Removal of Typical Industrial Gaseous Pollutants: From Carbon, Zeolite, and Metal-organic Frameworks to Molecularly Imprinted Adsorbents

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ABSTRACT

In recent years, various adsorbents have been developed to alleviate atmospheric pollution and remove harmful gases, such as carbon dioxide, sulfur dioxide, nitrogen oxides, hydrogen sulfide and volatile organic compounds. Polymer-based adsorbents are a novel type of material now being used for gas separation and purification; in particular, molecular imprinted polymers (MIPs) can achieve selective adsorption of target gas molecules. However, existing review papers have not yet discussed the application of MIPs in gas purification. In this paper, therefore, we exhaustively summarize recently developed adsorbents, including the materials based on carbon, zeolite, and metal-organic frameworks as well as MIPs, to analyze the status of these materials and identify promising adsorbents for gas purification.

Keywords: Adsorption; Industrial gas; Molecule imprinting technique; Porous materials; Selectivity.

INTRODUCTION

Currently, 85% of demanded energy is supplied by thermal power plants that use fossil fuels (Akinyele et al., 2014). However, these processes generate a considerable amount of hazardous gases, such as carbon dioxide (CO₂), sulfur dioxide (SO₂), hydrogen sulfide (H₂S), nitrogen oxides (NOₓ), and volatile organic compounds (VOCs). The methods of capturing CO₂ can be categorized to pre-combustion and post-combustion capture (Jiang et al., 2019; Pai et al., 2019). Air pollution caused by SO₂ has received considerable research attention recently because of its contributions in the forms of acid rain and secondary pollutants (Li et al., 2018). H₂S is so toxic and corrosive that the U.S. Environmental Protection Agency (EPA) reported corrosion of concrete wastewater pipes (due to H₂S) at a rate of 3.6 m² year⁻¹, and of sewer pipes at a rate of 2.5–10 m² a⁻¹ (Habeeb et al., 2017). NOₓ has severe effects on the global ecosystem, particularly on human health. In addition, VOCs are the precursors of particles and ozone.

Therefore, separation and removal approaches, mainly adsorption and catalysis, have been developed to remove harmful gases. Among them, the adsorption method using solid adsorbents as separation media has been widely used in processes such as airflow drying, hydrogen purification, and nitrogen and oxygen production (Sevilla and Fuertes, 2012; Huang and Wang, 2018; Pai et al., 2019). Traditional adsorbents have poor active sites, selectivity, and regeneration properties. Therefore, developing novel adsorbents with excellent properties is necessary for highly effective removal of these gases.

Molecular imprinting technique (MIT) is an interdisciplinary method that integrates polymer chemistry, materials science, chemical engineering and biochemistry. Molecularly imprinted polymers (MIPs) can be used to identify specific target molecules by mimicking the interaction between enzyme and substrates. According to the binding forms between templates and functional monomers, MIT can be categorized into covalent, noncovalent, and semicovalent methods. Covalent methods are also referred to as pre-organized methods, in which templates and functional monomers form precomplexes through covalent bonds (Shin et al., 2018). Noncovalent methods are also called self-assembly methods, in which templates and functional monomers form precomplexes through noncovalent bonds through hydrogen bonding, electrostatic attraction, charge transfer, ion-pair interactions, metal coordination, hydrophobic interactions, and van der Waals forces (Shin et al., 2018).

MIPs are a type of polymer material with a built-in recognition property that can be purposefully designed by changing templates, functional monomers, cross-linkers and initiators (Boysen, 2018). In other words, the polymerization
processes of MIPs can be divided into three stages, as indicated in Fig. 1. First, prepolymers form between templates and functional monomers. They are subsequently chemically fixed by cross-linkers to create three-dimensional (3D) polymer networks. Finally, template molecules are removed from the polymers, thus producing specific cavities. MIPs have the advantages of simple preparation, high selectivity and easy regeneration because of a lot of active sites with spatial shapes and sizes similar to those of templates (Ying and Nan, 2010). They have been studied in a wide range of fields, such as adsorption, solid-phase extraction, catalysis, sensors, and electron probes (Cheong et al., 2013; Xu et al., 2019).

This study reviews advances in the development of absorbents for gas removal. Emphasis is placed on functional adsorbents, such as MIPs and carbon-based, zeolite-based, and metal-organic framework (MOF) materials, as well as their selectivity and separation properties.

**ADSORPTION AND CAPTURE OF COMMON GASES**

**Carbon Dioxide**

Major sources of CO₂ are thermoelectric power plants and industrial plants, which account for approximately 45% of CO₂ emissions (Lee and Park, 2015; Beidari et al., 2017). Many successful technologies have been developed and applied for CO₂ capture, such as solvent absorption, chemical or physical adsorption, membrane separation, and cryogenic separation (Santiago et al., 2018). In addition, novel adsorbents have also been developed to reduce CO₂ emissions, as indicated in Table 1. These adsorbents are capable of capturing and storing CO₂ to directly reduce the CO₂ emissions from operational coal power plants (Tobiesen et al., 2018; Wawrzyńczak et al., 2019). Rezakazemi et al. (2019) conducted CO₂ adsorption experiments using nanofluids in a gas-liquid hollow fiber membrane contactor and analyzed the results with a two-dimensional (2D) mathematical model. Simulation results revealed that the adsorption rate of 0.05 wt% SiO₂ nanoparticles increased to 16%. However, using a 0.05 wt% carbon nanotubes (CNTs) increased the adsorption rate by up to 34%. This result suggested that CNTs have markedly superior adsorption capacity and hydrophobicity compared with SiO₂ nanoparticles. Louis et al. (2018) reported that membrane capacitive deionization (MCDI) could be used to capture CO₂ as bicarbonate and carbonate ions produced by the reaction of CO₂ and water at room temperature and atmospheric pressure. In this process without using chemicals, the absorption-desorption behavior of CO₂ can be driven by the adsorption and desorption of bicarbonate ions from water.

**Activated Carbons**

Marszewska and Jaroniec (2017) prepared highly-porous carbon spheres by combining silica template and CO₂ activation. The experimental results showed that mesoporosity could improve mass transfer, leading to high and fast CO₂ adsorption, and the CO₂ adsorption capacity reached 4.0 mmol g⁻¹ at 23°C and 1 bar. Ogungbenro et al. (2018) studied activated carbon synthesized from jujube seeds prevalent in the United Arab Emirates (UAE) for CO₂ adsorption. The results suggested that the adsorbent with rich pores had high CO₂ adsorption capacity of 141.14 mg g⁻¹ at room temperature. Tehrani et al. (2019) prepared nitrogen-sulfur-doped nanoporous carbon with a

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**Fig. 1.** Schematic of the preparation of imprinted polymers (Huang and Wang, 2018).
Table 1. Functional adsorbents for CO₂ removal.

