Review Article

Hydrophobic and hydrophilic functional groups and their impact on physical adsorption of CO_2 in presence of H_2O: A critical review

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ABSTRACT

Surface functional groups (SFGs) play a key role in adsorption of any target molecule and CO_2 is no exception. In fact, due to its quadrupole nature, different SFGs may attract either the oxygen or the carbon atoms to facilitate improved sorption characteristics in porous materials, hence the proliferation of this approach in the context of carbon capture *via* solid adsorbents. However, actual processes involve CO_2 capture/removal from a mixed gas stream that may have a non-negligible water content. The presence of humidity significantly hampers the sorption properties of classical physisorbents. To overcome this, the surface of the adsorbent can be modified to include hydrophobic/hydrophilic SFGs making the materials more resilient to moisture. However, the mechanisms behind H_2O-tolerance depend greatly on the characteristics of SFGs themselves. Herein, a multitude of hydrophobic and hydrophilic SFGs (e.g. carbonyls, halogens, hydroxyls, nitro groups, phenyls, various alkyl chains and etc.) for physical CO_2 adsorption are reviewed within the context of their separation performance in a humid environment, highlighting their merits and limitations as well as their impact on cooperative or competitive H_2O – CO_2 adsorption.

1. Introduction

Carbon capture and storage (CCS) is regarded as a prominent pathway for reducing CO_2 emissions from various processes and decarbonising different industries [1], thus allowing for a smoother transition from fossil fuels to renewable energy sources. For instance, the UK is heavily relying on CCS as part of the national plan to achieve net-zero, with the current aims being capturing and storing $20 - 30$ Mt of CO_2 per annum by 2030 and >50 Mt/y by 2035 [2]. Therefore, CCS technologies are widely regarded as indispensable and imperative for mitigating the adverse effects of climate change [3,4]. Within that, adsorption is believed to be a second-generation CCS technology [5] with a technology readiness level (TRL) of $\sim 6 - 7$ [6]. As such, front-end engineering design (FEED) studies and large-scale pilot plant demonstrations are currently under investigation [7,8]. Be it direct air capture (DAC), CO_2 removal from confined spaces (e.g. submarines, space shuttles) or post-combustion CO_2 separation from flue gases, adsorption processes offers merits over alkanolamine (absorption) solvents (e.g. lack of toxicity and corrosiveness, equipment fouling, lesser energy penalties and etc.). However, the inlet gas streams to the capture units contain moisture, which classically adsorbs preferentially over CO_2 (or

at least significantly diminishes the adsorption capacity of the target molecule) on many conventional adsorbents. For example, ~ 4 % of the flue gas from the steel industry is H_2O vapours, $6 - 12$ % in cement [9] and $10 - 18$ % in waste incineration [10]. Further, tail gas from a hydrogen production process can present ~ 0.75 % (mol) of H_2O coupled with high (>50 mol%) CO_2 contents [11,12]. Conditions encountered in submarines present low CO_2 concentrations ($\sim 0.5 - 1$ %) coupled with high (90+%) relative humidity (RH) values [13], whilst ambient air contains $0 - 3$ % H_2O [14] apart from ~ 426.9 ppm (as of May 2024 [15]) of carbon dioxide. Moreover, within the power generation context, a variety of moisture partial pressures have also been reported, ranging from 3.4 % up to 10 % [16–18]. The exact H_2O content, though, would vary greatly depending on the temperature, fuel and context of the separation: at 1 atm and 30 °C the maximum is 4.2 mol% [19] for boiler flue gas, whilst for a cement kiln the numbers would be ~ 5 % H_2O at 45°C (followed by 17 % CO_2, 10 % O_2, balance N_2) [20] and at 50 °C natural gas combustion flue gas can present values as high as 7.3 % H_2O [20]. For DAC these parameters would also depend on the location, season and even time of day or weather conditions. Finally, novel CCS technologies focused on removing CO_2 from seawater (e.g. the works of Digdaya *et al.* [21] or the SeaCURE project [22]), often termed direct ocean capture (DOC), deal with gas streams, where the RH could be as

Nomenclature		MS	Mass spectrometer
		ODTMS	Octadecyltrimethoxysilane
AC	Activated carbon	PEI	Polyethyleneimine
ACF	Activated carbon fibre	PSA	Pressure swing adsorption
APTES	3-amino-propyl-triethoxysilane	PVDF	Polyvinylidene difluoride
BT	Breakthrough	RH	Relative humidity
BTESE	1,2-bis(triethoxysilyl)ethane	SBS	Polystyrene-block-polybutadiene-block-polystyrene
CCS	Carbon capture and storage	SFG	Surface functional group
COF	Covalent organic framework	TGA	Thermogravimetric analysis
DAC	Direct air capture	TRL	Technology readiness level
DOC	Direct ocean capture	TSA	Temperature swing adsorption
FEED	front-end engineering design	TVSA	Temperature & vacuum swing adsorption
FTIR	Fourier Transform Infrared Spectroscopy	VOC	Volatile organic compound
GCMC	Grand Canonical Monte Carlo simulations	VPSA	Vacuum pressure swing adsorption
KPI	Key performance indicator	VSA	Vacuum swing adsorption
LC50	Lethal concentration in 50 % of cases	XPS	X-ray photoelectron spectroscopy
MOF	Metal organic framework	ZIF	Zeolitic imidazolate frameworks

high as 100 % further highlighting the prominence of this matter.

For amine solutions moisture content of inlet gas is a lesser issue as they are themselves (commonly) water based. Solid adsorbents, on the other hand, may perform below par due to the presence of H_2O. The kinetic diameter of the water molecule (265 pm) is smaller than that of CO_2 (330 pm) [23] and the permanent dipole moment of the H_2O makes it strongly adsorbable on many surfaces [24]. Therefore, H_2O often acts as a competitor to CO_2, since water molecules can often preferentially occupy a given adsorption site. Additionally, the presence of H_2O may affect the stability of an adsorbed carbon dioxide molecule by potentially displacing it off the surface [25]. Further, an adsorbed H_2O molecule would also impact the charge distribution of the surface. These aspects present a significant challenge for many applications/adsorbents and require specific attention. Dehydration of the inlet stream is possible (and would often help) but adds significant operational expenses [26], additional footprint and complexity. Some estimates suggest dehumidification to be equivalent to 30 % of the required energy for CO_2 recovery [27,28]. Moreover, if water is adsorbed by the material, then the energy penalty for regeneration would increase further due to the need to alleviate H_2O from the adsorbent. As such, development of moisture-tolerant physisorbents is imperative for wide deployment of adsorption-based CCS. An ideal/target physisorbent should be moisture-tolerant, i.e. possess a high mechanical stability upon exposure to H_2O in order to facilitate adsorbent regeneration by steam - a common industrial practice. This aspect is particularly important for MOFs (as highlighted in Section 2.3). Secondly, an ideal moisture-tolerant sorbent should have a high (or at least acceptable) ability to capture CO_2 from humid gas streams. These properties should also be coupled with the general low regeneration energy, high cyclic capacity and cost-effectiveness (and etc.) to suit industrial applications.

Within a laboratory setting most material-oriented publications focus on either pure CO_2 adsorption by gravimetric/volumetric methods or dynamic breakthrough studies from a simulated (yet often dry) gas stream. For these investigations, modifying a generic adsorbent to incorporate a desired surface functional group (SFG) that benefits CO_2 affinity is a popular approach. However, this approach often does not consider the aspects of interactions between the generated SFG and moisture. Such interactions may significantly alter the equilibrium capacities and/or kinetics of adsorption (and a plethora of further critical parameters for the actual industrial implementation of this technology). In the realm of material development, the questions and benefits from an engineering standpoint are less relevant and are only discussed (or discovered) at a later stage once manifested [19]. As such, investigations into materials that would be viable over a prolonged period of dealing with large scale multicomponent (*not just binary*) flows are necessary.

The prominence of this issue can be highlighted by the recency of some review publications that focus on CO_2 adsorbing materials and their interactions with H_2O ([10,29]) as well as the effects of water on chemisorbing amine SFG (dedicated manuscript [30] and elaborate discussions in [10,29]). Other SFGs, however, do not attract as much attention in the context of CCS (despite successful industrial deployment of physisorbents for point-source capture [14], their lower regeneration energy requirements and other advantages). Non-chemisorbing SFGs are also often overlooked in studies that evaluate resistance to moisture (although, some are mentioned in [29]). As such, this *state-of-the-art* review is focused on hydrophobic/hydrophilic properties of (non--amine) SFGs within the context of CO_2 capture *via* physisorption. This is prefaced with a brief discussion on generalised pristine material characteristics and their relationship to H_2O (as noted earlier, a dedicated manuscript can be found elsewhere [10]). Our previous works evaluated the impacts of individual SFGs and their affinity towards CO_2 [31,32]; whilst guidelines, good practices and considerations on experimental assessment (and computational predictions) of water competition in adsorbents can be found in [19].

When evaluating number of publications (within the realm of chemical engineering) based on keywords of: "*Carbon Dioxide*", "*Adsorption*" and "*Hydrophobicity*", whilst excluding various terms referring to "*Absorption*" and "*Membrane separation*" as well as "*Catalysis*", an emerging tend can be seen with the number of publications increasing by an order of magnitude within the past decade (as can be visualised from Fig. 1).

Despite this review paper having a narrower scope (focusing on physisorbents) than the above literature search, the increasing prominence of this issue cannot be ignored, especially when contrasted with the number of publications on the topic of CO_2 adsorbent development that do not investigate the questions of impacts of moisture. If deploying the same keyword structure as above but without any mention of hydrophobicity, the number of studies published in 2023 *alone* dwarfs the cumulative number from Fig. 1 (namely, 2088 versus 532). As such, this review aims to raise awareness of this particular aspect of CO_2 adsorbent deployment and to inform practitioners on the potential issues (or merits) that would manifest upon applications in humid conditions, thus guiding towards an appropriate paradigm for designing moisture-tolerant physisorbents for "real-life" CCS *via* deployment of appropriate SFGs.

In the next section, a brief introduction of a number of pristine CO_2 adsorbents (i.e. without specific functional groups) is presented in order to envisage their generalised material-specific properties with regards to humidity. Thereafter, a plethora of different SFGs (with some key examples provided in Fig. 2) are described in the context of CO_2
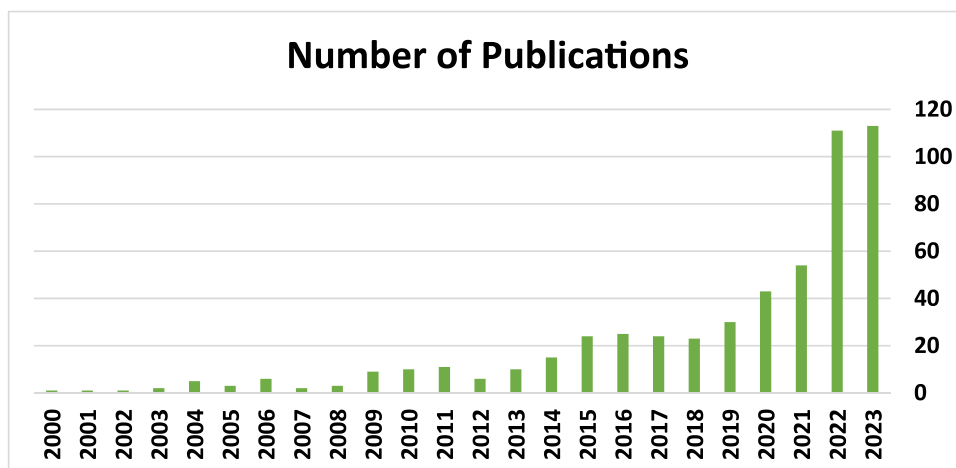
Fig. 1. Number of Scopus-indexed publications referring to the topic of hydrophobicity of CO_2 adsorbents since between 2000 and 2023.
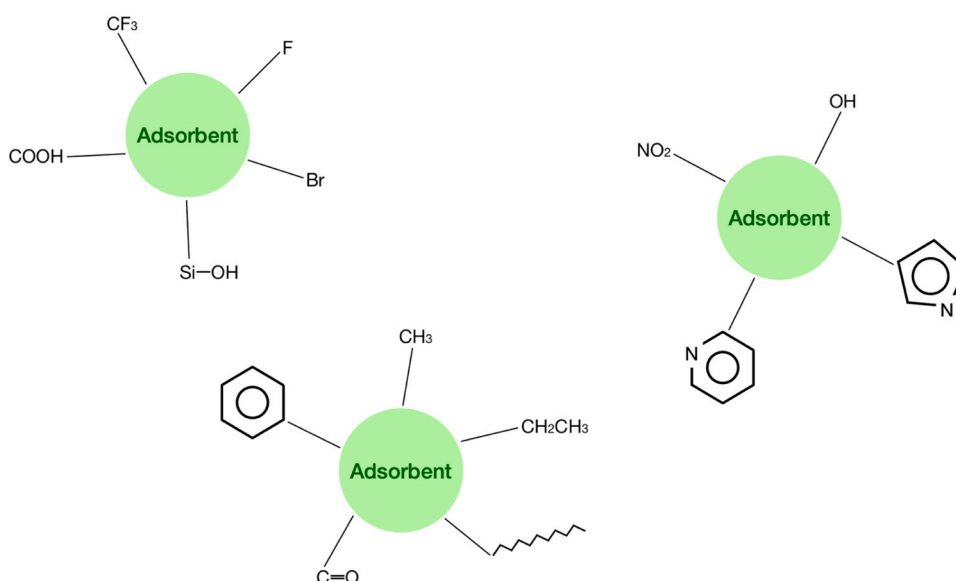

Fig. 2. Examples of SFGs discussed in this review paper.

physisorption in a humid environment, their hydrophobic/hydrophilic properties as well as any stand-out aspects. These are separated into sections based on the main (hetero)atom present.

