Dalton Transactions



PAPER

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Cite this: *Dalton Trans.*, 2019, **48**, 1006

Received 20th September 2018, Accepted 13th December 2018 DOI: 10.1039/c8dt03812k

rsc.li/dalton

Introduction

Metal–organic frameworks (MOFs), a family of porous polymer materials, are becoming a rising star in materials science by virtue of their huge porosity, exceptional surface area, and tunable surface chemistry.^{1–3} MOFs are constructed from metal ions/clusters and organic ligands. The abundance of various metal ions and organic linkers provides MOFs with considerable diversity. Examples of typical MOF series include ZIFs (zeolitic imidazole frameworks),⁴ UiOs (University of Oslo),⁵ MILs (Materials of Institute Lavoisier),⁶ and CAUs (Christian-Albrechts University).⁷ Given the extraordinary properties of MOFs, they have been used in a broad range of appli-

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Pressure-regulated synthesis of Cu(TPA)·(DMF) in microdroplets for selective CO₂ adsorption[†]

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The synthesis of metal-organic frameworks (MOFs) by using traditional wet-chemistry methods generally requires very long durations and still suffers from non-uniform heat and mass transfer within the bulk precursor solutions. Towards addressing these issues, a microdroplet-based spray method has been developed. In a typical spray process, an MOF's precursor solution is first atomized into microdroplets. These droplets serve as microreactors to ensure homogeneous mixing, fast evaporation, and rapid nucleation and crystal growth to form MOF particles. However, the fundamental MOF formation mechanisms by using this strategy have not been fully understood. In this work, the role of the operating pressure in the synthesis of a representative MOF (i.e., Cu(TPA) (DMF); TPA: terephthalic acid, DMF: dimethylformamide) was systematically investigated. Detailed characterization showed that the pressure variations significantly affected both the morphologies and crystalline structures of Cu(TPA) (DMF). Numerical simulations revealed that the morphology changes are mainly attributed to the variations in supersaturation ratios, which are caused by different microdroplet evaporation rates due to the regulation of operating pressure, while the crystalline structure variations are closely related to the dissociation of DMF molecules at lower operating pressures. Besides, the dissociation of DMF molecules decreased the surface area of the MOF crystals, but gave rise to massive coordinatively unsaturated metal sites, which greatly enhanced the interaction of CO₂ with the MOF crystal and thus led to improved CO₂ adsorption capacity and selectivity. The outcome of this work would contribute to the fundamental understanding of MOF synthesis using the microdroplet-based spray method.

cations, including gas separation,⁸ gas storage,⁹ catalysis,^{10,11} water treatment,^{12,13} sensing,¹⁴ and biomedical applications.¹⁵ MOFs can also be integrated with other materials (*e.g.*, metals and semiconductors) to enhance their functionalities and efficiencies by boosting molecule adsorption, facilitating charge transfer, and promoting molecule activation.^{16–19}

Conventionally, MOFs are synthesized through heating bulk precursor solutions via wet-chemistry processes (e.g., the solvothermal method), where the structure evolution takes place, including deprotonation, coordination, nucleation, and crystal growth.³ Wet-chemistry methods, however, are usually plagued with long synthesis durations due to inhomogeneous mixing and slow heat transfer within the bulk precursor solutions. For example, in a typical solvothermal process, it generally takes hours even days to obtain well-crystallized ZIF-8 crystals.²⁰ Various forms of external energies have been used to assist the MOF synthesis, such as microwave irradiation,²¹ ultrasound,²² electric potential,²³ and mechanical force.²⁴ Recently, a microdroplet-based spray strategy was developed for the fast and high-throughput synthesis of MOFs.^{25,26} In a typical spray process, MOF precursor solutions are firstly atomized into droplets with their size ranging from micrometers to millimeters. These droplets serve as microreactors, where uniform mixing

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[†]Electronic supplementary information (ESI) available: Assumptions for the simulation of microdroplet evaporation; calculation of the supersaturation ratio; the crystal structure of Cu(TPA)·(DMF) synthesized under 1 atm; FTIR and Raman spectra of Cu(TPA)·(DMF) synthesized under various pressures; XPS spectra of Cu(TPA)·(DMF) synthesized under various pressures; determining the surface areas of MOFs using the BET method. See DOI: 10.1039/c8dt03812k

and fast heat transfer can be easily achieved to promote efficient deprotonation and coordination. The microdroplets are then subjected to heating for solvent evaporation, nucleation, and crystal growth to form the final MOF crystals. The whole process takes only about several seconds to complete, making the spray route a rational strategy for the fast synthesis of MOFs. Besides, the spray method can also be used for the postsynthetic modification of MOFs²⁷ and manufacture of multicomponent MOF superstructures²⁵ and hierarchical MOFs.²⁸ It should be noted that the synthesis of MOFs by using the spray method is still in its early stage. More work needs to be conducted to unravel the formation mechanism of MOFs in this rapid process.

