

Superior Metal–Organic Framework Activation with Dimethyl Ether

Keenan R. Wright, Karabi Nath, and Adam J. Matzger*

Abstract: Metal–organic frameworks (MOFs) are demonstrated to be readily activated by treatment with the low surface tension, low boiling point solvent dimethyl ether (DME). The mildness of the method enables access to high surface areas by avoiding structural changes in the framework that often plague thermal activation methods. A distinction from previous methods is that DME activation succeeds for materials with coordinatively unsaturated sites (CUS) and non-CUS MOFs as well. DME displaces solvent molecules occupying the pores of the MOF as well as those coordinated to metal centers; reducing evacuation temperature by using a coordinating, yet highly volatile guest enables low temperature activation with structural retention as demonstrated surface area measurements that match or exceed existing activation protocols.

Porosity is central to most applications of metal–organic frameworks (MOFs). To access pores for gas adsorption, MOFs must undergo removal of the synthesis solvent. Known as activation, this process usually involves two steps. The first step is solvent exchange, where a high boiling point, often high surface tension solvent, is exchanged from the pores of the MOF for a lower boiling point and lower surface tension solvent.^[1] This process typically involves multiple exchanges with solvent choice depending on the fragility of the MOF. Process cost and environmental impact depend on this step of activation because the solvent volume used here often exceeds that used in MOF synthesis. The second step in activation requires solvents to be evacuated, usually using a combination of dynamic vacuum (mTorr range) and elevated temperature to remove solvent present inside the pores and, depending on the MOF, coordinated to metal centers. During evacuation, heating is typically required to complete solvent removal; however, damage to

MOF structural integrity and collapse can occur (Figure 1a), which is especially challenging for fragile frameworks with high potential surface areas.^[2–4] These challenges motivate reducing the number of exchange steps needed and the use of milder evacuation conditions: a delicate balance that can be potentially reached through judicious selection of activation solvent. Ideally, an activation solvent would allow for direct exchange from the synthesis solvent and have a low enough boiling point to be removed at temperatures as close to room temperature as possible.

MOFs with coordinatively unsaturated sites (CUS) are promising candidates for many applications including hydro-

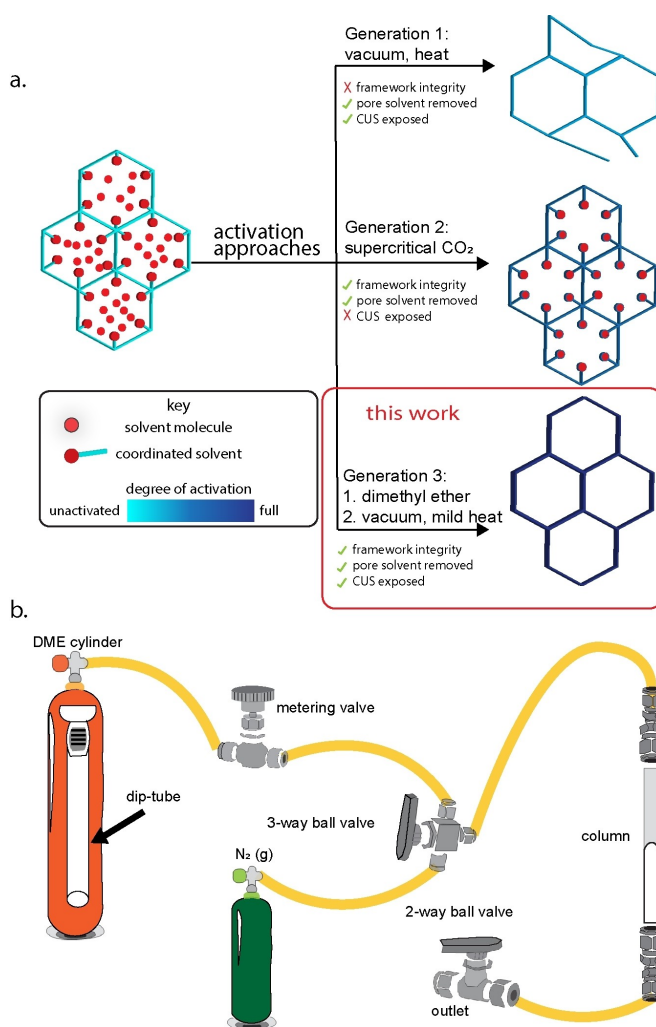


Figure 1. a) Comparison of current activation methods and the method introduced in the present study and b) schematic of dimethyl ether (DME) activation apparatus.