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>mg CO₂ g⁻¹ adsorbent</th>
<th>T (°C)</th>
<th>composition</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC-ZnAC₂</td>
<td>63.61</td>
<td>room temperature</td>
<td>CO₂ in H₂</td>
<td>Sevilla and Fuertes (2012)</td>
</tr>
<tr>
<td>N-S-rich nanoporous carbon</td>
<td>7.15</td>
<td>25</td>
<td>CO₂/CH₄</td>
<td>Sidek et al. (2019)</td>
</tr>
<tr>
<td>NC-Cu-BTC</td>
<td>8.24</td>
<td>0</td>
<td>CO₂ in N₂</td>
<td>Zhao et al. (2015)</td>
</tr>
<tr>
<td>zeolite/activated carbon honeycomb</td>
<td>4.51</td>
<td>25</td>
<td>CO₂ in N₂</td>
<td>Belmabkhout et al. (2010)</td>
</tr>
<tr>
<td>hierarchical carbon nanosheet-based networks (GPC)</td>
<td>4.62</td>
<td>0</td>
<td>CO₂ in N₂</td>
<td>Chen et al. (2010)</td>
</tr>
<tr>
<td>Ni (II)-Mofs</td>
<td>118.2</td>
<td>30</td>
<td>CO₂/N₂</td>
<td>An et al. (2009)</td>
</tr>
<tr>
<td>MIL-91(Al)</td>
<td>2.4</td>
<td>25</td>
<td>CO₂/N₂</td>
<td>Zhao et al. (2014)</td>
</tr>
<tr>
<td>HKUST-1</td>
<td>102.6</td>
<td>25</td>
<td>CO₂/N₂</td>
<td>Nabavi et al. (2017)</td>
</tr>
<tr>
<td>MOF-591</td>
<td>36</td>
<td>25</td>
<td>CO₂/N₂</td>
<td>He et al. (2016)</td>
</tr>
<tr>
<td>MOF-592</td>
<td>42</td>
<td>25</td>
<td>CO₂/N₂</td>
<td>He et al. (2016)</td>
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<tr>
<td>unconventional MOFs</td>
<td>0.86</td>
<td>25</td>
<td>CO₂/N₂</td>
<td>Gupta et al. (2016)</td>
</tr>
<tr>
<td>PCN-250(Fe₃)</td>
<td>1.82</td>
<td>25</td>
<td>CO₂/N₂</td>
<td>Chen et al. (2018b)</td>
</tr>
<tr>
<td>Inorganic-organic composite sorbent</td>
<td>4.54</td>
<td>25</td>
<td>CO₂ in H₂O</td>
<td>Nowicki et al. (2014)</td>
</tr>
<tr>
<td>hexagonal mesoporous silica</td>
<td>184</td>
<td>75</td>
<td>CO₂ in N₂</td>
<td>Xu et al. (2014)</td>
</tr>
<tr>
<td>PEI/monolith</td>
<td>210</td>
<td>75</td>
<td>CO₂ in N₂</td>
<td>Kazmierezak-Razna et al. (2015)</td>
</tr>
<tr>
<td>TEPA/monolith</td>
<td>260</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>TEPA/MSU-1</td>
<td>3</td>
<td>75</td>
<td>CO₂ in N₂</td>
<td>Lau et al. (2015)</td>
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<tr>
<td>MIP Adsorbent</td>
<td>0.48</td>
<td>60</td>
<td>CO₂ in H₂O</td>
<td>Balsamo et al. (2016)</td>
</tr>
<tr>
<td></td>
<td>0.49</td>
<td></td>
<td>CO₂ in O₂</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.57</td>
<td></td>
<td>CO₂ in SO₂</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.50</td>
<td></td>
<td>CO₂ in NO₂</td>
<td></td>
</tr>
<tr>
<td>poly[acrylamide-co-(ethylene glycol dimethacrylate)] polymer particles</td>
<td>1.1</td>
<td>0</td>
<td>CO₂ in N₂</td>
<td>Lee et al. (2017)</td>
</tr>
<tr>
<td>IPEIA-R</td>
<td>8.56</td>
<td>25</td>
<td>CO₂ in H₂O</td>
<td>Sun et al. (2018)</td>
</tr>
</tbody>
</table>
large surface area of 2186 m² g⁻¹ and pore volume of 1.3 cm³ g⁻¹. CO₂ adsorption capacity reached 7.15 mmol g⁻¹ at 1 bar and 25°C and reached 29.29 mmol g⁻¹ at 35 bar and 25°C, indicating that pressure significantly influenced CO₂ adsorption. Sidek et al. (2019) evaluated the CO₂ adsorption performance of activated carbon (AC) impregnated by zinc acetate in terms of breakthrough time and adsorption capacity. The maximum CO₂ adsorption capacity of the AC was 63.61 mg g⁻¹, and the longest breakthrough time was 25.7 min under the optimum feed gas flow rate of 0.25 L min⁻¹. Liu et al. (2019) designed novel composite adsorbents by combining a copper and benzene-1,3,5-tricarboxylate-(BTC) framework with a series of porous carbons, including ordered mesoporous non-activated carbon (OMC), ordered mesoporous AC, and nitrogen-containing microporous carbon (NC), and used these adsorbents to capture CO₂. Zhao et al. (2019) designed a new hybrid zeolite/AC honeycomb to achieve electrical swing adsorption for CO₂. When the power-on time was extended from 30 to 180 s, electrical swing adsorption achieved 15%-34% purity of CO₂ products and 29%-78% recovery rate. In a vacuum and electrical swing adsorption process, however, the CO₂ purity and recovery rate reached 33% and 72%, respectively, under the conditions of 10 kPa and electrochemical time of < 30 s. Zhang et al. (2018) prepared nitrogen-doped activated carbon (AC-N) using melamine as the nitrogen source and studied its catalytic performance for CO₂. The results revealed that AC-N had 60% and 75% conversion rates for methane (CH₄) and CO₂, respectively. Li et al. (2019) prepared AC from petroleum coke through the potassium post-combustion CO₂ capture from dry flue gas through a direct carbonization and KOH-activation method. The results indicated that AC had a high adsorption capacity of CO₂ by volume. Different from the above adsorbents, Xie et al. (2017) studied the amine-modified carbon aerogel for CO₂ capture, and found that the maximum adsorption capacity was 2.06 mmol g⁻¹ when the amine loading of carbon aerogel was 55 wt.%. Shao et al. (2018a) fabricated the porous carbon with the organic-inorganic hybrid framework thorough the direct carbonization and KOH-activation carbonization of triazine-based hyper-cross-linked polymers. Under the optimum preparation conditions, the surface area could attain 2058 m² g⁻¹. At 298 K and 10 bar, the adsorption capacity of the adsorbent for CO₂ was 590 mg g⁻¹. The CO₂/N₂ selectivity experiment suggested the best Henry’s law S_{CO2/N2} was 16.1. The result showed that the porous carbon with excellent surface area and microporosity structure had good adsorption and selectivity properties for CO₂.

Metal-organic Frameworks

MOFs have been studied for laboratory-scale applications such as gas separation, purification, storage, and heterogeneous catalysis. Zhao et al. (2015) discovered that some MOFs have favorable CO₂ capacity and high CO₂ selectivity with regard to dinitride (N₂). Pai et al. (2019) prepared five MOFs modified by diamine and evaluated post-combustion CO₂ capture from dry flue gas through a vacuum swing adsorption process. Among them, the mmen-Mn₄(dobpcd) and mmen-Mg₄(dobpdc) resulted in CO₂ purity and recovery of 95% and 90%, respectively. In the presence of N₂, these MOFs exhibited higher selectivity for CO₂. Gholidoust et al. (2019) discovered that compared with other solid physical adsorbents, some MOFs had higher CO₂ capture capacities under high pressure but poorer capacities at low CO₂ partial pressures. Elsabawy and Fallatah (2019) prepared an amorphous nickel-(II)-MOF with an ultrahigh BET surface area, and the maximum adsorption capacity was 118.2 mg CO₂ g⁻¹ under the conditions of 30°C and 27 bar. Kong et al. (2018) synthesized a stable layered bisphosphonate, MIL-91(Al), for adsorbing CO₂ under various environmental conditions. The MIL-91(Al) exhibited a maximum adsorption capacity of 2.4 mmol g⁻¹, and higher selectivity for CO₂ than for N₂ and CH₄. Shalini et al. (2018) investigated the potential of MOFs to separate CO₂ from industrial-rich greenhouse gas mixtures. Silva et al. (2018) synthesized a new type of microporous zirconate material using formaldehyde as the solvent. When evaluated on the basis of ideal adsorption solution, the results revealed that the material had higher selective adsorption capacity for CO₂ than for N₂ and CH₄. Zhou et al. (2018b) modified the metal-organic skeleton (HKUST-1) by doping lithium to improve its CO₂ adsorption performance; the modified HKUST-1 with a moderate concentration of lithium nitrate solution as the dopant demonstrated the best adsorption capacity for CO₂. Nguyen et al. (2018) employed the solvothermal method to synthesize three new lanthanide MOFs, namely MOF-590, MOF-591, and MOF-592. Among them, MOF-590 exhibited best conversion efficiency (96%), selectivity (95%) and yield (91%). MOF-591 and MOF-592 had moderate CO₂ adsorption capacities of 36 and 42 cm³ g⁻¹, respectively, at 800 Torr and 298 K.

