

Review



Removal of Hydrogen Sulfide From Various Industrial Gases: A Review of The Most Promising Adsorbing Materials

Amvrosios G. Georgiadis, Nikolaos D. Charisiou and Maria A. Goula *D

Laboratory of Alternative Fuels and Environmental Catalysis (LAFEC), Department of Chemical Engineering, University of Western Macedonia, GR–50100 Koila, Greece; amvro23@gmail.com (A.G.G.); ncharisiou@uowm.gr (N.D.C.)

* Correspondence: mgoula@uowm.gr; Tel.: +30-24610-68296

Received: 23 April 2020; Accepted: 6 May 2020; Published: 8 May 2020



Abstract: The separation of hydrogen sulfide (H_2S) from gas streams has significant economic and environmental repercussions for the oil and gas industries. The present work reviews H₂S separation via nonreactive and reactive adsorption from various industrial gases, focusing on the most commonly used materials i.e., natural or synthetic zeolites, activated carbons, and metal oxides. In respect to cation-exchanged zeolites, attention should also be paid to parameters such as structural and performance regenerability, low adsorption temperatures, and thermal conductivities, in order to create more efficient materials in terms of H_2S adsorption. Although in the literature it is reported that activated carbons can generally achieve higher adsorption capacities than zeolites and metal oxides, they exhibit poor regeneration potential. Future work should mainly focus on finding the optimum temperature, solvent concentration, and regeneration time in order to increase regeneration efficiency. Metal oxides have also been extensively used as adsorbents for hydrogen sulfide capture. Among these materials, ZnO and Cu–Zn–O have been studied the most, as they seem to offer improved H₂S adsorption capacities. However, there is a clear lack of understanding in relation to the basic sulfidation mechanisms. The elucidation of these reaction mechanisms will be a toilsome but necessary undertaking in order to design materials with high regenerative capacity and structural reversibility.

Keywords: zeolites; activated carbons; metal oxides; adsorption; H₂S

1. Introduction

Hydrogen sulfide (H₂S) is a colorless, corrosive, water-soluble, highly toxic, and flammable acid gas which has the characteristic foul odor of rotten eggs [1,2]. Due to the fact that it is heavier than air, it is prone to accumulation in low–lying areas with poor ventilation. Its detection limit is equivalent to 4.7 ppb in air, the concentration at which 50% of people can detect its distinctive "rotten egg" odor. The primary route of human exposure is inhalation, whereby the gas is rapidly absorbed by the lungs, while cutaneous absorption is minimal. H₂S affects the eyes, nose, and throat at very low concentrations (5 ppm) and can be lethal at over 1000 ppm [3]. Thus, it is an extremely lethal gas, second only to carbon monoxide (CO) as a cause of inhalational deaths [4]. A mortality rate of 6% has been reported for exposure to concentrations exceeding the highest permissible limit [5]. Moreover, with continuous low–level exposure (approximately 30 ppm), or at high concentrations (100–150 ppm), the individual loses the ability to smell the gas even though it is still present, as the olfactory nerve is paralyzed. Considering the health hazards caused by H₂S, it is of paramount importance for industry to adapt protective measures through trained personnel, effective exhaust

and ventilation systems, proper rescue procedures, and respiratory as well as other types of personal protective equipment. Table 1 summarizes the physicochemical properties of H₂S.

| Property | Value |
|------------------------------|---------------------------------|
| Molar mass | 34.08 g mol^{-1} |
| Melting point | −82 °C |
| Boiling point | −60.25 °C |
| Density | 1.363 g dm^{-3} |
| Dipole moment | 0.97 D |
| Critical temperature | 100.25 °C |
| Critical pressure | 89.7 bar |
| Acidity | 7 pKa |
| Solubility in water (H_2O) | 4 g dm ⁻³ (at 20 °C) |
| Lower explosive limit (LEL) | 4% |
| Upper explosive limit (UEL) | 44% |

Table 1. Physicochemical properties of H₂S [6].

Generally, H₂S is generated from industrial processes such as petroleum refining, natural gas, landfill and biogas processing, coal gasification, and wastewater treatment works. Due to its toxic and corrosive nature it affects steel equipment, poisons catalysts used in fuel cells, and contributes to the formation of acid rain [7,8]. Acceptable H₂S limits can vary depending on the end use. For example, for the exploitation of biogas in high-temperature fuel cells, an H₂S concentration lower than 1 ppm is required as the electrodes are vulnerable to sulfur poisoning [9,10].

Therefore, the removal of H_2S from industrial gases is a necessity and various physicochemical methods such as chemical oxidation, biological treatment, catalytic conversion, precipitation, electrochemical abatement, adsorption catalysis, incineration, and chemical scrubbing have been developed and commercially adopted [11,12]. H_2S capture by means of biological treatment is efficient and cost-effective, but it requires high capital investment in comparison to processes that are dry-based. Liquid-based and membrane techniques ensure appropriate regeneration processes; however, in addition to the fact that there is limited adsorption capacity of H_2S even at low concentrations, these methods are not economically and energetically viable [13]. The most widely used method for both large- and small-scale applications is adsorption, a dry process with superior performance in terms of H_2S removal efficiency even at low concentrations and temperatures [14,15].

The adsorbents normally used in dry adsorption desulfurization processes are natural or synthetic zeolites, activated carbons, and metal oxides. These materials can have crystalline (zeolites) and/or amorphous structures (activated carbons) at both the macro and nanoscale [16], but they can be further modified to alter their physicochemical properties, thereby upgrading their adsorption capacity toward target molecules. However, there are a number of issues that need to be clarified. Since gas mixtures such as natural gas often contain polar (H₂S/H₂O) and non–polar molecules (CH₄), a polar adsorbent surface is required in order to perform this separation (H₂S/CH₄). The presence of H₂O, which has a dipole moment that is two times higher compared to H₂O, H₂S is a stronger acid; thus, use of amino–functionalized groups is a viable alternative for the sweetening of sour gas. Nevertheless, this use of amines exhibits certain limitations with regard to $CO_2 \neg \neg/H_2S$ separation, on the grounds that CO_2 has higher acidity in comparison to H₂S. Due to the fact that both H₂S and CO₂ are electron acceptors (Lewis concept of acids), they have a close effect to that of amine groups. Hence, reactive and non-reactive adsorption cannot achieve highly efficient separation of CO_2/H_2S since H₂S has to be selectively adsorbed.

Taking into account the aforementioned considerations and the fact that there is only a one other literature report [17] that exclusively focuses on solid materials used as adsorbents towards H_2S removal, in this work we probe the design of adsorbents that can bear corrosion by H_2S and achieve acidity-based and polarity-based separations. To accomplish this, we have exhaustively compiled data

from the latest scientific works for the materials under consideration and attempted to shed light on new perspectives.

2. Adsorption

Adsorption is a surface–based exothermic process that leads to the transfer of a molecule from a fluid bulk to the solid surface of the adsorbent [18]. The substance that is adsorbed to the adsorbent is called adsorbate. The process may also be classified as physical adsorption (physisorption) or chemical sorption (chemisorption), depending on the interactions between the molecules and surface. Physical adsorption is dominated by weak Van der Waals forces and electrostatic interactions, while in chemisorption, strong chemical bonds such as covalent bonds are formed between the surface and the adsorbed species. Chemical adsorption is slow-paced compared to physical adsorption usually entails the formation of a thick multilayer on the surface [19] (Figure 1). Table 2 summarizes the main differences between physical and chemical adsorption.



Figure 1. Scheme of (a) physisorption and (b) chemisorption.

| Physisorption | Chemisorption | | |
|--|--|--|--|
| Electrostatic interactions and Van der Waals forces are involved | Covalent bonds are formed between the surface and the adsorbed molecules | | |
| Fast | Slow | | |
| Occurs in at low temperature | Occurs at high temperature | | |
| Is reversible | Is irreversible | | |
| Multilayers are formed | Monolayers are formed | | |
| Activation energy is not required | Activation energy is required | | |

 Table 2. Differences between physisorption and chemisorption.

Along with interaction–based separation, the shape and size of molecules may also affect the adsorption selectivity of one compound over another. Generally, it is desirable for the adsorbent to exhibit increased separation selectivity and adsorption capacity towards target molecules (e.g., H_2S) as well as stability under acid conditions, and structural regenerability in order to increase its cost-effectiveness.

2.1. Zeolites

Zeolites are widely used as catalytic materials in the petrochemical industry and as water softeners in detergents [20]. They are also considered molecular sieves with the capacity to selectively remove a target molecule from a fluid mixture, e.g., they have been extensively used in order to remove H_2S from biogas. Structurally, zeolites are microporous crystalline materials principally comprised of a three-dimensional framework of SiO₄ and AlO₄ tetrahedra. Their frameworks are typically anionic and have charge–compensating cations such as Na^+ and Ca^{2+} to retain electrical neutrality. These cations can be a part of ion-exchange processes, making them ideal selective H_2S adsorbents, as is the case in the well-known Claus process [21].

Several papers published so far have attempted to shed light on the retention mechanism of H_2S in different types of zeolites, such as zeolite–A (LTA), zeolite–Y (FAU), zeolite–X (FAU), and ZSM–5 (MFI), as well as natural zeolites (i.e., mordenite, clinoptilolite, erionite, phillipsite, and ferrierite), without however reaching a consensus, as some studies support that the formation of elemental sulfur predominates [22], while others propose an acid–base reaction [23]. Moreover, whether the water formation during the adsorption of H_2S is attributed to the presence of oxygen contained either in the inlet gas mixture or in the zeolite framework or to the metal oxides of the extra-framework cations remains unclarified [24]. Sigot et al. [25] attempted to provide an exegesis by studying the retention mechanism of H_2S on NaX zeolites with a Si/Al ratio of 1.4, suggesting a mechanism based on adsorption-oxidation and the formation of elemental sulfur. The authors argued that the formation of stable sulfur polymers affects the thermal regeneration of the zeolite, and they proposed regeneration by high-temperature desorption at 500–600 °C in an inert atmosphere, which is nevertheless an energy-consuming process damaging the zeolite's crystalline pore structure. Desorption-oxidation at a temperature <400 °C was also considered as an alternative. The authors suggestion of chemical dissolution with organic solvents maybe feasible but is not an environmetally sustainable solution.

As mentioned above, most industrial gases contain both acid (H_2S , CO_2) and polar species (CO and H_2O), which compete and at times supplant H_2S adsorption. Kumar et al. [26] throrougly investigated the effect of the presence of molar compounds on the adsorption of H_2S for Na, Ag, and Cu–exchanged FAU at high and low Si/Al ratios. The authors concluded that NaX exhibited almost zero capability for capturing H_2S in the presence of CO, CO_2 , or H_2O , while CuX and CuY demonstrated reduced H_2S selectivity in the presence of CO. AgX and AgY zeolites showed H_2S adsorption capacities of approximately 30–40 mg/g_{ads} when H_2S concentration in the mixture was 10 ppm, even in the presence of all three components.

