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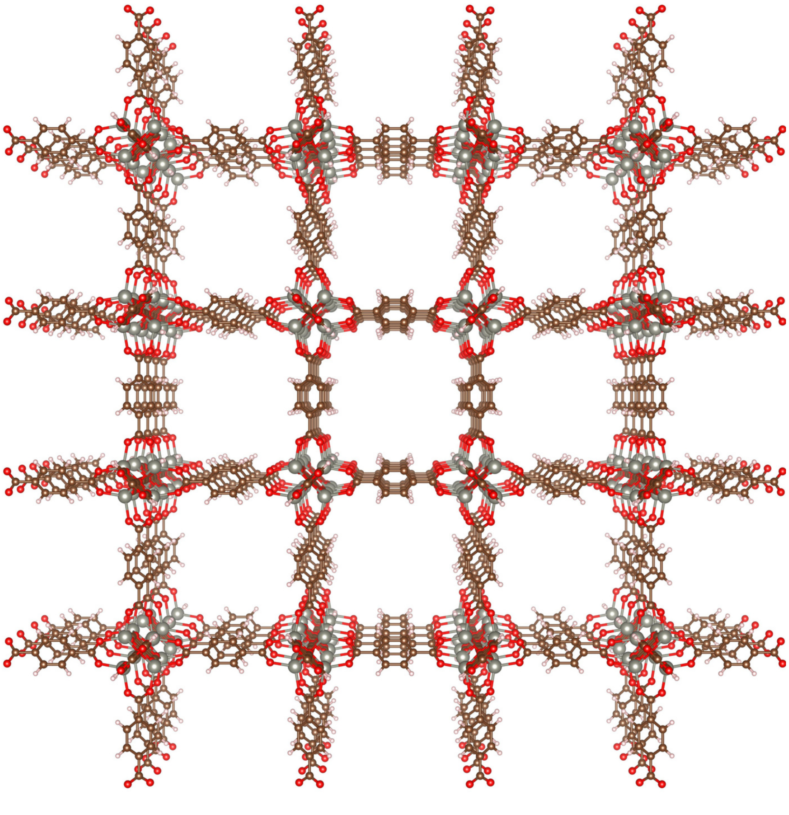

Department of Physics, Prithvi Narayan Campus, Pokhara
Nepal Physical Society, Gandaki Chapter, Pokhara

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Chief Editor

Aabiskar Bhusal

Cover: Ball-and-stick model of MOF-5. © Roshani Sharma. Printed with permission.

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Himalayan Physics

Adsorption of toxic gases by metal-organic frameworks

Review Article

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Abstract: Along with global economic development and population growth, the discharge of highly toxic and corrosive anthropogenic byproducts into the atmosphere or aquatic habitats creates a serious threat to human health. In order to remove such byproducts, more attention should be paid to innovative materials with high uptake capacity and performance. Metal-organic frameworks (MOFs) are crystalline, porous, hybrid materials that are made up of organic ligands as linkers and metal cluster-based nodes. Because of their beneficial features such as their large surface area, tailorable pore sizes, structural diversity, catalytic activity, and wide range of chemical and physical properties, MOFs offer significant potential as adsorbents. As a result, these materials have drawn a significant amount of attention for the capture and/or detoxification of hazardous and toxic chemicals. This review will focus on recent advancements on MOF based experimental and computational studies related to the capture of toxic gases including hydrogen sulfide (H_2S), ammonia (NH_3) sulfur dioxide (SO_2) carbon monoxide (CO), and nitrogen oxides (NO_x).

Keywords: Adsorbent • Adsorption • Hazardous • MOF • Toxic chemical

I. Introduction

Globally, there is an attraction to air pollution, which is harmful to individuals. The main pollutants include NO_x, SO_x, CO, H_2S, NH_3, other nitrogen or sulfur-containing compounds, hydrocarbons, and volatile organic compounds [1]. It leads to various serious problems like global climate change, ozone depletion, acid rain, and crop and forest damage. These pollutants are mainly caused by human activity including combustion, chemical reaction, leaks of harmful industrial gases and vapors as well as the deliberate emission of chemical warfare agents. So the sources of these gases are anthropogenic. For instance, the primary cause of emissions of SO_2, NO_2, and CO is the burning of fossil fuels to meet the current energy demand. Photochemical smog and acid rain, which pose a serious risk to the environment and human health, are produced by SO_x and NO_x. Another toxic, caustic, and odorous gas is H_2S. Both biogas and natural gas naturally contain it. In the pharmaceutical and chemical

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industries, NH_3 is another pollutant that is frequently used for a variety of purposes, such as a fertilizer, cleanser, fermentation agent, antibacterial agent, refrigerant, a precursor to most of N-containing chemicals, etc.

Metal-organic frameworks (MOFs) have attracted a lot of attention in recent years due to their potential application in separation, gas storage, chemical sensing, water harvesting, drug delivery, catalysis, and other applications [2]. Because of their high porosity, large surface area, and structural tunability, these materials are appealing for these applications. MOFs are made up of organic linkers that connect inorganic metal (or metal oxide) nodes and form a repeating cage-like structure. To adjust the MOF's characteristics, the organic linkers can be changed with functional groups. Some MOFs additionally contain open metal sites which can act as catalytic or chemisorption sites. The open metal sites allow for the thoughtful selection of metals for particular purposes. There are an infinite number of possible combinations of nodes, linkers, and functional groups that may be coupled in various topologies to produce an almost infinite number of distinct MOFs. As a result, there is an enormous opportunity for designing MOFs for specialized purposes. Through the efforts of several research teams over the last three decades, several thousand distinct MOFs have already been synthesized and described. But this number only represents a small portion of the potential structures that need to be discovered. Therefore, the design and discovery of new materials via computational means are now possible for MOFs.

Table 1. Physical properties and toxicity data for selected gases [3–5].*IDLH stands for "Immediately Dangerous to Life and Health" and is the concentration at which a toxic substance is likely to cause death or permanent adverse health effect*

Gas	Kinetic diameter (pm)	Normal boiling point(K)	Dipole moment (D)	IDLH (ppm)
NH_3	290	239.82	1.4718	300
H_2S	362.3	212.84	0.97	100
CO_2	330	216.55	0	40000
SO_2	411.2	263	1.62	100
NO_2	401-512	302.22	0.316	20
NO	349.2	121.38	0.15872	100
CO	369	81.66	0.1098	1200
H_2O	264.1	373.13	1.8546	-

The periodic density functional theory (DFT), which has been used for years to analyze a variety of systems from silicon to metal oxides to graphene, is well suited for studying MOFs because of their crystalline structure. The accurate calculation of interaction energies, electronic structures, and reaction processes in MOFs is made possible by the use of DFT. Ab initio calculations need a lot of computing power, so applying less expensive methods like Monte Carlo simulations with conventional force fields is frequently more beneficial. Scientific progress in the field of MOFs could be greatly accelerated by the use of computational tools, which are developing into a potent strategy for facilitating the development of valuable novel materials.

