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Flue-gas and direct-air capture of CO_2 by porous metal–organic materials

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Sequestration of CO_2, either from gas mixtures or directly from air (direct air capture), is a technological goal important to large-scale industrial processes such as gas purification and the mitigation of carbon emissions. Previously, we investigated five porous materials, three porous metal–organic materials (MOMs), a benchmark inorganic material, **Zeolite 13X** and a chemisorbent, **TEPA-SBA-15**, for their ability to adsorb CO_2 directly from air and from simulated flue-gas. In this contribution, a further 10 physisorbent materials that exhibit strong interactions with CO_2 have been evaluated by temperature-programmed desorption for their potential utility in carbon capture applications: four hybrid ultramicroporous materials, **SIFSIX-3-Cu**, **DICRO-3-Ni-i**, **SIFSIX-2-Cu-i** and **MOOFOUR-1-Ni**; five microporous MOMs, **DMOF-1**, **ZIF-8**, **MIL-101**, **UiO-66** and **UiO-66-NH$_2$**; an ultramicroporous MOM, **Ni-4-PyC**. The performance of these MOMs was found to be negatively impacted by moisture. Overall, we demonstrate that the incorporation of strong electrostatics from inorganic moieties combined with ultramicropores offers improved CO_2 capture performance from even moist gas mixtures but not enough to compete with chemisorbents.

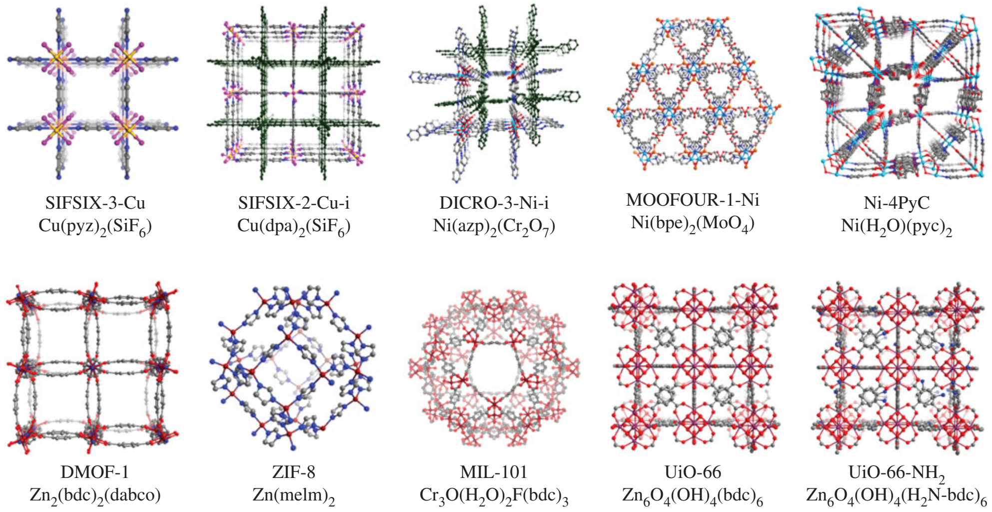
This article is part of the themed issue 'Coordination polymers and metal–organic frameworks: materials by design'.

1. Introduction

Anthropogenic emissions of carbon dioxide (CO_2) are accepted as a significant risk to global climate. 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]. At the 2015 United Nations Climate Change Conference, the 196 parties in attendance signed an agreement calling for zero net anthropogenic greenhouse gas emissions to be reached during the second half of the twenty-first century [2]. There are two pathways currently being considered for the reduction of CO_2 emissions: (i) CO_2 removal from CO_2-rich post-combustion industrial point sources (i.e. flue-gas capture) and (ii) the removal of CO_2 from the atmosphere via direct air capture (DAC) [3]. Although addressing the increase in global CO_2 concentrations presents a scientific and technological challenge of the highest order [4], it also presents an opportunity because DAC becomes more viable at higher CO_2 levels and CO_2 is a useful commodity. Carbon capture and storage technologies focus on capturing and storing CO_2. Carbon capture and utilization looks to exploit the large volumes of CO_2 produced by industrial practices for use in other applications [5]. For example, CO_2 is currently used as a feed gas in the chemical industry for the production of various alcohols [6], dimethyl ether [7], biodiesel [8] and polymers [9]. These large-scale processes are suited to the high volumes of CO_2 associated with post-combustion CO_2 capture. However, other niche applications such as the use of CO_2 gas in greenhouses to encourage photosynthesis or in algae farms to promote biofuels production may be more applicable to smaller scale CO_2 capture via DAC technologies. DAC may also be feasible for mitigating emissions from mobile sources and, if recycling costs are minimal, might represent an approach to the introduction of new carbon negative technologies. The catch is that DAC is handicapped by the relative availability of CO_2 in the atmosphere (0.0004 atm versus 0.15 atm in post-combustion capture) and, in the case of physisorption, by competition with other gases and vapours, such as N_2 and H_2O [10]. DAC is therefore much more challenging to physisorbents than post-combustion CO_2 capture, but it may be practical if an adsorbent offers optimum uptake, appropriate CO_2 selectivity over N_2 and H_2O and facile recyclability [11].

