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Monolithic metal-organic frameworks for carbon dioxide separation

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Carbon dioxide (CO₂) is both a primary contributor to global warming and a major industrial impurity. Traditional approaches to carbon capture involve corrosive and energy-intensive processes such as liquid amine absorption. Although adsorptive separation has long been a promising alternative to traditional processes, to this point, there has been a lack of appropriate adsorbents capable of capturing CO₂ whilst maintaining low regeneration energies. In this context of CO₂ capture, metal-organic frameworks (MOFs) have gained much attention in the past two decades as potential materials. Their tuneable nature allows for exquisite control over pore size and chemistry, which allows for tailoring of their properties for selective adsorption of CO₂. While many candidate materials exist, the amount of research into materials shaping for use in industrial processes has been limited. Traditional shaping strategies such as pelletisation involve the use of binders and/or mechanical processes, which can have a detrimental impact on the adsorption properties of the resulting materials or can result in low-density structures with low volumetric adsorption capacity. Herein, we demonstrate the use of a series of monolithic MOFs (monoUio-66, monoUio-66-NH₂ & monoHKUST-1) for use in gas separation processes.
Introduction

Anthropogenic emissions of carbon dioxide (CO$_2$) are accepted as a significant risk to the global climate. The atmospheric CO$_2$ concentration has surpassed 400 ppm on several occasions since 2013, which represents an increase of over 100 ppm since pre-industrial revolution levels.$^1$ Carbon capture will be a crucial technology in achieving carbon neutrality by 2050.$^2$ While clean technologies such as wind and solar power will play a major role in energy provision over the coming decades, increasing energy demands dictate that fossil fuels will remain a key component of the global energy system into the second half of the century.$^3$ Additionally, CO$_2$ represents a significant impurity in industrial processes and its removal from important gases such as methane (CH$_4$) can help improve the overall quality of pipeline grade natural gas (NG). The upgrading of alternative forms of CH$_4$ such as biogas and landfill gas to produce biomethane is also an incredibly attractive source of renewable NG that, once purified, can be pumped directly into the national grid. The development of next-generation carbon capture and sequestration (CCS) technologies in the coming decades will be imperative in the fight against global climate change.

To date, CCS has been hampered by high costs (>100 US$/t CO$_2$ captured) and techno-economic uncertainties of liquid amine-based technologies.$^4$ Liquid amine-based CCS technologies have been around for over half a century. However, liquid amine chemical capture relies upon chemical reactions and is energy-intensive, therefore reducing the overall efficiency of a power plant by up to 40%.$^5$ Additionally, liquid amines are volatile and prone to foaming, leading to corrosion of industrial equipment. Liquid amines are thus not economically viable and offer little room for innovation. With the advent of the 2015 Paris agreement,$^6$ there has been a political shift towards reducing CO$_2$ emissions globally. In particular, Canada announced recently a direct tax on carbon emissions of at least 10 C$/t$, rising by 10 C$/t per year until it reaches 50 C$/t by 2022.$^7$ At 50 C$/t, this will significantly improve the competitiveness of CCS technologies. Similar ambitious CO$_2$ emissions reduction targets have been set in Europe and, right now, it is required a new approach to CCS technologies, since renewable and new energy technologies alone will be unable to sustain the growing demand for energy in Europe. This requires a new paradigm for CCS technologies that will fundamentally improve the environmental footprint environmental and cost effectiveness of CSS technologies.

As an alternative to traditional amine-based technologies, solid adsorbents represent a viable alternative for the next generation of low-temperature CCS technologies. To date, much of the research into solid adsorbent based CO$_2$ capture has focused on traditional porous materials such as zeolites, activated carbons and amine-modified silicas.$^7$-$^{11}$ While significant progress has been made, there are many drawbacks to these materials. In the case of zeolites and activated carbons, these materials lack the tuneability and chemical functionalities to improve important process parameters...
such as chemical interactions, selectivity and hydrophobicity, giving way to high CO₂ capture costs as a result of low working capacities and high regeneration costs. Similarly, amine-modified adsorbents rely on similar capture mechanisms to liquid amines and require elevated temperatures (>100 °C) for adsorbent regeneration. Besides, gas constituents such as NOₓ, SOₓ and CO₂ itself can negatively impact amine-modified solids by poisoning the chemisorbent and deactivating the amine adsorption sites. Further, amine-modified materials are sometimes subject to thermal and oxidative degradation.