An interesting study in the context of polarity-based adsorption on zeolites was reported by Mohammed and Nassrullah [27], who prepared zeolite 5A using kaolin clay and tested H₂S removal from liquefied petroleum gases (LPG) in the presence of H₂O. The authors used breakthrough curves to draw conclusions with regard to the characteristics of the zeolite, and as expected, found that H₂O was a strongly adsorbed component, in comparison to H₂S which was a weakly adsorbed component. As has been argued, even traces of water may essentially decrease the adsorption capacity for other gasses on zeolites and lower their intracrystalline diffusivity [28]. Mohammed and Nassrullah [27] also demonstrated better adsorption capacities for H₂S when increasing flow rates from 3 to 5 liters/minute due to the fact the contact time between the water vapor and adsorbent was decreased. The adsorption capacity for H₂O when the flow rate was 5 liters/minute reached 7.547 g/g while for H₂S it reached 1.734 g/g.

Bulow et al. [29] examined H_2S/CO_2 reactive adsorption on LTA and FAU zeolites. Owing to the highly preferred adsorption of H_2O on these materials, which follows the order $H_2O \gg H_2S \ge$ $CO_2 \approx COS$, the equilibrium of the reaction $H_2S + CO_2 \rightleftharpoons COS + H_2O$ moves to the right; therefore, according to the reaction stoichiometry, one H_2S molecule is converted to another COS molecule, with infinitesimal enrichment of sulfur on the adsorbent. The impact of various parameters such as, Si/Al ratio, type of zeolite, cation exchange degree, pre-adsorption of appropriate gases (NH₃) and temperature was also investigated during this work. At ambient temperature, H_2S conversion on LTA reached 50% for a Si/Al ratio of 1, but it was decreased to almost zero for a Si/Al ratio of 3. The authors reported that when ion exchange increased, wherein higher activation energy was required, the conversion of H_2S was between 20% and 75%, depending on the time of reaction. Thereby, due to the difficulty in repressing this reaction, the authors suggested short–time adsorption techniques such as pressure swing adsorption (PSA)/vacuum swing adsorption (VSA). Tomadakis et al. [30] used three different types of molecular sieve adsorbents (4A, 5A, 13X) to separate mixtures containing bulk quantities of H_2S and CO_2 by means of PSA. Following the adsorption step, CO_2 was removed from the column by blowdown to increase the purity of the H_2S stream during desorption. According to the study results, 5A and 13X exhibited higher selectivity (84–85%) in comparison to 4A (61%) for adsorbing H_2S over CO_2 . The authors also observed that H_2S was the strongest adsorbed component in all cases. Desorption recovery for 4A zeolites was the greatest at 76–91%, followed by 5A and 13X (40–44% and 12–14%, respectively).

Another study focused on short-time adsorption techniques was reported by Wynnyk et al. [31], who performed extensive high-pressure experiments for selective adsorption of CO₂, COS, CH₄, and H₂S using 4A zeolite (LTA). Two different Si/Al ratios were used, i.e., 1.14 and 1.15. Prior to H_2S adsorption tests, the 4A zeolite was activated under ultra-high vacuum (10⁻¹⁰ bar) up to 400 °C. The comparison of the saturation loadings derived from the fitted adsorption isotherms for CH_4 (9.16 mmol/g), CO₂ (7.25 mmol/g), H₂S (5.87 mmol/g), and COS (3.11 mmol/g), revealed considerable differences between these species. Computational calculations for highest occupied molecular orbital (HOMO) bond orientation suggested that zeolite 4A did not perform well in the presence of COS in the gas stream. The positive correlation between CO_2 saturation loading and temperature was not clarified by the authors. In particular, lower temperatures (0, 25, and 50 °C) resulted in reduced saturation loadings for CO₂. Moreover, the enthalpy of adsorption was calculated using isotherms at different temperatures. It was found that at low loadings, COS as well as CH₄ provided identical values of 20 kg/mol, whilst the vigorously interacting H_2S and CO_2 yielded values of ~35 kJ/mol (close to saturation loading). The low enthalpy values indicated that chemical adsorption was favored. Nevertheless, it is worth mentioning that these interactions may be susceptible to even very small concentrations of H₂O contained in the feed gas.

However, despite the fact that the latter two separation methods (PSA/VSA) are of relevance with respect to acidity/based separations (i.e. CO_2/H_2S), they are economically unattractive due to their high operating costs. For this reason, numerous works attempted to achieve selective H₂S adsorption by applying more cost-efficient methods. Sigot et al. [32], carried out both laboratory-scale (with synthetic gas) and on-site (with real biogas) adsorption tests. The laboratory-scale adsorption tests were performed using 80 ppmv of H₂S, simulating a partly desulfurized gas, and compared the efficiencies of 13X zeolite (Z) and a coal-based impregnated activated carbon (IAC) in different humidity conditions (up to 80%). With respect to IAC, suppliers generally recommend 40-80% relative humidity (RH) for an optimal efficiency, and this is confirmed by data in the literature [14,33]. The absolute gas humidity at the column inlet was ~14.5 g·m⁻³. At the laboratory scale, dry N₂ (containing ~1% O₂ due to incomplete air separation in the N₂ generator) was used as diluent stream. A 25 mm diameter and 25 cm high stainless steel adsorption column was used. For each experiment, 10–30 g of adsorbent was introduced in the adsorption column. The 13X zeolite (Z) demonstrated a sufficient H_2S uptake on dry gas but its capacity decreased almost to zero in the presence of humidity due to its high affinity for water. On the other hand, IAC, which was treated with alkaline solution, showed enhanced performance in the presence of humidity owing to its lower affinity for water. In summary, the presence of water decreased the adsorption efficiency of Z towards H_2S , but enhanced the removal of H_2S by IAC. Another conclusion of the study was that CH₄ was not adsorbed regardless of the adsorbent. Moreover, Z had the ability to retain CO_2 (corresponding to approximately 90 mg CO_2/g Z adsorbed), which is expected to reduce its H_2S adsorption capacity. This was anticipated, considering that zeolites are commonly used for biogas upgrading (biogas to biomethane) [34]. Concerning the on-site adsorption tests (H₂S concentration of 4000 ppmv), the authors, taking into to account the laboratory-scale experiments, concluded that the H_2S adsorption capacity of Z was 142 mg H_2S/g Z. With respect to IAC, an adsorption capacity of 785 mg H_2S/g IAC was demonstrated, without reaching saturation of the adsorbent.

Barelli et al. [9] also tested a 13X zeolite treated with Cu ions (13X Ex–Cu) by impregnation or ion exchange as sorbent for H_2S removal from biogas. Material behavior was characterized over

several operating conditions typical of biogas mixtures (high H₂S contents, 200 and 1000 ppmv CH₄ (60%)/CO₂ (40%) matrices) and compared to specific conventional adsorbents. The impact of changing parameters such as reactor temperature, space velocity, gas matrix compositions, and particles size was investigated. The material demonstrated its best performance at reduced space velocity (850 h⁻¹), at increased reactor temperature (120 °C), and in high CH₄ concentrations in the gas mixture (1000 ppmv), with H₂S uptake of 40 mg/g. Brunauer-Emmet-Teller (BET) and X–ray diffraction (XRD) analysis showed that the improved performance was related to the high concentrations of Cu²⁺ ions, confirming the well–known affinity of Cu²⁺ for S^{2–} ions [23].

Another work that highlighted the increased capacity of 13X in H₂S adsorption was reported by Melo et al. [35], who used the material as adsorbent for the removal of H₂S from natural gas. The composition of the zeolite was Na₂O:Al₂O₃:2.8 \pm 0.2SiO₂:XH₂O, and X depended on the dryness or activation of the material according to X–ray diffraction peaks of zeolite 13X similar to the Faujasite structure. The authors concluded that its maximum adsorption capacity, at a surface area of 16.15 m²/g, was 53 mg H₂S/g_{ads} at 25 °C.

As was previously mentioned, there are numerous types of zeolites used for H₂S removal. Lee et al. [36] conducted an intriguing study focusing on the adsorption capacity of LTA. They tested iron-incorporated Na–A zeolites prepared from FeCl₃ solution and melting slag, which contained sodium silicate solution and sodium aluminate (main constituent), as adsorbents for hydrogen H₂S removal. The gas mixture comprised of N₂ and H₂S (1%) and the flow rate was 100 ml/min. The samples were packed into a bed (length 30 cm and diameter 15 mm) which was placed inside an oven maintained at 30 °C. The tests were stopped at a breakthrough concentration of 2000 ppm for H₂S. With respect to H₂S adsorption capacity, it was directly proportional to Fe³⁺ concentration and inversely proportional to calcination temperature. In particular, there was an increase in the surface area from 20 m²/g to 85 m²/g when the Fe³⁺ concentration increased from 0 nM to 78 nM. The highest H₂S adsorption capacity of Fe–Na–A (0.2–1.5%) was compared to other adsorbents, it was found to be lower than that of the commercial activated carbons (1.2–2.4%) and higher than that of commercial zeolites 13X (0.91%) and 4A (0.15%), owing to acidic surface properties presented by the Fe–Na–A, which is attributed to the incorporation of the Fe³⁺ ion.

Abdullah et al. [37] studied the adsorption of H_2S from a gas stream (200 ppmv H_2S in 30 mL min⁻¹ N_2 flow) in a fixed-bed reactor at room temperature (28 °C, 1 atm) using zinc oxide (ZnO) (10–30 wt% loading) impregnated on Na–A zeolite prepared from kaolin. Increasing zinc oxide loading concentration over a critical dispersion capacity led to the formation of bulk zinc oxide at the external surface of the material. The material provided its optimum adsorption capacity, 15.75 mg S/g sorbent, when 20 wt% ZnO was loaded on Na–A zeolite. Crystallinity was negatively affected when wt% ZnO increased above 20 wt%, resulting in lower H_2S adsorption capacity.

Liu et al. [38] also investigated LTA zeolites. In particular, they prepared and tested a 4A zeolite using attapulgite in different conditions in order to remove H_2S from various industrial gases such as natural gas, coal gasification gas, and digester gas. The gas mixture used for the experiment contained nitrogen as carrier gas and 1000 mg/m³ of H_2S , while the flow rate was 1000 mL/min. The temperature range was between 25 and 75 °C. The authors concluded that the highest amount of adsorbed H_2S onto zeolite was 8.36 mg/g_{ads}, accomplished at 50 °C. The regeneration performance of the sorbent was also studied and significant damage of the particle structure during the regeneration process was observed, leading to reduced adsorption capacity. Finally, it was revealed that the adsorption of H_2S molecules was hindered at high temperatures due to the exothermic reaction resulting in decreased adsorption capacity at 75 °C (6.5 mg/g_{ads}).

In a number of papers in the literature, comparative assessments of the performance of different types of zeolites were performed. For example Yokogawa et al. [39] prepared LTA (zeolite–A), MFI (ZSM–5), Ag–grafted LTA, and Ag–grafted MFI zeolites in order to remove volatile sulfur compounds (VSCs), and compared their capacity in capturing H₂S. Experiments were conducted

for an initial H_2S concentration of 30 ppm and the authors showed that H_2S adsorption capacity of LTA was higher than that of MFI. In addition, Ag–grafted LTA and Ag–grafted MFI exhibited higher adsorption capacity over LTA and MFI. This was due to the exchange of alkali metal or alkaline earth metal atoms of zeolite material to univalent metal ions, which improved the H_2S reduction effect. The authors considered that the etiology of the lower H_2S adsorption of the MFI was due to its lower surface potential in comparison to that of the LTA zeolite framework. Results showed that after 24 h, the H_2S concentration fell to 60% for the LTA and to 87% for the MFI. For the Ag–grafted zeolites, the H_2S concentration dropped to almost 0%; an important difference was that this was achieved after 4 h for the Ag–grafted LTA and after 8 h for the Ag–grafted MFI.