Composite Materials

Amine-based chemical adsorption has been commercially used for CO₂ separation in the natural gas industry (Rayer et al., 2018). Chen et al. (2009, 2010) synthesized a series of hexagonal mesoporous silica (HMS) materials with different textural porosities by using dodecylamine as a structure-directing agent and loaded polyethyleneimine (PEI) on the surface of HMS to prepare PEI/HMS adsorbents for CO₂ capture. They found that PEI/HMS adsorbents exhibited a CO₂ capture capacity superior to that of other silica-supported amine sorbents and had adequate regeneration performance. Wang et al. (2011) proposed tetraethylennepentamine (TEPA)/MSU-1, which was prepared by incorporating TEPA with self-prepared mesoporous silica MSU-1 using cheap sodium silicate as the silica source; they discovered that the TEPA/MSU-1 has a high adsorption capacity for CO₂. Lai et al. (2018) prepared an inorganic-organic composite solid sorbent by using aminoethylethanolamine to impregnate nanoporous silicic acid and thereby capture CO₂ from flue gas. In another study, PEI was immobilized in a silica substrate to capture CO₂ through a pressure swing adsorption process (An et al., 2009). Recently, Zhao et al. (2014) synthesized molecularly imprinted CO₂ adsorbents (CO₂-MIPs) by using ethanedioic acid, acrylamide, and ethylene glycol dimethacrylate as the template, functional monomer, and cross-linker, respectively.
They investigated the CO₂-MIPs’ ability to separate CO₂ from coal-fired flue gas after desulfurization; under the optimum adsorption temperature of 60°C, the maximum adsorption capacity of CO₂ was 0.57 mmol g⁻¹. The researchers also prepared a series of CO₂-MIPs by employing the molecular self-assembly method. They discovered that MIP1b with a high amine content demonstrated favorable CO₂ capacity compared with MIP3 and remained stable after 50 adsorption-desorption cycles. In an atmosphere of 15% CO₂ and 85% N₂, the CO₂ separation coefficients of all adsorbents were over 100 (Zhao et al., 2012). Nabavi et al. (2017) also synthesized CO₂-MIPs in oil-in-oil emulsion through suspension polymerization. The CO₂-MIPs had selectivity of 49% for CO₂/N₂ at 0.15 bar CO₂ partial pressure, and of 97% at ultralow CO₂ partial pressure. Liu et al. (2018b) synthesized molecularly imprinted solid amine adsorbents through a simple cross-linking reaction by using PEI as the framework, glycidyl ether as the cross-linker, and a CO₂ molecule as the template. The synthesis process of the molecularly imprinted solid amine adsorbent is displayed in Fig. 2. The amine content of MIP-PEI reached 11.41 mmol g⁻¹, but the diffusion resistance of CO₂ was low during the CO₂ adsorption process. The adsorption capacity of MIP-PEI for CO₂ (6.58 mmol g⁻¹) was higher than that of nonimprinted NIP-PEI (5.87 mmol g⁻¹). Water significantly improved the adsorption capacity of CO₂ by promoting the chemical adsorption of CO₂ on solid amine adsorbents. He et al. (2016) prepared a CO₂-imprinted solid amine adsorbent, and the adsorption results revealed that the imprinting of sodium borohydride (NaBH₄) on CO₂ and the reduction of imino groups led the adsorbent to have a high adsorption capacity for CO₂. The solid amine adsorbent based on PEI exhibited a remarkable CO₂ adsorption capacity of 8.56 mmol g⁻¹ in the presence of water at 25°C, which was attributed to its high amine content and strong swelling performance. The regeneration experiment revealed that the CO₂ adsorption capacity remained unchanged after 15 adsorption-desorption cycles, suggesting that the prepared adsorbents had adequate regeneration performance.

In the future, CO₂ will be one of the most important energy sources because it has the potential to be converted into various value-added chemicals, such as methanol, formic acid, carbonates, and carboxylic acid (Yang and Wang, 2015). However, the concentration of CO₂ in the industrial gases is too low and cannot meet the reaction requirement of catalytic conversion. Therefore, developing cheap and functional adsorbents with highly effective adsorption and catalytic properties is the key research direction to develop new and enabling processes. As a whole, new functional adsorbents, cheap and readily available, environment-friendly, selective and reusable, are desirable.

**Hydrogen Sulphide**

H₂S, which is an odorous, poisonous, and corrosive gas, is found in many industrial fields, such as oil production, coal gasification, natural gas, digester gas, and metal smelting (Liu and Wang, 2017a). The use of H₂S not only hinders industrial production and leads to high running costs but also has considerable effects on human health, such as headaches, dyspnea, dizziness, and even asphyxiation, loss of consciousness, and fatality (Gupta et al., 2016). The Occupational Safety and Health Administration (OSHA) categorized H₂S concentrations into three levels of toxicity: 10 ppm or less denotes low toxicity, between 10 ppm and 30 ppm is considered medium toxicity, higher than 30 ppm is high toxicity for humans (OSHA, 2015). Therefore, the removal of H₂S would considerably influence industrial production, environmental quality and the occurrence of human health problems. In addition, raw industrial gases commonly contain H₂S, CO₂, CH₄ and other light alkanes. Among the methods used to remove H₂S, adsorption is regarded as one of the most suitable approaches because of the advantages of low running costs, low corrosion and

![Fig. 2. The synthesis process of molecularly imprinted solid amine adsorbent (Liu et al., 2018).](image-url)
flexibility. In recent years, novel functional adsorbents have been widely studied for their ability to achieve H2S selective separation and removal; as indicated in Table 2, these adsorbents include MOF-based, carbon-based, zeolite-based, metal oxide-based, and composite materials.

**Carbon-based Functional Materials**

AC with abundant pore channels is a well-known adsorption material that can be easily prepared through the carbonization of biomass such as wood, coconut shells and straw. Nowicki et al. (2014) prepared carbonaceous materials by using coffee industry waste and found that an appropriate amount of steam promoted H2S adsorption. Xu et al. (2015) also proved that the introduction of steam increased the adsorption capacity of AC for H2S; the adsorption capacities of AC from sewage sludge and pig manure increased from 43.9 and 59.6 to 47.5 and 65.5 mg g\(^{-1}\), respectively, under a 25wt% humidity. For safer and easier AC preparation, Kazmierczak-Razna et al. (2015) utilized sawdust pellets to synthesize AC through microwave radiation. However, the adsorption capacity of the prepared AC for H2S was 6.2 mg g\(^{-1}\), which may be caused by its low surface area of 426 m\(^2\) g\(^{-1}\). Lau et al. (2015) prepared AC derived from palm shell by loading cerium oxide (CeO\(_2\)) and sodium hydroxide (NaOH) to remove H2S from biogas, and the adsorbent exhibited adequate removal capability for H2S in the presence of CO\(_2\) and CH\(_4\). To enhance the interaction between the carbon surface and H\(_2\)S, Yu et al. (2015) introduced N heteroatoms into the carbon matrix, thereby obtaining nitrogen-doped porous carbons (NPCs) by using \(\alpha\)-glucose and melamine as the carbon source and nitrogen source, respectively. The binding energy result demonstrated that the interaction between pyridinic N and H\(_2\)S (–14.6 kJ mol\(^{-1}\)) was greater than that at the raw carbon surface (–1.8 kJ mol\(^{-1}\)). Fauteux-Lefebvre et al. (2015) prepared iron-functionalized carbon nanofilaments (Fe-CNFs) to study their removal ability for H\(_2\)S at low (100°C) and high (300°C) temperatures. The CNFs acted as not only a sulfur adsorbent but also the carrier for evenly dispersing the iron, which had two roles in the Fe-CNFs: at 100°C, it enhanced the H\(_2\)S retention capacity of the CNFs, and at 300°C, it reacted with H\(_2\)S to form iron sulfide. Balsamo et al. (2016) studied the H\(_2\)S removal property of AC loaded with Zn and Cu and demonstrated that functional AC had superior adsorption ability to that of raw AC. Temperature-programmed desorption of the saturated adsorbents revealed that a combination of H\(_2\)S adsorption and oxidation led to the formation of metal sulfates, thus exhibiting surface reaction complexity. Lee et al. (2017) used goethite (alpha-FeOOH) to modify AC for H\(_2\)S removal from a gas stream. The composite adsorbent had superior removal ability, which is because the introduction of AC as support prevented the agglomeration of alpha-FeOOH and further increased the utilization rate of active sites. Goncalves et al. (2018) evaluated the H\(_2\)S adsorption capacities of ACs with different pore sizes from monocomponent H\(_2\)S and mixture gases of H\(_2\)S, CO\(_2\) and CH\(_4\) and discovered that CO\(_2\) promoted H\(_2\)S adsorption in AC with 8.9 Å pores. To achieve the effective regeneration of adsorbents, Farooq et al. (2018) applied a new regeneration method, electric potential swing desorption, for the regeneration of saturated AC; this method resulted in H\(_2\)S desorption that was three times faster than that resulting from the nonpotential desorption method. In addition, structured carbons, including CNTs and graphene-based materials, are mainly applied in sensor research to detect H\(_2\)S (Asad and Sheikh, 2014; Choi et al., 2014; Duong-Viet et al., 2016; Song et al., 2016; Chu et al., 2018; Liao et al., 2018).

