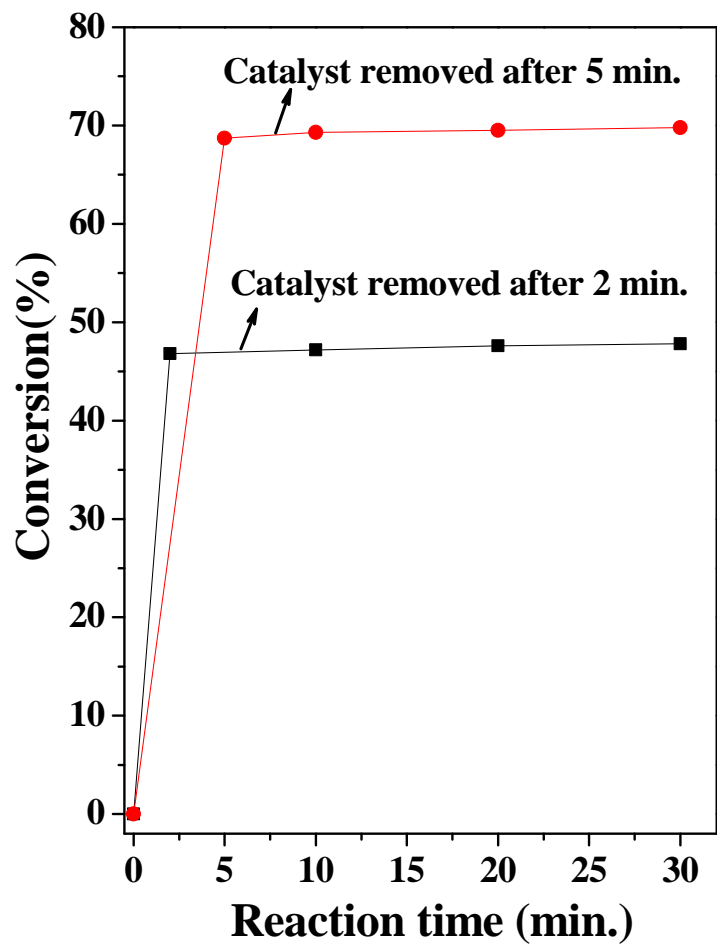
**Fig. S3.** SEM micrographs of various base grafted Zr-BDC-MOF.