It is also worth briefly mentioning the work carried out by Karge et al. [40], which pioneered the investigation of the properties of FAU–type zeolites. They found that similar to hydrogen FAU (HY) zeolites, on FAU (NaX) zeolites (Si/Al ~ 2.5), OH groups and S^{2–} are produced due to the fact that the first H₂S molecules are adsorbed dissociatively. However, the authors also showed that increased coverage not only led to the dissociation of H₂S into HS[–] and H⁺ (Figure 2), but also to physical adsorption. Nevertheless, on NaY–type zeolites (Si/Al > 2.5) H₂S molecules are adsorbed without dissociation. The authors concluded that H₂S adsorption capacity of X–type zeolites was four times higher relative to Y–type zeolites.



Figure 2. Dissociative H₂S adsorption on an aluminosilicate zeolite (adopted from [40]).

Recently, De Oliveira et al. [41] published an interesting study in which they used a Na-Y zeolite (hydrophilic structure due to Si–OH groups) as an adsorbent for H₂S removal from simulated natural and biogas mixtures in equilibrium and fixed bed conditions. Adsorption and desorption isotherms were acquired for various temperatures and H₂S partial pressures and modeled using Tóth and Dubinin-Astakhov equations with a view to determining the interactions that occurred. In particular, experiments were conducted at 20, 30, and 40 °C and partial pressures from 0.01 to 1.2 bar. The ranges of operating conditions were typical of natural gas and biogas processing in Brazil. A linear driving force (LDF) model was used to evaluate the adsorbent particle's effective mass transfer coefficient. Equilibrium results specified maximum adsorption capacities above 6.0 mol kg⁻¹ for the highest partial pressures. Isotherm modeling revealed the prevalence of physisorption of H₂S in the zeolite. Nevertheless, a hysteresis effect was detected for desorption curves and ascribed to H₂S chemisorption on the zeolite surface. The breakthroughs recorded were non-symmetrical and illustrated the presence of internal and external mass transfer resistances. Mass transfer zones showed no major changes with inlet flow rate, while higher availability of H₂S at the sorbent's surface, promoted the mass transfer in the intraparticle region. The authors concluded that the results obtained demonstrated that the LDF model could accurately depict the behavior of fixed bed adsorption data.

Ratnasamy et al. [42] also studied the adsorption capacity of FAU–type zeolites. They fabricated Ca–X and Na–X synthetic zeolites with a view to purifying natural gas at ambient conditions of pressure and temperature for use in polymer electrode membrane (PEM) fuel cells. Additionally, mixed metal oxides (Cu–Mn, Fe–Mn) supported on Al₂O₃ were also studied. As expected, none of the materials

tested managed to remove all the sulfur species, which led to the use of a sequential bed system. The results showed that the removal of H_2S was achieved in the third bed. It is worth mentioning that the sequential location and quantity of the sorbents also affected the overall adsorption performance. More specifically, a sequential bed system composed of zeolite Ca–X followed by Fe–Mn–Al₂O₃ oxides had notable desulfurization capacity at 38 °C, 15 psig, and a natural gas space velocity of 6000 h⁻¹. This work divulged that the adsorption capacity of alkali exchange zeolites was Ca–X > Na–X, but also showed that Al–supported Cu–Mn and Fe–Mn adsorbents demonstrated the best performance toward the H_2S capture.

Another interesting work was reported by Rong et al. [43], who carried out regeneration and sulfidation experiments with cerium ions and active copper supported onto zeolite-Y (Ce-Y, Cu-Y) with a view to examining the removal of hydrogen sulfidefrom fuels (such as JP-8). Ion exchange was carried out by exchanging Na⁺ with Cu²⁺. The Cu–exchanged zeolite was further exchanged by a triple positively charged cerium (Ce³⁺) ion, thus preparing a mixed metal supported sorbent. Sulfidation experiments were performed for the conditions of 50% H₂-10% H₂O-balanced He with a space velocity of $80,000 \text{ h}^{-1}$. Results showed that the overall sulfidation capacity of the mixed metal oxides was higher compared to the corresponding zeolite-supported counterparts (i.e., at 800 $^{\circ}$ C the maximum capacity for Cu–Ce–Y was 1.78 mg S/g_{ads}, while the maximum capacity for 5% CuO/CeO_2 was 2.45 mg S/g_{ads}). However, neither copper nor cerium oxide were able to resist sintering above 650 °C, thus resulting in a reduced capacity. On the other hand, the sulfidation capacity of the zeolite-supported mixed metal oxide (Cu-Ce-Y), seemed unaffected by the temperature at both 650 and 800 °C, suggesting that the Cu–Ce–Y zeolite is resistant to the sintering at high temperatures. In particular, during 12 sulfidation/regeneration cycles at 650 and 800 °C the capacity ranged between 1.38 and 1.58 mg S/gads. Ce-Y and Cu-Ce-Y exhibiting increased stability in surface area than Cu-Y at 800 °C may represent good candidates for H₂S removal.

Crespo et al. [44] provided a comparison of H₂S breakthrough capacities of four different molecular sieves, namely Cu(I)Y, Cu(II)Y, CuCl/MCM–41, CuCl/SBA–15, and AgY, and showed that the adsorption energy degraded as follows: Cu(I)Y > AgY > Cu(II)Y. Considering the chemical composition of AgY zeolites, $Ag_{63}Al_{57}Si_{135}O_{384}$, it was detected that the Ag/Al ratio was above unity, suggesting that there are cations found at sites other than cation exchange sites. Regeneration of the Cu(I)Y zeolite reached about 70% when heating at 450 °C using He; complete regeneration was achieved when Cu(I)Y reacted with air at 350 °C, indicating the presence of cations in an oxide form. Due to their high CH₄ selectivity, high H₂S adsorption capacity at low H₂S concentrations (100 ppm), and capability to fully regenerate at 350 °C, CuCl/SBA–15 and CuCl/MCM–41 can also be regarded as promising adsorbents.

A noteworthy work in the context of silicoaluminophosphate zeolites was reported by Hernandez–Maldonado et al. [45] who employed SAPO–43 (partially calcined), to separate CO₂, H₂O, and H₂S, gas molecules typically found in natural gas streams. A major drawback of this material was its lack of thermal stability over 300 °C, which limits its potential use in separation achieved by adsorption. The authors performed elemental analysis as well as CO₂ heats of adsorption, which helped them identify amine-containing compounds; the presence of the latter helped the framework from being dilapidated. For SAPO–43 and at ambient temperature and pressure, the authors recorded capacities of 1.1, 4.93, and 2.52 mmol/g towards the adsorption of CO₂, H₂O, and H₂S, respectively. Regeneration using pure helium at low temperatures (180 °C) removed nearly all the captured water, while 40% of the captured H₂S was restored. Using chemicals such as hydrogen peroxide (H₂O₂) instead of thermal regeneration may also be an alternative for the regeneration of the sorbent.

Several works in the literature have shown that compared to synthetic zeolites, natural zeolites can exhibit sufficient H₂S adsorption capacities, easier regeneration, and lower operating costs. For example, Yasyerli et al. [46] probed natural clinopltilolite for the capture of 1.06% H₂S from carrier gas at different temperatures between 100 and 600 °C, and found that its adsorption capacity was 0.087 g S/g_{ads} at 100 °C, which was higher compared to that at 600 °C (0.03 g S/g_{ads}). Thus, the authors concluded that increasing temperature reduced the capacity of the zeolite in capturing H₂S. Pourzolfaghar et al. [47] studied

 H_2S removal efficiency of a virgin zeolite for palm oil mill effluent (POME) biogas desulfurization at ambient temperature and pressure. One of the key points of the investigation was that at higher Si/Al ratios, the adsorption efficiency was increased. Moreover, it is worth mentioning that after the zeolite had been exposed to fresh air for four days or more, regeneration was not only achieved without the need for an extra regeneration process, but the adsorption capacity of the sorbent also increased. Experimetal results showed that the natural zeolite reached 94% capacity of H_2S removal.

2.2. Activated Carbons

Activated carbons (ACs) represent another group of materials extensively used as adsorbents or catalysts for H_2S removal due to their surface chemistry, high degree of microporosity, and developed surface area (that can exceed 1000 m²/g) [48]. They are amorphous materials usually produced from easily available carbonaceous materials such as wood, coal, coconut shells, and rice husks at high temperatures in an inert atmosphere. Steam activation of the highly microporous resultant carbon is usually performed to expand the pore structure in order to facilitate the adsorption. Although the retention mechanism of H_2S on activated carbons has been thoroughly investigated, it is almost impossible to rationalize all the emerging phenomena. This is due to differences in the pH of adsorption, the presence of multiple species in the activated carbon, and the wide variety of carbonaceous materials with different functional groups. Several studies reported high H_2S adsorption using different kinds of activated carbons, but the precise reasons that led to it are not perfectly comprehended.

Pure activated carbon is considered as an attractive candidate for adsorbing sulfur compounds due to its cost–effectiveness [49,50], but its performance can be further increased by surface modification with chemicals, such as transition metals and/or their salts, leading to the production of metal sulfide [51,52] or basic compounds [53] which promote H₂S removal through acid-base reactions or strong oxidizing agents, which result in H₂S oxidation. For example, Turk et al. [54] suggested that the impregnation with compounds that are basic in nature (e.g., ammonia) and/or caustic solutions can improve the adsorption of H₂S. However, impregnated activated carbons may demonstrate a decreased capacity for physical adsorption as a result of the reduction of the available micropore volume.

Adib et al. [55] prepared an activated carbon impregnated with urea in order to increase basicity, but the H₂S conversion dropped from 298 to 272 mg/g for the impregnated sorbents relative to the bare AC, which was probably caused by a substantial drop in the surface area of the sorbent (18%). Similarly, Tian et al. [56] tried to enhance the removal of H₂S by employing 3-aminopropyltriethoxysilane-surface-functionalized activated carbon (APTES), which is basic in nature, hoping that it would improve interaction with acidic H₂S. However, they noticed decreased breakthrough capacities (lower than 1 mg/g at 1600 ppm), possibly owing to the occlusion of the pores by APTES impregnation. The authors also reported that at a concentration of 8200 ppm of H₂S, the adsorption capacity values for APTES–AC, Na₂CO₃–AC, and AC were 18.13, 8.88, and 6.03 mg/g, respectively.

The average pH of the carbon surface coupled with the pH of the areal environment can also affect the adsorption capacity of the sorbent. An acidic environment hinders the dissociation of H_2S , leading to low concentrations of H_2S ions and thereby to the formation of highly dispersed sulfur species. Notwithstanding, for a less acidic surface, the degree of H_2S dissociation is higher, and the creation of polymeric elemental sulfur species resistant to further oxidation is favored. In summary, an alkaline environment promotes the formation of elemental sulfur, whilst an acidic environment favors the formation of sulfur oxides and sulfuric acid. Bandosz et al. [57–59] conducted various studies on the removal of H_2S using ACs that differ in their acidity, pore volumes, and surface areas.

