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Application Research of Metal-Organic Frameworks in the Treatment of NO_2 and SO_2

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Abstract:

With the acceleration of industrialization, emissions of nitrogen oxides (NO_2) and sulfur oxides (SO_2) have been increasing significantly, becoming major sources of global atmospheric pollution. Traditional treatment methods suffer from high energy consumption, high costs, and secondary pollution, driving the research and application of new materials. Adsorption materials offer advantages such as high selectivity, environmental friendliness, and renewability. Compared to traditional adsorption materials such as zeolites and activated carbon, metal-organic frameworks (MOFs) exhibit tunable pore structures, a high specific surface area, and ease of functionalization, demonstrating significant potential in the adsorption treatment of NO_2 and SO_2. This paper focuses on the application of MOFs in end-of-pipe pollution control, systematically analyzing the key factors influencing their adsorption performance, including pore size, specific surface area, functional group types, adsorption mechanisms (such as physical adsorption, chemical adsorption, and synergistic mechanisms), and environmental factors (temperature and humidity). The study found that the matching of pore size with gas molecule diameter and the chemical properties of functional groups, in conjunction with adsorption mechanisms, jointly determine the adsorption efficiency, reversibility, and stability of MOFs. Finally, directions for future improvements of MOFs are proposed.

Keywords: MOF; air pollution control; NO_2; SO_2.

1. Introduction

With the acceleration of industrialization, the emission of large amounts of nitrogen oxides (NO_2) and sulfur oxides (SO_2) has become a prominent global environmental pollution issue. These acidic gases are not only the primary precursors of acid rain and smog but also pose severe hazards to human health, ecosystems, and infrastructure. Traditional desulfurization and denitrification technologies, such as wet scrubbing and catalytic reduction, have mitigated pollution to some extent but generally suffer from drawbacks such as high costs, high energy consumption, or secondary pollution. To achieve more efficient, green, and sustainable air pollution control, the development of novel high-performance adsorbent materials has become a research hotspot.

Metal-organic frameworks (MOFs) have demonstrated significant potential in gas separation and storage due to their extremely high specific surface area, tunable pore structure, and excellent functionalization capabilities [1-4]. In recent years, increasing research has focused on the application of MOFs in the adsorption and treatment of NO_2 and SO_2, aiming to achieve efficient capture and recovery of these pollutants. Currently, the mainstream treatment methods primarily utilize activated carbon and zeolites for gas adsorption. Compared to traditional materials, MOFs offer advantages such as high selectivity and large specific surface areas [5]. For some MOFs, the specific surface area can even reach four to five times that of activated carbon. This paper primarily summarizes the adsorption performance of various MOFs for NO_2 and SO_2. The different adsorption effects of MOFs are analyzed, and the reasons for these differences are discussed.

2. Factors influencing the adsorption performance of MOFs

2.1 Material Properties

MOFs are a class of porous materials composed of metal ions and organic ligands connected by coordination bonds. They are widely used in gas storage, catalysis, adsorption, and separation. MOFs primarily consist of metal nodes, organic ligands, and a framework structure. Metal nodes primarily serve as connectors, influencing MOF stability, adsorption performance, and catalytic activity. Organic ligands are key factors determining the chemical environment and pore structure of MOFs, with different ligands leading to distinct pore structures and chemical environments. The framework structure is the periodic porous structure formed by the connection of metal nodes and ligands. Pore volume and pore size are jointly determined by the types of nodes and ligands, as well as their spatial arrangement [6].

2.1.1 Pore size

The pore size of MOFs determines whether gas molecules can effectively enter the material interior for adsorption. Generally, for adsorbing small molecules such as NOx and SO_2, microporous structures (pore size < 2 nm) are typically selected. When the pore size of MOFs is very close to the kinetic radius of gas molecules, selective penetration occurs during the entry of molecules into the pores, and adsorption is primarily limited by molecular size matching [1]. This effect significantly enhances the adsorption selectivity and efficiency of MOFs toward specific gases, particularly in multi-component gas mixtures. Therefore, designing pore structures with diameters matching the target gas molecules is a key strategy for improving MOF adsorption performance.