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gen storage and catalysis.^[5-7] CUS MOFs contain metal sites that are not bound to molecules, when fully activated, allowing direct binding of solvents and gases based on their affinity (a property tunable through metal choice); however, the challenge with CUS MOFs is activation. The same feature that makes them interact strongly with guest molecules are precisely the reason for the difficulty they present in activation: the metal sites are high affinity binding locations for dative ligands of all types.^[8] For highly porous CUS MOFs there are all the same concerns as non-CUS MOFs as well. If high surface tension solvents are employed, the pores can collapse due to capillary forces.^[9-12] The method to overcome this is well understood to be exchange with low boiling point and low surface tension solvents.^[13] The ultimate demonstration of this approach is supercritical fluid exchange using CO₂.^[10,14,15] The limitation when applying this approach to CUS MOFs is that CO₂ is too weak of a ligand to remove solvents directly bound to the metals, and therefore CUS exposure is incomplete (Figure 1a). To overcome this problem, we propose using dimethyl ether (DME) as an activation solvent because of its very low boiling point (−24 °C) which will make evacuation facile.^[16-19] Moreover, the surface tension of DME (12 mNm^{−1}) is much lower than commonly used activation solvents such as CH₂Cl₂, acetone, DMF, minimizing capillary forces during solvent removal. We propose that DME can displace solvent that is adsorbed in the pores as well as solvent coordinated to the framework. From an industrial perspective, DME is an inexpensive gas and the lab scale DME exchange apparatus (Figure 1b) can be fabricated for ≈\$100 which is a considerable improvement when compared to the ≈\$10 K critical point dryer^[14] or the more effective \$30 K flowing supercritical activation system.^[15]

MOF-5^[20] was chosen as a representative system for non-CUS MOFs to test the functional compatibility with and displacement of solvent in pores directly without the need for intermediate solvent exchange steps. Activation of MOF-5 with DME at room temperature (Figure S12 in Supporting Information) yielded a material with an average BET surface area of (3400 ± 50) m²g^{−1}, consistent with full activation.^[13] This result demonstrates that DME can directly displace dimethylformamide (DMF) in the pores (Figure S1 in Supporting Information) and degradation due to impurities in DME is not significant.^[21] Encouraged by our results for a non-CUS microporous MOF, DME activation was applied to a mesoporous system. For this demonstration Cu-DUT-23^[22] was chosen because it is a mesoporous MOF, previously activated by supercritical CO₂. After performing DME activation the average surface area is 3047 m²g^{−1} a value somewhat lower than supercritical CO₂ activation (Figure S19 in Supporting Information).

With success demonstrated for both microporous and mesoporous non-CUS MOFs, attention was turned to HKUST-1. This MOF is a model system for CUS MOFs due to its copper paddlewheel secondary building unit (SBU) in which four carboxylates are bound equatorially to the Cu₂ dimer and, when activated properly, there are two open copper sites in the axial positions of the SBU. What makes

HKUST-1 challenging to fully activate is that solvent molecules coordinate on the copper sites. HKUST-1 was first reported in 1999^[23] and synthesized in a solvent mixture of DMF:ethanol:water with a surface area of 695 m²g^{−1}. About twenty years later, the upper limit for surface area has risen to ≈2000 m²g^{−1}^[24] and this slow evolution to achieve high surface area is consistent with the complexities of achieving full activation of CUS MOFs.^[24] The higher surface areas have been achieved when activating from methanol (MeOH);^[25] however, high temperature (≈200 °C) is required for complete guest evacuation and overcoming the strong coordination of solvent remains a challenge.