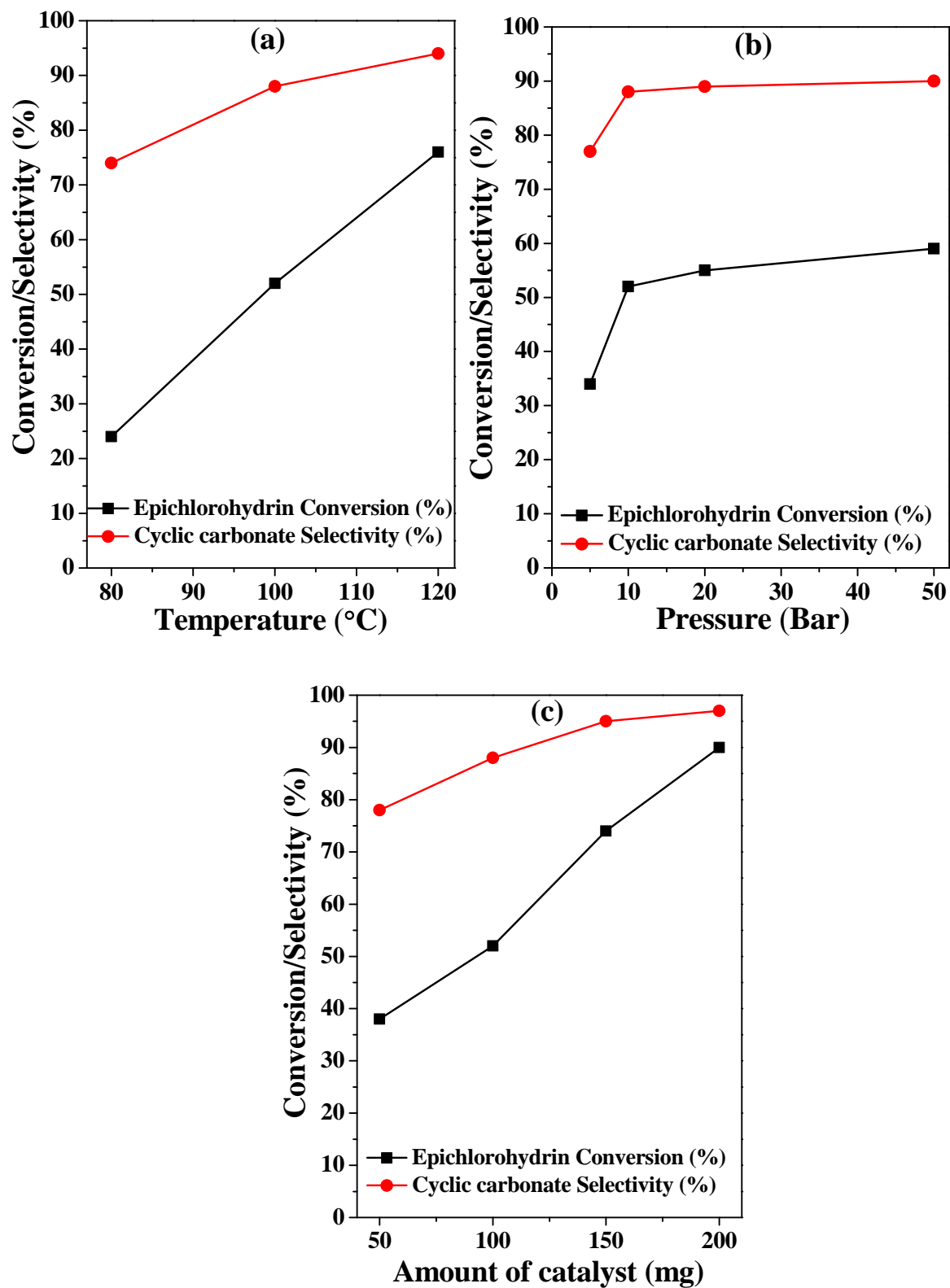
**Fig. S4.** CO<sub>2</sub> adsorption (filled) and desorption (open) isotherms of Zr-BDC-MOF and DMAP-Zr-BDC-MOF at 298 K.



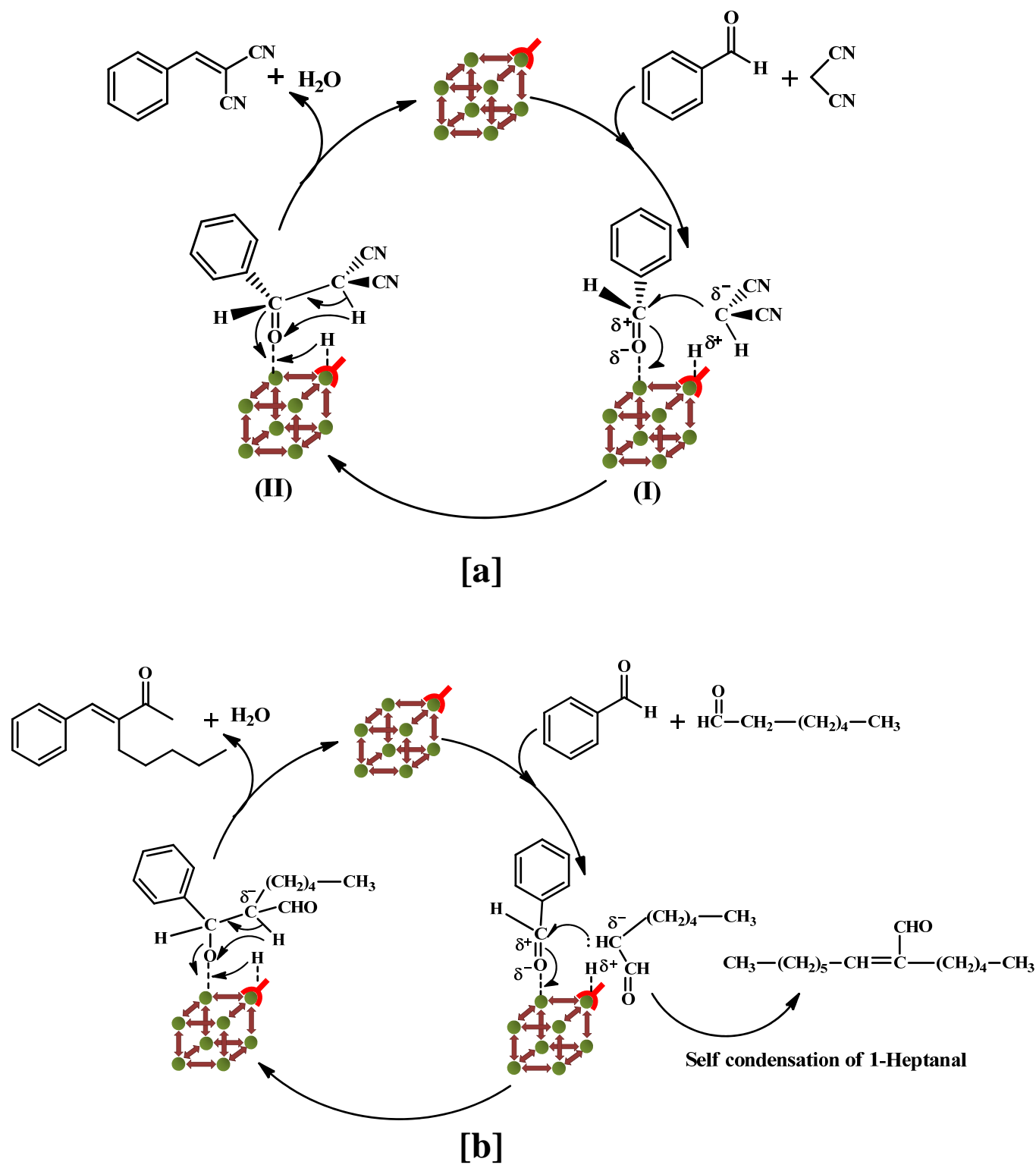
**Fig. S5.** XRD patterns of the fresh catalyst and the catalyst obtained after five recycles in the Knoevenagel condensation reaction.



