

Removal of Hydrogen Sulfide (H₂S) Using MOFs: A Review of the Latest Developments [†]

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Abstract: The removal of hydrogen sulfide (H₂S) from gas streams with varying overall pressure and H₂S concentrations is a long-standing challenge faced by the oil and gas industries. The present work focuses on H₂S capture using metal–organic frameworks (MOFs), in an effort to shed light on their potential as adsorbents in the field of gas storage and separation. MOFs hold great promise as they make possible the design of structures from organic and inorganic units, but also, they have provided an answer to a long-time challenging issue, i.e., how to design extended structures of materials. Moreover, the functionalization of the MOF's surface can result in increased H₂S uptake. For example, the insertion of 1% of a fluorinated linker in MIL-101(Cr)-4F(1%) allows for enhanced H₂S capture. Although noticeable efforts have been made in studying the adsorption capacity of H₂S using MOFs, there is a clear need for gaining a deeper understanding in terms of their thermal conductivities and specific heats in order to design more stable adsorption beds, experiencing high exothermicity. Simply put, the exothermic nature of adsorption means that sharp rises in temperature can negatively affect the bed stability in the absence of sufficient heat transfer. The work presented herein provides a detailed discussion by thoroughly combining the existing literature on new developments in MOFs for H₂S removal, and tries to provide insight into new areas for further research.

Keywords: MOFs; H₂S; adsorption; gas sweetening

1. Introduction

The removal of hydrogen sulfide (H₂S), released from different industrial sources, is a matter of great importance as it can cause corrosion and environmental damage even at low concentrations. This work thoroughly focuses on H₂S capture using a relatively new type of material, namely, metal–organic frameworks (MOFs), with a view to shed light on their desulfurization performance (i.e., principally via adsorption) [1]. Crystalline MOFs are formed by reticular synthesis, resulting in strong bonds between organic and inorganic units. The proper selection of MOF constituents can lead to crystals of ultrahigh porosity and high chemical, thermal, and mechanical stability. These properties allow the interior of MOFs to be chemically modified for the use in the field of gas storage and separation, among other applications. The ability to expand their metrics without changing the underlying topology and the precision generally exercised in their chemical modulation has not been achieved in other materials. The work presented herein discusses the existing literature on new

developments in MOFs for H₂S removal, opening new avenues for further research in terms of desulfurization processes [2].

2. H₂S Capture via Materials of the Institute Lavoisier (MILs)

Hamon et al. [3] pioneered the investigation of H₂S adsorption at room temperature by using different MIL-series MOFs, including MIL-47(V), MIL-53(Al, Cr, Fe), MIL-100(Cr), and MIL-101(Cr). The authors observed that larger-pore MOFs such as MIL-100 (16.7 mmol g⁻¹) and MIL-101 (38.4 mmol g⁻¹) exhibited higher H₂S uptake in comparison to smaller-pore MOFs such as MIL-47 (14.6 mmol g⁻¹) and MIL-53 (Al, Cr and Fe, 13.1 mmol g⁻¹, 11.8 mmol g⁻¹, and 8.5 mmol g⁻¹, respectively). However, large-pore MIL-100 and MIL-101 MOFs demonstrated irreversibility, which was due either to the strong interaction of H₂S with the framework, or structural collapse after H₂S exposure. Soon thereafter, these findings were confirmed by the same group using a combination of IR measurements and modeling [4].

H₂S capture using MIL-53(Al), in both powder and pellet form, was also examined by Heymans et al. [5] who carried out a joint experimental/theoretical approach. Their focus was on the synchronous removal of H₂S and CO₂ from biogas streams. The results showed that MOF-53(Al) was fully regenerable at moderate temperatures (200 °C), indicating that no chemisorption took place. It was also reported that the powdered form of MOF-53(Al) exhibited a higher desulfurization performance in comparison to that of the pelleted form, probably due to its increased specific surface area (SSA) and pore volume.

MIL-68(Al) was probed at high H₂S pressures up to 12 bar at room temperature by Yang et al. [6] using both experimental and theoretical (Grand Canonical Monte Carlo; GCMC) approaches. Given the results obtained, one can conclude that the triangular pores of this MOF were locked by some remaining organic or solvent molecules, because of the incomplete activation of the material. This partially activated sorbent was proven to be fully regenerable for at least five consecutive sulfidation cycles. This notwithstanding, it needs further elucidation whether the MIL-68(Al) can resist corrosiveness following H₂S exposure if fully activated.