To assess the effectiveness of DMF displacement by DME and to test binding affinity of DME to Cu, DME removal from HKUST-1 was probed with thermogravimetric analysis coupled to infrared spectroscopy (TGA-IR). TGA is advantageous for two reasons: (i) it distinguishes between bound and unbound solvent molecules for CUS MOFs and (ii) it places an upper limit on the temperature required to remove solvent from the MOF. IR spectroscopy identifies residual solvent after exchange, which informs if DMF remains after a single wash, and therefore additional DME exchanges are required. Additionally, the DME exchanged samples were digested and analyzed by Nuclear Magnetic Resonance (NMR) spectroscopy to quantify residual DMF in the MOF and the corresponding percentage of DMF-coordinated metal centers in HKUST-1.

As synthesized HKUST-1 was washed 3 times in fresh DMF to fully exchange the MOF into DMF and remove residual starting reagents. The MOF was analyzed by TGA; a dramatic decrease in the mass at temperatures between 25–100 °C is associated with DMF in intercrystalline regions or weakly held inside of the pores (Figures S9 in Supporting Information). At temperatures above 250 °C an acceleration in mass loss is observed indicating that coordinated DMF evolves from the MOF.

After 1 hour of DME exchange, HKUST-1 was analyzed by TGA-IR. A relatively constant rate of mass loss occurs until 125 °C (Figure 2). This corresponds to DME inside of the pores evolving. Relatively little change occurs at temperatures between 125 °C and 250 °C; however, a second drop in

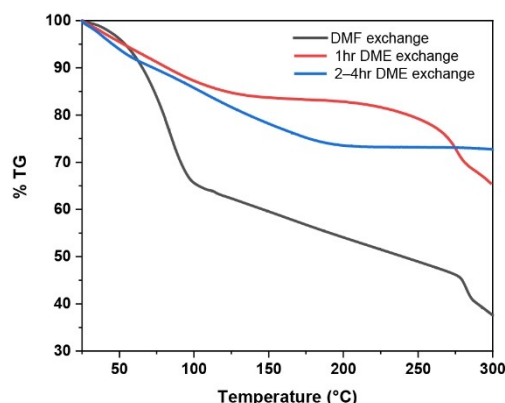


Figure 2. TGA of DMF and DME exchanged HKUST-1 from room temperature to 300 °C.

mass is observed at temperatures above 250 °C associated with DMF (Figure 2) coordinated to the Cu^{II} sites. This temperature corresponds closely to the more tightly bound DMF when TGA-IR is conducted on HKUST-1 exchanged for 1-hour in DME (see Figure S7 and S10 in Supporting Information). Digesting this MOF after 1 hour of DME exchange corresponds to 15 % of Cu^{II}^[26] still being coordinated to DMF (Figure S2 in Supporting Information). These results justify longer exchange times and/or multiple exchange steps to fully displace DMF.

Observing incomplete exchange after 1-hour of DME incubation, two washes with DME (over 8 hours) on HKUST-1 were performed to more fully displace DMF. The TGA trace shows an initial drop in mass that slows slightly above 50 °C (see Figure S11 in Supporting Information). The IR spectrum at all temperatures confirms DME evolution (Figure S8 in Supporting Information). Further into the experiment, no significant change in mass is found at temperatures greater than 175 °C (Figure 2), indicating that all solvent is removed. This contrasts with the 1-hour exchange wherein at 175 °C DMF remains. After the two DME exchanges, the MOF was digested for NMR analysis and 3 % of copper coordinated to DMF (see Figure S3 in Supporting Information).