The ability of MOFs to catch harmful substances has attracted a lot of interest. Due to their large specific surface areas and varied functionalities, many MOFs make effective adsorbents and can be adjusted to increase or decrease their binding affinity for various adsorbates. Toxic gases including industrial chemicals (TICs) have been captured using MOFs. These substances are frequently used as reagents in industrial processes. So chemical workers are at risk of exposure to spills and personal protective equipment is crucial for maintaining worker safety. Many of these deadly substances are easily accessible in large amounts and could perhaps be used as homemade chemical weapons in a terrorist strike. An activated carbon broad-spectrum filter is currently the most effective method of eliminating these compounds but it has low selectivity and limited capacity to adsorb polar molecules like H_2S or NH_3. A significant study has been concentrated on identifying MOFs with high adsorption capacity for a variety of TICs, and several MOFs have been proven over activated carbon in ground-breaking tests. Also, in-depth research has been done on MOFs as adsorbents for the removal of SO_2, NO_x, CO, and CO_2 from flue gas. It is well known that these chemicals have harmful impacts on the environment, such as smog, acid rain, and anthropogenic climate change. Although materials like MOF-74 that have open metal sites can bind these target molecules strongly, they also suffer from the competing adsorption of water. Stable MOFs that specifically bind SO_2 or NO_x in humid environments have been the focus of many studies in recent years. In this paper, we review recent experimental and computational work on the utilization of MOFs for toxic chemicals/gases detoxification applications. Toxic gases have a variety of physical and chemical characteristics, some of which are given in Table 1. It is difficult to develop high-performance materials for gas collection or separation that can accommodate these features.

Table 2. Dynamic adsorption capacities of the benchmark MOFs for gaseous contaminants measured in grams of gas per gram of adsorbent [6]
[a] *Expresses the ratio of dynamic adsorption capacity of the best-performing MOF [b] to that of BPL carbon.*
[b] *Best-performing MOFs.*
[c] *Experiments were not performed because of the corrosion of the apparatus by chlorine.*

Gas	MOF-5	IRMOF-3	MOF-74	MOF-177	MOF-199	IROMF-62	BPL carbon	Impprovement factor[a]
Sulfur dioxide	0.001	0.006	0.194[b]	$<$ 0.001	0.032	$<$ 0.001	0.033	5.88
Ammonia	0.006	0.105[b]	0.093	0.042	0.087	0.023	0.001	105
Chlorine	c	0.0335[b]	c	$<$ 0.001	0.036	0.092	0.190	1.76
Tetrahydrothiophene	0.001	0.007	0.090	$<$ 0.001	0.351[b]	0.084	0.123	2.85
Benzene	0.002	0.056	0.096	0.001	0.176[b]	0.109	0.155	1.14
Dichloromethane	$<$ 0.001	0.001	0.032	$<$ 0.001	0.055[b]	0.019	0.053	1.04
Ethylene oxide	0.001	0.002	0.110	$<$ 0.001	0.095[b]	0.011	0.010	9.50

Britt et al. carried out some of the first research on TIC adsorption in MOFs, carrying out column breakthrough tests for a variety of toxic gases, including NH_3, SO_2, CO, and benzene, in a variety of MOFs (MOF-5, IRMOF-3, MOF-74, MOF-177, IRMOF-62, and HKUST-1), as well as activated carbon [6]. They found that these MOFs' adsorption performance is significantly influenced by their pore functionality and that reactive MOFs can perform better than activated carbon in terms of adsorption capacity.They found that these MOFs' adsorption performance is significantly influenced by their pore functionality and that reactive MOFs can perform better than activated carbon in terms of adsorption capacity. As a result, it was proposed that functional groups or open metal sites may be used to design MOFs for particular adsorbates. The results of their work are summarized in Table 2.

II. Capture of Hydrogen Sulfide (H_2S)

The toxic material H_2S is a reagent used in numerous industrial processes like oil and gas industries. It is a significant component of flue gas, natural gas, and bio-gas and is also frequently present in groundwater sources. Due to its high toxicity (Table 1) and corrosiveness, numerous investigations were conducted in an effort to eliminate it from these sources. Here, we concentrate on desulfurization in regard to eliminating toxic materials from the atmosphere. With MOFs, binding/active site position at the spatially separated nodes or linkers can be precisely tuned for H_2S abatement. A functional group that would specifically encourage interaction with the target molecule can be added to or incorporated into MOFs due to their high degree of modularity. Due to the MOFs' crystallinity, computational approaches can be used to optimize these materials rather of spending countless hours on the bench. There have been numerous reports and reviews of materials for detecting H_2S, both in the atmosphere and in physiological situations [7]. This review will concentrate on adsorbents even though multiple studies show that MOFs can catalyze the conversion of H_2S to sulfate or elemental sulfur, respectively [8, 9] and these kinds of materials have been used in industrial applications.

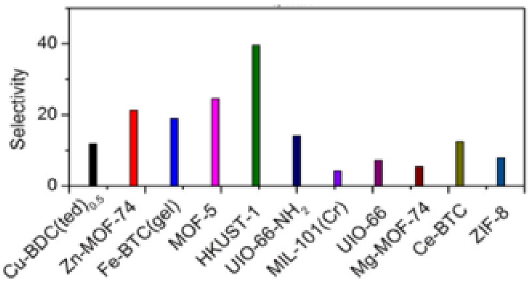

Figure 1. H_2S/CO_2 selectivities of the MOFs [10]

Hamon et al. were used MIL-47(V), MIL-53(Al,Cr,Fe), MIL-100, and MIL-101) MOFs to demonstrate H_2S collection at 303 K. (up to 20 bar) [11]. They demonstrated the complete reversibility of the H_2S adsorption isotherms in the microporous MOFs MIL-53(Al, Cr) and MIL-47(V). It was discovered that MIL-53(Cr) had a loading capacity of up to 13 mmolg^{-1} at 16 bar. MIL-53(Cr) showed a structural change as a result of H_2S adsorption, but MIL-47(V) remained its rigidity. H_2S adsorption was measured to be partially irreversible in MOFs having mesoporous architectures (MIL-100 and MIL-101). Strong interactions between the framework and H_2S molecules are to responsible for this behavior, which results in partial framework collapse. A huge amount of H_2S adsorption (about 38 mmol g^{-1} at 20 bar) was seen in MIL-101 due to the high pore volume of the material.

DFT was used by Chen et al. [12] to investigate the binding strength of numerous sulfur compounds, including H_2S, for a variety of ligands and metal nodes. It was found that there was weak interaction between H_2S and organic ligands having binding energies less than 50 kJ mol^{-1} that suggested a physisorption process. However, ligands functionalized with -NH_2 had a strong interaction for H_2S. It indicates that there is acid-base interaction between adsorbate and the functional group. Fe adsorbs stronger than Zn or Cu, while H_2S molecules were shown to bind strongly to the open metal sites in MOF-74 and HKUST-1.

According to Xu et al. [13], adding halogen groups to MIL-47(V) can make the pore more polar, which strengthens the interaction between polar H_2S and the framework and improves the selectivity for H_2S over non-polar gases like methane and nitrogen. GCMC simulations was performed for a range of temperatures, pressures, and H_2S/N_2 (and CH_4) compositions. MIL-47(Br) exhibits much higher H_2S selectivity than unfunctionalized MIL-47(V) for the complete range of mixture compositions at 1 bar and 273 K.