2. Materials

2.1. Carbon-based adsorbents

Generally, pristine carbonaceous adsorbents are hydrophobic [33], hence, materials like carbon nanofibres [34] or activated carbons (ACs) [35] present surface hydrophobicity. This is ascribed to their non-polar C-C bonds [36]. This is mostly correct when dealing with low RH but they still present water vapour adsorption uptakes at high partial pressures of H_2O (i.e. high RH, generally over 50 % [37]), which may be even higher than their CO_2 uptakes at same adsorption temperatures [24] due to capillary condensation [37]. This can be resembled by a characteristic S-shaped isotherm of carbonaceous adsorbents as opposed to type I and II for hydrophobic adsorbents [38]. The latter present significant H_2O loading even at low water partial pressures. Due to the aforementioned properties (coupled with the low RH values of 4 – 18 % commonly associated with most flue gases [39]), ACs may be of particular interest in the context of Vacuum-Pressure Swing Adsorption

(VPSA) applications from wet industrial flue gases [40]. ACs have also been shown to deliver high CO_2 purities (>85 %) as well as product recoveries (>82 %) and (comparatively) low energy consumption (<0.9 GJ/t) up to RH = 50 % in Vacuum Swing Adsorption (VSA) processes [41]. These results were contrasted to two different mixed/hybrid sorbents (i.e. Al_2O_3+Zeolite 13X and K_2CO_3/Al_2O_3) suggesting ACs to be favourable for applications with low RHs.

The pristine carbon surface is hydrophobic, hence, oleophilic (i.e. a strong affinity towards non-polar compounds). Therefore, it is prominently used in water treatment applications. However, even for ACs, the CO_2 adsorption capacity decreases due to competitive adsorption with H_2O. Moisture in the flue gas may also cause partial pore mouth closure, which, in turn, imparts diffusion resistance for the transport of CO_2 to the active adsorption sites [42]. However, this may also be ascribed to functional groups stemming from the organic precursor and/or activation method as well as any post-treatment (e.g. functionalisation, modification, impregnation, grafting and etc.) present on the surface. Generally, chemical activation is believed to lead to a more hydrophilic surface than physical activation [43]. This is ascribed to the former producing more SFGs (and expelling more heteroatoms stemming from precursor) and can corroborated by evaluating the differences in Fourier Transform Infrared Spectroscopy (FTIR) plots of a physically [44] and

chemically [45] activated AC from the same precursor, in this case – biomass (wood pellet) combustion bottom ash. These functionalities impact the surface properties of the material leading to increased/decreased affinities towards given molecules. For example, ACs impregnated with MgO and CaO can be used for chemisorbing CO_2 for applications of indoor air quality control [46]. Within the context of post-combustion CCS, however, other functionalisation pathways are more prevalent. Carbonaceous adsorbents containing O- and N-heteroatom SFGs are often described as increasing the uptake capacity of ACs due to the quadrupole nature of the adsorbate (CO_2) and polarity of the SFGs, which alter the electrostatic properties of the pores. Yet these surface heteroatoms can also demonstrate highly hydrophilic behaviour [47].

2.2. Zeolitic adsorbents

Zeolites are known to be hydrophilic and preferentially interact with moisture. Due to high affinities towards H_2O, full regeneration of some zeolites require temperatures over 250 °C [48] (other suggest up to 320 °C [35]). High hydrophilicity of these mineral materials allows for their industrial deployment (e.g. cryogenic air separation) as dessicants [19]. Drying fixed-beds in Temperature Swing Adsorption (TSA) applications can employ zeolite 3 A (or silica gel) [13]. Molecular sieves are also employed in dehydration of liquified natural gas [48]. This name (i.e. molecular sieves) for zeolites is frequently used to highlight their uniform pore sizes. However, this feature does not prevent co-adsorption of CO_2 and H_2O (since the latter molecule is smaller). As such, modification of the zeolite surface can be viewed as the pathway to adapt them for CCS. However, as zeolites are typically more expensive than silicas, their functionalisation is often questioned and may require further justification [10].

Within the context of CCS, zeolites type X and type A (large and small pore zeolites, respectively [49]) have been mostly studied. These zeolites interact with moisture as well as with CO_2. Both gaseous molecules may be adsorbed in the primary inner cavity of such zeolites. Yet due to different kinetic diameters (H_2O is ~0.26 nm and CO_2 is ~0.33 nm [23]), the larger CO_2 molecule would not have access to the sodalite cage (~0.27 nm) of the material [50]. With the sodalite, also referred to as the β-cage, being the primary building unit of such zeolites, accessibility of it for water molecules, increases their moisture adsorption capacity compared to CO_2. Once inside the zeolite's porous framework, the adsorbed water may also build hydrogen bonds with other H_2O molecules, resulting in formations of water agglomerations [51]. These, further drastically impact the CO_2 uptake of zeolites.

For example, CO_2 adsorption capacity of zeolite 13X (one of the most popular commercially available sorbnets; also known as NaX) decreases by 90 % in the presence of moisture due to competitive adsorption [51]. When comparing 13X to 4 A, both materials present similar CO_2 adsorption capacities (under humid conditions) that are miniscule compared to the amounts of co-adsorbed water (where 13X presents a larger relative capacity) [50]. One pathway that has been proposed is coating the zeolite with an AC, thus producing a hybrid adsorbent with surface hydrophobicity (due to the AC's properties) that still presents high CO_2 uptakes (due to the zeolitic phase). Such modification only slightly (~5 %) lowered the CO_2 adsorption capacity, whilst halving the H_2O uptake [52]. The concpet of coating, however, can be viewed as a macro-modification to the outer surface of a given not mositure-tolerant adsorbent. By adding a layer of a (normally, but not neccesarily) hydrophobic material, the hydrophylic active adosprtion sites may be protected from occupation by H_2O molecules.

Water may also hinder CO_2 adsorption not only *via* occupation of sites but also by steric hinderance effects. This is due to the shielding of the O-Si-O sites by H_2O agglomerations [51]. In order to avoid such issues (and, since, the silica-rich regions of the zeolites are more hydrophobic than the alumina [51]), zeolites with high Si/Al ratios (> 50) are proposed to be more hydrophobic [28]. However, such materials may exhibit low CO_2 adsorption capacities [23]. To benefit from the high capture capacity of conventional (e.g. type X) zeolites and the hydrophobicity of high-silica zeolites, an alternative hybrid adsorbent can be designed. For example, by coating a ZSM-5 (a medium-sized pore zeolite [49]) core (SiAl = 34 [53]) with an all-silica zeolite shell, the moisture uptake decreased significantly (~30 – 40 % depending on RH), whilst the CO_2 capacity dropped by 9 % compared to parent ZSM-5 beads [54].

Similarly, zeolitic imidazolate frameworks (ZIFs) have been used to protect the surface of zeolite type Y [55] as well as 5 A [56] and modified 13X [57]. The assosiated SFG is described further in the manuscript as its hydrophobicity stems from the n-heterocycle ligand.

Non-modified 5 A zeolites were also shown to be largely inapplicable to capture CO_2 from humid gases by Suzuki *et al.* [58]. They evaluated and compared cylindrical pellets of a standard commercial 5 A zeolite (a classic hydrophilic zeolite [10]) against a modified (non-disclosed; assumed to be proprietary) type Y (analogous to type X yet with a higher (1.5 minimum [49]) Si/Al ratio) zeolite, produced by Mitsubishi Heavy Industries for Pressure Swing Adsorption (PSA) applications. It was found that the reference 5A zeolite had significantly lost the capacity to adsorb CO_2 (and even N_2) at high humidity levels. In contrast, with the studied type Y (SiO_2/Al_2O_3 ratio of 70 was reported for this particular material), the CO_2 uptake dropped by one-third and two-thirds from dry (RH = 0 %) to wet conditions (RH = 50 and 80 %, respectively). Interestingly, elevated RH values had negligible influence on the kinetics of diffusion for the modified zeolite.

2.3. Metal organic frameworks

Many adsorbents, particularly Metal Organic Frameworks (MOFs), underperform in the presence of H_2O. Alumina supports are more resistant to moisture compared to some silica-based materials [30]. The latter class of materials may face pore collapse after prolonged steam treatments [26]. However, exposure to moisture may facilitate the destruction of the framework of some MOFs (e.g. slow hydrolysis induced collapse of HKUST-1 [16]). Without suitable mechanical stability a material cannot be deployed at scale, which in turn influences process viability. Industrial ACs cost around (and normally below) £5/kg, whilst MOFs are normally much more expensive. A number of MOFs have been commercialised (e.g. by BASF under the family name Basolite) and are currently priced at over £10,000/kg. Other estimates suggest USTA-16 to cost ~ €83.2/kg [59], while for some other MOFs, the raw materials (alone, no profit margin included or equipment amortisation and etc.) to cost more: UiO-66 > $500/kg; Ni-MOF-74 > $850/kg [60]. In order to justify such prices, a long operational life is a must. The presence of moisture decreases the number of regeneration cycles [60], therefore, it is critical to develop adsorbents with sustained performance upon increased regeneration cycles, when treating wet gases.

Apart from mechanical stability, moisture tolerance with regards to CO_2 adsorption should be addressed. Generally, MOFs have uptakes much higher than those of conventional adsorbents. For example, commercialised by BASF homologues of HKUST-1, MIL-53(Al) and MIL-100(Fe) present CO_2 adsorption capacities (pure CO_2 stream at ambient temperature and pressure) of 117.5 mg/g, 58.3 mg/g and 48.8 mg/g, respectively [61]. However (similar to zeolites), these values are known to decrease drastically (75 – 100 % loss) if capturing from a wet (5 – 10 vol% H_2O vapour) flue gas stream [10,62]. These are associated with competition between the two molecules in question for a given adsorption site. Interestingly, out of the three homologues mentioned, MIL-100(Fe) was suggested to be most water-stable due to the presence of amorphous content (which hampered water access) [61]. Nevertheless, they presented reduced surface areas and micropore volumes upon 24 hours of aging under 100 % RH. Furthermore, MIL-101(Cr) [60], M-MOF-74 family [10] among others are considered hydrophilic [36] adsorbents, whilst the ZIF family of materials have a much higher

tolerance to moisture and are labelled as hydrophobic [63]. Various ZIFs possess different functionalities (as described in Table 1).

However, ZIFs as a class of materials are believed to be hydrophobic. As such, this characteristic also (i.e. apart from the SFGs) stems from their common ligand basis, i.e. imidazole. Imidazole is a member of the azole family. Azoles are N-containing five-membered heterocycles. However, unlike pyrrole, they must contain at least one additional heteroatom in the ring [71,72]. As such, oxazoles and thiazoles exist alongside a plethora of other di/triazoles as well as tetrazole heterocycles (with some examples provided in Fig. 3).

Utilising these building blocks is a known approach for producing water-stable MOFs [73]. This approach can be corroborated by a particular stand out material in recent years is CALF-20, a Zn-based framework connected with oxalic acid and triazolate ligands. Interestingly, despite a reduced CO_2 uptake in the presence of H_2O (due to volumetric exclusion), the affinity between the adsorbent and the adsorbate increases in the presence of moisture [74]. For CALF-20, the H_2O adsorption is suppresed due to the pore sizes of ~0.5 nm, where interaction with CO_2 (i.e. overlapping var der Waals forces from the pore walls) are stronger than hydrogen-bonding with water [19].

On the other hand, low water concentrations (RH <20 % [19]) may facilitate CO_2 adsorption. This is the case for MIL-100(Fe), as the pre-adsorbed H_2O molecules in the mesopores of this MOF form micropore "pockets", that could adsorb CO_2 [60]. These phenomena, however, are often RH-dependent and at high partial pressures of water vapours, the CO_2 adsorption capacity of many MOFs (and non-functionalised adsorbents in general) declines dramatically.

High levels of structural defects have been proposed to induce hydrophilicity into MOFs [75] (and vice versa) since they can act as strong binding sites for the water molecules [19]. For example, higher synthesis temperatures lead to a lower amount of defects on UiO-66, which in turn decreases its' hydrophilicity (and vice-versa) [76]. Yet the hydrophilic metal clusters (or unsaturated metal sites) as part of the framework preferentially bind with water molecules over CO_2 [77]. As such, protective functionalisation and/or hydrophobic coating are great avenues for developing moisture-tolerant MOFs (and, by extension, adsorbents in general) for carbon capture [73].

