

Monolithic metal–organic frameworks for carbon dioxide separation†

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Carbon dioxide (CO_2) 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, up to this point there has been a lack of appropriate adsorbents capable of capturing CO_2 whilst maintaining low regeneration energies. In the context of CO_2 capture, metal-organic frameworks (MOFs) have gained much attention in the past two decades as potential materials. Their tuneable nature allows for precise control over the pore size and chemistry, which allows for the tailoring of their properties for the selective adsorption of CO_2 . While many candidate materials exist, the amount of research into material 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 capacities. Herein, we demonstrate the use of a series of monolithic MOFs ($_{\text{mono}}\text{UiO-66}$, $_{\text{mono}}\text{UiO-66-NH}_2$ & $_{\text{mono}}\text{HKUST-1}$) for use in gas separation processes.

Introduction

Anthropogenic emissions of carbon dioxide (CO₂) are acknowledged to be a significant risk to the global climate. The atmospheric CO₂ concentration has surpassed 400 ppm on several occasions since 2013, which represents an increase

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of over 100 ppm compared to 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 this century.³ Additionally, CO₂ represents a significant impurity in industrial processes and its removal from important gases such as methane (CH₄) can help improve the overall quality of pipeline grade natural gas (NG). The upgrading of alternative forms of CH₄ 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\$ per t CO₂ captured) and the 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 the 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 CO₂ emissions globally. In particular, Canada recently announced a direct tax on carbon emissions of at least 10 C\$ per t, rising by 10 C\$ per t per year until it reaches 50 C\$ per t by 2022.⁷ At 50 C\$ per t, this will significantly improve the competitiveness of CCS technologies. Similar ambitious CO₂ emission reduction targets have been set in Europe and, right now, a new approach to CCS technologies is required, 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 and cost effectiveness of CCS 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 CO₂ 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 tunability and chemical functionalities to improve important process parameters such as chemical interactions, selectivity and hydrophobicity, leading to high CO₂ capture costs as a result of their 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 NO_x, SO_x and CO₂ itself can negatively impact amine-modified solids by poisoning the chemisorbent and deactivating the amine adsorption sites.^{12–14} Furthermore, amine-modified materials are sometimes subject to thermal and oxidative degradation.^{15,16}

As an alternative to traditional porous materials, metal–organic frameworks (MOFs)^{17,18} or porous coordination polymers (PCPs)¹⁹ represent a broad class of



Despite their potential, the lack of a suitable method for production scale-up and shaping has thus far been a barrier to maximising the potential of MOFs for numerous applications. Their synthesis traditionally relies on solution-based methods, *i.e.* layering or solvothermal synthesis, both of which are time-consuming and require large amounts of solvent. Mechanochemical synthesis has recently garnered attention for adsorbent scale-up,^{22–29} where the synthesis can be conducted at scale using continuous processes such as twin-screw extrusion (TSE).^{30–36} While the scale-up of MOFs has been well-studied, these processes generally lead to powdered materials that require post-synthetic shaping. Indeed, the shaping of MOF powders into bulk samples with desired sizes, shapes, densities and mechanical stabilities 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).²² To date, mechanical shaping

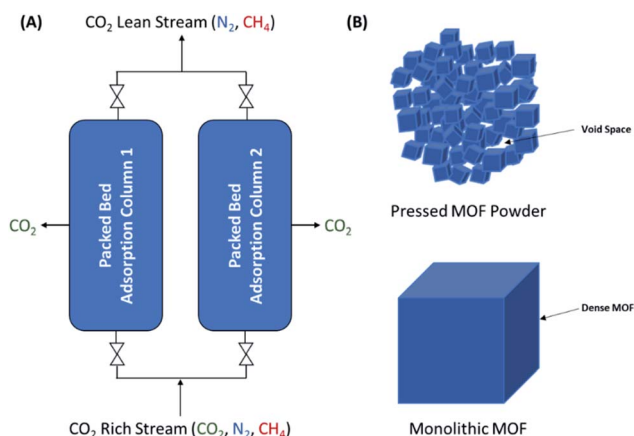


Fig. 1 (A) Schematic of a dual-column pressure swing adsorption/temperature swing adsorption (PSA/TSA) system with MOF packed beds. (B) Representation of the abundant void spaces amongst pressed MOF particles compared with a densified monolithic MOF.

