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Review

Selective adsorption of volatile organic compounds in metal-organic frameworks (MOFs)

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ABSTRACT

Volatile organic compounds (VOCs) are common air pollutants that are harmful to humans and to the environment, commonly originating as crude materials from various industrial chemical processes. It is increasingly important to develop cost-effective and highly adsorptive materials for VOC capture. To this end, metalorganic frameworks (MOFs) have been studied as a potentially effective class of adsorbents due to their flexible structure and pore size, large surface area, and adjustable chemical functionality. This review summarizes recent developments in the selective adsorption of four different classes of VOCs - aliphatic, aromatic, oxygenated, and sulfur-containing, and their distinctive mechanisms of capture by MOFs. Aliphatic hydrocarbons form weaker van der Waals dipolar interactions with MOF pore walls, while aromatic hydrocarbons predominantly form π-π host–guest interactions. Oxygenated volatile organic compounds rely on capture by the formation of polar interactions with suitable adsorption sites within MOFs. Lastly, sulfur-containing VOCs tend to form strong bonds with MOFs that contain unsaturated metal sites. Additionally, synthetic methods for enhancing the hydrophobicity of MOF micropores to improve their stability with respect to slow hydrolysis, in the presence of realistic, humid environments are presented. In this comprehensive review article, commercialization, scale-up and nascent companies that utilize and/or produce MOFs are also discussed.

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1. Introduction

The rise in energy consumption and industrial activity has made air pollution regulation a priority to many countries and organizations. Particularly, volatile organic compounds (VOCs) are among the most common air pollutants emitted from industrial chemical processes, household products, and construction materials [1,2]. VOCs are defined as organic compounds with high vapor pressure and low water solubility [3], and common VOCs can be divided into several classes based on their molecular structure, boiling point, and polarity [4]. The most ubiquitous VOCs are formaldehyde, acetone, halocarbons, BTEX aromatics (benzene, toluene, ethylbenzene, and xylenes) and hydrocarbons. These primarily originate from anthropogenic industrial sources such as petroleum refinement, solvent production, coal combustion, and fossil fuel usage [5]. When released into the atmosphere, they contribute to the formation of ozone (O_3) which has adverse effects on ecosystems, the climate, air quality, and human health [6]. For instance, formaldehyde ($O = CH_2$) can cause chronic health problems to the human body upon exposure [7]; typical emitters of formaldehyde come from wood-based products in housing materials such as wall papers and paints; or, reaction between ozone and VOCs released from computers, laser printers, or photocopiers [8]. Aromatic VOCs have been reported to react with atmospheric oxidants like NO_x molecules to form secondary organic aerosols, of particulate matter that can be inhaled, or which further negatively impact the atmosphere [9]. Furthermore, VOCs pose a particular risk to human health by inhalation in confined (*i.e.*, indoor) spaces such as tobacco smoke [10]; indeed, studies have linked VOC exposure to major short and long-term health effects, including nausea, central nervous system damage, fatigue, and conjunctival irritation [5,11].

Thus, the development of effective VOC adsorption strategies is of timely significance for a broad range of industrial sectors and in controlling outdoor and indoor air quality. In terms of VOC abatement, recovery techniques are more environmentally beneficial and energy efficient compared to the alternative destructive techniques such as, catalytic oxidation, because they can produce more toxic byproducts [12]. Among available recovery techniques (membrane separation, absorption, adsorption, or condensation), adsorption is by far the most popular and economical [5,13]. Ideal properties for an adsorbent include, having a large specific surface area, high pore volume, thermal and chemical stability, easy regeneration, long-term activity, and cost-efficiency. The current state-of-the-art porous materials employed in VOC control include, activated carbons (ACs), zeolites, and hypercrosslinked organic polymers. These materials physically and chemically interact with the guest VOC molecules and can be subsequently desorbed through thermal and/or reduced pressure conditions to regenerate the adsorbent for continued use [14-17].

Among these three adsorbents, activated carbon is widely used commercially, owing to its large surface area (> 3,000 $m^2\ g^{-1}$) and ease of chemical modification (*e.g.*, by impregnation of metal ions) [5]. However, several issues with ACs exist due to aging effects (incomplete desorption of VOC species which leads to lower adsorptive capacities) [18], flammability concerns from enthalpies of adsorption by the VOCs [19], and the inability to adsorb VOCs at medium–high concentrations [20]. Due to the nature of pure physisorption onto ACs, desorption can occur. For instance, Gallego *et al.* noted the desorption of heptanal and nonanal on coconut shell activated carbon due to the weak binding interaction for aldehydes [21]. Secondly, synthetic zeolites (*i.e.*, mesoporous aluminosilicates) are commonfor VOC adsorption due to their high adsorption capacities, good thermal stability, and large surface areas [22]. These remain highly popular for industrial applications, but achieving optimal properties requires expensive reagents and complex synthetic protocols [23]. Lastly, hypercrosslinked organic polymers are microporous materials composed of light atoms (C, H, O, N, and B atoms) that form an interconnected framework and usually preferred in applications because they are the most resistant to hydrolysis in aqueous media across a wide range of pH conditions [24]. However, hypercrosslinked polymers are not selective enough for VOCs separations [25].

In contrast, metal–organic frameworks (MOFs) have emerged as a promising, alternative class of microporous adsorption materials. Along with coordination polymers, MOFs are prime candidates for applications in VOC capture and detection based on their high internal surface areas (1,140–4,293 $m^2\ g^{-1}$ for reported MOFs used in VOC capture) and their vast chemical functionalities which enable advanced adsorbate specificity [5]. The particular network structures of MOFs are predictable, versatile, and tunable towards VOC capture, which has made them a prime choice for VOC adsorption and separation [26]. MOFs can be modified to impart additional properties for diverse applications [27], and structures of the most common MOFs used for VOC adsorption are shown in Fig. 1**.** An ideal MOF for VOC capture would have wide pore windows that guest molecules could enter; however, the repeating units could form within each other leading to interpenetration [28]. Since effective molecular sieving requires careful matching of the MOF pore apertures with adsorbates, structure directing agents are often added to solvothermal MOF-forming reactions to prevent framework interpenetration from reducing the total accessible void spaces. Most microporous MOFs (*i.e.*, having pores < 2 nm) display diffusion-limited transport of similarly sized VOC molecules through the pores. In comparison, mesoporous structures (*i.e.*, having pores between 2 and 50 nm) show unrestricted VOC transport [29].

According to a review by Li *et al.*, the average VOC adsorptive capacity of MOFs is 1.7 times greater than ACs, 5.8 times greater than zeolites, and 2.1 times greater than polymeric resins [5]. These hybrid materials are synthesized using specific combinations of organic ligands and metal ions that give rise to desired chemical and topological properties in the solid-state: high porosity, large surface areas, tunable pore sizes, and functionalized adsorption sites [24,30-33]. Consequently, the wide array of possible MOF structures permits fine chemical modifications in their components that can significantly enhance sorption selectivity, the pore topology and size, as well as relative hydrophobicity [4]. Indeed, imparting water-resistance and minimal water selectivity is a key aspect to any VOC adsorbent's success because their effectiveness is often hampered by more favorable adsorption of H_2O from gas streams [34].

Over the last two decades, numerous MOFs with novel network types have been identified – a subset of which have been shown to exhibit exceptional properties and stability and can be synthesized at-scale. Examples such as MOF-74 [39], UiO-66 [40], MIL-53 [41], and NU-1000 [42] have been intensively studied in a range of environments, demonstrating viability for gas storage [43], separation [44], catalysis [45] and sensing [46]. In 2016, Sholl and Lively identified the capture of greenhouse gases from automotive and industrial emissions as one among the seven most important chemical separations [47]. MOFs have been used for CO_2 capture [48], water harvesting from desert air [49], adsorption heat pump [50], and refrigeration [51]. Sensing of VOCs is another important application for MOFs. To use MOFs as sensors, it is important to achieve selective adsorption of the desired compound and to have resistance to humidity which normally present at much higher concentrations compared to the concentration of VOCs. By utilizing novel adsorbents such as MOFs, these necessary processes could be improved efficiently, economically, and environmentally.

The volume of literature focused on selective gas adsorption by MOFs has been increasing steadily from 2017 to 2022 as seen in Fig. 2. There have been several reviews summarizing VOC capture using MOFs. Lai and group reviewed studies involving MOFs for

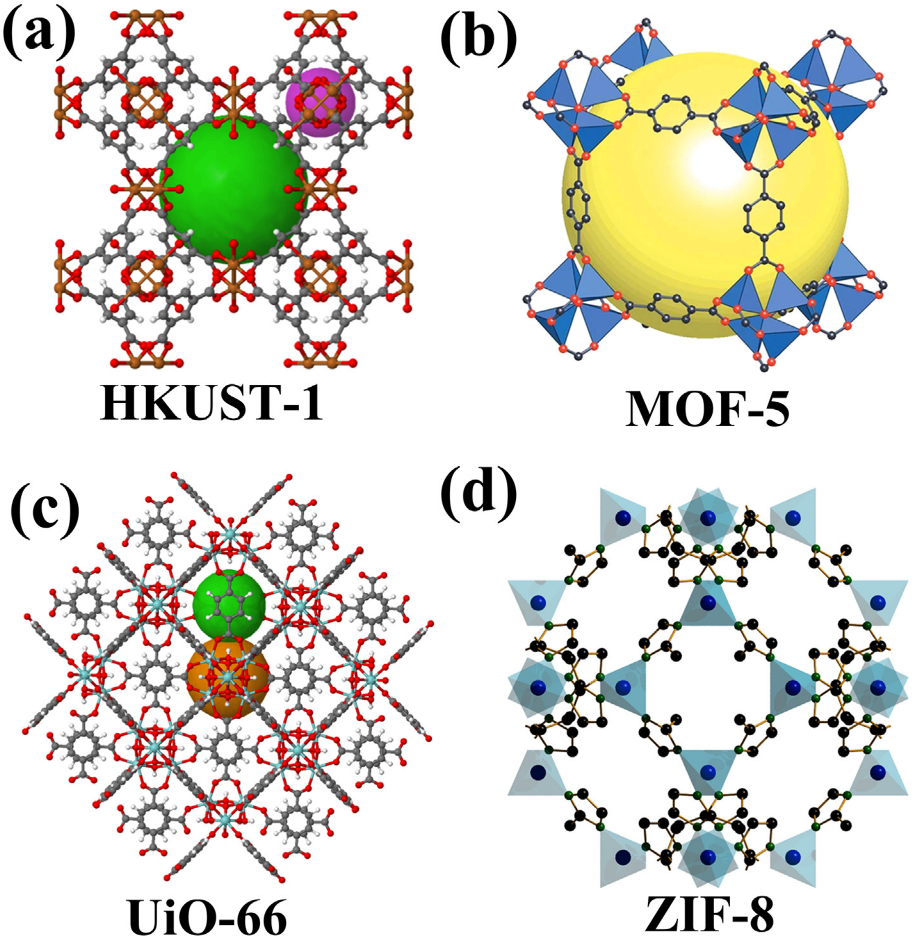

Fig. 1. a) HKUST-1,[35] reproduced with permissions. Copyright 2023, published by ChemTube3D. (b) MOF-5,[36] reproduced with permissions. Copyright 2020, published by IOP (c) UiO-66,[37] reproduced with permissions. Copyright 2023, published by ChemTube3D and (d) ZIF-8.[38] reproduced with permissions. Copyright 2018, published by Springer. All of which have been used for VOC capture.