Vaesen et al. [7] tested the adsorption performance of the amino-functionalized titanium terephthalate MIL-125(Ti)-NH₂ towards its parent MIL-125(Ti) analogue, for the simultaneous removal of CO₂ and H₂S from biogas and natural gas, applying a joint experimental/modeling approach. The pure-component adsorption runs at a low temperature (30 °C), and low pressures resulted in decreased H₂S capture for both MOFs. A key finding was that compared to other sorbents, such as 13X zeolites, these materials exhibited lower H₂S adsorption enthalpies, and thus a lower energy footprint for recycling the sorbent.

Recently, Díaz-Ramírez et al. [8] reported the partial functionalization of MIL-101(Cr) with fluorine using 2,3,5,6-tetrafluoro-1,4-benzenedicarboxylate (BDC-4F). The authors aimed to investigate the adsorption performance of MIL-101(Cr)-4F(1%) at a low temperature (30 °C) and 15% of H₂S volume. The results showed that this MOF outperformed other mesoporous MOFs mentioned in the literature. However, a serious downside was that H₂S exposure partially led to structural degradation.

3. H₂S Capture via HKUST-1 (Hong King University of Science and Technology)

Petit et al. [9] prepared HKUST-1 composites with graphite oxide (GO) (5 to 46 wt. %) and reported a synergistic effect on H₂S capture for the hybrid materials. The authors reported that the composite material GO/MOF (5 wt. % of GO) outperformed both GO and HKUST-1 sorbents, with an H₂S adsorption capacity of 199 mg g⁻¹. The enhanced desulfurization performance of the GO/MOF solid was ascribed to the formation of newly formed pores in its structure. H₂S molecules were captured through physisorption and reactive adsorption. Nevertheless, it was claimed that HKUST-1 suffers from structural collapse due to H₂S molecules that strongly bind to the unsaturated copper centers of the MOF, resulting in the formation of CuS.

Pokhrel et al. [10] also studied the H₂S adsorption on HKUST-1 and HKUST-1/GO. The authors claimed that GO did not enhance the adsorption of H₂S molecules, but it was the presence of well

dispersed crystals of the MOF that promoted the H₂S uptake. It was also shown that both physical and reactive adsorption took place, due to the unsaturated Cu sites in the MOF structure, which interact with H₂S. Regardless, since physical adsorption predominates, an increasing temperature resulted in favorable kinetics but a reduced H₂S uptake. In the presence of water, the stability of both materials presented gradual degradation, indicating that chemisorption occurred.

An interesting theoretical study was carried out by Watanabe et al. [11] who tried to calculate the binding energies of different molecules, namely, H₂S, H₂O, CO, NO, pyridine, C₂H₂, and NH₃, using HKUST-1. The results showed that H₂S exhibited a binding strength of 0.49 eV on Cu dimers, quite close to that of H₂O, which demonstrated a large affinity for the metal center of HKUST-1.

In general, the results obtained from the theoretical studies differ from the ones adopted from the experimental results. Modeling suggests that H₂S physisorption prevails on HKUST-1, thus failing to explain the conversion of H₂S to CuS in the presence of moisture. Contrary to experimental approaches, theoretical studies do not consider the host–guest interactions which are required to explain the CuS formation.

All things considered, experimental studies denote that H₂S molecules bind stronger with Cu atoms in the center of HKUST-1, thereby displacing the existing H₂O molecules.

4. H₂S Capture via Isoreticular Metal–Organic Frameworks (IRMOF-n)

Isoreticular MOFs (IRMOF-n, where n = 1–16) based on a skeleton of Zn-based MOF were first prepared by Eddaoudi et al. [1] To exemplify the structure of IRMOF-1 (also known as MOF-5), Figure 1 is presented; this solid has a stable cube-like structure with a regular, three dimensional cubic lattice, with BDC as the edges and Zn₄O clusters as vertexes 5.