using binders has already been widely utilised for shaping MOFs.^{33,38–43} 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 collapsing under high mechanical pressures, leading to crumple zones of amorphous material.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 the gas separation performance is critical for the real-world applications of solid adsorbents.

In contrast to traditional shaping, self-shaping methods can effectively circumvent the issues related to the 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 the performance-related issues of MOF shaping whilst simultaneously reducing the cost for shaped MOF production. So far, there have been a limited number of reports on self-shaping MOFs.^{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.^{53–56} 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 (monoMOFs). Similar to previously reported monolithic gels, monoMOFs have been formed *via* a sol–gel synthesis approach which has offered a viable alternative to traditional MOF shaping processes. monoMOFs 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 monoMOF synthesis came with the development of monoZIF-8 .⁶⁰ The transparent, glassy-looking material displayed a high BET area ($S_{\text{BET}} = 1423 \text{ m}^2 \text{ g}^{-1}$) and a density of $\rho_{\text{b}} = 1.05 \text{ g cm}^{-3}$ (single crystal $\rho_{\text{b}} = 0.95 \text{ g cm}^{-3}$).

The sol–gel synthesis approach in MOFs was subsequently extended to other classical MOFs such as HKUST-1 and UiO-66.^{49,50} The remarkable physical properties displayed by monoHKUST-1 ($\rho_{\text{b}} = 1.06 \text{ g cm}^{-3}$ and $S_{\text{BET}} = 1288 \text{ m}^2 \text{ g}^{-1}$) resulted in an outstanding volumetric methane uptake capacity of 261 cm^3 (STP) cm^{-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.⁶¹ Recently, the formation of monoUiO-66 was achieved by varying the sol–gel drying conditions employed during synthesis.⁴⁹ The bulk physical properties of monoUiO-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^{-3} (single crystal $\rho_{\text{b}} = 1.20 \text{ g cm}^{-3}$). The inclusion of mesoporosity and its resultant alteration of the adsorptive properties of the MOF yielded outstanding improvements in the methane working capacity of monoUiO-66 (261 cm^3 (STP) cm^{-3} , 5–100 bar, 298 K). This demonstrated that unprecedented levels of synthetic control can be exerted on local structures of monoMOFs , enabling the enhancement of the gas adsorption properties beyond those of purely microporous materials. While the field of





Table 1 Textural and adsorption properties of the monolithic and powdered MOF samples. BET area (S_{BET}), total pore volume (V_{Tot}), bulk density (ρ_{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