As an alternative to traditional porous materials, metal-organic frameworks (MOFs) or porous coordination polymers (PCPs) represent a broad class of materials that have received a great deal of attention over the past two decades. MOFs are composed of metal ions or clusters, commonly referred to as nodes, bridged by organic ligands, and in some cases organic and inorganic pillars, to form various structures and networks. There are currently ca. 100,000 MOF structures included in the Cambridge Structural Database – MOF subset vs. ca. 1,000 silica’s and zeolites; their tuneable nature enables precise control of material design at the molecular level. Using crystal engineering and reticular chemistry approaches, it is possible to tailor the pore size and chemistry by rational selection of the organic ligand, functional group, metal ion, and activation method. MOFs have already displayed exceptional performance for a wide array of applications including gas storage, catalysis and drug delivery. Their performance for gas separations has also been widely studied, with MOFs holding benchmark physisorptive performance for numerous processes including carbon capture, CO₂ direct air capture (DAC), C2/C3/C4 separations, and natural gas processing. The tuneability of MOFs and the vast array of platforms available gives MOFs great promise for revolutionising industrial processes over the coming decades.

Despite their potential, the lack of a suitable method for production scale-up and shaping has thus far been a barrier to MOFs in maximising their potential for numerous applications. Their synthesis traditionally relies on solution-based methods, i.e. layering or solvothermal, both of which are time-consuming and require large amounts of solvent. Mechanochemical synthesis has recently garnered attention for adsorbent scale-up, where they can be conducted at scale using continuous processes such as twin-screw extrusion (TSE). While scale-up of MOFs has been well-studied, these processes generally give way to powdered materials that require post-synthetic shaping. Indeed, the shaping of MOF powders into bulk samples with desired size, shape, density and mechanical stability, is a critical step for their industrial deployment, as it is required to minimise pressure drops and to increase the volumetric adsorption capacity in adsorption columns (Fig. 1). To date, mechanical shaping using binders has already been widely utilised for shaping MOFs. While mechanical shaping is relatively simple and fast, the resulting materials often display two major issues. On one hand, extruded materials where low mechanical pressures are applied display low bulk densities due
to the presence of large void spaces. Conversely, in powder pressing, the delicate crystalline structures of MOFs are prone to collapse under high mechanical pressures, leading to crumple zones of amorphous material.\textsuperscript{20} These amorphous phases can give way to pellets with high bulk densities but with large reductions in the overall porosity. The development of strategies that can address the issues of powder processing, whilst maintaining gas separation performance is critical for real-world applications of solid adsorbents.

**Figure 1.** (A) Schematic of a dual-column pressure swing adsorption/temperature swing adsorption (PSA/TSA) system with MOF packed beds. (B) Representation of the abundant void space amongst pressed MOF particles compared with a densified monolithic MOF.

