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Supporting Information

2-Methylimidazole-Assisted Synthesis of Two-Dimensional MOF-5 Catalyst with Enhanced Catalytic Activity for the Knoevenagel Condensation Reaction

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1. General Information

1.1. Materials and Reagents

All chemicals were purchased from Adamas-beta, Sigma-Aldrich and used as received.

1.2. Materials Characterization

XRD:

The product was characterized by XRD using a Rigaku D/max-ga X-ray diffractometer at a scan rate of 6 º min $^{-1}$ in 2 θ ranging from 5 º to 40 º with Cu Kα radiation (λ = 1.54178 Å).

SEM:

Scanning electron microscopy (SEM) was conducted on a Hitachi S-8010 with an accelerating voltage of 100 kV.

TEM:

Transmission electron microscopy (TEM) images were obtained with a JEM-2100.

IR:

FT-IR spectra were obtained with a Bruker EQUINOX-55 spectrophotometer within the wavenumber interval of 400-4000 cm^{-1}.

TGA:

Thermogravimetric analysis (TGA) was performed on a Shimadzu DTG-50 thermal analyzer from room temperature to 800 ºC at a heating rate of 10 ºC min^{-1} under an air atmosphere.

XPS:

X-ray Photoelectron Spectroscopy (XPS) was obtained with the AXIS UltraDLD

AFM:

Atomic force microscopy (AFM) was obtained with the Bruker Multimode 8.

TPD:

NH_3/CO_2-TPD was performed using Micromeritics AutoChem II 2920. In a typical TPD experiments, 100 mg of sample was pretreated in He (30 mL/min) at required temperature for 1 h. After cooling down to desired temp, ammonia /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/CO_2. The sample was carried out by increasing the temperature linearly from 50 to 400 ^{o}C with a heating rate of 10 ^{o}C /min and a helium flow rate of 20 mL/min.

GC:

Gas chromatographic (GC) analyses were performed using a Shi-madzu GC 2010-Plus equipped with a flame ionization detector (FID) and an SPB-5 column (length = 30 m, inner diameter = 0.25 mm, and film thickness = 0.25 μm). The temperature program for GC analysis held samples at 100 ^{o}C for 1 min, heated them from 100 to 280 ^{o}C at 20 ^{o}C /min, and held them at 280 ^{o}C for 5 min. Inlet and detector temperatures were set constant at 280 ^{o}C.

GC–MS:

GC–MS analyses were performed using a Shimadzu GCMS-QP2010 Ultra with a ZB-5MS column (length = 30 m, inner diameter = 0.25 mm, and film thickness = 0.25 μm). The temperature program for GC–MS analysis held samples at 100 ^{o}C for 1 min, heated samples from 100 to 250 ^{o}C at 20 ^{o}C /min and held them at 250 ^{o}C for 5 min. Inlet temperature was set constant at 250 ^{o}C. MS spectra were compared with the spectra gathered in the NIST library.

NMR spectrum:

^{1}H NMR spectra were collected on 400 MHz NMR spectrometers (Varian Inova-400) using $CDCl_3$. Chemical shifts are reported in parts per million (ppm). Chemical shifts for protons are reported in parts per million downfield and are referenced to residual protium in the NMR solvent ($CHCl_3$ = δ 7.26). Data are represented as follows: chemical shift, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants in Hertz (Hz), integration.

2. Experimental

2.1. The synthesis procedure for cube-shaped MOF-5.

Cube-shaped MOF-5 was synthesized according to the method reported by Cheng and co-workers;[1] 1,4-benzenedicarboxylic acid (H_2BDC) (0.017 g, 0.1 mmol) and $Zn(NO_3)_2{\cdot}6H_2O$ (0.149 g, 0.5 mmol) were dissolved in 15 mL of *N,N*-dimethylformamide (DMF) at room temperature. The mixture solution was then transferred to a 25 mL Teflon-sealed and placed in an oven at 120 °C for 21 h. After which the solid was isolated by centrifugation and washed with DMF three times, and then two more times with methanol. Methanol was finally removed under high vacuum ($<10^{-7}$ bar) at 60 °C, yielding the cube-shaped MOF-5.