Materials	Single component gas adsorption						Dynamic breakthrough studies		
	S_{BET} $\text{m}^2 \text{g}^{-1}$	V_{Tot}^a $\text{cm}^3 \text{g}^{-1}$	ρ_{bulk}^b g cm^{-3}	ρ_{crystal} g cm^{-3}	S_{BET} $\text{m}^2 \text{cm}^{-1}$	V_{Tot} $\text{cm}^3 \text{cm}^{-3}$	CO ₂ uptake		
							CO ₂ uptake (0.15 bar) $\text{cm}^3 \text{cm}^{-3}$	CO ₂ uptake (0.5 bar) $\text{cm}^3 \text{g}^{-1}$	CO ₂ uptake 50/50 CO ₂ /N ₂ $\text{cm}^3 \text{g}^{-1}$ CH ₄ $\text{cm}^3 \text{cm}^{-3}$
mon _o HKUST-1	1512	0.634	1.060	0.883	1603	0.672	18.5 (19.6)	53.8 (57.0)	23
pow _d HKUST-1	1871	1.290	0.500	0.883	936	0.645	23.8 (11.9)	76.2 (38.1)	—
pel _l HKUST-1 ^c	1340	0.570	0.824	0.883	1102	0.470	—	—	—
mon _o UiO-66	1015	0.530	1.050	1.237	1066	0.557	14.9 (15.6)	33.1 (34.8)	28
pow _d UiO-66	1288	2.050	0.560	1.237	721	1.148	18.1 (10.1)	39.9 (22.3)	—
pel _l UiO-66 ^d	1459	0.540	0.430	1.237	627	0.232	—	—	—
mon _o UiO-66-NH ₂	1226	1.040	1.250	1.246	1533	1.300	15.1 (18.9)	34.9 (43.6)	30
pow _d UiO-66-NH ₂	1094	0.941	0.660	1.246	722	0.621	17.2 (11.4)	39.7 (26.2)	—
pel _l UiO-66-NH ₂ ^d	625	0.250	0.930	1.246	581	0.234	—	—	—

^a Obtained at $P/P_0 = 0.98$, ^b Quantified using Hg porosimetry, ^c Quantified using ideal adsorption solution theory (IAST), ^d Physical properties for _{pel}HKUST-1 obtained from the study by Peng *et al.*, ^e Physical properties for _{pel}UiO-66 and _{pel}UiO-66-NH₂ obtained from the study by Dhainaut *et al.*⁶⁸

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†),⁶⁵ as well as the total (V_{tot}) pore volumes and bulk densities (ρ_{bulk}) of each material synthesised. All of the materials were fully activated by heating under vacuum before performing the 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.^{62–64} The BET areas of the *mono*MOFs were also consistent with previous reports.^{57,58} For both the powdered and monolithic variants, the N₂ isotherms displayed high gas uptake below 0.1 P/P_0 , indicating extensive microporosity within the samples. N₂ uptake was also observed at higher relative pressures ($>0.8 P/P_0$) for the Zr-MOFs, indicating the presence of mesoporosity. *mono*UiO-66-NH₂ displayed a relatively large mesoporous step, while the lower N₂ uptake above 0.8 P/P_0 for *mono*UiO-66 indicates a relatively low amount of mesoporosity. This mesoporosity has been previously observed for *mono*Zr-MOFs and can be attributed to the void spaces between the crystallites and UiO-type material defects.⁵⁷

To investigate the bulk density properties of the synthesised materials, we performed Hg porosimetry on the monolithic and powdered MOF materials (Table 1). We have shown previously that *mono*MOFs display higher bulk densities than powders and pelletised materials due to the exceptional control and close packing of the primary particles (*i.e.* crystallites) during the sol-gel synthesis. In turn, this leads to materials that maintain their porosity and performances and overcomes 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 *mono*HKUST-1 ($\rho_{\text{bulk}} = 1.06 \text{ g cm}^{-3}$), *mono*UiO-66 ($\rho_{\text{bulk}} = 1.05 \text{ g cm}^{-3}$), and *mono*UiO-66-NH₂ ($\rho_{\text{bulk}} = 1.25 \text{ g cm}^{-3}$) were comparable to previous reports.^{57,58} In contrast, the bulk densities of the powdered materials were significantly lower for HKUST-1 ($\rho_{\text{bulk}} = 0.5 \text{ g cm}^{-3}$), UiO-66 ($\rho_{\text{bulk}} = 0.56 \text{ g cm}^{-3}$) and UiO-66-NH₂ ($\rho_{\text{bulk}} = 0.66 \text{ g cm}^{-3}$). The lower density can be attributed to the poor packing, leading 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-NH₂, respectively, compared to their powdered variants.