One of the most prominent approaches to hydrophobisation of the surface is to endow a given CO_2 adsorbent with polar CH-chains.

3. CH-chain functionalisation

Introduction of long chain carbon molecules is believed to impart hydrophobic properties to sorbents. Yet shorter CH-based functionalities are also known to decrease sensitivity to moisture in CO_2 adsorbents. For example, polar adsorption sites of CALF-25 are believed to be protected by ethyl groups as part of the ligand [65]; other MOFs employed ethylene and benzene linkers [78], whilst introduction of methyl groups to another MOF enhanced CO_2 adsorption despite an RH of 85 % [79]. However, apart from aliphatic SFGs (Section 3.2), aromatic groups (Section 3.1) also facilitate hydrophobic surface properties. Nevertheless, in general, due to the non (or slightly) polar nature of most

CH-based SFGs, they do not provide strong H_2O adsorption sites. Additionally, with an increase in chain length, a hindrance of gas molecule diffusion to the surface of the adsorbent is anticipated. This often leads to a drop in CO_2 capture capacity (compared to a pristine sorbent) in dry environments. However, when adsorbing from humid streams, such SFGs can often "protect" the adsorption sites by decreasing their accessibility for H_2O molecules. This, in turn, results in a lesser (in percentage) drop in performance for the modified sample as opposed to the significant losses in capacity common for many non-functionalised adsorbents when comparing their performance in dry and humid environments.

3.1. Aromatic/Aryl functionalisation

Despite benzene rings being less hydrophobic than cyclohexane rings [80] (their aliphatic counterpart), aromatic SFGs are still considered as great modifying agents to induce hydrophobicity. For example, tolyl groups are widely regarded as hydrophobic due to their non-polar nature and, therefore, they have been applied to tune the hydrophilic surface of a silica-based xerogel [81]. Based on low temperature thermal decomposition, this was successfully achieved yet at the expense of volumetric CO_2 uptake (ascribed to lower surface areas and pore volumes upon addition of tolyl SFG). Also, non-polar benzene rings can act as hydrophobic linkers in MOFs [78].

A variety of phenyl-based SFGs on a Li-exchanged beta-zeolite (with a Si/Al ratio of 12.5) have been investigated for CO_2 adsorption under humid conditions [23]. The phenolic moiety of this SFG was successfully grafted to the bridging O atom of the micropore wall *via* strong covalent bonds. Such functionalisation facilitated hydrophobicity by hindering diffusion of H_2O into the pores, hence, leaving adsorption sites accessible to carbon dioxide. With regards to dynamic adsorption of CO_2 from moist gas, the parent zeolite presented a drop in capacity of ~22 % compared to dry conditions, whilst for the functionalised adsorbent, the uptakes were very similar. The authors have also investigated further functionalisation of their Ph-modified zeolite (i.e. the addition of various SFGs (COOH, OH, NH_2 and CH_2-NH_2) to the existing surface aryl chain). These have been described in their respective sections in this review.

Alternative SFGs containing aromatic rings (as well as an oxygen and phosphorous heteroatom) have also been investigated. A derivative of 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide has been applied to various silicates (SBA-15, SBA-16 and KIT-6) owing to an electron-rich condensed aromatic structure [82]. As a result of such functionalisation, all three bases demonstrated higher adsorption capacities than the pristine silicas. In the presence of 1 % water vapour (from a 3 % CO_2 stream; balance N_2), a further enhancement was reported. The latter increase was ascribed to chemisorption reaction between the amine moiety present as part of the modifier, yet the hydrophobic properties of the adsorbents were further evidenced by minimal mass loss (0.5 %) below 150 °C.

Polynaphthalene-modified MOF-5 was shown to significantly outperform the pristine material under both dry and humid adsorption conditions [83]. Despite possessing merely a third of parent's MOF-5 surface area, CO_2 adsorption uptake was doubled. The heat of adsorption was also noticed to be larger while the CO_2/N_2 selectivity was increased by a factor of 23. With regards to hydrophobicity, when evaluating a mixture of 16 vol% of CO_2, 84 vol% of N_2 (dry basis) and a RH of 65 %, the breakthrough (BT) time was noted to change minimally due to introduction of humidity (656 seconds – wet; 688 seconds – dry), whilst for the pristine MOF, the values were not registered due to equipment limitations (i.e. very short BT time). Finally, after a singular (humid) adsorption-desorption cycle, MOF-5 lost a significant portion (approximately half) of its capacity, whilst for naphthalene-MOF-5, the capacities almost remained the same.

Table 1
Examples of ZIFs with various functional groups.

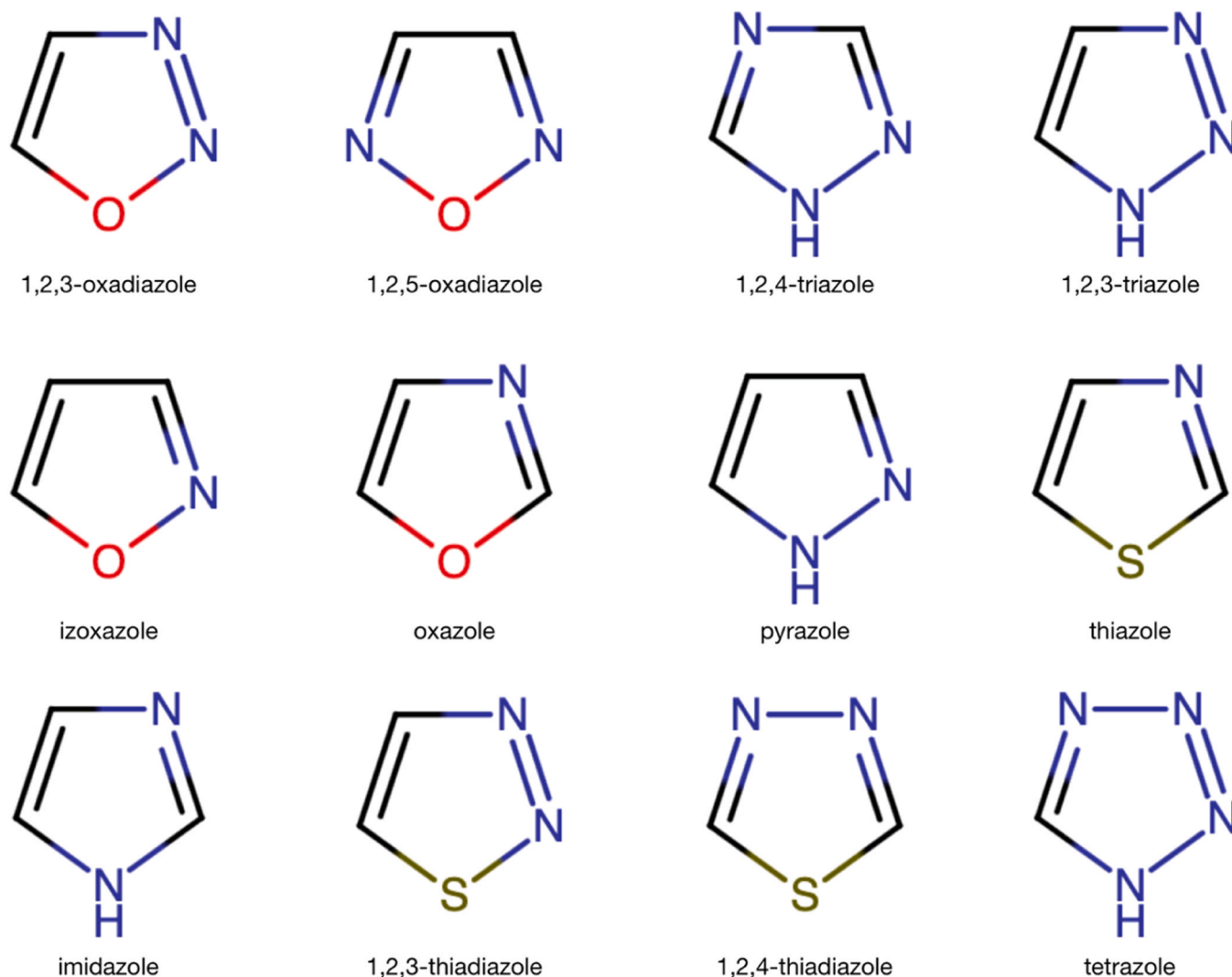| Functionality	Name
Methyl	ZIF−8 [64] (also labelled as MAF−4 [65])
	ZIF−79 [66]
	ZIF−79 [66]
Carbonyl	ZIF−90 [65]
Bromine	ZIF−81 [67]
	ZIF−300 [68]
Chlorine	ZIF−69 [67,69]
	ZIF−301 [68]
	ZIF−71 [70]
	ZIF−80 [67]

Fig. 3. Examples of azole molecules.

3.2. Aliphatic/Alkyl chain functionalisation

A further type of CH-chain functionalisation is achieved *via* grafting alkyl chains to the surface of the adsorbent. Alkyl chains are hydrophobic species. However, grafting their moieties often leads to a trade-off between CO_2 adsorption capacities and hydrophobic properties of materials [84]. Nevertheless, alkyl functionalisation is a feasible strategy. For example, the hydrophobicity of ZIF-8 is also assosiated with the presence of a methyl group that hinders diffusion of water molecules into the pores [85]. On the other hand, the methyl group can also contribute to CO_2 adsorption *via* electrostatic interactions between the partially positive hydrogen atoms (of the methyl SFG) and the partially negative oxygens of carbon dioxide [46].

Hydrophobicity of a given SFG typically increases with the length of the alkyl chain. For example, functionalisation with MIL-101(Cr) with n-propylamine (C3), n-hexylamine (C6), and 1-dodecylamine (C12) has led to a rise in hydrophobic properties in the same order as described above (starting from the pristine MOF) [86]. As such, not only introducing a surface alkyl SFG but also increasing its chain length can be a practical pathway to increase hydrophobicity of the adsorbent.

From the previously described investigation on a beta-zeolite [23], some information (albeit minimal) on increasing the alkyl chain can be gathered. The authors have grafted their zeolite with an aniline (Ph-NH$_2$) SFG as well as a benzylamine (Ph-CH$_2$-NH$_2$) SFG. The main

benefits (compared to the unmodified sample) were attributed to the presence of the amino functionality (which produced a new type of adsorption (i.e. chemisorption) site), yet when comparing the two, the longer chain SFG had a higher (0.87 mmol/g versus 0.78 mmol/g) CO_2 uptake from a simulated wet flue gas, whilst the BT were similar. The authors however, did not further discuss the results (i.e. how a single additional C-chain could dramatically increase uptake). We hypothesise, however, that this phenomenon may stem from synergistic effects between the amine and hydrophobic SFGs. A similar sentiment has been observed for a fluoroalkyl-modified polyallylamine adsorbent, where incorporation of the hydrophobic groups (fullerene, alkyl and F moieties) drastically enhanced amine accessibility (4.1-fold) as well as CO_2 capture capacity (2.8-fold) [87]. The authors have ascribed this effect to inclusion of additional free void volume upon modification. These features, however, do not necessarily describe the properties of alkyl-functionalisation per say, as there are other hydrophobic SFGs on the surface of the adsorbent.

Hexadecane [88] or cetyltrimethylammonium ions [89] can serve as an example of such long chains (both C$_{16}$) alkyl-based hydrophobic modifiers. The latter agent can be used for developing a hydrophobic surface layer on MCM-41 silicas [89] but other alternatives also exist.

In addition to long chain alkyls, short chain alkyl (e.g. methyl) SFGs have been shown to improve resistance to moisture. This can be gathered based on data for a hybrid (perfluorosilica-Ni) adsorbent [46] as

well as a methyl-containing Al-based MOF, namely, ZJU-620(Al) [90]. This material presented minimal changes in BT time under 15/85 CO_2/N_2 in both RH = 80 % (141.5 s) and dry (145.2 s) conditions. As expected with most MOFs, the water molecules were largely adsorbed around the metallic (in this case, AlO_6) clusters, whilst the alternative (and preferential for CO_2) adsorption sites (between two parallel benzene rings as part of the ligand) were protected from moisture by the methyl functionality (based on Grand Canonical Monte Carlo (GCMC) simulations). As such, the more high-energy site was "shielded" by the hydrophobic methyl SFG.

Another successful methyl functionalisation is described in a recent study on CALF-20 [91]. Such functionalised MOFs presented a (dry) CO_2 uptake of ~70 – 78 % of the parent MOF. More importantly, however, is the fact that at high RH (70 – 80 %), the methyl-functionalised adsorbents retained ~20 % of their dry capacity (between 0.5 and 0.6 mmol/g). The pristine adsorbent's ability to capture CO_2 at RH values over 70 % is nearly entirely compromised [92]. The high moisture tolerance was ascribed to the methyl SFG limiting formation of hydrogen bonding networks (based on GCMC simulations) [91]. The combination of this data suggests pristine CALF-20 to be more suitable for capture from relatively dry (RH< ~47 % [92]) gas streams (due to lower CO_2 heat of adsorption values, higher adsorption capacities and etc. [91]), whilst methyl-functionalised adsorbents would be more favourable for highly humid applications.