In particular, the evaporation of microdroplets is the first and foremost step of the synthesis of MOFs by using the spray process, because the solvent evaporation of microdroplets directly influences the kinetics of supersaturation of precursors,²⁹ which will have great effects on the subsequent MOF formation steps, *i.e.*, nucleation and crystal growth.^{3,30} Fundamentally, the evaporation of microdroplets is a macroscopic phenomenon of microscopic heat and mass transfer,³¹ which is generally controlled by several factors, including solvent types, operating temperature, and pressure. In a recent study, we studied the effect of operating temperature on the synthesis of $[Cu_3(TMA)_2(H_2O)_3]_n$ (TMA: trimesic acid) via the microdroplet-based spray method.²⁶ The results showed that the operating temperature affected not only the crystal size but also the accessible open coordination sites. It should be noted that $[Cu_3(TMA)_2(H_2O)_3]_n$ became amorphous at operating temperatures higher than 300 °C due to the disintegration of organic ligands. Compared with temperature, the adjustment of operating pressure is a milder way to regulate the synthesis of MOFs in microdroplets. Based on the previous studies of the formation of inorganic materials in microdroplets,^{32,33} the regulation of operating pressure would dramatically change the evaporation behaviors of microdroplets,³⁴ which will alter the supersaturation ratios, nucleation and crystal growth kinePaper

tics, and eventually give rise to different properties of the final products. However, the role of operating pressure in the formation of MOFs in microdroplets has not yet been explored thus far.

Herein, the current work aims to investigate the effect of operating pressure on the formation of MOFs in microdroplets. To be specific, a spray process equipped with a pressure control system was built. A representative MOF, Cu(TPA) (DMF) (TPA: terephthalic acid, DMF: dimethylformamide), was chosen and synthesized under different operating pressures ranging from 0.2 atm to 1 atm (Scheme 1). Systematic material characterization and numerical simulations of microdroplet evaporation were conducted to investigate the changes in the MOF's properties brought by the variation in operating pressure. The results showed that the operating pressure has significant effects on the MOF in terms of morphology, chemical structure, and gas adsorption ability (Scheme 1). Based on the results, a reasonable mechanism was proposed to explain the dependence of MOFs' properties on operating pressure. The results from this work would advance the understanding of MOFs' synthesis by using the spray strategy.

Materials and methods

Synthesis process

As illustrated in Scheme 2, the microdroplet-based spray process is composed of several parts, including a Collison nebulizer, a tube furnace, a sample collector (*i.e.*, a microfiber filter) and a pressure control system. In a typical synthesis process, the precursor solution was firstly prepared by dissolving 0.2174 g of Cu(NO₃)₂·3H₂O and 0.0997 g of terephthalic acid (TPA) in 15 mL of dimethylformamide (DMF). Subsequently, the precursor solution was nebulized into microdroplets, which were carried by an air flow (1.5 L min⁻¹) passing through the tube furnace at a pre-set temperature (200 °C). Flying through the furnace, the microdroplets under-



Scheme 1 Schematic illustration of the synthesis of Cu(TPA) (DMF) in microdroplets under various operating pressures.



Scheme 2 Schematic illustration of the experimental set-up for the microdroplet-based synthesis of MOFs under various operating pressures.

went solvent evaporation, nucleation, and crystallization. The particles were finally collected by using the microfiber filter. During the spray process, the pressure inside the tube was adjusted within the range of 0.2 atm to 1 atm.

Material characterization

Detailed characterization of the as-synthesized samples was carried out by using scanning electron microscopy (SEM, Hitachi SU-70), X-ray powder diffraction (XRPD, PANalytical X'Pert Pro Diffractometer: Cu-K α radiation source (λ = 1.5401 Å); reflection mode; step size = 0.026°; time per step: 27.54 s), Fourier transform infrared spectroscopy (FT-IR, Thermo Scientific Nicolet iS50), Raman spectroscopy (Horiba LABRam Spectrometer), X-ray photoelectron spectroscopy (XPS, Thermofisher ESCALab 250), and surface area and pore structure analysis (Autosorb iQ).