Single-component gas adsorption isotherms and kinetic studies

The exceptional physical properties of the *mono*MOFs prompted us to examine their CO₂ adsorption and separation performances. We collected CO₂, N₂ and CH₄ single-component isotherms at 298 and 273 K for all monolithic materials (Fig. 3 & S14–S16†). We also collected CO₂ single-component isotherms at 298 K for the powdered variants for comparison (Fig. 3 & S17–S19†). The CO₂ uptake values at 298 K and 1 bar observed for *mono*HKUST-1, *mono*UiO-66 and *mono*UiO-66-NH₂ were found to be 4.2, 2.2 and 2.1 mmol g^{−1}, respectively. The CO₂ uptake values for the



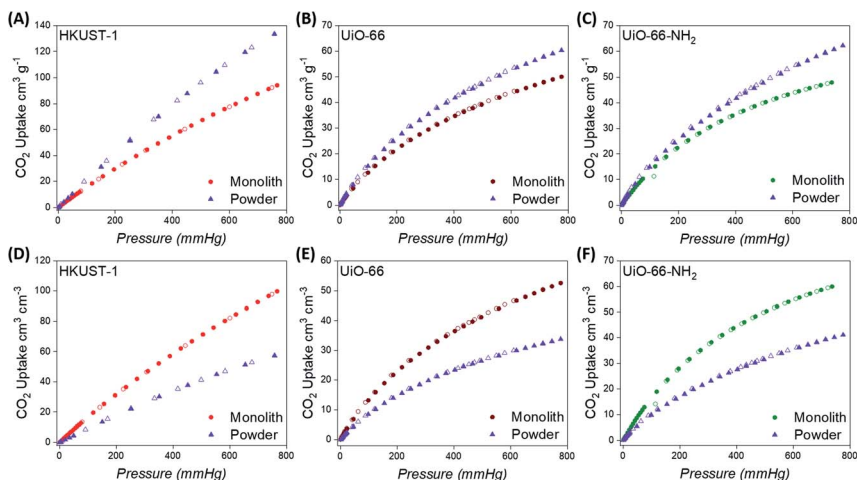


Fig. 3 Gravimetric (A–C) and volumetric (D–F) CO_2 adsorption isotherms at 298 K for monolithic and powdered HKUST-1, UiO-66 and UiO-66- NH_2 materials. Closed symbols represent adsorption while open symbols represent desorption.

monolithic MOFs were found to be consistent with values reported for the powdered variants of each material in the literature and in the NIST/ARPA-E Database of Novel and Emerging Adsorbent Materials.^{9,69,70} Similarly, the lower uptake values for N_2 and CH_4 gases observed for the monoliths were also consistent with previous reports for powdered variants of each MOF material.^{9,69,70} Although the powdered materials display higher gravimetric CO_2 adsorption performances compared to the monolithic materials for each MOF variant, this trend is once again reversed when the bulk density is used to calculate the volumetric CO_2 adsorption performance (Fig. 3). In this case, the monolithic variants display a superior volumetric performance. While many studies report the gravimetric CO_2 uptake performances of MOF materials, the volumetric performances of MOFs are often reported based on the crystal densities of the MOFs as opposed to the experimental bulk densities. To the best of our knowledge, the volumetric CO_2 uptake value for monoHKUST-1 of $99.7 \text{ cm}^3 \text{ cm}^{-3}$ at 1 bar represents a new benchmark for volumetric performance under these conditions for MOF materials.