capture and sensing of VOCs and radon gases under practical conditions [52]. Prior to this, Wen *et al.*, Barea *et al.*, and Vellingiri *et al.* summarized progress in the fields of VOCs capture and degradation using metal-organic frameworks [53–55]. Wen *et al.* and Barea *et al.* summarized capture and degradation of toxic gases in MOFs, while Vellingiri *et al.* focused of VOC adsorption at ambient conditions. Furthermore, Li *et al.* summarized and compared different adsorption materials for VOC adsorption and concluded that the MOF have most adsorption capacity compared to other adsorption materials such as activated carbons and hypercrosslinked polymeric resin [5]. Yet, there has not been any review focused on selective adsorption of VOCs.

This review paper summarizes and categorizes the current state-of-the-art with respect to metal–organic framework applications in VOC adsorption based on the type of volatile organic compound studied and addresses important practical considerations, including MOF stability under realistic (*i.e.*, humid) operating conditions. Aspects of MOFs' chemical modifications to improve VOC sequestration, important molecular interactions, and their impact on sorption selectively are also featured. Furthermore, this work discusses current applications, near-term commercialization activities, and current challenges in the field.

2. VOC adsorption performance of MOFs

Volatile organic compounds are a group of organic chemical compounds with high vapor pressures, allowing them to easily vaporize under atmospheric temperatures and pressures [56]. The major classes of VOCs include aliphatic hydrocarbons, aromatic hydrocarbons, oxygenated VOCs (OVOC), and sulfur-containing VOCs (SVOC) [57], as shown in Table 1. While further classification of VOCs is possible (by their polarities, boiling points, and functional groups), these four groups encompass most common VOCs. Judicious selection and optimization of the metal–organic framework is necessary to maximize sorption of VOC ('guest') within the MOF ('host'), and the interactions are fundamentally different for each major class of VOC. For instance, benzene, toluene, ethylbenzene, and xylene (BTEX) containing waste streams require a MOF that exploits the metal-π coordination effectively. Therefore, the review individually discusses how MOFs address each category of VOCs through their mechanism of sequestration and relevant progress.

2.1. Adsorption of aliphatic hydrocarbons

Aliphatic volatile organic compounds such as acetylene (C_2H_2), ethylene (C_2H_4), and hexanes (C_6H_{14}) are among the most common industrial feedstocks and are therefore common air pollutants [59]. The removal of these compounds generated from vehicle emissions and chemical processes are especially significant for safety concerns since they are highly flammable and explosive [13,82]. To improve the separation efficiency of aliphatic hydrocarbons and carbon dioxide, a newly constructed MOF [Co(btzip)(H_2btzip)]·2DMF·$2H_2O$ (H_2btzip = 4,6-bis(triazol-1-yl)isophthalic acid) was chosen for the presence of uncoordinated Lewis basic N-atoms

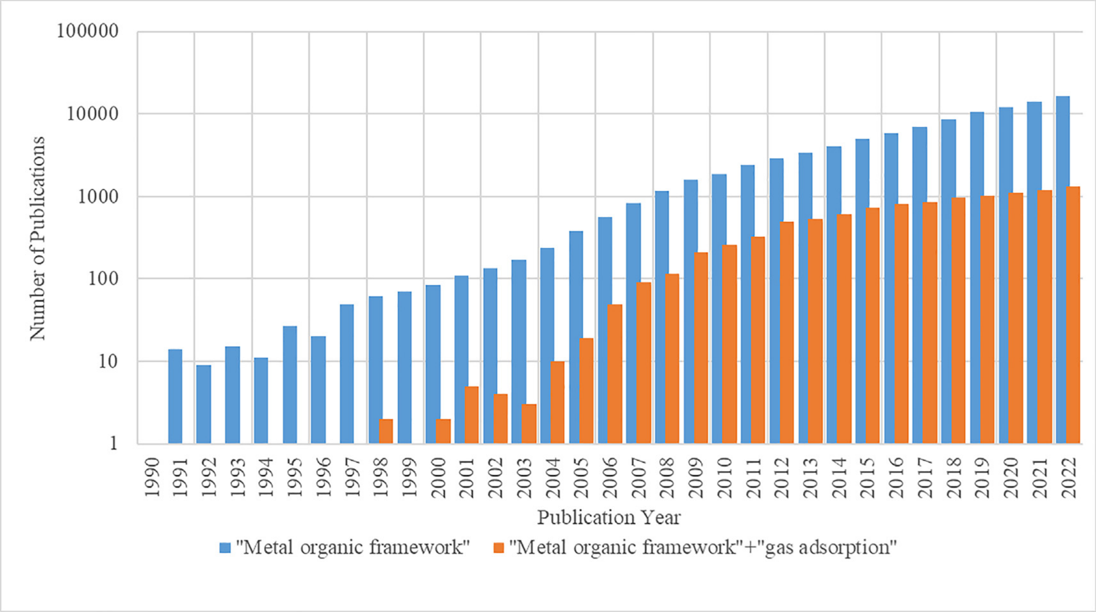

Fig. 2. Number of publications of gas adsorption on metal organic framework between 1990 and August 2022. The key search words “metal–organic frameworks” and “metal–organic framework” + “gas adsorption” were used in Web of Science.

Table 1
MOFs categorized by the four major classes of VOCs: aliphatic, aromatic, oxygenated, and sulfur-containing.

VOC Classes	VOCs	MOFs
Aliphatic	Ethylene C_2H_4	[Co(btzip)(H_2btzip)] [58]
Aliphatic	Acetylene C_2H_2	[Co(btzip)(H_2btzip)] [58]; Cu-CPAH [59]
Aliphatic	n-Pentane C_5H_{12}	M-MIL-101(Cr) [60]
Aliphatic	n-Hexane C_6H_{14}	M-MIL-101(Cr) [60]
Aliphatic	n-Heptane C_7H_{16}	M-MIL-101(Cr) [39]
Aromatic	Benzene C_6H_6	Bio-MOF-11 [61]; MOF-5 [62,63]; MOF-199 (MC-T-n) [64]; MIL-125-NH_2 [65]; IRMOF-5 [63]; MOF-74 [63]; MOF-177 [63]; MOF-199 [63]; IRMOF-62 [63]; Cu_3@MIL-10 [66]; BUT-66 [67]; BUT-67 [67]
Aromatic	Toluene C_7H_8	Bio-MOF-11 [61]; MOF-5 [62]; MOF-177 [63]; MIL-125-NH_2 [65]; BUT-66 [67]; BUT-67 [67]; Fe-MOF [68]; CAU-1 [69]; MIX UiO-66(Zr) [70]; UiO-66 [71]; MIL-101 [72]
Aromatic	Ethylbenzene C_8H_{10}	MOF-5 [62]; MOF-177 [73]; MIL-101 (Cr) [72,74]; MIL-53(Fe) [74]; BUT-66 [67]; BUT-67 [67];
Aromatic	Xylenes C_8H_{10}	MOF-5 [62]; MOF-177 [73]; MIL-101(Cr) [72]; MIL-125-NH_2 (*p*-xylene) [65]; BUT-66 [67]; BUT-67 [67]
Aromatic	Chlorobenzene C_6H_5Cl	N-coordinated M-UiO-66 (Zr-Nx) [75]
Oxygenated	Formaldehyde CH_2O	MIL-125-NH_2 [65]; MIL-100 (Fe)/ M-350 [76]
Oxygenated	Acetaldehyde C_2H_4O	N-coordinated M-UiO-66 (Zr-Nx) [75]
Oxygenated	Acetone C_3H_6O	MOF-177 [73] Bio-MOF-11 [61]; MIL-125-NH_2 [65]; MIL-101/ TC-30 [77]; MIL-101(Cr) [72]; MIL-100 (Fe)/ M-350 [76]
Oxygenated	Methanol CH_3OH	Bio-MOF-11 [61]; MIL-100 (Fe)/ M-350 [76]
Oxygenated	Isopropanol C_3H_8O	MIL-125-NH_2 [65]
Oxygenated	Ethyl Acetate $C_4H_8O_2$	ZIF-8 [78]
Sulfur containing	Dimethyl sulfide CH_3SCH_3	IRMOF- 3 [79]; MOF-199 [80]; Zn-MOF-74 [81]
Sulfur containing	Ethyl mercaptan C_2H_5SH	IRMOF- 3 [79]; MOF-199 [80]; Zn-MOF-74 [81]

and acidic carboxylic acid (–CO_2H) functional groups present in its structure [58]. Several intermolecular forces between guest acetylene molecules with the MOF influenced the capture, which were attributed to a combination of the acidic hydrogens coordinating with the π system of the MOF (C–H$\cdots\pi$), π bond electrons with the MOF (C$\cdots\pi$), acetylene guest molecules and the –CO_2H groups, and uncoordinated triazolyl-N atoms in the MOF (Fig. 3). When exposed to a C_2H_2/CO_2 binary gas mixture, the MOF showed a sorption preference for acetylene (1.51 mmol g^{-1}) over carbon dioxide (0.64 mmol g^{-1}). This finding has great industrial potential due to the difficulty in separating C_2H_2/CO_2 because both molecules have similar kinetic radii and boiling points.