2.1.2 Specific surface area

A larger specific surface area means that MOFs have more adsorption sites. A higher specific surface area provides MOFs with greater adsorption capacity [2, 4]. Additionally, a higher specific surface area enhances physical adsorption efficiency and gas diffusion rates [3]. However, due to the influence of controlled structure, a higher specific surface area only results in higher physical adsorption efficiency when the pore size matches the diameter of the adsorbed gas molecules. However, it is important to note that an increase in specific surface area is not always linearly correlated with adsorption efficiency. Effective adsorption in MOF structures can only fully realize its physical adsorption potential when the pore size matches the size of the target gas molecules. Otherwise, even with a large specific surface area, gas molecules may struggle to enter due to pore size being too small, or intermolecular forces may weaken due to pore size being too large, thereby impairing overall adsorption performance. Therefore, in MOF material design, optimizing specific surface area should be combined with pore size regulation to achieve efficient adsorption of specific gases.

2.1.3 Functional groups

Functional groups on MOFs are categorized into two main types: basic functional groups (e.g., $-NH_2$, -OH) and acidic functional groups (e.g., -COOH, $-SO_3H$)

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Table 1. Adsorption interaction mechanisms of functional groups in MOFs with two gases

Gas/functional group	$-NH_2$	-OH	-COOH	$-SO_3H$
SO_2	1. Base-acid interactions[7] 2. Hydrogen bonding [8]	1. Hydrogen bonding [11]	1. Acid-base interactions [13] 2. Hydrogen bonding	1. Acid-base interactions [14]
NO_2	1. Acid-base interactions [8-9] 2.Hydrogen bonding [10]	1. Hydrogen bonding [12] 2.Coordinate bond interaction [12]	1. Hydrogen bonding	1. Electrostatic interactions[13] 2. Hydrogen bonding [13]

This Table 1 lists only some of the adsorption interaction mechanisms between functional groups and gases, primarily acid-base interactions and hydrogen bonding. In the structural design of MOFs, introducing appropriate functional groups is one of the key methods for regulating their adsorption performance. The presence of functional groups in MOFs not only provides more active sites but also forms various types of intermolecular forces with target gas molecules, thereby significantly influencing their adsorption capacity, adsorption selectivity, thermodynamic stability, and the reversibility of adsorption/desorption. It is important to note that these interactions not only enhance the adsorption capacity of gas molecules but also improve the selectivity and stability of MOFs during the adsorption process, while promoting their reversibility and regenerative capacity in multiple adsorption/desorption cycles. Therefore, the rational selection and introduction of functional groups are key strategies for achieving efficient adsorption performance in the design and functionalization of MOFs

2.2 Adsorption Mechanisms

The adsorption mechanisms of MOFs can primarily be categorized into physical adsorption, chemical adsorption, and special synergistic mechanisms. Different adsorption mechanisms influence the reversibility and cyclability of MOFs. MFM-300(Al) adsorbs NO_2 through hydrogen bonding and coordination bonding, achieving high capacity and complete reversibility. NH_2-MIL-125(Ti): Partial capacity loss after adsorbing SO_2 indicates the presence of irreversible chemical adsorption. Pore size matching, functional group type, and adsorption mechanisms are all critical factors determining adsorption performance.

