Electronic Supplementary Information

Solvent-Free Synthesis of ZIF-8 from Zinc Acetate with the Assistance of Sodium Hydroxide

Peng Ji,[a,b,c] Renbing Tian,[a] Hua Zheng,[a] Jin-gang Jiang,[d] Junbiao Peng*,[b] and Jinghua Sun*,[a]

[a] School of Electrical Engineering & Intelligentization, Dongguan University of Technology, No. 1 Daxue Road, Dongguan 523808, PR China. E-mail: sunjh@dgut.edu.cn (J. Sun)

[b] State Key Laboratory of Luminescent Materials and Devices, South China University of Technology, No. 381 Wushan Road, Guangzhou 510640, PR China. E-mail: psjbpeng@scut.edu.cn (J. Peng)

[c] Qingdao Haiwan Science and Technology Industry Research Instituite Co., Ltd., No. 27 South Banghai Road, Qingdao 266031, PR China.

[d] Shanghai Key Laboratory of Green Chemistry and Chemical Processes, School of Chemistry and Molecular Engineering, East China Normal University, No. 3663 North Zhongshan Road, Shanghai 200062, PR China.

1. Experimental Section

2.1. Chemicals and material preparation.

Zinc Acetate ($Zn(OAc)_2$, > 99 %), sodium hydroxide (NaOH, > 99 %), 2-methylimidazole (MeIM, > 98%), methanol (> 98%) were purchased from Tokyo Chemicals Ind (TCI). $Zn(NO_3)_2 \cdot 6H_2O$ was purchased (> 99 %) from Sinopharm Chemical Regant Co., Ltd. All the chemicals were used as received without further purification.

In a typical synthesis of ZIF-8-DGUT, 0.183 g of $Zn(OAc)_2$ and 0.18 g of MeIM (MeIM to Zn molar ratio of 2.25) were mixed together in an agate mortar with diameter of 6 cm in a dry atmosphere, and fully ground for 5 min. Later, 0.064 g of NaOH power was added and fully ground for 10 min. The synthesis was carried out in a 50-mL Teflon-lined stainless-steel autoclave at 343 K for 24 h. The product was washed by suction filtration with water (1.0 to 1.5 mL), and dried overnight in a vacuum-oven at room temperature to obtain ZIF-8-DGUT. The total yield was 97.4% based on $Zn(OAc)_2$.

ZIF-8-ST was prepared according to the literature reported by Lee.[1] In the experiment, 0.67 g (2 mmol) of $Zn(NO_3)_2 \cdot 6H_2O$ and 0.167 g (2 mmol) of MeIM were mixed in 80 mL of methanol, and the mixture was left at room temperature for 24 h without stirring. The product was washed several times with MeOH, centrifuged, and dried overnight in a vacuum-oven at room temperature to obtain ZIF-8-ST.

2.2. Physicochemical characterizations.

The X-ray diffraction (XRD) patterns were collected on a Rigaku Ultima IV X-ray diffractometer using Cu-Kα radiation (λ = 1.5406 Å) at 35 kV and 25 mA to check the structure and crystallinity of materials. High resolution XRD data for the pawley fits was recorded on a Bruker D8 Advance X-ray diffractometer using CuKα radiation (35 kV, 25 mA) with an incident monochromatic X-ray wavelength of 1.5406 Å. To improve accuracy, the sample was continuously rotated in a 0.5 mm glass capillary, and Pawley fits were performed using FULLPROF. To determine the morphology,

scanning electron micrographs (SEM) were collected on a Hitachi S4800 microscope. The nitrogen adsorption isotherms were performed at 77 K on a BELSORP-MAX instrument after activating the samples at room temperature under vacuum for at least 5 h. The Brunauer-Emmett-Teller (BET) analysis was carried out using the data in the relative pressure region of P/P_0 = 0.05 - 0.25, which provided the specific surface area. The thermogravimetric and differential thermal analyses (TG-DTA) were performed on a METTLER TOLEDO TGA/SDTA 851 apparatus from 298 K to 1073 K at a heating rate of 10 K min^{-1} in air. Fourier transform infrared (FT-IR) spectra were collected on a Nicolet Nexus 670 FT-IR spectrometer operated at a spectral resolution of 2 cm^{-1} using KBr pellets of the solid samples. The solid state ^{13}C MAS NMR spectra was obtained on a VARIAN VNMRS-400WB NMR. The X-ray photoelectron spectroscopy (XPS) measurements were carried out by a ThermoFischer ESCALAB 250Xi spectrometer with Al Kα (hν = 1253.6 eV).