Compared to their double and triple bonded counterparts, saturated aliphatics are challenging to capture as they inherently have less avenues of chemical interactions. From Table 1, MIL-101(Cr) $[Cr_3F(H_2O)_2O(BDC)_3]\cdot nH_2O$ (n ~ 25; BDC = benzene-1,4-dicarboxylate) is an extremely common MOF used for VOC capture, especially for aromatics. This MOF features trimeric Cr (III) octahedral clusters joined together by BDC molecules to create two cages of 29 Å and 34 Å diameter, granting extremely high surface area of *ca.* 2500–3200 m^2 g^{-1} [83,84]. Alongside that, it has excellent hydrothermal and chemical stability and retains its crystallinity for months in ambient conditions or when treated with organic solvents [83]. Accordingly, Shafiei *et al.* explored the efficacy of using MIL-101 and its variant for linear aliphatic hydrocarbons. Instead of using a 1:1 ratio of reactants (linker H_2BDC to metal cluster $Cr(NO_3)_3\cdot 9H_2O$), they synthesized MIL-101(Cr) with an alternative ratio of 2:1, yielding M-MIL-101 [60]. In comparison with their synthesized MIL-101 vs M-MIL-101 without the use of modulators, the latter exhibited a BET surface area of 4293 m^2 g^{-1} compared to 1758 m^2 g^{-1}, leading to a 244% increase in surface area. The enhancement in adsorption capacity is due to increased surface area resulting from increase in the ratio of micropore volume to total volume from 0.45 to 0.88 (for MIL-101@HNO_3) and 0.85 (for MIL-101@HF) where the @ symbol denotes what modulator was used when synthesizing the MOF. Most importantly, the equilibrium adsorption capacity of n-pentane, n-hexane, n-heptane, and gasoline was changed to 89 wt %, 135 wt%, 150 wt%, and 116 wt% respectively when using M-MIL-101 compared to MIL-101@HNO_3. Indeed, the efficacy for VOC capture is made even more explicit when comparing M-MIL-101 to a commercial AC where equilibrium adsorption capacity for M-MIL-101 was 179.2 wt% as opposed to 49.8 wt% for AC, resulting in a 260% increase.

2.2. Adsorption of aromatics

Aromatic volatile organic compounds make up a substantial portion of the total VOC emissions in the atmosphere which primarily originate from fossil fuel combustion, fuel evaporation, biofuel burning, and solvent uses in commercial products (e.g., paint and paint thinners) [85,86]. These aromatics have the highest ozone-forming potential, resulting in 69% of the total ozone production potential; additionally, aromatic hydrocarbons bring severe health effects upon exposure [87]. Benzene (C_6H_6) is one of the most extensively studied aromatic VOCs and has wide applications in the chemical industry as a chemical precursor and fuel additive, but it is also a known carcinogen with increased incidence of leukemia in humans [88]. Therefore, limiting the exposure and release of BTEX compounds into the atmosphere is critical.

Generally, non-polar aromatic VOCs rely on the π-π interactions with a given adsorbent; it is therefore reasonable to assume its selective adsorption by a MOF requires the presence of abundant, accessible aromatic moieties in the pore walls to sequester them. Saccoccia *et al.* performed single-crystal X-ray diffraction studies of solvent-loaded samples of Mg-CUK-1 $[Mg_3(2,4\text{-}pdc)_2(\mu_3\text{-}OH)_2]\cdot 9H_2O$ (2,4-pdc = 2,4-pyridinedicarboxylic acid) [89]. When Mg-CUK-1 was dehydrated and activated, treatment of the crystals with dry aromatic molecules (pyridine, benzene, toluene, *p*-xylene, or *p*-divinylbenzene) for 1–5 days at room temperature yielded X-ray resolvable crystallites. Fig. 4**a** illustrates the crystal structure of the MOF with benzene inside of the 1-D channels of the MOF, and **4b** shows the solvent positions relative to the polymer walls. As hypothesized, the face of one benzene molecule coordinates with the conjugated aromatic system of CUK's pyridine ring (*i.e.*, π-π interactions) while a separate, perpendicular benzene ring coordinates via C-H···π interaction – a positive H in benzene coordinating with pyridine's negative π system of the MOF [90]. Similarly, Fig. 4**c and 4d** correspond to the toluene/Mg-CUK-1 experiment with single-crystal images and reveal the same type of π-π coordination that is necessary for aromatic VOC adsorption [89].

In another study, Xie *et al.* demonstrated the effectiveness of hydrophobic BUT-66 $[Zr6(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_4(BDB)_6)]$ (BDB^{2-}= 4,4′-(benzene-1,3-diyl)dibenzoate) and BUT-67 $[Zr6(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_4(NDB)_6)]$ (NDB^{2-} = 4,4′-(naphthalene-2,7-diyl)dibenzoate) to adsorb trace toluene, ethylbenzene, *o*-xylene, *m*-xylene, and *p*-xylene from humid flow of air [67]. BUT-66 and BUT-67 have been reported with a benzene uptake of 3.97 mmol g^{-1} and 6.14 mmol g^{-1}, respectively. This utility is due to the formation of hydrophobic groups present in the ligand. This uptake volumes are twice as high as carbon-based adsorbent carboxen-1000.

In comparison to the conventional active carbon used for aromatic VOC adsorption, MOFs such as MIL-101(Cr) show a higher adsorption capacity (170 mg g^{-1}) for 500 ppm ethylbenzene at 25 ℃ [74]. As a common industrial derivative of benzene, ethylbenzene exhibits similar non-polar characteristics which allows it to form stronger π-π interactions with MIL-101(Cr) compared to the host–guest interactions (such as O···π) responsible for aromatic adsorption over activated carbon. Wang *et al.* synthesized MOF-199 $[Cu_3(BTC)_2(H_2O)_3]$ (BTC = benzene-1,3,5-tricarboxylate) derived porous carbon materials (MC-T-n, where T indicates the carbonization temperature and n refers to the mass ratio of KOH

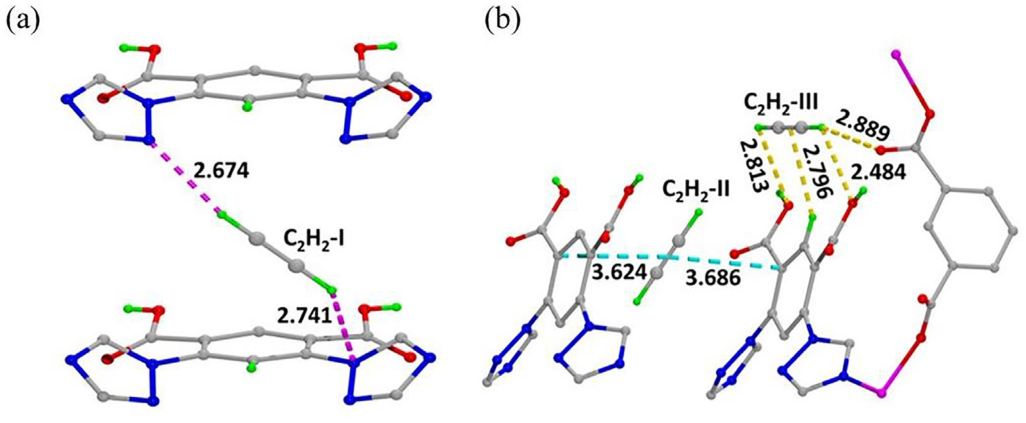

Fig. 3. Adsorption sites and intermolecular interactions between C_2H_2 and $[Co(btzip)(H_2btzip)]\cdot 2DMF\cdot 2H_2O$ generated by Grand Canonical Monte Carlo method [58] (Reproduced with permissions, Copyright 2020, published by American Chemical Society).

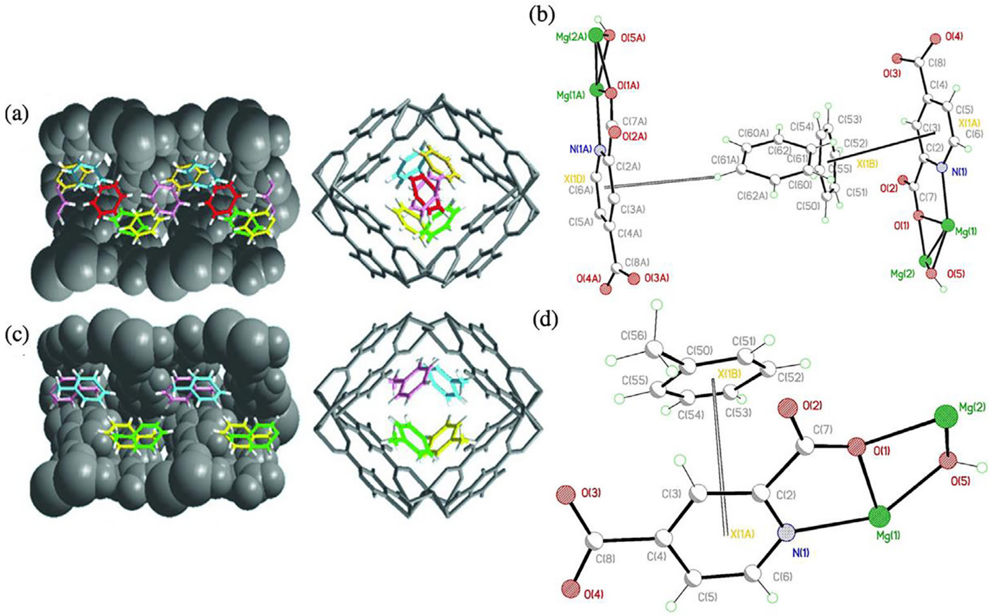

Fig. 4. (a,b) Single crystal x-ray images of Mg-CUK-1 with adsorbed benzene and (c,d). toluene. Mg-CUK-1 walls are colored gray while each unique guest solvent is in multiple colors. (b,d) ball-and-stick representations of the spatial arrangements of benzene or toluene relative to Mg-CUK-1 atoms. [89] (Reproduced with permissions, Copyright 2015, published by John Wiley and Sons).

and carbonized sample) and investigated their performance for benzene and water vapor sorption [64]. For example, the material that demonstrated the highest quantity of benzene adsorbed was MC-500-6 (12.8 mmol g^{-1} at 25 °C), which outperformed both MOF-199 and other conventional adsorbents; preparation of this material required a carbonization temperature of 500℃ and used a 6:1 ratio of KOH and carbonized sample. Compared to AC and zeolites, MC-500-6 is 2 to 11 times greater in its capacity for benzene adsorption.

