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Activation-dependent breathing in a flexible metal-organic framework and the effects of repeated sorption/desorption cycling

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Abstract: A non-interpenetrated metal-organic framework with a paddle-wheel secondary building unit has been activated by direct thermal evacuation, guest exchange with a volatile solvent, and supercritical CO₂ drying. Conventional thermal activation yields a mixture of crystalline phases and some amorphous content. Exchange with a volatile solvent prior to vacuum activation produces a pure breathing phase with high sorption capacity, selectivity for CO₂ over N₂ and CH₄, and substantial hysteresis. Supercritical drying can be used to access a guest-free open phase. Pressureresolved differential scanning calorimetry was used to confirm and investigate a systematic loss of sorption capacity by the breathing phase as a function of successive cycles of sorption and desorption. A corresponding loss of sample integrity was not detectable by powder X-ray diffraction analysis. This may be an important factor to consider in cases where flexible MOFs are earmarked for industrial applications.

During synthesis of a metal-organic framework (MOF) the reaction solvent is usually trapped as a guest within cavities or channels of the porous framework. These typically high-boiling guest molecules are routinely removed by heating under dynamic vacuum. However this form of direct activation often leads to irreversible framework changes that reduce porosity.1 MOF crystals often maintain their single-crystal character during solvent exchange,² i.e. when the MOF is submerged in a new guest solvent, allowing for guest exchange by diffusion. Employing a relatively volatile solvent for exchange potentially lowers the activation temperature, thereby increasing the probability of obtaining high-quality single crystals of an activated phase. Similarly, activation methods such as supercritical drying³ and freeze-drying⁴ have been shown to affect MOF properties by improving surface areas and pore performance.

A recent study of activation effects on the threedimensional Zn carboxylate MOF FIR-3 included solvent exchange, freeze drying and supercritical drying.⁵ Large

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variations in the resulting sorption capacity were observed for these three methods. In a separate study Park and co-workers investigated the effect of activation methods on the fine structure of SNU-77, also a three-dimensional Zn carboxylate.⁶ Yang *et al.* were also able to optimise the sorption capacity of Cu-BTC by solvent exchange with various solvents prior to activation.⁷ In general, however, detailed *structural* investigations of the effect of solvent-mediated activation are limited.

MOFs have been extensively studied for their potential applications in gas capture and separation. In this context, the separation of commercially important gas mixtures such as flue gas emissions,⁸ natural gas⁹ and short-chain alkanes¹⁰ are of particular interest, as is the direct-air capture of carbon dioxide.¹¹

Flexible MOFs, often described as having soft porosity,¹² generally interpenetrate and the prevention of interpenetration is sometimes advantageous for maximising potential guest-free volume.¹³ A variety of strategies¹⁴ have been employed with success, including the selection of sterically bulky ligands.¹⁵ In the present study we have prepared an analogue of the known doubly-interpenetrated MOF-508,^{10,16} but we have appended phenyl groups to the dicarboxylic acid bridging ligand in order to prevent interpenetration.

We synthesised 2,5-diphenylbenzene-1,4-dicarboxylic acid (DPT) according to a literature procedure.¹⁷ The noninterpenetrated MOF **1** was prepared by combining DPT, 4,4'bipyridine and zinc nitrate tetrahydrate in DMF, and incubating at 100 °C for 24 h (Scheme 1). The framework has molecular formula $[Zn_2(C_{20}H_{12}O_4)_2(C_{10}H_8N_2)]_n$ and its as-synthesised, solvated phase is referred to as **1A**.



Scheme 1. Solvothermal synthesis of 1.

Phase **1A** crystallizes in the space group *P4/ncc* and contains highly disordered DMF guest molecules, which could not be modelled (the residual electron density in the guest-accessible channels amounts to 1160 electrons per unit cell – see ESI). The pillared-layered structure of **1A** is based on zinc paddle-wheel secondary building units and is analogous to that of MOF-508 but prevention of interpenetration greatly increases the potential free volume from 28% for MOF-508 (according to Hupp *et al.*^{16a}) to 50.1% for **1A**. Both estimates were made using

PLATON¹⁸ (probe radius 1.2 Å). Figure S1 shows partial packing diagrams of **1A**, where phenyl substituents protrude into channels along [110] and [001].