Regeneration of activated carbons via cold and hot water washing at 300 °C in air atmosphere following the first adsorption run resulted in a considerable decrease (approximetely 60%) in H₂S adsorption capacity of the carbon owing to the irrevesible chemical adsorption in the active sites of the material [60,61]. Boudou et al. [62] tried to regenerate an activated carbon used as adsorbent for H₂S removal, in nitrogen by heating for 10 min at 500 °C. However, while it is possible to maintain

inert atmosphere at laboratory scale (thus eliminating the chance of AC self-ignition), this is not the case at industrial scale. Moreover, the authors observed that used activated carbons were virtually unwashable with water, owing to the agglomeration of sulfur polymers that are resistant to oxidation, making them very difficult to be reused. Therefore, replacement with fresh activated carbon is a frequently used industry practice for lowering the operational cost and overcoming conventional regeneration issues [63,64].

The presence of moisture and oxygen (Figure 3) may also affect the adsorption capacity of activated carbons, and numerous studies have investigated their impact on H₂S uptake. It is generally accepted that the presence of water may have a positive or negative effect on the adsorption mechanism depending on the type of adsorbent used [32]. When activated carbons are impregnated with metal oxides, water competes with H₂S on carbon active sites, resulting in the gradual catalyst deactivation [65,66]. In contrast, for carbons treated with basic compounds, humidity considerably enhances H₂S adsorption capacity [67]. Moreover, the presence of oxygen also increases the breakthrough time of H₂S adsorption for the latter adsorbents [68–70].



Figure 3. Physical and chemical adsorption mechanism of H₂S onto activated carbons (adopted from [71]).

Several studies published so far have dealt with the effect of oxygen and humidity on the adsorption capacity of activated carbons. As an example, Papurello et al. [72] tested three commercial

activated carbons, namely AirDep CKC (impregnated with 5% potassium bicarbonate (KHCO₃)), Sulfa Trap R&G (Fe: 8.3 wt%, Cu: 19.8 wt%), and AirDep CKI (impregnated with 2% potassium iodide (KI)), for the removal of H_2S from low- H_2S level biogases (50–200 ppm) at 30 °C. They found that SulfaTrap R&G exhibited the best adsorption capacity (10.87 mg/g) under anoxic conditions due to a catalytic oxidation mechanism promoted by copper and iron particles identified on the surface of activated carbon. Results also revealed that by adding 0.1% of oxygen in the gas mixture, the alkaline AirDep CKC increased its adsorption capacity from 3.91 to 84.87 mg/g, surpassing both Sulfa Trap R&G (47.91 mg/g) and AirDep CKI (27.04 mg/g) (Figure 4). Finally, the authors concluded that the presence of oxygen led to the formation of elemental solid sulfur that is adsorbed on carbon pores yielding water release, as depicted by the following equations (Equation (1)-(2)):

$$H_2S + 1/2O_2 \to S + H_2O$$
 (1)

$$H_2S + O_2 \rightarrow 1/4S8 + 2H_2O$$
 (2)



100

80

60

40

Absence of O Presence of O₂ (0.1%)

Figure 4. Adsorption capacities of the selected materials before and after 0.1% oxygen addition (adopted from [72]).

In a very interesting study, Ciahotny et al. [73] tested several commercially available carbons impregnated with oxidants to emphasize the functionality of impregnated adsorbent materials for H_2S removal from biogas in the presence of O_2 at ambient temperature. In terms of the experimental test conditions, the adsorption capacity of the selected impregnated sorbents was evaluated under four different atmospheres i.e., (1) containing approximately 20% O₂, 15 g/m³ H₂O, and 7.5 g/m³ H₂S, balanced with nitrogen, (2) without oxygen, (3) without moisture, and (4) without oxygen and moisture. Experimental results showed that the presence of oxygen in the gas mixture was beneficial for H₂S removal. Moreover, the authors concluded that copper, iodine, and potassium salts outperformed the other impregnating agents. In contrast, sorbents impregnated with Mn or Mg were not regarded as suitable candidates due to their decreased sulfur adsorption capacity (below 5%) (Table 3).

In particular, in the presence of humidity and under oxic conditions, iodine-impregnated sorbents reached a sulfur adsorption capacity of close to 25% (Table 3), followed by sorbents impregnated with copper or potassium salts (close to 10%). Under anoxic conditions, a considerable decrease in adsorption capacity of the adsorbent to values as low as one-tenth of the initial ones was noticed. This behavior is probably related to changes on the H_2S bond mechanism of the sorbent. Under anoxic conditions, H₂S bonds as a result of physisorption instead of chemisorption. The authors also concluded that the CuO-impregnated sorbent was an exception, demonstrating a lower adsorption capacity decrease to one-third of the initial value, probably due to the strong oxidation properties of CuO. Compared to the absence of oxygen (Table 3), the absence of humidity did not have such a strong influence on the adsorption capacity of the impregnated sorbents. A dry environment (Table 3) led to a decrease of adsorption capacities for H₂S to almost half the value reached in a humid environment. CuO once again demonstrated exceptional behavior, with minor changes in adsorption capacities or no changes at all.

| Mixture recommended by Norm ASTM D6646-03 | Sample label | Sample weight (g) | Total feed volume (m ³) | H ₂ S concentration (g/m ³) | Adsorption capacity for S (%) |
|--|-----------------|----------------------|--|--|-------------------------------------|
| (containing approximately | Ι | 49.55 | 1.380 | 7.88 | 22.78 |
| $20\% O_2$, 15 g/m ³ H ₂ O, and | Cu I | 54.40 | 0.606 | 7.93 | 9.88 |
| 7.5 g/m ³ H ₂ S, balanced | Mn | 65.50 | 0.158 | 7.89 | 4.64 |
| with nitrogen). | Cu II | 50.40 | 0.424 | 7.89 | 6.45 |
| | K | 48.35 | 0.686 | 6.76 | 9.57 |
| | Mg | 55.68 | 0.289 | 6.76 | 3.47 |
| | I | 50.18 | 0.016 | 7.44 | 0.33 |
| | Cu I | 54.59 | 0.031 | 6.87 | 0.26 |
| Mixture without overgon | Mn | 67.33 | 0.056 | 6.87 | 0.13 |
| Mixture without oxygen | Cu II | 50.93 | 0.077 | 6.87 | 2.27 |
| | K | 50.33 | 0.062 | 6.87 | 0.38 |
| | Mg | 56.99 | 0.027 | 7.44 | 0.17 |
| | I | 48.83 | 1.004 | 6.09 | 11.90 |
| | Cu I | 53.86 | 0.421 | 5.63 | 9.77 |
| Mixture without water | Mn | 68.75 | 0.248 | 5.63 | 1.87 |
| vapor | Cu II | 50.00 | 0.420 | 5.56 | 7.48 |
| | Κ | 51.54 | 0.871 | 5.16 | 11.21 |
| | Mg | 55.56 | 0.230 | 5.16 | 1.85 |
| | I | 50.04 | 0.027 | 6.36 | 0.47 |
| | Cu I | 53.31 | 0.043 | 6.36 | 0.56 |
| Mixture without oxygen | Mn | 66.83 | 0.042 | 6.36 | 0.23 |
| and water vapor | Cu II | 50.47 | 0.075 | 6.36 | 2.87 |
| | Κ | 0.079 | 6.36 | 0.97 | 51.62 |
| | Mg | 0.028 | 6.36 | 0.31 | 57.12 |

Table 3. Sorbent test results using several gas mixtures (adopted from [73]).

This subject has been studied recently by Barelli et al. [74], who compared two commercial activated carbons, namely AC Ultra DS (treated with KOH-KI) and Norit RGM1 (which contains Cu (II)-Cr (IV) salts), and performed several dynamic adsorption tests in order to study their performance under the influence of humidity and oxygen content in concentration and conditions typical of biogas mixtures $(50\% \text{ CH}_4/50\% \text{ CO}_2, \text{RH }90\%, \text{ and } \text{O}_2 2\%_v)$. Unlike Norit RGM1, humidity, in the presence of oxygen, enhanced the adsorption capacity (at RH 90% and O_2 2%v, with the highest capacity found for the N_2 carrier at 65.60 mg/g) of alkaline-treated carbon (AC Ultra DS). The authors reported that a humid atmosphere was required in order to ensure the dissociation of H₂S and to facilitate the completeness of chemical reactions needed for H₂S oxidation on the carbon surface. In contrast, the negative effect of humidity on AC RGM1 was attributed to sorbent deactivation, caused by the reduction of amorphous copper oxide (Cu_2O) species [75]. Moreover, considering that H_2S adsorption by Cu–coated AC is an exothermic reaction, when humidity is present in the inlet gas mixture, water vapor condensation and water film formation may not occur. Therefore, moisture (water vapor) and H₂S species compete with each other for carbon active sites, leading to decreased H₂S adsorption. The authors also investigated and confirmed the competitive adsorption between H₂S and CO₂, and highlighted the negative effect of CO₂ towards H₂S capture. Concerning the impact of gas matrix composition, enhanced performance was noted when using high percentages of CH_4 under dry and anoxic conditions. Thus, the latter three works clearly explain the determining effect of water and oxygen on H_2S adsorption capacity of activated carbons.

The increasing interest in developing new cost–effective materials as sorbents for H_2S removal from industrial gases (i.e. biogas treatment) has led to the investigation of industrial and agricultural wastes and sewage sludge as alternative sorbents. In terms of this, the group of Awe [76] used solid

wastes as adsorbents for H₂S removal from air and biogas. More specifically, they used CaCO₃-based solid wastes (CCW-D and CCW-S (a calcium carbonate-based form of solid waste, D and S indicate the number of the sample), commercial activated carbon, and pure commercial calcite as adsorbents for H₂S removal from air and biogas. Experimental tests were carried out in two phases, firstly with synthetic waste gas (dry air containing 200 ppmv H₂S) and secondly with synthetic biogas (CH₄: 64%, CO₂: 31%, H₂S: 200 ppmv) balanced with N₂ (approximately 5%) under room temperature and atmospheric pressure. It was observed that, in the first case, AC showed the highest adsorption efficiency toward H₂S, followed by CCW–D, CCW–S, and pure commercial calcite. Physisorption was promoted when using AC, whilst the acid-base reaction and catalytic oxidation was favored with calcium carbonate-based adsorbents. Unlike calcium carbonate-based wastes, AC gradually lost its reactivity. With respect to biogas mixture, only CCW-D and AC were studied. CCW-D rapidly lost its reactivity because no oxidation reaction occurred, due to the anoxic conditions in the biogas matrix used. Besides, AC again demonstrated increased performance for H₂S removal through physisorption, though its reactivity was decreased in the biogas matrix compared to the air matrix, which may be explained by the competitive adsorption of CO_2 and CH_4 present in the biogas matrix. The authors concluded that that the adsorption of H₂S was dependent on the porous structure and presence of alkali elements, which is because of the acidic nature of H₂S. Both solid wastes presented higher performance as opposed to the pure commercial calcite for H₂S removal. The pairing of AC and CaCO₃ led to better results in terms of sorption performance compared to pure commercial CaCO₃ and AC used alone.

Another study devoted to low–cost adsorbents for H_2S removal was reported by Skerman et al. [77]. The authors, aiming at reducing H_2S concentrations in piggery biogas, tested and compared H_2S removal by a commercial iron–oxide H_2S scavenger (cg5) with alternative solid media i.e., granulated steel furnace slag (GSFS), red soil, compost, composted beef feed lot manure, granular activated carbon (GAC), and biochar. Experiments measured single-pass H_2S removal from a pre–humidified standard gas (2000 ppm H_2S in nitrogen) onto solid media contained in a cylindrical plastic column (DN 25 mm, depth 110–147 mm). Results showed that all carbon–based materials exhibited poor physisorption, leading to decreased H_2S adsorption capacity. On the other hand, the commercial medium (cg5) performed significantly better than the other media, achieving sulfur removal of 143 g S/kg medium at breakthrough (>10 ppm outlet H_2S). The red soil was regarded as the most promising alternative medium (2–12 g S/kg medium at breakthrough).