2.2.1 Physical adsorption

Physical adsorption is a process by which gas molecules bind to the surface of an adsorbent through weak intermolecular forces (such as van der Waals forces, hydrogen bonding, and dipole-dipole interactions). The hydrogen bonding mentioned in Table 1 is a typical example of physical adsorption. In MOFs, physical adsorption primarily occurs within their highly porous framework structures. Due to their high surface-to-volume ratios, which can reach several hundred to several thousand m^2/g, MOFs provide a large number of accessible adsorption sites for gas molecules. One of the distinctive features of physical adsorption is that no new chemical bonds are formed during the entire adsorption process. This means that gas molecules are in a relatively weak binding state on the adsorbent surface, resulting in good reversibility of the adsorption-desorption process. This property is particularly important for gas separation and storage, such as the recovery and reuse of acidic gases like SO_2 and NO_2 or cyclic adsorption-desorption processes, which can significantly reduce operational costs and extend material lifespan. In MOF applications, the physical adsorption mechanism is often closely related to its pore size distribution. For the capture of acidic gases, if the pore size of the MOF is similar to the kinetic diameter of the gas molecules, a pronounced size-exclusion effect [15] occurs, enhancing the weak intermolecular forces and thereby improving adsorption selectivity. For example, in the adsorption of SO_2 (kinetic diameter approximately 0.36 nm) and NO_2 (approximately 0.32 nm), appropriate pore sizes not only enhance the strength of hydrogen bonding and dipole interactions but also reduce competitive adsorption by other gas molecules. Physical adsorption exhibits high stability under varying operating temperatures, typically showing increased adsorption at lower temperatures due to the lower thermal energy required to keep molecules adsorbed at the adsorption sites. However, compared to chemical adsorption, physical adsorption has lower adsorption enthalpy (generally 5-40 kJ/mol), making it prone to desorption at high temperatures. This characteristic is both an advantage (facilitating regeneration) and a limitation (reduced adsorption capacity at high temperatures) in gas separation applications. Overall, the advantages of MOFs in physical adsorption lie in their high reversibility, rapid kinetic response, and low-energy regeneration. However, their drawbacks include reduced adsorption capacity under high-temperature or high-humidity conditions. Therefore, when designing MOF materials based on physical adsorption, it is essential to comprehensively consider pore size, surface polarity, and framework stability to balance adsorption capacity and regenerability.

2.2.2 Chemical adsorption

Chemical adsorption is the process by which gas molecules bind to an adsorbent through the formation of chemical bonds (such as covalent bonds, coordination bonds, or strong acid-base bonds). The coordination bond effects and acid-base interactions mentioned in Table 1.1 are typical examples of chemical adsorption. Unlike physical adsorption, chemical adsorption has higher binding energies (typically 40-800 kJ/mol), and the adsorption process is often irreversible or requires high energy for regeneration. Chemical adsorption in MOFs primarily relies on two types of active sites: the first are metal nodes (metal nodes/clusters), which include metal ions or metal cluster structures and possess abundant coordinatively unsaturated sites (CUS), enabling direct formation of stable coordination bonds with gas molecules; the second are functional groups on organic ligands (e.g., $-NH_2$, -OH, -COOH, $-SO_3H$, etc.), which can undergo chemical reactions or strong acid-base interactions with acidic or basic gases, thereby achieving efficient fixation. In the treatment of acidic gases, chemical adsorption often manifests as Lewis acid-base interactions or Brønsted acid-base interactions. For example, SO_2 acts as a Lewis acid and forms stable coordination bonds with alkaline sites on the MOF framework (such as nitrogen-containing functional groups), NO_2 can bind to unsaturated coordination sites on metal nodes via oxygen atoms [16]. This binding mechanism significantly enhances adsorption capacity and selectivity while improving resistance to water vapor and temperature fluctuations. However, the irreversibility of chemical adsorption imposes certain limitations. During repeated use, adsorbents may become deactivated due to the formation of stable compounds, leading to regeneration difficulties or performance degradation. Additionally, the kinetic process of chemical adsorption is typically slow, as gas molecules must overcome a certain activation energy to enter the reaction state. In MOF design, chemical adsorption mechanisms are commonly employed in scenarios requiring high selectivity and high affinity, such as the deep capture of SO_2 or NO_2 in industrial exhaust gases. However, to balance adsorption capacity, selectivity, and regenerability, researchers adjust the coordination environment of metal centers or introduce reversible functional groups (e.g., protonatable/deprotonatable groups) to impart partial reversibility to chemical adsorption, thereby achieving both high efficiency and recyclability.