Crystals of **1A** lose guest DMF (total percentage mass loss = 30.0%) in at least two steps according to thermogravimetric analysis (TGA) (Figure S2). A sample of **1A** was activated at 423 K under dynamic vacuum for 12 h but the resulting guest-free phase lost its single-crystal character. Powder X-ray diffraction (Figure S7) showed that the sample had transformed to what appeared to be a mixture of unknown phases and some amorphous content.

In an attempt to lower the temperature of activation, crystals of **1A** were submerged in diethyl ether for solvent exchange. The new solvent was replaced once a day for three days to ensure complete exchange of the included guest. The crystals showed minimal signs of cracking or other damage as a result of the exchange process and TGA (Figure S4) confirmed that all included guest is expelled below 330 K. Solvent-exchanged crystals were activated at ambient temperature under dynamic vacuum; some crystals had maintained their single-crystal character and it was therefore possible to record single-crystal diffraction data. The activated phase **1B** is an empty, collapsed version of **1A** (Figure 1) in which the connectivity of the MOF is preserved.



Figure 1. Perspective view along [001] showing the open-channel nature of 1A as compared to its closed counterpart 1B. Hydrogen atoms and guest molecules have been omitted for clarity.

A sample of **1A** was similarly subjected to solvent exchange with ethyl acetate (TGA provided as Figure S5) and activated at 353 K under dynamic vacuum. Powder X-ray diffraction (PXRD, Figure S8) confirms that the same transformation to **1B** occurs for the samples activated *via* diethyl ether and ethyl acetate exchange, and that the single-crystal X-ray structure of **1B** is representative of the bulk. For further investigation, **1B** was routinely prepared by activation of **1A** *via* diethyl ether exchange. It has been reported that treatment of a MOF with supercritical CO₂ can produce an activated phase of higher porosity than might be obtained by heating under dynamic vacuum.^{3a} We treated **1A** with supercritical CO₂ for 48 h and PXRD (Figure S9) shows that the framework structure of the resultant activated phase resembles that of the as-synthesised version, **1A**.

Some of the crystals that had been subjected to the supercritical drying experiment were suitable for single-crystal X-ray diffraction. One of these was mounted in an environmental gas cell, which was then evacuated at $\sim 2 \times 10^{-3}$ mbar at room temperature for 12 h and thereafter sealed under these conditions. Single-crystal diffraction data were recorded at ambient temperature and, as expected, the structure resembles that of guest-free **1A** (we refer to this apohost form as **1C**; summation the residual electron density amounts to 18 electrons per unit cell – see ESI). In **1C** the phenyl rings of DPT are

disordered over two positions, as are the pyridyl rings of the pillaring ligand, whereas in **1A** there is no crystallographic disorder. There is a related change in space group from P4/ncc for **1A** to P4 for **1C**, and a change in the orientation and size of the unit cell. The disorder may be due to either the absence of guest molecules, the higher temperature of data collection (data for **1A** were collected at 173 K) or a combination of these factors. Nevertheless the connectivity and overall structure are preserved. For clarity, a summary of the three phases of **1** is provided in Table 1.

Phase	Details	Method
1A	As-synthesised version containing DMF guest molecules	Solvothermal synthesis
1B	Collapsed framework free of guest molecules	Obtained from 1A by solvent exchange with diethyl ether or ethyl acetate followed by vacuum activation
1C	Open framework free of guest molecules	Obtained from 1A by supercritical CO ₂ drying

 Table 1. Phases of 1 along with the methods used to obtain these phases.