At present, DAC systems typically employ solid supported amine-based adsorbents, wherein amine functional groups are tethered to the surface of cellulose [12,13], porous polymer networks [14,15] and porous silica materials [10,16–19]. Chemisorption of CO_2 is feasible but in order for chemisorbents to be recycled one must reverse the chemical reaction that captures CO_2. Therefore, although chemisorbents achieve moderate CO_2 adsorption capacities ($0.5–3.6\,\mathrm{mmol\,g^{-1}}$) for DAC, they also typically require elevated temperatures for sorbent regeneration (more than 100°C). It has also been found that gas constituents such as NO_x, SO_x and CO_2 itself can negatively impact amine-modified solids by poisoning the chemisorbent and deactivating the amine adsorption sites [20–22]. Furthermore, amine-modified materials are sometimes subject to thermal and oxidative degradation [23,24]. DAC using physisorbent materials has been much less studied, presumably due to the lack of suitable candidate materials. In principle, advanced sorbents that capture CO_2 through highly selective physisorption offer great promise, because they require much less energy for recycling. Unfortunately, existing classes of physisorbent materials do not meet the requirements for DAC, mainly high CO_2 selectivity over N_2 (S_{CN}) and H_2O (S_{CW}), which are major constituents of air.

Recently, we reported a systematic study of DAC performance for a number of benchmark physisorbents [10]; prototypal metal–organic materials (MOMs) **HKUST-1** and **Mg-MOF-74**, a zeolite, **Zeolite 13X**, and a hybrid ultramicroporous material (HUM) [25], **SIFSIX-3-Ni**. A highly adsorbent amine-modified chemisorbent material, **TEPA-SBA-15**, was included in the



SIFSIX-3-Cu $Cu(pyz)_2(SiF_6)$

SIFSIX-2-Cu-i $Cu(dpa)_2(SiF_6)$

DICRO-3-Ni-i $Ni(azp)_2(Cr_2O_7)$

MOOFOUR-1-Ni $Ni(bpe)_2(MoO_4)$

Ni-4PyC $Ni(H_2O)(pyc)_2$

DMOF-1 $Zn_2(bdc)_2(dabco)$

ZIF-8 $Zn(melm)_2$

MIL-101 $Cr_3O(H_2O)_2F(bdc)_3$

UiO-66 $Zn_6O_4(OH)_4(bdc)_6$

UiO-66-NH$_2$ $Zn_6O_4(OH)_4(H_2N\text{-}bdc)_6$

Figure 1. Ten physisorbent materials were evaluated in this study. Elements C, O, N, Si, F, Cu, Cr, Ni, Mo, Zn and Zr are represented by grey, red, blue, yellow, pink, salmon, dark red, sky blue, orange, brown and purple, respectively; H atoms have been omitted for clarity. The dark green net represents the second interpenetrated network in **SIFSIX-2-Cu-i** and **DICRO-3-Ni-i**.

study for comparison. All four physisorbent materials were observed to exhibit a dramatic decrease in performance with respect to CO_2 uptake in the presence of water vapour. **SIFSIX-3-Ni** exhibited the highest CO_2 uptake from DAC of the physisorbent materials at 4.07 l CO_2 kg^{-1} adsorbent. While the chemisorbent **TEPA-SBA-15** was unaffected by water vapour, its energetics and recyclability were not as favourable as those of **SIFSIX-3-Ni**. In this contribution, we examine the performance of 10 additional benchmark physisorbent materials for capturing CO_2 from flue-gas and DAC using a combination of temperature-programmed desorption (TPD), thermogravimetric analysis (TGA) and mass spectrometry (MS). **SIFSIX-3-Cu** [26], **DICRO-3-Ni-i** [27], **MOOFOUR-1-Ni** [28], **SIFSIX-2-Cu-i** [26], **Ni-4-PyC** [29], **ZIF-8** [30], **DMOF-1** [31], **UiO-66** [32], **UiO-66-NH$_2$** [33] and **MIL-101** [34] were evaluated for their performance with respect to DAC and five other CO_2-rich gas mixtures. The 10 physisorbents studied herein represent two classes of MOMs that have been widely studied for carbon capture (figure 1).

