Supporting information

Spray drying of zeolitic imidazolate frameworks: Investigation of crystal formation and properties

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1) Synthesis and characterization

1.1. Experimental

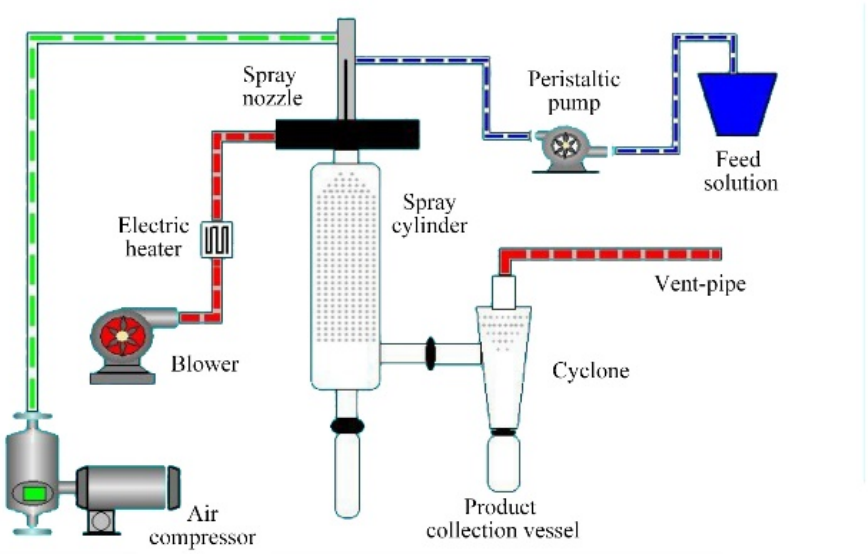
All sample were synthesized via spray drying technique. The metal salt and ligand were dissolved in up-water (25 mL) followed by addition of the adequate amount. The amount of metal salt and ligand are provided in Table S1. The mixture obtained from the two solutions (metal and ligand solution) was fed to the spray drying instrument with a feed rate of 400 mL/h, a flow rate of 160 m^3/h and an inlet temperature of 180 °C. The solid powders (as-synthesized) were collected in the collecting bottle of the instrument and immersed in solvent (200 mL) followed by drying to obtain the final product.

Table S1 Mole and mass/volume of reagent used to synthesize ZIF-8, ZIF-67 and dual metal Zn/Co-ZIF.

Sample	Metal salt		Ligand	Total solvent
	$Zn(OAc)_2{\cdot}2H_2O$	$Co(OAc)_2{\cdot}4H_2O$	2-IMI	Water
ZIF-8	6 mmol, 1.32 g	-	8 mmol, 0.66g	50 mL
ZIF-67	-	6 mmol, 1.49g	8 mmol, 0.66g	50 mL
Zn/Co-ZIF	3 mmol, 0.66 g	3 mmol, 0.745g	8 mmol, 0.66g	50 mL

1.2. General description of the spray drying process

A complete diagram of the spray drying apparatus is illustrated in Scheme S1. In a typical experiment, the drying gas enters the apparatus from the top and is heated up to the pre-set inlet temperature, then flows through the drying chamber and is filtered, before finally leaving the instrument to remove the fine particles. The inlet temperature is measured just after the heating, and the outlet temperature, just before the cyclone. The feed solution is introduced to the spray head by a peristaltic pump, and is then atomized in a nozzle with a standard diameter of 0.8 mm, in order to disperse the solution into the drying chamber as fine droplets.



Scheme S1. Schematic illustration of the laboratory spray dryer (AF-8000).

1.3 Characterization instruments

The powder X-ray diffraction spectra (XRD) were collected using an Empyrean instrument Bruker D8 applying a monochromatic Cu Kα radiation at ambient conditions. Data were collected in 2θ range from 3 to 30º, with a scanning rate of 5º/min. All gas adsorption measurements were analyzed using ASAP 2020 (Micromeritics) apparatus. The BET and Langmuir surface areas were calculated at P/P_o = 0.01-0.05 from the nitrogen isotherm. The data of pore volume and pore size were estimated using the H-K equation at the relative pressure of P/P_o = 0.5. The sample pretreatment (degas) at 200°C for 3h before analyzed samples. The morphology studies were conducted on a Scanning Electron Microscope (SEM) from JEOL (JSM-5610LV, 0.5–35 kV). Elemental analysis was performed using ICP-AES (Optima4300DV).