**Zeolite-based Functional Materials**

As a type of porous crystalline material, zeolites have the advantages of high surface area and regular pore size and shape, which have led to their wide application in the fields of adsorption and catalysis. For desulfurization, zeolite-based materials are mainly used as adsorbents because of their high sulfur capacity, strong regeneration performance, and stable structure. Tomadakis et al. (2011) studied the H\(_2\)S separation properties of 4A, 5A, and 13X molecular sieves from CO\(_2\) through pressure swing adsorption. They discovered that the fresh 13X sieves exhibited the highest separation factor (11.9) for H\(_2\)S/CO\(_2\) compared with the 5A (5.4) and 4A (2) zeolites. Maghsoudi et al. (2013) first investigated the adsorption ability of pure silica chabazite (Si-CHA) for H\(_2\)S, CO\(_2\) and CH\(_4\), reporting that the adsorption capacity in order was H\(_2\)S > CO\(_2\) > CH\(_4\). That the H\(_2\)S capacity was 4 mmol g\(^{-1}\) at 25°C and 2 bar. Shah et al. (2015) investigated the separation of seven all-silica zeolite frameworks (CHA, DDR, FER, IFR, MFI, MOR and MWW) for H\(_2\)S/CH\(_4\) through Gibbs ensemble Monte Carlo simulations. When the H\(_2\)S concentration was low, MOR exhibited the highest selectivity and the most favorable enthalpy of adsorption for H\(_2\)S; this was attributed to the favorable interactions between H\(_2\)S and adsorbents in its smaller pores. However, MFI demonstrated the highest degree of selectivity for H\(_2\)S at a high H\(_2\)S concentration (Shah et al., 2015). To improve the H\(_2\)S removal capacity of zeolite, Liu et al. (2015a) prepared a material with the dual functions of adsorption and photocatalysis by combining zeolite with titanium dioxide (TiO\(_2\)). The adsorbent had selective removal ability for H\(_2\)S and could be effectively regenerated through calcination. Hao et al. (2016) also investigated the H\(_2\)S removal ability of TiO\(_2\)-zeolite, and the material exhibited an excellent H\(_2\)S removal rate (97%) and low SO\(_2\) selectivity (9.2%). Sigot et al. (2016b) studied the regeneration property of 13X zeolite through thermal desorption and discovered that zeolite had poor desorption behavior at a lower temperature (350°C) in an inert atmosphere. From an industrial perspective, Liu and Wang (2017b) used cheap attapulgite to synthesize a 4A molecular sieve from zeolite for H\(_2\)S removal. The experimental result indicated that the zeolite had a higher sulfur saturation capacity of 12.4 mg g\(^{-1}\) at 50°C compared with pure sieves, and the saturated 4A zeolite could be effectively regenerated through N\(_2\) purging at 350°C; moreover, the highest removal rate for H\(_2\)S could be maintained at 100% in every cycle experiment. Similarly, Abdullah et al. (2018) utilized local kaolin as the alumina and silica source
### Table 2. Functional adsorbents for H$_2$S removal.

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>Room temperature</th>
<th>T ($^{\circ}$C)</th>
<th>Composition</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC from coffee waste</td>
<td>47.5</td>
<td>28.1</td>
<td>0.1% H$_2$S in air</td>
<td>Asad and Sheikhi (2014)</td>
</tr>
<tr>
<td>AC from sewage sludge</td>
<td>42.6</td>
<td>18.1</td>
<td>1% H$_2$S in air</td>
<td>Liao et al. (2018)</td>
</tr>
<tr>
<td>AC from pig manure</td>
<td>46.7</td>
<td>42.1</td>
<td>1% H$_2$S in N$_2$</td>
<td>Wang et al. (2015)</td>
</tr>
<tr>
<td>CeO$_2$/NaOH/AC from palm shell</td>
<td>49.8</td>
<td>30</td>
<td>H$_2$S in CO$_2$/CH$_4$</td>
<td>Song et al. (2016)</td>
</tr>
<tr>
<td>NPCs</td>
<td>51.8</td>
<td>30</td>
<td>H$_2$S in CO$_2$/CH$_4$</td>
<td>Chu et al. (2013)</td>
</tr>
<tr>
<td>Cu$<em>{0.5}$Zn$</em>{0.5}$/AC</td>
<td>54.2</td>
<td>50</td>
<td>H$_2$S in CO$_2$/CH$_4$</td>
<td>Magirsoudi et al. (2013)</td>
</tr>
<tr>
<td>Darco AC</td>
<td>57.8</td>
<td>30</td>
<td>H$_2$S in N$_2$</td>
<td>Shah et al. (2015)</td>
</tr>
<tr>
<td>Cu$<em>{0.05}$Zn$</em>{0.9}$/AC</td>
<td>61.6</td>
<td>30</td>
<td>H$_2$S in N$_2$</td>
<td>Huang et al. (2015)</td>
</tr>
<tr>
<td>Cu$<em>{0.1}$/Zn$</em>{0.9}$/AC</td>
<td>64.4</td>
<td>30</td>
<td>H$_2$S in N$_2$</td>
<td>Song et al. (2016a)</td>
</tr>
<tr>
<td>Cu$<em>{0.25}$Zn$</em>{0.75}$/AC</td>
<td>67.6</td>
<td>30</td>
<td>H$_2$S in N$_2$</td>
<td>Inagaki et al. (2018)</td>
</tr>
<tr>
<td>Cu$<em>{0.5}$Zn$</em>{0.5}$/AC</td>
<td>70.8</td>
<td>30</td>
<td>H$_2$S in N$_2$</td>
<td>Wu et al. (2016)</td>
</tr>
<tr>
<td>Cu$<em>{0.5}$Zn$</em>{0.5}$/AC</td>
<td>74.1</td>
<td>30</td>
<td>H$_2$S in N$_2$</td>
<td>Wu et al. (2016)</td>
</tr>
<tr>
<td>α-FeOOH/AC</td>
<td>77.3</td>
<td>30</td>
<td>H$_2$S in N$_2$</td>
<td>Shah et al. (2015)</td>
</tr>
<tr>
<td>Cu/AC from rice husk</td>
<td>80.6</td>
<td>30</td>
<td>H$_2$S in N$_2$</td>
<td>Huang et al. (2015)</td>
</tr>
<tr>
<td>AC from tobacco stem</td>
<td>84.0</td>
<td>30</td>
<td>H$_2$S in N$_2$</td>
<td>Sigot et al. (2016a)</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>87.3</td>
<td>30</td>
<td>H$_2$S in N$_2$</td>
<td>Cimino et al. (2018)</td>
</tr>
<tr>
<td>ZnO/Na-A zeolite</td>
<td>89.3</td>
<td>30</td>
<td>H$_2$S in N$_2$</td>
<td>Li et al. (2014)</td>
</tr>
<tr>
<td>Cu/13X zeolite</td>
<td>92.3</td>
<td>30</td>
<td>H$_2$S in N$_2$</td>
<td>Song et al. (2011)</td>
</tr>
<tr>
<td>Ag/NaX zeolite</td>
<td>94.1</td>
<td>30</td>
<td>H$_2$S, COS, CO$_2$ in N$_2$</td>
<td>Lange et al. (2015)</td>
</tr>
<tr>
<td>5Ce$_5$Mn/ZSM-5</td>
<td>97.3</td>
<td>30</td>
<td>H$_2$S in N$_2$</td>
<td>Hamon et al. (2011)</td>
</tr>
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<td>0.10Co/NaX zeolite</td>
<td>99.5</td>
<td>30</td>
<td>H$_2$S in N$_2$</td>
<td>Kim et al. (2014)</td>
</tr>
<tr>
<td>0.15Co/NaX zeolite</td>
<td>101.7</td>
<td>30</td>
<td>H$_2$S in N$_2$</td>
<td>Kim et al. (2014)</td>
</tr>
<tr>
<td>ZnAl-MMO</td>
<td>104.9</td>
<td>30</td>
<td>H$_2$S in N$_2$</td>
<td>Cimino et al. (2018)</td>
</tr>
<tr>
<td>MCM-41@ZIF-8</td>
<td>107.3</td>
<td>30</td>
<td>H$_2$S in N$_2$</td>
<td>Al-Jadir and Spierstein (2018)</td>
</tr>
<tr>
<td>SBA-15@ZIF-8</td>
<td>110.6</td>
<td>30</td>
<td>H$_2$S in N$_2$</td>
<td>Al-Jadir and Spierstein (2018)</td>
</tr>
<tr>
<td>ZnAl-MOMO</td>
<td>113.9</td>
<td>30</td>
<td>H$_2$S in N$_2$</td>
<td>Blatt et al. (2017)</td>
</tr>
<tr>
<td>13X zeolite</td>
<td>117.2</td>
<td>30</td>
<td>H$_2$S in N$_2$</td>
<td>Liu et al. (2017)</td>
</tr>
</tbody>
</table>
instead of pure chemicals to synthesize low-cost Na-A zeolite and then introduced zinc oxide (ZnO) into its pore channels to remove H2S from the biogas. On the basis of previous work on NaX zeolite, Chen et al. (2018a) used Zn, Co, and Ag to modify NaX zeolite though the ion-exchange method; the NaX modified by Ag had the highest adsorption capacity for H2S (1.53 mmol g⁻¹). Tran et al. (2016) also investigated Co-doped NaX zeolite. To study the effects of the pore structures and wall thickness of zeolites on H2S removal, Cara et al. (2018) used maghemite (γ-Fe₂O₃)-modified hexagonal MCM-41 and cubic MCM-48. They discovered that the adsorbent based on hexagonal MCM-41 had more stable adsorption and superior regeneration performance compared with that based on cubic MCM-48.