2.2. The synthesis procedure for 2D MOF-5 nanosheets.

4 mM of 2-MI was dissolved in 10 mL of DMF, which was added dropwise into 60 mL of DMF solution dissolved H_2BDC (0.017 g, 0.1 mmol) and $Zn(NO_3)_2{\cdot}6H_2O$ (0.149 g, 0.5 mmol). The mixture solution was stirred at room temperature for 10 min, and then transferred to a 100 mL Teflon-sealed and heated at 110 °C for 24 h. The resulting precipitates were collected by centrifugation, washed with DMF and MeOH for three more times respectively. Methanol was finally removed under high vacuum ($<10^{-7}$ bar) at 60 °C, yielding the 2D MOF-5 nanosheets.

2.3. SEM image of 2D-MOF-5

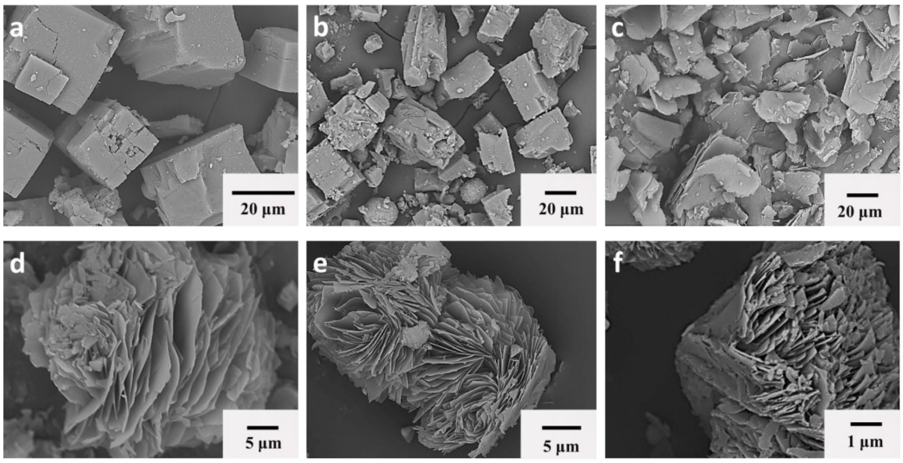


Fig. S1 SEM image of the MOF-5 obtained in DMF:EtOH:H_2O (1:1:1, v/v/v) at 120 °C for 24 h, and the MOF-5 samples prepared with different molar ratios of H_2BDC and 2-MI. a: in the absence of 2-MI; n(H_2BDC):n(2-MI) = b: 1:1; c: 1:2; d: 1:3; e: 1:4; f: 1:5.

2.4 N_2 adsorption/desorption isotherms of the 2D MOF-5 nanosheets

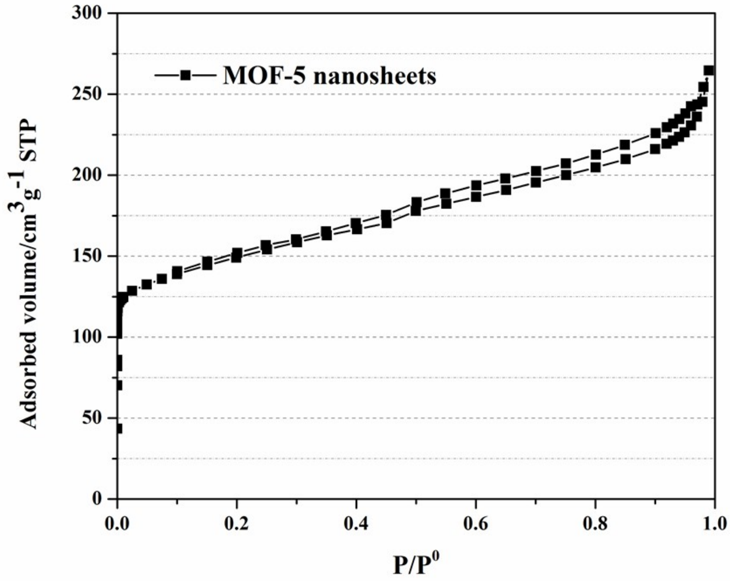


Fig. S2 N_2 adsorption/desorption isotherms of the 2D MOF-5 nanosheets.

Table S1. Values of the 2D MOF-5 nanosheets estimated from the N_2 adsorption/desorption isotherms presented in Figure 5.