2) Characterization of materials

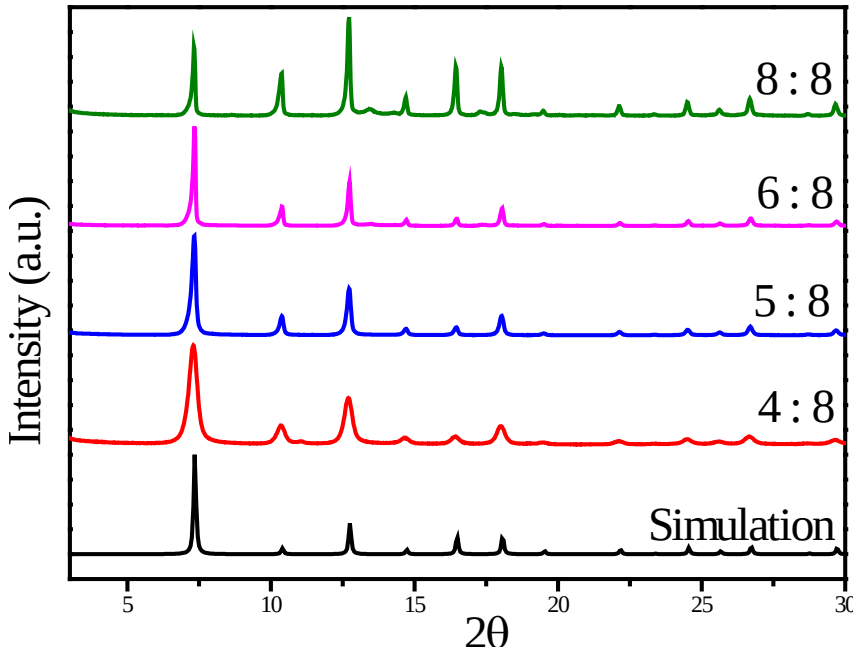


Figure S1. XRD analysis: effect of M:L mmol ratio (M= mole of zinc acetate, L= mole of 2-methylimidazole) in 50 mL water with 2-methylimidazole (8 mmol) kept constant.

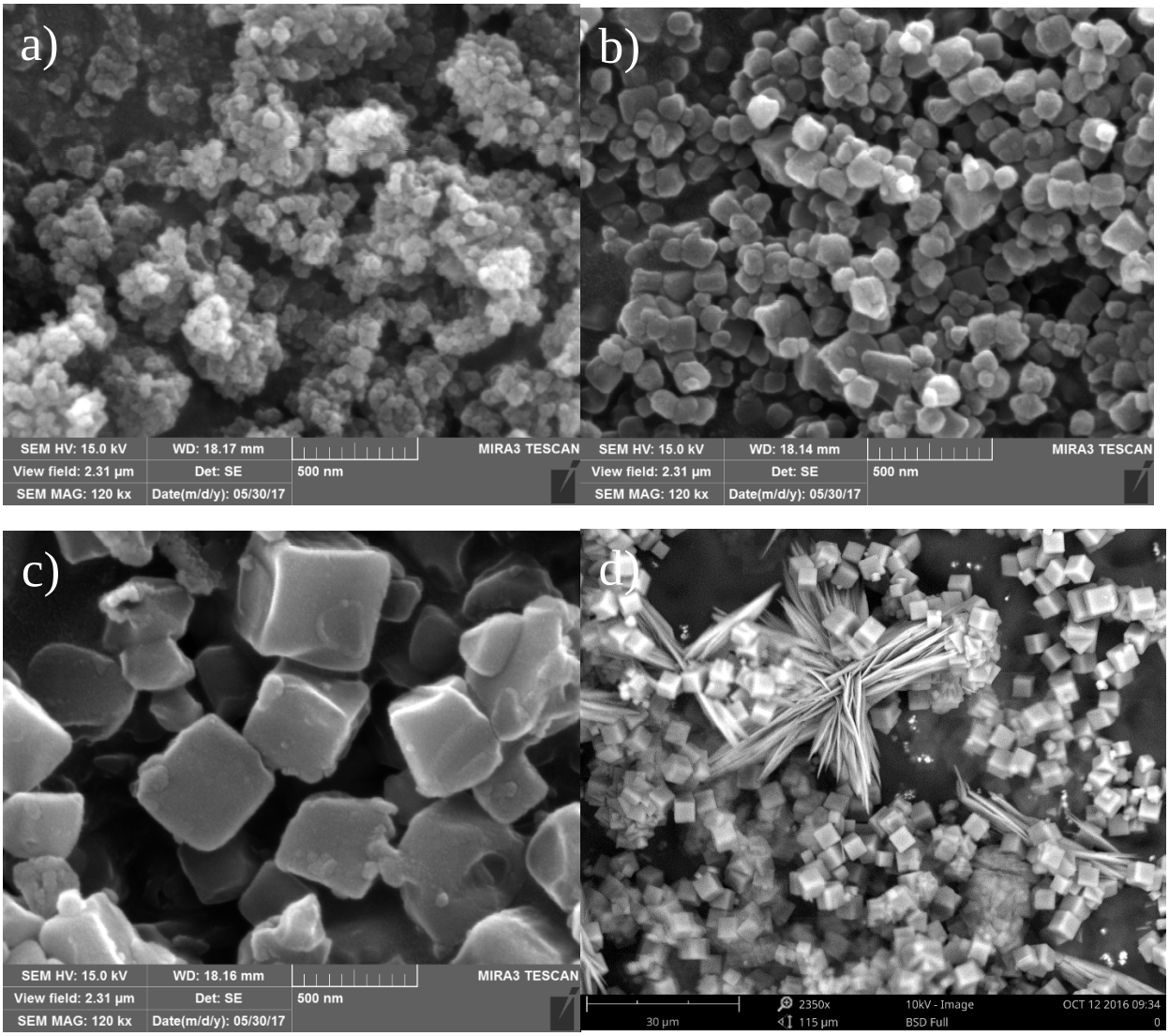


Figure S2. The morphologies of obtained products by variation of zinc acetate concentration in the feed solution (50 mL water, 0.66 g or 8 mmol 2-MIM); a) 4 mmol or 0.88 g, b) 5 mmol or 1.10 g, c) 6 mmol or 1.32 g, and d) 8 mmol or 1.76 g.

