Title: Rapid Guest Exchange and Ultra-low Surface Tension Solvents Optimize Metal-organic Framework Activation

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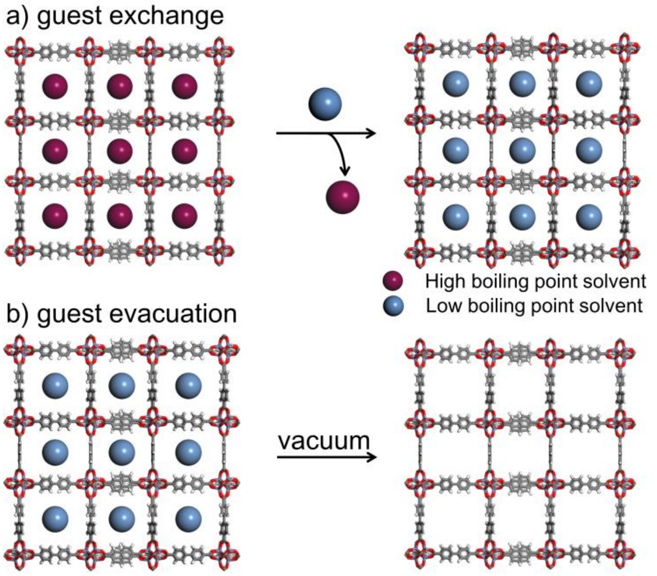
Rapid Guest Exchange and Ultra-low Surface Tension Solvents Optimize Metal-organic Framework Activation

Jialiu Ma, Andre P. Kalenak, Antek G. Wong-Foy and Adam J. Matzger*[a]

Abstract: Exploratory research into the critical steps in metal-organic framework (MOF) activation involving solvent exchange and solvent evacuation are reported. It is discovered that solvent exchange kinetics are extremely fast, and minutes rather days are appropriate for solvent exchange in many MOFs. It is also demonstrated that choice of very low surface tension solvent is critical in successfully activating challenging MOFs. MOFs that have failed to be activated previously can achieve predicted surface areas provided that lower surface tension solvents such as n-hexane and perfluoropentane are applied. The insights herein aid in the efficient activation of MOFs in both laboratory and industrial settings and provide best practices for avoiding structural collapse.

Porous materials, including carbons, zeolites, and certain coordination polymers, often require regimens of chemical, thermal, and/or pressure treatment to achieve their highest levels of surface area[1]. Such processes are collectively termed ‘activation’ and the details of these processes are particularly important for metal-organic frameworks (MOFs);[2] nonporous materials are often obtained if, after synthesis, the solvent (guest) is not removed properly.[3] Synthesis of MOFs is typically carried out solvothermally in high boiling point formamide solvents such as N,N-dimethylformamide (DMF), N,N-diethylformamide (DEF), N-methyl-2-pyrrolidone (NMP) or in dimethylsulfoxide (DMSO) and rarely can the high inherent porosity of the material be accessed by direct evacuation to remove these solvents. Despite progress in developing new strategies for guest removal,[4] it is frequently reported that after activation, MOFs show broadened powder X-ray diffraction (PXRD) patterns (compared to solvent filled ones) and lower surface areas and pore volumes compared to those calculated from single crystal X-ray structures.[5] Furthermore, considerable variations in surface area and gas storage properties pervade the literature even for well-established MOFs.[6] When such discrepancies are encountered they are often ascribed to ‘incomplete activation’ and attributed to capillary forces leading to partial or full structural collapse.[7] To address such discrepancies, it is necessary to understand the nature of activation; insights into this process and best practices for MOF activation form the content of this communication.

Current activation strategies are largely empirical in nature and rely on two steps to remove guest molecules: guest exchange and guest evacuation (Scheme 1).[8] The approach, first established to reveal the permanent porosity in MOF-5,[4d] involves submerging MOFs into low boiling point solvents such as CH_2Cl_2, $CHCl_3$ and CH_3OH (guest exchange) for days, replacing the solvent multiple times each day before vacuum evacuation (guest evacuation). If this conventional activation method fails to generate theoretical surface areas, another milestone discovery - supercritical CO_2 ($scCO_2$) processing - has been demonstrated to be extremely useful in unveiling a MOF’s true porosity, especially highly porous Zn-based MOFs.[4a, 9] Though the protocols have been widely performed and work successfully for many MOFs, how key factors such as solvent exchange time and the number of solvent washes influence outcome are unknown. With regard to the evacuation step, the type of solvent and the rate of guest evacuation also require further exploration to understand their roles in the activation process. Understanding these factors is critical, especially when empirical protocols fail to activate challenging MOFs and further tuning of these factors is necessary to achieve the highest surface area. Moreover, as the desire to transition more MOFs to industrial scale mounts, efficiency in activation protocol will have a pivotal effect on the economics of production.[10]



Scheme 1. (a) Guest exchange in MOFs from high boiling point to low boiling point solvent. (b) Guest evacuation to remove solvent from MOFs by vacuum.