Sample	S_{BET}[a] ($m^{2}\cdot g^{-1}$)	S_{mcrop}[b] ($m^{2}\cdot g^{-1}$)	S_{ext}[c] ($m^{2}\cdot g^{-1}$)	V_{pore}[d] ($cm^{3}\cdot g^{-1}$)	Pore size[e] (nm)
2D-MOF-5	550	367	183	0.41	3.83

2.5 CO_2-/NH_3-TPD spectra of the cubic MOF-5 and MOF-5 nanosheets

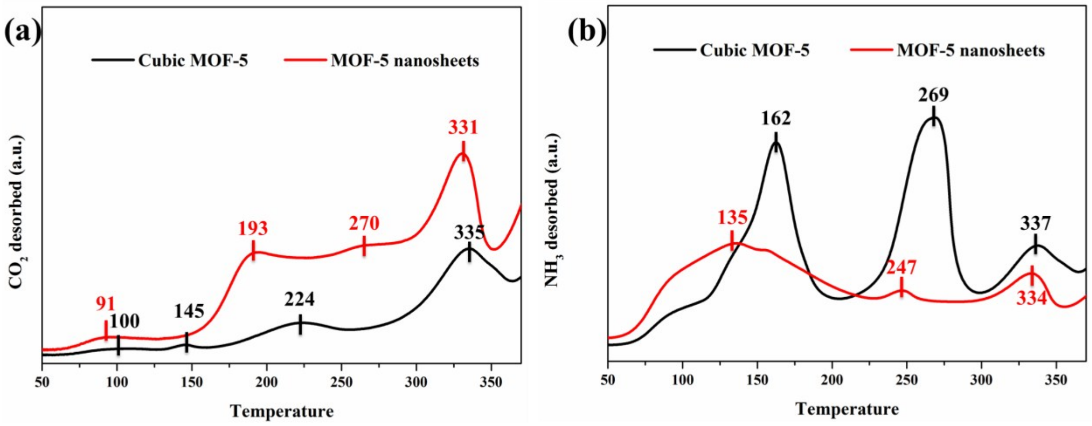
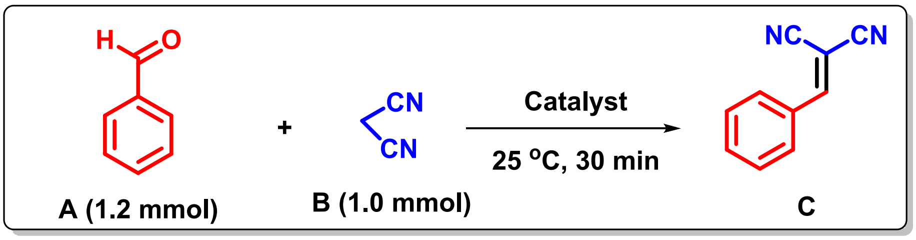


Fig. S3 (a) CO_2-TPD spectra of the cubic MOF-5 and MOF-5 nanosheets; (b) NH_3-TPD spectra of the cubic MOF-5 and MOF-5 nanosheets.

2.6. Control Experiments



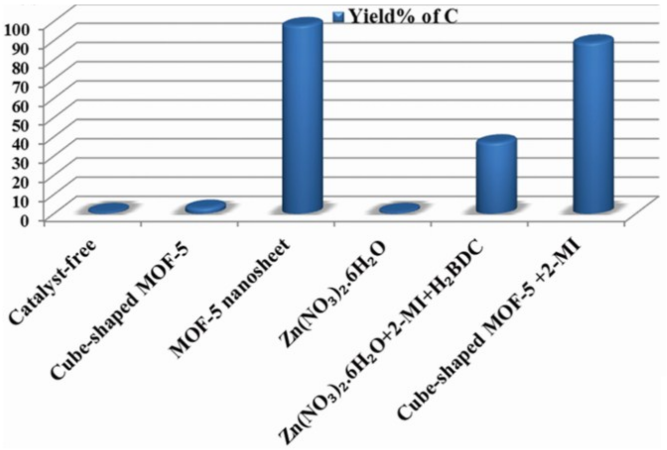
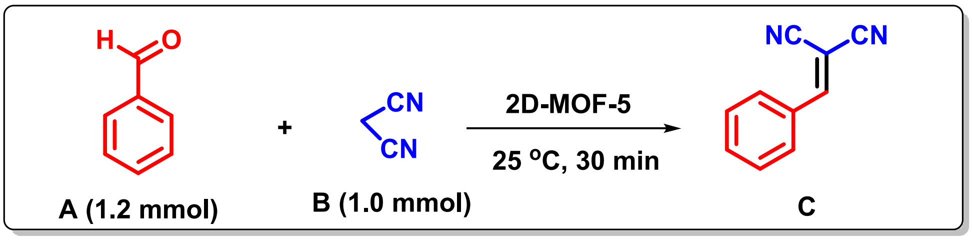


Fig. S4 The catalytic activity of different homogeneous and heterogeneous catalysts for Knoevenagel condensation.