In contrast to traditional shaping, self-shaping methods can effectively circumvent the issues related to extrusion and high-pressure pressing of MOFs. Self-shaping can eliminate the need for additives and/or the use of mechanical presses or extruders. These unique methodologies hold promise for reducing performance-related issues for MOF shaping whilst simultaneously reducing the cost for shaped MOF production. So far, there have only been a limited number of reports on self-shaping MOFs.\textsuperscript{44-52} In early self-shaping MOFs, researchers utilised precursor MOF gels to form self-shaped materials via syneresis when the MOF gel was dried under ambient conditions, while elevated drying temperatures gave way to powder formation.\textsuperscript{53} These materials displayed similar properties to xerogels, displaying large volumes of hierarchical porosity and low bulk densities. The development of MOF xerogels gave way to the development of the first monolithic MOFs (\textit{mono}MOFs). Similar to previously reported monolithic gels, \textit{mono}MOFs are formed via a sol-gel synthesis approach and has offered a viable alternative to traditional MOF shaping processes. \textit{mono}MOFs enable the synthesis of high-density, mechanically and chemically stable, centimeter-scale shaped materials, which retain their porosity during synthesis. The first such report on \textit{mono}MOFs synthesis came with the development of \textit{mono}ZIF-8.\textsuperscript{60} The transparent, glassy-looking material displayed a high BET area ($S_{BET} = 1423$ m$^2$ g$^{-1}$) and a density of $\rho_b = 1.05$ g cm$^{-3}$ (single crystal $\rho_b = 0.95$ g cm$^{-3}$).
The sol-gel synthesis approach in MOFs was subsequently extended to other classical MOFs such as HKUST-1 and UiO-66.\textsuperscript{49, 50} The remarkable physical properties displayed by monomono\textsubscript{HKUST-1} (\(\rho_b = 1.06 \text{ g cm}^{-3}\) and \(S_{\text{BET}} = 1288 \text{ m}^2 \text{ g}^{-1}\)) resulted in an outstanding volumetric methane uptake capacity of 261 cm\textsuperscript{3} (STP) cm\textsuperscript{-3} (65 bar, 298 K). This was found to substantially exceed the previously reported results for pelletised HKUST-1 compacted under a range of pressures and effectively rendered it as the first material to reach the DOE target for NG storage.\textsuperscript{61} Recently, the formation of monomono\textsubscript{UiO-66} was achieved by varying the sol-gel drying conditions employed during synthesis.\textsuperscript{49} The bulk physical properties of monomono\textsubscript{UiO-66} were tuned with a high level of experimental control, resulting in materials with bulk densities varying between 0.43 and 1.05 g cm\textsuperscript{-3} (single crystal \(\rho_b = 1.20 \text{ g cm}^{-3}\)). The inclusion of mesoporosity and its resultant alteration to the adsorptive properties of the MOF yielded outstanding improvements in the methane working capacity of monomono\textsubscript{UiO-66} (261 cm\textsuperscript{3} (STP) cm\textsuperscript{-3}, 5–100 bar, 298 K). This demonstrated that unprecedented levels of synthetic control can be exerted on local structures of monomono\textsubscript{MOFs}, enabling the enhancement of the gas adsorption properties beyond those of purely microporous materials. While the field of monomono\textsubscript{MOFs} is relatively new, these materials have shown the potential as a viable alternative to traditional shaping methods to produce high-density materials for industrial utility.

In this contribution, we examine the gas separation performance of monomono\textsubscript{MOFs} in comparison to their powdered variants under both gravimetric and volumetric conditions. The performance of all materials was then evaluated using single-component isotherms, gravimetric gas uptake and mixed gas dynamic breakthrough experiments. We used single-component isotherms to determine important parameters such as gas uptake and mixed gas selectivity values, while we used gravimetric uptake experiments to determine gas uptake kinetics. Finally, we analysed these materials for mixed gas separation in gas streams associated with carbon capture (15/85 \(v/v\) CO\textsubscript{2}/N\textsubscript{2}, dry and 74\% relative humidity) and natural gas/biogas upgrading (50/50 \(v/v\) CO\textsubscript{2}/CH\textsubscript{4}). This work represents the first demonstration of the use of monomono\textsubscript{MOFs} for gas separation applications.

Results & Discussion

Synthesis, characterisation and physicochemical properties

Monolithic and powdered variants of HKUST-1, UiO-66 and UiO-66-NH\textsubscript{2} were initially synthesised via previously reported methodologies.\textsuperscript{57, 58, 62-64} The crystallinity and thermal stability of pristine samples were investigated using powder X-ray diffraction (PXRD) and thermogravimetric analysis (TGA), respectively. Experimental PXRD patterns were found to match the calculated PXRD patterns for each material. The PXRD patterns for the monolithic samples display Scherrer line broadening, caused by the non-convergence of the diffraction line in nano-size particles (Fig. S1-S3). Besides,
monolithic HKUST-1, UiO-66 and UiO-66-NH₂ were found to be thermally stable to 300 °C, 400 °C and 280 °C, respectively (Fig. S4), which is consistent with previous reports for these materials.

