Supporting Information for:

Gas promotes the crystallization of nano-sized metal-organic framework in ionic liquid

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1. Experimental Section

Materials: CO₂ (> 99.95%), H₂ (> 99%), N₂(> 99%), CH₄(> 99%) were provided by Beijing Analysis Instrument Factory. [BMIM]BF₄ was purchased from Centre of Green Chemistry and Catalysis, LICP, CAS (purity>99%). Acetonitrile , ethanol, DMF and DMSO were provided by Beijing Chemical Reagent Company. Copper (II) acetate monohydrate (Cu(OAc)₂·H₂O) (A. R. Grade) and DEF were purchased from Alfa Aesar. H₃BTC (purity 99%) was purchased from J&K Scientific Co., Ltd.

MOF synthesis. In a gas promoted experiment, H₃BTC (0.3mmol) and Cu(OAc)₂·H₂O (0.54 mmol) were added into the [BMIM]BF₄ (5 g), which was loaded in a stainless steel autoclave (50 ml). Gas was charged into the cell under stirring until the desired pressure was reached. After the mixture was stirred at 25 °C for a certain time, the stirrer was stopped and gas was released. For the synthesis reaction with acetonitrile, 1mL acetonitrile was added into the [BMIM]BF₄ instead of gas. For the solvothermal synthesis, 0.05 g H₃BTC was dissolved in 10 mL of DMF/EtOH/H₂O (1:1:1 v/v). Then 0.087 g Cu(OAc)₂·H₂O was dissolved in 10 mL of the same solvent mixture and both solutions were combined with stirring at 120°C.¹ The solid was collected by filtration after stirring for 3 h. For the synthesis reaction in DMSO or DEF, H₃BTC (0.3mmol) and Cu(OAc)₂·H₂O (0.54 mmol) were added into DMSO (5g) or DEF (5g), which was loaded in a stainless steel autoclave. Gas was charged into the cell under stirring until the desired pressure was reached. After the mixture was stirred at 25 °C for a certain time, the stirrer was stopped and gas was released. The product was then washed with ethanol for several times and dried at 100 °C under vacuum for 24 h

MOF characterization. The products were characterized by XRD (Model D/MAX2500, Rigaka) with Cu K α radiation at a scanning rate of 3°/min. The morphologies were characterized by a HITACHI S-4800 scanning electron microscope and JEOL-1010 transmission electron microscope at 100 kV. The porosity properties were gained from N₂ adsorption-desorption isotherms using a Micromeritics ASAP 2020M system. FT-IR spectra were obtained using a Bruker Tensor 27 spectrometer, and the samples were prepared by the KBr pellet method. TG measurements were carried out using a HITACHI-STA 7300 with N₂ flow of 50 mL/min.

Catalytic test. The procedure of catalytic reaction was similar to those reported by Li and coworkers.² The oxidation of cyclohexene was carried out in a 5 mL roundbottom flask equipped with a reflux condenser and an oxygen balloon. In a typical reaction, catalyst (0.04 mmol) and cyclohexene (19.7 mmol) were heated at 80 °C under atmospheric pressure. After the desired time, the heterogeneous mixture was cooled and centrifuged. The products were analyzed by a gas chromatograph (Agilent 6820). For the reusability investigation, after 5 h of reaction the catalyst was recovered by centrifugation, washed with ethanol and dried under vacuum. Then the solid was reused for a consecutive run.

2. Results and Discussion



Fig. S1 XRD patterns of the samples synthesized in pure [BMIM] BF_4 at reaction time of 9 h (a), 84 h (b), 132 h (c) and 192 h (d).



Fig. S2 SEM images of the samples synthesized in pure [BMIM]BF₄ without CO_2 at 9 h (a), 84 h (b) and 132 h (c).



Fig. S3 FT-IR spectra of H₃BTC (a) and HKUST-1 synthesized in pure [BMIM]BF₄ (b), at CO₂ pressure of 6.14 MPa (c). The FT-IR spectra of the HKUST-1 synthesized in pure [BMIM]BF₄ (b) and at CO₂ pressure of 6.14 MPa (c) display the characteristic asymmetric (1618 cm⁻¹, 1558 cm⁻¹) and symmetric vibration (1443 cm⁻¹, 1375 cm⁻¹) of carboxylate anions in deprotonated H₃BTC. In comparison with the IR spectrum of H₃BTC (a), the wavenumber difference of asymmetric and symmetric vibration of carboxylate anions is narrowed. This indicates that carboxylate groups of H₃BTC are coordinated to Cu (II) ions.³