On multiple occasions samples of 1A were dried under supercritical conditions. Although this produced phase pure 1C several instances, the experiment was not always in reproducible. The method appears to be more reliable for smaller samples and we postulate that the presence of residual DMF interferes with this activation process (owing to the small volume of the supercritical fluid compartment of the apparatus). A phase-pure sample of 1C from supercritical drying was analysed by FTIR, TGA and PXRDs. The FTIR spectrum (Figure S14) shows no evidence for entrapped CO₂, (i.e. no peak is observed at approximately 2300 cm⁻¹). However, the peak at 3430 cm⁻¹ suggests that 1C adsorbs water under ambient conditions, which is consistent with the TGA result for the same sample (Figure S6). A sample of 1C was heated at 373 K under dynamic vacuum for 12 h, removed from the oven subjected to PXRD analysis under ambient conditions. This process was repeated for the same sample using temperatures of 423 K and then 523 K. From the resulting PXRD patterns (Figure S10) it is clear that the sample does not collapse or transform under these conditions.

Phase **1B** was exposed to supercritical CO_2 for 36 h, after which PXRD (Figure S11) indicated partial conversion to **1C**. A second, freshly activated sample of **1B** was also subjected to the same conditions for one week, after which the sample appeared to have almost entirely converted from **1B** to **1C**. However, most of the sample reverted to **1B** when subsequently evacuated at 523 K. Since this result is inconsistent with that for **1C** produced solely by supercritical drying, we propose that the conversion from **1B** to **1C** occurs *via* a metastable frustrated phase¹⁹ that easily reverts to **1B**.

High pressure sorption analysis with N₂, CH₄ and CO₂ were carried out on a single sample of **1B** at 298 K. Informed by preliminary experiments, the order of gases was chosen to minimise carry-over effects. We tested N₂ first, then CH₄ and finally CO₂. It is clear from the sorption isotherms presented in Figure 2 that the compound has a far greater affinity for CO₂

over N₂ and CH₄. We have presented two cycles of CO₂ sorption. In the first cycle the sorption isotherm shows a broad gateopening step beginning at ~25 bar. During the desorption leg of the first cycle most of the adsorbed CO₂ is retained down to a pressure of ~10 bar, below which it appears that gate closing occurs abruptly. In the second cycle, the gate-opening step is broader and begins at a lower pressure of ~20 bar. At 35 bar the sorption isotherm begins to resemble that of cycle 1. The desorption leg of cycle 2 also resembles that of cycle 1. The maximum uptake of CO₂ under the conditions used is 8.4 mmol g⁻¹, which is equivalent to 37 g of gas per 100 g of sorbent. In stark contrast the maximum uptakes of N₂ and CH₄ under the same conditions are a mere 0.081 and 0.23 mmol g⁻¹, respectively.



Figure 2. Sorption (filled symbols) and desorption (empty symbols) isotherms for 1 recorded at 298 K with test gases CO_2 (cycles 1 and 2), CH_4 and N_2 .

Variable-pressure PXRD (Figure S12) data were recorded with incremental CO_2 loading to further investigate the gateopening event. A sample of **1B** was subjected to vacuum for the first data collection and then loaded with CO_2 in steps of 5 bar (all at ambient temperature). The structure remains unchanged over the pressure range 0-25 bar. However, between 25 and 30 bar there are clear changes in the PXRD pattern, indicating a phase transformation.

A comparison of the PXRD traces for **1B** under vacuum (Figure 3b) and of the same sample exposed in situ to 50 bar CO_2 (Figure 3d) shows that **1B** transforms, at least partially, to **1C** under CO_2 pressure. The gate-opening (or breathing)²⁰ event appears to be a transformation from **1B** to an open form that is a metastable frustrated variant of **1C**.



Figure 3. Comparison of (a) the calculated PXRD trace of 1B from singlecrystal diffraction data with (b) the experimental trace of a sample of 1B under vacuum, (c) the calculated trace of 1C and (d) the experimental trace recorded for the sample exposed *in situ* to 50 bar CO₂ pressure.

The phase transformation to an open form is consistent with the definition of MOF breathing by Schneemann et al: "(reversible) transitions of metal-organic frameworks, during which the (substantial) displacement of atoms of the framework is accompanied by a change in unit cell volume ($\Delta V \neq 0$). Characteristic distances and angles of the unit cell change and the crystallographic space groups of the two distinct phases ... may be different."²¹ Reversibility is evident from the CO2 sorption and desorption isotherms in Figure 2 as well as from the PXRD pattern (Figure S13) recorded after multiple sorption-desorption cycles.