Solvent exchange in Zn_4O based MOFs[11] is generally conducted on timescales ranging from hours to days in various established solvent exchange procedures, a suggestion of a slow kinetic process. However, slow exchange is not consistent with our observations on solvent exchange of, for example, UMCM-9 (Zn_4O(naphthalene-2,6-dicarboxylate)$_{1.5}$(biphenyl-4,4’-dicarboxylate)$_{1.5}$), a highly porous mixed-linker Zn_4O based MOF.[12] During our experiments in exchanging solvent from DMF to CH_2Cl_2 for UMCM-9, as synthesized crystals were found to float upon addition of CH_2Cl_2. Almost immediately, the crystals begin to sink back to the bottom on the timescale of seconds and with a rate that is slower for larger crystals (Figure 1a and video in Supporting Information). Such behavior indicates a fast

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guest exchange process wherein DMF (density=0.94 g/cm^3) molecules are replaced by CH_2Cl_2 (density=1.43 g/cm^3) causing a dramatic density increase for the UMCM-9 crystals. To confirm the hypothesis of fast kinetics observed in solvent exchange, we focused on MOF-5 (Zn_4O(benzene-1,4-dicarboxylate)$_3$) because its limiting pore aperture (8 Å) is larger than most solvent molecules; in addition MOF-5 has been made in labs around the world using established procedures. To perform real-time monitoring of solvent exchange, ~50 mg of MOF-5 crystals (300-500 µm in diameter) soaked in DMF were collected by filtration and transferred into a 5 mm NMR tube. After introducing 600 µl of CH_2Cl_2 to the NMR tube to mimic the solvent exchange process, the solution was monitored using ^{1}H-NMR spectroscopy (no sample spinning) where a spectrum was taken every 30 s over a 20 minute period (Figure 1b). The DMF signal (corresponding to DMF exiting the MOF and equilibrating with the exchange solvent) increases steadily in the first 5 min and after 10 min a plateau is reached (Figure 1c); monitoring for up to 3 hours reveals no further concentration change. A second solvent exchange was also performed where the previously exchanged CH_2Cl_2 was decanted before another 600 µl of fresh CH_2Cl_2 was replenished; this mimics the common practice of multiple washes in MOF solvent exchange protocols. The DMF signal increases steadily and after 20 min the change is insignificant (Figure 1d).

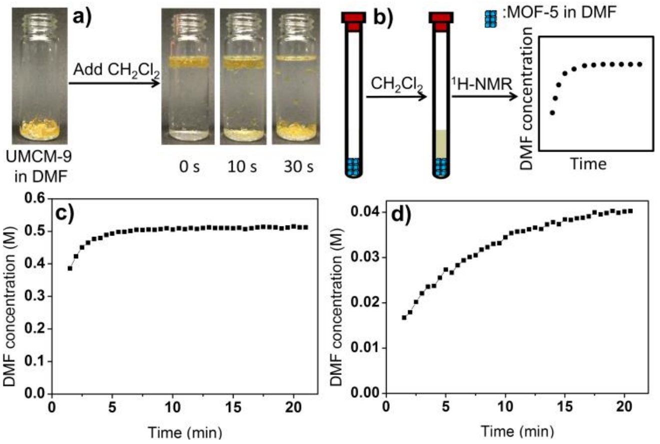

Figure 1. (a) Images of UMCM-9 in DMF exchanged into CH_2Cl_2. Crystals were found to float (0s) and then sink back to the bottom (10s) completely (30s). (b) ^{1}H-NMR spectroscopy monitoring of the amount of DMF diffusing into CH_2Cl_2 during the (c) first and (d) second solvent exchange process of MOF-5.