2.2.2 Special synergistic adsorption mechanisms

Special synergistic adsorption mechanisms refer to the cooperative action of multiple adsorption mechanisms (physical, chemical, or other molecular recognition mechanisms) during the adsorption process of MOFs, thereby significantly enhancing adsorption efficiency and selectivity. The electrostatic interactions mentioned in Table1 and the size-sieve effect discussed before are important examples of such mechanisms. Electrostatic interactions primarily occur between charged or polar gas molecules and the charged surfaces of the MOF framework. For example, some MOFs contain positively charged metal nodes or protonated functional groups that can form strong electrostatic attractions with polar molecules such as SO_2 and NO_2. Compared to single physical adsorption, this electrostatic attraction not only increases adsorption capacity but also significantly enhances selectivity under low-pressure conditions. The size-sieving effect depends on the matching relationship between MOF pore sizes and gas molecule dimensions. When the pore size is close to or slightly smaller than the kinetic diameter of the target gas molecules, larger molecules are excluded, while molecules of suitable size can preferentially enter the pores and be adsorbed. For example, MOFs with pore sizes of 0.33-0.38 nm exhibit extremely high selectivity toward NO_2 (0.32 nm) but limited adsorption of larger molecules such as CO_2 (0.33 nm). In synergistic adsorption, these mechanisms often do not exist in isolation. For example, in some fluorine-containing MOFs (such as MFM-190(F)), fluorine atoms can simultaneously provide polar sites and suitable pore sizes, enabling synergistic effects between electrostatic interactions and size screening. Additionally, weak hydrogen bonding within the framework further enhances their performance in acid gas capture, demonstrating ultra-high selectivity and reversibility. Furthermore, synergistic adsorption mechanisms are particularly important in multi-component gas separation, as real industrial exhaust gases contain complex gas mixtures, and a single mechanism often fails to achieve efficient separation. By designing MOFs with multifunctional active sites, multiple interactions can be simultaneously triggered during adsorption, such as electrostatic + chemical adsorption, size-sieve+ and hydrogen bonding, thereby effectively overcoming competitive adsorption issues. In summary, special synergistic adsorption mechanisms are a hot research direction in MOF studies, offering the advantage of achieving performance enhancements through mechanism, resulting in a “1+1>2” effect. However, this mechanism demands extremely precise structural design of MOFs, requiring a balance between pore size control, functionalization modification, and framework stability [1].

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2.3 Environmental Factors

The performance of MOFs in the adsorption of acidic gases (SO_2, NO_2) is not only determined by their own structure and functional modifications but also significantly influenced by external environmental conditions. Among these, humidity and temperature are the two most critical environmental variables, which directly alter the pore structure stability, availability of active sites, and gas-material interaction energy of MOFs, thereby affecting adsorption capacity, selectivity, and cycling stability.

