Chemistry Proceedings

Proceedings

Removal of Hydrogen sulfide (H_2S) using MOFs: A review of the latest developments

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† Presented at the 1st International Electronic Conference on Catalysis Sciences, 10–30 November 2020; Available online: https://sciforum.net/conference/ECCS2020
Published: 10 November 2020

Abstract: Removal of hydrogen sulfide (H_2S) from gas streams with varying overall pressure and H_2S concentration is a long-standing challenge faced by the oil and gas industries. The present work focuses on H_2S 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 objective, i.e., how to design extended structures of materials. Moreover, the functionalization of the MOF's surface can result in increased H_2S uptake. For example, the insertion of 1% of a fluorinated linker in MIL-101(Cr)-4F(1%) allows for enhanced H_2S capture. Although noticeable efforts have been made in studying the adsorption capacity of H_2S 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 H_2S removal, and tries to provide insight into new areas for further research.

Keywords: MOFs; H_2S; Adsorption; Gas sweetening;

1. Introduction

The removal of hydrogen sulfide (H_2S), 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 H_2S 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. 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 met in other materials. The work presented herein discusses the existing literature on new developments in MOFs for H_2S removal opening new avenues for further research in terms of desulfurization processes [2].

2. H_2S Capture via Materials of the Institute Lavoisier (MILs)

Hamon et al. [3] pioneered the investigation of H_2S 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 H_2S uptake in comparison to smaller MOFs pore MOFs involving 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 either due to the strong interaction of H_2S with the framework or structural collapse after H_2S exposure. Soon thereafter, these findings were confirmed by the same group using a combination of IR measurements and modeling [4].

H_2S 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 synchronous removal of H_2S and CO_2 from biogas streams. 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 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 H_2S 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 tat 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. Notwithstanding, it needs further elucidation whether the MIL-68(Al) can resist corrosiveness following H_2S exposure if fully activated.

Vaesen et al. [7] tested the adsorption performance of the amino-functionalized titanium terephthalate MIL−125(Ti)-NH_2 towards its parent MIL−125(Ti) analogue, for the simultaneous removal of CO_2 and H_2S from biogas and natural gas, applying a joint experimental/modeling approach. The pure-component adsorption runs at low temperature (30 °C) and low pressures showed decreased H_2S capture for both MOFs. A key finding was that compared to other sorbents, such as 13X zeolites, these materials exhibited lower H_2S adsorption enthalpies, thus 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 low temperature (30 °C) and 15% of H_2S volume. Results showed that this MOF outperformed other mesoporous MOFs mentioned in the literature. However, a serious downside was that H_2S exposure partially led to structural degradation.

3. H_2S Capture via HKUST−1 (Hong King University of Science and Technology)

Petit et al. [9] prepared HKUST-1 composites with GO (5 to 46 wt% graphite oxide) and reported a synergistic effect on H_2S 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 H_2S adsorption capacity of 199 mg g^{-1}. The enhanced desulfurization performance of GO/MOF solid was ascribed to the formation of newly formed pores in its structure. H_2S molecules were captured through physisorption and reactive adsorption. Nevertheless, it was claimed that HKUST-1 suffers from structural collapse due to H_2S 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 H_2S adsorption on HKUST-1 and HKUST-1/GO. The authors claimed that GO did not enhance the adsorption of H_2S molecules, but it was the presence of well dispersed crystals of the MOF that promoted the H_2S uptake. It was also showed that both physical and reactive adsorption took place, due to the unsaturated Cu sites in the MOF structure, which interact with H_2S. Howbeit, since physical adsorption predominates, an increasing temperature resulted in favoring kinetics, but reducing H_2S 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, H_2S, H_2O, CO, NO, pyridine, C_2H_2, and NH_3) using HKUST−1. Results showed that H_2S exhibited a binding strength of 0.49 eV on Cu dimers, quite close to that of H_2O, 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 H_2S physisorption prevails on HKUST-1, thus failing to explain the conversion of H_2S 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 H_2S molecules bind stronger with Cu atoms in the center of HKUST-1, thereby displacing the existing H_2O molecules.

4. H_2S 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 edges and Zn_4O cluster as vertexes 5.

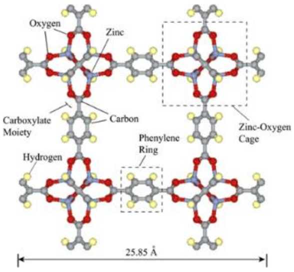

Figure 1. The cubic structure of MOF-5. The lattice constant at 27 °C is 25.85 Å. The diameter is 7.16 Å. Reproduced with permission from Ref. [1]. Copyright 2007 International Journal of Heat and Mass Transfer.

In a theoretical study by Gutiérrez-Sevillano et al. [12], the adsorption of H_2S on MOF-5 was examined. Results showed 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 H_2O (~ −22.5 kJ mol^{-1}) on MOF-5 was higher than that of H_2S (~ −16.7 kJ mol^{-1}), suggesting that the presence of moisture negatively affects the H_2S 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 H_2S removal (Figure 2). Results showed that the glucose-promoted Zn-based sample exhibited increased H_2S 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 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.