Further characterisation of the synthesised materials was performed using 77 K N₂ adsorption isotherms (Fig. 2) and Hg porosimetry (Table 1) to analyse the porosity and bulk densities, respectively, of the powdered and monolithic materials. Table 1 displays the BET areas (S_{BET}) calculated using our extended Rouquerol’s criteria using our BETSI protocol (Fig. S8-S13), as well as the total (V_{tot}) pore volumes and bulk densities (ρ_{bulk}) of each material synthesised. All materials were fully activated by heating under vacuum before performing porosimetry experiments. The experimental BET areas calculated for the powdered materials were consistent with those previously reported for HKUST-1, UiO-66 and UiO-66-NH₂. The BET areas of the mono-MOFs were also consistent with previous reports. For both powdered and monolithic variants, N₂ isotherms display high gas uptake below 0.1 P/P₀, indicating extensive microporosity within the samples. N₂ uptake was also observed at higher relative pressures (>0.8 P/P₀) for the Zr-MOFs, indicating the presence of mesoporosity. monoUiO-66-NH₂ displayed a relatively large mesoporous step while the lower N₂ uptake above 0.8 P/P₀ for monoUiO-66 indicates a relatively low amount of mesoporosity. This mesoporosity has been previously observed for monoZr-MOFs and can be attributed to void space between crystallites and UiO-type material defects.

Figure 2. Gravimetric (A-C) and volumetric (D-F) N₂ adsorption isotherms at 77 K for monolithic and powdered HKUST-1, UiO-66 and UiO-66-NH₂ materials. Closed symbols represent adsorption while open symbols represent desorption.

To investigate the bulk density properties of the synthesised materials, we performed Hg porosimetry on monolithic and powdered MOF materials (Table 1). We have shown previously that
MOFs display higher bulk densities than powders and pelletised materials due to the exceptional control and close packing of primary particles (i.e. crystallites) during the sol-gel synthesis. In turn, this gives way to materials that maintain their porosity and performance and overcome the limitations of traditional shaping techniques (i.e. pore collapse or low density due to high or low pressure, respectively, during the compression or pore blockage due to the use of binders). The bulk densities observed for the monolithic HKUST-1 (ρ_{bulk} = 1.06 g cm\(^{-3}\)), monolithic UiO-66 (ρ_{bulk} = 1.05 g cm\(^{-3}\)), and monolithic UiO-66-NH\(_2\) (ρ_{bulk} = 1.25 g cm\(^{-3}\)) were comparable to previous reports.\(^{57,58}\) In contrast, the bulk densities of the powdered materials were significantly lower for HKUST-1 (ρ_{bulk} = 0.5 g cm\(^{-3}\)), UiO-66 (ρ_{bulk} = 0.56 g cm\(^{-3}\)) and UiO-66-NH\(_2\) (ρ_{bulk} = 0.66 g cm\(^{-3}\)). The lower density can be attributed to poor packing, giving way to large amounts of void space in the powder samples. When the bulk density is taken into account to calculate the volumetric BET area and volumetric total pore volume of each material (Table 1), the monolithic materials display significantly higher values compared to the powdered variants. In terms of performance, the monolithic materials display volumetric BET areas which are 79%, 48% and 150% higher for HKUST-1, UiO-66 and UiO-66-NH\(_2\), respectively, compared to their powdered variants.

**Table 1.** Textural and adsorption properties of monolithic and powdered MOF samples. BET area (S\(_{\text{BET}}\)), total pore volume (V\(_{\text{Tot}}\)), bulk density (ρ\(_{\text{bulk}}\)) and gravimetric and volumetric CO\(_2\) uptake measured for monolithic, pelletised and powdered HKUST-1, UiO-66 and UiO-66-NH\(_2\) via single component adsorption isotherms and dynamic mixed gas breakthrough studies.