Table S2 Influence of the feed concentration on product yield and porosity (surface area).

Items	Zn (mmol)	2-MIM (mmol)	Immersed	Yield of product (g)	BET (m^2/g)
1	4	8	3h	0.11155	1569
2.1	4	8	1day	0.13255	1614
2.2	4	8	1day	0.13625	1630
2.3	4	8	1day	0.1392	1652
3	5	8	3h	0.17925	1517
4.1	5	8	1day	0.2225	1695
4.2	5	8	1day	0.2095	1703
4.3	5	8	1day	0.1825	1616
5	6	8	3h	0.2025	1600
6.1	6	8	1day	0.2025	1755
6.2	6	8	1day	0.2148	1728
6.3	6	8	1day	0.2313	1717
7	3.34	6	1day	0.1743	1728
8	5.66	10	1 day	0.22885	1732
9	8	8	3h	0.1816	1273
10.1	8	8	1Day	0.18435	1328
10.2	8	8	1Day	0.16915	1433
10.3	8	8	1Day	0.19445	1431

Note: Total volume of mixture (feed solution) is 50 mL and water as solvent. The synthesis repeatability was investigate *such as* 2.1, 2.2, 2.2 *etc.*

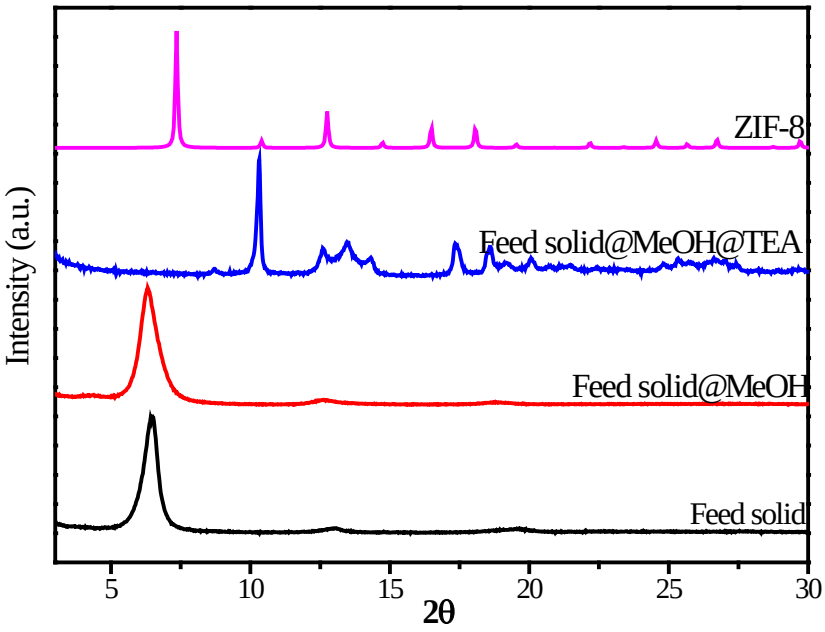


Figure S3. The XRD analysis of precipitated solid from the feed solution and after treatment at different conditions and XRD of ZIF-8 as reference.

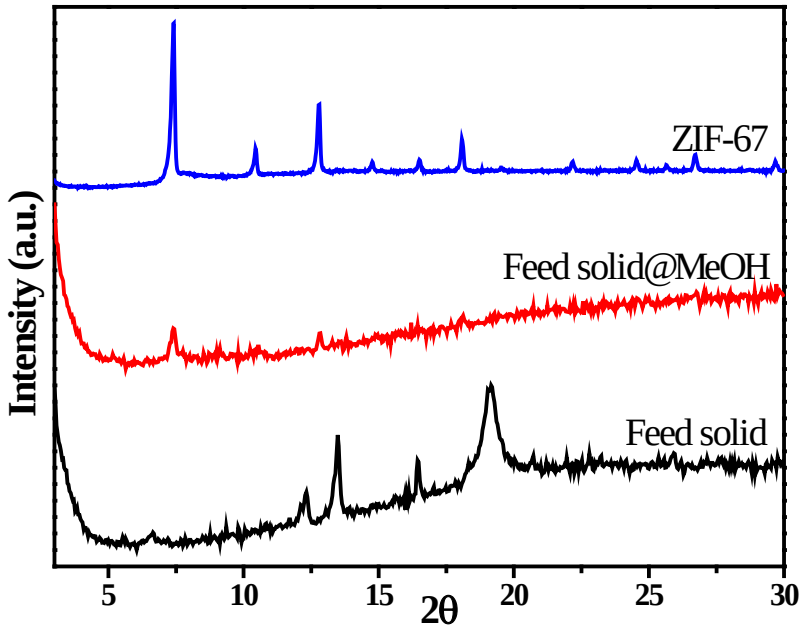


Figure S4. The XRD analysis of precipitated solid from the feed solution and after treatment at different conditions and XRD of ZIF-67 as reference.