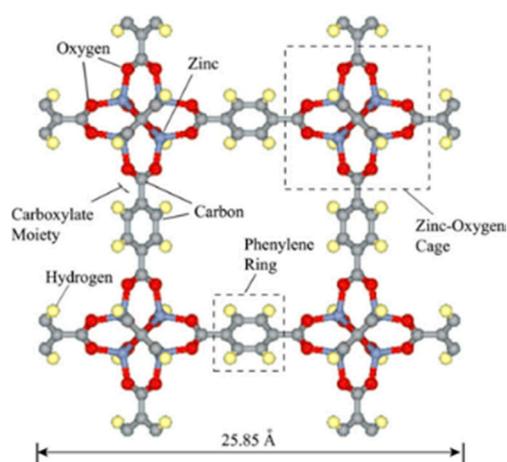


Figure 1. The cubic structure of metal-organic framework 5 (MOF-5). The lattice constant at 27 °C is 25.85 Å. The diameter is 7.16 Å. Reproduced with permission from Ref. [1]. Copyright 2007 International Journal of Heat and Mass Transfer.

In a theoretical study by Gutiérrez-Sevillano et al. [12], the adsorption of H₂S on MOF-5 was examined. The results showed a lower heat of adsorption for the material under consideration (~15 kJ mol⁻¹) compared to that of HKUST-1 (~30 kJ mol⁻¹), probably because of the wider pores of the MOF-5. Moreover, the energy of adsorption of H₂O (~22.5 kJ mol⁻¹) on MOF-5 was higher than that of H₂S (~16.7 kJ mol⁻¹), suggesting that the presence of moisture negatively affects the H₂S uptake.

Another study was carried out by Huang et al. [13], who prepared composites of Zn-based MOF (MOF-5) and GO in the presence of glucose for H₂S removal (Figure 2). The results showed that the glucose-promoted Zn-based sample exhibited increased H₂S uptake at 5.25% of GO loading, reaching a maximum capacity of 130.1 mg g⁻¹. Nevertheless, even though the loading of GO enhanced the dispersive force in the porous structure, when the GO loading surpassed the optimum value of 5.25%, it led to the crystal distortion of the MOF-5. It was also mentioned that the insertion of glucose can help maintain structural stability and prevent distortion.

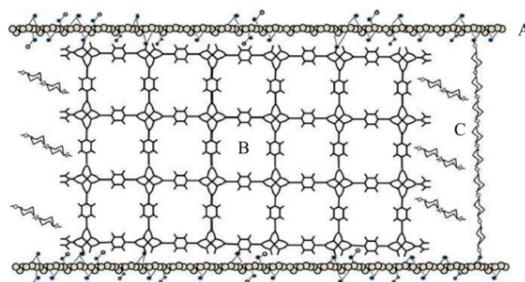


Figure 2. Schematic view of the glucose-promoted MOF-5/GO structure unit: (A) GO layer, (B) MOF-5, and (C) glucose polymer. Reproduced with permission from ref. [13]. Copyright 2012 Applied Materials & Interfaces.

5. H₂S Capture via M-MOF-74

M-CPO-27, also known as M-MOF-74 [$M_2(2,5\text{-dihbdc})(\text{H}_2\text{O})_2$], (2,5-dihbdc = 2,5-dihydroxyterephthalate $M = \text{Ni}^{2+}, \text{Zn}^{2+}$), was investigated by Allan et al. [7] because of its strong affinity for H₂S. It was reported that the H₂S uptake on Ni-MOF-74 was approximately 6.4 mmol g⁻¹ at room temperature and relative pressures (under 5 kPa). The highest H₂S removal of 12 mmol g⁻¹ was attained at 100 kPa and 25 °C. However, after regeneration, the H₂S adsorption capacity was reduced in the second run, corroborating the irreversibility of H₂S binding on the Ni sites.

Chavan et al. [14] also studied H₂S removal (relative pressures, 10 mbar) on Ni-MOF-74 and reported the formation of H₂S adducts on almost 80% of the Ni sites. It was also claimed that Ni-MOF-74 had a reversible behavior upon thermal activation at 200 °C for 12 h, and that after desorption, there was an increase in H₂S adsorption capacity probably because of the additional active sites produced by means of heat treatment.

6. H₂S Capture via Universitetet I Oslo MOF (UiO-66)

UiO-66 (Universitetet I Oslo) is an MOF built of [$\text{Zr}_6\text{O}_4(\text{OH})_4$] clusters (octahedra) that are 12-fold connected with adjacent octahedra through BDC struts (linkers), leading to a highly face-centered cubic structure [15].

Li et al. [16] performed a theoretical study to probe the adsorption performance of the pristine UiO-66(Zr) and its functionalized derivatives in removing sulfur from binary gas mixtures. UiO-66-(COOH)₂ and UiO-66-COOH displayed the highest H₂S uptake compared to that of the other tested solids, probably owing to their higher adsorption isosteric heats. The isosteric heat of adsorption under infinite dilution and radial distribution functions suggests that the hydrophilic groups and polar H₂S molecules strongly interact with one another, favoring H₂S removal.