In experimental studies [14, 15], it has been proposed that the mechanism of HKUST-1 degradation upon H_2S adsorption is influenced by the fact that H_2S binds to the copper sites preferentially over H_2O. But according to various classical and ab initio calculations, H_2O binds to Cu more strongly than H_2S. To resolve this disagreement, Gutie'rrez-Sevillano et al. built three new sets of interatomic potentials to explain H_2S binding from experimental data [16]. The GCMC simulations, even with these new potentials, still show the same result. In order to confirm the findings of the classical simulation, they also carried out DFT calculations and reported binding energies of 43.3 kJ mol^{-1} for H_2S and 46.7 kJ mol^{-1} for H_2O on HKUST-1. As a result, earlier computational research is confirmed by the results of this work and still contradicts the most recent interpretation of experimental data. The literature still doesn't have a solution for this issue, thus more research is definitely necessary.

Eddaoudi and colleagues focused on a variety of fluorinated MOFs (NbOFFIVE1-Ni, AlFFIVE-1-Ni, SIFSIX-2-Ni-I, and SIFSIX-3-Ni) with different pore volumes [17]. Although (SIFSIX-2Ni-I) showed a high CO_2 affinity, H_2S condensed in the pores, resulting in a material with a high H_2S/CO_2selectivity ratio. SIFSIX-3-Ni was used to improve charge density. The H_2S/CO_2 selectivity ratio was significantly reduced as a result of the reduced pore volume, which allowed for increased CO_2 interaction with the framework. The selectivity was quite similar to the selectivity of NbOFFIVE-1-Ni that had been previously reported. The isostructural Al-analog of NbOFFIVE-1-Ni is used to improve H_2S affinity. AlFFIVE-1-Ni was used in this case. This MOF provides distinct sites for adsorptive interaction between H_2S and open Al metal sites and CO_2 and fluorine moieties. AlFFIVE-1-Ni was stable and recyclable in the presence of CH_4 and was able to achieve the required selectivity ratio of 1:1 for H_2S: CO_2 over a wide range of temperatures and gas concentrations.

Due to competing adsorption at Lewis basic sites, it can be challenging to selectively remove H_2S from CO_2 in natural gas streams. Using DFT calculations, molecular dynamics simulations, and ground-breaking tests, Zou and coworkers [10] assessed 11 common MOF-based materials to determine the characteristics that lead to high/reversible H_2S adsorption. After the first cycle, all MOFs lost the majority of their capacity with the exception of Mg-MOF-74, MIL-101(Cr), UiO-66, and UiO-66-NH_2. Despite having high surface areas and open metal sites, these MOFs have poor H_2S/CO_2 selectivity (Fig. 1). Despite not corroding and having reversible sorption, Ce-BTC and ZIF-8 only have a little amount of absorption because they lack open active sites. It has been shown that Cu or Zn-containing MOFs, such as Cu-BDC$(ted)_{0.5}$, Zn-MOF-74, Cu-BTC, and MOF-5, can bind H_2S quickly and irreversibly, creating metal sulfides and causing structural damage as a result. Although these MOFs have a high H_2S uptake and selectivity, they cannot be recycled, which limits their potential applications. The Fe(III) centers in MIL-100(Fe) gel (also described at Fe-BTC) were converted to Fe(II) in the presence of H_2S, which also caused H_2S to be oxidized to S_8. In this study, the oxidative capability of the MOF gel was not fully studied, but it is promising for the catalytic abatement of H_2S.

Walton and colleagues [18] discovered that ligand functionalization is a potential method to improve adsorption without sacrificing stability in order to prevent MOF degradation through the binding of H_2S on open metal sites. The effect of amine-functionalized linkers on H_2S extraction from natural gas simulant mixtures was studied using three MOFs, UiO-66(Zr), MIL-125(Ti), and MIL-101(Cr), each with different pore size. Comparable breakthrough times and adsorption capacities were observed for MIL-101 and MIL-101NH_2 as the pore size expanded from MIL-125 to UiO-66 to MIL-101, indicating that the effect of amine functionalization decreased with increasing pore size. This effect might be brought on by the confinement effect produced by MIL-125's smaller pores or by the topology-driven orientation of the amines along the pore walls.

III. Capture of Amonia (NH_3)

Ammonia is one of the most significant industrial gases, with a global production of roughly 176 million tons per year [19]. This is owing to its application in a variety of fields, including cleaners, fertilizer, refrigerants, and as a chemical intermediate. The public should be concerned about pollution due to its high toxicity, which has an IDLH value of 300 ppm in the air (Table 1). Ammonia contamination often comes from two main sources: farming such as fertilizers, as well as urine and dung produced by livestock and industrial ammonia spills. When ammonia enters the atmosphere, it reacts with NO_x or SO_x, which are both in the atmosphere as a result of emissions from fossil fuels. As a result particulate matter less than 2.5 m wide ($PM_{2.5}$), which has the potential to have a harmful impact on the environment, can be created. The most efficient strategy to lower the concentration of $PM_{2.5}$ in the atmosphere is regarded to be reducing ammonia emissions [20]. Effective methods of capturing ammonia are required to protect industrial and emergency workers who could be in danger of exposure in the case of an unintentional spill because of its high toxicity and strong irritant to the eyes and respiratory system. Activated carbon is the most popular porous material utilized for this application, however, its ammonia capacity is quite low and it is better suited to absorbing organic molecules than highly polar gases, like ammonia . Therefore, it is urgently necessary to create high-capacity, selective, efficient, and cost-effective sorbents in order to advance the ammonia adsorption technology now in use.

In a ground-breaking study, Yaghi and colleagues investigated ammonia capture by a variety of MOFs using kinetic breakthrough measurements [6]. They found that MOFs containing functional groups such as IRMOF-3, an amino-functionalized version of MOF-5 or open metal sites, such as MOF-199 or MOF-74, have significantly better dynamic adsorption capabilities than unfunctionalized MOFs like MOF-5 or MOF-177. This is true even though the unfunctionalized MOFs have far higher porosities and surface areas. In the years that followed, scientists looked into both approach functionalized linkers and the utilization of open metal sites to capture ammonia in MOFs.

In four MOFs (MIL-47, IRMOF-1, IRMOF-10, and IRMOF-16) functionalized with -OH, -C=O, -Cl, and -COOH groups, Yu and colleagues used a hierarchical modeling technique to predict NH_3 capacity [21]. They fitted force fields to be used in grand canonical MonteCarlo (GCMC) calculations using single-point energies computed at the MP2 level of theory. They discovered that functionalized MOFs have greater NH_3 absorption at low pressure, but that at high pressure, the overall capacity may be decreased because of a reduction in pore volume brought on by large functional groups.

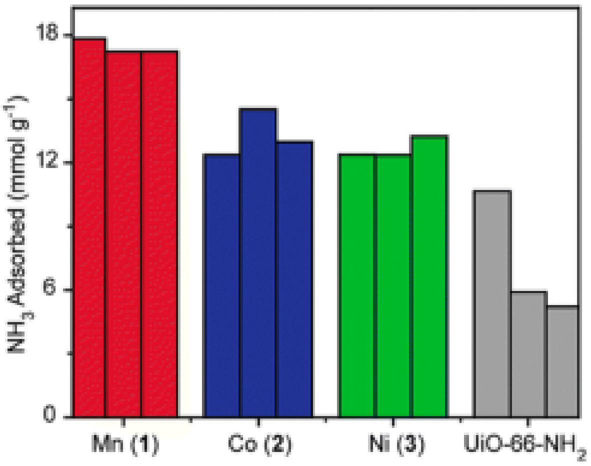

Figure 2. NH_3 adsorption uptake at 1 bar, 293 K for activated MOFs of $Mn_2Cl_2BTDD(H_2O)_2$ (1; red), $Co_2Cl_2BTDD(H_2O)_2$ (2; blue), and $Ni_2Cl_2BTDD(H_2O)_2$(3; green), and UiO-66-NH_2 (gray) for three cycles [22].