<table>
<thead>
<tr>
<th>Materials</th>
<th>S(_{\text{BET}}) m(^2) g(^{-1})</th>
<th>V(_{\text{Tot}}) cm(^3) g(^{-1})</th>
<th>ρ(_{\text{bulk}}) g cm(^{-3})</th>
<th>ρ(_{\text{crystal}}) g cm(^{-3})</th>
<th>S(_{\text{BET}}) cm(^2) g(^{-1})</th>
<th>V(_{\text{Tot}}) cm(^3)</th>
<th>CO(_2) Uptake (0.15 bar) cm(^3) g(^{-1})</th>
<th>CO(_2) Uptake (0.5 bar) cm(^3) g(^{-1})</th>
<th>S(_{\text{Cyc}}) cm(^2) g(^{-1})</th>
<th>CO(_2) Uptake (0.15 bar) cm(^3) g(^{-1})</th>
<th>CO(_2) Uptake (0.5 bar) cm(^3) g(^{-1})</th>
<th>CO(_2) Uptake 50/50 cm(^3) g(^{-1})</th>
<th>CO(_2) Uptake 70/30 cm(^3) g(^{-1})</th>
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</thead>
<tbody>
<tr>
<td>mon-HKUST-1</td>
<td>1512</td>
<td>0.634</td>
<td>1.060</td>
<td>0.883</td>
<td>1603</td>
<td>0.672</td>
<td>18.5 (19.6)</td>
<td>53.8 (57.0)</td>
<td>23</td>
<td>12</td>
<td>21.3 (22.6)</td>
<td>53.3 (56.5)</td>
<td></td>
</tr>
<tr>
<td>pow-HKUST-1</td>
<td>1871</td>
<td>1.290</td>
<td>0.500</td>
<td>0.883</td>
<td>936</td>
<td>0.645</td>
<td>23.8 (11.9)</td>
<td>76.2 (38.1)</td>
<td>-</td>
<td>-</td>
<td>24.7 (12.4)</td>
<td>61.7 (30.8)</td>
<td></td>
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<tr>
<td>pel-HKUST-1</td>
<td>1340</td>
<td>0.570</td>
<td>0.824</td>
<td>0.883</td>
<td>1102</td>
<td>0.470</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
<td>mon-Uio-66</td>
<td>1015</td>
<td>0.530</td>
<td>1.050</td>
<td>1.237</td>
<td>1066</td>
<td>0.557</td>
<td>14.9 (15.6)</td>
<td>33.1 (34.8)</td>
<td>28</td>
<td>36</td>
<td>15.2 (16.0)</td>
<td>42.0 (44.1)</td>
<td></td>
</tr>
<tr>
<td>pow-Uio-66</td>
<td>1288</td>
<td>2.050</td>
<td>0.560</td>
<td>1.237</td>
<td>721</td>
<td>1.148</td>
<td>18.1 (10.1)</td>
<td>39.9 (22.3)</td>
<td>-</td>
<td>-</td>
<td>17.9 (10.0)</td>
<td>44.0 (24.6)</td>
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<tr>
<td>pel-Uio-66(^{d})</td>
<td>1459</td>
<td>0.540</td>
<td>0.430</td>
<td>1.237</td>
<td>627</td>
<td>0.232</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>mon-Uio-66-NH(_2)</td>
<td>1226</td>
<td>1.040</td>
<td>1.250</td>
<td>1.246</td>
<td>1533</td>
<td>1.300</td>
<td>15.1 (18.9)</td>
<td>34.9 (43.6)</td>
<td>30</td>
<td>54</td>
<td>16.0 (20.0)</td>
<td>36.2 (45.2)</td>
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<tr>
<td>pow-Uio-66-NH(_2)</td>
<td>1094</td>
<td>0.941</td>
<td>0.660</td>
<td>1.246</td>
<td>722</td>
<td>0.621</td>
<td>17.2 (11.4)</td>
<td>39.7 (26.2)</td>
<td>-</td>
<td>-</td>
<td>17.6 (11.6)</td>
<td>38.6 (25.5)</td>
<td></td>
</tr>
<tr>
<td>pel-Uio-66-NH(_2)(^{d})</td>
<td>625</td>
<td>0.250</td>
<td>0.930</td>
<td>1.246</td>
<td>581</td>
<td>0.234</td>
<td>-</td>
<td>-</td>
<td>-</td>
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</tr>
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</table>

\(^{a}\)Obtained at P/P\(_{0}\) = 0.98; \(^{b}\)quantified using Hg porosimetry; \(^{c}\)quantified using Ideal Adsorption Solution Theory (IAST).\(^{66}\) Physical properties for pel-HKUST-1 obtained from the study by Peng et al.\(^{67}\) Physical properties for pel-Uio-66 and pel-Uio-66-NH\(_2\) obtained from the study by Dhainaut et al.\(^{68}\)
Single-component gas adsorption isotherms and kinetics studies