An alternative option for introducing alkyl-SFGs is to use hydrophobic polymers as binders, thus, solving two issues simultaneously. Firstly, this could serve as a quasi-modification of the surface which addresses the questions of moisture in the feed gas. The second one is associated with industrial deployment (especially in fixed-bed reactors), as in this case, individual adsorbent particles should be large enough to avoid operational challenges (e.g. bead, pellet, granule and etc.), and not powder [93]. This is done to minimise dust formation [94], facilitate handling [95], increase the heat transfer rate [96] and reduce pressure drop in the column. This approach has been trialled with a polystyrene-block-polybutadiene-block-polystyrene (SBS) binder, which was used to coat polyethyleneimine (PEI) mesoporous cellular foam onto ceramic fibre honeycombs for DAC applications [97]. Incorporation of SBS polymer counteracted the hydrophilic nature of both the silica and PEI. Following this methodology, an adsorbent was developed that performed better (in terms of both uptake and BT) under humid conditions than in a dry environment. This was ascribed to the mechanism of reaction between amines and CO_2 which is promoted by moisture. Nevertheless, competitive adsorption between H_2O and CO_2 still influenced the process as evidenced by the maximised CO_2 uptake at moderate RH values (50 %) and a drop at a high RH of 80 %. Moreover, steam regeneration was studied (since prolonged exposure to steam may collapse the silica microstructure [26]). The produced material presented consistent and stable performance after three consecutive adsorption-desorption cycles (7 L/min of steam at 105 °C).

Alternatively, binders may also be hydrophilic – alginate, which was used for moulding zeolite beads [98]. This approach has been criticised for pore blockage (which is to be expected) and for increasing adsorbent's water uptake, whilst dropping the CO_2 adsorption capacity [55].

Alternatively, prefabricated shaped adsorbents can be coated with hydrophobic powders. This has been trialled on K_2CO_3/Al_2O_3 beads, which were coated with polyethylene (and compared to TiO_2 and SiO_2) powder to produce surface hydrophobicity of a adsorbent [99]. This was done by drop casting the adsorbent sol onto a layer of powder-like hydrophobic modifier (to achieve coating), followed by aging and calcination at different temperatures. The alkyl chain polymer presented most resilient adsorbent particles with a compressive strength of ~27.2 MPa and the average maximum pressure equal to ~85.4 N. Simultaneously, this adsorbent possessed the least CO_2 uptake (0.24 mmol/g) compared to TiO_2 and SiO_2 coated samples (0.50 and 0.36 mmol/g, respectively) from a simulated flue gas stream of 10 vol% CO_2 and 10 vol% of H_2O, balanced with N_2. However, this was only true

for the sample calcined at 300 °C, as at higher calcination temperatures (>500 °C), all three samples were shown to lose some of their mechanical and surface hydrophobic properties, with decomposition of polyethylene (due to its organic nature). With regards to the SiO_2- and TiO_2-coated adsorbents, deterioration of the microstructure (induced by the increased temperatures) was believed to be culpable for enhanced water diffusion to the K_2CO_3/Al_2O_3 core. Finally, the CO_2 adsorption capacity presented a maximum for samples calcined at 500 °C. The values for 850 °C were, however, greater than those for 300 °C across all modifying species reported in the work.

4. N-heteroatom

Functionalisation with amine moieties is one of the most prominent surface modification methods in the context of CCS. Their high selectivity and strong affinity towards carbon dioxide offer significant benefits, especially in DAC. Amines are hydrophilic [100] and the reaction of this SFG with CO_2 is promoted by presence of moisture. However, due to chemisorption, the regeneration energy is higher than the physisorption counterparts.

The interaction between the NH_2 SFG and H_2O has been recently rigorously described elsewhere ([10,30]). They are, therefore, left out in this review, where more focus is drawn towards other N-containing functional groups. Nevertheless, incorporation of this SFG has been reported to increase hydrophilicity of a Zr fumarate-based MOF due to enhanced surface basicity [75]. Additionally, since quaternary N (i.e. quaternary ammonium) can be viewed as a fully (or rather overly) substituted amine, this SFG also presents hydrophilic properties [101]. Finally, employment of long-alkyl chain amines can enhance hydrophobicity whilst also facilitating CO_2 adsorption [102], which may stem from synergistic effects between these two SFGs.

However, other polar nitrogen SFGs can also attract H_2O *via* hydrogen bonding [103]. As such, N-containing functionalities and their impact on adsorbent's hydrophobicity/hydrophilicity and affinity towards CO_2, are discussed hereafter.

4.1. Imide

Imides are a type of compound that present two carbonyl groups bound to a nitrogen heteroatom, hence, a structure that can be represented as: O=C-N-C=O (as can be visualised from Fig. 4). Imides offer different adsorption sites. Presence of H_2O with CO_2 was found to have both a cooperative and a competitive nature in an investigation of an imide-containing covalent organic framework (COF) [104]. At low (< 40 %) RHs, the capture capacity of the COF was raised by 25 %. This was ascribed to the hydrophilic carbonyl-site attracting the H_2O, which, once bound to the SFG, enhanced CO_2 adsorption, compared to adsorption from dry gas. To verify whether the imide group partook in the adsorption process, FTIR spectroscopy was employed. An increased "red shift" of the resulting wavenumber with a rise in RH was seen. This
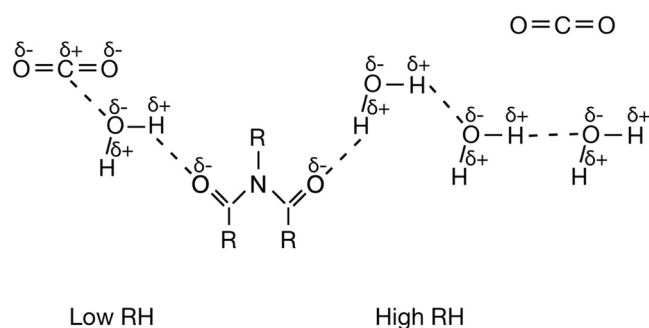

Fig. 4. Proposed cooperative (low RH) and competitive (high RH) interactions between the imide SFG with H_2O and CO_2.

suggests the presence of the imide carbonyl bond that may be visualised as: N-C=O⋯H_2O⋯CO_2 (Fig. 4).

In contrast, elevated RH values (~30 % – 40 %) are associated with water cluster (i.e. multilayer adsorbed H_2O) formation that negatively impacts CO_2 adsorption. This can sterically hinder access to pores of the adsorbent for CO_2. This also has been the case for the imide-containing COF with the onset at RH = 38 – 42 % [104]. The authors observed the red shift associated with carbonyl, suggesting attraction of H_2O molecules. At high RH values, H_2O molecules not only bind to this SFG, but also form water clusters on the COF (resulting in pore filling).

With regards to the N atom of the imide group, the reverse was noted (i.e. blue shift of the C-N band from 1340 cm^{-1} for dry to 1344 cm^{-1} at RH 80 %). In the imide SFG, the N is less likely to participate in H-bonding as its lone electron pair is delocalised through resonance with the carbonyls. This phenomenon was corroborated by the enhanced bond strength between the C and the N upon water loading [104].

4.2. N-containing heterocycles

Azole-derivatives are often found as ligands of hydrophobic MOFs [65] such as imidazole-based ligand of various ZIFs. Despite the presence of hydrophobic ligands, they often present low affinities towards CO_2. For example, ZIF-8 was shown to adsorb nearly three times less carbon dioxide than a commercial AC (based on single-component isotherms at 1 bar and 25 °C); on the other hand, its H_2O adsorption was only ~16 % of that of the (conventionally relatively hydrophobic) AC [105]. However, when a ZIF was produced on the AC as a hydrophobic layer, synergetic effects were observed, resulting in a hybrid adsorbent with superior qualities for CO_2 adsorption at an RH of 50 %. Since the mesoporosity of the AC was largely protected from water intrusion and competitive adsorption, the hybrid sample only presented a drop in capacity of ~17 % from dry to humid (resulting in a CO_2 uptake of ~1.43 mmol/g). In contrast, the parent commercial AC's capacity dropped by ~61 % (i.e. displaying a capacity of ~0.77 mmol/g) [105]. Therefore, azole-based SFGs can be viewed as appropriate modifiers for CO_2 adsorbents under realistic (i.e. humid) conditions.

Pyridine is a six-membered heterocycle made up of five carbon atoms and a single N atom, whilst the pyrrole molecule is a pentagonal heterocycle. These SFGs have been investigated in the context of carbon capture and their interaction with moisture. For example, addition of pyridine groups resulted in the synthesis of more hydrophobic Ni-MOF-74 [65]. A different MOF (Ni-DOBDC) was modified with pyridine in order to transform its hydrophilic surface to a more hydrophobic one [106]. The pyridine-functionalised sample presented a decreased uptake for both CO_2 and H_2O (based on pure-gas isotherms) ascribed to smaller surface areas and pore volume upon modification. Furthermore, the affinity to water declined dramatically more than for carbon dioxide, resulting in a higher selectivity (308) when compared to the pristine MOF (1844). These tests were conducted having saturated the samples with H_2O at an RH of ~45 %. This methodology, however, has been criticized recently as it relies on assumptions that water loading would not change during CO_2 adsorption (which is only true for highly hydrophilic (e.g. zeolites) adsorbents) [19]. This may lead to erroneous results. An improved approach is suggested elsewhere [19].

Such SFGs have also been found to influence water and CO_2 sorption in carbonaceous adsorbents. For example, to benefit from the presence of N-5 heterocycles, a polypyrrole precursor has been utilised to prepare a KOH-activated carbonaceous adsorbent [107]. Based on X-ray Photoelectron Spectroscopy (XPS) results, both N-5 and N-6 heterocycles were identified with the pyrrolic/pyridonic (i.e. N-5 SFGs) prevailing (86.8 %) over pyridinic nitrogen atoms (13.2 %). Applying this adsorbent under humid conditions (3 vol% H_2O and 10 % CO_2 at 25 °C) corresponded to a 22 % decrease in uptake (from 1.45 to 1.13 mmol/g) and a shorter BT compared to a dry gas. Further, the presence of trace amount (ppm) of acidic gases (SO_x, NO_x) was also investigated which led to a 14 % drop in capacity. A combination of both acidic gases and water

vapours was not studied. Nevertheless, the SFG-containing sample did not present a strong decline in adsorption capacities over 10 cycles regardless of the inlet gas condition (dry, humid and acidic). Working or cyclic capacity studies are of critical importance for industrial deployment of adsorbents [45] and should not be overlooked in favour of purely maximising the adsorption capacity of a sample. As such, apart from investigations into moisture tolerance, experimental evaluation of cyclic performance is also suggested by the authors as a further key performance indicator (KPI) of a CO_2 adsorbent.

Similar N-containing heterocycle composition (i.e. domination of N-5 over N-6) was observed for an $NaNH_2$-activated carbonised phenolic resin Wang et al. [108]. In their studies, the inlet gas was passed through a water bottle to maintain an RH of 28 %. Despite a rise in water vapour content, the functionalised adsorbent performed well, losing only 9 % of capacity (0.86 mmol/g) compared to the dry dynamic test (0.94 mmol/g). CO_2 BT times were also impacted negatively yet not substantially. The adsorbent lost 5.4 % of its original uptake after eight adsorption-desorption cycles (dry and pure CO_2).

4.3. Nitro groups

Nitro (NO_2) functionality is more seldomly reported in the context of carbon capture, due to its acidic nature. However, due to its high polarity, it may also positively impact CO_2 adsorption and influence interactions with H_2O. For example, it has been shown that by functionalising a ZIF with the NO_2 SFG (ZIF-78), the material would outperform other SFGs (namely, CN, Br, phenyl and methyl) and the parent (plus a commercial AC) in terms of both uptake and selectivity (over methane, oxygen and nitrogen), based on pure component isotherm studies [67]. Further, four hyper-cross-linked polymers of intrinsic microporosity were also functionalised with the nitro group [109]. As a result of such modification, the equilibrium single-component CO_2 capture capacity (at 1 bar and 25 °C) increased substantially (ranging from an additional 13 % up to ~76 %) for all sorbents. Interestingly, at 1 bar and 0 °C, the modification provided a meaningful increase of ~29 % for only one material, while the others demonstrated negligible change. The authors compared these adsorbents to their NH_2-modified and sulphonated analogues concluding the nitro-functionalisation to slightly outperform the amino SFG and the HSO_3 group to present best results. However, the impact of moisture in the gas-phase on the adsorbents was not investigated and was acknowledged by the authors.