HKUST-1 and MOF-74 are two examples of MOFs with OMSs that have been shown through experimental studies to have the ability to act as Lewis acids and interact strongly with Lewis bases, such as ammonia, resulting in extremely high ammonia absorption[23, 24]. The fact that NH_3 gas molecules do not desorb in the presence of an inert gas shows that this strong connection is chemisorptive. Additionally, it has been demonstrated that MOF-74 has a better capacity than activated carbon for the efficient binding of phosphine [25].

Huang et al. used molecular dynamics (MD) simulations using a ReaxFF force field to examine the ammonia and water adsorption on HKUST-1 (also known as CuBTC or MOF-199), which has unsaturated Cu^{2+} sites in the nodes [26]. They discovered that HKUST-1 is hydrostatically stable at concentrations up to 4.0 water molecules per Cu site and up to 550 K using the ReaxFF method. Dehydrated HKUST-1 collapses, even at low water concentrations, at temperatures higher than 550 K. Additionally, they discovered that HKUST-1 breaks down when there is more than 1.0 NH_3 molecule per Cu site in the ammonia solution. At 348 K, $Cu_2(NH_2)_4$ and $(NH_4)_3$BTC structures start to develop because the NH_3 molecules prefer to bind to the unsaturated Cu sites over forming dimers with other NH_3 molecules.

Zhang et al. discovered that water can exchange for ammonia that is attached to the metal sites in Mn-MOF-74 by the analysis of competitive adsorption of water and ammonia using DFT . The H_2O-NH_3 exchange process has an energy barrier of 28 kJ mol^{-1} and is endothermic (107 kJ mol^{-1}), but it might still take place if the system provides enough energy to cross the barrier. When the NH_3 is initially linked to the Mn, the water molecule is stabilized by a hydrogen bond with the H on the NH_3 molecule.[27]

Tan et al. used a DFT analysis to identify the function of hydrogen bonds in the competitive adsorption of CO_2 with NH_3, H_2O, and SO_2 in M-MOF-74 (M = Mg, Co, and Ni) [28]. They discovered that while SO_2 and NO_2 have stronger binding affinities with the metal sites (about 70–90 kJ mol^{-1}) than water does (about 60-80 kJ mol^{-1}), CO_2 can be replaced by H_2O and NH_3 more readily than NO_x and SO_x molecules do because H_2O and NH_3 are stabilized by a hydrogen bond with an O atom on the framework node. This demonstrates how crucial it is to take electrostatic effects into account in systems where hydrogen bonding may be common, as well as interactions between the adsorbates and the nearby framework atoms outside of the precise adsorption sites.

Since ammonia capture faces a difficult problem with competitive binding with water, several researchers have proposed that hydrophobic MOFs might bind ammonia while displaying a minimal affinity for water. Three hydrophobic MOFs, ZIF-8, Zn4O(3,5-dimethyl-4-carboxy-pyrazolato) Zn(pyrazole), and Al(NDC), was used in GCMC simulations by Ghosh et al. to determine the isotherms for water and ammonia [29]. The TIP4P/2005 model was used for water, and the simulated single-component water isotherms agreed well with experimental isotherms. The authors demonstrated that even in the presence of water, the ammonia capacity of these hydrophobic MOFs is not significantly reduced. But ZIF-8 only has a small capacity (2 mmol g^{-1}) in comparison to the other two, which have capacities of 6-7 mmol g^{-1} (at 1 bar partial pressure of NH_3). At low partial pressures of NH_3, Zn(pyrazole) and Al(NDC) are able to significantly adsorb water; however, when the partial pressure rises to close to 1 bar, the water absorption decreases and ammonia is instead preferentially absorbed.

In order to find hydrophobic MOFs based on Henry's constant for water, Moghadam et al.[30] evaluated a database of 137953 hypothetical MOFs. Using GCMC simulations to detect water, ammonia, and methane absorption, 45975 MOFs were identified as hydrophobic, and 2777 MOFs were chosen for a more thorough investigation. They discovered that the most effective NH_3 selectivity is found in hydrophobic materials with pore sizes close to the NH_3 kinetic diameter. Pore diameters in the top 97 structures range from 5 - 7.5 A^o and have void fractions of 0.6 – 0.7. Furthermore, MOFs with halogen functional groups have the lowest ammonia selectivity, whereas MOFs with alkyl functional groups have the best selectivity because of the increased hydrophobicity from the alkane and the smaller pore size.

Dinca and coworkers conducted ammonia sorption investigations on a variety of isostructural, mesoporous triazolate-based MOFs, $M_2Cl_2(BTDD)(H_2O)_2$ (M = Mn, Co, and Ni) and revealing that activated samples of $Mn_2Cl_2(BTDD)(H_2O)$, $Co_2Cl_2(BTDD)(H_2O)$, and $Ni_2Cl_2(BTDD)(H_2O)_2$ adsorb 15.47, 12.00, and 12.02 mmol g^{-1} at 1 bar and 298 K, respectively(Fig. 2 and Table 3) [22]. It should be noted that under comparable conditions, these ammonia uptake values are higher than the corresponding value for UiO-66-NH_2. Interestingly, despite these MOF materials having open metal sites, ammonia uptake is reversible after a few of cycles. Additionally, because to the higher density of open metal sites in the $M_2Cl_2(BTDD)$ family of MOFs [31], the smaller pore variants (e.g., $M_2Cl_2(BBTA)$; M = Mn, Co, and Ni) have higher capacities for NH_3, especially at low pressures. Last but not least, dynamic breakthrough measurements of NH_3 show that $Co_2Cl_2(BBTA)$ performs better than its bigger pore equivalent, Co_2Cl_2 (BTDD).

Table 3. Overview of the NH_3 adsorption capability of different MOFs

MOFs	Uptake(mmol g^{-1})	Temp (K)	Ref
Mn_2Cl_2BTDD	15.47	298	[22]
Co_2Cl_2BTDD	12	298	
Ni_2Cl_2BTDD	12.02	298	
Cu_2Cl_2BTDD	16.74	298	[31]
Co_2Cl_2BBTA	17.95	298	
Ni_2Cl_2BBTA	14.68	298	
Cu_2Cl_2BBTA	19.79	298	
MFM-300(Al)	13.9(15.7)	293 (273)	[32]
Prussian blue	12.5	298	[33]
CoHCC	21.9	298	
CuHCF	20.2	298	
POP-PO_3H_2	18.7	298	[34]
POP-CO_2H	16.1	298	
UiO-66-NH_2	9.84	298	[22]
HKUST-1	12.1	298	[35]
DUT-6	12	298	[36]
DUT-6$(OH)_2$	16.4	298	
Fe-MIL-101-SO_3H	17.8	298	[37]
Al-PMOF	7.67	298	[38]
Ga-PMOF	10.50	298	
In-PMOF	9.41	298	
NU-300	8.28	298	[39]