The fast kinetics of solvent exchange in MOF-5 is clear from the above experiments; however, if there are some more tightly held solvents the completeness of exchange may not be well reflected.[13] Thus MOF-5 was subjected to N_2 isotherm measurement and digestion after each solvent exchange to determine the influence of the exchange protocol on surface area. Approximately 40 mg of MOF-5 was exchanged with 10 mL CH_2Cl_2 for 1, 2 or 3 times (each exchange conducted for 20 min) before evacuation and N_2 isotherm measurement. The activated MOF-5 crystals were further digested under acidic conditions to determine the DMF content. The results are shown in the Table S1, Figure S4 and Figure S6. After only one exchange, the DMF concentration is reduced to 0.78 DMF molecules per unit cell in MOF-5 and exhibits a BET surface area of 2650 ± 20 m^2/g. The DMF content is further reduced to 0.12 molecules per unit cell after two exchanges with a higher surface area of 3410 ± 30 m^2/g. After three solvent exchanges, a surface area of 3640 ± 40 m^2/g, matching the theoretical value (3527 m^2/g), is obtained with only 0.014 DMF molecules detected per unit cell. Thus the completeness of exchange after multiple short timescale exchanges is confirmed. These observations are echoed by experiments with IRMOF-2, the brominated analog of MOF-5, a compound with slightly smaller pores and additional solvent interacton sites.[14] Though both of these factors would be expected to slow exchange kinetics, the effect is minor (Figure S3) and rapid exchange occurs.

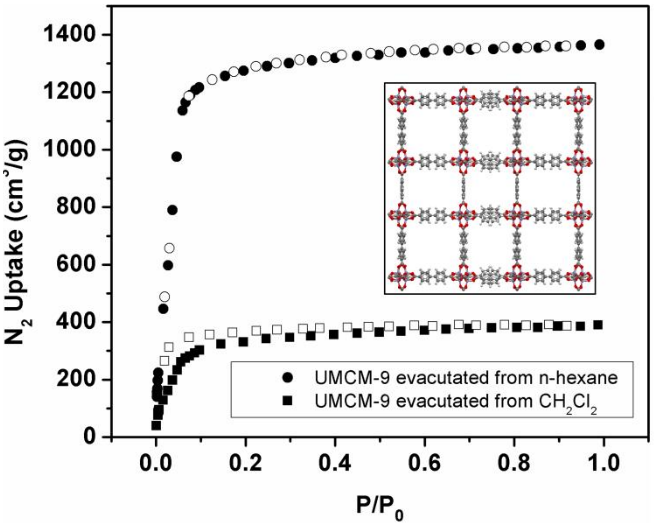

Figure 2. N_2 isotherm plots of UMCM-9 activated from n-hexane and CH_2Cl_2 exchanged materials. Inset: Structure of UMCM-9 (Zn_4O(naphthalene-2,6-dicarboxylate)$_{1.5}$(biphenyl-4,4'-dicarboxylate)$_{1.5}$).

Armed with an understanding of the timescale for solvent exchange, we turned our attention to guest evacuation in MOFs. If capillary forces caused by surface tension are indeed the major contributor to these failures,[15] structural collapse may be avoided by filling the pores with ultralow surface tension solvents via exchange before evacuation, providing a convenient alternative solution to $scCO_2$ for the activation of extremely fragile MOFs. To test this hypothesis, we attempted to activate a Zn_4O-based MOF, UMCM-9 that has previously failed to be activated by the conventional solvent exchange method. UMCM-9 was reported to show partially collapsed structure when evacuated from material completely exchanged in CH_2Cl_2 and a low surface area of 1330 m^2/g. Only by applying the flowing $scCO_2$ method, a surface area of 4970 m^2/g was achieved, matching the theoretical value of 4900 m^2/g.[12] The solvent n-hexane was chosen as the exchange medium due to its low surface tension (17.9 mN/m) compared to CH_2Cl_2 (27.2 mN/m). UMCM-9 was fully exchanged with n-hexane (through a two-step exchange procedure due to the immiscibility of DMF and n-hexane, see experimental section for details) before evacuation and a high surface area of 4980 ± 50 m^2/g was obtained (Figure 3).[16] Furthermore, no structural changes after activation of UMCM-9 were found by powder X-ray diffraction analysis (Figure S7). It should be noted that exchange of all loosely bound solvent is possible by this procedure, but for MOFs with coordinatively unsaturated metal sites, heating under vacuum may be required for full activation.[17] This is also true for MOFs activated by $scCO_2$.[4b]

Solvent evacuation rate is known to affect porosity in some classes of materials.[18] However, as commonly practiced in MOF activation, the solvent evacuation rate uncontrolled and the impact of this factor on MOF activation is unknown. To investigate this activation variable, controlled evacuation of hexane from UMCM-9 was carried out at three rates: 380 torr/h, 9,990 torr/h and >225,000 torr/h (Figure S11). A two-step procedure was applied to evacuate ~40 mg of UMCM-9 wherein the pressure was reduced from atmospheric pressure (760 torr) to 1 torr at the specified rate and then maintained under a dynamic vacuum (~0.05 torr) for another 2 hours before N_2 isotherm measurement. The activated materials all demonstrated full surface area indicating evacuation rate does not impact surface area (Figure S12).