To displace DMF in HKUST-1, two exchanges with DME and heating were employed (see Figure 3 and Activation Protocol in Supporting Information). With CUS MOFs, higher temperatures are often required to remove coordinated solvent. This is operationally disadvantageous and degrades thermally sensitive MOFs. Experiments were targeted at activating the MOF at different temperatures (RT, 60, 100, 120 °C) to find the lowest temperature that can be used to obtain high surface area. The overlay of nitrogen adsorption isotherms shows that nitrogen uptake, corresponding to accessible pore volume, increases as activation temperature increases consistent with more complete guest removal (Figure 3). At 120 °C, a surface area of 1900 m²g⁻¹ is accessed, which is near the upper limit of surface areas for

HKUST-1 (further heating to 200 °C did not lead to higher surface area). While heating is required, it is important to note that temperatures 50–80 °C less than conventional practice achieved activation, which is promising for thermally sensitive MOFs. Because other ethers have low surface tensions and boiling points, we performed exchange and activation of HKUST-1 using diethyl ether (DEE) to compare the degree of activation. Longer exchange times are required to displace only a fraction of DMF and the resulting surface area is below 1000 m²g⁻¹.

Two thermally sensitive MOFs were activated using the developed DME activation method: UMCM 151^[27] and DUT-34.^[22,28] Activating UMCM-151 from acetone yields a BET surface area of 263 m²g⁻¹, activation by supercritical CO₂ yields a surface area of 455 m²g⁻¹; however, by employing DME, a BET surface area of 950 m²g⁻¹ is obtained (Figure 4 and Figures S5, S14, S15, and S16 in Supporting Information). The shape of the isotherm changes dramatically consistent with collapse when activating from acetone. DUT-34 is a copper paddle-wheel MOF for which the surface area has not been reported in the literature, a common occurrence for thermally sensitive MOFs. Supercritical CO₂ activation was performed, and a surface area of 744 m²g⁻¹ was obtained (See Figure S17 in Supporting Information). Through DME activation, a surface area of ≈1600 m²g⁻¹ is reached (Figures S6 and S18 in Supporting Information). Activating UMCM-151 and DUT-34 at room temperature demonstrates the mildness and ease of solvent evacuation using DME being able to achieve high surface areas where all previous approaches fail.

Although copper paddlewheels are the most common SBU for CUS MOFs, there are many other SBUs and metals that are used to construct MOFs. For example, MOF-74 contains an infinite rod SBU and can be synthesized using different metals (including Co, Ni, Mg, Zn)^[29,30] each with its own adsorption affinity for solvents and gases. To activate MOFs with this SBU, the DME exchange and

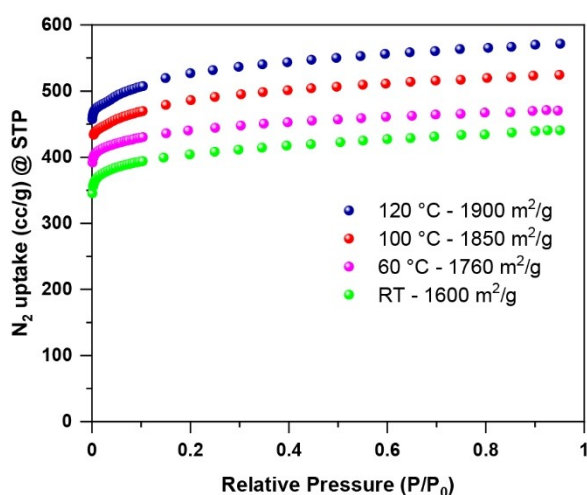


Figure 3. Nitrogen adsorption isotherm of DME exchanged HKUST-1 at different activation temperatures.

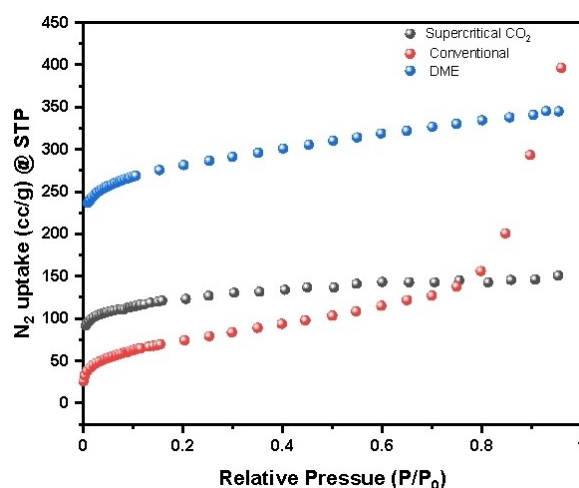


Figure 4. Nitrogen adsorption isotherms of UMCM-151 activated by supercritical CO₂, conventional solvent exchange, and DME.

evacuation method developed with HKUST-1 was applied to MOF-74 made with Mg and with Zn.