The exceptional physical properties of \textit{mono}MOFs prompted us to examine their CO\textsubscript{2} adsorption and separation performance. We collected CO\textsubscript{2}, N\textsubscript{2} and CH\textsubscript{4} single-component isotherms at 298 and 273 K for all monolithic materials (Fig. 3 & Fig. S14-S16). We also collected CO\textsubscript{2} single-component isotherms at 298 K on the powdered variants for comparison (Fig. 3 & Fig. S17-S19). The CO\textsubscript{2} uptakes at 298K and 1 bar observed for \textit{mono}HKUST-1, \textit{mono}UiO-66 and \textit{mono}UiO-66-NH\textsubscript{2} were found to be 4.2, 2.2 and 2.1 mmol g\textsuperscript{-1}, respectively. The CO\textsubscript{2} uptake values for the monolithic MOFs was found to be consistent with values reported for powdered variants of each materials in literature and in the NIST/ARPA-E Database of Novel and Emerging Adsorbent Materials.\textsuperscript{9, 69, 70} Similarly, the lower uptake for N\textsubscript{2} and CH\textsubscript{4} gases observed for the monoliths was also consistent with previous reports for powdered variants of each MOF material.\textsuperscript{9, 69, 70} Although the powdered materials display higher gravimetric CO\textsubscript{2} adsorption performance compared to monolithic materials for each MOF variant, this trend is once again reversed when the bulk density is used to calculate the volumetric CO\textsubscript{2} adsorption performance (Fig. 3). In this case, the monolithic variants display a superior volumetric performance. While many studies report gravimetric CO\textsubscript{2} uptake performance of MOF materials, the volumetric performance of MOFs is often reported based on crystal densities of MOFs as opposed to experimental bulk densities. To the best of our knowledge, the volumetric CO\textsubscript{2} uptake for \textit{mono}HKUST-1 of 99.7 cm\textsuperscript{3} cm\textsuperscript{-3} at 1 bar, represents a new benchmark for volumetric performance under these conditions for MOF materials.

\textbf{Figure 3.} Gravimetric (A-C) and volumetric (D-F) CO\textsubscript{2} adsorption isotherms at 298K for monolithic and powdered HKUST-1, UiO-66 and UiO-66-NH\textsubscript{2} materials. Closed symbols represent adsorption while open symbols represent desorption.
To examine the effect of MOF shaping on the adsorbent-adsorbate interactions, we collected variable temperature gas adsorption isotherms to determine the CO$_2$ isosteric heats of adsorption ($Q_{st}$) for the mono-MOF materials. To obtain the CO$_2$ adsorption energy for these compounds, we fitted the CO$_2$ adsorption data at 273 and 298K using the virial equation (Fig. S20-S22), calculating the $Q_{st}$ using the Clausius–Clapeyron equation (Fig. S23). mono-HKUST-1 displays a CO$_2$ $Q_{st}$ of ca. 25 kJ mol$^{-1}$, while mono-UiO-66 and mono-UiO-66-NH$_2$ display values of ca. 25 and 37 kJ mol$^{-1}$, respectively, similar to previous reports for powdered variants of each MOF material.$^{69,70}$ The higher $Q_{st}$ displayed by mono-UiO-66-NH$_2$ can be attributed to the higher electrostatic contribution of the amino group which, in turn, gives way to stronger adsorbent-adsorbate interactions.

To estimate the CO$_2$/N$_2$ ($S_{CN}$) and CO$_2$/CH$_4$ ($S_{CM}$) selectivities of the materials, we first fitted the adsorption isotherms to a dual-site Langmuir-Freundlich (DSLF) model (Tables S1-S3) and then we used the ideal adsorbed solution theory (IAST)$^{66}$. We estimated the selectivities under relevant conditions for carbon capture and natural gas purification (CO$_2$ mole fraction of 0.15 and 0.5, respectively) for all monolithic MOF materials (Fig. S24-S26). For CO$_2$ separations associated with carbon capture, mono-HKUST-1, mono-UiO-66 and mono-UiO-66-NH$_2$ exhibited IAST $S_{CN}$ (at 1 bar and 298K) of 23, 28 and 30, respectively. For CO$_2$ separations associated with natural gas purification, mono-HKUST-1, mono-UiO-66 and mono-UiO-66-NH$_2$ exhibited IAST $S_{CM}$ (at 1 bar and 298K) of 12, 36 and 54, respectively. The high $S_{CN}$ and $S_{CM}$ values exhibited by the monolithic MOFs suggest they have potential for use in gas separations relevant to post combustion carbon capture (15/85 v/v CO$_2$/N$_2$) and natural gas purifications (50/50 v/v CO$_2$/CH$_4$).