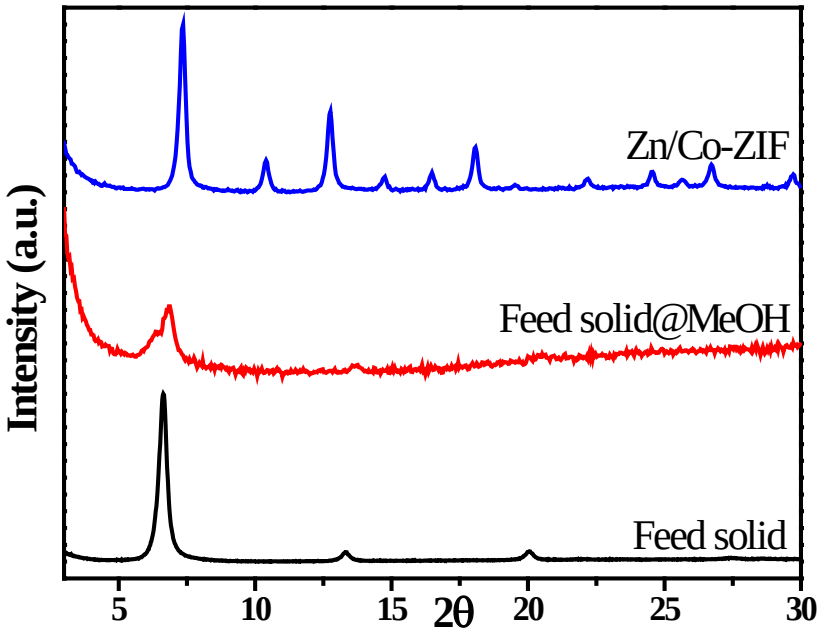
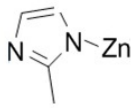
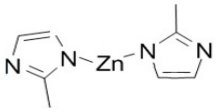
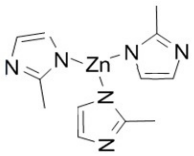
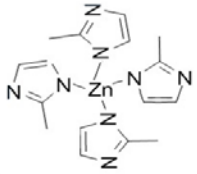
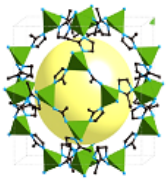
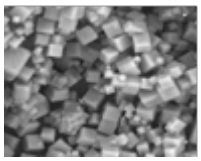
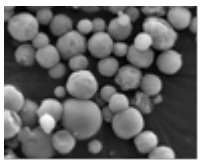


Figure S5. The XRD analysis of precipitated solid from the feed solution and after treatment at different conditions and XRD of Zn/Co ZIF as reference.

Table S3. Elemental analysis and theoretical calculated element analysis.

Compound	Structure	Element content (%)				Element ratio		
		Zn	N	C	H	N/Zn	C/Zn	H/Zn
Zn-1L[a]		44.63	19.12	32.79	3.44	0.429	0.735	0.077
Zn-2L[a]		28.73	24.62	42.22	4.43	0.857	1.470	0.154
Zn-3L[a]		21.18	27.22	46.69	4.90	1.285	2.205	0.231
Zn-4L[a]		16.77	28.75	49.30	5.17	1.714	2.940	0.308
ZIF-8[a]		28.73	24.61	42.22	4.42	0.857	1.469	0.154
ZIF-8[b]		31.50	23.05	40.83	3.49	0.732	1.296	0.111
		31.50	22.93	40.78	4.03	0.728	1.295	0.128
P 1[b]		27.43	14.47	34.78	4.679	0.528	1.268	0.170
		27.43	14.47	34.43	4.58	0.528	1.255	0.167

Note; [a] Calculation based on theoretical structure.