**Metal Oxide-based Functional Materials**

In solid adsorbents for H2S removal, the reaction temperatures of carbon-based materials are relatively low; nevertheless, the desulfurization process is discontinuous. Although their reaction temperatures are relatively high, metal oxides are the most widely used adsorbents in practical applications because of their high affinity for H2S. However, their disadvantages of low surface areas and lack of pores lead to poor regeneration and reutilization. To solve these problems, many scholars have studied the desulfurization performance of metal oxides loaded on solid matrices. Kim et al. (2014) prepared carbon nanofiber webs loaded with ZnO through electrospinning, as presented in Fig. 3; the webs demonstrated a desulfurization ability that was three times greater than that of pure ZnO adsorbent. Sun et al. (2014a) used ferric oxides to modify the surface of AC and reported that the sulfur saturation capacity reached 50.1%. Wu et al. (2018) studied the H2S removal property of a Zn-Al mixed metal oxide (Zn-Al-MMO) derived from layered double hydroxide in hot coal gas desulfurization. The adsorbent demonstrated an adequate sulfur capacity of 318.8 mg g⁻¹, and X-ray photoelectron spectroscopy (XPS) indicated the production of elemental sulfur during the desulfurization process, as shown in Fig. 4. Cimino et al. (2018) dispersed Zn and Cu oxides onto γ-Al₂O₃ and studied the desulfurization ability at room temperature; their experiments revealed that Cu₀.₅Zn₀.₅/γ-Al₂O₃ had the best adsorption capacity (27.9 mg g⁻¹) for H2S under both dry and humid conditions.

**MOF-based Functional Materials**

MOFs are a type of porous crystalline materials consisting of a combination of organic ligands and metal ions or clusters. Because of their unique advantages of adjustable functionality, high porosity, and controllable composition, MOFs have attracted a considerable amount of attention in various fields, such as gas adsorption and catalysis. Hamon et al. (2011) compared the desulfurization performance of MIL-53(Cr) and MIL-47(V) at 30°C and discovered that the interactions of H2S with both MIL-53(Cr) and MIL-47(V) were relatively weak and that the simulated adsorption enthalpies for H2S were in decreasing order, MIL-53(Cr) (narrow pore) > MIL-47(V) > MIL-53(Cr) (large pore). Nickeral et al. (2014) investigated the H2S removal ability
of metal salts (Cu\textsuperscript{2+}, Ni\textsuperscript{2+} and Co\textsuperscript{2+}) loaded on UiO-67; the adsorbent loaded with 86.8% Cu(NO\textsubscript{3})\textsubscript{2} had the highest H\textsubscript{2}S capacity (7.8 wt.%). In addition, polyoxometalates (POMs) are widely used as catalysts in desulfurization because of their excellent redox ability. However, because pure POMs are solid materials and thus have low surface area, they do not exhibit ideal removal of H\textsubscript{2}S, because of a poor utilization rate of activated sites. Therefore, some scholars have attempted to combine MOFs with POMs, using MOFs as support to improve the desulfurization and regeneration of POMs. Song et al. (2011) investigated a material that combined a Keggin-type POM ([CuPW\textsubscript{11}O\textsubscript{39}]\textsuperscript{5–}) with MOF-199 for H\textsubscript{2}S removal. Solid octasulfur (S\textsubscript{8}) was produced by using the composite, whereas pure MOF-199 did not produce S\textsubscript{8}. Lange et al. (2015) also investigated the removal performance of the aforementioned composite material for H\textsubscript{2}S and methyl parathion at room temperature. Demir et al. (2017) evaluated the selective H\textsubscript{2}S adsorption of functionalized UiO-66 with a series of functional groups through computational methods. Al-Jadir and Siperstein (2018) assessed the selective H\textsubscript{2}S/CH\textsubscript{4} adsorption of UiO-66, UiO-67, and UiO-68 to study the effects of the pore sizes of MOFs on H\textsubscript{2}S removal. The result revealed that linkers had no obvious influence on macroscopic properties at low pressures, but the differences among linkers increased at high pressures. Analysis of the selective adsorption parameter revealed that UiO-67 had the greatest potential for separating H\textsubscript{2}S from natural gas. Sánchez-González et al. (2018) prepared Mg-CUK-1 using water as the solvent for H\textsubscript{2}S and CO\textsubscript{2} adsorption. An adsorption experiment demonstrated that the ecofriendly adsorbent could achieve reversible adsorption of H\textsubscript{2}S; a regeneration experiment revealed that the adsorption performance could be maintained after multiple cycles, and long-range crystallinity could be retained during the regeneration process. Liu et al. (2017) investigated the selective separation of 11 MOFs for H\textsubscript{2}S
and CO$_2$ reporting that Mg-MOF-74, MIL-101(Cr), UiO-66, ZIF-8, and Ce-BTC had completely reversible physical adsorption of H$_2$S; among them, MIL-101(Cr) exhibited the best separation performance for H$_2$S/CO$_2$. Liu et al. (2018a) reported a novel hybrid membrane, a rare earth, face-centered cubic-MOF (RE-fcu-MOF), modified by polymers, to remove H$_2$S and CO$_2$ from natural gas. Recently, Huang and Wang (2019) reported core-shell structure H$_2$S-imprinted polymers loaded on a polyoxometalate@Zr-based metal-organic framework using water as a substitution template to achieve the selective removal of H$_2$S from gases containing CO$_2$. They found that this functional adsorbent had excellent separation for H$_2$S/CO$_2$, and could transform H$_2$S to sulphur. The results suggested that the adsorbent had excellent selectivity and desulfurization properties.

Nitrogen Oxides

NO$_x$ compounds are the products of reactions between nitrogen and oxygen in high-temperature combustion processes, such as those associated with internal combustion engine exhaust and power station boilers. NO$_x$ is a general term for all nitrogen oxides, including nitric oxide (NO) and nitrogen dioxide (NO$_2$), which belong to a type of air pollutants that can cause smog and acid rain (Hu et al., 2019). In addition, NO$_2$ can react with ammonia, moisture, and other compounds to produce nitric acid, which causes considerable harm to lung tissue. Thus, the OSHA stipulated that the permissible exposure levels of NO and NO$_2$ were 25 and 5 ppm, respectively (Decoste and Peterson, 2014). Current NO$_x$ removal methods mainly include adsorption, absorption, catalytic decomposition, and selective catalytic reduction (Jiang et al., 2018). Adsorption has been widely studied for NO$_x$ removal because of its advantages of a relatively high removal rate, no secondary pollution, and no energy loss. Therefore, various functional adsorbents, including MOF-based, carbon-based, zeolite-based, and composite materials (listed in Table 3), have been proposed to achieve highly effective removal of NO.