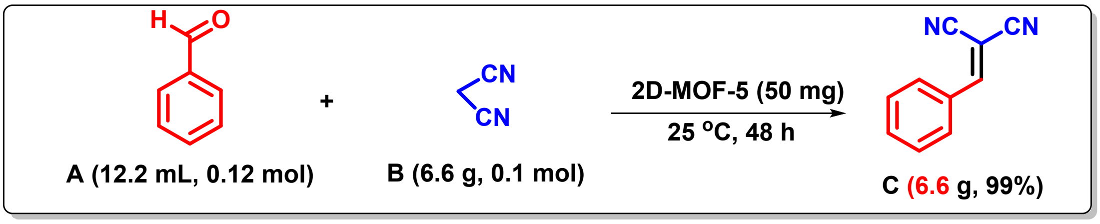
2.7. Catalytic studies

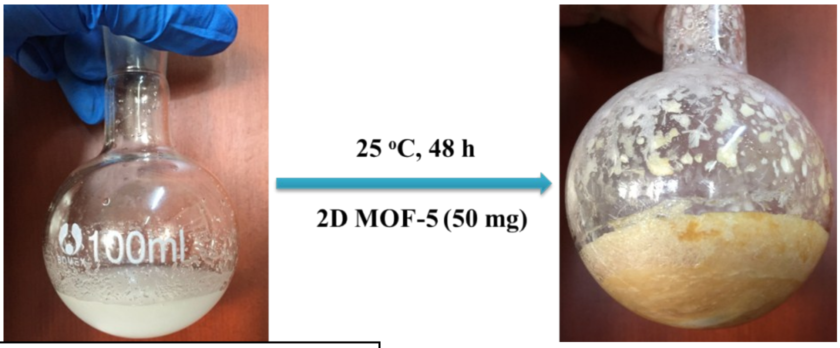


The catalytic Knoevenagel condensation reaction was carried out in a glass tube equipped with a magnetic stirrer. In a typical reaction, the mixture of 2D-MOF-5 (7 mg), benzaldehyde (0.12 mL, 1.2 mmol) and malononitrile (0.066 g, 1.0 mmol) were added into the tube, and stirred for 30 min at room temperature. After the reaction was complete, the reaction mixture was extracted with ethyl acetate and then the solid catalyst was filtered. The filtrate mixture was evaporated under vacuum and then recrystallized from ethanol to afford the pure product 2-benzylidenemalononitrile, 98% isolated yield, white solid. The product identity was further confirmed by ^{1}H NMR, ^{13}C NMR and GC-MS. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94-7.88 (m, 2H), 7.78 (s, 1H), 7.67-7.61 (m, 1H), 7.58-7.51 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.95, 134.65, 130.91, 130.74, 129.64, 113.70, 112.54, 82.87; MS: 154.

2.8. Gram Scale Experiments

Gram Scale for Synthesis of 2-benzylidenemalononitrile



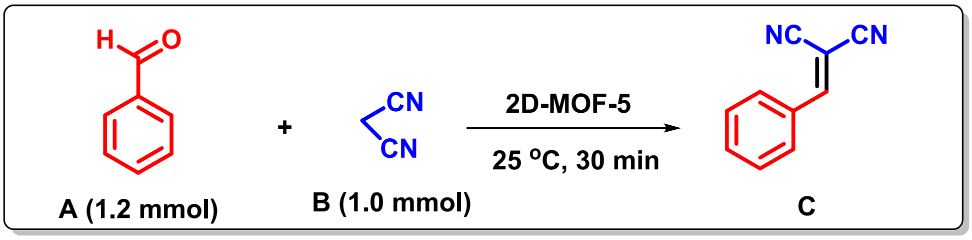


Reaction mixture of 2D-MOF-5 and reactant (before reaction)

Upon completion of the reaction

A mixture of 2D-MOF-5 (50 mg), benzaldehyde (12 mL, 0.12 mmol) and malononitrile (6.6 g, 0.1 mol) were added into a 100 mL flask, and stirred for 48 h at room temperature. After the reaction reached completion, the reaction mixture was extracted with ethyl acetate and then the solid catalyst was filtered. The filtrate mixture was evaporated under vacuum and then recrystallized from ethanol to afford the pure product 2-benzylidenemalononitrile, 99% isolated yield, white solid.