A viable platform for ammonia capture is provided by MOF materials with Bronsted acidic binding sites in addition to the good ammonia capture capability of MOFs with open metal sites. Through kinetic microbreakthrough experiments, Rosseinsky and colleagues reported the acidloaded $Al_2(OH)_2(H_2TCPP)$ (Al-PMOF), which contains infinite rod SBUs, for ammonia capture. They discovered that both the HCl- and formic acid-loaded versions of Al-PMOF exhibit superior ammonia capture performance to the parent Al-PMOF [40]. With the uptake of 15.7 mmol g^{-1} at 1 bar and 273 K, MFM-300(Al), made of 3,3',5,5'-biphenyl-tetracarboxylate, and infinite Al rod SBUs, exhibits reversible ammonia adsorption performance [32]. Also according to Moribe and his coworkers, isoreticular MOFs Al-PMOF, Ga-PMOF, and In-PMOF that have Bronsted acidic sites exhibited better performance for ammonia capture [38]

Kitagawa et al. systematically investigated the stability of MOFs in the presence of ammonia, showing that MOFs made from oxophilic metal cations, such as Al^{3+}, Ti^{4+}, and Zr^{4+}, are more stable in the presence of NH_3 gas than MOFs made from labile cations, such as Cu^{2+} and In^{3+} [41]. Also, it was discovered that MOFs made of neutral nitrogen donors are less stable in the presence of ammonia than MOFs made of anionic nitrogen donors, such as ZIF-8. The results of ammonia sorption tests showed that MOFs with open metal sites, such as MOF-74(Mg), are strongly adsorptive, whereas MOFs with Bronsted acidic sites, such as MIL-53(Al), are moderately adsorptive, and MOFs without functional groups, such as ZIF-8, are not.

IV. Capture of Carbon Monoxide(CO)

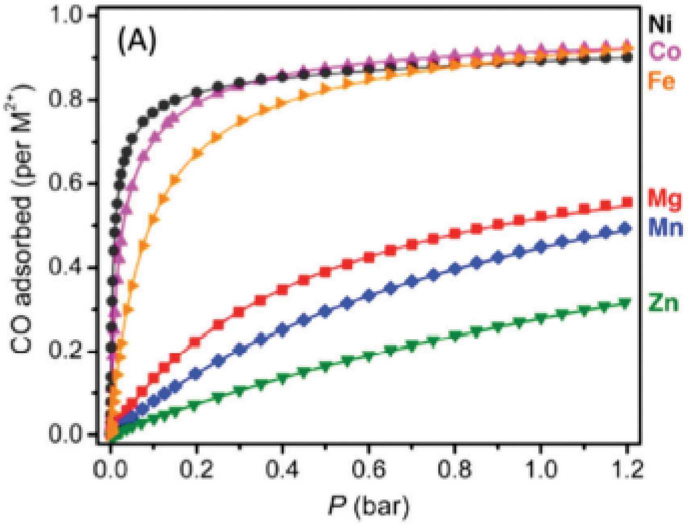

Figure 3. Carbon monoxide isotherms for M-MOF-74/M-CPO-27 analogues measured at 298 K [42]

Carbon monoxide, also known as the "silent killer", is a colorless, odorless gas that can be lethal if inhaled accidentally because it coordinates with hemoglobin roughly 200 times stronger than oxygen does, thus depriving cells of oxygen [43]. Exposures to CO more than 70 ppm cause noticeable symptoms. Inhaling concentrations of 150-200 ppm often results in dizziness or unconsciousness and can occasionally result in death [44]. According to the Centers for Disease Control and Prevention, more than 400 American lose their lives from carbon monoxide poisoning each year. Contrarily, it is an important chemical feedstock for the production of various chemical products, including oxo-alcohols, aldehydes, esters, and organic acids [45]. Pure CO is also used as a reference material for semiconductors, electronics, and calibration service systems. So, for the scientific community, it is essential that CO be detected and stored in a secure manner. Conventional porous materials like activated carbon and zeolites are used most frequently in catalytic oxidation or separation of CO. However, the focus of this study will be on MOF-based CO capture and purification applications.

One interesting type of CO adsorbent has been suggested: MOFs with open metal sites, commonly known as undercoordinated metal sites [46, 47]. The CO molecule binds to the exposed metals in these materials by the chemisorption process, even at modest loadings. MOF-74, which is also known as CPO-27, is made of divalent metal cations (Mg^{2+}, Ni^{2+}, Zn^{2+}, Fe^{2+}, Co^{2+}, Cu^{2+}, and Mn^{2+},) and 2,5-dioxido-1,4-benzenedicarboxylate (dobdc) linkers. It crystallizes as a collection of one-dimensional hexagonal channels [42]. Among its M-MOF-74 analog series, Ni-MOF-74 has the highest interactions with CO (Fig. 3) and the smallest M-C distance (2.148 Å). The total CO uptakes in the Fe, Co, and Ni counterparts were 6.04, 5.95, and 5.79 mmol g^{-1}, respectively (at 298 K and 1.2 bar) which is beyond the benchmark zeolite material. Additionally, Ni-MOF-74 has been reported to have binding energies greater than 50 kJ mol^{-1}.

Dynamic column breakthrough experiments and density functional theory (DFT) calculations revealed that Co and Ni MOFs had much higher binding affinities for CO than for CO_2, while Mg-MOF had a higher affinity for CO_2 than for CO due to a lack of overlapping orbitals or valence electrons. The strong interactions between the low-spin state Fe(II) and CO are to responsible for this high capacity [48]. FeBTTri (H3BTTri = 1,3,5-tris(1H-1,2,3-triazol-5-yl) benzene) was another promising MOF for CO adsorption that was reported by Long and colleagues where CO interacts with coordinatively unsaturated Fe^{2+} to produce a spin state transition mechanism. Significant CO uptake is feasible at very low pressures (1.49 mmol g^{-1} at 0.1 bar and 2.7 mmol g^{-1} at 0.27 bar at 298 K) because of the framework's strong affinity for CO gas (about 65 kJ mol^{-1}). Using the pressure-temperature swing adsorption (PTSA) technique between 373 and 423 K under vacuum, this MOF was successfully recycled ten times with little to no capacity loss. Also, they examined the adsorption of CO in the MOFs Fe_2Cl_2(bbta) and Fe_2Cl_2(btdd) whose uptakes were 5.75 mmol g^{-1} and 3.40 mmol g^{-1} at 298 K [49].

Because of the huge number of open metal sites in the structure, HKUST-1, $Cu_2(btc)_2$, is a well-researched MOF for tiny gas separation applications [50]. However, compared to MOF-74, Cu(II) open metal sites in HKUST-1 exhibited substantially weaker interactions with CO [46]. A Cu^{2+} based MOF (PCP-2) with a sharp absorption in the CO isotherm was described by Kitagawa et al. in their paper. This MOF changes structurally when the CO partial pressure rises above 0.05 bar at 120 K [51].

Adsorption sites can be added through postmetalation of the framework in addition to using the open metal sites already present on a MOF's nodes for the selective adsorption of CO molecules. For instance, Cu^{1+} sites have been added via postmetalation to MIL-100Fe and MIL-101Cr [52] After metalation, the MOF's ability to absorb CO dramatically improved. 90% of the initial CO intake of the Cu-impregnated MIL-101-Cr was retained even after exposure to air for a month during its regeneration at room temperature under vacuum conditions [53].