2.3.1 Humidity

The impact of water molecules in air on MOF adsorption performance manifests in two primary aspects: competitive adsorption and reduced framework stability. First, water molecules possess strong polarity and a small molecular diameter (approximately 0.265 nm), enabling them to readily occupy the hydrophilic active sites on the MOF framework during acid gas adsorption. For example, coordination-unsaturated metal sites (CUS) and polar functional groups (-OH, $-NH_2$, etc.) in MOFs can form hydrogen bonds or coordination interactions with water molecules [17], thereby inhibiting the adsorption of SO_2 molecules at these sites. This competitive adsorption effect significantly reduces the actual available adsorption capacity of SO_2, particularly under high relative humidity conditions. Second, some MOFs undergo structural degradation or pore collapse under high humidity conditions. For example, the pore volume of NH_2-MIL-100(Al) decreases by over 50% in humid environments [4], primarily due to water molecules entering the framework and undergoing irreversible hydrolysis reactions with metal nodes or forming new hydrogen bond networks with ligands, leading to framework contraction or collapse. Such structural changes not only reduce the specific surface area but also decrease the diffusion pathways for gas molecules, slowing down the adsorption kinetics. Additionally, in aqueous environments, SO_2 may react with water molecules to form sulfurous acid (H_2SO_3), which further undergoes acid corrosion reactions with the MOF, accelerating material deactivation [18]. To address this issue, researchers typically enhance the moisture stability of MOFs through hydrophobic modification (e.g., introducing hydrophobic groups such as $-CF_3$ or -F) or post-synthesis treatment (e.g., organosilane modification) to reduce water molecule intrusion and competitive adsorption effects. Therefore, in actual industrial exhaust gas treatment, if the exhaust gas humidity is high, MOF materials with high moisture resistance stability must be prioritized, such as fluorine-containing MOFs or Zr-based MOFs (e.g., UiO series), combined with pre-dehumidification processes to maximize SO_2 adsorption capacity and material lifespan [4].

2.3.2 Temperature

The influence of temperature on the gas adsorption behavior of MOFs primarily manifests in two aspects: adsorption thermodynamics and structural stability. From a thermodynamic perspective, gas adsorption is an exothermic process (especially physical adsorption, with adsorption enthalpy typically ranging from 5-40 kJ/mol, and chemical adsorption being even higher). Therefore, the kinetic energy of gas molecules grows, as temperature increases, making them more likely to desorb from adsorption sites, thereby reducing the equilibrium adsorption capacity [19]. For the same MOF material, gas molecules are more easily fixed on the pore wall surface at low temperatures, while at high temperatures, the molecular-surface interaction forces are difficult to overcome the thermal motion energy, thereby significantly reducing the adsorption capacity. Additionally, high-temperature environments may cause partial degradation of the MOF framework structure or thermal decomposition of organic ligands, leading to a decrease in specific surface area and porosity. For example, the decrease in specific surface area with increasing temperature has been reported in various MOFs, which not only reduces the number of available adsorption sites but may also alter the pore size distribution, affecting the size-selective screening effect. For chemisorptive MOFs, high temperatures may initially promote reaction rates (overcoming adsorption activation energy), but prolonged high-temperature operation can destabilize chemical bonds, leading to the deactivation of active sites. For example, certain nitrogen-containing functional groups may undergo thermal desorption or chemical degradation at high temperatures, reducing acid-base exchange sites and thereby affecting the adsorption performance of NO_2 and SO_2. In practical applications, temperature changes may also interact with humidity effects to produce composite impacts [20]. High temperatures not only reduce adsorption capacity but also accelerate the diffusion and reaction of water molecules within the framework, further damaging the structure. Therefore, in industrial operations, it is essential to consider the operating temperature range of the target gas during the MOF design stage and prioritize materials with higher thermal stability (e.g., Zr-based UiO series, Cr-based MIL series, certain carbonized MOFs). Additionally, thermal-humidity dual stability can be enhanced through surface hydrophobic modification or strengthening metal-ligand bonds. In summary, temperature changes not only directly affect adsorption equilibrium but also indirectly influence material structural stability and cycling performance. In industrial acidic gas treatment, temperature control and material selection must be integrated to ensure long-term operational stability and efficiency.