We examined further the CO$_2$ adsorption performance of monolithic materials using kinetics studies on pristine samples of mono-HKUST-1, mono-UiO-66 and mono-UiO-66-NH$_2$ (Fig. S30-S32). We exposed activated samples of monolithic MOFs to a constant 20 ml min$^{-1}$ flow of 1.0 bar CO$_2$ at 308 K, while constantly recording the weight change. We found that, despite having shaped the MOFs into larger bodies than the microcrystalline powder, the CO$_2$ uptake kinetics were consistent with previous reports,$^{32,33}$ with mono-HKUST-1, mono-UiO-66 and mono-UiO-66-NH$_2$ achieving 90% of saturation loading in 60, 80 and 40 min, respectively. This demonstrates negligible loss in terms of gas adsorption kinetics between powdered and monolithic materials, something that is critical when evaluating the utility of monolithic materials for use in gas separation applications.

**Dynamic mixed gas breakthrough studies**

At this point, we examined the gas separation performance of mono-MOFs using experimental breakthrough studies on pristine samples of powdered and monolithic variants of mono-HKUST-1, mono-UiO-66 and mono-UiO-66-NH$_2$. We examined gas mixtures associated with post-combustion carbon capture (15/85 v/v CO$_2$/N$_2$, dry and 74% relative humidity) and natural gas purifications (50/50 v/v CO$_2$/CH$_4$).
CO$_2$/CH$_4$) at room temperature (Fig. 4-5 & Fig. S33-S41). All of the materials examined under both dry and moist conditions achieved efficient CO$_2$/N$_2$ and CO$_2$/CH$_4$ separation. N$_2$ and CH$_4$ gases eluted through the bed immediately, whereas CO$_2$ was retained in the adsorbent bed. For 15/85 v/v CO$_2$/N$_2$ gas mixtures, mono-HKUST-1 and the powdered variant achieved CO$_2$ uptake capacities of 21.3 and 24.7 cm$^3$ g$^{-1}$, respectively, under dry conditions (Table 1). The CO$_2$ uptake value for mono-HKUST-1 was in agreement with the IAST predicted value (Fig. S27). Importantly, when the bulk density of the monolithic and powdered variants of HKUST-1 is taken into account, the mono-HKUST-1 material displays a volumetric CO$_2$ uptake of 22.6 cm$^3$ which is nearly double that of the HKUST-1 packed powder at 12.4 cm$^3$ cm$^{-3}$. Similar trends were observed for the volumetric CO$_2$ uptake performance of UiO-66 (monolith = 16.0 cm$^3$ cm$^{-3}$; powder = 10.0 cm$^3$ cm$^{-3}$) and UiO-66-NH$_2$ (monolith = 20.0 cm$^3$ cm$^{-3}$; powder = 11.6 cm$^3$ cm$^{-3}$) materials for 15/85 v/v CO$_2$/N$_2$ gas mixtures (Table 1 & Fig. S34-S35). When we exposed the materials to a humid (ca. 74% relative humidity) 15/85 v/v CO$_2$/N$_2$ gas stream, both packed powder and monolithic MOF materials displayed a ca. 40% drop in performance compared to the dry gas mixture (Fig. S36-S38). The drop in performance is attributed to the competitive adsorption between CO$_2$ and H$_2$O molecules.$^{9,32,33}$ Interestingly, despite this reduction in performance, mono-MOFs exhibit nearly double the volumetric CO$_2$ uptake performance under humid conditions compared to powders for each of the MOF variants studied.

**Figure 4.** Gravimetric (A-C) and volumetric (D-F) CO$_2$ breakthrough curves for a 15/85 v/v CO$_2$/N$_2$ gas stream at 298 K for monolithic and powdered HKUST-1, UiO-66 and UiO-66-NH$_2$ materials.