The rich structural and functional diversity of MOMs means that they can be tuned for specific purifications and separations of gas mixtures [35]. **SIFSIX-3-Cu** [26], **SIFSIX-2-Cu-i** [26], **DICRO-3-Ni-i** [27] and **MOOFOUR-1-Ni** [28] are hybrid ultramicroporous materials (HUMs) [11,25,26,28,36], which exhibit ultramicropores (less than 0.7 nm) and comprise metal cation nodes linked by two types of linkers: neutral organic ligands and anionic inorganic pillars. The use of an appropriately charged inorganic pillar means that the resulting network is uncharged and creates a relatively high electrostatic contribution that, when combined with tight binding sites, enables strong interactions between adsorbent and adsorbate (large Q_{st}) and ultra-high selectivity for polarizable gases such as CO_2 versus less polarizable gases such as N_2. **ZIF-8** [30], **DMOF-1** [31], **UiO-66** [32], **UiO-66-NH$_2$** [33] and **MIL-101** [34] are prototypal examples of physisorbent MOMs, also known as metal–organic frameworks, MOFs [37,38], or porous coordination polymers, PCPs [39–41]. **Ni-4-PyC** [29] is a recently reported example of an ultramicroporous MOM and, being built from a single small ligand; **Ni-4-PyC** exhibits similar pore dimensions to HUMs (0.35 and 0.48 nm). However, there is a reduced electrostatic contribution due to the lack of an inorganic pillar. These sorbents were synthesized following the literature methods (see the electronic supplementary material). Each of the sorbents was characterized via powder X-ray diffraction (PXRD; electronic supplementary material, figures S3–S12) to verify phase purity. Sorbents were then subjected to solvent exchange and activation using published procedures; details for the exchange process and activation protocols are given in the electronic supplementary material. After activation, each sorbent was subjected to sorption experiments to verify a match with their

Table 1. TPD coupled with mass spectrometry.