3. Common MOFs for adsorbing SO_2 and NO_2

Table 2. Summary of adsorption capacity and pore size of MOFs

Adsorbed gas	Material	Adsorption Capacity/Temperature, Pressure	Pore size/ Å
SO_2	MFM-190(F) [21]	18.7 mmol g^{-1} (298 K, 1 bar)	7-9
	MFM-101 [21]	18.3 mmol g^{-1} (298 K, 1 bar)	7-9
	MIL-96(Al) [22]	4.27 mmol g^{-1} (313 K, 2 MPa)	11
	MOF-177 [23]	25.7 mmol g^{-1} (293 K, 1 bar)	10.6-11.8
	NH_2-MIL-125(Ti) [23]	10.8 mmol g^{-1} (293 K, 1 bar)	N/A
	MIL-160 [23]	7.2 mmol g^{-1} (293 K, 1 bar)	5
NO_2	MOF-801[24]	4.35 mmol g^{-1} (298 K, 1 bar)	5.6
	MFM-300(Al)[25]	14.1 mmol g^{-1} (298 K, 1 bar)	6.5 [24]
	HKUST-1[26]	4.1 mmol g^{-1} (298 K, 1 bar)	8-10
	UiO-66-NH_2[27]	1.4 g NO_2 g^{-1} (298 K, 1 bar)	5.9

The Table 2 presents the performance parameters of common metal-organic framework materials for the adsorption of SO_2 and nitrogen dioxide NO_2, including the type of adsorbate gas, material name, adsorption capacity at specific temperatures and pressures, and pore size. For SO_2, MFM-190(F) and MFM-101 exhibit adsorption capacities of 18.7 mmol·g^{-1} and 18.3 mmol·g^{-1} at 298 K and 1 bar, respectively, with pore sizes of 7-9 Å; MIL-96(Al) exhibited an adsorption capacity of 4.27 mmol·g^{-1} at 313 K and 2 MPa, with a pore size of 11 Å; MOF-177 exhibited a high adsorption capacity of 25.7 mmol·g^{-1} at 293 K and 1 bar, with a pore size of 10.6-11.8 Å; NH_2-MIL-125(Ti) showed an adsorption capacity of 10.8 mmol·g^{-1}under the same conditions, with pore size data not provided; MIL-160 exhibits an adsorption capacity of 7.2 mmol·g^{-1} at 293 K and 1 bar, with a pore size of 5 Å. For NO_2, MOF-801 exhibits a capacity of 4.35 mmol·g^{-1} at 298 K and 1 bar, with a pore size of 5.6 Å; MFM-300(Al) exhibits an adsorption capacity of 14.1 mmol·g^{-1} under the same conditions, with a pore size of 6.5 Å; HKUST-1 has a capacity of 4.1 mmol·g^{-1}, with a pore size of 8-10 Å; UiO-66-NH_2 exhibits a mass adsorption capacity of 1.4 g NO_2 g^{-1} under conditions of 298 K and 1 bar, with a pore size of 5.9 Å. This data comparison highlights the differentiated adsorption capabilities and pore size characteristics of different MOFs in the treatment of acidic gases, providing important references for material screening and optimization.

Table 3. Summary of MOFs' regenerability and specific surface area

Adsorbed gas	Material	Renewability	Specific surface area (m^2/g)
SO_2	MFM-190(F) [21]	No total adsorption capacity loss after 10 cycles	253
	MFM-101 [21]	Fully reversible, no total adsorption capacity loss	2300
	MIL-96(Al) [22]	N/A	N/A
	MOF-177 [23]	N/A	4100
	NH_2-MIL-125(Ti) [23]	Partially irreversible	130
	MIL-160 [23]	Can be achieved with no loss after nitrogen purging	1170
NO_2	MOF-801[24]	Formic acid treatment for reuse	N/A
	MFM-300(Al)[25]	Fully reversible 5-cycle cycle with no total adsorption capacity loss	N/A
	HKUST-1[26]	N/A	N/A
	UiO-66-NH_2[27]	Total loss after 7 cycles is less than 15%	800-1100