2.3. Catalytic Characterizations.

The catalytic evaluation of cycloaddition reaction was carried accord to the literature.[2] In a typical reaction, 18 mmol of epichlorohydrin and 100 mg of catalyst were placed in a 250 mL stainless-steel high pressure Parr reactor. The reactor was pressurized with CO_2 at 7 bar, and the reaction was carried out at 343 - 373 K for 4 h. After the reaction, the reactor was cooled to room temperature, the unreacted CO_2 was vented out, the catalyst was separated by centrifugation, and the products were analysed by GC/MS (Shimadzu 2014).

Reference

(1) Y.-R. Lee, M.-S. Jang, H.-Y. Cho, H.-J. Kwon, S. Kim and W.-S. Ahn, *Chem. Eng. J.,* 2015, **271**, 276-280.

(2) C. M. Miralda, E. E. Macias, M. Zhu, P. Ratnasamy and M. A. Carreon, *ACS Catal.,* 2012, **2**, 180-183.

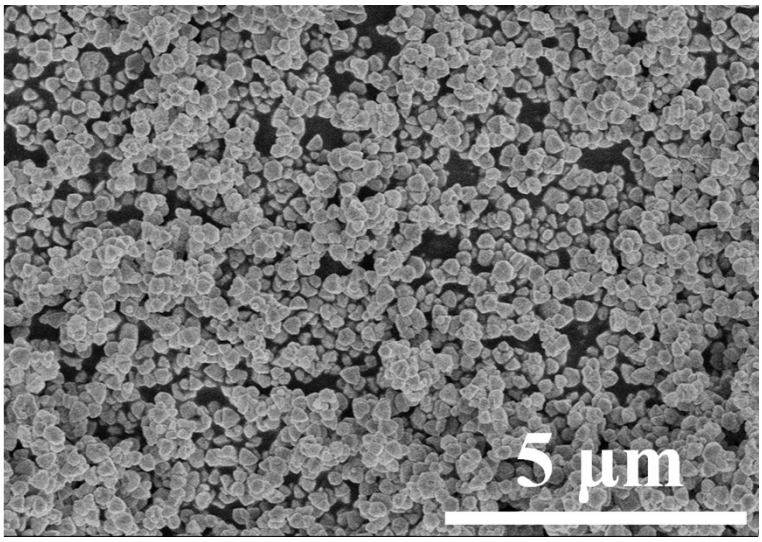

Fig. S1 SEM image of ZIF-8-ST.

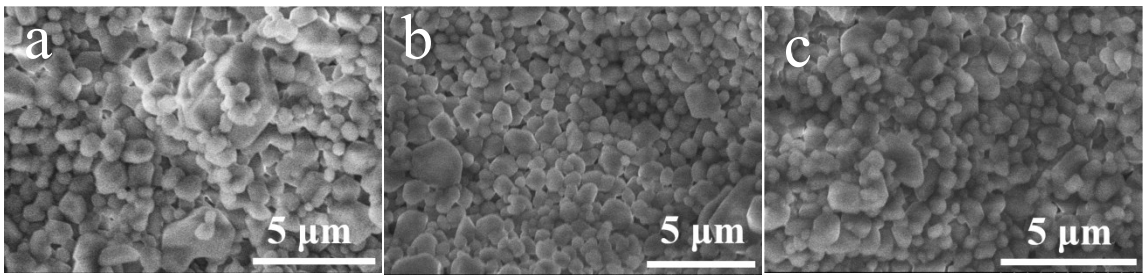

Fig. S2 SEM images of ZIF-8-DGUT as-synthesized at 323 (a), 373 (b) and 423 (c) K. The synthesis was conducted for 24 h, 4 h and 1 h, respectively.