H_2O tolerance was, however, investigated for a different material (a type of MOF not often employed for CCS purposes), i.e. CAU-10 [110]. From a pure component isotherm standpoint (at 1 bar and 25 °C), the introduction of any functionality caused the capacity to decrease following the order of: pristine > NO_2 > F > CH_3 > OH > NH_2; whilst at partial pressures resembling post-combustion CCS conditions (i.e. 0.15 bar), the nitro group outperformed the unfunctionalized CAU-10 (0.62 and 0.56 mmol/g, respectively). With regards to moisture tolerance, the authors also evaluated a bi-functional adsorbent CAU-10-CH_3-NO_2 (note that these two SFGs were not tethered linearly (as has been sometimes used previously in the manuscript); a linear chain would be denoted at CAU-10-CH_2-NO_2). Based on dynamic column experiments at 30 °C with an RH = 80 % and 1 vol% CO_2 (balance N_2), the absolute values of CO_2 BT time (both dry and wet) followed the order of: nitro-functionalised MOF, CAU-10-CH_3-NO_2 followed by methyl-modified CAU-10. However, if evaluating exclusively the percentage decline of BT time between dry and humid conditions (used as measure of hydrophobicity), the reverse is true. The calculated values showed a 19 % reduction for the methyl SFG, 21 % for the bi-functional CAU-10 and 26 % for the NO_2-modified material. Similar conclusions were derived from thermogravimetric analysis (TGA) after an overnight exposure to 85 % RH. Upon heating to 100 °C (hold time and ramping rate were not described) CAU-10-CH_3 lost 9.4 wt%, CAU-10-CH_3-NO_2 – 11.2 % and CAU-10-NO_2 presented a 13.5 % mass loss due to removal of

water.

The superior ability to retain moisture was also shown in the context of a modified AC, where a sample with NO_2 groups presented a larger moisture content than the parent material [111]. This may, however, also been impacted by the presence of OH moieties on the surface of the AC, as oxygen containing polar groups also attract water molecules, which is discussed in the following section. Grafting of nitro SFG however, typically involves the formation of brown gas (NO_2) as a by-product – a poisonous and acutely toxic substance with a Lethal Concentration in 50 % of cases (LC_{50}) of 115 ppm (based on a one hour exposure of a population of rats) [112]. Nevertheless, exposure of the AC to the nitration mixture leads to an increase in CO_2 uptake from a dry stream. Additionally, apart from surface functionalisation, the acidic treatment has also provided a further benefit of purification of the carbonaceous adsorbent *via* dissolution of inorganic impurities, namely, ash species [111].

5. O-heteroatom

Polar functional groups are highly hydrophilic [33] and, since O-containing SFGs (Fig. 5) often present high polarities, they are known to play a crucial role in promoting moisture uptake at low partial pressures, forming H_2O vapour clusters [113].

As such, a reduction (or elimination) of O-content, in the context of carbonaceous adsorbents, is a way to suppress adsorbents' affinity to moisture [114]. For example, AC directly extracted (without secondary pyrolysis) from biomass combustion bottom ash is believed to be more hydrophobic than its virgin carbon precursor (based on the moisture content of the adsorbents acquired *via* proximate analysis) due to the reduction of O-containing volatile functionalities (evidenced by FTIR spectra and volatile organic compounds (VOCs) content) as a result of prolonged thermal treatment (i.e. physical activation under a slow (0.9 °C/min) ramping rate) [44]. A similar sentiment has been expressed by Pokrzywinski *et al.,* where the activation conditions were carefully selected specifically to eliminate (confirmed *via* XPS) the hydrophilic O-heteroatom based SFGs, whilst preserving the porous structure of their milk-derived ACs [115].

5.1. Carboxyl groups

Carboxyl groups are highly hydrophilic [116], and therefore, are often described to have drastically enhanced affinity to water. This can be ascribed to the strength of the COOH – OH_2 hydrogen bond as evidenced by its short length (<0.25 nm) [117]. However, some carboxylic acids present hydrophobic qualities, e.g. oleic acid [88], yet that stems from the long alkyl/aryl chain (C18 in the case of oleic acid) rather than the highly polar carboxyl. For example, oleic acid has been used to
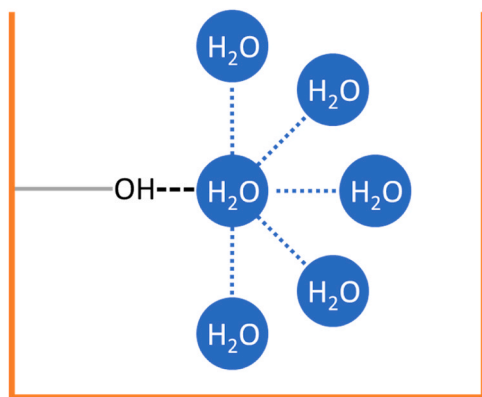

Fig. 5. Schematic representation (not to scale) of water agglomeration/clustering.

produce a hydrophobic aerogel for CO_2 capture, where the terminal COOH has been shown to react with the NH_2 moiety of 3-amino-propyl--triethoxysilane (APTES) to form the adsorbent [118]. Additionally, carboxylic acid ligands can be used for synthesising hydrophobic MOFs [65].

This sentiment can be corroborated when evaluating a reported family of azolyl-carboxylate MOFs developed by Nandi et al. and their performance in humid conditions: selective CO_2 adsorption even at 75 % RH [119]. Despite their "family name", the hydrophobic properties of the pores stem from the methyl radicals, whilst the oxygen atoms of the carboxylic SFG act as the connectors to the metal centres. The origin of these properties has been acknowledged by the authors.

The phenyl-modified zeolite (described extensively in Section 3.1) was also further modified to include a terminal COOH [23]. This affected both the adsorption capacity and the BT time. The CO_2 uptake for the beta-zeolite with the SFG of Ph-COOH presented a lower (0.58 mmol/g) capacity than the purely phenyl modified (0.65 mmol/g) and pristine (0.68 mmol/g) adsorbent at 40 °C and 1 bar (10.5 kPa of CO_2 and 5 kPa of H_2O). A similar trend was observed in breakthrough measurements. The least favourable performance of the COOH-phenyl functionalised sample may be attributed to the higher polarity of the carboxylic group, which facilitated greater competitive H_2O adsorption (*via* stronger hydrogen bonding) despite the hydrophobic nature of the benzene SFG.

5.2. Carbonyl groups

Carbonyl groups are believed to be highly hydrophilic [104]. This is ascribed to their polar nature. For example, ZIF-90 is believed to be less hydrophobic than ZIF-8 and ZIF-71 due to carbonyl SFGs [65]. Yet this may depend on the comparative/baseline material. For example, a variety of Schiff-base COFs were studied and cross compared based on different functionalities present [77]. The keto group (resulting from keto-enol tautomerism) was found to outperform other imine-based COFs in terms of both selectivity and uptake. Therefore, they were selected for breakthrough studies under wet flue gas conditions. Under 17 % RH (15/85 CO_2/N_2 feed), the keto-COFs retained ~70 % of their dry capacities and adsorbed ~0.4 mmol/g of CO_2. This was contrasted to UiO-66, which lost 80 % at the nearly the same (RH=16 %) conditions resulting in an adsorption capacity of 0.34 mmol/g of CO_2. At 51 % RH, the keto-COFs adsorbed ~0.25 mmol/g of CO_2, suggesting the produced adsorbents to be moderately hydrophobic due to the presence of the carbonyl SFG.

A further study investigated the impact of different O-heteroatom SFGs (namely, the carbonyl, carboxyl and the hydroxyl groups) on a simulated AC followed by experimental trials [120]. The conducted TGA experiments, however, did not distinguish between the amounts of CO_2 and H_2O adsorbed and therefore, cannot lead to accurate conclusions on the impact of these SFGs on CO_2 adsorption from humid streams. Nevertheless, the findings from their simulations suggest the adsorption energies between the surface and both CO_2 and H_2O to decrease (compared to a pristine AC with no SFGs) upon incorporation of a carbonyl group, whilst an increase was observed with addition of hydroxyl and carboxyl groups. The authors attribute these changes to differences in polarity, suggesting multiple times the C=O bond to be non-polar [120], which is debatable to say the least. Indeed, the polarity of an SFG plays a crucial role and the carbonyl bond is less polar than either the hydroxyl or the carboxyl (with the latter being the most polar out of the three). Yet the main difference between the carbonyl (C=O) functionality and the COOH and the OH groups is the presence of a terminal hydrogen atom for the latter two. This feature facilitates further hydrogen bonding between either of the adsorbates' oxygen atoms and the hydrogen atoms from the SFGs on the AC surface, thus, increasing the affinity towards both adsorbates to a stronger extent than a comparable carbonyl SFG.

Regardless, the conducted simulations suggest an interaction

between the adsorbate molecules to occur upon co-adsorption of the gases leading to a drop in CO_2 adsorption [120]. Here, again, a similar trend is noticed, where the C=O SFG presents different results to the COOH and the OH functionalities. The co-adsorption energy for the carbonyl-functionalised material is nearly the same as the pristine AC (-22.66 and −22.84 kJ/mol, respectively), whilst the more polar and H-containing SFGs present a declined value that follows their order of polarity (i.e. −16.06 kJ/mol for the OH-containing adsorbent and −4.59 kJ/mol for the more polar AC-COOH).

5.3. Hydroxyl groups

OH groups can act as very strong adsorption sites for CO_2 due to the very short distance between the adsorbate's oxygen atom and the hydrogen atom of the SFG (~0.22 nm [121]). At the same time, OH groups can also interact strongly with H_2O *via* hydrogen bonding [65]. For example, polyols have been shown to increase hydrophilicity [122] indicating the highly hydrophilic nature of the hydroxyl SFG [116,123]. As such, CO_2 and H_2O may compete for the same hydroxyl adsorption sites within the structure of the adsorbent [124]. However, the high hydrophilicity of this SFG may bring beneficial effects for some CO_2 physisorbents. In some MOFs, pore confinement and bottleneck effects (as a result of presence of moisture) may accommodate more efficient packing of CO_2 molecules [125]. A simplified description of this phenomenon can be visualised from Fig. 6.

Following this approach, MOFs constructed with OH functional groups present increased CO_2 uptakes. For example, $CO_2 \cdots H_2O$ interactions inside the microchannels of Mg-CUK-1 (a hydroxyl-containing MOF), led to a (nearly) twofold increase in the CO_2 adsorption capacity (from 4.6 to 8.5 wt% at 30 °C and 1 bar), when switching from dry conditions to RH = 18 % [121]. This, however, was achieved having saturated the sample with moisture, which allowed the hydroxyl SFG to "pin down" the water molecule. This impacted the micropores (*via* confinement), allowing for more efficient (hence, larger) CO_2 loading of the adsorbent. Similar observations have been made for InOF-1, NOTT-400 and NOTT-401 [126] as well as MIL-53(Al) [127] (all containing OH groups) as well as the imide-containing (i.e. O=C-N-C=O) COF [104] described earlier in the manuscript.

Hydroxyl groups were added onto the aromatic phenyl moiety of the previously mentioned beta-zeolite (Section 3.1). The OH-Ph-β-zeolite presented a lower uptake (0.60 mmol/g) than the parent Ph-β-zeolite (0.65 mmol/g) and the unfunctionalised adsorbents (0.68 mmol/g) [23]. Similarly to the COOH modification (Section 5.1) case, the hydrophilic nature of the polar O-containing hydroxyl SFG lead to comparatively worse performance under a humid environment. It is worth mentioning that β-zeolites have pores of ~0.7 nm [128].

Based on the above discussions, a conflicting picture of the impact of OH (as well as other polar functional groups) on adsorption in humid conditions can be realised. Granted, in all studies reported in this review, different adsorption conditions (e.g. temperatures, concentrations, etc.) are employed. Yet the main difference seems to stem from the material and its relationship with the functionality in terms of resulting pore size. A CO_2 molecule is preferentially adsorbed on a high-energy site of the adsorbent as opposed to multi-layer adsorption on H_2O. However, if the water molecule(s) is capable of reducing the pore size, and producing a more high-energy environment (i.e. narrowing mesopores into micropores of appropriate sizes), then an enhancement in uptake may be observed. This allows to benefit from the confinement phenomenon mentioned earlier in the manuscript. As such, enhanced CO_2 sorption has been noted on adsorbents with somewhat larger pores. For example, MIL-100(Fe) with mesoporous cages (2.5 and 2.9 nm [49]) presented an enhanced uptake under humid conditions, whereas more microporous studied adsorbents (NaX, HKUST-1 and UiO-66) did not [129,130]. This was ascribed to development of "microporous pockets" within the larger pore structure that were filled with CO_2. However, this phenomenon has been presented in the context of a polar O-based SFG attracting an H_2O (due to their hydrophilic nature) and inducing creation of these "micropore pockets" or pore confinement/bottleneck effects. As such, functionalisation with hydrophilic moieties may be preferable for adsorbents with smaller mesopore and/or larger micropore structures, whilst protective functionalisation with hydrophobic SFGs should be more suitable for ultramicroprous adsorbents (i.e. pore size <0.7 nm). There are, however, exceptions: the cage openings of the Mg-CUK-1 (inclusive of the hydroxyl SFG) are 0.81 and 1.06 nm [121]. Therefore, the question of which SFG to opt for has to be decided holistically (considering the cost of treatment and its environmental impact as well as the properties of the pristine adsorbent) on a case-by-case basis.