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>NO$_2$ (mg g$^{-1}$)</th>
<th>NO (mg g$^{-1}$)</th>
<th>composition</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC</td>
<td>39</td>
<td>NO$_2$ in N$_2$</td>
<td>Yu et al. (2018)</td>
<td></td>
</tr>
<tr>
<td>C$_{CO2}$</td>
<td>129</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C$_{Zn}$</td>
<td>124</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GAC</td>
<td>127</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>GAC-O</td>
<td>78</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GAC-O-T</td>
<td>136</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ordered mesoporous carbon (OMC)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ce-OMC</td>
<td>16.35</td>
<td>NO, O$_2$ in Ar</td>
<td>Ebrahim et al. (2014)</td>
<td></td>
</tr>
<tr>
<td>AC from sawdust</td>
<td>54.7</td>
<td>NO$_2$ in N$_2$</td>
<td>Choi et al. (2014)</td>
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<tr>
<td>AC</td>
<td>11.3</td>
<td>NO$_2$ in N$_2$</td>
<td>Mendt et al. (2017)</td>
<td></td>
</tr>
<tr>
<td>Cu/AC</td>
<td>42.39</td>
<td>NO, O$_2$ in N$_2$</td>
<td>Zhao et al. (2017)</td>
<td></td>
</tr>
<tr>
<td>Zn/AC</td>
<td>34.23</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M5AC7</td>
<td>16.3</td>
<td>0.1 % of NO$_2$</td>
<td>Chen et al. (2014)</td>
<td></td>
</tr>
<tr>
<td>M7AC7</td>
<td>13.4</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>M5AC8</td>
<td>12.0</td>
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<td></td>
</tr>
<tr>
<td>M7AC8</td>
<td>29.2</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>A-N$_2$-D-N$_2$</td>
<td>11.1</td>
<td>NO, O$_2$ in N$_2$</td>
<td>Severa et al. (2015)</td>
<td></td>
</tr>
<tr>
<td>A-O$_2$-D-N$_2$</td>
<td>11.4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A-N$_2$-O$_2$-D-N$_2$</td>
<td>11.4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>UiO-66 (dry)</td>
<td>73</td>
<td>NO$_2$ in N$_2$</td>
<td>Babu et al. (2016)</td>
<td></td>
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<tr>
<td>UiO-66 (moist)</td>
<td>40</td>
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<td></td>
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<tr>
<td>UiO-67 (dry)</td>
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<tr>
<td>UiO-67 (moist)</td>
<td>118</td>
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<td></td>
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<tr>
<td>Urea/UiO-66 (dry)</td>
<td>37</td>
<td>NO$_2$ in N$_2$</td>
<td>Sun et al. (2016)</td>
<td></td>
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<td>Urea/UiO-66 (moist)</td>
<td>101</td>
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<tr>
<td>Melamine/UiO-66 (dry)</td>
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<td></td>
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<tr>
<td>Melamine/UiO-66 (moist)</td>
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<td>Urea/UiO-67 (dry)</td>
<td>74</td>
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<td></td>
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<tr>
<td>Urea/UiO-67 (moist)</td>
<td>154</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Melamine/UiO-67 (dry)</td>
<td>41</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Melamine/UiO-67 (moist)</td>
<td>93</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>MIPa (AA as functional monomers)</td>
<td>0.121</td>
<td>NO in N$_2$</td>
<td>Iberahim et al. (2018)</td>
<td></td>
</tr>
<tr>
<td>MIPb (AAM as functional monomers)</td>
<td>0.112</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Carbon-based Functional Materials

Belhachemi et al. (2014) compared the NO$_2$ adsorption capacities of different ACs, which were prepared through physical and chemical activation of date pits or obtained through the modification of commercialized AC.
results demonstrated that the AC from date pits had a high NO$_2$ adsorption capacity (129 mg g$^{-1}$) similar to that of commercialized adsorbents. They also discovered that the presence of strong acidic groups such as carboxylic acids, anhydrides, and lactones inhibited the reduction of NO$_2$ into NO. Wang et al. (2014) prepared AC fibers loaded with manganese dioxide (MnO$_2$) and studied the effect of the amount of MnO$_2$ loading on the NO removal efficiency at room temperature. They found that appropriate amounts of MnO$_2$ can improve the NO removal efficiency of AC; moreover, the oxidation efficiency of NO reached 30.6% when the amount of MnO$_2$ was 3.64 wt%. Saputro et al. (2017) investigated the selectivity adsorption of the ZnO (0002) surface for NO and carbon monoxide by performing density functional theory (DFT) calculations. They found that a clean ZnO (0002) surface exhibited better selectivity for NO than for CO. Sager et al. (2014) prepared AC under different carbonization and activation temperatures to analyze the effects of these two factors on NO$_2$ removal. Under dry conditions, AC that was prepared using carbonization and activation temperatures of 700°C and 800°C, respectively, had the best NO$_2$ adsorption capacity of 29.2 mg g$^{-1}$. However, AC that was prepared using carbonization and activation temperatures of 500°C and 700°C, respectively, exhibited the best removal capacity of 102.1 mg g$^{-1}$ under mix-dry conditions. Guo et al. (2018) conducted the first study that used DFT to investigate the NO and NO$_2$ adsorption behavior of pristine and B-atom-embedded $\gamma$-graphene. B-atom-embedded $\gamma$-graphene had stronger chemical interactions with NO and NO$_2$ than pristine $\gamma$-graphene.

Zeolite-based Functional Materials

Sun et al. (2014b) compared the performance of 12 porous materials as adsorbents for removing NO$_x$ from flue gases; these materials comprised four all-silica zeolites, six MOFs, and two zeolitic imidazolate frameworks (ZIFs). The results indicated that Cu-BTC had the best adsorption of NO$_x$, and the other adsorbents could not provide effective separation with large adsorption capacities for NO$_x$; this shortcoming was attributed to the small dipole moment of NO$_x$. Skarlis et al. (2014) investigated the storage of NO$_x$ on Fe-BEA zeolite through Fourier transform infrared spectroscopy. Liu et al. (2015b) proposed a novel and ultrafast method to prepare high-silica zeolite SSZ-13 in 10 min. After copper ion exchange, the prepared SSZ-13 exhibited excellent removal of NO$_x$. Pan et al. (2015) studied the NO$_x$ adsorption of Fe/zeolites in the presence of SO$_2$, CO$_2$ and water (H$_2$O). The results revealed the NO$_x$ adsorption capacities of the Fe/zeolite, which in descending order were as follows: Fe/MOR > Fe/FER > Fe/ZSM-5 > Fe/Beta; moreover, the adsorption capacity of Fe/MOR for NO$_x$ was approximately 3.2 mg g$^{-1}$. In the presence of 100-ppm SO$_2$, 10% CO$_2$, and 10% H$_2$O, the adsorption capacity of Fe/MOR for NO$_x$ decreased to approximately 2.0 mg g$^{-1}$.

Yu et al. (2018b) investigated the NO removal of HZSM-5 from flue gas through adsorption-plasma processes, including A-N$_2$-D-N$_2$ (adsorption-N$_2$ flushing-nonthermal plasma decomposition-N$_2$ flushing), A-O$_2$-D-N$_2$ and A-N$_2$O$_2$-D-N$_2$.

MOF-based Functional Materials

Ebrahim et al. (2012) studied the NO$_2$ adsorption properties of UiO-66 and UiO-67 at ambient temperatures. An experiment comparing UiO-66 and UiO-67 indicated that the size and chemistry of a ligand influenced the adsorption property. In addition, UiO-66 demonstrated a more favorable adsorption capacity in dry conditions than in moist conditions, suggesting that water has a negative effect on NO$_x$ adsorption. By contrast, the adsorption capacity of UiO-67 was higher under moist conditions than under dry conditions. On the basis of relevant research, the group utilized urea and melamine with NH$_3$ groups to modify UiO-66 and UiO-67 and thus be capable of effectively removing NO$_2$ under either dry or moist conditions. A series of experiments revealed that the adsorption capacity of every adsorbent was higher under moist conditions than under dry conditions. The adsorption capacities of both UiO-66 and UiO-67 modified with urea exhibited obvious increases compared with pure UiO-66 and UiO-67 under moist conditions. However, the introduction of melamine negatively affected the adsorption performance of UiO-66 and UiO-67 for NO$_x$ (Ebrahim et al., 2014). Mendt et al. (2017) investigated the NO adsorption of MIL-100 (Al) at low temperatures by employing pulsed electron paramagnetic resonance spectroscopy and DFT calculations.