[b] Calculation based on the analysis result

Zn-1L theoretical elemental analysis: Zn, 44.63; N, 19.12; C, 32.79; H, 3.44

Zn-2L theoretical elemental analysis: Zn, 28.72; N, 24.62; C, 42.22; H, 4.43

Zn-3L theoretical elemental analysis: Zn, 21.18; N, 27.22; C, 46.69; H, 4.89

Zn-4L theoretical elemental analysis: Zn, 16.77; N, 28.75; C, 49.30; H, 5.17

ZIF-8 theoretical elemental analysis: Zn, 28.73; N, 24.61; C, 42.22; H, 4.42

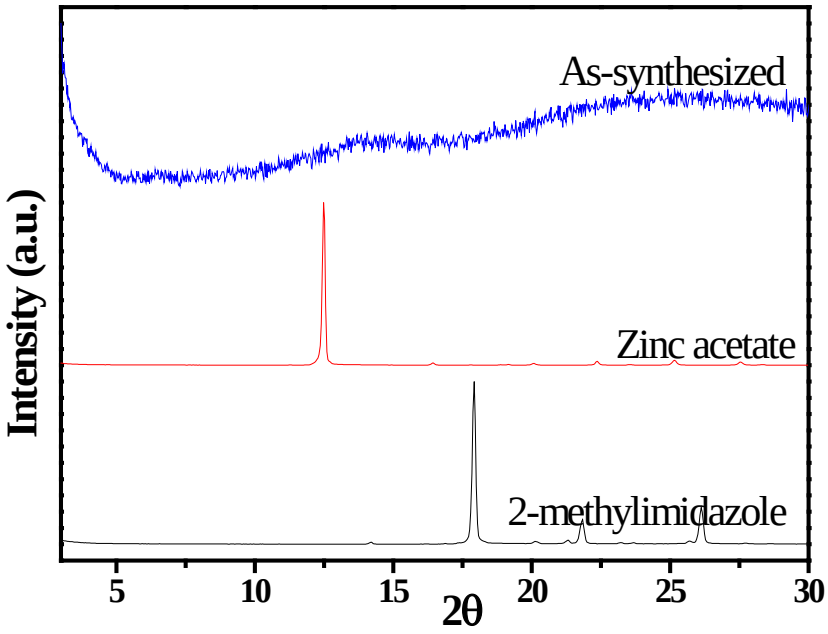


Figure S6 XRD analysis of metal salt, ligand precursor and product as-synthesized.

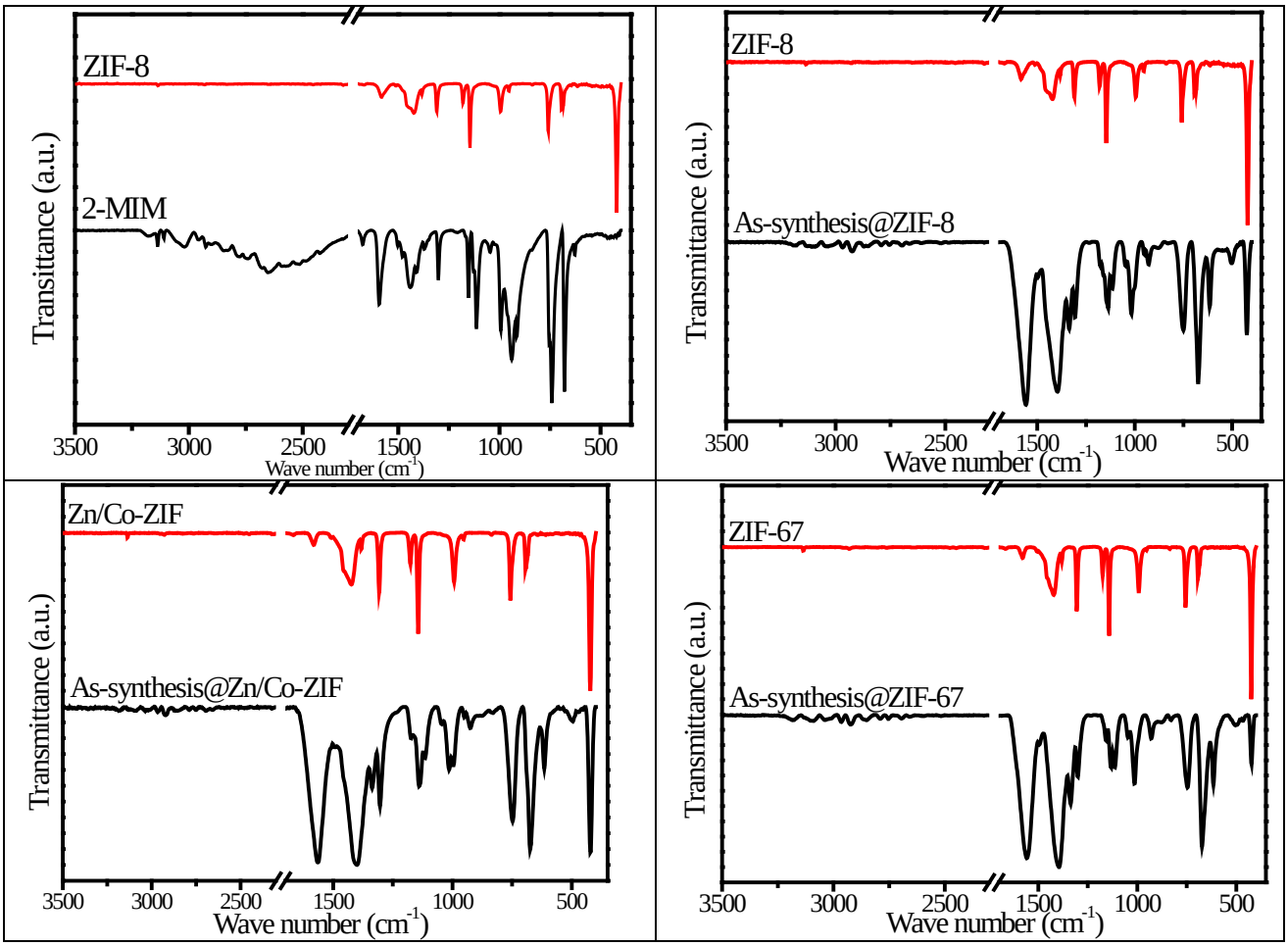


Figure S7 FTIR analysis ZIF-8, ZIF-67, Zn/Co-ZIF and spray dried product (as-synthesis).