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 monoMOF materials. To obtain the CO_2 adsorption energies for these compounds, we fitted the CO_2 adsorption data at 273 and 298 K using the virial equation (Fig. S20–S22†), calculating the Q_{st} using the Clausius–Clapeyron equation (Fig. S23†). monoHKUST-1 displays a CO_2 Q_{st} of ca. 25 kJ mol^{-1} , while monoUiO-66 and monoUiO-66-NH_2 display values of ca. 25 and 37 kJ mol^{-1} , respectively, similar to previous reports for the powdered variants of each MOF material.^{69,70} The higher Q_{st} displayed by monoUiO-66-NH_2 can be attributed to the higher electrostatic contribution of the amino group which, in turn, leads 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 the relevant conditions for carbon capture and natural gas purification (CO₂ mole fractions of 0.15 and 0.5, respectively) for all monolithic MOF materials (Fig. S24–S26[†]). For the CO₂ separations associated with carbon capture, _{mono}HKUST-1, _{mono}UiO-66 and _{mono}UiO-66-NH₂ exhibited IAST S_{CN} values (at 1 bar and 298 K) of 23, 28 and 30, respectively. For the CO₂ separations associated with natural gas purification, _{mono}HKUST-1, _{mono}UiO-66 and _{mono}UiO-66-NH₂ exhibited IAST S_{CM} values (at 1 bar and 298 K) of 12, 36 and 54, respectively. The high S_{CN} and S_{CM} values exhibited by the monolithic MOFs suggest that they have potential for use in gas separations relevant to post combustion carbon capture (15/85 v/v CO₂/N₂) and natural gas purification (50/50 v/v CO₂/CH₄).

We examined further the CO₂ adsorption performances of the monolithic materials using kinetic studies on pristine samples of _{mono}HKUST-1, _{mono}UiO-66 and _{mono}UiO-66-NH₂ (Fig. S30–S32†). We exposed the activated samples of the monolithic MOFs to a constant 20 ml min^{−1} flow of 1.0 bar CO₂ 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 CO₂ uptake kinetics were consistent with previous reports,^{32,33} with _{mono}HKUST-1, _{mono}UiO-66 and _{mono}UiO-66-NH₂ achieving 90% saturation loading in 60, 80 and 40 min, respectively. This demonstrates negligible loss in terms of the gas adsorption kinetics between the 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 performances of the monoMOFs using experimental breakthrough studies on the pristine samples of powdered

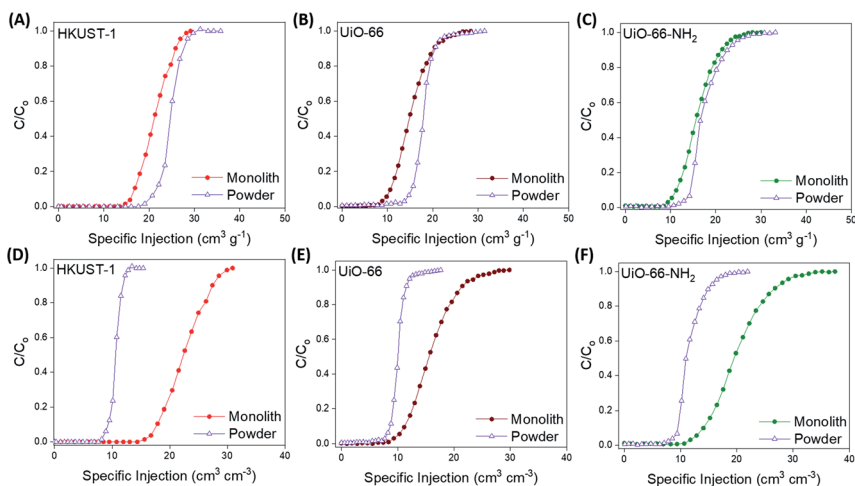
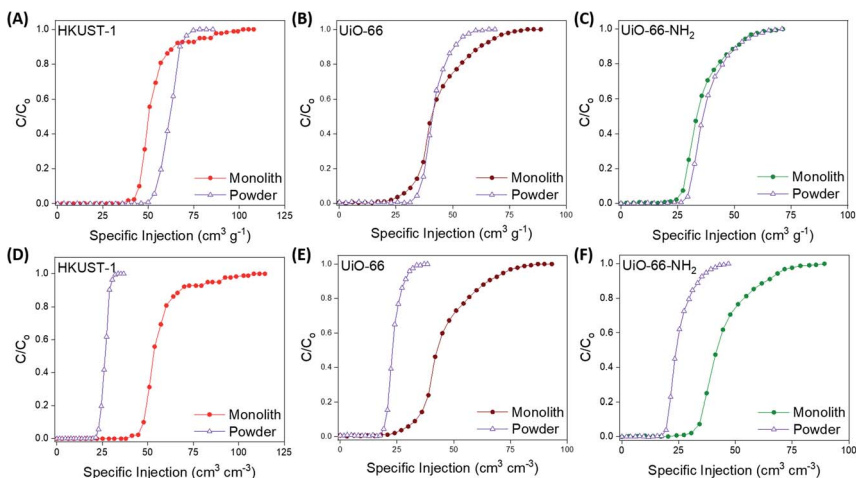