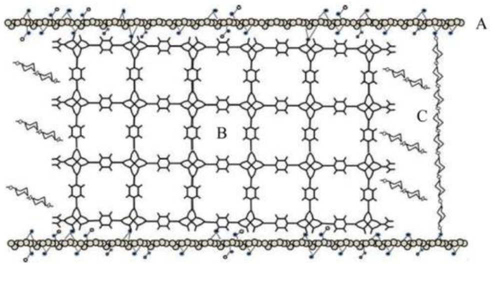

Figure 2. Schematic view of the glucose-promoted MOF-5/GO structure unit: (A) GO layer, (B) MOF-5, and (C) glucose polymer. Reproduced with permission from ref. [13]. Copyright 2012 Applied Materials & Interfaces.

5. H_2S Capture via M-MOF-74

M-CPO-27 also known as M-MOF-74 [M_2(2,5-dhbdc)(H_2O)$_2$], (2,5-dhbdc = 2,5-dihydroxyterephthalate M = Ni^{2+}, Zn^{2+}) was investigated by Allan et al. [14] because of its strong affinity for H_2S. It was reported that the H_2S uptake on Ni-MOF-74 was approximately 6.4 mmol g^{-1} at room temperature and relative pressures (under 5 kPa). The highest H_2S removal of 12 mmol g^{-1} was attained at 100 kPa and 25 °C. Howbeit, after regeneration, H_2S adsorption capacity was reduced in the second run, corroborating the irreversibility of H_2S binding on the Ni sites.

Chavan et al. [15] also studied H_2S removal (relative pressures, 10 mbar) on Ni-MOF-74 and reported the formation of H_2S 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 H_2S adsorption capacity probably because of additional active sites produced by means of heat treatment.

6. H_2S Capture via Universitetet I Oslo MOF (UiO-66)

UiO-66 (Universitetet I Oslo) is a MOF built of [$Zr_6O_4(OH)_4$] clusters (octahedra) that are 12-fold connected with adjacent octahedra through BDC struts (linkers), leading to a highly face centered cubic structure [16].

Li et al. [17] 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 H_2S uptake compared to that of other tested solids probably owing to their higher adsorption isosteric heats. The isosteric heat of adsorption at infinite dilution and radial distribution functions suggest that the hydrophilic groups and polar H_2S molecules strongly interact with one another, favoring H_2S removal.

Huang et al. [18] studied the antagonistic adsorption between CO_2 and H_2S by synthesizing core-shell-structure H_2S imprinted polymers (PMo_{12}@UiO-66@H_2S-MIPs) based on the surface of UiO-66 modified by phosphomolybdic acid hydrate. At the outset, it was mentioned that the use of H_2O as substitution template for H_2S can surmount limitations associated with H_2S molecules, such their toxic and instable nature. It was reported that PMo_{12}@UiO-66@H_2S-MIPs presented increased H_2S adsorption capacity (24.05 mg g^{-1}) compared to that of carrier PMo_{12}@UiO-66, suggesting that the capacity of the latter in capturing H_2S was further improved by the H_2S imprinted polymers. In addition, PMo_{12}@UiO-66@H_2S-MIPs exhibited decent H_2S adsorption capacity at room temperature and in the presence of water, while it successfully separated H_2S/CO_2 mixtures.

7. H_2S 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 H_2O exposure, even at mild conditions (low pressure and temperature) [19]. Given that MOFs have hydrophilic properties, the strongly interact with H_2O. That said, even small amounts of moisture, can disintegrate the coordination bonds, resulting in the 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 a 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 m^2 g^{-1}) and notable chemical resistance to boiling organic solvents and alkaline H_2O [20].

8. Conclusions

H_2S 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 H_2S.

Reversibility after H_2S sulfidation can be achieved through noncovalent bonding between functionalized ligands H_2S molecules. However, the need to elucidate further the preferred H_2S adsorption sites arises to optimize this kind of H_2S separations.

Moreover, a deeper understanding for 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 H_2S, generating metal sulfides. A solution to this shortcoming may be the use of MOF-composites, such as MOF/GO, where graphene oxide is used as a support. However, these composite materials suffer from poor H_2S uptake.

Conversely, mild interactions between H_2S and the open metal sites, can promote the adsorption of H_2S molecules without breaking the material's structure offering the opportunity of reversible adsorption processes.

In addition, the functionalization of the MOF's surface can lead to increased H_2S adsorption capacities, as in the case of MIL−101(Cr)-4F(1%), which exhibited noticeably H_2S uptake at low temperature and pressure.

At this point, it 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 the H_2S capture in MOFs in the presence of moisture. However, the results obtained are somehow misleading, as they contradict with the ones obtained from the experimental H_2S 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 H_2S selectivity, higher H_2S adsorption capacities, regenerability, long-term stability, and lower cost remains a challenge to be addressed to reach industrialization standards.

Author Contributions: Conceptualization, A.G.G.; data curation, A.G.G.; formal analysis, A.G.G.; funding acquisition, I.V.Y. and M.A.G.; investigation and methodology, M.A.G.; project administration, M.A.G. and I.V.Y.; project coordination, I.V.Y.; resources, M.A.G.; supervision, N.C.; writing—original draft, A.G.G. and N.C.; writing—review & editing, N.C., I.V.Y., and M.A.G. All authors have read and agreed to the published version of the manuscript.

Funding: This research has been co-financed by the European Union and Greek national funds through the operational program Competitiveness, Entrepreneurship, and Innovation, under the call Research-Create-Innovate (Project code: T1EDK-00782).

Conflicts of Interest: The authors declare no conflict of interest.

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