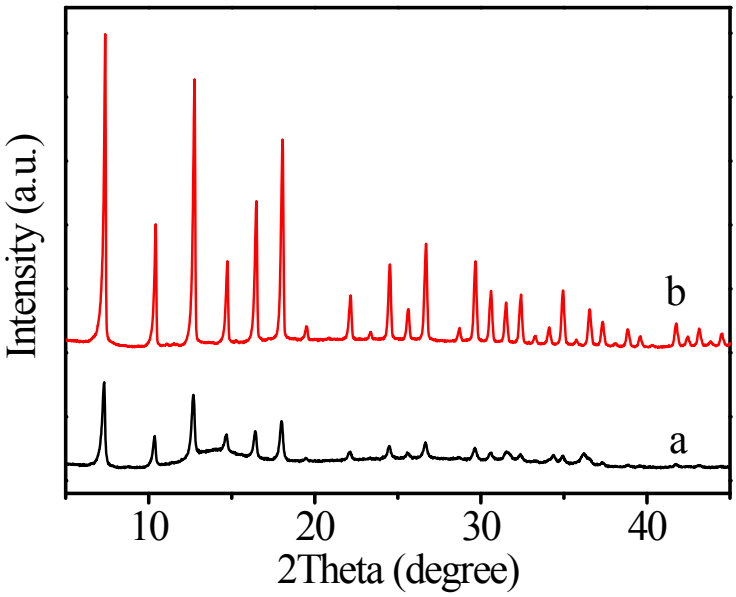

Fig. S3 XRD patterns of as-synthesized products obtained at 298 (a) and 323 (b) K for 48 h and 24 h, respectively.

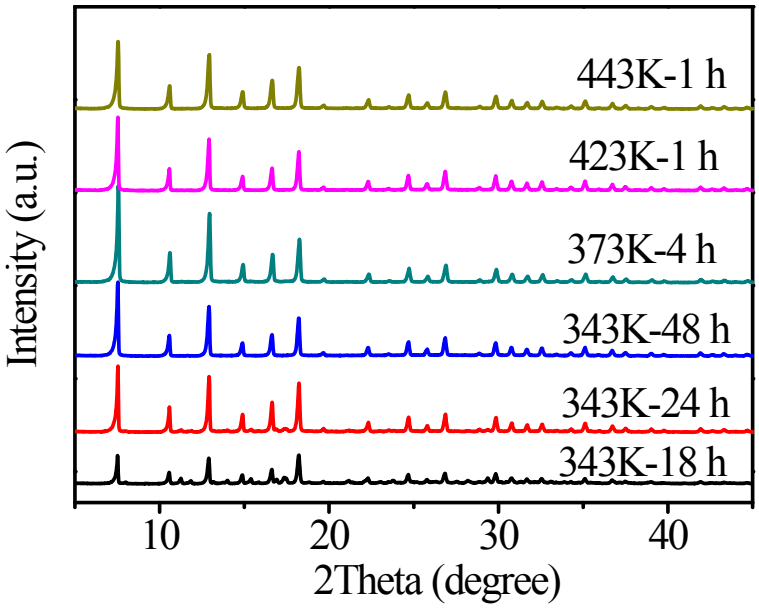

Fig. S4 XRD patterns of as-synthesized products obtained at different temperature and time.

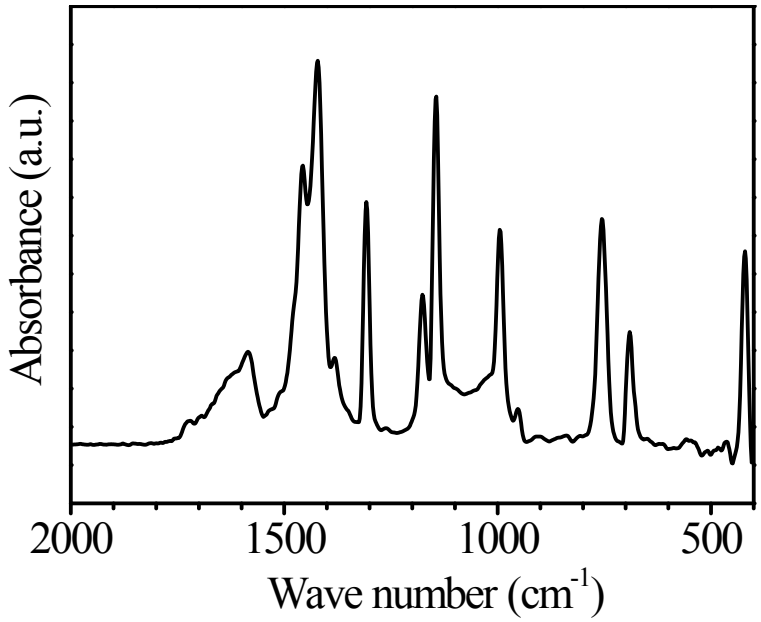

Fig. S5 FT-IR spectra of ZIF-8-DGUT.