Toluene is another common VOC found in both indoor and outdoor environments, which can induce an inflammatory response in the mucous membranes of the lungs [91]. Abundant accessible Fe^{2+} sites in FeMOF-0.25 were found to contribute to its excellent ability to remove 100% of toluene vapor tested at a concentration of 460 ppm [68]. Using UiO-66(Zr) $[Zr_6O_4(OH)_4(BDC)_6]$ and its isostructural amine counterpart UiO-66(Zr)–NH_2 $[Zr_6O_4(OH)_4(\text{BDC-}NH_2)_6]$, Vo *et al.* showed that toluene adsorption capacity at a concentration of 1,000 ppm was found to reach as high as 180 mg g^{-1}, facilitated by hydrogen bonding interactions formed between toluene's polarized hydrogens and the amine group of the MOF [70]. Tangentially, Zhang *et al.* focused on engineering the pores in a Zr-MOF (UiO-66) for toluene capture by adding a non-ionic triblock copolymer (Ploronic P-123) into the MOF crystallization step as a secondary structure directing agent [29]. In the presence of P-123, UiO-66 formed with larger average measured pore sizes. As a result, the modified structure prepared using a 0.2 ratio of P-123:Zr^{4+} showed a higher toluene uptake of 394 mg g^{-1} in comparison to pristine UiO-66 (166 mg g^{-1}; Fig. 5**a-c**). Different ratios of P-123:Zr^{4+} were also explored, but the ratio of 0.2 (denoted as P-U-0.2) was the best performing material that yielded the highest uptake capacity (2.6 times greater than pristine UiO-66). This observation was attributed to the higher degree of mesoporous defect sites inside the micropore network (based on the presence of broad peaks at low angles in the PXRD patterns of P-U-0.1 through 0.4) which enabled improved molecular diffusion of toluene. As expected, the sorption performance of the MOF decreased when the relative humidity was increased from 0 to 70 % relative humidity (%RH), resulting in an 82 % decrease in performance to 70 mg g^{-1} of toluene adsorbed on P-U-0.2.

To investigate the observed differences in adsorption capacity among various aromatic hydrocarbons, Wang *et al.* focused on the competitive adsorption among benzene, toluene, and ethylbenzene (BTE) mixtures by doping copper nanoparticles into MIL-101 (Cr) (Cu@MIL-101) [66]. A lower adsorption capacity was observed in their system due to mutual interference among the three substances. For VOC concentrations below 1500 mg m^{-3}, the MOF showed an adsorption preference in the order: ethylbenzene > toluene > benzene. Wang and coworkers attributed this difference to the polarity and structure of the different adsorbate molecules: in comparison to a benzene ring, the increasingly longer alkyl substituent on toluene and ethylbenzene allowed for an increasingly greater interaction with deeper parts of the MOF pores via van der Waals forces. Doping MIL-101(Cr) with copper(II) nitrate post-synthetically improved the adsorption capacity of MIL-101 by providing additional favorable adsorption sites by taking advantage of π- complexation. This example demonstrates a secondary strategy to sequester aromatic VOC's by employing unsaturated metal sites.

To explore the influence of shape and positioning in aromatics, Yang *et al.* investigated the efficacy of MIL-101(Cr) to capture acetone and BTEX molecules [72]. The pore sizes in MIL-101 range from 8.5 to 26 Å with a total pore volume of 1.85 cm^3 g^{-1} at P/P_o = 0.55; the two dominant pore domains are 12 and 18 Å in diameter. Adsorption of VOC molecules was found to follow a Type-I pore-filling mechanism akin to other porous materials like zeolites and activated carbons where the guest molecules rapidly fill the micropore channels. Yang *et al.* observed that the volume adsorption capacity decreased with increasing VOC molecular diameter since the cylindrical micropores of MIL-101 are smaller than the target VOCs. However, the shape and their geometrical orientation relative to the pores in MIL-101 greatly affect their adsorptive capacity. Acetone, benzene, toluene, ethylbenzene, and *p*-xylene could approach the pores in MIL-101 in orientations that present minimum critical diameters (Fig. 6). Conversely, *m*-xylene and *o*-xylene were predicted to approach at planes that result in maximum critical diameters due to the favorable interactions between their -CH_3 groups and the MIL-101 pore surfaces.

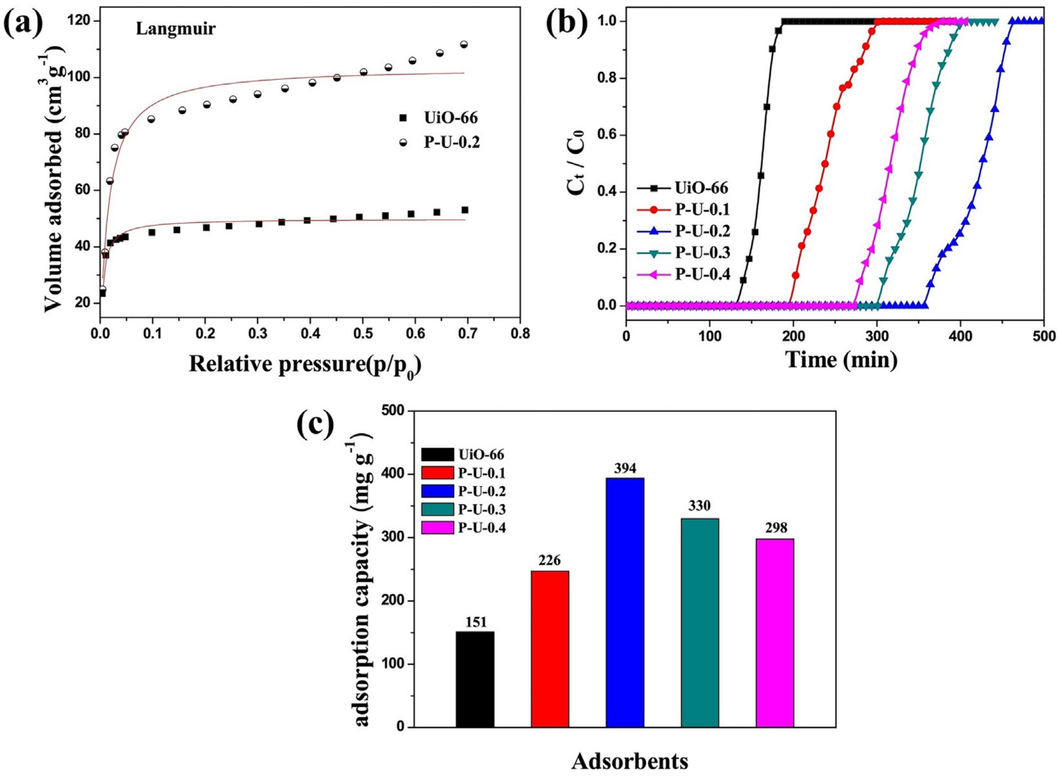

Fig. 5. (a) Freundlich isotherm fitting of toluene adsorption data on UiO-66 and P-U-0.2 (UiO-66 with P123:Zr4+= 0.2) at 298 K. (points: experimental data; lines: model curves); (b) Breakthrough curves for UiO-66, P-U-0.1, P-U-0.2, P-U-0.3 and P-U-0.4; (c) Adsorption capacity values for gaseous toluene in UiO-66 and P-U-0.1 to P-U-0.4 [29] (Reproduced with permissions, Copyright 2019, Elsevier B.V.).

2.3. Adsorption of oxygenated volatile organic compounds (OVOC)

Oxygenated volatile organic compounds (OVOCs) such as alcohols, aldehydes, and ketones are primarily generated by incomplete combustion of fuels and oxidation of hydrocarbons in the atmosphere [92,93]. Oxygenated organic compounds are generally more “active” compared to other VOCs due to the higher polarity of C–O and related O–X bonds. Cation-π bonding interactions, strong dipolar forces between host-guest functional groups, and coordinatively unsaturated sites (CUS) synergistically contribute to favorable OVOC adsorption capacities observed by some MOFs [94-96]. A MOF’s secondary building unit (SBU) is the environment and bonding that the metal ion or clusters have formed which repeats accordingly with the organic linker. While most frameworks feature regions where guest molecules could interact with the metals, they are often hindered by solvents during synthesis or small molecules from the air; therefore, activation of the solid via high temperature and low pressure in an inert atmosphere liberates the MOF from these extraneous molecules along with removing any that are adsorbed onto the pores as well.

An adenine-based metal–organic framework Bio-MOF-11 [$Co_2(ad)_2(CH_3CO_2)_2 \cdot 0.3EtOH \cdot 0.6H_2O$, ad = adeninate] with a specific surface area of 580 m^2 g^{-1} was synthesized via a facile solvothermal method and studied for the adsorption of methanol vapor [61]. Bio-MOF-11 displayed a strong preference for adsorption of polar species due to the abundant exposed heterocyclic-N donors and pendant amino ($-NH_2$) groups in its structure. Having a small molecular diameter of 6.16 Å, acetone can interact with the N-atoms of adeninate linkers within the pores of Bio-MOF-11 as well [61]. Bio-MOF-11 largely favors polar VOC molecules, having equilibrium adsorption capacities of 2.65, 1.86, 1.17, and 0.79 mmol g^{-1} for methanol, acetone, benzene, and toluene, respectively, at 1 kPa and 288 K.

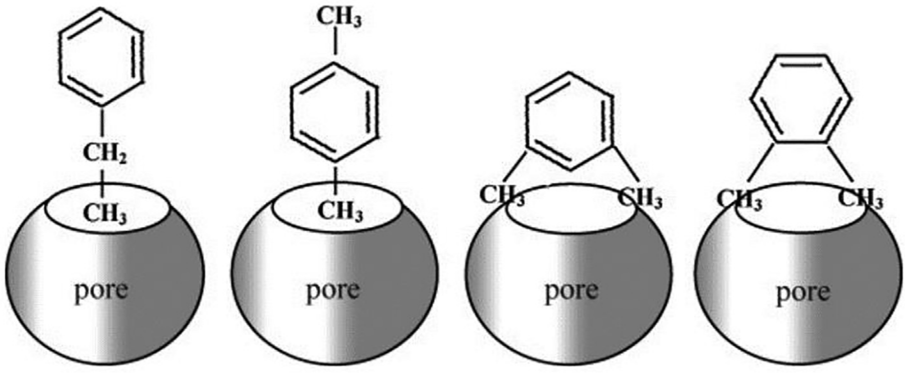

Fig. 6. Schematic representation of ethylbenzene, p-xylene, m-xylene, and o-xylene entering the pores of MIL-101 [72] (Reproduced with permissions, Copyright 2011, Elsevier B.V.).