From an economical and technical perspective, petcoke is also considered as a competitive raw material for activated carbon production owing to its high carbon content, low volatile matter, and ash content. As has been extensively reported in the literature, KOH chemical activation is regarded as a prominent activation method for preparing highly porous activated carbon from different raw materials, including petcoke [78]. In this regard, Mochizuki et al. [79] used activated carbon fabricated from petcoke via KOH chemical activation (the KOH/petcoke weight ratio and activation temperature were varied in the ranges of 2–6 and from 873 K to 1073 K, respectively). Surface chemistry, pore structure, and adsorption capacity towards H₂S of the synthesized material were studied. It was found that rising activation temperature led to an increased specific area of activated carbon, and at the same time to a reduction in the acidic surface functional groups. Enlargement in the KOH/petcoke weight ratio favored the development of the pore structure. Regarding the H₂S adsorption, experiments were carried out at room temperature, showing that the adsorption of H₂S proceeded slowly. It was also reported that the adsorption capacity of H₂S was correlated with distinguishing features of pores of activated carbons.

Considering the recent momentum towards promoting cost–effective promising materials for H_2S removal, Asaoka et al. [80] explored and tested carbonated steel slag in order to reveal the removal mechanism of H_2S by these materials and to quantify its removal performance. The authors reported that the reduction of MnO_2 in carbonated steel slag emerged at the same time as the decomposition of H_2S , whereby H_2S adsorption proceeded on the carbonated steel slag with an adsorption capacity of 7.5 mg/g. Results also showed that H_2S was captured via two reactions such as the formation of

pyrite, and the oxidation to elemental sulfur combined with the reduction of manganese oxide on the carbonated steel slag. The promising functions of steel slag as an adsorbent for the removal of H_2S have also been reported by other studies [81].

In a subsequent work by the same group [82], granulated coal ash (GCA), a mixture of coal fly ash (CFA) and blast furnace cement (BFC), was employed in order to reduce H_2S concentration in water. This group demonstrated that GCA adsorbed and oxidized H_2S efficiently [83]. The authors focused on optimizing the mixing ratio of GCA with a view to improving the rate of H_2S removal. Results showed that the highest removal rate of H_2S was detected for 87 wt% of coal fly ash owing to reduced adsorption competition between hydroxyl ions and sulfide.

As mentioned above, activated carbons can be derived by a variety of materials such as wood, peat, coal, coconut shells, fruit stones, and peels. Bazan-Wozniak et al. [84] used pistachio nutshells in order to create carbonaceous sorbents for H_2S capture. The activated carbons were fabricated using physical, chemical, and direct activation, and their surface area ranged from 277 to 1204 m²/g. According to the results reported, physical activation of pistachio nutshells could result in carbonaceous sorbents with high sorption capacity for acid gases.

Similarly, Zulkefli et al. [85] used commercial coconut shell activated carbon (CAC) treated with zinc acetate (ZnAc2), copper sulfate (CuSO₄), potassium hydroxide (KOH), sodium carbonate (Na₂CO₃), and potassium iodide (KI) in order to enhance its selectivity towards H_2S removal. The authors used two types of gas mixtures (containing $H_2S/N_2/CO_2$ and H_2S/N_2), and the operating parameters for the H_2S adsorption varied in L/D ratio (0.5–2.5) and feed flow rate (1.5–5.5 L/min), corresponding to gas hourly space velocity (GHSV) (212.4–780.0 h⁻¹). Characterization results showed that the impregnated solution homogeneously covered the adsorbent surface and morphology. BET analysis further revealed that the treated sorbents surface area lessened by up to 96%. Among the tested sorbents, ZnAc2–CAC not only demonstrated the best performance ranging within 1.3–1.7 mg H_2S/g , but also exhibited "reuse potential" for the adsorption–desorption process in numerous cycles.

Very recently, Nam et al. [86] employed an activated carbon derived from rice husks as an adsorbent for H_2S removal. The experimental results showed that the surface area of activated rice husk carbon as well as their adsorption capacity were largely dependent on carbonization temperature. Moreover, as is usually the case, when activated carbon was modified via impregnation with copper, the adsorption capacity of the Cu–treated material was increased, reaching its maximum efficiency at 450 °C, as it eliminated H_2S in 15 minutes. An interesting observation was that the regenerated Cu–treated activated carbon successfully re-adsorbed the H_2S gas, making this carbonaceous material a promising sorbent for the removal of H_2S .

Generally, the structure of activated carbons depends on the activation processes, conditions of carbonization, and type of precursor [87]. Conventional heating is considered as the most extensively used method for obtaining activated carbons. Nevertheless, this technique is associated with certain limitations such as non–uniform heating, and thus increased pyrolysis and activation temperatures are required. In this context, the group of Kazmierczak–Razna [88] applied radiation as a possible alternative for heating trying to obtain carbonaceous adsorbents from sawdust in order to remove H_2S from biogas. This method of conversion of electromagnetic energy into thermal energy is fast, occurs in the whole volume, and can be tuned. Hence, the authors used sawdust pellets and coniferous wood to fabricate (through pyrolysis at 400 °C using N₂) activated carbon and assessed its adsorption capacity for H_2S in dry and wet conditions (70% humidity). They verified that the adsorption capacity of activated carbon is reliant on the pH and activation procedure and can reach up to 4.1 mg H_2S/g_{ads} and 6.2 mg H_2S/g_{ads} in dry conditions, respectively.

Obviously, the adsorbent used in adsorption applications must exhibit high separation selectivity for the compound targeted (i.e., H_2S). In this context several studies have investigated the competitive adsorption of CO_2 and H_2S on the porous structure of the sorbent since they are both acid gases and concluded that this adverse effect can be partly eliminated by adding O_2 and humidity in the gas stream. In a recent and very promising study, De Oliveira et al. [89] examined the selectivity of an activated carbon, fabricated by Brazilian babassu coconut hush, towards a $H_2S/CO_2/CH_4$ mixture as well as H_2S and CO_2 partition coefficients (K) at different pressures and temperatures. The data obtained were also correlated by Langmuir and Toth models, and multicomponent adsorption was predicted using the extended Langmuir, extended Toth, and ideal adsorption solution theory (IAST) methods. Results demonstrated that the activated carbon adsorbed roughly 26 wt% of H_2S or CO_2 . Partition coefficients (K) values for H_2S and CO_2 reached more than 26 and 3, respectively, according to the predictive model applied, and were superior for diluted mixtures (high CH_4 content in the gas phase). Selectivity values for H_2S and CO_2 were greater than 25 for Toth and IAST. Moreover, selectivity toward CO_2 was approximately 5.6 times less than H_2S , which can be ascribed to a chemisorption phenomenon. The multicomponent results signaled S and K value degradation as the temperature rose. Results showed that the separation of H_2S and CO_2 from mixture containing CH_4 using this activated carbon as adsorbent is possible, especially for low H_2S and CO_2 concentrations and lower temperatures.

2.3. Metal Oxides

Metal oxides have exhibited high efficiency with respect to the desulfurization of coal gas, syngas, H_2 for fuel cells, and Claus tail gas etc., depending on their acid–base properties. However, pure metal oxides without a framework are characterized by low porosity, low surface area, and metal evaporation, and they are not able to resist sintering at higher temperatures, resulting in a reduced capacity for capturing H_2S [90,91]. For example, Ganwal et al. [92] mentioned that the exposure of the metal oxides to temperatures over 500 °C led to the formation of iron carbide due to excessive reduction and limited operating conditions caused by decreasing H_2S adsorption reactivity. The general reaction between H_2S and a metal oxide is as follows (where M is the representative metal):

$$M_xO_v(s) + yH_2S(g) \leftrightarrow M_xS_v(s) + yH_2O(g)$$
(3)

These limitations have led to mixed metal oxides in order to improve sulfur efficiency, prevent or delay the reduction to elemental metal, prevent sulfate formation (not reactive but occupies active material), improve dispersion and modify porosity and pore size, and impart structural strength and stability. Therefore, mixed metal oxides have gained in popularity in desulfurization processes owing to their wide range of operating temperatures (300–800 °C) and feasibility of compositional changes [93]. Zinc–, manganese–, copper–, iron–, cobalt–, nickel–, chromium–, and calcium–based oxides are the most extensively studied oxides for desulfurization in solid–gas reactions due to their high affinity to S. Of note is the work of Westmoreland et al. [94], who pioneered studies of metals and metal oxides for high temperature desulfurization. In particular, they screened the high–temperature desulfurization potential of 28 solids, mainly metal oxides, and came up with 11 candidate solids based upon the metals Fe, Zn, Mo, Mn, V, Ca, Sr, Ba, Co, Cu, and W, as these exhibited thermodynamic feasibility for high-temperature desulfurization.

Portela et al. [95] showed that among different tested metal oxides, ZnO exhibited the highest equilibrium constant for sulfidation, reducing H₂S levels to fractions of 1 ppm. However, ZnO has certain limitations associated with the desulfurization process. In the highly reducing atmosphere of syngas it is partially reduced to elemental zinc, which is volatile above 600 °C, and thus a part of the sorbent may be lost. Hence, adding TiO₂ as a stabilizer is recommended when it comes to high-temperature applications. In contrast, for low operating temperatures such as in coal gas desulfurization using ZnO with different morphologies, including an interesting review by Samokhvalov [96], but it is extremely difficult to provide a direct comparison between them owing to the different operating parameters used in each study, for example with respect to GHSV, gas-feed compositions, and definitions of breakthrough concentration.

In an early work, Jalan et al. [97] studied the initial rate of sulfidation of ZnO at 650 °C and showed that the adsorption capacity was low as the high temperatures prompted an occlusion of the material's

pores. The authors tried to regenerate the metal oxide by means of a mixture comprised of steam and air at 650 °C, but the pore structure was damaged by this process. Davidson et al. [98] published results on the adsorption of H_2S onto 300–710 μ m particles of ZnO, studied in flow reactors at low H_2S concentrations and in the presence of H_2O . These reactions were conducted at ambient conditions (25-45 °C), and approximately 40% conversion of H₂S was noted. Nevertheless, the reactions were not performed to saturation, so the total percentage of ZnO converted to ZnS was not reported. Another study focusing on ZnO was reported by Sasaoka et al. [99], who discussed the effects of the presence of CO, CO₂, and H₂O on the reaction. The authors concluded that CO inhibited the reaction by adsorbing onto the active sites, while H₂O inhibited the reaction by causing a back reaction with the ZnO to form H_2S and ZnO. Rodriguez et al. [100] published a work in which a direct comparison between the adsorption of H₂S on ZnO and MgO was attempted. The results showed that the reaction of ZnO toward H₂S was more effective. The same group compared their results to previously studied Al₂O₃, Cr₂O₃, Cr₃O₄, and Cu₂O and found a trend between the band gap energy and chemical reactivity (availability to adsorb H_2S). In particular, they investigated H_2S adsorption on different metal oxide frameworks by means of synchrotron-based high-resolution photoemission and argued that H₂S principally interacts with the metal centers of the oxides. Moreover, they also stated that at nearly ambient temperature (26.85 °C), it undergoes complete decomposition [101,102]. The authors concluded that for these systems, the smaller the band gap in the oxide, the greater its reactivity over S-containing species. The theoretical results of ab initio self consistent field (SCF) calculations and experimental results suggested that the oxide's reactivity mostly depended on the degree of the interaction between its band and the orbitals of H₂S or HS. Oxides with high ionic character, such as Al_2O_3 (band gap ~9 eV) and MgO (band gap ~6.5 eV), exhibited low reactivity in relation to H_2S , illustrating that the electrostatic interactions taking place between the dipole of H₂S and the ionic field being generated by the charges in an oxide were of subordinate importance in the adsorption process. On the other hand, Cr₃O₄ (band gap ~0 eV) interacted strongly with H₂S, CuO, and Cu₂O. Therefore, it was found that the lower the band gap energy, the more H_2S was adsorbed. Another effort in drawing comparisons of the adsorption of H_2S on ZnO and other metal oxides was reported by Carnes et al. [103], who investigated the adsorption of H_2S on microcrystalline metal oxides of Zn, Ca, Mg, and Al at high (250 ~ 500 °C) and low temperatures (25 ~ 100 °C) and they concluded that at elevated temperatures, CaO was the best choice for H₂S adsorption and ZnO appeared to be superior at temperatures lower than 100 °C.