	DAC (1 atm; 49% RH)				moist CO_2 (0.15 atm; 75% RH)[b]				dry CO_2 (0.15 atm)	
sorbent	CO_2	H_2O	CO_2 l kg^{-1} (l l^{-1})	S_{CW}	CO_2	H_2O	CO_2 l kg -1 (l l^{-1})	S_{CW}	CO_2	CO_2 l kg^{-1} (l l^{-1})
SIFSIX-3-Ni[a]	<8% (8.0)	>92% (93)	4.07 (6.55)	5.43	62% (76)	38% (46)	38.69 (62.29)	0.27	100% (109)	55.49 (89.34)
HKUST-1[a]	1% (2.1)	99% (178)	1.07 (0.95)	0.63	8.5% (12.8)	>91% (137)	6.52 (5.78)	0.02	100% (70)	35.64 (31.61)
Mg-MOF-74[a]	<4% (6.3)	>96% (171)	3.21 (2.94)	2.60	51% (68)	49% (65)	34.62 (31.71)	0.17	100% (235)	119.64 (109.59)
Zeolite 13X[a]	1% (1.5)	99% (146)	0.76 (0.99)	0.63	22% (26.3)	78% (93)	13.39 (17.54)	0.05	100% (140)	71.27 (93.36)
TEPA-SBA-15[a]	93% (158)	7% (12)	80.44 n.a.[c]	830	92% (130.3)	8% (11)	66.33 n.a.[c]	1.92	100% (152)	77.38 n.a.[c]
SIFSIX-3-Cu	13.8% (14.1)	>86% (88)	7.18 (11.55)	10.03	65% (101)	35% (54)	51.42 (82.68)	0.31	100% (119)	60.58 (97.41)
DICRO-3-Ni-i	>2% (1.9)	<97% (80)	0.97 (1.40)	1.47	<53% (19.2)	>47% (17,2)	9.77 (14.08)	0.19	100% (23.9)	12.17 (17.54)
SIFSIX-2-Cu-i	1% (1.6)	99% (155)	<1.00 (1.247)	0.63	59.5% (18.1)	40.5% (12.3)	9.21 (11.48)	0.24	100% (31)	15.78 (19.68)
MOOFOUR-1-Ni	>5% (2.5)	<95% (49)	1.27 (1.60)	3.29	60% (39)	40% (26)	19.85 (25.01)	0.25	100% (58)	29.53 (37.21)
Ni-4-PyC	2% (3.3)	98% (154)	1.68 (1.74)	1.28	61% (15.6)	39% (10.1)	7.94 (8.20)	0.26	100% (26)	13.24 (13.68)
DMOF-1	>2% (1.3)	<98% (56)	1.00 (0.83)	1.28	56% (9.7)	44% (7.7)	4.94 (4.08)	0.21	100% (17.3)	8.81 (7.28)
ZIF-8	23% (2.3)	77% (7.6)	1.20 (1.10)	18.67	75% (2.5)	25% (>1)	1.27 (1.16)	0.50	100% (1.8)	0.92 (0.84)
MIL-101	<1% (<1.0)	>99% (95)	<1.00 (0.62)	<0.63	40% (11.2)	60% (16.8)	5.70 (3.53)	0.11	100% (33.1)	16.85 (10.45)
UiO-66	<1% (0.7)	>99% (195)	0.36 (1.45)	<0.63	29.6% (8.4)	70.4% (19.6)	4.28 (5.30)	0.07	100% (31.8)	16.19 (20.04)
UiO-66-NH_2	<2% (11.2)	>98% (237)	5.70 (7.38)	1.28	46.7% (51.3)	53.3% (58.5)	26.12 (33.83)	0.15	100% (59)	30.04 (38.90)

[a] Previously reported adsorbents [10].

[b] Water saturated gas feeds were obtained by bubbling each pure gas through deionized water.

[c] Density for TEPA-SBA-15 is indeterminable. Mass of analyte in mg g^{-1}.

reported apparent surface area, uptake capacity and isosteric enthalpy of adsorption for CO_2 (Isotherms; electronic supplementary material, figures S13–S22).

The CO_2 adsorption performance of each physisorbent was evaluated using pristine, activated samples exposed to a specific gas mixture for a prescribed time period before being subjected to TPD. In a typical TPD experiment, a sample was placed in a quartz reactor cell positioned within a tube furnace. This cell was heated to a temperature that promotes expulsion of guest molecules from the host in the presence of He carrier gas. The exhaust gas was continuously monitored using a mass spectrometer. These experiments provide the identity and relative quantity of gases and vapours desorbed by the sample as a function of temperature, or, if temperature is held constant, as a function of time. They also afford an understanding of the energy required for recycling the adsorbent. In short, TPD experiments address relative CO_2/H_2O uptake and afford at least a qualitative indication of the ease with which the sorbent can be recycled. In conjunction with the DAC experiments where the material was exposed to laboratory atmosphere, the 10 physisorbents were also subjected to TPD–TGA experiments in which each material was exposed to five additional gas mixtures following a protocol previously established [10]. Each of the five gas mixtures was selected to address a different aspect of the sorbent's performance with respect to CO_2 sorption. Data from the DAC and TPD–TGA experiments on the 10 adsorbents, as well as the five previously studied materials [10], are presented in table 1 (for full dataset of results, see the electronic supplementary material).

2. Results and discussion

In terms of DAC from laboratory atmosphere, **SIFSIX-3-Cu** exhibits the highest gravimetric uptake of CO_2 (7.18 l CO_2 kg^{-1}) of the 10 physisorbents examined during this study, outperforming **SIFSIX-3-Ni**, the top physisorbent from our previous study. **SIFSIX-3-Cu** was previously found to exhibit a high Q_{st} (56 kJ mol^{-1}) and high CO_2 uptake at low partial pressure (1.24 mmol g^{-1}) during single-component CO_2 adsorption experiments [11]. **SIFSIX-3-Cu** exhibits a higher Q_{st} and gravimetric uptake at 400 ppm than **SIFSIX-3-Ni** (50.8 kJ mol^{-1}, 1.10 mmol g^{-1} respectively), which explains why the DAC uptake of CO_2 for **SIFSIX-3-Cu** (7.18 l CO_2 kg^{-1}) is larger than that of **SIFSIX-3-Ni** (4.07 l CO_2 kg^{-1}). The ultramicroporous pore channel and high electrostatic contribution of the inorganic $SiF_6{}^{2-}$ pillar is key to the DAC performance of the **SIFSIX-3-M** compounds [26]. However, whereas pristine **SIFSIX-3-Cu** performs best in terms of DAC performance, it was found to be inherently unstable when exposed to elevated temperature and humidity (40°C, 75% RH). Indeed, the PXRD pattern was completely changed (electronic supplementary material, figure S100) and surface area lost (electronic supplementary material, figure S101).