Alternatively, a MOF with highly accessible coordinatively unsaturated sites accomplishes OVOC capture as well. MIL-100(Fe) $[Fe_3O(H_2O)_2F_{0.81}(OH)_{0.19}BTC_2]\cdot nH_2O$ (n ≈14.5) is composed of iron(III) trimesate, forming trimers of Fe^{3+} octahedra, and two of its three iron octahedra are coordinated with two H_2O and F^-/OH^- [95]. Pei *et al.* activated MIL-100(Fe) by calcining it at 300, 350, or 400 ℃ to remove these ancillary ligands [76]. Based on XPS and FTIR spectroscopies, subjecting MIL-100 to a calcination temperature of 350 ℃ was the most optimal, while a temperature above 350 ℃ caused thermal degradation of the MOF, and a temperature below 350 ℃ caused incomplete activation. Formaldehyde and acetone breakthrough studies were performed with this optimized M-350 material (MIL-100 calcined at 350 ℃). Breakthrough experiments are defined as adsorption studies where a stream of constant concentration gas is passed through a packed bed of the MOF to determine the mass of gas that was captured; the experiment is finished when the concentration of the adsorbate is at 1% of the inlet concentration. In this case, breakthrough for a formaldehyde stream at 10 ppm would entail determining the mass of formaldehyde that is adsorbed until concentration of the outlet stream becomes 0.1 ppm. Those studies yielded capacities of 17.8 mg g^{-1} for 10 ppm formaldehyde and 197 mg g^{-1} for 300 ppm acetone.

Besides methanol, the adsorption of other alcohols such as isopropanol was studied over a related amine-functionalized framework MIL-125-NH_2 [65]. This highly porous is composed of octahedral titanium (IV) oxide (from titanium(IV) isopropoxide) nodes and 2-aminobenzenedicarboxylate $(BDC-NH_2)^{2-}$ linkers with triangular openings (5–7 Å), resulting in basic units of $Ti_8O_8(OH)_4(-BDC-NH_2)_6$. For isopropanol, enthalpy of adsorption values ranged between 103 and 57 kJ mol^{-1} for different pressures. This likely originates from a strong hydrogen bonding (–N···HOR and –NH_2-···O(H)R) formed between the MOF pendant amine groups and isopropanol molecules, leading to the observed adsorption capacity 452 mg g^{-1} at 293 K.

In addition to alcohols, numerous studies have investigated the adsorption of aldehydes and ketones by various MOFs. The simplest ketone acetone ($O = C(CH_3)_2$) is a widely used industrial solvent. Li *et al.* reported that MIL-101 doped with porous carbon showed high acetone uptake capacity (1,137 mg g^{-1}) due to interaction between the polar adsorbate and the hydroxyl (–OH) group in the MOF [77]. The adsorption capacity increased by 19.8% with the addition of 40 mg of porous carbon compared to the original MIL-101 (949 mg g^{-1}). This improvement was attributed to two possible reasons: the addition of porous carbon hindered unreacted H_2BDC from poisoning Cr (III) sites, leading to more accessible Cr (III) ions at the nodes, and the contribution of the porous carbon to the surface area for acetone capture. The sorption enhancement observed for this type of MOF-carbon composite is a promising method for the straightforward preparation of VOC removal agents for applications in the industry.

An effective adsorption method has yet to be developed for the removal of formaldehyde from indoor environments [8]. Currently, AC is the most accepted technology for adsorption; however, formaldehyde's low boiling point (-19.5℃) makes it difficult to bind to AC along with the issue of better adsorption of water compared to formaldehyde [97]. To enhance the adsorption capacity of a polar compounds like formaldehyde, an amine-tagged material is often best utilized to aid in its sequestration [67]. Kim *et al.* showed in their study of MIL-125-NH_2 that polar interactions (–NH···O = CH_2) resulted in an enhanced adsorption capacity (40.2 mg g^{-1}) for formaldehyde (2.1 mg g^{-1}; average pore size of 0.61 nm; 298 K; 60 ppm formaldehyde in 1 bar N_2) [65]. Additionally, they exploited MIL-125′s micropore opening (0.4 nm) to favorably adsorb formaldehyde molecules since its kinetic diameter is close in size (0.25 nm) [65]. It is worth noting that most general studies of formaldehyde adsorption are performed on activated carbon or graphene, while few have used MOFs as the exclusive adsorbent. Therefore, research on formaldehyde adsorption with MOFs, including competitive adsorption studies from humid air, warrants further exploration.

2.4. Adsorption of sulfur-containing VOCs

Small organosulfur molecules like mercaptans, thioethers, and disulfides are SVOCs that are often emitted naturally from the anaerobic decomposition of organic materials inside landfills and composts, industrial processes in hydrodesulfurization units in petroleum refining, sewage treatment, and more [80,81,98,99]. Current EPA gasoline standards require less than 10 ppm [100], but hydrodesulfurization sacrifices H_2 to form H_2S. Not only does this produce the serious health hazard of H_2S, but hydrogen is becoming more valuable as a fuel and needs to be used judiciously. Aside from the human health and environmental repercussions, SVOCs are the chief cause for catalyst poisoning, corrosion of equipment infrastructure, and odor pollution in urban environments [80]. Their capture majorly relies upon abundant coordinately unsaturated metal sites within MOF's nodes [95,101]. According to Pearson's hard-soft acid-base principles (HSAB), soft Lewis acids like Cu^+, Cu^{2+}, Ag^+ and Ni^{2+} would be most effective for MOF synthesis since they can coordinate with the soft Lewis bases of sulfur-containing VOCs [80,102].

Therefore, Zhang *et al.* examined the adsorption capacity of two common organosulfur compounds dimethyl sulfide $S(CH_3)_2$ and ethyl mercaptan C_2H_5SH by Zn-MOF-74 $[Zn_2(dhtp)(H_2O)_2\cdot 8H_2O]$ (dhtp = 2,5-dihydroxy terephthalate) [81]. With the VOC concentration fixed at 200 mg m^{-3}, Zn-MOF-74 reached a maximum adsorption capacity of 1.14% for ethyl mercaptan at 80 °C while the highest adsorption for dimethyl sulfide was 1.33% at 30 °C. In addition to the strong (Zn^{2+}···S) intermolecular interactions formed between metal centers and ethyl mercaptan, hydrogen bonding interactions between the thiol groups on the sulfur compounds and accessible hydroxyl groups present in the nodes (–OH···S) of Zn-MOF-74 also contributed to the adsorption capacity. In contrast, the two methyl groups of dimethyl sulfide created sufficient steric hindrance that resulted in weaker (*i.e.*, longer-range) interactions with Zn^{2+} centers. It is important to note that Zn-MOF-74 displayed excellent regeneration stability for dimethyl sulfide sorption due to the weaker binding, while the regeneration performance for ethyl mercaptan was accordingly poor.

Wang *et al.* performed a series of breakthrough experiments with MOF-199 $[Cu_3(BTC)_2]$, also known as HKUST-1 and Cu-BTC, to capture hydrogen sulfide, dimethyl sulfide, and ethyl mercaptan [79]. MOF-199 is known for its copper paddlewheel geometry on its secondary building units; subsequent activation of the MOF leaves behind two highly accessible Cu^{2+} sites for VOC capture [103]. CH_3-SCH_3 and CH_3CH_2SH were set at a concentration of 600 ppm in a stream of nitrogen at 30, 50, 60, and 80 ℃ and passed through a fixed bed of MOF-199 after activation at 180 ℃. MOF-199 shwed a capacity for both gasses that decreased at higher temperatures, while CH_3SCH_3 performed the best with values of 8.48%, 7.68%, 5.55%, and 1.97% at their respective temperatures. The structure of MOF-199 collapsed when exposed to H_2S and CH_3CH_2SH, as evidenced by the powder X-ray diffraction (PXRD) spectra's loss of peaks compared to the freshly activated sample. Additionally, from FTIR, a new Cu-S bond at 672.9 cm^{-1} and thiol at ∼ 2500 cm^{-1} denoted chemical adsorption had occurred. Similar to the poisoning that occurs with catalysts, the group's evidence for chemisorption was the overwhelmingly stable Cu-S bond formation from hydrogen sulfide and ethyl mercaptan with the Cu^{2+}, since the interaction is between a soft acid and soft base, leads to free carboxylate protonation which destroys the linkages (O-Cu-OOC to O-Cu-S-C_2H_5). However, CH_3SCH_3 adsorption was reversible, and Wang *et al.* attribute this discrepancy to the steric hindrance of the methyl groups hindering a chemical change to the MOF as sulfur capacity was unchanged after 2 more additional cycles.

2.5. Selectivity of VOC adsorption in MOFs

Achieving selective adsorption and selective separation has been a major effort in the field of VOCs adsorption in MOFs. Several researchers have attempted to achieve selective separation of VOCs from a mixture of VOCs [61]; Huang *et al.* have experimented adsorption properties of MIL-101 with mixture of six VOCs (n-hexane, toluene, methanol, butanone, dichloromethane, and n-butylamine) [104]. MIL-101 has been found to have strongest affinity to n-butylamine, and the weakest affinity to n-hexane. In their experiment, adsorption isotherms using the Dubinin–Astakhov equation have shown adsorption capacity ranging from 0.08 for n-hexane to 12.8 mmol g^{-1} for n-butylamine. In another study by Yang *et al.*, the team tested adsorption of BTEX compounds in MOF-177 [73], which showed adsorption capacity of 800 mg g^{-1} for benzene and adsorption capacity of 589 mg g^{-1} for acetone. This demonstrates MOF-177′s affinity towards benzene over acetone.

In another recent work by Brantuas *et al.* demonstrated the effectiveness of MIL-160(Al) [AlOH(fdc)] (fdc = on separating engine fuel from mixture of VOCs [105]. The hierarchy of sorption has been found as follow: n-hexane $\gg$ n-pentane $\gg$ 2-methylpentane > 3-methylpentane $\ggg$ 2,3-dimethylbutane > isopentane $\approx$ 2,2-dimethylbutane. This study demonstrates low octane number engine fuel is more favorable for sorption in MIL-160 (Al) than low octane number engine fuel. Other than these studies, there have not been many other investigations focusing on selective adsorption of VOCs from a mixture.