For example, if the adsorbent possesses amine SFGs, they can be modified in a particular way that would incorporate an OH group. This functionalisation approach relies on the ring opening of an epoxy modifier, which tethers a carbon atom of the modifier to the NH_2 whilst the epoxy ring is transformed into a given CH tail with a hydroxyl branched out from the β-carbon (second C atom from amine SFG as can be visualised form Fig. 7).

This approach is often used to impart hydrophobic properties (mainly by stepping away from the hydrophilicity of amines) as well as to impede urea formation during regeneration (i.e. loss of amine/
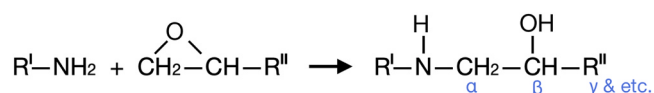
$$R'\!-\!NH_2 \;+\; \underset{\text{O}}{CH_2\!-\!CH\!-\!R''} \;\longrightarrow\; R'\!-\!\underset{\alpha}{\overset{H}{N}}\!-\!\underset{\beta}{CH_2}\!-\!\underset{\gamma \,\&\, etc.}{\overset{OH}{CH}}\!-\!R''$$

Fig. 7. Schematic of an epoxy ring opening reaction with the amine SFG.
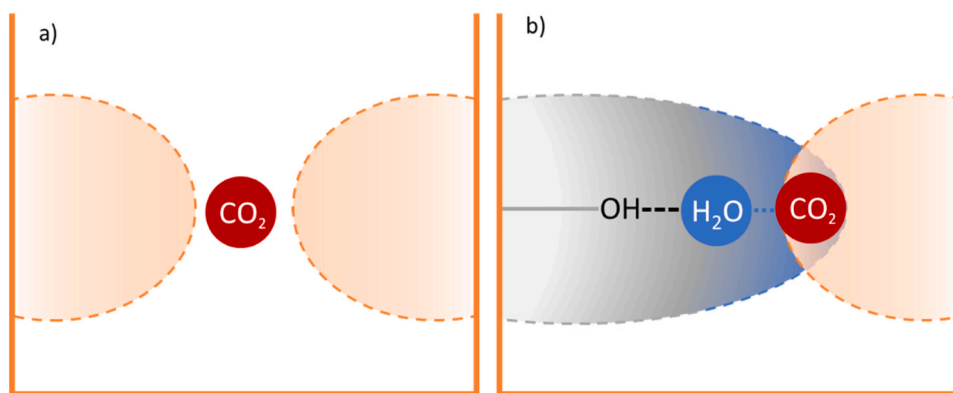

Fig. 6. Schematic representation (not to scale) of a bottleneck facilitating CO_2 adsorption: a) prior to incorporation of SFG and/or H_2O molecule the electrostatic field from the pore walls (dashed orange gradient oblongs) did not interact with the CO_2 molecule; b) due to the presence of SFG and/or H_2O molecule the electrostatic fields (dashed gradient oblongs) of the wall as well as from the SFG (and/or H_2O molecule) can allow CO_2 to be adsorbed on this site.

degradation of the adsorbent). This degradation is inhibited *via* the change from primary to secondary amines as the latter have weaker interactions with CO_2 and avoid dehydrative condensation [131]. Nevertheless, this is often referred to as alkyl-functionalisation (due to the hydrophobic properties of the SFG); however, due to the presence of the hydroxyl functionality, the performance of adsorbents upon such modification are described in this section.

Acrylate copolymer beads with grafted amine groups have been functionalised with propylene oxide (i.e. 1,2-epoxypropane, i.e. $CH_2(O)$ CH-CH_3) to enhance moisture tolerance of the adsorbent [131]. The authors expected and achieved a better cyclic performance to trade-off with an inhibited adsorption capacity. Evaluating the samples in a fluidized bed reactor at 60 °C under a stream of 8 % steam, 6 % oxygen and 30 ppm SO_2 (balance CO_2) resulted in adsorption of 2.87 and 2.15 mmol/g of CO_2 for parent and functionalised adsorbents, respectively. The parent material lost 43.2 % of original adsorption capacity after 1000 adsorption/desorption cycles (3 % steam in pure CO_2, 120 °C), in contrast to the modified-material, which maintained 90.2 % [131]. The prepared adsorbents were not only moisture-tolerant but also resistant to acidic gases.

Choe *et al.* [94] evaluated an elaborate diamine-appended alumina/silane-modified $Mg_2(dobpdc)$-based MOF (in bead form) that was further functionalised to induce hydrophobicity of the porous structure *via* mechanism explained above. Addition of a C1 structure (binding with the amine groups *via* ring opening of 1,2-epoxypropane (epoxy ring-CH_3)) led to a reduction in water adsorption by 3.33 wt% (described in relation to the non-functionalised MOF with 9.2 %). The results were collected based on TGA apparatus using 5 % H_2O in N_2 at 40 °C. Moreover, the C2-functionalised (here ring opening of 1,2-epoxybutane (epoxy ring-CH_2-CH_3)) MOF performed slightly worse (-3.13 wt%). Similar trends were observed for the C10 and C12 modified samples (-1.53 and -2.54 wt%, respectively). This was associated with diffusion limitations of the longer chain molecules resulting in unreacted, hence, not protected from moisture, H_2O adsorption sites (in this case, the diamines). However, alongside the decreased affinity to moisture, the CO_2 adsorption capacity also declined, which was also attributed to the availability of free amines.

5.4. Ethers

In the previous section, a particular MOF (diamine-functionalised and Al/Si modified member of the $Mg_2(dobpdc)$ family) was described. The MOF was functionalised with numerous hydroxyl-containing alkyl chains with varying lengths (C1 to C12) [94]. The results suggested a trade-off between CO_2 and H_2O adsorption capacities due to diffusion limitations induced by the longer modifiers. As a result, in the cases of C10 and C12 modifiers, unreacted amine groups endow the sorbent with a higher CO_2 adsorption capacity and a lower resistance to moisture (since the amine group acts as both the modifier tethering and adsorption site). The reverse (i.e. lower capture capacity yet higher hydrophobicity) is noted for the C1 and C2 functionalised adsorbents. This observation can be visualised from Fig. 8. This figure also displays the sample corresponding to the highest moisture tolerance and CO_2 uptake simultaneously (i.e. een-MOF/Al-Si-C17) that has not been discussed prior (Section 5.3).

Adsorbents een-MOF/Al-Si-C1 through C12 have all been modified with various alkylepoxides (facilitating the O atom from the heterocycle to form a hydroxyl group), which acted as the binding agent to the amine functional groups of the parent MOF. In contrast, C17 has been modified with 2,3-epoxypropyl hexadecyl ether (epoxy ring–C–O–C16). The authors also investigated the impact of different loading of this functionality within the material. The reason behind changing the SFG type as well as the investigation approach has not been highlighted. Perhaps, this stems from the additional electronegativity provided by the O-atom in the ether structure that facilitated the attraction of more CO_2, whilst the longer alkyl chain shielded the MOF from water.
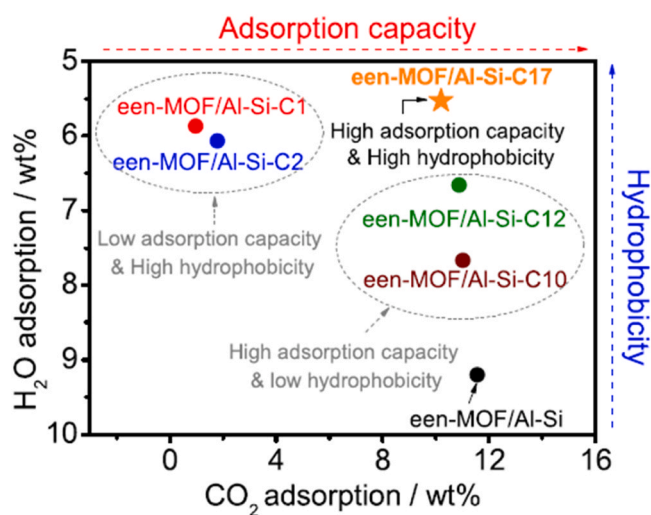

Fig. 8. Adsorption capacities of CO_2 and H_2O on a number of modified MOFs, adapted from [94].

Regardless, with an increased loading of this SFG, a drop in uptake of both adsorbates has been registered and linked to lower surface areas as well as micropore (specifically, 0.6 – 0.8 nm) volumes. Choe *et al.* [94] compared dry (pure) CO_2 adsorption and humid (i.e. 5 % water vapour) *via* isobars. Due to limitations of this technique (i.e. a TGA apparatus without an additional modules), the adsorbed species cannot be determined directly and the results can only be indicative of mass increase. Nevertheless, the *total* adsorption capacity for the maximally loaded C17 ether-modified MOF remained unchanged despite introduction of H_2O molecules alongside CO_2, whilst the parent material presented significant differences as a result of presence of moisture. To verify selective adsorption of CO_2 under humid conditions on the modified MOF, a temperature programmed desorption approach has been employed using a 15 % CO_2 gas stream ((if humid then 3.75 % of H_2O was added) balance He) and a mass spectrometer (MS). Following this investigation, selectivity has been confirmed as the H_2O signal was registered later and at higher temperatures after the CO_2 signal on the MS. Further, the introduction of water vapour has little impact on CO_2 uptake (10.22 wt % versus 10.11 wt% for dry and humid, respectively) at the post-combustion flue gas concentrations (in this case, 15 % CO_2).

A similar approach was undertaken by Hamdy *et al.* [132]. Here, the ether SFG was not directly employed in functionalisation. Ethers were employed as the modifier (in this case, the cross-linking agent). The moisture tolerance observed (or even benefits from applications in humid environments) stems from the branched hydrocarbon (e.g. fluorinated, aromatic, aliphatic) tail and the amine groups of the adsorbent (as described earlier in the context of opening of the epoxy ring).

5.5. Esters

Ester modification is less often described in the literature. Nevertheless, pore surface lining with ethyl ester groups has increased the moisture tolerance of CALF-33 [65]. Alkyl chains have been added to UiO-66-$(OH)_2$ to produce ester-like structures on the surface of the MOF to render the surface hydrophobic [133]. The authors studied two different tail-end radicals: a C_3 (propionic) and a C_2 (acetate-like). The results suggest that even the longer C_3 ester SFG was not sufficiently long as the H_2O molecules could still penetrate the framework and access the hydrophilic metal centre. The esterification was realised to be an unviable approach for hydrophobic modification as the loss in capacity (mean value of 1.73 mmol/g for the parent and 1.08 mmol/g for the modified MOF) was not counterbalanced by suppressed moisture adsorption. In fact, at room temperature and an RH of 60 %, only a

minimal 0.04 mmol/g of CO_2 was captured by the propionic ester-functionalised UiO-66. Therefore, bulky, long chain alkyl groups are believed to be more effective SFGs for producing hydrophobicity on the adsorbent's surface.

6. Halogens

Halogen atoms (such as F, Cl, Br) are regarded as hydrophobic [134], hence, their potential applicability in CO_2 separation from humid environments. Within this introduction of fluorine moieties onto various MOFs seems to be most prominent, yet other halogens have also been incorporated into various ligands. For example, ZIF-81 [67] and ZIF-300 [68] posess Br; whilst ZIF-69 [67,69], ZIF-301 [68] have a thethered Cl and ZIF-71 [70] and ZIF-80 [67] have two Cl atoms on the linker. Additional chlorine atoms were also shown to provide an increase in CO_2 adsorption energies and uptake in general (from a CO_2/CH_4 mixture) for a ZIF termed COK-17 [70].

Firstly, focus will be drawn to non-fluorine halogens followed by a more in-depth discussion on F-containing adsorbents.

6.1. Bromine

Most halogen functionalisation studies have employed fluorine (F) as the modifying SFG; however, addition of bromine (Br) moieties has also been investigated within the context of CCS. Molecular simulations of UiO-66 have been conducted to compare the introduction to the linkers of bromine atoms against amine and hydroxyl SFGs [135]. Pure component isotherms suggest UiO-66-Br to have a smaller dry capacity than other modifications. Secondly, simulation of a humidified post-combustion feed gas (15 % CO_2 (fixed); X% H_2O (varied); balance N_2), suggested that a 5 % water content could decrease the capture capacity significantly for all samples. However, at concentrations of 0.5 % and 1 % and pressures below 1 bar, other studied SFGs presented a decline in adsorbed CO_2, whilst the capacity of the Br-modified MOF remained nearly unchanged. UiO-66-Br was shown to have a smaller water uptake than UiO-66-NH_2 or UiO-66-OH. Based on the findings, the authors suggest a degree of drying to be necessary for deploying the MOF with aniline-type ligand (i.e. UiO-66-NH_2) as the binding energy with H_2O was higher than for CO_2. The phenol-type ligand of UiO-66-OH was also shown to interact more strongly with moisture than with carbon dioxide. In contrast, UiO-66-Br presented a much smaller water binding energy (3.06 kcal/mol), suggesting such modification to endow the adsorbent with a degree of hydrophobicity.