UiO-66-NH$_2$ was observed to exhibit the next highest gravimetric uptake of CO_2 (5.71 l CO_2 kg^{-1}) of the 10 physisorbents examined during this study. The 'decoration' of the terephthalic acid linker with an amine group to form **UiO-66-NH$_2$** has a significant effect on the CO_2 uptake by this adsorbent compared with the parent material, **UiO-66** (DAC < 1.0 l CO_2 kg^{-1}), under all adsorption conditions. The reason **UiO-66-NH$_2$** outperforms **UiO-66** is again correlated with isosteric enthalpy of adsorption (Q_{st}). **UiO-66** and **UiO-66-NH$_2$** exhibit Q_{st} values of 25.5 kJ mol^{-1} and 35.1 kJ mol^{-1}, respectively [42,43]. High Q_{st} values are reflective of stronger adsorbate/adsorbent interactions, but they also require higher regeneration energies during the desorption process to liberate the adsorbed CO_2 [44]. The improvement in CO_2 adsorption and increase in enthalpy of adsorption of **UiO-66-NH$_2$** over **UiO-66** is attributed to the addition of the highly polar amine group; this in turn increases the affinity of **UiO-66-NH$_2$** towards polarizable gases such as CO_2 [43,45]. The addition of highly polar ligands also leads to a considerable enhancement of CO_2/N_2 selectivity (S_{CN}) [46,47]. The affinity of **UiO-66-NH$_2$** towards CO_2 $SiF_6{}^{2-}$ has previously been observed to increase with an increase in the amine density [48]. This phenomenon also has been observed in other amine functionalized MOMs [49–53]. The increase in the amount of CO_2 adsorbed may also be as a result of a *quasi*-chemisorption interaction between CO_2 and the functional amino group in **UiO-66-NH$_2$**, whereby CO_2 interacts with the amine to form anhydrous carbamates in the absence of H_2O or bicarbonate species under moist conditions as observed in other amine functionalized porous materials [54]. This increased affinity towards CO_2 also improves S_{CW} compared with that of the parent **UiO-66** material and is supported by TPD experiments, which estimate the relative ease of regeneration of the sorbent. The DAC plot in figure 2 reveals that **UiO-66-NH$_2$** requires

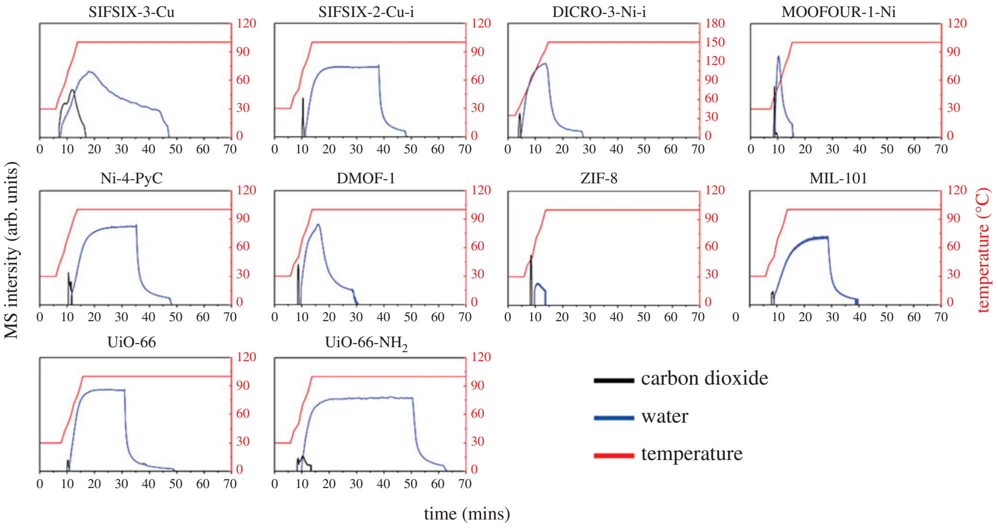


Figure 2. TPD plots for DAC for the 10 sorbents studied. The red curve depicts the temperature profile used for desorption. The MS signal for CO_2 and H_2O are given by the black and blue curves, respectively.

notably more energy and time to liberate CO_2 compared with **UiO-66** and the other physisorbents studied herein.