Gas sorption analysis

Autosorb iQ was used to obtain the sorption isotherms of N₂ and CO₂ at 273 K and 298 K. After the measurements, the CO₂ adsorption isotherms at these two temperatures were fitted with the virial equation (eqn (1)) to calculate the isosteric heats of CO₂ adsorption (Q_{st}) (eqn (2)).^{35,36}

$$\ln(p) = \ln(n) + \frac{1}{T} \sum_{i=0}^{A} a_i n^i + \sum_{i=0}^{B} b_i n^i$$
(1)

$$Q_{\rm st} = -R \sum_{i=0}^{A} a_i n^i \tag{2}$$

where p = gas pressure (Torr); n = amount of adsorbed gas molecules (mmol g⁻¹); T = temperature (K); a and $b = \text{virial coefficients with no dependence on the temperature; <math>Q_{\text{st}} = \text{isosteric heat of adsorption (J mol⁻¹)}$; R = gas constant (8.314 J (K mol)⁻¹).

Analysis of CO₂/N₂ adsorption selectivity

The ideal adsorbed solution theory (IAST), which has been demonstrated to be an accurate method to predict gas adsorption selectivity in numerous prior studies,^{37–39} was employed here to analyze the CO_2/N_2 adsorption selectivity of various Cu(TPA)-(DMF) samples. To be specific, the pure-component adsorption isotherms of CO_2 and N_2 were firstly fitted by using

the dual-site (eqn (3)) and single-site (eqn (4)) Langmuir-Freundlich models, respectively.

$$q = q_{\rm A, \, sat} \frac{c_{\rm A} p^{\alpha_{\rm A}}}{1 + c_{\rm A} p^{\alpha_{\rm A}}} + q_{\rm B, sat} \frac{c_{\rm B} p^{\alpha_{\rm B}}}{1 + c_{\rm B} p^{\alpha_{\rm B}}} \tag{3}$$

$$q = q_{\rm A,sat} \frac{c_{\rm A} p^{\alpha_{\rm A}}}{1 + c_{\rm A} p^{\alpha_{\rm A}}} \tag{4}$$

where q = adsorption quantity (mmol g⁻¹); $q_{A,sat}$ and $q_{B,sat}$ = saturated adsorption quantities; subscripts A and B indicate various adsorption sites; c_A and c_B = Langmuir–Freundlich coefficients (bar^{- α}, temperature-dependent); p = gas phase pressure (bar); α_A and α_B = dimensionless exponents.

Subsequently, the fitting parameters were incorporated into eqn (5) to calculate the mole fraction of individual components in the adsorbed phase.

$$\int_{0}^{P y_1/x_1} \frac{q_1}{P} dp = \int_{0}^{P y_2/x_2} \frac{q_2}{P} dp$$
(5)

where P = total pressure (bar); x and y = mole fractions of the gas component in the adsorbed and bulk phases, respectively; q = adsorption quantity (mmol g⁻¹); subscripted numbers were used to differentiate the gas components.

Finally, the adsorption selectivity (S_{ads}) was calculated using eqn (6).

$$S_{\rm ads} = \frac{x_1/y_1}{x_2/y_2}$$
 (6)

Results and discussion

Morphology characterization

The Cu(TPA)·(DMF) samples synthesized under various pressures were subjected to detailed characterization. As shown in Fig. 1a, all of the Cu(TPA)·(DMF) samples synthesized by the spray process have a sheet morphology, which is consistent with the lamellar crystal structure of Cu(TPA)·(DMF).⁴⁰ Notably, the operating pressure affects the size distribution of Cu(TPA)·(DMF) (Fig. 1b), and lower pressures give rise to smaller crystal sizes and more homogeneous size distributions. To be specific, the mean lengths of the Cu(TPA)·(DMF) crystals synthesized under 1, 0.8, 0.6, 0.4 and 0.2 atm were found to be 915, 502, 453, 334 and 299 nm,



Fig. 1 (a) SEM images and (b) size distribution histograms of Cu(TPA)·(DMF) synthesized under various pressures. Scale bars in SEM images: 2 μ m (up) and 500 nm (down).

respectively. Besides, Cu(TPA)·(DMF) crystals synthesized under ambient pressure (1 atm) have a wide size distribution, ranging from 400 nm to 1600 nm, while the size distribution becomes narrower with decreased pressures. The smaller size and narrow size distribution under lower pressures can be ascribed to a faster nucleation rate induced by rapid solvent evaporation. In addition, the operating pressure also has a significant effect on the length/thickness ratio of the samples. As shown in Fig. 2, under ambient pressure, Cu(TPA)·(DMF) exhibits the highest length/thickness ratio (~7.8). With the operating pressure being lower than 0.8 atm, the length/thickness ratio stabilizes to around 2.6 to 3.4. The variations in crystal size, size distribution, and length/thickness ratio might be related to the pressure-modulated evaporation of the microdro-



Fig. 2 Effect of operating pressure on the length/thickness ratio of the samples.

plets during the spray process, as explained in detail in the following section.