Figure S17 shows the CO₂ sorption isotherm for **1** together with those reported for MIL-53(Cr) hydrate^{20a} and COMOC-2^{20b} for qualitative comparison. The total sorption capacities for MIL-53(Cr) and **1** are comparable although **1** reaches equilibrium at higher pressure. In contrast to MIL-53(Cr), where selectivity of CO₂ over CH₄ is dependent on hydration of the framework,^{20a} **1** shows comparatively high selectivity in its guest-free state. Both COMOC-2 and **1** retain CO2 over a remarkably large pressure range during desorption.

We used pressure-resolved differential scanning calorimetry (P-DSC) to investigate repeated cycling and its effect on the sorption capacity of 1. We were thus able to obtain data for 13 sorption-desorption cycles over a period of 13 days, whereas the standard method of recording multiple sorption isotherms would have taken an estimated 50 days or more. The instrumental setup comprises a differential scanning calorimeter coupled to a gas syringe pump (details in ESI). The syringe pump is controlled by a computer programme to ensure delivery of a constant pressure gradient to the sample and reference chambers. The P-DSC output yields a thermogram of heat flow vs pressure (Figure S18) and from these data we derived plots of integral heat vs pressure for each sorption cycle (Figure S19). The first cycle is omitted for reasons described below. The integral heat is proportional to sorption loading and the profile of the integral heat vs pressure plot is thus a reliable approximation of expected sorption isotherms.

The maximum integral heat (proportional to the maximum sorption loading) was plotted against sorption-desorption cycle number to reveal systematic deterioration in sorption capacity with extended cycling (Figure 4). For all of the cycles, the gateopening event occurs with an onset pressure of approximately 20 bar. However, the response to pressure, as evident from the sorption thermogram above this value, does not follow the same trend for cycle 1 as for subsequent cycles (Figure S18). This implies that the first sorption experiment conditions the sample for subsequent gas inclusion - i.e. a 'memory' effect. Thus cycle 1 has been omitted from our analysis of the systematic decline in sorption capacity (Figure S19). The fitted curve in Figure 4 tends to a final value of 61.92 J g⁻¹ from an initial value of 160.35 J g⁻¹ (details in ESI), implying that the sorption capacity of the material will ultimately be reduced to approximately 39% of its initial value.

Although no appreciable loss of crystallinity was evident from PXRD analysis of **1** after 13 sorption/desorption cycles (Figure S13), subtle peak broadening occurs and we believe that partial sample degradation is responsible for the reduction in sorption capacity. Hupp and co-workers have described a robust paddle-wheel type MOF that maintains its sorption capacity through several sorption/desorption cycles.²² They suggest that, in contrast, most MOFs that display dynamic sorption tend to lose uptake capacity because of extreme strain on coordination

bonds, leading to bond breakage. However, we were not able to locate reported examples of this phenomenon for breathing MOFs. Kitagawa and co-workers described the effect of crystal downsizing, providing experimental to support the assertion that "reduction in the number of repeating units should be sufficient to regulate the cooperative nature of [structural transformations] and the effect of stress."²³ We postulate that the reduction in particle size in a sample of **1** with repeated fracturing of crystallites finally results in a particle size for which the stress induced by breathing is minimised. The mechanical degradation of particles of **1** is evident in the SEM images in Figure S20.



Figure 4. The maximum integral heat from pressure-DSC plotted against the cycle number of CO_2 sorption-desorption.

Direct activation of **1A** results in a loss of framework integrity, leaving **1** unusable for gas sorption. On the other hand, activation *via* solvent exchange not only preserves framework integrity but yields a collapsed phase **1B**, which exhibits gated breathing with relatively high uptake of CO_2 . We have provided direct structural evidence of the difference between **1B** and **1C**, obtained by different activation methods. Our analysis of the effects of repeated CO_2 sorption-desorption cycling for **1** reveals a systematic decline in sorption capacity, suggesting that cycling effects may need to be investigated more routinely where MOFs, and particularly flexible MOFs, are proposed as industrial molecular storage and separation materials.

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