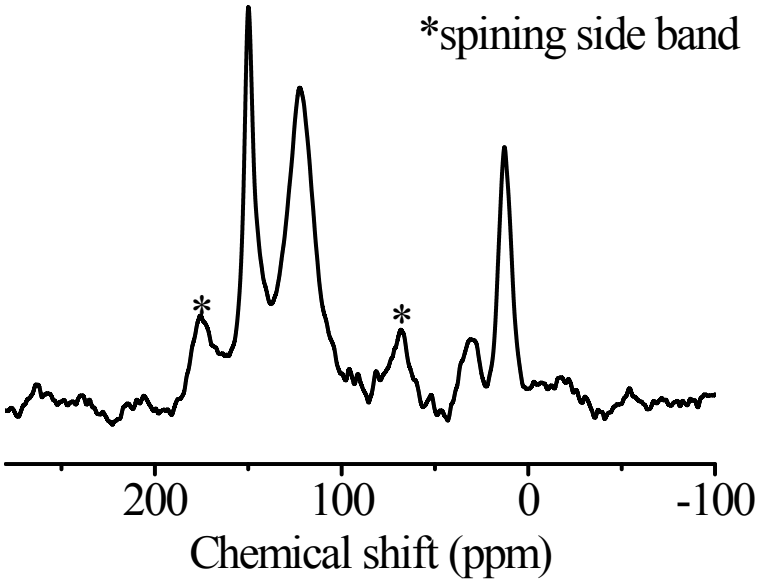

Fig. S6 Solid state ^{13}C MAS NMR spectra of ZIF-8-DGUT.

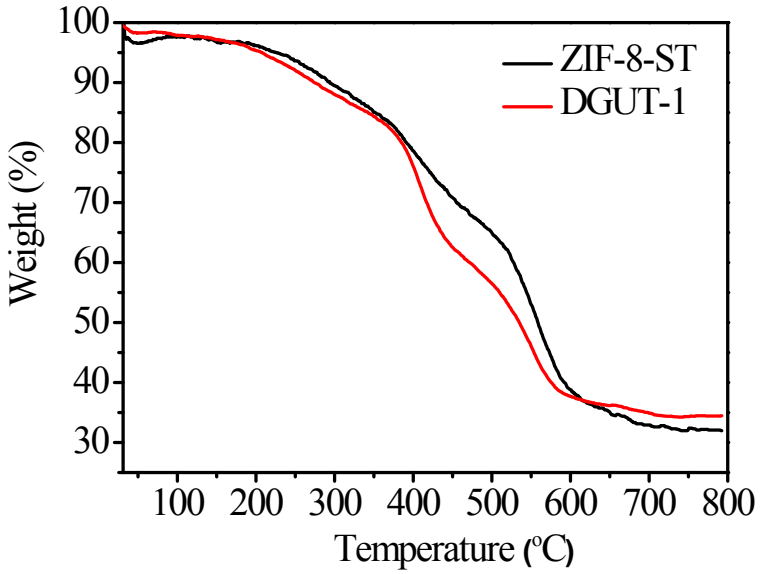

Fig. S7 Thermogravimetric analyse (TGA) curves of ZIF-8-ST and ZIF-8-DGUT.

Table S1. The parameters of powder diffraction data collection for ZIF-8-DGUT.

Diffractometer	D8A
Condition of data collection	Room temperature
Sample holder	Rotating 0.5 mm capillary
Wavelength (Å)	1.5406
2θ range (degree)	5 - 120
Step size 2θ (degree)	0.008135

Table S2. Crystallographic data from the Pawley fits of ZIF-8-DGUT.

Unit cell composition	$C_{69}N_{48}Zn_{12}$
Lattice parameters	
a [Å]	16.99714(4)
b [Å]	16.99714 (4)
c [Å]	16.99714 (4)
$\alpha = \beta = \gamma$ (°)	90
Space group	I-43M(217)
Number of points	6763
Contributing reflections	91
Peak profile	Pseudo-Voigt
R_p	0.1548
R_{wp}	0.0685
Rwp(w/o bck)	0.0739

Table S3. Catalytic Performance of ZIF-8-ST and ZIF-8-DGUT in the Cycloaddition of CO_2 to Epichlorohydrin

Catalyst/ Temperature (°C)	Epichlorohydrin conversion (%)	Selectivity (%)		
		chloropropene carbonate	diol	dimer
ZIF-8-ST (70)	64.6	59.6	29.7	10.7
ZIF-8-DGUT (70)	61.2	54.4	34.8	10.8
ZIF-8-ST (80)	77.9	44.7	33.1	22.2
ZIF-8-DGUT (80)	80.2	48.8	26.9	24.3
ZIF-8-ST (90)	85.6	45.2	24.3	30.5
ZIF-8-DGUT (90)	86.9	47.6	22.5	29.9
ZIF-8-ST (100)	92.1	41.3	27.6	31.1
ZIF-8-DGUT (100)	94.2	36.1	32.3	31.6

Reaction conditions: catalyst, 100 mg; epichlorohydrin, 18 mmol; pressure, 7 bar; time, 4 h.