Simulation of microdroplet evaporation

To better understand the dependence of microdroplet evaporation (*i.e.*, droplet temperature and size) on the operating pressure, numerical simulations were carried out based on the fundamental heat and mass transfer principles.⁴¹ The models are composed of four differential equations (eqn (7)–(10)), describing the evolution of the droplet diameter (D_d), solvent vapor concentration in air (n), droplet temperature (T_d), and air temperature (T_a) as a function of time, respectively. The assumptions are provided in ESI, S1.†

$$\frac{\mathrm{d}D_{\mathrm{d}}}{\mathrm{d}t} = \frac{4D_{\mathrm{v}}m_{\mathrm{d}}(n-n_{\mathrm{s}})}{\rho_{\mathrm{d}}D_{\mathrm{d}}} \tag{7}$$

$$\frac{\mathrm{d}n}{\mathrm{d}t} = -2\pi D_{\mathrm{d}} D_{\mathrm{v}} N(n-n_{\mathrm{s}}) \tag{8}$$

$$\frac{dT_{\rm d}}{dt} = \frac{3L\frac{dD_{\rm d}}{dt} + 6\frac{h_{\rm d}}{\rho_{\rm d}}(T_{\rm a} - T_{\rm d})}{C_{\rm d}D_{\rm d}}$$
(9)

$$\frac{dT_{a}}{dt} = \frac{-\pi^{2}R^{2}D_{d}^{2}Nh_{d}(T_{a} - T_{d}) + 2\pi Rh_{t}(T_{t} - T_{a})}{FC_{a}} \times \frac{Q}{\pi R^{2}} \left(\frac{T_{a}}{T_{a}^{0}}\right) \left(\frac{1 - f_{d}^{0}}{1 - f_{d}}\right)$$
(10)

where D_d = droplet diameter (m), t = residence time (s), D_v = diffusion coefficient of DMF vapor (m² s⁻¹, derived from eqn (11) (ref. 42)), m_d = molecular mass of DMF (kg), n = number concentration of DMF vapor molecules in air (1 m⁻³), n_s = saturated DMF vapor concentration (1 m⁻³), ρ_d = DMF density (kg m⁻³), N = number density of microdroplets in air (1 m⁻³), T_d = temperature of microdroplets (*K*), K_m = mass transfer

coefficient of DMF vapor (m s⁻¹), n_t = DMF vapor concentration at the tube wall (1 m⁻³), L = latent heat of DMF evaporation (J kg⁻¹), h_d = heat transfer coefficient around microdroplets (W (m² K)⁻¹), T_a = air temperature (K), C_d = heat capacity of DMF (J (kg K)⁻¹), R = tube radius (m), h_t = heat transfer coefficient near the tube (W (m² K)⁻¹), F = mass flow rate of air (kg s⁻¹), C_a = heat capacity of air (J (kg K)⁻¹), Q = volume flow rate of air (m³ s⁻¹), f_d = mole fraction of DMF vapor in air. Superscripted "0" indicates the initial values.

$$D_{\rm v} = \frac{2.66T_{\rm a}^{1.5} \times 10^{-7}}{pM_{\rm ad}^{0.5}\sigma_{\rm ad}^2\Omega_{\rm D}} \tag{11}$$

where $M_{\rm ad} = \frac{2}{1/M_{\rm a} + 1/M_{\rm d}}$, $M_{\rm a}$ = molecular weight of air (g mol⁻¹), $M_{\rm d}$ = molecular weight of DMF (g mol⁻¹), $\sigma_{\rm ad} = \frac{\sigma_{\rm a} + \sigma_{\rm d}}{2}$, $\sigma_{\rm a}$ = hard sphere diameter of air (Å), $\sigma_{\rm d}$ = hard sphere diameter of DMF (Å), and $\Omega_{\rm D}$ is almost unity.