Huang et al. [17] studied the antagonistic adsorption between CO₂ and H₂S by synthesizing core-shell-structure H₂S-imprinted polymers (PMO₁₂@UiO-66@H₂S-MIPs) based on the surface of UiO-66 modified by phosphomolybdic acid hydrate. At the outset, it was mentioned that the use of H₂O as a substitution template for H₂S can surmount the limitations associated with H₂S molecules, such as their toxic and instable nature. It was reported that PMO₁₂@UiO-66@H₂S-MIPs presented an increased H₂S adsorption capacity (24.05 mg g⁻¹) compared to that of the carrier PMO₁₂@UiO-66, suggesting that the capacity of the latter in capturing H₂S was further improved by the H₂S-imprinted polymers. In addition, PMO₁₂@UiO-66@H₂S-MIPs exhibited a decent H₂S adsorption capacity at room temperature and in the presence of water, while it successfully separated H₂S/CO₂ mixtures.

7. H₂S Capture via Zeolitic Imidazolate Frameworks (ZIFs)

It is widely known that MOFs exhibit hydrothermal stability. For example, MOF-5's structure irreversibly collapses after only 10 min of H₂O exposure, even at mild conditions (low pressure and temperature) [18]. Given that MOFs have hydrophilic properties, they strongly interact with H₂O. That said, even small amounts of moisture can disintegrate the coordination bonds, resulting in framework degradation. Another downside that is associated with the hydrophilic properties of

MOFs is that the access of hydrophobic organic substrates is hampered, compromising the catalytic activity of some reactions. In this regard, many scientists trying to take advantage of the stability of zeolites, combined with the diverse structures and the MOFs tailorability in terms of chemical functionality, synthesized zeolitic imidazolate frameworks (ZIFs), which are classified as an MOF subclass.

ZIFs are zeolite-like structures which are built of transition metal ions that replace aluminum or silica atoms and maintain the topology of a zeolitic material. Furthermore, the organic ligands displace the oxygen atoms in the lattice of the zeolite. For instance, ZIF-8 was thoroughly examined owing to its high thermal stability (up to 550 °C), high surface area (1630 m² g⁻¹) and notable chemical resistance to boiling organic solvents and alkaline H₂O [19].

8. Conclusions

H₂S removal using MOFs can be limited by the formation of strong and often irreversible bonds. To avoid this issue, one can regulate the host–guest binding interaction between MOFs and H₂S.

Reversibility after H₂S sulfidation can be achieved through noncovalent bonding between functionalized ligands H₂S molecules. However, the need to elucidate further the preferred H₂S adsorption sites arises in order to optimize this kind of H₂S separation.

Moreover, a deeper understanding of the structural characteristics of MOFs is key. For example, the structure of MOFs with open metal sites (i.e., HKUST-1, IRMOF-3 and MIL-53(Fe)) degrades when challenged with the toxic H₂S, generating metal sulfides. A solution to this shortcoming may be the use of MOF composites, such as MOF/GO, wherein graphene oxide is used as a support. However, these composite materials suffer from poor H₂S uptake.

Conversely, mild interactions between H₂S and the open metal sites can promote the adsorption of H₂S molecules without breaking the material's structure, offering the opportunity of reversible adsorption processes.

In addition, the functionalization of the MOFs' surface can lead to increased H₂S adsorption capacities, as in the case of MIL-101(Cr)-4F(1%), which exhibited noticeable H₂S uptake at low temperatures and pressures.

At this point, it is worth mentioning the lack of studies in the literature in terms of MOFs' thermal conductivities. The designing of adsorption beds with high stability when experiencing high exothermicity is critical.

Further research should focus on the benefits provided by reticular chemistry for the developments of stable porous MOFs, suitable for sweetening applications.

Moreover, several theoretical studies studied the mechanism of H₂S capture in MOFs in the presence of moisture. However, the results obtained are somehow misleading, as they contradict the ones obtained from the experimental H₂S adsorption tests.

Finally, even though significant improvements have been made in terms of MOFs' structural characteristics in the past two decades, the development of MOF structures with high H₂S selectivity, higher H₂S adsorption capacities, regenerability, long-term stability, and lower cost remains a challenge to be addressed in order to reach industrialization standards.

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