3. Strategies for improving MOFs' resistance to hydrolysis

Despite the potential applications in environmental abatement and air quality control, majority of MOFs are quite sensitive to water, which is concerning as the relative humidity present in air separation units is around 40%, and industrial flue gas contains approximately 10% water vapor [34]. According to Xie *et al.*, out of the tens of thousands of metal–organic frameworks synthesized, approximately 100 structures are considered hydrophobic *i.e.*, materials that exhibit low affinity for water. To illustrate the issue, the seminal MOF-5 [$Zn_4O(BDC)_3$] is featured widely with excellent porosity but is significantly weak in moist environments at room temperature while HKUST-1 has much greter stability at higher relative humidities and temperatures [106]. When exposd to VOCs, Xian *et al.* demonstrated that the adsorption capacities of dichloroethane, ethyl acetate, and benzene in MIL-101 decreased by 45%, 62%, and 60.8%, respectively, when the relative humidity (%RH) of the mixture gas increased from 0 to 80% [107]. Similarly, Yang and group measured the adsorption capacity of toluene in MOF-177 which sharply decreased when the % RH was increased from 0 to 50% [73].

VOC adsorption capacity of MOFs decreases drastically in the presence of water since they competitively occupy the most favorable adsorption sites within the pores of the MOFs [17,107]. Additionally, water is often detrimental to the crystallinity of MOFs and can induce slow hydrolysis of metal–organic linkages, leading to eventual structural collapse and loss of porosity [108]. To characterize the effects of water exposure, the loss of crystallinity can be generally determined by a change in the PXRD patterns via the loss in sharpness of peaks or shifting altogether in the pattern, indicating a change in the space group and/or breakdown of the crystallographic faces. However, a relatively unaffected PXRD pattern can still indicate degradation due to loss of multiple adsorbent sites Therefore, comparing the BET surface area and adsorption capacity of the material after a prescribed dose of water vapor can be necessary [34]; furthermore, more methods such as water contact angle measurements or competitive breakthrough adsorption of water vs toluene can elucidate the effects of humidity [109].

Three main physical factors contribute to the relative robustness of MOFs, relating to thermodynamic and kinetic stability that results from a particular combination of organic ligand and metal ions used : (i) the metal–ligand coordination bond strength, (ii) connectivity within the SBU, and (iii) the number of metal sites available for ligand coordination [34,106,110,111]. The primary factor for MOF thermodynamic stability is the metal–ligand bond strength. According to HSAB theory, high-valent metal cations such as Ti^{4+}, Zr^{4+}, Al^{3+}, Fe^{3+}, and Cr^{3+} combined with acidic organic ligands such as carboxylates ($-COO^-$) or soft divalent metals like Zn^{2+}, Cu^{2+}, and Ni^{2+} with soft acids like azolates ($-N-N^-$) can form strong coordinative bonds. For example, the UiO series of MOFs feature tetravalent Zr^{4+} ions with BDC ligands ($C_6H_4-(COO^-)_2$), and this highly acidic Zr^{4+} ion with the hard carboxylate base endows UiO-66 with an unchanged nitrogen BET surface area after 100 days under a 75% humidity environment [112]. On the other hand, the zeolitic imidazolate framework (ZIF) family is both water stable and thermally stable, owing to their excellent bond stability between the N^- from variations of 2-methylimidazolate with the Lewis acid Zn^{2+} (a low valent, d^{10} ion) with an 8 mg g^{-1} water adsorption at 25℃ and P/P_0 = 0.8 [109,113].

In terms of kinetic stability, water molecules must approach the metal ion at a critical distance for a hydrolysis reaction to occur. If the metal cations are sufficiently protected by hydrophobic or steric methods, then the loss of crystallinity cannot occur. Indeed, hydrophobicity can be defined as the incorporation of low surface energy moieties such as alkyl, aryl, and fluorinated alkyl/ aryl groups to the internal (MOF pore system) or external (bulk material) that hinder water molecules approach to the metal ion in the secondary building units [109]. Other tactics like increasing the connectivity of the SBU can prevent water from approaching the proper geometry for hydrolysis, and if one linkage were to be undone, there is more margin before lattice collapse due to the increased coordinations present to stabilize the SBU [34].

Wang and group featured two metal–organic frameworks by synthesizing 3-ethyl-5-trifluoromethyl-1,2,4-triazole (Hfetz) with Ag^+ and Cu^+ to form MAF-9 [Ag(fetz)] and MAF-2F [Cu(fetz)], [114]. The incorporation of $-CH_2CH_3$ and $-CF_3$ groups is an exemplary use of imparting hydrophobicity to the MOF's pores as these low surface energy groups disfavor water adsorption while each N atom (as part of the triazole moiety) is coordinated to an individual Ag^+/Cu^+ metal. From thermogravimetric analysis (TGA) measurements, both MOFs decompose at 280℃ and exhibit no other onset temperatures, meaning their only mass loss contributions are from decomposition and not from water desorption. MAF-9 showed no change in its pristine PXRD pattern when submerged in water at room temperature for a year while MAF-2F was stable for at least 3 months; indeed, MAF-9 excludes water almost completely with a 0.07 mmol g^{-1} water adsorption at P/P_0 = 0.99. With respect to VOC adsorption, MAF-2F achieves methanol, ethanol, and benzene adsorption capacities of 4.8, 4.4, and 2.1 mmol g^{-1}, respectively. This dual-fold approach by Wang *et al.* demonstrates thermodynamic stability in the triazolate to Ag/Cu bond and kinetic stability by preventing water approach with low surface energy functional groups, creating highly water stable metal-organic frameworks.

Zhu *et al.* grafted C_2-C_8 alkyl chains onto the organic linkers of UiO-67 [$Zr_6O_4(OH)_4(BPDC)_6$] (BPDC = 4,4′-biphenyl- dicarboxylate) to improve the hydrophobicity by lowering the internal pore surface energy as well as creating surface roughness to obstruct water adsorption [115]. To achieve this, methyl-2-hydroxy-4-iodobenzoate was used to form an analogous UiO-67 linker containing *ortho*-OH groups; once inside the MOF, the OH groups could be deprotonated and appended, giving the general form UiO-67-Rs, where R = ethyl, n-butyl, n-hexyl, and n-octyl. Untreated UiO-67 displayed a water contact angle of 0°, indicating complete sorption of the water since the MOF surface is hydrophilic (Fig. 7**a**). With the addition of appended alkyl groups of increasing chain length, contact angles increased to 121.1 – 154.0°, with UiO-67-Oct having the greatest. Additionally, water uptake isotherms measured at 298 K showed that UiO-67-Oct had the lowest mL g^{-1} capacity while un-modified UiO-67 had the greatest (Fig. 7**b**). While Zhu and group's work did not test VOC adsorption, it still maintains an example of hydrophobicity modifications to an originally hydrophilic MOF by inserting low surface energy alkyl groups.

An example of sterically hindering the metal node includes MIL-53-Al [$(Al(OH)BDC]\cdot H_2O)$] which was modified by Shi *et al.* to improve the capture of the oxygenated VOC acetone [116]. MIL-53-Al suffers from the same hydrophilicity issues as many other MOFs; therefore, alkyl phosphonic acids (with C_{12}, C_{14}, and C_{18} chains) were post-synthetically substituted into a proportion of existing Al–OH bonds in the nodes, yielding chemically stronger Al–O–P linkages and decorating the pores with hydrophobic aliphatic appendages. Consequently though, the addition of low surface energy alkyl groups simultaneously lowers the adsorption capacity due to the decreased pore sizes, so MIL-53-Al@C_{14} exhibited an optimal balance of these two competing factors: the acetone adsorption capacity of this material was 39.04% and 102.98% higher than pristine MIL-53-Al at 60 and 90 %RH, respectively.

A third route for tuning hydrophobicity by pore structure modifications has been achieved by modifying the bulk crystalline surfaces of a MOF with a hydrophobic coating. Zheng *et al.* chose an aluminum-based MOF CAU-1 [$Al_4(OH)_2(OCH_3)_4(H_2N\text{-}BDC)_3$] ($H_2N$-BDC = 2-aminoterephthalic acid [69]. Before modifications, at > 30% RH, water was found to condense in its pores. Their solution was to use anhydrides (butyric, valeric, or benzoic anhydride) to transform the hydrophilic –NH_2 group to form corresponding amides; then, a polydimethylsiloxane (PDMS) film was deposited on the crystal surfaces by physical vapor deposition for external hydrophobicity. This method shows both internal ligand modifications as well as coating the bulk material with a hydrophobic layer. The modified CAU-1 shows an uptake of 6.82 mg g^{-1} (at 1 ppm and 50 %RH) with an 85% increase in adsorption capacity for toluene in comparison to the untreated CAU-1.

Another method to impart hydrophobicity in MOFs is by replacing each linear ligand with a pair of angular ligands with non-coordinated aromatic bridging backbones. These angular ligands with bridging backbones form small and hydrophobic pores because of the space segmentation by the angular aromatic entities and rotational dynamics of the phenyl rings, preventing a water molecule to approach the metal node. This method has been exploited by Xie *et al.* in their study where BUT-66 uses BDB^{2-}ligands which is similar to terphenyl but bent and BUT-67 uses NDB^{2-} which has a naphthalene center with phenyl rings at side positions as well. [67].Because of their bent orientations, this causes their structures to form interpenetrated nano- and microporous hydrophobic surfaces. Then, BUT-66 and BUT-67 have been proved to be a better adsorbent for BTEX in presence of 50 and 80% relative humidity than carboxen-1000, MIL-101(Cr) and ZIF-8. This demonstrates the effectiveness of replacement of linear ligands with long angular ligands in MOFs to impart hydrophobicity.

Thus, the thermodynamics and kinetic factors affecting stability between coordination bonds in a MOF ought to be considered for their VOC adsorption. Pearson's HSAB rules are the chief guidelines for maximizing metal–organic framework stability. And for kinetic stability, adding hydrophobic functional groups like alkyl, aryl, or fluorinated groups and high connectivity in the metal ion can disable water vapor's approach to a metal node that would cause ligand displacement and lattice collapse.