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This Table 3 systematically compares the regenerability and specific surface area characteristics of various MOFs in the adsorption of SO_2 and NO_2, providing a data foundation for the applicability of different materials in the treatment of acidic gases. In terms of SO_2 adsorption, both MFM-190(F) and MFM-101 exhibit excellent cyclic stability, with MFM-190(F) showing no significant loss in adsorption capacity after 10 cycles and a specific surface area of 2538 $m^2 \cdot g^{-1}$; MFM-101 also achieves fully reversible adsorption with a specific surface area of 2300 $m^2 \cdot g^{-1}$. MIL-96(Al) and MOF-177 lack cyclic performance data, but MOF-177 has a higher specific surface area (4100 $m^2 \cdot g^{-1}$), offering potential advantages for high-capacity adsorption; NH_2-MIL-125(Ti) exhibits partial irreversibility during adsorption, while MIL-160 can be regenerated without loss after nitrogen purging, with a specific surface area of 1170 $m^2 \cdot g^{-1}$. In terms of NO_2 adsorption, MOF-801 can be reused after formic acid treatment, MFM-300(Al) achieves fully reversible adsorption, and its adsorption capacity remains unchanged after five cycles, demonstrating high stability; UiO-66-NH_2 exhibits a total adsorption loss of less than 15% after seven cycles, with a specific surface area of 800-1100 $m^2 \cdot g^{-1}$. Although HKUST-1 lacks data on cycling and specific surface area, as a classic MOF material, its performance remains worthy of further study. Overall, the table reveals differences in specific surface area, cyclic reversibility, and regeneration methods among various MOFs during the adsorption of acidic gases. These differences not only stem from variations in framework structure, ligand functionalization, and metal node types but are also closely related to gas molecule polarity, size, and interaction mechanisms, providing important references for the subsequent targeted design of efficient and regenerable MOF adsorbents. In terms of renewability, adsorption capacity, and pore size, MFM-190(F) is more suitable for SO_2 adsorption, while MFM-300(Al) is more suitable for NO_2 adsorption[28]. This is because both materials utilize physical adsorption mechanisms, resulting in excellent renewability and pore sizes that are more conducive to size-selective adsorption, thereby enhancing adsorption efficiency. Additionally, both materials exhibit high adsorption capacities compared to similar materials. Among them, MFM-190(F) is constructed using fluorine-containing ligands, forming a three-dimensional framework structure with pore sizes of 7-9 Å. The introduction of fluorine atoms significantly enhances the material's affinity for SO_2 molecules [1]. This material demonstrates outstanding performance in SO_2 adsorption, with an adsorption capacity as high as 18.7 mmol/g, and can undergo 10 cycles of adsorption-desorption without performance loss. Its adsorption mechanism primarily involves hydrogen bonding and acid-base interactions. MFM-300(Al), on the other hand, utilizes Al^{3+} metal nodes to form 6.5 Å pores. The abundant μ_2-OH and carboxylic acid functional groups in the framework can effectively adsorb NO_2 through coordination and hydrogen bonding, achieving an adsorption capacity of 14.1 mmol/g and complete reversibility after five cycles, demonstrating excellent regenerability and structural stability [1]. Although MFM-190(F) and MFM-300(Al) have achieved outstanding results under laboratory conditions, MOFs still face numerous challenges in practical applications [1]. First, some MOFs are prone to structural collapse under strong acidic, humid, or high-temperature conditions; second, low-energy regeneration and efficient desorption of gases remain key challenges hindering their industrialization; Additionally, the selective adsorption capacity of MOFs toward mixed gases requires further improvement. To address these bottlenecks, future research should focus on introducing functional groups (e.g., -F, -OH, -SO_3H) to enhance gas recognition ability, developing multifunctional MOF materials capable of simultaneously adsorbing NO_2 and SO_2, and employing stable metal ions such as Zr and Al along with cross-linking strategies to enhance structural stability [29]. Additionally, green regeneration technologies at low temperatures or under light/electricity assistance, combined with in situ characterization techniques to deeply understand adsorption mechanisms, exploring application tests under real flue gas conditions, and developing low-cost, green, and sustainable synthesis processes are all important directions for the industrial application of MOFs. In summary, MFM-190(F) and MFM-300(Al) provide important research foundations for the application of MOFs in the adsorption and treatment of acidic gases, and clearly indicate future research directions for improving material performance and practicality [30].