DMF droplets with an initial diameter of 2 μ m were selected for simulation. As shown in Fig. 3a and b, upon evaporation, the DMF vapor number density in air increased drastically with time, which also leads to a decrease in droplet diameter (Fig. 3c and d). Notably, a lower operating pressure would enhance the diffusion



Fig. 3 Evolution of DMF vapor density (a and b), droplet diameter (c and d), and droplet temperature (e and f) as a function of reaction time under various operating pressures. (a, inset) The color bar used to indicate various operating pressures (unit: atm) for a, c, and e.

coefficient of DMF vapor (eqn (11)), which would speed up the droplet evaporation and thus give rise to a higher DMF vapor number density and a smaller droplet diameter. To be specific, at the evaporation time of 0.04 ms, the diameter of the microdroplets was calculated to be 1.64 μ m under the operating pressure of 1 atm, but decreased to 1.44 µm under 0.2 atm. The rapid decrease in droplet diameter under lower operating pressures would significantly increase the concentration of reactants, and therefore result in a faster increase in supersaturation ratio. As shown in Fig. S1,[†] the supersaturation ratio of the solute at 0.04 ms under 0.2 atm was 1.46 times that under 1 atm. The increase in supersaturation ratio would drastically promote the nucleation process.²⁶ In particular, more seed nuclei can be obtained under lower operating pressures, which would yield smaller crystals. The simulation results are consistent with the SEM images (Fig. 1). Meanwhile, a lower operating pressure also reduces the equilibrium temperature of the microdroplets (Fig. 3e and f). For instance, the equilibrium temperature of the droplet under 1 atm is 355 K, while the equilibrium temperature decreases to 329 K when the process is operated under 0.2 atm. The results indicate that the evaporative cooling effect³⁴ becomes more prominent under lower operating pressures, which will also make partial contributions to the increased supersaturation ratios.

Chemical properties analysis

In addition to the morphology variations, pressure also plays a significant role in the crystallinity of the products. As shown in Fig. 4a, the XRPD patterns of the as-prepared samples agree well with the one reported previously.40 The corresponding crystal structure (CCDC-687690)40 of Cu(TPA)·(DMF) synthesized under 1 atm is illustrated in Fig. S2.† It is clear from the structure that the DMF molecules are coordinated with the Cu sites from one end, leaving the other end dangling inside the pores, which become vulnerable upon the variations of temperature and pressure during the synthesis process. Interestingly, with decreasing pressures, the diffraction peak at 12° gradually splits into two peaks. When synthesized at a very low pressure (*i.e.*, 0.2 atm), a new diffraction peak shows up at 8.2°. The variations in crystallinity may be attributed to the loss of DMF coordinated to Cu^{II} sites during the spray process under low-pressure conditions (Fig. 4b), which is analogous to the temperature-modulated changes in crystal structures as reported previously.⁴⁰ Despite the various crystal structures, the samples synthesized under various pressures possess similar functional groups as demonstrated from the FT-IR (Fig. S3a[†]) and Raman spectra (Fig. S3b[†]). All of the functional groups stem from the Cu(TPA)·(DMF) crystals.40,43 The assignments of the primary IR frequencies and Raman shifts are summarized in Table 1. For instance, the IR bands at 676,



Fig. 4 (a) XRPD patterns; (b) schematic illustration of the effect of pressure on the crystal structure of Cu(TPA) (DMF).

FT-IR		Raman		
Wavenumber (cm ⁻¹)	Assignment	Raman shift (cm^{-1})	Assignment	
676	$\delta(OCN)$	182	ν (Cu–Cu)	
882	$\nu_{\rm s}({\rm C'N})$	316	ν (Cu–O)	
1105	$r(CH_3)$	1430	$\nu_{s}(COO)$	
1255	$\nu_{a}(C'N)$	1609	$\nu(C = C)$	
1386	δ(CH)		()	
1439	$\delta_{s}(CH_{3})$			
1604	$\nu_{a}(COO)$			
1663	ν (CO)			

1105, 1255, 1386, and 1663 cm⁻¹ can be assigned to δ (OCN), r(CH₃), ν_a (C'N), δ (CH) and ν (CO), respectively. All of these peaks originate from the DMF molecules existing inside

Cu(TPA)·(DMF) crystals. Compared with those of the free DMF molecules (Fig. S3a†), these peaks redshift a little bit to higher wavenumbers. The IR band at 1604 cm⁻¹ corresponds to ν_a (COO) of TPA. More information was obtained from the Raman spectra (Fig. S3b†). In particular, the bands at the Raman shifts of 182 and 316 cm⁻¹ can be ascribed to ν (Cu–Cu) and ν (Cu–O), respectively.