2.9. Recycling Experiment



Run times

Fig. S5 Catalyst recycling studies.

A mixture of 2D-MOF-5 (7 mg), benzaldehyde (0.12 mL, 1.2 mmol) and malononitrile (0.066 g, 1.0 mmol) were added into the tube, and stirred for 30 min at room temperature. After the reaction reached completion, the mixture was extracted three times by ethyl acetate (5 mL×3), and then the remaining solid catalyst 2D-MOF-5 was separated by simple centrifugation after reaction, washed with ethanol for three times, and then reused in the next run under the same conditions. The combined organic layer was evaporated under vacuum and then recrystallized from ethanol to afford the pure product 2-benzylidenemalononitrile white solid.

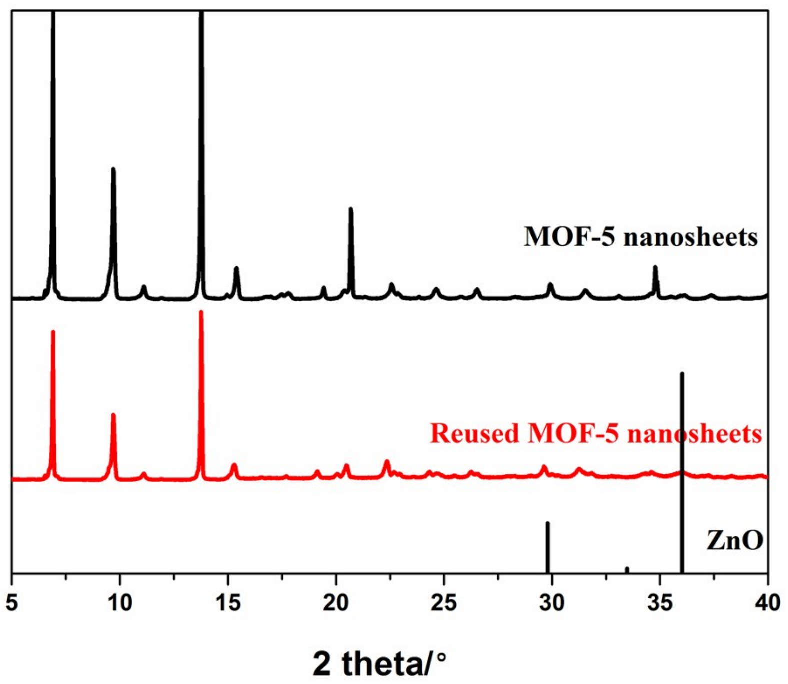
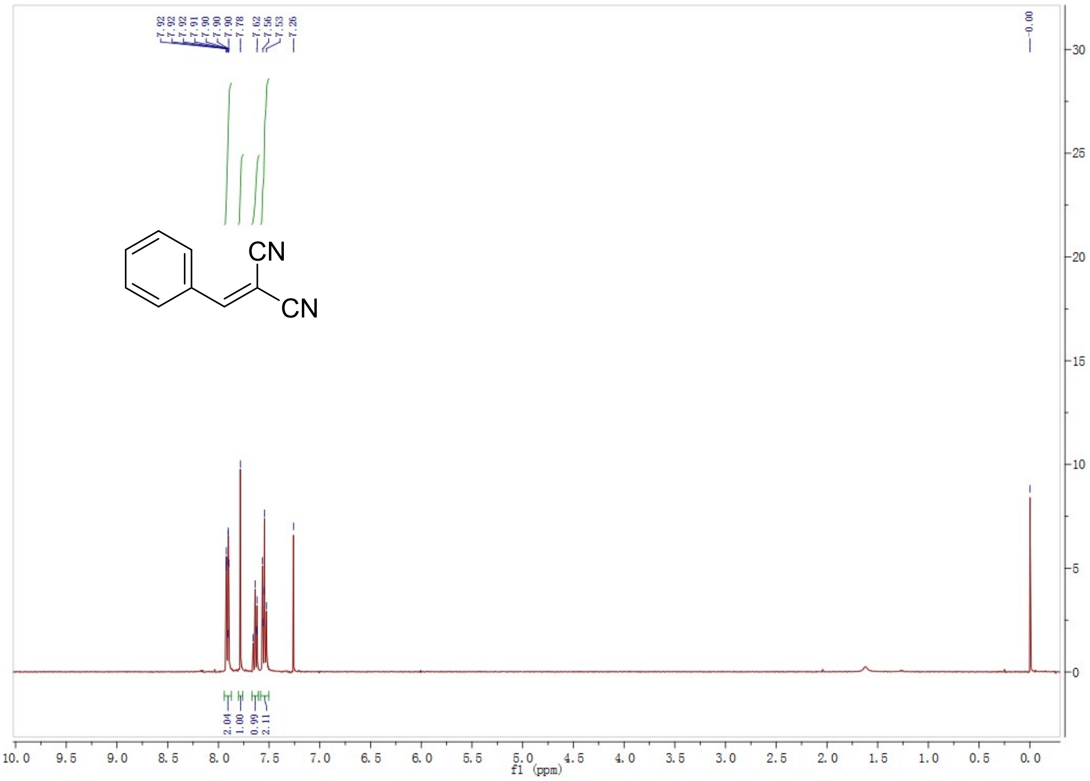