Composite Materials

Zhao et al. (2016) synthesized NO-MIPs by using methanoic acid as a dummy template because the solubility of NO is low in organic solvents under ambient conditions. In their study, they used acrylic acid (AA) and acryl amide (AAM) as functional monomers to prepare MIPa and MIPb, respectively. The results demonstrated that the NO adsorption ability of MIPa was superior to that of MIPb, suggesting that the acidic functional monomer AA is beneficial for improving NO adsorption capacity. Selectivity experiments revealed that O$_2$ had no influence on NO adsorption capacity; the introduction of CO$_2$ and SO$_2$ led to the decrease of NO adsorption capacity. On the basis of their previous study, the group prepared two groups of NO-MIPs using methanoic acid, acetic acid, and ethanoic acid as templates and AA and AAM as functional monomers. They discovered that the adsorbents with different functional monomers and templates had different pore sizes and surface areas, resulting in variations in adsorption capacity (Zhao and Wang, 2017).

Sulfur Dioxide

SO$_2$ is a poisonous and colorless gas that is released mainly by the combustion of fossil fuel and waste incineration. SO$_2$ can react with water vapor, O$_2$, and other compounds to form acid rain. Moreover, it can cause the development of respiratory diseases and severely harm human organs such as stomachs, livers, and kidneys.
removal is key method for improving air quality and human health (Hussain and Luo, 2019). In the past few years, researchers have proposed novel functional adsorbents such as carbon-based, zeolite-based, MOF-based, and composite materials to remove SO2, as indicated in Table 4.

**Carbon-based Functional Materials**

Peng et al. (2014) studied the selective adsorption ability of AC for SO2 and the desorption behavior of AC under microwave radiation. The selectivity result indicated that the presence of other gases in flue gas reduced the adsorption capacity to 28.73 mg g⁻¹ for SO2. Yi et al. (2014) investigated the SO2, NO and CO2 removal abilities of coconut shell ACs modified with Cu, Ca, Mg, and Zn, respectively. They reported that the following order of SO2 adsorption capacity of each adsorbent: Zn/AC < Cu/AC < Mg/AC < Ca/AC. Tailor et al. (2014) prepared a series of adsorbents, including PEI, and poly(propyleneimine) second and third generation ((PPI-G2 and PPI-G3, respectively) dendrimers supported on SBA-15 and MCM-41, and investigated the selective adsorption ability of each material for SO2. In the presence of mixture gas of SO2 and N2, the MCM-41 loaded with PPI-G3 exhibited the best selectivity for SO2/N2 compared with the other adsorbents. In addition, the SO2 adsorption of MCM-41 loaded with PPI-G3 or PEI increased considerably under 19% relative humidity. Zhang et al. (2015) investigated the SO2 adsorption of modified graphene oxides by performing DFT calculations and discovered that hydroxyl groups on graphene oxides can not only improve SO2 adsorption but also promote the oxidation of SO2 to SO3. To adsorb trace SO2, Ling et al. (2015) utilized a one-pot fabrication method of a calcium oxide (CaO)-carbon foam adsorbent, as shown in Fig. 5; the adsorbent had a hierarchical porous structure and retained a stable structure even after five cycles.

Severa et al. (2015) prepared ionic liquids (ILs) supported on AC to study SO2 adsorption. They discovered that ILs based on acetate and lactate imidazolium anions demonstrated favorable adsorption capacity for SO2 compared with those based on sulfate and halide anions. Sun et al. (2016)

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>SO2 (mg g⁻¹)</th>
<th>Temperature (°C)</th>
<th>composition</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-OMC</td>
<td>119.1</td>
<td>25</td>
<td>SO2 in N2</td>
<td>Song et al. (2014)</td>
</tr>
<tr>
<td>MnO2</td>
<td>200</td>
<td>250</td>
<td>SO2, CO2, O2 and H2O</td>
<td>Savage et al. (2016)</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>450</td>
<td></td>
<td></td>
</tr>
<tr>
<td>GO</td>
<td>150</td>
<td>25</td>
<td>SO2</td>
<td>Zhang et al. (2016)</td>
</tr>
<tr>
<td>Pure PC</td>
<td>12.2</td>
<td>25</td>
<td>SO2 in N2</td>
<td>Glomb et al. (2017)</td>
</tr>
<tr>
<td>4.25% NPC</td>
<td>24.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7.57% NPC</td>
<td>35.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10.2% NPC</td>
<td>48.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Macro and micro GO</td>
<td>190.1</td>
<td>20</td>
<td>SO2</td>
<td>Elder et al. (2018)</td>
</tr>
<tr>
<td>POSB</td>
<td>10.04</td>
<td>400</td>
<td>SO2 in N2</td>
<td>Mon et al. (2018)</td>
</tr>
<tr>
<td>MDEA/AC after CO2 activation</td>
<td>156.22</td>
<td>120</td>
<td>1% SO2 in N2</td>
<td>Carter et al. (2018)</td>
</tr>
<tr>
<td>PILs-xerogels</td>
<td>514</td>
<td>25</td>
<td>SO2 in N2</td>
<td>Xia et al. (2018)</td>
</tr>
<tr>
<td>Propyldiethanolamine/MCM-41</td>
<td>181.8</td>
<td>23</td>
<td>1% SO2 in N2</td>
<td>Khan et al. (2000)</td>
</tr>
<tr>
<td>Triethylamine/SBA-15</td>
<td>146.3</td>
<td>25</td>
<td>SO2 in N2</td>
<td>Quijano et al. (2011)</td>
</tr>
<tr>
<td>MF3-300(In)</td>
<td>529.9</td>
<td>25</td>
<td>SO2, CO2 in N2</td>
<td>Wang et al. (2017b)</td>
</tr>
<tr>
<td>MFM-601</td>
<td>787.2</td>
<td>25</td>
<td>SO2</td>
<td>Zhou et al. (2018)</td>
</tr>
</tbody>
</table>

**Fig. 5.** SEM images of CaO/ carbon foam before heat treatment (a), before use (b) and after 5 cycles (c) (Ling et al., 2015).
investigated how the amount of nitrogen loaded on the surface of NPs affects SO2 adsorption. The results demonstrated that the introduction of N can noticeably enhance the SO2 adsorption capacity of porous carbon. On the basis of research on the use of palm oil mill sludge, Ibrahim et al. (2018) prepared biochar through the pyrolysis method and studied its SO2 adsorption ability. To further improve the SO2 adsorption of AC, Shao et al. (2018b) used CO2 activation and methyl diethanolamine (MDEA) impregnation to modify AC; the SO2 adsorption capacity of AC increased from 57.78 to 156.22 mg g⁻¹ after MDEA impregnation, demonstrating that MDEA impregnation treatment can effectively enhance the adsorption capacity of AC. Xia et al. (2018) designed a highly cross-linked nonporous poly(ionic liquid) xerogels through the polymerization of gemini ILs. Selectivity experiments demonstrated that the xerogels had no adsorption ability for CO2, CH4, or N2, but the adsorption capacity for SO2 reached 514 mg g⁻¹. The SO2 adsorption capacity exhibited no remarkable changes after 50 cycle experiments. The results demonstrated that the prepared xerogels had remarkable adsorption performance for SO2 and excellent regeneration ability.