Mg-MOF-74 exhibits exceptional CO₂ adsorption affinity at ambient temperatures and low pressures relevant to flue gas applications;^[32,33] however, the coordination to DMF (residual from synthesis) and MeOH presents a challenge for complete activation. In the case of Mg-MOF-74 the MOF was first exchanged into MeOH, to remove residual synthesis solvent, and then activated from DME at 120 °C. An average BET surface area of 1575 m²g⁻¹ was achieved (Figure 5) which matches well with fully activated material made by heating at 270 °C under vacuum.^[30] In the case of Zn-MOF-74, this MOF has a reported BET surface area ranging from 800–1100 m²g⁻¹ which is lower than its theoretical surface area of 1336 m²g⁻¹.^[31] Part of this gap in accessible surface area is due to potential collapse, or the presence of residual coordinated solvent after activation. When activating this MOF by supercritical CO₂, an additional vacuum and heating step at 270 °C is required to remove coordinated solvent.^[15] Under these activation conditions a surface area of 1119 m²g⁻¹ has been accomplished.^[15] While this result is an improvement over the reported surface area of ≈800 m²g⁻¹,^[32–34] supercritical CO₂ only clears solvent molecules from the pores with the subsequent heating step required to remove coordinated strongly solvent molecules. Using DME, both the unbound and bound guest molecules are displaced (See Figure S4 in Supporting Information), and evacuation yields a reproducible surface area higher than supercritical CO₂ at a temperature of 120 °C (150 °C less than conventional): 1250 m²g⁻¹ (Figure 5 and Figure S13 in Supporting Information). These results further support DME as an activation solvent that can maximize performance for CUS MOFs with different SBUs.

The functional capability of DME is demonstrated of MOF activation for both non-CUS and CUS MOFs using liquid DME and relatively low evacuation temperatures. Under the same protocol, microporous MOFs with different SBUs have been activated with surface areas that meet or exceed literature values (see Table 1 in Supporting Informa-

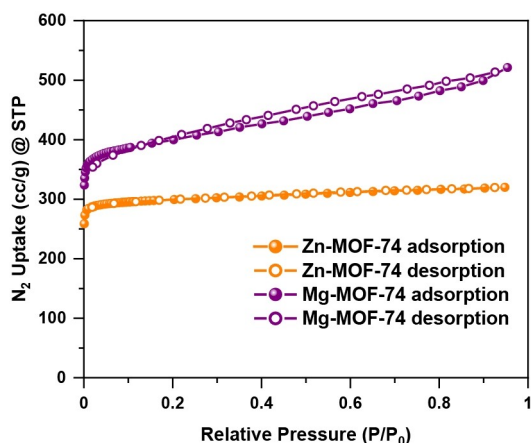


Figure 5. Nitrogen adsorption isotherm of DME exchanged MOF-74 (Zn and Mg) activated at 120 °C.

tion for comparison of pore volumes). Moreover, these results are achieved with mild activation conditions. These data further support the previous work that ultralow surface tension, low boiling point solvents allow for milder activation conditions^[1] but now enable activation of the challenging class of MOFs with coordinatively unsaturated metal centers. This is expected to become the method of choice for activating MOFs displaying surface areas below theoretical values.

Acknowledgements

The authors would like to acknowledge the financial support of the United States Department of Energy BES Grant no. (DE-SC0004888). K.R.W. would like to also acknowledge the Rackham Graduate School, Gates M.S.P., and Sachs Foundation for additional support. K.R.W. would like to acknowledge Roy Wentz for creating the glassware for experiments.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the Supporting Information of this article.

Keywords: Coordination Chemistry · Metal–Organic Frameworks · Microporous Materials · Structural Collapse · Surface Area

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Manuscript received: September 6, 2022

Accepted manuscript online: November 2, 2022

Version of record online: November 23, 2022