Fig. S4 Thermogravimetric curves of HKUST-1 synthesized in pure [BMIM]BF₄ (black) and at CO₂ pressure of 6.14 MPa (red). The weight loss in the temperature range of 30-200 °C is assigned to the desorption of surface adsorbed water and ethanol. A weight loss of about 36% after 350 °C corresponds to the decomposition of Cu-MOF. The HKUST-1 synthesized in pure [BMIM]BF₄ and at CO₂ pressure of 6.14 MPa can keep stable up to 290 °C.⁴



Fig. S5 XRD patterns of the samples synthesized in [BMIM] BF_4 at CO₂ pressure of 2.36 MPa in 3 h (a), 9 h (b), 15 h (c) and 24 h (d).



Fig. S6 XRD patterns of the samples synthesized in $[BMIM]BF_4$ at CO₂ pressure of 4.60 MPa in 3 h (a), 6 h (b) and 9 h (c).



Fig. S7 FT-IR spectra of H_3BTC (a) and HKUST-1 synthesized in [BMIM]BF₄ at CO₂ pressure of 2.36 MPa (b) and 4.60 MPa (c).



Fig. S8 Thermogravimetric curves of HKUST-1 synthesized in $[BMIM]BF_4$ at CO₂ pressure of 2.36 MPa (black) and 4.60 MPa (red).



Fig. S9 SEM images of the HKUST-1 synthesized in $[BMIM]BF_4$ at CO₂ pressure of 2.36 MPa (a) and 4.60 MPa (b).



Fig. S10 N_2 adsorption-desorption isotherms of the HKUST-1 synthesized in pure [BMIM]BF₄ (A) and at CO₂ pressure of 2.36 MPa (B), 4.60 MPa (C), 6.14 MPa (D).



Fig. S11 XRD patterns of the HKUST-1 synthesized in $[BMIM]BF_4$ with H_2 (A), N_2 (B), and CH_4 (C). The gas pressure is 4.60 MPa.



Fig. S12 SEM images of the HKUST-1 synthesized in [BMIM]BF₄ with H_2 (a), N_2 (b), and CH_4 (c). The gas pressure is 4.60 MPa.



Fig. S13 FT-IR spectra of H_3BTC (a) and HKUST-1 synthesized in [BMIM]BF₄ with H_2 (b), N_2 (c), and CH_4 (d). The gas pressure is 4.60 MPa.



Fig. S14 Thermogravimetric curves of HKUST-1 synthesized in [BMIM] BF_4 with H_2 (black), N_2 (red), and CH_4 (blue). The gas pressure is 4.60 MPa.



Fig. S15 N_2 adsorption-desorption isotherms of the HKUST-1 synthesized in [BMIM]BF₄ with H₂ (A), N₂ (B), and CH₄ (C). The gas pressure is 4.60 MPa.



Fig. S16 Comparition of XRD patterns of the HKUST-1 synthesized in pure IL in 9h (black), with acetonitrile in [BMIM]BF₄ (acetonitrile/[BMIM]BF₄: 1/4 v/v) in 9 h (red) and with CO₂ pressure of 4.60 MPa in 9h (blue). The volume expansibility of the

[BMIM]BF₄ with CO₂ pressure of 4.60 MPa measured in our work is 25% (Δ V/V₀).



Fig. S17 Left: XRD patterns of the MOFs synthesized in DMSO (black) and in CO_2 -present DMSO (red). The reaction time was 0.5 h. The CO_2 pressure was 6.0 MPa. **Right:** XRD patterns of the MOFs synthesized in DEF (black) and in CO_2 -present DEF (red). The reaction time was 0.5 h. The CO_2 pressure was 6.0 MPa.



Fig. S18 XRD pattern of the HKUST-1 synthesized by solvothermal reaction in DMF/EtOH/H₂O (1:1:1 v/v) in 3h.



Fig. S19 SEM image of the HKUST-1 synthesized by solvothermal reaction in DMF/EtOH/H₂O (1:1:1 v/v) in 3h.



Fig. S20 XRD pattern of the HKUST-1 synthesized in $[BMIM]BF_4$ at CO₂ pressure of 6.14 MPa in 9 h after it was used five times for oxidation reaction.



Fig. S21 SEM images of the HKUST-1 synthesized in $[BMIM]BF_4$ at CO₂ pressure of 6.14 MPa in 9 h after it was used four times (a) and five times (b) for oxidation reaction.

3. Reference

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