When we examined the synthesized materials for 50/50 v/v CO$_2$/CH$_4$ gas mixtures, mono-HKUST-1, mono-UiO-66 and mono-UiO-66-NH$_2$ displayed exceptional volumetric CO$_2$ uptakes of 56.5, 44.1 and
45.2 cm$^3$ cm$^{-3}$, respectively (Table 1 & Fig. S39-S41). The gravimetric performance of each material was in agreement with the IAST predictions (Fig. S27-S29). Once again, the monolithic materials significantly outperform the packed powders in terms of volumetric CO$_2$ uptake performance in breakthrough studies, with each monolithic variant adsorbing nearly double the amount of CO$_2$ per cm$^3$ compared to the powdered materials. The CO$_2$/CH$_4$ separation performance of $\text{mono}$HKUST-1, $\text{mono}$UiO-66 and $\text{mono}$UiO-66-NH$_2$ was comparable to a number of benchmark MOFs such as TIFSIX-3-Ni, NbOFFIVE-1-Ni and TIFSIX-2-Cu-i, with only materials such as Mg-MOF-74 and UTSA-16 displaying superior gravimetric CO$_2$ uptake under similar conditions.$^{37-39, 71}$ While many MOFs demonstrate benchmark performance for gravimetric CO$_2$ capture, their performance does not translate well to volumetric performance. Many studies rely on theoretical crystal densities when calculating volumetric performance which are often not achievable during traditional MOF shaping and densification processes such as extrusion and pressing due to mechanical degradation and pore collapse.$^{38, 50, 54}$ Again, to the best of our knowledge, the CO$_2$ removal performance of $\text{mono}$HKUST-1 represents the highest CO$_2$ removal performance achieved by any adsorbent after successful pelletisation and shaping under these conditions. Finally, we carried out recyclability tests on $\text{mono}$HKUST-1, $\text{mono}$UiO-66 and $\text{mono}$UiO-66-NH$_2$ for 50/50 v/v CO$_2$/CH$_4$ gas mixtures (Fig. S42). In order to examine the recyclability of the materials, we heated the adsorbents to 120 °C under a helium flow between tests. The $\text{mono}$MOFs were stable under dry conditions, displaying negligible reduction in performance over five successive adsorption/desorption cycles.

Figure 5. Gravimetric (A-C) and volumetric (D-F) CO$_2$ breakthrough curves for a 50/50 v/v CO$_2$/CH$_4$ gas stream at 298 K for monolithic and powdered HKUST-1, UiO-66 and UiO-66-NH$_2$ materials.
Conclusions

Adsorption based gas separation processes have shown huge potential for important industrial processes such as carbon capture and gas purifications. The deployment of porous adsorbents in these processes, however, has been hampered by a lack of suitable shaping processes which enable high density materials while maintaining gas sorption performance. In conclusion, we have demonstrated that \textit{mono}MOFs display superior volumetric gas separation performance compared to packed powder materials. Single-component gas adsorption isotherms suggest that all six materials examined herein are efficient at removing CO$_2$ from CO$_2$/N$_2$ and CO$_2$/CH$_4$ gas mixtures. However, when the bulk density of each material is evaluated to determine the volumetric performance in both gas adsorption isotherms and dynamic breakthrough studies, \textit{mono}MOFs exhibit superior CO$_2$ separation performance under all conditions. \textit{mono}MOFs display similar kinetics to their powdered variants suggesting kinetic limitations do not existing after \textit{mono}MOFs synthesis. While many benchmark MOFs display exceptional gravimetric CO$_2$ adsorption performance, this rarely translates to volumetric CO$_2$ adsorption due to issues regarding MOF shaping and densification. Many reports for MOF materials rely on theoretical crystal structure densities when reporting volumetric performance which rarely translate to experimental bulk densities upon powder processing and pelletisation. While high-density \textit{mono}MOFs have previously demonstrated benchmark performance for gas storage applications, this report represents the first demonstration of gas separation performance of \textit{mono}MOFs. This work further illustrates the potential of this unique class of materials for a myriad of commercially relevant gas separation applications and paves the way for the development of next generation \textit{mono}MOFs with superior physical properties and enhanced gas adsorption performance.

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Conflicts of interest

D.F.-J. has financial interests in the start-up company Immaterial, which is seeking to commercialise metal-organic frameworks.

References