The surface elemental information of the Cu(TPA)·(DMF) crystals synthesized under various pressures was examined through XPS measurements. As shown in Fig. S4,† all samples exhibit almost identical XPS spectra, including survey scans and high-resolution spectra. Primary elements in the Cu(TPA)·(DMF) crystal were identified. In particular, the peaks at 932.5 eV and 952.5 eV can be assigned to Cu 2p3/2 and Cu 2p1/2, respectively.¹⁶ While the peaks centered at 398.3 eV and 529.7 eV correspond to N 1s and O 1s, respectively.^{44,45} The minimal differences in the FTIR, Raman and XPS results among the samples indicate that even though the DMF mole-



Fig. 5 Nitrogen sorption isotherms and Density Functional Theory (DFT) pore size distributions of Cu(TPA) (DMF) synthesized under various pressures (NLDFT-N₂-carbon equilibrium transition kernel at 77 K based on a slit-pore model).

cules are dissociated from the copper sites at low operating pressures, they might be still trapped inside the pores of the MOF crystals.

The dissociation of DMF from copper sites in Cu(TPA)·(DMF) samples also gives rise to the changes in other properties, including surface area and the availability of coordinatively unsaturated copper sites. The surface area and pore size distribution of the samples were analyzed with nitrogen sorption experiments. In particular, the Brunauer-Emmett-Teller (BET) method was used to derive the surface areas (S6[†]). The results show that the Cu(TPA) (DMF) sample synthesized at 1 atm (hereafter Cu(TPA)·(DMF)_1) has a BET surface area of 1187 m² g⁻¹, while the one synthesized at 0.4 atm (hereafter $Cu(TPA)\cdot(DMF)_0.4$ has only a BET surface area of 57 m² g⁻¹. The nitrogen sorption isotherms of the samples are shown in Fig. 5. For Cu(TPA) (DMF)_1, the rapid increase in nitrogen uptake observed at low relative pressure ($P/P_0 < 0.01$) indicates the abundance of micropores, while the slight increase at high relative pressure and the existence of hysteresis suggest the presence of mesopores. For Cu(TPA) (DMF)_0.4, a similar nitrogen sorption isotherm was observed but with fewer micropores. The

co-existence of micropores and mesopores is also confirmed by the pore size distribution results. As shown in Fig. 5b and d, Cu(TPA)·(DMF)_1 and Cu(TPA)·(DMF)_0.4 exhibit similar pore size distributions. Fewer micropores are observed in the case of Cu(TPA)·(DMF)_0.4, which is consistent with the nitrogen sorption isotherms. The change in the porous structures becomes more apparent when a lower pressure (0.2 atm) was used, where the sample was designated as Cu(TPA)·(DMF)_0.2. In particular, Cu(TPA)·(DMF)_0.2 has a BET surface area of 49 m² g⁻¹, with a dominated pore diameter of 27.7 Å.

The variations in the porosity and crystal structures of Cu(TPA)·(DMF) lead to different performances in gas adsorption as demonstrated with N₂ and CO₂ adsorption experiments (Fig. 6). The analysis of pure gas adsorption was performed at 273 K and 298 K, after which in-depth modelling was conducted to analyze the isosteric heats and adsorption selectivity. Specifically, at 273 K, Cu(TPA)·(DMF)_1 has a N₂ uptake of 1.23 mmol g⁻¹ at 1.0 bar, which is 52% higher than that of Cu(TPA)·(DMF)_0.2 (Fig. 6a), while at a higher temperature (298 K), these two samples possess a similar N₂ adsorption capacity (~0.10 mmol g⁻¹ at 1.0 bar). Interestingly,



Fig. 6 (a) N_2 adsorption isotherms; (b) CO_2 adsorption isotherms; (c) isosteric heats of CO_2 adsorption; (d) adsorption selectivity for CO_2/N_2 mixtures estimated using IAST. Note: The pressure values indicate the operating pressures used during the synthesis process; the temperature values indicate the temperatures used for gas adsorption tests.