**Fig. S6.** Leaching test for the catalyst removed after 2 minutes and 5 minutes after the start of reaction from the reaction mixture in the Knoevenagel condensation reaction.

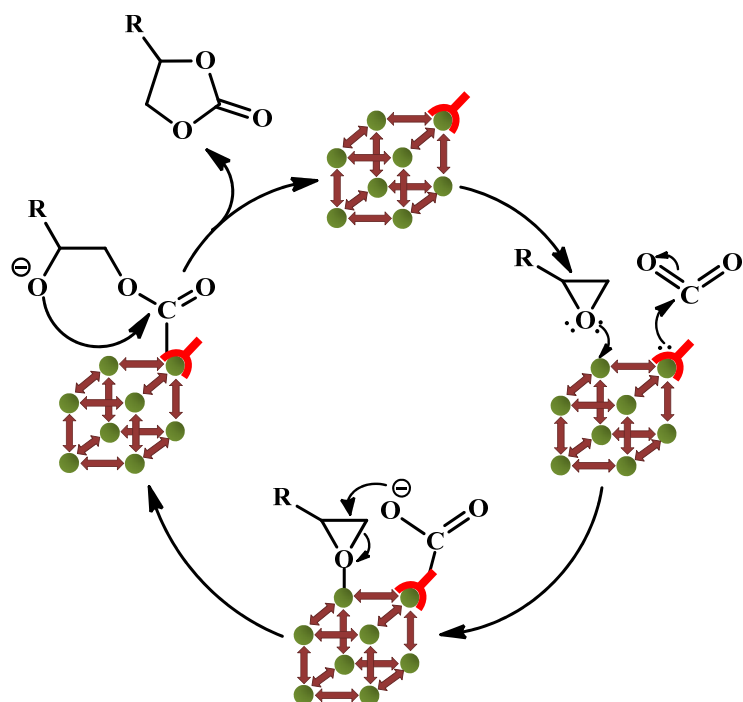


**Fig. S7.** Influence of reaction parameters in the cycloaddition reaction using Zr-BDC-MOF catalyst.



**Scheme S1.** Plausible mechanism for the condensation reaction of (a) benzaldehyde with malononitrile and (b) benzaldehyde with 1-heptanal.





**Scheme S2.** Plausible mechanism for the cycloaddition reaction of CO<sub>2</sub> to an epoxide.