In a more recent study, Rosso et al. [104] reported an interesting contribution devoted to the impact of calcination temperature on H₂S adsorption capacity of the ZnO sorbent. The authors tested several pure ZnO materials prepared with different methods and calcined at different temperatures (ZnO₆₀₀, ZnO₅₀₀, ZnO₄₀₀, ZnO₃₀₀) as low-temperature desulfurizing sorbents for syngas. The sulfidation performance was evaluated in a fixed-bed reactor by breakthrough curves at 250 °C. ZnO_{300} and ZnO_{400} sorbents, calcined at the lowest temperatures and hence with the highest specific surface area (SSA) and pore volume, exhibited the highest capacity in capturing sulfur, with breakthrough times varying from 430 to 530 min measured at a space velocity of 105 h^{-1} . The ZnO₄₀₀ sorbent, due to its higher structural stability, was identified as the most effective candidate for application in syngas purification. The authors evaluated the regenerability of the sorbent by subsequent sulfidation-thermal regeneration cycles (for six in particular). They found that the ZnO_{400} sorbent recovered about 50% of its initial sulfur-capturing capacity following the first regeneration and about 25% after the second regeneration, while it stabilized to a value of about 15% from the third to the sixth regeneration. A numerical model was developed and validated using the experimental data of the ZnO_{400} . The ZnO_{400} sulfidation rate was limited by the internal mass transfer resistance (which results in the rate determining step (RDS) of the process), due to the difficulty of for H_2S molecules to reach the adsorbent core, while the impact of the external mass transfer became rapidly irrelevant. Therefore, only the external layers of the sorbent participated in the sulfidation process.

However, despite the fact that the ZnO desulfurization reaction has been extensively investigated, little is known in terms of the transformation at the crystal scale, its detailed mechanism, and kinetics. Most works found in the literature presume that the diffusion of H_2S on ZnO is inward; however, Neveux et al. [105] argued that the growth mechanism was an outward one. The authors noticed the presence of voids in the interior of ZnS particles, indicating Zn^{2+} and O^{2-} diffusion from the ZnO–ZnS internal interface to the surface of the ZnS particle. Nevertheless, the formation of voids at the internal interface led to a decrease in the ZnO–ZnS internal interface and to a strong slowing down of the reaction rate while the external interface increased. Thereby, the authors suggested that diffusion through the ZnS layer was probably the rate limiting step. They also suggested a sequence of steps for the sulfidation reaction that included the outward growth of ZnS and diffusion of Zn and O₂ through ZnS. A rate expression was obtained that took into account the void evolution by means of random nucleation. The authors were able to show that the model predictions were in good agreement with the experimental rates obtained. A schematic representation of an inward and an outward growth mechanism is shown in Figure 5 [106].



Figure 5. (a) Inward ZnS mechanism and (b) outward ZnS mechanism (adopted from [105]).

Apart from ZnO–based adsorbent, CuO–based adsorbents have also received considerable attention in recent decades due to their high equilibrium sulfidation constants, which can allow extremely low-equilibrium H₂S concentration [107]. However, CuO is readily reduced to metallic copper in the presence of CO and H₂ in the fuel, downgrading its desulfurization efficiency [108,109].

In a recent study, Pola-Albores et al. [110], compared ZnO and Cu–based adsorbents for biogas desulfurizaion at room temperature. Powder–X ray diffraction and X–ray fluorescent spectroscopy analysis showed a unique zincite phase for ZnO and three phases in copper samples: Cu⁰, Cu₂O, and CuO (76.3, 18.3, and 5.4 wt%). Experiments were conducted in a fixed bed glass reactor using a simulated gas mixture containing N₂ and H₂S (100 ppm) measured at a space velocity of 9120 h⁻¹. Both sorbents became saturated after 5 min, while the presence of metallic sulfides at amounts of less than 0.05 wt% was observed. An interesting point was that following gas–phase desulfurization, desorption tests did not reveal the presence of H₂S, indicating that the adsorbed compound was chemisorbed, forming solid metallic sulfide phases.

However, the growing demand for low temperature desulfurization for environmental and economic reasons is driving the search for more efficient solutions. In this regard, Xue et al. [111] prepared a series of mixed oxide adsorbents of Zn containing Fe, Ni, Co, Mn, Cu, Al, Ti, and Zr; the H₂S adsorptive capacity of ZnO could be enhanced considerably by the doping of these metal ions. An important contribution was reported by Skrzypski et al. [112], who found that the breakthrough capacity of Cu–doped ZnO was higher than that of pure ZnO. More specifically, they probed mixed Cu–Zn oxides (Cu_{0.03}Zn_{0.97}O) and found that at 200 °C the breakthrough capacity of the sample containing 6 mol% Cu (Cu_{0.06}Zn_{0.94}O) was six times higher than that of pristine ZnO. Moreover, there was an absence of voids on the Cu–doped ZnO, which is a good indication that the growth mechanism was an inward one, in which the anions of sulfur diffused from the external surface to the internal ZnO/ZnS interface and exchanged with active oxygen species (O^{2–}). This was in contrast to pure ZnO, which at 250 °C showed the formation of voids at the interface of ZnO/ZnS. These vacancies resulted in the diffusion enhancement of sulfur and thus, in increased conversions of Cu–Zn oxides. XRD analysis revealed that the ZnS crystallite size remained unchanged during

the reaction. On the other hand, the presence of copper increased the mobility of sulfur anions in Cu–containing ZnS particles. Several other studies [113,114] also attributed the positive role of copper in improving the conversion degree of ZnO to reduced diffusional resistance in the ZnS product layer with a transition from an outward (for pure ZnO) to an inward (for Cu–doped ZnO) growth mechanism.

Very recently, Cimino et al. [115] studied the reactive adsorption of H₂S from gaseous streams at room temperature (30 °C) and 500–3000 ppm H₂S concentration (N₂ carrier gas) using a mixed Zn–Cu active phase supported onto γ -alumina (Zn–Cu/Al) in order to highlight the role of the support and the possible synergic effect between the two metals on the adsorption mechanism. XRD, diffuse reflectance infrared fourier transform spectroscopy DRIFTS, and temperature programmed desorption (TPD) NOx studies on fresh sorbents calcined at 250 °C showed that the active phase contained both metal hydroxides and hydroxynitrates, owing to the alumina support acting as a stabilizer preventing the complete decomposition of metal nitrates precursors during the calcination stage. The deposition of Cu–Zn on the support determined a negligible decrease of the pore size distribution and BET surface area in proportion to the weight increase, testifying to the high dispersion of the active face, that, in contrast, considerably increased the H₂S adsorption capacity of the bare support. The interaction between Zn and Cu entailed a gradual enhancement in the H₂S adsorption capacity, which, on the contrary, was barely affected by the inlet H_2S concentration. The sorbent exhibited its best capacity (0.82 mmol g^{-1}) in trapping H₂S at the maximum copper content (Cu_{0.5}Zn_{0.5}/Al) under both dry and wet environments. Moreover, the authors attempted to draw comparisons between the sorbent ($Cu_{0.5}Zn_{0.5}/Al$) and a respective material with similar nominal active phase composition, supported on activated carbon (Cu_{0.5}Zn_{0.5}/AC). The Cu_{0.5}Zn_{0.5}/AC exhibited an immensely higher breakpoint time and adsorption capacity at saturation compared to $Cu_{0.5}Zn_{0.5}/Al$. This behavior is most likely attributable to the significantly larger surface area of AC promoting dispersion of the Cu–Zn nanoparticles, and to the fixation of metal hydroxynitrates on the surface of the alumina support, which were less reactive compared to the corresponding oxides formed on the activated carbon.

However, inorganic supports such as alumina and silica usually offer the advantage of high thermal stability and hence potential regenerability after sulfidation/regeneration cycles, frequently carried out under oxygen/air streams [116]. Elyassi et al. [113] reported that a sequence of oxidation (in a 5%/95% O_2/N_2 mixture at 400 °C) followed by reduction (in a 10%/90% H₂/He mixture at 400 °C to reduce CuSO₄ species) of a spent silica-supported (Cu–ZnO–SBA–15) sorbent was efficient in fully restoring the capacity of the sorbent in trapping H₂S. On the other hand, Wang et al. [117] noticed that the CuO–SiO₂ 3DOM sorbents, whose behavior on adsorption applications will be further analyzed later, exhibited poor H₂S capture capacity at ambient temperature when performing the regeneration stage at 650 °C in air, owing to the agglomeration of CuO upon exposure to high temperature. Therefore, the issues associated with the sorbent's regenerability has to be evaluated depending on different factors including the nature of the substrate/sulfation products, their chemical interaction, and possible sintering phenomena.

The preparation of metal–supported catalysts by co-precipitation (cp) or multi–precipitation (mp) was also investigated. Jiang et al. [118] examined the performance of Cu–Zn and Cu–Zn–Al synthesized by means of cp and mp and found that adsorbents with high Cu concentrations were more efficient in capturing H₂S compared to adsorbents with high Zn concentrations. As an example, at 80 °C, mp–Cu₈₀Zn₁₀Al₁₀ showed almost complete conversion. The etiology for the increased efficiency of Cu–rich adsorbents was the faster sulfidation rate of CuO as compared to ZnO.

In general, mixed metal oxides that were prepared using the co-precipitation method exhibited higher SSAs, smaller particle sizes, and improved H₂S capacity in comparison to their counterparts that were prepared by simple impregnation [119]. Baird et al. [120] also probed H₂S adsorption on a Co-Zn-Al-O that was synthesized using co-precipitation. As expected, the presence of alumina led to a higher SSA, but the doped materials were not able to increase their capacity in trapping H₂S. Notwithstanding, mixed metal oxides (Co-Zn) with different Co/Zn ratios exhibited positive correlations between the increase in percent utilization and the increase in the surface area. Generally, Co doping

leads to increased SSA by decreasing the size of the particle. From a thermodynamic perspective, ZnO has more positive free energy for sulfidation in comparison with Co_3O_4 [121].