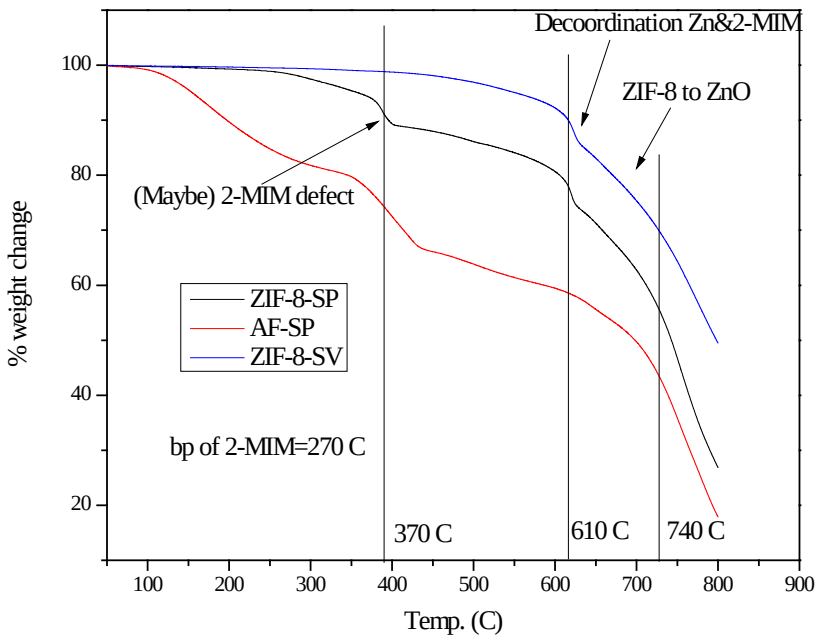


Figure S8 Thermal analysis of as-synthesized (AF-SP), solvothermal (ZIF-8-SV) and spray dried product (ZIF-8-SP).

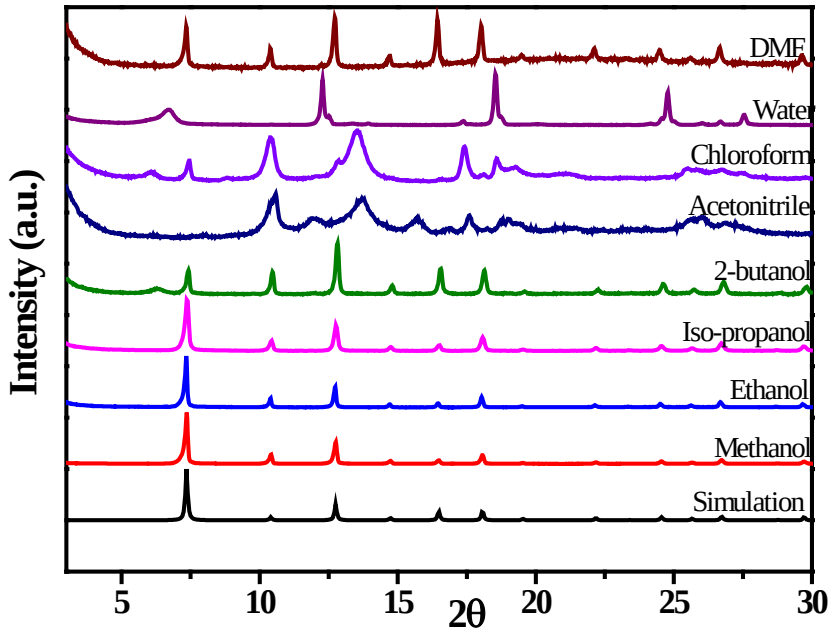
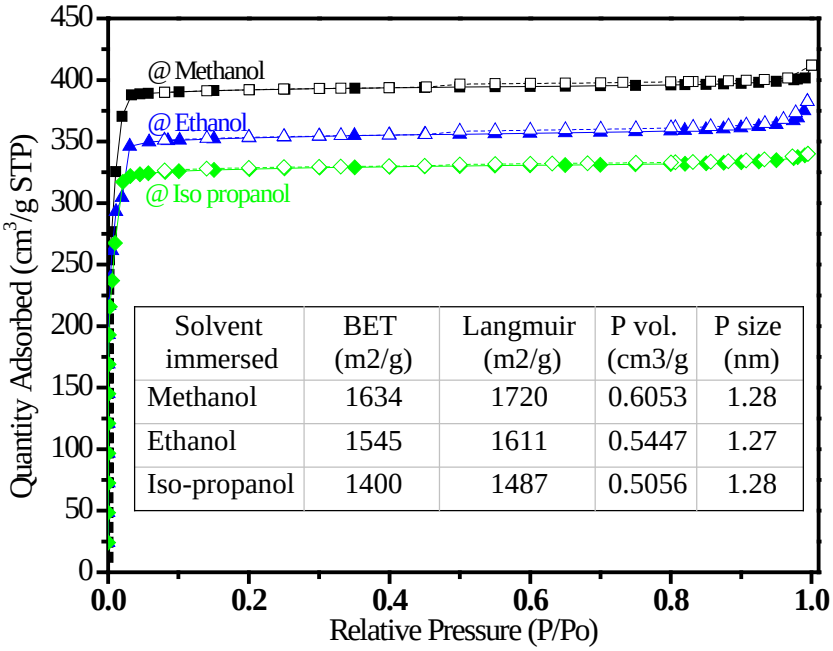


Figure S9. XRD analysis of spray dry samples after immersion in different solvents.