Comparing **SIFSIX-3-Cu** and **Ni-4-PyC** provides insight into the relative impact of two key aspects of HUMs: the presence of ultramicropores and the strong electrostatics by use of inorganic pillars. The use of ultramicropores alone has been shown to significantly enhance the selective adsorption of H_2 over CO_2 [55] or CO_2 over other gases [17,56,57] via size-selective exclusion. However, size exclusion requires very precise and uniform pore size, which is difficult to design and has only been observed in a few instances. While both adsorbents exhibit similar pore dimensions (3.5 and 4.8 Å for **Ni-4-PyC** and 3.5 Å for **SIFSIX-3-Cu**), **Ni-4-PyC** lacks inorganic pillars (SiF_6^{2-} anions), which results in a reduced electrostatic contribution and Q_{st} values (34 versus 56 $kJ\,mol^{-1}$) [29]. This, in turn, results in lower CO_2 uptake at very low partial pressures such as those in the atmosphere [26]. **Ni-4-PyC** exhibits lower CO_2 uptake (1.68 l $CO_2\,kg^{-1}$) from the laboratory atmosphere compared with **SIFSIX-3-Cu** (7.18 l $CO_2\,kg^{-1}$), which further suggests that electrostatics plays an important role in the performance of physisorbent materials in terms of S_{CN} and S_{CW} and that pore size alone does not determine the adsorption performance of ultramicroporous materials.

SIFSIX-2-Cu-i and **MOOFOUR-1-Ni** performed only marginally better than the non-HUM physisorbents. While **MOOFOUR-1-Ni** (1.27 l $CO_2\,kg^{-1}$) has a very high Q_{st} (56 $kJ\,mol^{-1}$), its larger pores (*ca* 7 Å) are borderline supermicroporous [36]. Comparing **SIFSIX-2-Cu-i** (less than 1.0 l $CO_2\,kg^{-1}$) with **SIFSIX-3-Cu**, we see the former has a somewhat larger pore size (*ca* 5 Å), but also a lower density of inorganic pillars than the latter due to the interpenetrated nature of this compound. These two factors combine to create a lower Q_{st} (31.9 $kJ\,mol^{-1}$) for **SIFSIX-2-Cu-i** and presumably account for the decreased DAC performance. Of the non-HUM physisorbents in this study, **UiO-66-NH$_2$** aside, **ZIF-8** performed the best, adsorbing 1.2 l $CO_2\,kg^{-1}$ from the laboratory atmosphere. **DMOF-1**, **MIL-101** and **UiO-66** all adsorbed less than 1.0 l $CO_2\,kg^{-1}$ under these conditions.

When the materials were exposed to simulated flue-gas (moist 0.15 atm CO_2/0.85 atm N_2), **SIFSIX-3-Cu** was again the top performer of the 10 adsorbents studied herein in terms of gravimetric CO_2 uptake, adsorbing 51.42 l $CO_2\,kg^{-1}$. This is comparable to **SIFSIX-3-Ni** and **Mg-MOF-74**, which were previously found to adsorb 38.69 l $CO_2\,kg^{-1}$ and 34.62 l $CO_2\,kg^{-1}$, respectively [10]. **UiO-66-NH$_2$** (26.12 l $CO_2\,kg^{-1}$), **MOOFOUR-1-Ni** (19.85 l $CO_2\,kg^{-1}$) and **Ni-4-PyC** (12.57 l $CO_2\,kg^{-1}$) were the next best materials under simulated flue-gas conditions.