Westmoreland et al. [94] also defined the initial rates for the reaction between H₂S and MnO, ZnO, CaO, and V₂O₃ over a temperature range of 300 to 800 °C, using a thermos-balance reactor. It was shown that at temperatures between 300 and 800 °C the intrinsic reaction rate of H₂S with ZnO was almost 10 times less than that of MnO, despite the fact that the SSA of ZnO was almost 10 times higher than that of the MnO.

Zn metal oxides doped with Fe, Ni, Co, Mn, Cu, Al, Ti, and Zr exhibited higher conversions at ambient temperature, notably for $Zn_{2.9}MnO_{4.2}$. It is worth mentioning that pure manganese tetroxide (Mn₃O₄) is associated with poor conversion, but the reasons for this behavior remain unclear [111].

Polychronopoulou et al. [122] investigated the regeneration capacity of Zn–Ti–based mixed metal oxides and concluded that its doping with Mn, Cu, or Mo resulted in an enhancement in H₂S capture for the regenerated material, notably 41 mg/g for 10Mn–45Zn–45Ti–O (600 ppm H₂S in the feed). Moreover, the addition of 1% H₂O in the gas mixture resulted at a considerable increase in capacity (160 mg/g).

Liu et al. [123] studied CuO-based mixed oxides that were prepared by co-precipitation (Table 4) as adsorbents for H₂S removal and noted increased capacities for oxides that were doped by Fe. It was shown that CuO-based adsorbents were able to remove H₂S from a CO₂ stream to less than 0.1 ppm at 40 °C. Capacities were higher for H₂S in N₂/H₂S gas mixture (1000 ppm H₂S) in comparison to a CO₂/H₂S gas mixture (1000 ppm H₂S), indicating the competitive adsorption between these acid gases. Doped CuO (Fe–Cu–Al–O) exhibited the highest breakthrough capacity of 113.9 mg g⁻¹ at 40 °C. In the temperature range of 40–130 °C, the breakthrough capacity of the modified CuO increased with adsorption temperature, which nonetheless would have been below 100 °C in the presence of CO₂ owing to the possibility of generating COS impurities. As expected, at lower space velocities, increased breakthrough capacities were observed. It was also reported that the inhibitory effect (CO₂ inhibits the adsorption of H₂S) was higher for pristine CuO in comparison to doped CuO. Five cycles of adsorption and regeneration were performed using CuO, Cu–Al–O, and Fe–Cu–Al–O at 100 °C in air. Results showed that only CuO was able to maintain its regeneration capacity (75% of the capacity of the fresh adsorbent). The latter doped materials showed reduced regenerated capacities and became constant during the last two cycles at 50% and 43% of the initial value, respectively.

| Adsorbent | SSA (m ² /g) | mg S/g Sorbent | T (°C) | Gas Composition |
|---------------------------------------|-------------------------|----------------|--------|-------------------|
| CuO | 16.4 | 17.7 | | |
| Cu ₃ Al | 72.3 | 86.0 | | |
| Co _{0.44} Cu ₃ Al | 87.4 | 73.4 | 40 | |
| Ni _{0.44} Cu ₃ Al | 86.0 | 55.7 | | 0.1% HaS in COa |
| | | 91.1 | | 0.170 H20 HI CO2 |
| Con Cute Al | 00 1 | 207 | 70 | |
| Ce _{0.44} Cu ₃ AI | 82.1 | 212 | 100 | |
| | | 220 | 130 | |
| CuO | 16.4 | 25.3 | | |
| Cu ₃ Al | 72.3 | 106.0 | 40 | $0.1\%S$ in N_2 |
| Fe _{0.44} Cu ₃ Al | 96.7 | 125.0 | | |

Table 4. Brunauer–Emmet–Teller (BET) surface areas and breakthrough capacity in mixed copper–based metal oxides, prepared via co–precipitation, for H₂S adsorption (adopted from [123]). SSA: specific surface area.

Jung et al. [124], with a view to enhancing the poor regeneration properties of the $ZnO-Al_2O_3$ (ZA) sorbent featuring high sulfur removal capacity and fast H_2S adsorption rate, added 5–10 wt% of metal oxides such as Fe_2O_3 , Co_3O_4 , NiO, and CeO_2 . The method used for the preparation of the sorbents was co–precipitation, whilst their trapping capacities and regeneration properties were evaluated

in a fixed–bed reactor during multiple regeneration–sulfidation cycles at temperatures between 480 and 580 °C. All the sorbents exhibited sufficient sulfur removal (0.17–0.20 g S/g) and regeneration properties, which were maintained even after 10 cycles of sulfidation and regeneration, as compared with the conventional ZnO–Al₂O₃ and ZnO–TiO₂ prepared by the physical mixing method. Fe–, Co–, and Ni–containing adsorbents formed their aluminates, which did not transform to sulfide during sulfidation. The additives/aluminates strongly promoted the transformation of S contained in ZnS into SO₂. Cerium dioxide exhibited similar behavior to aluminates in terms of the sulfur oxidation.

The studies mentioned above clearly demonstrate that it is extremely difficult to achieve high regeneration capacities for mixed metal oxides. Thus, further research in this area should concentrate not only on increasing the capacity of these materials in capturing H₂S but also on enhancing regenerability issues.

Another very interesting study in the context of Fe_2O_3 desulfurization properties was reported by the group of Thanakunpaisit [125] who studied the removal of H_2S contained in biogas using Fe_2O_3 -rich laterite materials as adsorbents, which promote potential reactivity with H_2S . Initially, to predict the interaction among five principle compositions of biogas (CH₄, H_2S , CO₂, and N) and one composition of laterite (Fe₂O₃), the density functional theory with the B3LYP/6–31G(d,p) level was applied. Study results depicted that energy adsorption between Fe_2O_3 and H_2S was –26.06 kcal/mol, which was higher in comparison to that of other compositions of biogas and Fe_2O_3 due to the strong affinity between the sulfur atom of H_2S and the iron atom of Fe_2O_3 . Afterward, the adsorption of H_2S and CH₄ on laterite was investigated. Adsorption efficiency values for H_2S and CH₄ were 91.67% and 1.84%, respectively.

Thermodynamic investigations also concluded that sorbents doped with transition metal oxides such as oxides of Co, Cu, Mn, Cr, Fe, Ni, and W are potentially attractive replacements for low temperature desulfurization [126–128]. Among these, Co–doped sorbents are thought to have the highest degree of H_2S removal rates and subsequent metal sulfide conversions.

The group of Pahalagedara [129] studied mesoporous cobalt oxides calcinated in different temperatures (150, 250, 350, or 450 °C) as desulfurization sorbents and found that they may attain 100% capacity at 150 °C. A significantly high sulfur sorption capacity was also noted at room temperature (13.4 g S/100 g sorbent) as well as in the temperature range of 175–250 °C (65.0–68.9 g S/100 g sorbent). According to the literature, even though the sulfidation at low temperatures is kinetically slow, the mesoporous cobalt oxide materials showed high sulfur capacities and reached high oxide to sulfide conversions. The high breakthrough capacities recorded are probably due to H₂S physical adsorption. Other mesoporous materials (Cr_2O_3 , CuO, Mn_2O_3 , and Fe_2O_3) also showed superior H₂S removal capacity compared to their nonporous analogues (as high as 200 times).

Van Nisselrooya et al. [130] used a catalyst comprised of chromium and iron oxides supported on α -alumina in order to enhance the thermodynamically limited Claus process, introducing the term "Superclaus catalyst". Nevertheless, due to the toxic effects of chromium, further research into the development of new catalysts for this reaction is needed [131].

Several works have investigated vanadium–based catalysts supported on different metal oxides for H₂S abatement in the temperature range of 50–250 °C. It was reported that the catalyst supported on CeO₂ exhibited the higher catalytic performance at 150–250 °C with a moderate selectivity to SO₂ (13%) [132]. Having said that, Palma et al. [133] investigated vanadium–based catalysts supported on ceria for the direct and selective oxidation of H₂S to sulfur and water at low temperature. Two different vanadium-grafted catalysts (20–50 wt% of V₂O₅) were fabricated, and tested at temperatures varying from 150–200 °C with a view to identifying the optimum catalytic conditions. The most effective catalyst was that with the 20 wt% of V₂O₅, which exhibited 99% sulfur selectivity and equilibrium H₂S conversion at different operating conditions. Palma et al. [133] also studied the catalytic performance in the presence of three principle compositions of biogas stream (CH₄, CO₂, and H₂O) at 150 °C, in an attempt to investigate the possible formation of by–products such as COS and CS2. Results revealed that the presence of CO₂ and CH₄ had no impact regarding the formation of both SO₂ and undesired secondary products. Moreover, the authors studied the effect of the H₂S inlet concentration, contact time, molar feed ratio of O_2/H_2S , and temperature at 80 °C. The results obtained by changing the H_2S concentration in the feed stream verified that low concentrations ($H_2S = 80-100$ ppm) led to a complete H_2S conversion at 100 °C, yet with increased SO₂ selectivity. In the presence of higher H_2S concentrations (200 ppm) no catalyst deactivation occurred, while the deposition of the sulfur on the catalyst surface resulted in clogged pores of the carrier. The temperature at low contact time affected to an important extent the catalytic activity and catalyst stability, while strong deactivation and low H_2S conversion were detected at 80 °C as a result of the low reaction temperature that did not favor the reaction from a kinetic perspective. At the end, a stability experiment was performed at the minimum temperature (80 °C) and at the maximum contact time (240 ms) by using a specific molar feed ratio ($O_2/H_2S = 1$). Results showed a slight deactivation starting from 20 h of time on stream, probably owing to sulfur blocking the pores of the CeO₂. It is worth mentioning that when performing the same experiment at a higher temperature of 120 °C no deactivation occurred.

Researchers also investigated H₂S adsorption in three-dimensionally ordered macroporous (3DOM) structures. Recently, Fan et al. [134] synthesized an iron oxide sorbent with a structure composed of three-dimensionally ordered macropores (3DOM). The 3DOM media feature high porosity with interconnected macropores, large surface area, and nanosized active particles, and represent an alternative at medium–temperature desulfurization applications. Furthermore, stable γ –Fe₂O₃ proved to be easily prepared via a colloidal crystal templating method when silicon was added to the precursors.

Huang et al. [135] studied H₂S adsorption using iron oxide γ -Fe₂O₃ and silica-supported iron oxide γ -Fe₂O₃/SiO₂ (3DOM-FS) with different Fe:Si molar ratios from 1 to 16, at low temperatures (20–80 °C) in the presence and/or absence of humidity. Then, the performance of these materials was compared with that of a-Fe₂O₃ and the commercial sorbent HXT-1 (amorphous hydrated iron oxide). Adding the amorphous and highly dispersed silicon in γ -Fe₂O₃ improved the dispersion of Fe₂O₃ and hampered its transformation to α -Fe₂O₃ during calcination. The activity of γ -Fe₂O₃ was higher than that of HXT–1 at temperatures over 60 °C, whereas a–Fe₂O₃ had little activity. The vacancies in the lattice of γ -Fe₂O₃ promoted the ion diffusion. Moreover, the reference γ -Fe₂O₃ featuring lower density, larger surface area, and smaller particle size than that of α -Fe₂O₃ exhibited increased performance in trapping H₂S as compared with the reference α -Fe₂O₃, but lower performance when evaluated against 3DOM–FS. Decreased capacity at high Fe:Si ratios was ascribed to the fact that α –Fe₂O₃ was present. The authors also reported that relative humidity (approximately 10%) had a positive role in H₂S capture. Moreover, it was reported that at 300 °C, conventional regeneration by means of 5% O₂ in N_2 led to a significant drop in the capacity of the regenerated sorbent. As an alternative regeneration technique, the authors suggested the use of 5% O₂ in the feed stream and showed that desulfurization and regeneration could occur synchronously; this resulted in substantially increased breakthrough capacities (79.1% from 40.61%) in comparison to those achieved in the absence of oxygen from the gas mixture. It is not quite clear whether this alternative regeneration method promotes H_2S oxidation to SO2. Monitoring SO2 concentration may provide evidence of the presence or absence of sulfur during this process.