3.1. Selectivity of MOFs towards VOCs in the presence of water vapor

To reduce the adsorption of water, the strategy is to create hydrophobic MOFs; thus, the general approach is to introduce hydrophobic ligands in the MOFs [117]. However, if water molecules approach at coordinatively unsaturated sites, these MOFs could still be kinetically unstable. Simultaneously, by adding hydrophobic moieties to a metal–organic framework, these naturally decrease the available surface area and therefore the adsorption capacity for VOCs. Additionally, hydrophobic groups will naturally disfavor the binding of polar VOCs like acetone, ethyl

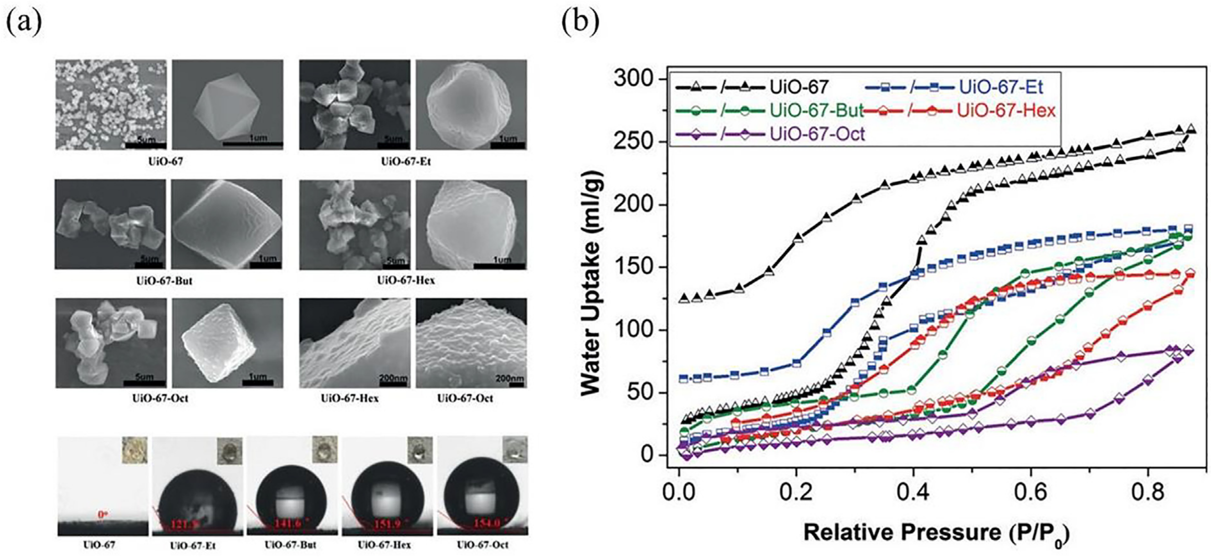

Fig. 7. (a) SEM images and digital photographs of static water contact angle measurements of UiO-67 and UiO67-Rs. Values for water contact angles are 0°,121.1°, 141.6°, 151.9°, and 154.0° for UiO-67, UiO-67-Et, UiO-67-But, UiO-67-Hex, and UiO-67-Oct. (b) Water adsorption isotherms of UiO-67 and UiO67-Rs at 298 K. Bottom filled shapes indicate adsorption and top-filled shapes indicate desorption [115] (Reproduced with permissions, Copyright 2019, published by John Wiley and Sons).

acetate, or formaldehyde, so a balance must be maintained to maximize selectivity.

Dedecker *et al.* have considered this hydrophobicity/hydrophilicity balance by studying dilute acetic acid adsorption in a variety of MOFs with different pore apertures, functional groups, etc., and they determined that UiO-66-2CF_3 (UiO-66 but with two -CF_3 groups adjacent to the carboxylic acid groups) was the most promising [118]. For instance, they tested UiO-66-NH_2 for its acetic acid capture but found that the basic polar group does not reduce its simultaneous adsorption of water, but when trifluoromethane groups were instead added, UiO-66-2CF_3 showed the highest adsorption capacity for acetic acid after 1 h. Their conclusion was that the addition of perfluoro groups coupled with optimal pore size for the adsorbate was the best for uptaking acetic acid.

Though there have been studies involving techniques of exclusion of water vapor to minimize water adsorption, there have not been many studies demonstrating the use of these techniques for optimizing selective VOCs adsorption. Wang *et al.* have showed adsorption selectivity for benzene/water vapor in MC-500–6 (derived from MOF-199) reached up to 16.3, which was superior to MIL-101 and MOF-199 [64]. In another work, Wang and coworkers demonstrated the effectiveness of BUT-66 for capturing benzene from airflow containing 10 ppm benzene and 80% humidity [67]. BUT-66 captured benzene selectively from water vapor due to its high hydrophobicity of the crystal's exterior surface. In addition to these studies, Virdis *et al.* reported a comparative study between adsorption of low concentrations of VOC mixtures of ethanol, ethyl acetate, 2-butanone, and 2,3-butanedione and 90% relative humidity for ZIF-8 and UiO-66 [119]. In this study UiO-66 exhibited significantly higher uptake of VOCs in the humid condition compared to ZIF-8. Not all experiments with relative humidity showed a successful adsorption of VOC in MOFs. Yang *et al.* experimented with MOF-177 to adsorb acetone, benzene, toluene, ethylbenzene, *o*-xylene, *m*-xylene, *p*-xylene and ethenylbenzene in air with relative humidities of up to 90% [73]. The experiment showed that the addition of water molecules reduces the available sites for VOC adsorption in MOF-177. Chevalier *et al.* demonstrated that HKUST-1 MOF's performance to adsorb common indoor air VOCs (toluene, acetone, *o*-xylene, ethanol, and acetaldehyde) can degrade up to 97% in presence of humidity [120]. Another study detailed a comparative analysis to understand the effectiveness of Cu-, Co–, and Zr-MOFs to absorb VOCs (1 ppm each) benzene, toluene, styrene, *m*-xylene, methyl ethyl ketone, methyl isobutyl ketone, butyl acetate, and isobutyl alcohol was explored both as single and multi-component system [121]. The adsorption performance series of experimented MOF can be shown as Co-CUK-1 < UiO-66 < UiO-66NH_2 < MOF-199. This study also demonstrated that activated carbon performs better for adsorbing non-polar VOCs than the above-mentioned MOFs.

Yang *et al.* reported reversible adsorption with a high capacity for n-hexane, cyclohexane, benzene, toluene, and *p*-xylene on flurous metal–organic frameworks FMOF-1 [$Ag_2[Ag_4(Tz)_6]$ and FMOF-2 [$Ag(Ag_3Tz_4)]_{3/2}$] (Tz = 3,5-bis(trifluoromethyl)-1,2,4-triazolate [122]. Adsorption of VOCs on FMOF-1 and FMOF-2 has been found to be unaffected in the presence of 100% relative humidity because of MOFs' highly hydrophobic perfluorinated inner surface.

3.2. Issues of MOFs for practical applications

Though MOFs have been used for industrial carbon capture [123], gas storage [124], and water treatment [125]. MOFs have potential be used for selective adsorption and separation of VOCs from a mixture of gases from indoor and industrial air. However, there have not been many studies involving multicomponent VOC separation using MOFs. A rare comparative study of multicomponent VOC separation using ZIF-8 and UiO-66 has been reported by Virdis *et al.* [119]. The study involved a mixture of 4–12 ppm of ethanol, ethyl acetate, 2-butanone and 2,3-butanedione in anhydrous condition at 25 and 6 °C using ZIF-8 and UiO-66. In this report, ZIF-8 adsorption capacities ranged between 0.3 and 1.8 mg g^{-1} while UiO-66 exhibited adsorption capacities between 1.8 and 51.9 mg g^{-1}. Both ZIF-8 and UiO-66 show a preferential adsorption towards hydrophobic VOCs. For ZIF-8, in the presence of humidity in the inlet flow, 2-butanone and diacetyl breakthrough begins relatively early, followed by ethanol and ethyl acetate. Whereas for UiO-66, a decline in the adsorption performance was observed due to presence of water in active sites on UiO-66.

In another study on removal of VOCs from the mixture of methyl ethyl ketone, methyl isobutyl ketone, butyl acetate, isobutyl alcohol, styrene, *m*-xylene, toluene, and benzene the following MOFs were used: HKUST-1, Co–(Co-CUK-1), Zr-(UiO-66) and UiO-66-NH_2 [121]. In this multicomponent VOC separation study, these MOFs adsorbed polar VOCs favorably, with the HKUST-1 outperforming the rest. For the Zr-(UiO-66) MOF, the presence of amine groups was seen to promote the adsorption of all eight VOC. Though this study involved multiple VOCs simultaneously, an additional study of VOC adsorption in presence of humidity would have been helpful.

Adsorption performance of HKUST-1 exposed to 0.5 to 2.5 ppm concentrations of toluene, acetone, o-xylene, ethanol & acetaldehyde has been studied and reported by Chevalier *et al.* [120]. Adsorption preference was found as *o*-xylene > acetone > toluene. VOC adsorption in the presence of humidity was also determined and found to degrade the capacity of up to 97%.

3.3. Commercial applications of MOFs and their scale-up

Since the early landmark work by Omar Yaghi in the 1990s, reports of new MOFs and their potential applications have continued to increase [126]. Since then, scientists like Gerard Ferey [127], Richard Robson [128], Abraham Clearfield [129], and Susumu Kitigawa [130] have contributed significantly to the development of MOFs. MOFs are examples of 'designer' materials that can achieve functions that are inaccessible to classical bulk adsorbents. As such, they are arguably presently most well-placed for integration into niche VOC applications, as well as many large-scale applications such as gas adsorption and storage, catalysis, drug delivery and chemical sensing [131].

The transition from benchtop quantities of a material (milligram or gram scales) to industrial/commercial sizes is critical to enable a novel technology to reach the wider market. Several companies are developing production methods to create kilogram scale amounts of MOFs for diverse commercial applications [108].

One of the biggest players in the field of industrial MOF is BASF [132]. In 2017, BASF held 2.5% of all the patents associated with MOFs. The company has produced over 100 types of MOFs on the lab scale with collaboration of Dr. Omar Yaghi. The company is selling small scale MOFs via Merck KGaA subsidiary of Sigma-Aldrich. In recent years, Svante and BASF have been working together to develop MOF for CO_2 capture and sequestration (CCS) on cement and hydrogen plants [133,134].

ExxonMobil is another big industrial contributor in the field of MOF [135,136]. They have developed a new type of MOF for selective CCS with 90% efficiency in collaboration with the University of California, Berkley. The company also partnered with Mosaic Materials to separate carbon dioxide from air or flue gas. The company is also working in collaboration with the Georgia Institute of Technology and Imperial College London to develop MOF based membranes for hydrocarbon fuel separation, which would help decreasing emission during fuel refining.

MOFworx is an Australian company working towards commercialization of MOF-based technologies. Their first industrially available MOF is Airthena, which can directly adsorb CO_2 from air [137].

SquairTech (France), founded in 2021, have developed two different MOFs for formaldehyde capture from indoor air and for NO and NO_2 degradation [138].