6.2. Fluorine

Despite being a polar SFG [136], fluorine presents hydrophobic properties [137]. However, post-synthetic grafting of fluorine SFG can involve use of expensive and toxic gases such as F_2 or XeF_2 [138], rendering the process environmentally unfriendly [23] and challenging. As with other SFGs, a particular adsorbent may not necessarily benefit from F incorporation, depending on the loading, pores size and other factors. For example, an activated carbon fibre (ACF) with an average pore size of 0.7 nm was grafted with fluorine atoms at different temperatures which correlated directly to the F content [139]. As a result, both higher and lower values of CO_2 uptake (compared to pristine ACF) were reported. The increased density of F atoms may have provided diffusional limitations, sterically hindering access to the pores (considering the C–F bond length of ~1.37 Å [140] which is nearly 20 % of the pore size of the studied [139] ultramicroporous ACF), whilst at lower F concentration (on the surface of the ACF), enhanced adsorption capacity stems from the interaction between the CO_2 quadrupole and the skewed electric field of the C-F bond. These results corroborate the hypothesis of a lack of a universal solution and highlight the value of careful case-by-case consideration of the SFG (similar sentiment has also been expressed recently in the context of fluorination of MOFs [141]).

Fluorine SFG has been shown to strongly interact with CO_2 as evidenced by isosteric heat of adsorption measurements of a carbonaceous adsorbent (although, in the presence of polar triazine moieties - aromatic six-memebered heterocycle with three nitrogen atoms in the framework) [136]. The degree of interaction between CO_2 and and this SFG has been shown to strongly correlate with the size of the channel between the pendant F moieties [142]. Upon fluorination of MOF-801, the window between the pores of the materials network reduced to 0.35 nm from 0.48 nm, which hindered diffusion, resulting in a decreased CO_2 uptake [140]. These findings underscore the imporatnce of pore size/ditribution changes upon incorporation of a SFG (as can be understood from the illustration in Fig. 6).

Incorporation of trifluoro moieties to the ligands of MOFs is believed to be a viable approach to their hydrophobisation. For example, FMOF-1 was decorated with CF_3 groups in a simulation-based study. The material successfully maintained the adsorption capacity (0.05 mmol/g at 0.15 bar and 25 °C) in a humid environment (RH = 80 %) [143].

Trifluoro SFGs were added to an amino-functionalised UiO-66 to induce hydrophobicity [144]. BT experiments were conducted to evaluate the efficacy of incorporation of a tetrafluoroterephthalate ligand to UiO-66(Zr)-NH_2 [62]. It was observed that the material lost only 30 % capture capacity when experimenting under dynamic conditions with 15 % CO_2 and a balance N_2 at 25°C under 70 % RH (0.76 mmol/g), compared to a dry (0.53 mmol/g) environment. In contrast, the capture capacity of the parent material decreased by 88 % (from 0.96 to 0.11 mmol/g) as can also be seen in Table 2. Moreover, this hydrophobic modification was shown to enhance CO_2 transport properties evidenced by a 2.7-fold increase in the mass transfer coefficient. This phenomenon

Table 2

Examples of some fluorine-containing adsorbents and the impact of H_2O presence on their CO_2 adsorption performance.

Adsorbent	Modification	Performance	Reference
UiO−66	Amino group	88 % loss in CO_2 adsorption capacity upon introduction of H_2O into the inlet gas compared to dry conditions.	[62]
	Amino and trifluoro	30 % loss in CO_2 adsorption capacity upon introduction of H_2O into the inlet gas compared to dry conditions.	
MIL−101(Cr)	Pristine	Up to 18 % loss in CO_2 adsorption capacity upon introduction of H_2O into the inlet gas compared to dry conditions.	[39]
	Fluorine	No direct proportionality. Results ranging between increase of 12–22 % loss in CO_2 adsorption capacity upon introduction of H_2O into the inlet gas compared to dry conditions.	
HKUST−1	Pristine	90 % loss in CO_2 adsorption capacity upon introduction of H_2O into the inlet gas compared to dry conditions.	
MIL−53(Al)	Pristine	80 % loss in CO_2 adsorption capacity upon introduction of H_2O into the inlet gas compared to dry conditions.	
MIL−101(Cr)	Amino group	22 % loss in CO_2 adsorption capacity upon introduction of H_2O into the inlet gas compared to dry conditions.	[138]
	Amino and fluorine	2 % loss in CO_2 adsorption capacity upon introduction of H_2O into the inlet gas compared to dry conditions.	
NbOFFIVE−1-Ni	Pyrazine and fluorine	32 % loss in CO_2 adsorption capacity upon introduction of H_2O into the inlet gas compared to dry conditions.	[142]

was associated with the reduction in the adsorbent–adsorbate interactions, which, in turn, decreases the unit operation time in an adsorption-based separation process [62].

Partial fluorination of MIL-101(Cr) resulted in a lower CO_2 uptake (based on single-component volumetric isotherms) which was linked to decreased surface area and pore volume [145]. At -77 °C, the parent MOF captured 25.8 mmol/g, whilst the modified MOF adsorbed 19.4 mmol/g. On the other hand, a higher isosteric enthalpy of adsorption at near zero loading (pristine $= -32.4$ kJ/mol versus F-functionalised with -43.2 kJ/mol [145]) was noted (although these near-zero values are notoriously unreliable [146]) which suggests stronger interactions between the adsorbate and the adsorbent and generation of more attractive/higher-energy sites upon incorporation of the F SFG. Nevertheless, the lower surface textural properties as a result of partial fluorination also led to a decline in water adsorption, whilst the isosteric enthalpy of adsorption at near-zero loading decreased (pristine $= -39.7$ kJ/mol; F-MIL-101(Cr) $= -18.2$ kJ/mol [145]). At lower vapour pressures, the parent sample presented a lesser water uptake, which was associated with the F atoms promoting the formation of efficiently packed hydrogen-bonded H_2O clusters.

In another study (by the same authors) on partial fluorination of MIL-101, the co-adsorption of CO_2 and H_2O was investigated [39]. Firstly, under dry conditions, similar trends in a slightly decreased CO_2 uptake upon modification were noted (0.086 mmol/g (F-MIL-101) and 0.092 mmol/g (pristine MIL-101) under 0.05 bar CO_2). Secondly, with an increase in RH up to 20 %, a 18 % decrease in parent's capacity was recorded, whilst the CO_2 uptake was promoted for the modified MOF upon introduction of moisture. At RHs $= 15$ %, a peak in uptake (0.097 mmol/g) was registered whilst at an RH of 20 %, a 22 % drop was observed. Both HKUST-1 and MIL-53(Al) were outperformed in the same moist conditions (as also highlighted in Table 2). Finally, CO_2 diffusion was shown to be aided (for parent and F-containing MOF) when water was introduced. This phenomenon was explained by H_2O adsorption, providing a more homogenous surface, thus, permitting easier CO_2 diffusion [39]. Interestingly, at RH=20 %, the diffusion coefficient also dropped (alongside the CO_2 adsorptive performance). These results suggest low to moderate H_2O contents to be most optimal for this physisorbent.

A different study involved co-functionalisation of MIL-101(Cr) with both amine and fluorine SFGs where the hydrophobicity of the material was significantly improved [138]. Firstly, both amine and fluorine SFG (in a ratio of 1:4) served as adsorption sites for CO_2 on this mixed-ligand MOF. Based on pure component adsorption data, the F-containing amino-MIL-101 outperformed the aminated-only (as well as the pristine) adsorbent under dry conditions. This was however, fluorine loading dependent (which may be due to smaller pore volume and surface area). After being subjected to 85 % RH for 12 hours, a mere 2 % reduction in adsorption capacity was noted for the optimally F-loaded adsorbent compared to the 22 % of its amine-based counterpart. BT tests were also conducted in a dry and RH=60 % environment at 30 °C and a 1 % CO_2 stream. Due to the presence of an additional adsorption site as a result of co-functionalisation, the MIL-101-NH_2-F outperformed (282 s – dry and 242 s – RH=60 %) MIL-101-NH_2 in both investigations (~200 s and 100 s, respectively) in terms of BT time (with similar results pertaining to adsorbed volumes). Incorporation of this SFG has been further shown to enhance hydrophobicity and performance of MOFs for CCS.

An alternative F-containing MOF is NbOFFIVE-1-Ni. Besides F atoms, this adsorbent also has pyrazine (aromatic six-memebered heterocycle with two N atoms in positions 1 and 4). Both of these functionalities interact with CO_2 *via* electrostatic interactions (i.e. van der Waals forces), between the pyrazine H atoms and the oxygen of CO_2, as well as the electropositive C in CO_2 and electronegative fluorine atoms, respectively. These facilitate adsorption of 1.25 mmol/g of CO_2 from a dry (400 ppm) stream at 25 °C based on single-component volumetric isotherm [142]. Further, BT experiments at the same temperature but under 1 % CO_2 (balance N_2) in a dry and humid (RH=75 %)

environments show the CO_2 capacity and BT time to decrease upon introduction of moisture (415 min/g and 8.2 wt% versus 283 min/g and 5.6 wt%, respectively). However, NbOFFIVE-1-Ni also demonstrated a higher water uptake (13.8 wt%) and a longer water BT (680 min/g) [142].

Based on the data initially collected in [142], a simulation study of performance for DAC conditions in a temperature-vacuum swing adsorption (TVSA) set-up was conducted [14]. In this work, NbOFFIVE-1-Ni presented a ternary CO_2 loading of 0.527 mmol/g with a water loading of 7 mmol/g based on a simulated gas stream containing 400 ppm CO_2, 1.15 % H_2O (i.e. 50 % RH at 20 °C) balance N_2.

This was compared to SIFSIX-18-Ni-β, another fluorinated (ultra-microporous) MOF (yet the pores are also decorated with the methyl SFG), that has a dry CO_2 capture capacity of 1.05 mmol/g (400 ppm CO_2 at 0 °C) [14]. Similar to NbOFFIVE-1-Ni, the SFGs of this adsorbent present both hydrophobic properties and attract CO_2 *via* comparatively strong C⋯F interactions coupled with six weak C-H⋯O interactions from methyl groups [46]. Based on the TVSA study [14], SIFSIX-18-Ni-β presented a lower ternary CO_2 loading (0.4 mmol/g) than NbOFFIVE-1-Ni. However, the water loading of this MOF was ten times lower (i.e. 0.7 mmol/g). This led to a significantly lower minimum specific energy demand for SIFSIX-18-Ni-β (~18.02 MJ$_{th}$/kg CO_2) than that of NbOFFIVE-1-Ni (~30.4 MJ$_{th}$/kg CO_2 captured) [14]. The authors have also contrasted this to amine-based MOFs and found lower productivity values of the chemisorbents and a correlation between increased water loading and a higher energy requirement.

In another study, to enhance the hydrophobicity of a quaternary ammonium cross-linked polystyrene resin (envisaged for a DAC setting), the adsorbent was doped with polyvinylidene difluoride (PVDF) [147]. As a result, the adsorption rates for both CO_2 and H_2O were enhanced significantly. Prior to doping, a 35 % drop in CO_2 adsorption capacity was observed as the RH was elevated from 21.2 % of 84.7 %. In contrast, having incorporated the hydrophobic modifying agent, the adsorbent presented an increased uptake (of ~0.9 mmol/g at 20 °C from a stream containing 400 ppm CO_2) across the whole RH spectrum. Also, the cyclic capacity over 10 adsorption-desorption cycles did not present significant deterioration. The desorption in this study was conducted *via* moisture swing, i.e. by increasing the RH to 100 % and at low temperatures (<60 °C). The fluorine-based modification was shown to increase this material's hydrophobic properties [147].

Another F-SFG modification approach to achieve hydrophobicity was used for fluorination of an AC, i.e. impregnation with an ionic liquid [148]. Based on weight loss data and FTIR, the addition of fluorine (as well as sulphonyl) moieties suppressed moisture adsorption by the AC (as evidenced by mass loss at < 200 °C). The CO_2 uptake, however, was compromised significantly, which was attributed to a lower surface area of the modified adsorbent. This further indicates high hydrophobicity of fluorine-based SFGs as sulphonyls also are prone to hydrogen bonding with H_2O [65], which highlights a non-negligible water uptake of S-based SFGs (a further example is that thiophenic moieties are believed to be hydrophobic [103]).