Table 4. Overview of the CO adsorption capability of different MOFs

MOFs	Uptake(mmol g^{-1})	Temp (K)	Ref
MOF-74-Fe	6.04	298	[42]
MOF-74-Co	5.95	298	
MOF-74-Ni	5.79	298	
MOF-74-Mg	4.58	298	
MOF-74-Mn	3.24	298	
MOF-74-Zn	1.95	298	
HKUST-1	1.20	298	[46]
MIL-101-Cr	1.03	298	[53]
$CuAlCl_4$ doped MIL-101-Cr	2.26	298	
MIL-100-Fe	0.38	298	[52]
Cu(I) supported MIL-100-Fe	2.78	298	
Cu(aip)(H_2O)	7.18	120	[51]
Fe_2Cl_2(bbta)	5.75	298	[49]
Fe_2Cl_2(btdd)	3.40	298	
Fe-BTTri	2.90	298	[54]
NH_2-functionalized MIL-125-Ti	0.22	303	[55]

Sieving is another method for improving the overall capacity of CO in MOFs. It traps gases inside the pores of MOFs. But when the pressure drops, these gases generally desorb quickly due to weak intermolecular interactions. In a recent work on MOF-74, it was discovered that adding ethylenediamine (EDA) after adsorption might preserve weakly adsorbing molecules like CO inside the MOF by forming a capping layer at the surface of the microcrystals. According to time-resolved infrared spectra, original Ni-MOF-74 may evacuate CO molecules from its pores as early as 30 minutes, whereas EDA-modified Ni-MOF-74 can keep more than 97% of the CO from the pores upon evacuation for two hours [56]. This spectroscopic study in association with ab initio calculations, demonstrated that water can be introduced to liberate the trapped gas molecules, opening a door to new reversible CO storage materials.

Since CO_2 is more polarizable than CO, it is possible to functionalize the linker with strongly polarizing groups to encourage CO_2 uptake and produce materials with greater CO_2/CO selectivities. Multivariate MOF-5 with substituted 1,4-benzodicarboylate linkers having functional groups such as NH_2, NO_2, Br, or Cl. has been described by Yaghi and coworkers [57]. Due to less surface area of functionalized materials, the uptake of CO_2 increased whereas that of CO decreased, which was as expected. In comparison to MOFs made from individual linkers, they reported that multivariate MOFs had up to 400% greater selectivity.

V. Capture of Sulfur Dioxide (SO_2)

Sulfur dioxide is one of the major atmospheric pollutants which reacts with ammonia to produce dangerous $PM_{2.5}$ particles. It is a highly toxic byproduct of fossil fuel emissions. Both the exhaust from marine engines and the flue gas from coal-fired power plants include sulfur dioxide. Due to its ability to interact with water and nitrogen oxides in the environment to create acid rain, this substance is especially concerning. Up to 95% of SO_2 can be removed from flue gases in power plants using desulfurization techniques including limestone scrubbing and the use of aqueous alkaline solutions [58]. However, the public is still at risk for health problems due to trace quantities of SO_2 in exhaust emissions. As a result, capturing trace SO_2 (down to 400 ppm) from flue gas is essential for maintaining air quality. Ahmed and Jhung reviewed the use of MOFs as adsorbents to capture sulfur and nitrogen compounds from both liquid and gas phases [59]. In this review, MOFs will be highlighted as a potential class of materials for the efficient removal of SO_2 from flue gas, along with some relevant recent studies.

Yang et al. investigated the process of SO_2 adsorption in an Al-based MOF called NOTT-300 (also known as MFM-300(Al)) utilizing in situ powder X-ray diffraction (PXRD), inelastic neutron scattering experiments, and density functional theory (DFT) calculations in one of the early publications [60]. They found that NOTT-300 has a significant SO_2 absorption at 1 bar, with values of 8.1 and 7.1 mmol g^{-1} at 273 and 298 K, respectively. Savage et al. reported an indium-based MOF, MFM-300(In), which showed the enhanced capacity of SO_2 uptake of 8.3 mmol g^{-1} at 1 bar and 298 K (Fig. 4) [61]. It is important to note that in both situations, the heat of adsorption rises with increasing loading and indicates strong adsorbate-adsorbate interactions. If the SO_2 concentration is at a low ppm level, selectivity is also a major concern for high gas uptake. At 298 K and 1 bar, the MFM-300(In) exhibits extremely high selectivities for SO_2 over CO_2, CH_4, and N_2 in equimolar mixtures. Yang et al found that at 1 bar, NOTT-202a exhibits a very high SO_2 uptake capacity of about 13.6 and 10 mmol g^{-1} , respectively, at 268 and 298 K [62]. It has been noted that MFM-601, a Zr-MOF with eight linked Zr6 nodes, has a high SO_2 uptake capacity of 12.3 mmol g^{-1} at 1 bar and 298 K [63]. MFM-600, which is created using four linked ligands and Zr_6 nodes, undergoes a phase shift, yielding MFM-601.

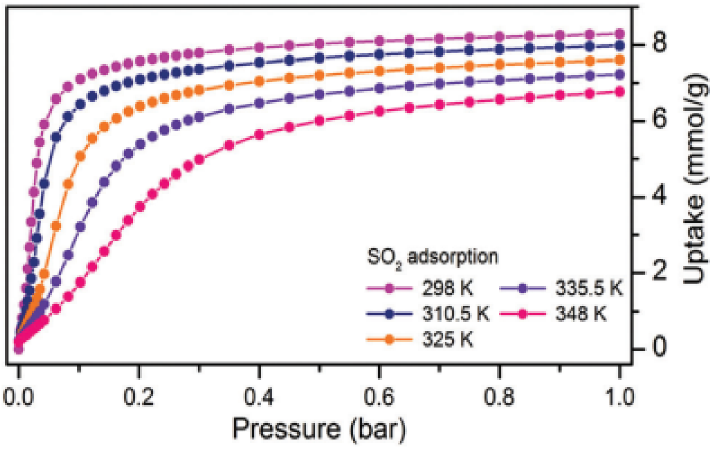

Figure 4. SO_2 adsorption isotherms of MFM-300(In) between 298 and 348 K up to 1 bar [61]

According to Navarro and colleagues, adding Ba^{2+} to a MOF made of nickel pyrazolates improved the interaction between the MOF and SO_2. The experiments showed that the Ba^{2+} -exchanged MOFs have a greater capacity to adsorb SO_2 than either the parent MOF or the K^+ -exchanged MOF. Additionally, it was demonstrated that extra-framework Ba^{2+} cations within the MOF outperform barium hydroxide for the capture of SO_2, highlighting the significance of the accessibility of the active adsorption sites [64]

Tan et al. examined in detail the mechanism of SO_2 adsorption into two microporous MOFs, $M(BDC)(TED)_{0.5}$ (M = Ni Zn), using a combination of experiments and DFT [65]. At 1 bar and 298 K, $Ni(BDC)\text{-}(TED)_{0.5}$ and $Zn(BDC)\text{-}(TED)_{0.5}$ display SO_2 uptake values of 9.9 and 4.4 mmol g^{-1}, respectively. In similar circumstances, $Ni(BDC)(TED)_{0.5}$ surpasses Mg-MOF-74, which adsorbed 8.6 mmol $g^{-1}$of SO_2. According to PXRD experiment, $Ni(BDC)(TED)_{0.5}$ preserves its crystallinity while $Zn(BDC)\text{-}(TED)_{0.5}$ partially disintegrates following SO_2 sorption. The outcomes of ab initio DFT calculations and infrared spectroscopy data both suggest a variety of interactions between the SO_2 guest molecules and the MOF hosts.