Fig. 4 Gravimetric (A–C) and volumetric (D–F) CO₂ breakthrough curves for a 15/85 v/v CO₂/N₂ gas stream at 298 K for monolithic and powdered HKUST-1, UiO-66 and UiO-66-NH₂ materials.



When we examined the synthesized materials with the 50/50 v/v CO₂/CH₄ gas mixture, monoHKUST-1, monoUiO-66 and monoUiO-66-NH₂ displayed exceptional volumetric CO₂ uptake values of 56.5, 44.1 and 45.2 cm³ cm⁻³, respectively (Table 1 & Fig. S39–S41†). The gravimetric performances of each material were in

agreement with the IAST predictions (Fig. S27–S29†). Once again, the monolithic materials significantly outperformed the packed powders in terms of the volumetric CO₂ uptake performance in the breakthrough studies, with each monolithic variant adsorbing nearly double the amount of CO₂ per cm^{−3} compared to the powdered materials. The CO₂/CH₄ separation performances of *mono*HKUST-1, *mono*UiO-66 and *mono*UiO-66-NH₂ were 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 CO₂ uptakes under similar conditions.^{37–39,71} While many MOFs demonstrate benchmark performances for gravimetric CO₂ capture, their performances do not translate well to volumetric performance. Many studies rely on theoretical crystal densities when calculating volumetric performances, 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 CO₂ removal performance of *mono*HKUST-1 represents the highest CO₂ removal performance achieved by any adsorbent after successful pelletisation and shaping under these conditions. Finally, we carried out recyclability tests on *mono*HKUST-1, *mono*UiO-66 and *mono*UiO-66-NH₂ for the 50/50 v/v CO₂/CH₄ gas mixture (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 *mono*MOFs were stable under dry conditions, displaying negligible reductions in performance over five successive adsorption/desorption cycles.

Conclusions

Adsorption based gas separation processes have shown huge potential for important industrial processes such as carbon capture and gas purification. The deployment of porous adsorbents in these processes, however, has been hampered by a lack of suitable shaping processes which allow high density materials while maintaining gas sorption performance. In conclusion, we have demonstrated that *mono*MOFs display superior volumetric gas separation performances compared to packed powder materials. Single-component gas adsorption isotherms suggest that all six materials examined herein are efficient at removing CO₂ from CO₂/N₂ and CO₂/CH₄ gas mixtures. However, when the bulk density of each material is evaluated to determine the volumetric performances in both gas adsorption isotherms and dynamic breakthrough studies, *mono*MOFs exhibit superior CO₂ separation performances under all conditions. *mono*MOFs display similar kinetics to their powdered variants, suggesting that kinetic limitations do not exist after *mono*MOF synthesis. While many benchmark MOFs display exceptional gravimetric CO₂ adsorption performances, these rarely translate to volumetric CO₂ adsorption due to issues regarding MOF shaping and densification. Many reports on MOF materials rely on theoretical crystal structure densities when reporting volumetric performances, which rarely translate to experimental bulk densities upon powder processing and pelletisation. While high-density *mono*MOFs have previously demonstrated benchmark performances for gas storage applications, this report represents the first demonstration of the gas separation performances of *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



monoMOFs with superior physical properties and enhanced gas adsorption performance.

Conflicts of interest

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

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