4. Conclusion

This study comprehensively reviews the research progress of metal-organic frameworks (MOFs) in the adsorption treatment of NO_2 and sulfur SO_2, systematically analyzes the influencing factors of their adsorption performance, and presents typical application cases. Compared with traditional adsorbents such as activated carbon and zeolite, MOFs possess higher specific surface area, more tunable pore size structures, and designable functional properties, thereby demonstrating significant advantages in the field of acidic gas treatment. From a mechanistic perspective, the adsorption performance of MOFs primarily depends on four factors: First, the matching of pore size with gas molecule diameter significantly enhances size exclusion effects and adsorption selectivity; Second, increased specific surface area provides a foundation for more active sites, but must be combined with pore size regulation to achieve maximum efficiency; Third, functional group modification not only enhances gas-scaffold interactions but also improves material stability and reversibility during cycling; Fourth, the synergistic combination of physical adsorption, chemical adsorption, and special synergistic mechanisms confers unique advantages to MOFs in terms of high selectivity and high capacity adsorption.

In typical cases, MFM-190(F) achieves high affinity for SO_2 molecules through the introduction of fluorine, maintaining high adsorption capacity while demonstrating excellent cyclic stability; whereas MFM-300(Al) effectively combines hydrogen bonding and coordination interactions via the synergistic action of μ_2-OH and carboxyl groups, enabling efficient and reversible capture of NO_2. These studies not only demonstrate the important role of MOFs' structural designability in acid gas treatment but also provide insights for future material development. However, it is important to note that while MOFs exhibit outstanding performance under laboratory conditions, they still face stringent challenges from external environmental factors such as humidity and temperature in industrial applications. Competitive adsorption of water molecules and framework hydrolysis may lead to structural collapse, while temperature fluctuations can affect specific surface area and the stability of active sites, all of which limit their practical application in real flue gas environments. Additionally, the regeneration process of MOFs requires further optimization, particularly in terms of reducing energy consumption and improving desorption efficiency.

Future research can be conducted in the following directions: First, at the material design level, the introduction of functional groups (such as -F, $-SO_3H$, $-NH_2$) should be used to achieve differential recognition of NO_2 and SO_2, and frameworks with multifunctional active sites should be developed to improve selectivity and capture efficiency in mixed gas systems. Second, to improve structural stability, high-stability metal nodes such as Zr and Al can be combined with cross-linking or post-synthesis modification techniques to effectively enhance the moisture resistance and thermal stability of MOFs. Third, in terms of regeneration and recycling, green regeneration methods such as low-temperature, light-assisted, and electrochemical approaches should be explored to reduce operational energy consumption and extend material lifespan. Fourth, in terms of practical application, it is urgent to conduct more long-term operational tests under real flue gas conditions and combine kinetic and thermodynamic models to deeply analyze the adsorption mechanisms of MOFs in complex systems, thereby realizing the transformation of laboratory results into engineering applications. Finally, economic and sustainability factors are also critical considerations for the industrial application of MOFs, so developing low-cost, scalable, and green synthesis processes is equally important for future research.

In summary, MOFs demonstrate unprecedented potential in the field of acidic gas adsorption and treatment, not only providing new approaches to addressing NO_2 and SO_2 emissions but also laying the foundation for environmentally friendly and sustainable atmospheric treatment technologies. Despite challenges such as environmental adaptability, regeneration energy consumption, and large-scale production, with continuous improvements in structural design, synthesis methods, and application testing, MOFs are expected to make the leap from laboratory research to industrial applications in the future, becoming an important material system for efficiently treating air pollution and promoting green development.

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