7. Other heteroatoms and functional groups

7.1. Silicon

The hydrophobicty of Si-heteroatom containing SFGs often stems from the modifier containing either long alkyl chains or a polymethylsiloxane – an O-Si-O polymer structure with surrounding CH_3 groups. Silicon atoms with a terminal hydrogen (Si-H functionality) are also hydrophobic, whilst the silanol (Si-OH) groups are regarded as hydrophilic [149]. Due to the presence of the latter SFG, silicon-based materials are often used as drying agents with a common example being silica gel (Fig. 9) as laboratory dessicants (with colour additives serving as humidity indicators).

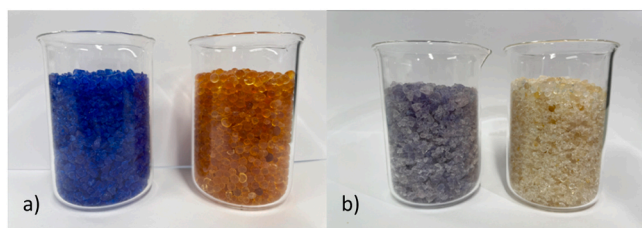On the other hand, the presence of surface silanol groups can be

Fig. 9. – a) Dry and b) saturated with moisture (i.e. exhausted) silica gel granules (left) and beads (right).

exploited for functionalisation [150]. Often amine moieties are tethered to these centres but other SFGs can also be grafted. For instance, recently mesoporous SBA-15 has been examined and compared to a adsorbent modified with 1,2-bis(triethoxysilyl)ethane (BTESE) as well as an amine-functionalised material (grafted with APTES) [124]. The former modifier is believed to impact hydrophobic properties *via* the addition of the ethyl SFGs. Following such modification the hysteresis loop of H_2O isotherms is moved to higher relative pressures suggesting improved hydrophobicity. However SBA-15 performed better (i.e. suppressed H_2O adsorption) at lower water partial pressures. This phenomenon was ascribed to a larger surface population of unprotected silanol groups due to an adjusted synthesis pathway of the modified adsorbent. Moreover, a decreased pure-component CO_2 uptake was observed which was linked to a lack of CO_2 affinity towards the ethyl moieties. Additionally, smaller pore volumes and surface areas of the modified samples could have also influenced the observations. When evaluating dynamic adsorption performance (10 % CO_2/N_2 stream at 30 °C), pure SBA-15 did not present a significant decline in CO_2 uptake (compared to dry conditions) under RH below 20 %. However, at 50 % RH, the adsorption capacity was reduced by nearly a third. The BTESE-modified silica adsorbent, on the other hand, presented a completely different picture. Firstly, as suggested by the pure CO_2 isotherm, the dry "baseline" capacity was 36 % lower for the functionalised sample than for SBA-15 (0.18 mmol/g and 0.29 mmol/g, respectively). Secondly, upon introduction of moisture into the inlet gas stream, a synergistic effect was noted, which resulted in a greater adsorption capacity at 20 % RH (0.24 mmol/g) and a maximum of 0.28 mmol/g under 50 % RH. Water vapour promoted CO_2 uptake on silnol groups, which was ascribed to bicarbonate formation. Finally, the adsorption enthalpy values were cross-examined. Evaluating the data for coverage ≤ 1 mmol/g, SBA-15 and the BTESE-modified samples presented values typical for physisorption of CO_2, i.e. in the range of -18 kJ/mol to -20 kJ/mol versus between -23 kJ/mol to -28 kJ/mol (depending on modified content), respectively. On the other hand, the NH_2-containing adsorbent presented much higher (typical of CO_2 chemisorption) values of -88 kJ/mol and -81 kJ/mol (for CO_2 coverage ≤ 1 mmol/g), depending on amine loading [124]. This significant disparity further highlights the relative advantages of physisorption.

A commercial zeolite 13X was coated with octadecyltrimethoxysilane (ODTMS) [151] – an organosilicon compound consisting of a long (C18) organic chain tethered to a Si atom with three terminal methoxy groups. Different ODMTS concentrations were studied to produce an adsorbent for deployment in simulated indoor conditions (i.e. RH = 50 ± 5 %, and CO_2 concentration of 3000 ppm, balance N_2 at ~20 °C). A rise in modifier loading was found to decrease both the CO_2 and moisture uptakes of the adsorbents in question. Compared to commercial 13X, the optimum sample (modified with 20 % ODTMS concentrated solution) presented different adsorption capacities for both gases. Under the simulated indoor conditions, the CO_2 uptake changed from 0.3 mmol/g (parent) to 0.4 mmol/g (modified), i.e. the functionalisation with ODTMS effectively increased the CO_2 adsorption capacity. Moisture uptake, under the same experimental conditions, dropped (as a result of hydrophobic coating) by ~41.5 % from 3.3 mmol/g (parent) to

1.9 mmol/g. These findings corroborate the hypothesis of hydrophobic functionalities generally being non or not highly polar (the three methoxies balance the charge) and possessing a long alkyl (18 carbon atoms) chain.

7.2. Boron

Incorporation of a carborane (three-dimensional aromatic boron-rich clusters) linkers has been shown to significantly increase hydrophobic properties and water stability of a MOF (mCB-MOF-1) [16], whilst negligibly impacting the adsorption capacity, even under 100 % RH. This was ascribed to the high hydrophobicity of the MOF channels which leave the Cu sites available for selective (over both N_2 and H_2O) adsorption of CO_2. The phenomenon of water not entering the pores was further corroborated by the lack of a significant impact of moisture on the breakthrough times and curves, suggesting this approach to provide highly H_2O-tolerant MOFs. Further, a comparison between the carborane-functionalised MOF and MOF-74(Ni) was performed by the authors (the latter was selected due to its high stability in the presence of moisture). They have further proved MOF-74(Ni) not to degrade under wet flue gas streams, yet the performance (in terms of CO_2 uptake) was significantly hampered by the presence of water and competitive adsorption.

An RHO zeolite (type A cages and small pore diameters [49]) was synthesised to include either a boron or a copper heteroatom [152]. This was done to reduce hydrophilic properties of the adsorbent in comparison to the pristine sample and was shown to increase the micropore volume and surface areas. The Si/Al ratio of the produced parent zeolite was 8.0 but changed to 8.2 upon heteroatom incorporation for B-containing, and to 7.3 for Cu-modified materials. Further differences were noted with regards to working capacity (difference between uptake at 1 and 0.1 bar). In line with their higher degrees of microporosity, both heteroatoms presented enhanced uptakes (based on single-component isotherms) of 2.81 (B) and 2.84 (Cu) mmol/g at 25 °C in comparison to the pristine (2.48 mmol/g). However, once the adsorbents were saturated with H_2O under varying RHs (25 %, 45 % and 75 %), the respective capacities dropped. Across all studied humid conditions, the heteroatom-containing samples adsorbed more CO_2 with Cu-containing zeolite presenting the highest moisture tolerance. Yet there is some discrepancy with the provided supporting data that most likely stems from a minor naming/typing issue in the paper, to the best of our understanding. Nevertheless, incorporation of either a copper or a boron heteroatom led to favourable performance under the humid conditions studied.

8. Conclusions, recommendations and future work

Introduction of particular SFGs onto adsorbents (be it post-synthetic modification, incorporation as part of the material or as part of a binding agent) can be viewed as an approach to developing moisture-tolerant CO_2 capture solid media. However, it is not straightforward.

Contradictory results of introduced functional groups onto adsorbents for CO_2 adsorption have been noted previously [134], suggesting that this has to be evaluated based on the material and system at hand, echoing the sentiment that the system and the adsorbent have to be "married" to one another [153,154]. As such, the given hydrophilic/hydrophobic SFG has to be evaluated in conjunction with the deployed material (its pore size, nature and location of the SFG(s) and its form (powder, pellet, bead and etc.)). Moreover, proposed reactor design and regeneration approach also need to be considered. Finally, the desired KPI (cyclic capacity, energy requirement, and etc.) has to be carefully selected aiming for successful industrial deployment of this technology.

Common threads across the evaluated studies suggest a possibility of pore blockage as a result of "*protective*" functionalisation (especially prominent with bulky hydrophobic SFGs) to occur. This may lead to a

decreased adsorption capacity of both (CO_2 and H_2O) adsorbates in question. This is unfavourable in terms of performance but may prolong adsorbent work-life, suggesting long-term benefits from such physisorbents. On the other hand, hydrophilic groups (classically polar and with a heteroatom that may form H-bonds with water as well as terminal hydrogens on the SFG to build hydrogen bonds with O atoms of the adsorbates) may be viewed as "*sacrificial*" functionalisation. In this case, affinity towards CO_2 is usually increased in a dry stream setting, whilst in humid environments the adsorbed water can act as a preferred adsorption site, which may also facilitate increased CO_2 mass transfer. An overarching concept, however, is the fundamental affinity of CO_2 to ultramicropores (or similarly sized "pockets"). As such, the ability to design these adsorption sites by addition of appropriate SFGs (i.e. producing an ultramicroporous pocket within the pore by tethering an SFG) can be viewed as a prominent pathway towards adsorbents that are not hindered (or even promoted) by the presence of moisture in the inlet gas.

With regard to the aims for designing moisture-tolerant adsorbents, we believe the "*protective*" SFG approach to be more attractive for wide industrial deployment, whilst the "*sacrificial*" functionalisation could lend itself for more niche applications in specific contexts (perhaps, in conjunction with amine-containing chemisorbents for DAC or DOC). Despite often presenting a decreased CO_2 adsorption capacity (compared to pristine adsorbent in dry conditions), the lack of an additional regeneration energy requirement (to strip the water off the surface of the material) would most likely outweigh the benefits of a higher capture capacity value. On the other hand (albeit unlikely), if the cyclic CO_2 capacity of a hydrophilic sorbent is substantial/acceptable, an alternative pathway of limiting the desorption of co-adsorbed water may be an avenue for "*sacrificial*" SFGs.

Any modification, however, would greatly depend on the pristine material and its porous network. To facilitate such selection, the hydrophobic/phylic properties as well as approximate sizes of some prominent SFGs are presented in Table 3. The length of the SFG was determined by measuring linearly the distance between the SFG connection point, i.e. *the substituted carbon* (the α-atom) of an anthracene molecule (used as a representation of adsorbent ligand/surface) and the *furthest atom* of the SFG (simulated *via* MolView.org). In contrast, the volume of the SFG was calculated based on the molar volume of the radical (used as representation of the given SFG) obtained *via* Gaussian 9, revision D (B3LYP/6–31 G(d,p)).

The numbers in Table 3 are indicative and would depend largely on the charge distribution and the electron density cloud of the exact adsorbent and SFG system at hand. This is particularly important for the N-containing functionalities (as well as aryls), where there are multiple options for tethering position as well as distortion of the electron cloud due to resonance. Therefore, to benefit from the interplay between SFGs (size and properties), pore sizes (both diameter and volume) as well as moisture presence molecular simulations can be employed evaluating various functionalised linkers of a given MOF, for example. Alternatively, experimental studies involving systematic target SFG modifications on cheaper conventional adsorbents (ACs, zeolites, silicas) would benefit the field of CO_2 capture from humid environments *via* physisortion.

CRediT authorship contribution statement

Mikhail Gorbounov: Writing – original draft, Methodology, Investigation, Formal analysis, Conceptualization. **Paul Halloran:** Writing – review & editing, Supervision, Funding acquisition. **Salman Masoudi Soltani:** Writing – review & editing, Supervision, Resources, Project administration, Funding acquisition, Conceptualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence

Table 3
Examples of some SFGs, their properties and their approximate sizes.

Functionality	Affinity to H_2O	Length, Å	Volume, nm^3	Additional information
Methyl	Hydrophobic	2.14	0.00340	
Ethyl	Hydrophobic	3.45	0.00497	
Hexadecanyl	Hydrophobic	21.29	0.03583	
Phenyl	Hydrophobic	5.32	0.01100	
P-Tolyl	Hydrophobic	6.21	0.01571	
Carboxyl	Hydrophilic	3.21	0.00533	C=O bond length is ~1.21 Å [155] C-OH bond length is ~1.30 Å [156]
Carbonyl	Hydrophilic	2.37	0.00595	C=O bond length is ~1.21 Å [155]
Hydroxyl	Hydrophilic	1.92	0.00213	C-OH bond length (in phenols) is ~1.36 Å [155]
Pyrrole	Hydrophobic	4.56	0.00903	N atom is in position 1 (i.e. directly connected to the ligand)
		4.70	0.01012	N atom is in position 2
		4.71	0.00923	N atom is in position 3
Pyridine	Hydrophobic	5.22	0.01058	N atom is in position 1 (i.e. directly connected to the ligand)
		5.26	0.01042	N atom is in position 2
		5.27	0.01258	N atom is in position 3
		4.61	0.01077	N atom is in position 4
Nitro	Hydrophilic	2.31	0.00335	N=O bond length is ~1.21 Å [155]
Fluorine	Hydrophobic	1.34	0.00222	C–F bond length is ~1.37 Å [140]
Trifluoromethyl	Hydrophobic	2.39	0.00546	
Bromine	Hydrophobic	1.91	0.00283	C-Br bond length is ~1.96 Å [157]

the work reported in this paper.

Data availability

No data was used for the research described in the article.

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