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Cu(TPA)·(DMF)_0.2 shows a much higher capacity for CO₂ uptake at both 273 K and 298 K (Fig. 6b), even though the surface area of Cu(TPA)·(DMF)_0.2 is much smaller than that of Cu(TPA)·(DMF)_1. To gain further understanding of the CO₂ adsorption with these two samples, the isosteric heats of CO₂ adsorption were calculated using the Clausius-Clapevron equation (eqn (2)). In the case of Cu(TPA) (DMF)_1, the isosteric heats of CO₂ adsorption gradually increased with higher loading of CO₂, which might arise from the enhanced CO₂- CO_2 interaction.³⁷ Compared with the isosteric heats of CO_2 adsorption for Cu(TPA) (DMF)_0.2 (~30 kJ mol⁻¹), higher values were observed with Cu(TPA)·(DMF)_1 (46 to 49 kJ mol⁻¹), which indicates that the interaction between CO₂ molecules and Cu(TPA)·(DMF)_1 was stronger than that with Cu(TPA)·(DMF)_0.2. Besides, it also suggests the tunability of isosteric heats of CO₂ adsorption through pressure-regulated synthesis of Cu(TPA) (DMF) samples, offering huge potential to optimize the sorption profiles of CO₂. As shown in Table 2, the isosteric heats of CO₂ adsorption of Cu(TPA)·(DMF) are comparable to other porous materials, such as Cu₃(BTC)₂ (29.8 \pm 0.2 kJ mol⁻¹), Mg-MOF-74 (22 to 42 kJ mol⁻¹), and zeolites (20 to 50 kJ mol⁻¹). It should be noted that the isosteric heats of CO₂ adsorption of Cu(TPA)·(DMF) samples can be further improved by modifying binding functionalities, just like the examples shown in Table 2 (i.e., cation-exchanged MCM-22 zeolite and modified SBA-15 mesoporous silica). In addition, the IAST model was used to analyze the adsorption selectivity for CO₂ from flue gas (75% N₂, 15% CO₂ and 10% other gases) based on the isotherms (see the Experimental section for details). As shown in Fig. 6d, the IAST selectivities of Cu (TPA)·(DMF)_0.2 at 273 K and 298 K are calculated to be ~3 and ~ 20 , respectively, which are much larger than those of Cu(TPA)·(DMF)_1, indicating that Cu(TPA)·(DMF)_0.2 has a better ability to selectively adsorb CO2 over N2.

On the basis of the above results, a plausible mechanism for the enhanced CO_2 uptake and selectivity with $Cu(TPA) \cdot (DMF)_0.2$ was schematically illustrated in Scheme 3. With lower operating pressures, DMF molecules tend to dissociate from the crystal structure due to the increased diffusiv-

Table 2 Companson of the isosteric fields of ausorptic	able 2	e 2 Comparison	of the	isosteric	heats	ot	adsor	ptic
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Adsorbate	Adsorbent	$Q_{\rm st} ({\rm kJ} {\rm mol}^{-1})$	Ref.
CO_2	Cu(TPA)·(DMF)_0.2	~30	This work
CO_2	Cu(TPA)(DMF)_1	46 to 49	This work
CO_2	$Cu_3(BTC)_2$	29.8 ± 0.2	49
CO_2	Mg-MOF-74	22 to 42	50
CO_2	CMP-1	24 to 26	51
CO_2	ZK-5	25 to 50	52
CO_2	Cation-exchanged MCM-22 zeolite	20 to 40	53
CO_2	Modified SBA-15 mesoporous silica	10 to 70	54

Note: BTC: Benzene-1,3,5-tricarboxylic acid; CMP: conjugated microporous polymer; ZK-5: an 8-membered-ring zeolite (Framework Type Code: KFI).



Scheme 3 Schematic illustration of CO_2 adsorption inside the framework of Cu(TPA) (DMF) synthesized under low pressures. H atoms are omitted for simplicity.

ity of DMF molecules (eqn (11)). Instead of leaving away from the framework, these dissociated DMF molecules are trapped inside the pores as suggested by the systematic characterization results (Fig. 4a, S3, and S4[†]). The dissociated but trapped DMF molecules led to a decreased surface area but created massive coordinatively unsaturated copper sites. As demonstrated in many prior studies,^{46,47} the coordinatively unsaturated metal sites would produce strong electric fields to bind polar molecules (*e.g.*, CO_2),⁴⁸ which would subsequently improve the CO₂ adsorption capacity. Generally, the open metal sites would also increase the isosteric heat (Q_{st}) . However, smaller Q_{st} values were observed for Cu(TPA)·(DMF) _0.2 compared with that for Cu(TPA)·(DMF)_1. This might be due to the fact that Cu(TPA) (DMF)_0.2 has lots of dissociated DMF molecules trapped inside the pores (Scheme 3), which would cause steric hindrance and thus decrease the isosteric heat.