Table 5. Overview of the SO_2 adsorption capability of different MOFs

MOFs	Uptake(mmol g^{-1})	Temp (K)	Ref
FMOF-2	1.8	298	[66]
MFM-305-CH_3	5.16	298	[67]
MFM-305	6.99	298	
SIFSIX-1-Cu	11.01	298	[68]
SIFSIX-2-Cu-i	6.9	298	
Ti-MIL-125	9.5	298	[69]
Ti-MIL-125-NH_2	9.5	298	
MFM-300(Al)(NOTT-300)	8.1 (7.1)	273(298)	[60]
MFM-300(In)	8.3	298	[70]
MOF-74(Mg)	8.6	298	[65]
$Zn(BDC)(TED)_{0.5}$	4.41	298	
$Ni(BDC)(TED)_{0.5}$	9.97	298	
MFM-202a	13.6 (10)	268 (298)	[62]
MFM-600	5.0	298	[63]
MFM-601	12.3	298	
CoCo	2.5	298	[71]
ZnCo	1.8	298	

Mounfield et al. highlighted the impact of functional groups on SO_2 adsorption performance in MOFs in humid circumstances, which is a crucial factor to take into account for adsorbent materials used for flue gas purification. The titanium-based MOF MIL-125 used in this work shows a loss of stability when exposed to humid SO_2, but not when exposed to dry SO_2 or water vapor [69]. But it was found that MIL-125-NH_2, an isoreticular analogue of MIL-125 with an amino functional, is stable toward humid SO_2. Both MIL-125 and MIL-125-NH_2 exhibit single gas adsorption isotherms and can adsorb roughly 9.5 mmol g^{-1} SO_2 at 1 bar and 298 K Another potential family of materials for effective SO_2 adsorption is microporous fluorinated MOFs. As part of their SO_2 capture research, Cui et al. reported the SIFSIX series of anion-pillared hybrid porous materials [68]. According to single gas SO_2 adsorption isotherms, SIFSIX-1-Cu has a very high SO_2 uptake capacity of 11 mmol g^{-1} at 1 bar and 298 K, which is higher than that of SIFSIX-2-Cu-i, SIFSIX-3-Ni, and SIFSIX-3-Zn. Additionally, at a very low SO_2 partial pressure of 2 mbar at 298 K, SIFSIX-2-Cu-i and SIFSIX-1-Cu demonstrate outstanding SO_2 absorption of 2.3 and 1.8 mmol g^{-1}, respectively. These MOFs might be used to separate SO_2/CO_2 and SO_2/N_2, as shown by mixture gas breakthrough investigations and DFT calculations that identify the preferential adsorption sites. Even though it is necessary to explore these materials' stability in the presence of water vapor, they are intriguing candidates for the flue gas desulfurization process.

The utilization of fluorinated MOFs, NbOFFIVE-1-Ni (KAUST-7) and AlFFIVE1-Ni (KAUST-8), for the selective removal of SO_2 from flue gas and the sensing of trace quantities of SO_2 was described by Eddaoudi and colleagues [72]. A good SO_2 absorption capacity of 2.2 mmol g^{-1} was found in both KAUST-7 and KAUST-8 during column breakthrough investigations using a gas mixture (SO_2/N_2 = 7/93). Additionally, both MOFs continue to absorb SO_2 even when exposed to a gas mixture containing only 500 ppm of SO_2 in N_2, with both demonstrating SO_2 absorption values of 1.4 mmol g^{-1} under these circumstances. It should be noted that this MOF platform is stable in humid SO_2 environments. The interaction of SO_2 molecules with electronegative fluorine atoms of the neighboring anionic pillars and hydrogens of pyrazines was clarified by a combination of theoretical and experimental studies on SO_2-loaded MOF crystals.

VI. Capture of Nitrogen Oxides (NO_x)

Major human sources include burning coal, oil and natural gas, vehicle exhaust, and agricultural activities all produce highly toxic chemicals called nitrogen oxides (NO_x). Nitric oxide (NO) and nitrogen dioxide (NO_2) are the two types of NO_x that are most frequently found in the atmosphere. Skin and eye irritation, as well as respiratory harm, are all results of exposure to high NO_x levels. In addition to the species' toxicities, acid rain, which is produced by NO_xin the presence of sunlight, is a serious environmental issue. The production of ozone and photochemical smog at ground level is also aided by NO_x species. NO has a significant role in a number of cardiovascular, neurological, and immunological systems, despite being dangerous to humans at high levels [73]. It is crucial to design the materials for NO absorption under certain biological circumstances. As of now, NO_x adsorbents include activated carbon, graphite oxides, iron composites, zeolites, and titania. Low adsorption capabilities and irreversible NO_2 absorption via disproportionation to NO^+ and ${NO_3}^-$ are two drawbacks of these materials. The selective catalytic reduction of NO_x to N_2 in the presence of ammonia, urea, and hydrocarbons from stationary sources is another method for removing NO_x. The usefulness of NO_x in some industries has led to an increase in interest in the development of novel adsorbent materials that remove NO_x rather than change the species. In the chemical industry, NO_2 is commonly used as a nitrating or bleaching agent and NO has been used therapeutically [74]. Therefore, the possible applications of NO_x pushed to create the materials that can both adsorb and deliver NO_x under particular conditions. In the last two decades, MOFs have become an innovative functional material based on host-guest interactions that have since been used for NO_x capture and release.

The efficiency of several MOFs for NO_2 uptake has been proven by ground-breaking experiments. The uptake capacity of Cu-based framework HKUST-1 under dry and 70% humidity at room temperature was found to be 2.30 and 1.17 mmol NO_2/g MOF respectively. In dry conditions, a graphite oxide composite of HKUST-1, known as GOHKUST-1, had a capacity of 2.43–2.91 mmol NO_2/g MOF, whereas at 70% humidity, it had a capacity of 0.83–1.28 mmolg^{-1}. Bandosz and colleagues claim that the Zr-based frameworks UiO-66 and UiO-67 had uptakes of 1.59 and 1.72 mmol NO_2/g MOF, respectively, under dry conditions [75]. The NO_2 dissolution inwater increased NO_2 absorption to 2.56 mmol g^{-1} at 71% relative humidity. However, after being exposed to NO_2, both MOFs collapsed. Peterson et al. tested UiO-66-NH_2 by modifying the linker on UiO-66 to remove NO_2 from air under humid and dry conditions. It was found that UiO-66-NH_2 captured 20.3 mmol g^{-1} NO_2 under dry conditions, while 31.2 mmol g^{-1} was adsorbed under 80% humidity [76]. This remarkable adsorption was far greater than the theoretical value indicated by its crystal structure and traditional adsorption theory. Metal dopants were investigated in order to functionalize the Zr6 UiO node in addition to the linker. Ce(III) was post-synthesized onto UiO-66 and UiO-67, which captured 2.1 mmol g^{-1} and 1.87 mmol g^{-1} NO_2 under dry circumstances and 1.15 mmol g^{-1} and 1.85 mmol g^{-1} NO_2 under 71% humidity conditions [77]. Due to the inclusion of extra adsorption sites, the adsorption of NO_2 by Ce(III)-doped UiO-66 and UiO-67 was greater than that of the corresponding parents.