Solvent immersed	BET (m2/g)	Langmuir (m2/g)	P vol. (cm3/g	P size (nm)
Methanol	1634	1720	0.6053	1.28
Ethanol	1545	1611	0.5447	1.27
Iso-propanol	1400	1487	0.5056	1.28

Figure S10. Nitrogen isotherm and porosity properties of spray dried product after immersion in different solvents.

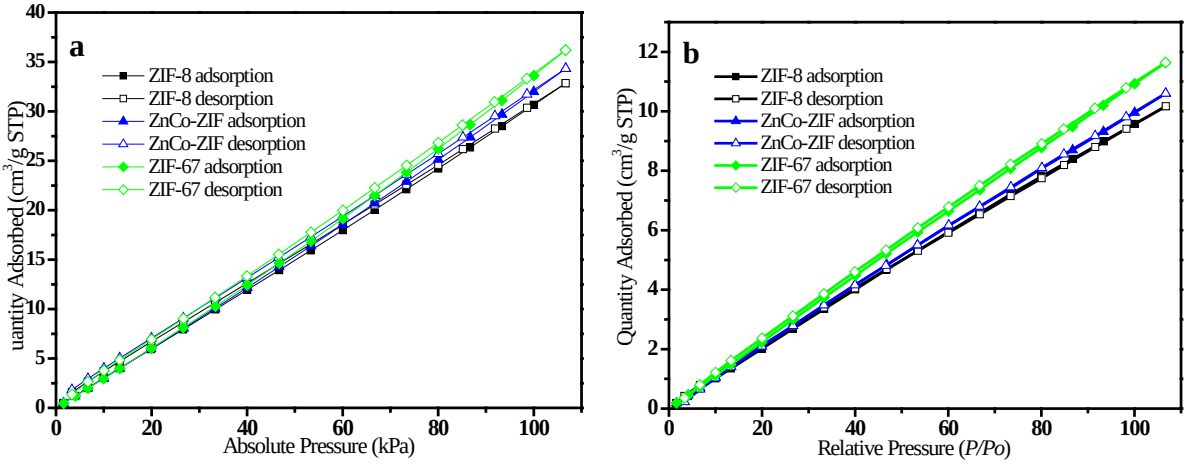


Figure S11. The gas adsorption capacity of CO_2 (a) and CH_4 (b) at 273K of ZIFs synthesized via spray drying technique

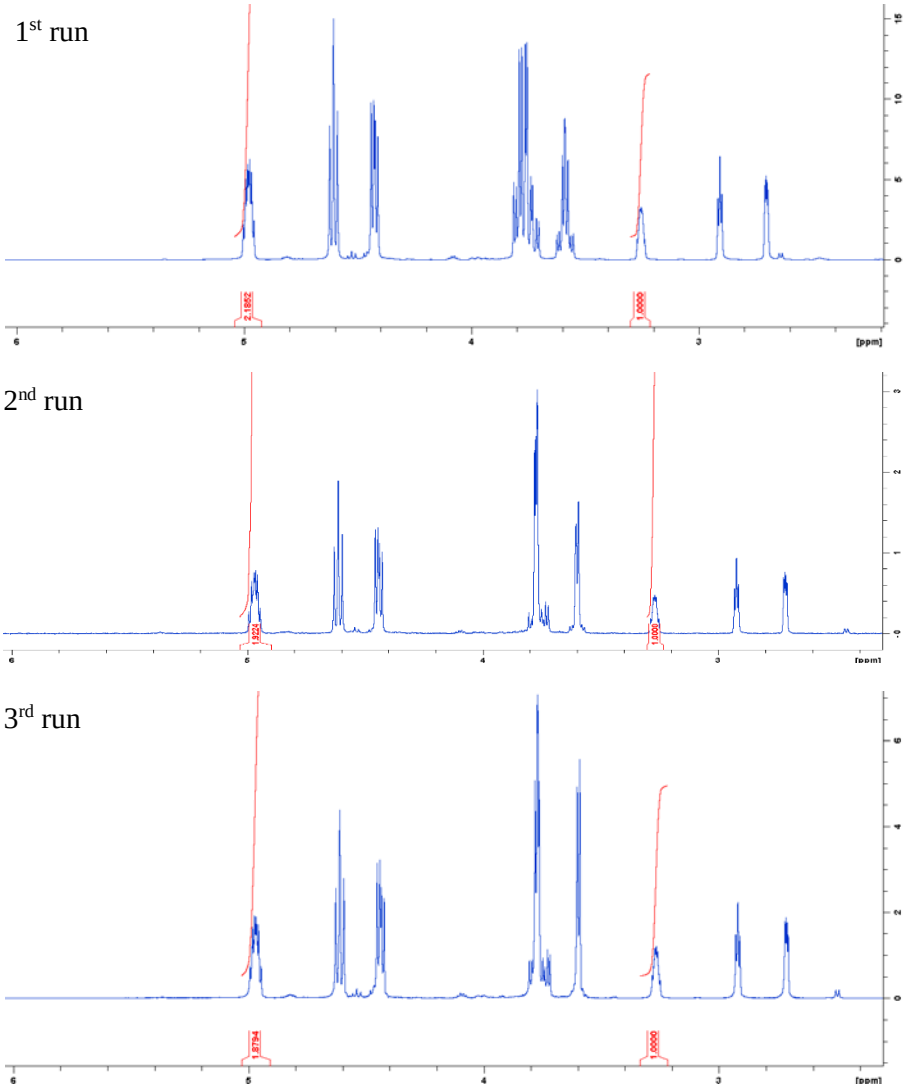


Figure S12. CO_2 conversion to chloropropene carbonate using NMR spectroscopy. The reaction progression was identified using ^{1}H-NMR in $CDCl_3$ 500 MHz,