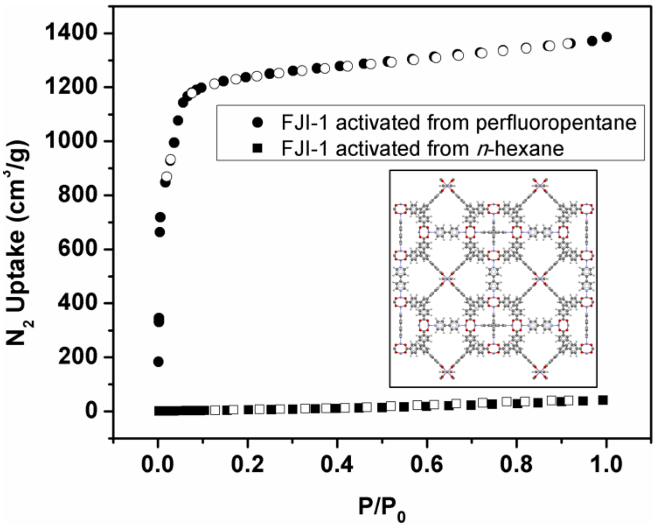

Figure 3. N_2 isotherm plots of FJI-1 activated from perfluoropentane and n-hexane exchanged materials. Inset: Structure of FJI-1 (Zn_2(benzene-1,3,5-tribenzoate)$_{4/3}$(4,4'-bipyridine)).

When expanding the scope of the conventional solvent exchange activation method to more delicate MOFs, further tuning of solvent surface tension is needed to avoid structural collapse as demonstrated below in the activation of a fragile Zn paddle-wheel ($Zn_2(CO_2R)_4$) based MOF, FJI-1.[19] FJI-1 was reported to amorphatize when evacuated from CH_2Cl_2 exchanged materials. Following the success in activation of UMCM-9, n-hexane was applied as the exchange medium in FJI-1 prior to evacuation. However, only negligible surface area (<100 m^2/g) was observed (Figure 4). Nevertheless, n-hexane is already one of the lowest surface tension solvents commonly found in a lab setting. To achieve even lower surface tension at room temperature and atmospheric pressure, we turn to fluorocarbons. Perfluoropentane possesses a surface tension of 9.42 mN/m. When FJI-1 is exchanged completely in perfluoropentane (see Supporting Information Section 6 for details) and then evacuated, the activated material shows a high BET surface area of 4890 ± 50 m^2/g, which matches well with the theoretical surface area (4741 m^2/g) and the state of art $scCO_2$ flowing processing (4813 m^2/g) (Figure 4).[4b] Powder X-ray diffraction analysis also confirmed the obtained phase matches with the crystal structure (Figure S8).

In this paper, we have shown that the solvent exchange process is rapid and that minutes rather than days are appropriate for solvent exchange in many MOFs. Lower surface tension solvents such as n-hexane and perfluoropentane are found to create much milder activation conditions during vacuum application and thus lead to better preserved MOF surface area and porosity. Finally we note that $scCO_2$ activation may not be required for the vast majority of MOFs. Practices such as shorter solvent exchange time and ultralow surface tension solvent should be regarded as the best practices in the field before claiming that conventional activation fails for a given material.

Experimental Section

Activation procedure for UMCM-9: UMCM-9 (~40 mg) initially washed with DMF (3 × 20 mL) was first exchanged with CH_2Cl_2. The crystals were soaked in 20 mL of CH_2Cl_2 3 times over 1 hour (20 minutes each). The crystals were then immersed in 20 mL of dry n-hexane over 1 hour replacing the solvent every 20 minutes. Once the solvent exchange is complete, the material was isolated by decanting the n-hexane and the crystals were evacuated under dynamic vacuum (0.05 torr) for 2 hours at room temperature before N_2 isotherm measurement.

Acknowledgements

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Keywords: Metal-organic framework • Microporous materials • Activation • Surface tension

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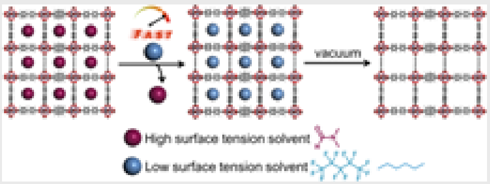
COMMUNICATION



Keeping it open: Activation involving solvent exchange and evacuation is crucial to achieve maximum surface area and gas storage properties in metal-organic frameworks (MOFs). Porosity is preserved when fast solvent exchange kinetics and ultra-low surface tension solvents are exploited yielding MOFs without structural collapse.

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