MOF Technologies (Belfast, United Kingdom) is a nanomaterial consulting company that specializes in assessing a company's needs and developing a tailored MOF-based solution [139,140]. To accomplish this, they use twin screw extrusion to produce up to 140,000 kg m^{-3} day^{-1} amounts of a given MOF and can tailor their reaction conditions to enhance the mechanical strength, packing efficiency, and/or bulk form factor; such properties are rarely considered on benchtop scales in R&D lab settings [141]. At present, MOF Technologies can supply up to 100 kg of 10 different MOFs as well as produce hundreds of grams of 15 other MOFs [140]. Indeed, MOF Technologies helped develop TruPick, a MOF-based solution to post-harvest preservation of produce to curtail food waste.

In the mechanism of fruit and vegetable ripening, ethylene is naturally produced which triggers ripening, thereby causing decay before the produce reaches the consumer. However, 1-methylcyclopropene can bind to the corresponding fruit receptors that ethylene normally would, retarding the whole process [142]. To this end, MOF Technologies developed TruPick along with the US Environmental Protection Agency to extend post-harvest freshness of produce by selectively adsorbing 1-methylcyclopropene into the pores of the MOF and slowly releasing it when in a sealed storage environment. MOFs typically require organic solvents that are anthropogenically harmful; MOF Technologies utilizes a solvent-free, mechano-chemical process to effectively scale production without compromising safety. TruPick is already employed in the United States and expected to expand to other countries in the future.

Swiss-based consultation company novoMOF AG (Zofingen, Switzerland) specializes in utilizing MOFs for addressing specific applications that a company is interested in solving. From the design to implementation and scale-up, novoMOF has focused its efforts on challenges such as toxic gas sensing and water harvesting from air [143]. Relevant for the capture of VOCs, novoMOF describes the use of a Eu-MOF where the material is inherently luminescent caused by the presence of Eu in the metal node, but it becomes quenched when ammonia is adsorbed, allowing for detection in the low ppm range with a threshold of 2.4 ppm – well below the OSHA detection safety limit value of 50 ppm. In addition, the regeneration time for this MOF sensor is only 10 min at room temperature and 5 min at 40 °C.

For traditional carbon-based energy sources to prevent growing climate change concerns, the capture and sequestration of carbon dioxide has become a tantamount focus in the 21st century. Normally, CO_2 scrubbing is performed by passing a flue gas stream through an aqueous amine solution then regenerating the solvent by heating and reversing the absorption. Not only is this process extremely energy intensive, but the CO_2-infused solution is acidic, leading to the risk of degradation of infrastructure which incurs higher capital and maintenance costs [144]. Mosaic Materials' (Berkeley, California, USA) approach to this issue utilizes a MOF called Mg_2(dobpdc) ($dobpdc^{4-}$ = 4,4′-dioxidobiphenyl-3,3′-dicarboxylate) for CO_2 sequestration; the MOF is further modified by attaching *N*, *N*′-dimethyl ethylenediamine to the exposed Mg^{2+} ions within the framework [144-146]. The presence of amines in the MOF pores causes synergistic adsorption of CO_2 by inducing the formation of a magnesium carbamate bond [144,145].

NuMat Technologies (Skokie, Illinois, USA) is another company that successfully produced large-scale economic MOFs through unit-level optimization and reagent recycling. Developed by Dr. Omar K. Farha, their signature ION-X gas storage cylinder uses a mixture of two MOFs to store highly toxic, but expensive gasses such as phosphine, arsine, and boron trifluoride at sub-atmospheric pressures, taking advantage of the inherent favorable interactions between the host–guest chemistry in MOFs [147]. Since these gasses are under reduced pressures, punctures or leaks in the gas cylinder would force air flow into the tank as opposed to the rapid discharge of those gasses when compressed, making it inherently safer. NuMat Technologies is currently able to produce hundreds of kilograms of their ION-X material [148].

Lantha Sensors Inc. (Austin, Texas, USA) uses MOFs as sensing devices by taking advantage of the luminescent properties of lanthanide ions [149]. MOFs constructed using Ln^{3+} ions as the nodes can be excited using UV light by the so-called antenna effect, whereby the organic components of the MOF act to harvest light, achieving indirect excitation of the Ln^{3+} ions by resonant energy transfer. Once excited, different Ln^{3+} ions emit visible light of specific wavelengths. At the same time, they are highly sensitive to changes in their local electronic environments, *i.e.*, due to which analytes are adsorbed inside the MOF pores. Unique to Lantha, their MOFs are composed of triphenylcarboxylate phosphine linkers instead of the commonly used polycarboxylate aromatics, drastically changing the electronic emission properties of the bulk material [150]. By varying the ratios of lanthanides used along with their phosphine linkers, Lantha can create disposable test strips that contain deposited MOFs, which detect the presence and concentration of D_2O in the presence of H_2O at the ppm level, which ordinarily requires nuclear magnetic resonance spectroscopy. Additionally, their test strips can determine the concentration of water in alcohols, which would need Karl Fischer titration along with other common laboratory solvents, compared to their handheld LanthaLux device [151].

Scientists from Canada have developed a highly water-stable MOF, Calgary Framework-20 CALF-20 [Zn_2(1,2,4-triazolate)$_2$(oxalate)] which has high selectivity and capacity for CO_2 over water with an estimated production speed of 550 kg m^{-3} day with an exceptional survivability in steam for > 450,000 cycles [152].

With the successful development and introduction of the above products into industry, metal–organic framework research is steadily progressing from academic concepts to tangible industrial implementations. However, the full potential of MOFs will not be reached until the production process becomes cost-competitive compared to other materials on the market. The potential of these novel materials inspired the establishment of numerous tech start-ups mentioned above which utilize cost-effective methods of VOC separation and VOC detection with MOFs. While there are several obstacles to overcome, MOFs are promising solid-state materials that can provide unique advantages over current zeolites and technologies.

3.4. Challenges with commercialization of MOFs

Despite the advantages of MOFs as a VOC adsorbent such as high surface area, good thermal stability, tunable porosity, functionality, there are several limitations and challenges associated with their structure, general development, and scale-up. Many MOFs preferentially interact with water molecules which inhibits the adsorption of VOCs into the pores. Unfortunately, this is due to the preferential coordination of the metal ions for water compared to the carboxylates *via* linker displacement reactions. The synthesis of hydrophobic MOFs with stable adsorption capacity in humid environment is crucial in expanding their industrial applications. Processes such as post-synthetic modification attempts to modify the organic linkers after the MOF is formed, while others, pre-modify the linkers before synthesis [153,154]. Another issue is the difficulty in generating isoreticular MOFs (*e.g.*, increasing the number of phenyl rings in a linker does not necessarily translate to a wider pore window – interpenetration may occur) or more generally designing shape-selective materials. While certain topologies can be predicted based on the metals and donor groups that are involved, shape-selective separations are largely challenging and less predictable in comparison to zeolites [155,156].

From an industrial perspective, Casaban *et al.* identified four major barriers to the expansion of MOFs to commercial markets: (1) commercial availability of MOFs, (2) customization of MOFs consistently without losing performance, (3) tailoring the framework's physical properties at a large scale, and (4) demonstrating MOF performance in real operating conditions [141]. The controlled environment required for the MOFs synthetic process has prevented further commercialization. The simplification of their production is required to move MOF production from specialized labs into large factories. Furthermore, the expensive equipment, organic reagents, and the reaction conditions (temperature and pressures) used for synthesis increase the cost of large-scale productions, so the amount of MOF produced in one batch does not compensate for the associated cost [157]. Thus, it is important to invent and implement continuous synthesis methods to lower production cost while increasing single-batch quantities. Moreover, toxicity and flammability associated with MOFs pose significant danger during synthesis and use; therefore, additional storage and safety precautions need to be implemented.

4. Conclusions

One of the most pressing environmental needs today is developing sustainable and cost-efficient gas sorption methods to improve quality of life and further abate climate change. Accordingly, volatile organic compounds have, and continue, to pose a threat as industrialization increases globally and the consequential emissions that arise from them. Metal-organic frameworks have emerged as promising adsorbents for VOCs due to their high surface areas, tuneability, and broad functionality that zeolites and activated carbons are unable to provide. The large surface area and porosity of MOFs provide abundant adsorption sites for target VOCs, and their physical and chemical characteristics such as pore size, hydrophobicity, functionality, and thermal stability can be uniquely tailored to capture specific adsorbates.

In this review, a variety of metal–organic frameworks for VOC sequestration and recent advancements of MOFs in the field were presented. Selective sequestration of aliphatic, aromatic, oxygenated, and sulfurous VOCs relies on taking advantage of metal–organic frameworks' large surface for adsorbing the most molecules as possible and the chemical moieties present in the pores or secondary building units. Saturated aliphatics like pentane or heptane can be effectively separated or encapsulated by size-sieving MOFs. If double or triple bonds are present in aliphatics (e.g., acetylene), polar functional groups coordinate effectively with them. Aromatic VOCs can be targeted with MOFs that size-selectively discriminate BTEX molecules; additionally, their adsorption is favored by wide windows with many aromatic groups in the pores for maximizing π-π interactions. Adsorption of oxygenated and sulfur-containing VOCs favor polar functional groups to create hydrogen bonding networks or coordinately unsaturated metal sites in the framework's secondary building units *i.e.*, oxygenated molecules would prefer MOFs that utilize hard metal acids while organosulfur molecules would interact more with softer metals. Therefore, MOF structures must be thoughtfully engineered to function as effective VOC sequestration material for a particular application, and this requires careful selection of the inorganic (node) and organic (linker) functional groups employed in their construction.

Most work involving metal–organic frameworks for volatile organic compounds capture report adsorption studies of pure component vapor streams that are at moderate to high concentrations. However, selectivity and adsorption capacity may be compromised when multiple VOCs are present in the gas stream. A key issue is MOFs' weakness in humid environments is due to decomposition from water displacing the organic linker and/or occupation of adsorbent sites. Fortunately, they can be tailored by pre-synthetic linker modification, post-synthetic modification, and hydrophobic coatings to be more resistant; examples of respective alteration would be changing the donor groups, reactively adding alkyl groups post-synthetically, or applying a polymeric hydrophobic coating. However, more work is required to demonstrate and validate MOFs for selective adsorption in real environments where multiple VOCs and humidity are present. Scaling up manufacturing and developing cost-effective processes remains a challenge.

Data availability

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

Declaration of Competing Interest

Simon M. Humphrey reports a relationship with Lantha Sensors Inc. that includes: equity or stocks.

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