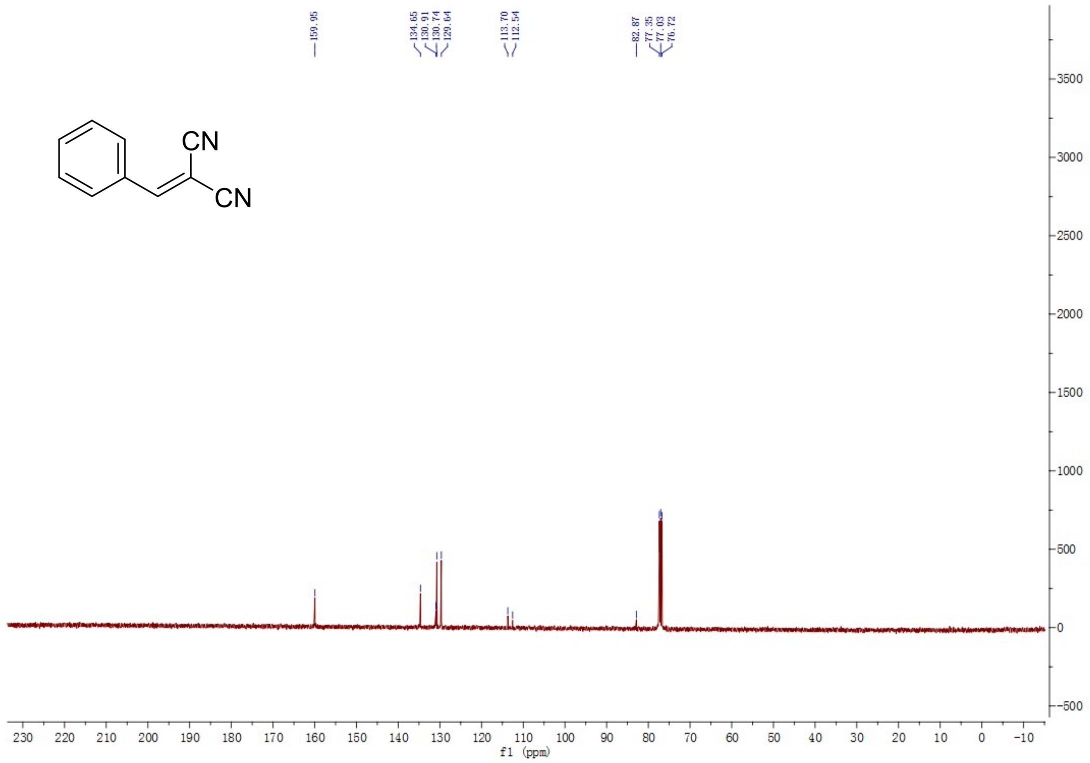
Fig. S7 PXRD of MOF-5 nanosheets, reused MOF-5 nanosheets and ZnO.

3. Copies of ^{1}H NMR and ^{13}C NMR

^{1}H NMR spectra of 2-benzylidenemalononitrile



^{13}C NMR spectra of 2-benzylidenemalononitrile



References

[1] H. Li, W. Shi, K. Zhao, H. Li, Y. Bing, P. Cheng, *Inorg. Chem.,* 2012, **51**, 9200-9207.