Table 6. Overview of the NO_2 adsorption capability of different MOFs at 298 K

MOF	Adsorption capacity (mmol g^{-1}	Ref
HKUST-1	2.30 (dry) 1.17 (wet)	[78]
GO-HKUST-1	2.43 - 2.91 (dry) 0.83 - 1.28 (wet)	
UiO-66	1.59 (dry) 0.87 (wet)	[75]
UiO-67	1.72 (dry) 2.56 (wet)	
UiO-66	3.8 (dry)	[79]
UiO-66-vac	3.9 (dry)	
UiO-66-ox	8.4 (dry)	
UiO-66-NH_2	20.3 (dry) 31.2 (wet)	[76]
MFM-300 (Al)	14.1(dry)	[80]
Ce(III)doped UiO-66	2.1(dry) 1.15(wet)	[77]
Ce(III)doped UiO-67	1.87 (dry) 1.85 (wet)	

Free carboxylate groups can be added to increase NO_2 uptake capabilities. DeCoste et al. introduced free carboxylic groups into UiO-66 to form UiO-66-ox. It was found that UiO-66-ox captured 8.4 mmol g^{-1} NO_2, which is significantly greater than UiO-66 (3.8 mmol g^{-1}) [79]. This is related to both the physical adsorption of NO_2 and a chemical reaction between free carboxylic acid and NO_2.

According to Han and his coworkers, the extremely robust MFM-300(Al) framework provided a demonstration of reversible, high NO_2 collection [80]. It was demonstrated that NO_2 could be selectively removed in low concentrations (less than 1 ppm) above an uptake capacity of 14.1 mmol g^{-1}. Additionally, at ambient temperature and 1.0 bar pressure, MFM-300(Al)preferentially adsorbed NO_2 with 18.1 over SO_2, 248 over CO_2, and >1000 over N_2. Reversible NO_2 adsorption was supported by Synchrotron PXRD, infrared and EPR spectroscopy, density function theory, and predictions based on molecular dynamics.

It is believed that open metal sites (OMS) are required for NO adsorption within MOFs. In order to use MOFs for biological purposes, NO storage and selective release have been investigated. For instance, the MIL-88 type of exceptionally adaptable iron(III) dicarboxylate MOFs were tested for their ability to absorb the pharmacologically active NO. Its uptake capacity was found to be 1-2.5 mmol g^{-1} [81]. This type MOFs might be suitable for NO adsorption because iron is less poisonous and more environmentally friendly. NO either physically adsorbed within the accessible pore of MOFs or was chemically adsorbed on either accessible Fe^{3+} or Fe^{2+} sites. Wang and his team claimed that MIL-100-Fe showed outstanding activity for the selective catalytic reduction of NO that contains both Lewis and Bronsted acidic sites [82]. The copper-containing framework, HKUST-1 adsorbed about 9 mmol g^{-1} NO at 296 K and 1.0 bar which was the highest capacity among the porous materials . It was due to a strong interaction between NO and Cu ions within the framework. During desorption, there was a decrease in material crystallinity and only 2 mol g^{-1} of NO were liberated. The addition of NH_2 to HKUST-1 caused an increase in NO emission of 65 mol g^{-1} [83]. However, the stability of the framework did not significantly improve.

Researchers are attracted to the MOF-74 series because of its high density of open metal sites. At room temperature, Ni-MOF-74 and Cu-MOF-74 absorbed 7.0 mmol NO/g of activated material [84]. NO can be stored in these materials for several months, which is advantageous for medical purposes. After the release of NO caused by flowing humid air, the MOFs entirely recovered without experiencing any structural alterations. Co(II) and Ni(II) are not biocompatible, which restricts the use of these metals in medical applications. Although transmetalation of MOF-74 with Mg(II) and Zn(II) can provide biocompatible materials. The rate of NO delivery from Mg-MOF-74 was too slow, but Zn-MOF-74 released NO too quickly. This was due to the fact that NO had an excessively strong interaction with Mg and a weak bond with Zn ions. However, the biocompatible Mg-MOF-74 framework was doped with Ni to improve adsorption. The Mg-MOF-74 with 40% Ni(II) doping successfully adsorbed and delivered the required amount of NO [85]. The Fe-MOF-74 framework was capable of capturing 6.21 mmol g^{-1} NO at 298 K, (7 mbar). Such absorption implied that NO was present at about 95% of Fe(II) open metal sites [86].

VII. Conclusions

The scientific community has always been primarily interested in the adsorption removal of toxic gases for human safety and air purification. For this objective, MOFs have been investigated as adsorbent and catalytic materials over the past ten years. It can be modified by changing the linkers, pore sizes, functional groups, and metal nodes. Due to this immense diversity compared to other conventional porous materials, it is possible to create materials to hold and degrade selected target molecules. Therefore, MOFs have demonstrated excellent potential as sorbents for numerous common toxic gases.

An effective method for enabling the adsorption of various gases can be achieved by adjusting the pore sizes and shapes in MOFs. However, this strategy cannot be applied generally to adsorb toxic gases. As a result, it is necessary to decorate the MOF pores with potent adsorption sites. It has been observed that introducing open-metal sites for enhanced interactions with specific Lewis basic gases is a potential method for gas adsorption, especially at low concentrations. Through the MOF node, open-metal sites can be introduced using strategies like postmetalation. Additionally, it has been observed that adding polar groups to the pore walls of MOFs increases the uptake capacity of polar gases like ammonia through hydrogen bonding or ionic interactions. However, amine functionalities have been observed to react only with NO_x gases.

Although there are considerable problems with competitive adsorption with water under humid conditions, MOFs with open metal sites, such as MOF-74 and HKUST-1, are particularly effective MOFs for capturing NH_3 and H_2S. It is necessary to understand how water and the desired gas interact. The majority of the proposed applications would be used in humid climatic circumstances. Therefore, the efficiency of the MOFs in humid conditions must be evaluated. It has been observed that through the proper application of functional groups or metals, the selectivity for the desired gas over water may be enhanced. The materials that are used in open-metal sites or polar functional groups in MOFs for selective adsorption over water are also important. Moreover, it has been observed that the high solubility of ammonia and NO_2 in water is favorable, which increases the adsorption capacity of MOFs in the presence of moisture than in dry conditions. The affinity of SO_2 and other non-coordinating gases for open metal sites was found to be low. A potential sorbent for NO_2 is UiO-66-NH_2. Some intriguing research has been done on composite materials made of MOFs and graphite oxide or ionic liquids. These composite materials should be studied further because they have potential as sorbents.

The adsorption behavior of toxic materials in MOFs has been extensively described using molecular simulation. The number of experiments with toxic materials can be decreased if the models are accurate enough. One of the key challenges in simulating materials is developing improved methods that take into account interactions and binding of adsorbates functional groups with open metal sites. The modeling of MOF flexibility, which is critical for some systems, can be tricky. The highly correlated electronic structure of the transition metal-oxide nodes in MOFs cannot be successfully explained by purely local DFT functionals, hence the degree of theory must be carefully chosen.

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