Epichlorohydrin: δ 3.57-3.63 (m, 2H), **3.23 (m, ^{1}H)**, 2.68 (m, 1H), 2.88 (m, 1H);

Chloropropene carbonate: 1H NMR (500 MHz, CDCl3): δ **4.90-5.02 (m, ^{1}H)**, 4.61 (t, J = 8.6 Hz, 1H), 4.45 (dd, J = 8.9, 5.7 Hz, 1H), 3.68-3.78 (m, 1H). 13C NMR (100 MHz, $CDCl_3$): δ 154.5, 74.5, 67.0, 44.1.

The catalytic performance was calculated using the peak ratio (3.23 (m, ^{1}H) of epichlorohydrin to 4.90-5.02 (m, ^{1}H) of chloropropene carbonate).

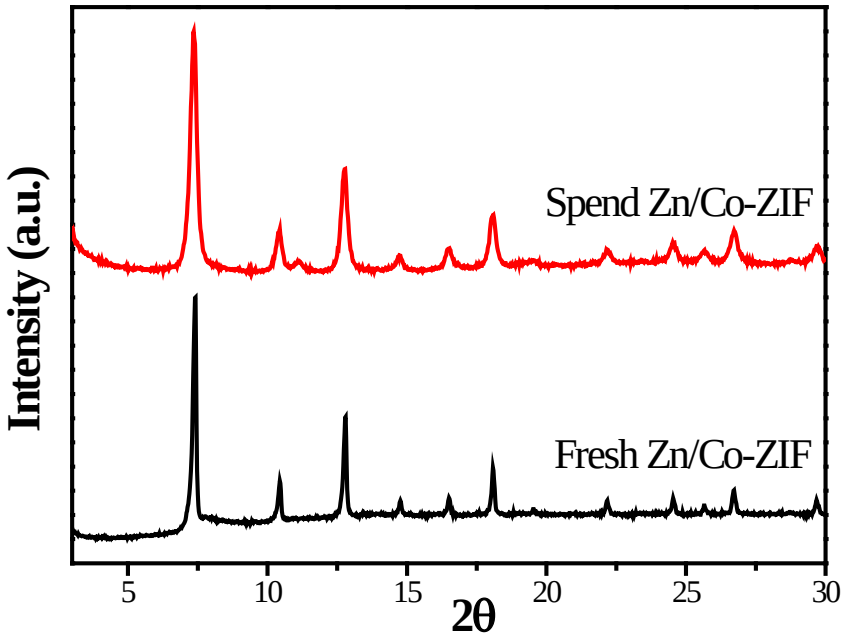


Figure S13. XRD analysis of fresh and spend (after 3rd cycle) Zn/Co ZIF for the CO_2 addition to epoxide.

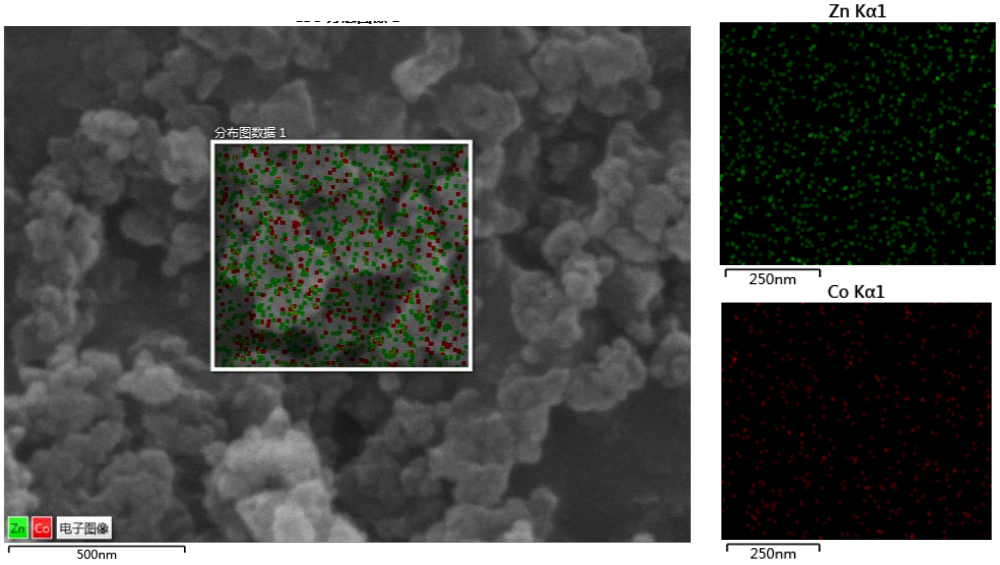


Figure S14 SEM-EDX metals mapping of Zn/Co-ZIF