Conclusions

A pressure-regulated microdroplet-based spray route has been developed for the synthesis of MOFs. Systematic experimental and modelling studies have been conducted to investigate the dependence of the properties of Cu(TPA)·(DMF) on the pressure in the spray process. Apparent variations in morphology and crystal structure were observed with different synthesis pressures, which could be attributed to the different evaporation rates of microdroplets and the dissociation of coordinated DMF under low pressures, respectively. The dissociation of DMF molecules would generate large numbers of coordinatively unsaturated metal sites, which leads to higher CO_2 adsorption capacity and selectivity. The outcome of this work would contribute to the fundamental understanding of the pressure-regulated synthesis of MOFs using the spray process.

Conflicts of interest

The authors declare no competing financial interest.

Acknowledgements

Financial support from the National Science Foundation (CMMI-1727553) is gratefully acknowledged.

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Paper

Supporting Information

Pressure-Regulated Synthesis of Cu(TPA)·(DMF) in

Microdroplets for Selective CO₂ Adsorption

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- S5. XPS spectra of Cu(TPA)·(DMF) synthesized under various pressures
- S6. Determining surface areas of MOFs using BET method

S1. Assumptions for the simulation of microdroplet evaporation

- 1) Chemicals reactions within the droplet during evaporation are ignored.
- 2) The initial diameter of the DMF droplets was assumed to be $2 \mu m$.
- 3) The initial temperature of the microdroplets was 298 K. During the spray process, the temperature was assumed to be uniform within the microdroplets, as the thermal equilibrium characteristic time is much shorter than the evaporation time.
- 4) Compared with solvent evaporation and vapor diffusion, other dynamics (e.g., droplet coagulation, diffusion and thermophoresis) are not important.
- 5) The sizes of all particles are larger than 100 nm, making the Kelvin effect negligible.
- 6) Free convention is not decisive and was not considered in this simulation.

S2. Calculation of the supersaturation ratio

The supersaturation ratio (S) of the solute was calculated by using the following equation:

$$S = \frac{c_t}{c_s} \tag{S1}$$

where, c_t is the concentration of solute at reaction time t; c_s is the solubility of the solute. At the same reaction time t, c_s was considered to have the same value under various operation pressures by neglecting the temperature variations. Given the same initial precursor, the supersaturation ratio in this case is proportional to c_t . Therefore,

$$\frac{S_{P1}}{S_{P2}} = \frac{c_{tP1}}{c_{sP2}} = \frac{V_{P2}}{V_{P1}} = \frac{(D_{dP2})^3}{(D_{dP1})^3}$$
(S2)

where, V is the volume of droplet; D_d is the droplet diameter; the subscripted P1 and P2 represent the operation pressures.



Figure S1. Normalized supersaturation ratios as a function of operation pressures at the

evaporation time of 0.04 ms. Note: All the supersaturation ratios were normalized to the value calculated under 1 atm.

S3. Crystal structure of Cu(TPA)·(DMF) synthesized under 1 atm



Figure S2. Crystal structure of Cu(TPA)·(DMF) synthesized under 1 atm (CCDC-687690). (a) view along a axis; (b) view along b axis; (c) view along c axis.

S4. FTIR and Raman spectra of Cu(TPA)·(DMF) synthesized under various pressures



Figure S3. (a) FTIR spectra and (b) Raman spectra of Cu(TPA)·(DMF) synthesized under various pressures.

S5. XPS spectra of Cu(TPA)·(DMF) synthesized under various pressures



Figure S4. XPS spectra of Cu(TPA)·(DMF) synthesized under various pressures (from top to down: 1, 0.8, 0.6, 0.4, 0.2 atm). (a) survey scan; (b) Cu 2p; (c) O 1s; (d) N 1s.

S6. Determining surface areas of MOFs using BET method

It should be noted that the BET theory assumes multilayer adsorption, while adsorption in MOFs is mainly interpreted through a pore-filling mechanism. This inconsistency makes it questionable to use the BET theory to get the surface areas of MOFs. In 2007, a solid work was carried out by Snurr's group at Northwestern University to justify applicability of the BET theory for the adsorption in MOFs by carefully selecting the pressure range based on the established consistency criteria.¹ Firstly, they derived the BET surface areas from N₂ adsorption isotherms predicted from grand canonical Monte Carlo simulations. Then, they compared these BET values with the accessible surface areas calculated directly from the crystal structures. They found that these values matched well with each other, which indicates that the BET surface area is proper to characterize MOFs over the pressure ranges selected based on the established consistency criteria. Since then, the BET method has been widely accepted in MOFs-related studies.²⁻⁵ In the current study, the surface areas of the samples were also derived using the BET theory based on the consistency criteria suggested in these prior literatures.

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