The addition of moisture to the gas stream significantly impacts CO_2 uptake by the physisorbent materials studied herein. The gravimetric CO_2 uptake from moist simulated flue-gas was reduced by up to 62% when compared with dry flue-gas results obtained for the 10 physisorbents examined in this study. The presence of water vapour in CO_2 containing gas streams can have a detrimental effect on physisorbent materials both in terms of CO_2 adsorption performance [10,58] and overall stability of the adsorbent [59–62]. The selectivity of sorbent materials for CO_2 over H_2O (S_{CW}) is an important aspect in determining the suitability of sorbent materials for CO_2 capture via post-combustion and DAC methods. From the current study, **ZIF-8** performed best in terms of S_{CW} for both DAC ($S_{CW} \sim 18.7$) and moist simulated flue-gas ($S_{CW} \sim 0.5$). ZIF frameworks are inherently hydrophobic as long as the imidazolate linkers do not contain hydrophilic functional groups [63–65]. Despite the high S_{CW} for **ZIF-8**, it exhibits low overall gravimetric CO_2 uptake for both DAC (1.2 l CO_2 kg^{-1}) and simulated flue-gas (1.27 l CO_2 kg^{-1}). **SIFSIX-3-Cu** was the next best physisorbent in terms of CO_2/H_2O selectivity (DAC $S_{CW} \sim 10.03$), which is almost double that of our previous benchmark physisorbent, **SIFSIX-3-Ni** (DAC $S_{CW} \sim 5.43$).

The regeneration performance of the 10 materials studied in this contribution was also examined using TPD experiments (figure 2). The results of these experiments correlates well with the isosteric enthalpy of adsorption (Q_{st}) determined from pure CO_2 adsorption isotherms. However, while pure gas isotherms can be used as an indicator of a material's likely ability to selectively adsorb CO_2 over competing gases such as N_2, TPD studies are necessary to examine the adsorption performance of MOMs when exposed to specific adsorption conditions such as atmosphere and simulated flue-gas conditions. The results of TPD experiments illustrate that water competition is a significant issue when carrying out adsorption studies under humid conditions on physisorbent materials. Consequently, chemisorbents are still the current benchmark materials for CO_2 capture via DAC, with CO_2 uptakes of up to 80.44 l CO_2 kg^{-1} reported in previous studies [10,12,16]. **TEPA-SBA-15** exhibits the highest S_{CW} under all adsorption conditions. However, as mentioned previously, chemisorbent materials can suffer from a high-energy penalty in terms of sorbent regeneration.

3. Conclusion

Capture of CO_2 either from flue-gas or directly from air presents a challenge but also an opportunity to play a significant role in tackling greenhouse gases such as CO_2 over the coming century. In this contribution, we examine the use of benchmark MOMs for their potential use in CO_2 adsorption processes under humid conditions, particularly DAC and moist-simulated flue-gas. Competition with water vapour was found to significantly reduce the CO_2 adsorption performance of the physisorbent materials compared with anhydrous conditions. However, there was quite a wide range in performance, with both pore size and pore chemistry affecting the performance of physisorbents studied herein. Humid conditions exacerbated the situation and even wider ranges of uptakes and selectivity were observed. The functionalization of organic ligands with hydrophobic decoration, such as methyl groups in the case of **ZIF-8**, may be an approach that could be used to improve S_{CW} of physisorbents. However, our results indicate that increased electrostatics generated by inorganic pillars in HUMs or grafted amines are most effective at improving Q_{st} and overall CO_2 adsorption performance. In conclusion, competition with water vapour is a significant challenge for implementation of physisorbent materials in CO_2 capture, either from DAC or from flue-gas. Control of pore size and pore chemistry through crystal engineering may be a successful strategy to improve CO_2 capture performance even in the presence of water vapour and must be further addressed if physisorbents are to compete with chemisorbents in terms of uptake. However, the best physisorbents studied herein were found to be much easier to recycle than the benchmark chemisorbent **TEPA-15-SBA**, suggesting that faster and less energy intensive recycling of physisorbents could compensate for the lower uptake values.

Data accessibility. The datasets supporting this article have been uploaded as part of the electronic supplementary material.

Authors' contributions. D.G.M., J.J.P. and M.J.Z. designed project; A.B. performed ligand synthesis; K.J.C., A.K., H.S.S., R.S. and D.G.M. performed MOMs synthesis; K.J.C., J.J.P. and M.L. performed sorption data collection and analysis; D.G.M. and T.C. performed temperature-programmed desorption; all authors contributed in manuscript writing and gave final approval for publication; M.J.Z. and T.C. performed project supervision.

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