MOF-based Functional Materials

Using the grand canonical Monte Carlo simulation method, Song et al. (2014) studied the SO2 adsorption properties of MOFs with different pore sizes and topologies, including IRMOF-1, -8, -9, -10, and -15; MOF-177 and -505; Cu-BTC; MIL-47; and ZIF-8. The simulation results revealed that the MOFs with pore sizes larger than 0.4 nm exhibited excellent adsorption of SO2. Savage et al. (2016) prepared porous MOF (MFM-300 (In)) and studied the selective adsorption of SO2 with interference of CO2, CH4, and N2 individually. The results demonstrated that MFM-300 (In) had a high SO2 adsorption capacity of 529.9 mg g⁻¹ and favorable selectivity for SO2/CO2 (60), SO2/CH4 (42.5), and SO2/N2 (5000) under ambient conditions. Mounfield et al. (2016) studied the adsorption performance of MIL-125 and MIL-125-NH2 for SO2 at 2.7 bar and found that the adsorption capacities were 10.9 and 10.3 mmol g⁻¹, respectively. In addition, they discovered that MIL-125-NH2 can retain a stable structure under dry, humid, and aqueous SO2 conditions. However, MIL-125 degraded when exposed to humid and aqueous SO2, indicating that its stability requires improvement. Considering that ZIFs demonstrate favorable stability with respect to temperature and humidity, Bhattacharyya et al. (2016) studied the adsorption performance of ZIF-8 for SO2 and analyzed its stability under dry, humid, and aqueous SO2 conditions. The SO2 saturation capacity was approximately 518.4 mg g⁻¹ at 25°C and 2.5 bar in a dry environment. Characterization revealed that dry SO2 had no influence on the stability of ZIF-8 at room temperature, humid SO2 attacked the structure of ZIF-8, and ZIF-8 exhibited no structural degradation under aqueous SO2 conditions. Ranbar and Taher (2016) studied the adsorption property of Ni-MOF-74 for SO2 at 25°C under the pressure range of 0 to 4 bar. The SO2 adsorption capacity of Ni-MOF-74 increased in with the pressure, and the maximum capacity of 105.06 mmol g⁻¹ was reached at 4 bar. Zhang et al. (2016) compared the SO2 adsorption capacities of four MOFs loaded with polyacrylonitrile (PAN)—PAN/ZIF-8, PAN/Mg-MOF-74, PAN/MOF-199, and PAN/UIO-66—NH2—and reported that the PAN supported by the four MOFs had an adsorption ability that was superior to that of pure PAN; moreover, PAN/UIO-66-NH2 exhibited the highest adsorption capacity of approximately 11 mg g⁻¹ at 25°C. Glomb et al. (2017) prepared four dicarboxylate modified MOFs for SO2 adsorption: 3D-[Zn6(μ4-O)(L1)], 2D-[Zn2(L1)2(DEF)2·2.5DEF], [Zn4(L1)2(bipy)] and [Zn2(L1)2(bipy)]. Among them, [Zn2(L1)2(bipy)] exhibited the highest SO2 adsorption capacity of 10.9 mmol g⁻¹ at 293 K and 1 bar. Elder et al. (2018) investigated the adsorption performance of copper benzenedicarboxylate (CuBDC), zinc benzenedicarboxylate (ZnBDC) and cobalt benzenedicarboxylate (CoBDC) for humid SO2; 88% of the SO2 was adsorbed by CuBDC in a reduced oxidation state. Moreover, the structures of ZnBDC and CoBDC underwent changes when exposed to SO2; this indicated that they were unsuitable for application in SO2 removal. Mon et al. (2018) proposed a novel 3D MOF with hydrated barium cations for selective adsorption of SO2, and the SO2 adsorption capacity reached 2.5 mmol g⁻¹ at 303 K and 0.025 bar. Carter et al. (2018) reported that a novel MFM-601 had a record-high SO2 adsorption capacity of 12.3 mmol g⁻¹ at 298 K and 1.0 bar; furthermore, the adsorbent exhibited fully reversible and highly selective adsorption for SO2 with respect to CO2 and N2.

Cui et al. (2017) designed an inorganic anion-pillared hybrid porous adsorbent (silicon hexafluoride, SiF6⁻) to achieve the efficient capture of SO2; a high SO2 adsorption capacity of 704.6 mg g⁻¹ was reached at 1.01 bar, and an excellent SO2/CO2 selectivity of 89% was achieved at a low pressure (0.002 bar).

Volatile Organic Compounds

VOCs are a type of common air pollutant emitted through production in chemical, petrochemical, and related industries; some examples of these pollutants are benzene, toluene, hexane, CH4, and sulfur compounds (Khan and Ghoshal, 2000). Deng et al. (2018) analyzed 36 VOCs from Longchuan Tunnel, Hefei, in eastern China, to study the atmospheric VOC pollution in urban areas of China. They found that alkanes (mainly branched alkanes) accounted for the largest proportion of 52%, and benzene homologues took the second place. These gases cause serious harm to the environment and human health, including by causing nausea, exposing humans to carcinogens, and contributing to global warming (Quijano et al., 2011). Therefore, many absorbents and catalysts have been developed for the removal of VOCs. For example, some researchers have investigated the potential of using ILs as absorbents for VOC removal (Park et al., 2017; Wang et al., 2017a). Quijano et al. (2011) assessed the feasibility of using imidazol ILs for VOC removal in a multiphase bioreactor. The results suggested that the acclimation of VOCs by microorganisms alone was insufficient for achieving effective biodegradation in heterogeneous systems such as nonaqueous-phase ILs.
Wang et al. (2017b) investigated the adsorption potential of a [Bmim] [NTf2] absorbent for toluene. The solubility of toluene in [Bmim] [NTf2] was 61.5% at 20°C and standard atmospheric pressure. The maximum adsorption rate of toluene for [Bmim] [NTf2] was 98.3%. At a concentration of 300 ppm and flow rate of 50 mL min⁻¹, the adsorption rate of toluene could exceed 94% at 20°C. The results indicated that [Bmim] [NTf2] absorbents can remove toluene easily. Biard et al. (2018) simulated the countercurrent adsorption of four hydrophobic VOCs and two heavy organic solvents, namely polydimethylsiloxane (PDMS) 50 and di-(2-ethylhexyl) adipate (DEHA), using fixed volume packed columns. VOC biodegradation experiments revealed that 5% (v/v) IL was toxic to activated sludge organisms, and the combination of IL and VOC may produce a synergistic toxic effect. After the domestication of target VOCs, only toluene biodegradability increased significantly in response to IL. The results revealed that ILs could strongly inhibit microbial activity in the presence of VOCs for more than 24 hours. Mo et al. (2019) reported that photocatalytic oxidation is a promising method for the removal of VOCs and reviewed the purification status of VOCs in indoor air. Park et al. (2017) investigated several strategies for removing VOCs from the atmosphere. VOCs could be effectively captured using activated carbon fiber (ACF) and mesoporous silica with high surface areas. Biard et al. (2016) utilized a simple dynamic adsorption method to evaluate the mass transfer performance of solvents for selective removal of VOCs. Four hydrophobic VOCs (toluene, acetone, dichloromethane, and isopropanol) were absorbed by water and two heavy organic solvents, namely DEHA and PDMS. The water had high selectivity, and the two organic solvents, especially DEHA, demonstrated strong binding affinity for all VOCs.

Fang et al. (2016) prepared a series of new paraffin/surfactant/water emulsion (PSW) materials, and studied their potential for VOC removal. PSW-5 (5%, v/v) had higher adsorption efficiency for toluene than did other absorbents. The adsorptivity of PSW-5 towards toluene reached 82.42%, and it remained 82.42% after three cycles. Yu et al. (2018a) selected benzene, toluene and xylene (BTX) as VOC representatives to measure the vapor-liquid equilibrium of BTX+ [EMIM] [Tf2N] mixtures. Cardoso et al. (2008) prepared ACs using cork powder waste as the raw material, and studied the adsorption potential of ACs for VOCs. Three ACs were prepared through the chemical activation of cork powder waste with KOH as the activator. The adsorbent had a large surface area exceeding 1300 m² g⁻¹ and a micropore volume greater than 0.5 cm³ g⁻¹. They discovered that the adsorbent at the highest activation temperature and KOH dosage exhibited the best removal and selective adsorption performance for VOCs.

Wang et al. (2016) developed hydrophobic functionalized SBA-15 through synthesis and post-modification of trimethylchlorosilane (TMCS) to remove VOCs. The adsorption and desorption properties of SBA-15-TMCS under various static and dynamic conditions were studied. The designed SBA-15-TMCS had high VOC adsorption capacity and recycling capacity. Zhou et al. (2018a) studied the effect of membrane adsorption on VOC recovery from oil and gas. The removal rate of heat-conducting oil absorbent was 86.50%, and that of an AbsFOV-97 absorbent was 90.44%. The performance of ABFOV-97 was superior to that of the heat-conducting oil. Moreover, a lower gas flow rate led to higher recovery from oil and gas. When the gas flow rate was less than 50 mL min⁻¹, the hydrocarbon removal rate was approximately 99.50%.

In addition, Iuga et al. (2011) used pyridine as the target molecules and MAA as the functional monomers to form a specific MIP, which demonstrated had strong selectivity for pyridine in the presence of toluene and benzene.

SUMMARY

In conclusion, the adsorption and regeneration properties of adsorbents require improvement in terms of working adsorption capacity, cycle life, and stability. To obtain a techno-economic system, the development of a new type of highly efficient absorbent is necessary. In addition, few studies have been conducted in recent years on MIPs in the field of gas separation and removal, especially that of H₂S, SO₂, and NO. Therefore, designing functional absorbents with excellent selectivity, adsorption and regeneration properties should be the focus of future research.

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