As already mentioned, zinc oxide–based materials have exhibited promising desulfurization properties. ZnO has the ability to react with H₂S, leading to the formation of zinc sulfide by means of an exothermic reaction. Accordingly, decreased temperatures give rise to higher desulfurization efficiency. Wang et al. [136] synthesized, via a colloidal crystal template method, a number of ZnO silica-based 3DOM structures with different weight ratios of ZnO (3D–SZx–500, where x (ZnO weight ratio) = 20%, 50%, and 73%) with a view to capturing H₂S at ambient temperature. The synthesized materials exhibited a well–ordered 3D–interconnected network consisting of macropores, mesopores, and micropores. It was reported that both the Zn/Si ratio and calcination temperature strongly affected structural parameters. Moreover, the surface areas and pore volumes reduced with increasing the Zn/Si ratio, presumably owing to the agglomeration of ZnO species in the pores. The same decreasing effect was observed for the surface areas and pore volumes at high calcination temperatures (>500 °C) due to

the shrinkage of the channels. Even lower calcination temperatures (400 °C) led to the production of carbon impurities, which affected the ZnO surface and occluded the pore channels, resulting in reduced sulfur adsorption capacity. Furthermore, the breakthrough time increased with increased ZnO content. In particular, 3DOM sorbents exhibited the highest utilization (69%) and sulfur capacity (135 mg g⁻¹) with 50 wt% of ZnO. It was also reported that moisture could have a positive effect on the removal of H₂S.

Another work in the context of 3DOM structure H₂S adsorbents was reported by the group of Wang [137] who prepared two types of cobalt oxide-silica composites via the sol-gel method using different alcohols (n-butyl alcohol and ethylene glycol) as sol precursors. The respective adsorbents with the 3DOM structure were also synthesized by means of the colloidal crystal template method. In order to understand the physicochemical properties of the materials, several characterization techniques were used, while the efficiency of the sorbent in capturing H_2S was evaluated at room temperature. It was shown that use of n-butyl alcohol in sol precursors could result in a sorbent (SCN57-500) featuring a very large surface area $(314.5 \text{ m}^2/\text{g})$ and ordered mesoporocity, with a diameter of 2–5 nm in grains. However, it exhibited extremely decreased capacity in capturing H_2S (12 mg/g). On the other hand, (SCE57–500) had a smaller surface area (137.2 m^2/g) but well–distributed particles, resulting in increased H₂S breakthrough capacity of 28 mg/g. It was reported that use of ethylene glycol could benefit the formation of 3DOM materials. Unlike 3D–SCN57–500 (159.5 m²/g), the surface area of 3D–SCE57–500 was considerably enhanced (257.4 m²/g). The decreased surface area of 3D–SCN57–500 was due to the sintering of the sorbent's grains, which affected the pore volume. It can be deduced that the increased surface area of 3DOM composites was attributed to the high dispersion, i.e., the newly formed puny nanoscale grains. The desulfurization performance of 3DOM composites was strongly affected by the calcination temperature as well as the Co_3O_4 content of the material. The 3DOM sorbents achieved higher capacities for trapping H₂S compared to their respective bulk counterparts. Study results suggested that the crystalline structure or dispersion contributed to the adsorbent's reactivity, along with the interconnected and well-ordered macropores. Despite the fact that sulfidation at low temperature was kinetically slow, the breakthrough sulfur capacity of 3D–SCE57–500 could reach as high as 189 mg/g with Co_3O_4 utilization of 63% at room temperature. The 3D–SCE57–500 showed increased performance compared with the reference mesoporous cobalt oxide. Using XRD and selected area (electron) diffraction (SAED) analysis, the presence of sulfide cobalt in amorphous form was observed, and regarded as CoS by XPS and thermogravimetric-mass spectrometric TG-MS analysis. Moreover, XPS and TG-MS analysis was carried out for 3D-SCE57-500S and the involved reactions for H_2S removal by Co_3O_4 in the discussed experimental conditions. The results exhibited the presence of at least five distinct sulfidation products (CoS, CoSO₄, CoSOH, CoOOH, and elemental sulfur) that were produced during the sulfidation and storage process.

2.4. Composite Materials

2.4.1. Metal Oxide/Mesoporous Silica

Despite the fact that metal oxides exhibit high H_2S affinity, they also have a number of shortcomings, which include low porosity, low surface area, and volatility. Moreover, metal oxides are also prone to sintering phenomena at high temperatures. Thus, the sulfur removal capacity of the sorbent declines during desulfurization–regeneration cycles. On the other hand, ordered mesoporous molecular silica, featuring control of reactions due to lower reactivity (i.e., in comparison to transition metals), the variety of possible structures, enhanced thermal stability, and the range of functionalization methods, constitutes an interesting alternative.

Wang et al. [138,139] was the first to investigate the adsorption of H_2S on mesoporous silica that was impregnated with metal oxides, namely, ZnO/SBA–15 and Fe₂O₃/SBA–15. However, the breakthrough capacities were inconsistent compared to the breakthrough times they reported, and hence recalculation of new ones based on the details of the experimental setup was performed by Shah et al. [121]. It was

found that H_2S reacted with metals oxides in an inert atmosphere and that it was possible to achieve complete utilization of metal oxides that were deposited on carriers with high surface areas. The authors also argued that the adsorption of H_2S could surpass the theoretical ceiling, as the Claus reaction is carried out between oxygen and hydrogen sulfide contained in the air, while the metal particles act as a catalyst for this reaction and are not involved in a chemical reaction with H_2S to yield metal sulfide.

Quite recently, Geng et al. [140], by means of melt infiltration and impregnation, prepared zinc oxide (ZnO) sorbents supported onto three molecular sieves (MCM-41, SBA-15, and MCM-48) for H₂S removal at room temperature. The physicochemical properties of the two aforementioned modification methods were compared to draw conclusions. X–ray diffraction, nitrogen adsorption, and TEM characterizations showed that due to penetration of the precursor into the pores of carrier via capillary force, melt infiltration could lead to more even ZnO dispersion in the pores of molecular sieve as compared to impregnation. Breakthrough curves exhibited that the best ZnO loading contents were 20 wt% on SBA-15 and MCM-41, and 30 wt% on MCM-48, and their equivalent utilization ratios were 69.8%, 52.2%, and 45.1% (Table 5), respectively. With respect to the impregnation method, the utilization ratio of the components was considerably lower. Breakthrough tests and several adsorption/regeneration cycles revealed that sorbents with a massive specific surface area, extensive pore size, and high strength were favorable. Nevertheless, high strength and small pore size molecular sieve could greatly benefit from melt infiltration.

Table 5. Breakthrough sulfur capacity of commercial desulfurizer and molecular sieves supported ZnO materials when outlet concentration reached 1.5 mg/m^3 at room temperature (25–30 °C) (adopted from [140]).

| Sorbent | Inlet H ₂ S (mg/m ³) | Sulfur Capacity mg S/g | Utilization Ration of ZnO (%) | Source |
|---------------------------|--|---------------------------|----------------------------------|--------|
| Commercial ZnO | 500 | 37.7 | 16.00 | [141] |
| ZnO (15%)/MCM-41 | 300 | 5.9 | 10.01 | [142] |
| ZnO (15%)/SBA-15-S | 300 | 18.5 | 31.37 | [142] |
| ZnO(15%)/SBA-15-F | 300 | 15.6 | 26.46 | [142] |
| Z ₃₀ /MCM-48 | 1200 | 14.8 | 12.60 | [143] |
| M-Z ₂₀ /MCM-41 | 500 | 54.9 | 69.80 | [140] |
| M-Z ₂₀ /SBA-15 | 500 | 41.0 | 52.20 | [140] |
| M-Z ₂₀ /MCM-48 | 500 | 53.2 | 45.10 | [140] |

Two different kinds of mesoporous materials, namely Cu–Mn mixed oxide/SBA–15 and La–Mn mixed oxide/KIT6, were prepared as sorbents for the removal of H₂S from hot coal gas [144]. In this approach, the deactivation kinetics model for the removal of H₂S was studied by investigating several kinetic parameters such as apparent activation energy, rate constants, reaction orders, and deactivation energy. Study results revealed the high adsorption capacity of mixed metal oxides (Cu1Mn9/S15 and La3Mn97/K6) toward H₂S along with the high structural stability of these materials at high temperatures.

The most significant limitation of this type of composite materials is the fact that the active component is a minor part of the overall material. Therefore, although it is possible to utilize the metal oxide to a high degree, the absolute amount of adsorbed H_2S per unit mass of the adsorbent is not significant. Several studies reported that increasing the loading of metal oxide may lead to improving the H_2S capacity but not without loss in percent utilization [140,144]. Further research to increase the fraction and the utilization of the active phase of these composite materials and high regenerability of the sorbents would result in more promising candidates.

2.4.2. Metal Oxide/Activated Carbon

Cu–Zn–Ni nanoparticles (NPs) were loaded on activated carbon and Ni–Co–NPs were loaded on γ –alumina (Al₂O₃). These nanocomposites were applied for hydrogen sulfide removal (H₂S) from natural gas, and their degree of effectiveness was tested at different reaction conditions, varying parameters such as the amount of adsorbent, flow rate, temperature, pressure, and volume of gas [145]. The best conditions for maximum removal of H₂S (94% and 91.6%) by Cu–Zn–Ni/AC and Co–Ni/ γ –Al₂O₃ were determined to be 0.3 g of adsorbent, flow rate of 0.15 L/min, 15 °C, and 7 Psi for both adsorbents, and 5.5 and 6.5 L of sample for Cu–Zn–Ni/AC and Co–Ni/ γ –Al₂O₃, respectively. The physisorption nature of adsorption was confirmed by the negative value of Δ G (Table 6).

| T (°K) | Adsorbent | Kc | r ² | ΔG° _{ads} (kj·mol ^{−1}) | ΔH° _{ads} (kj·mol ^{−1}) |
|--------|--|------|----------------|---|---|
| 288 | | 6.74 | | -4.54 | |
| 298 | $C_{\rm H}$ $T_{\rm m}$ NE/AC | 3.58 | 0.070 | -3.14 | 20.07 |
| 308 | Cu-Zn-MI/AC | 2.22 | 0.970 | -2.04 | -38.07 |
| 318 | | 1.66 | | -1.40 | |
| 288 | | 6.08 | | -4.32 | |
| 298 | Ni–Co/γ–Al ₂ O ₃ | 3.23 | 0.075 | -2.90 | 27.09 |
| 308 | | 2.09 | 0.975 | -1.88 | -37.96 |
| 318 | | 1.53 | | -1.13 | |

Table 6. Thermodynamic parameters calculated for the adsorption of H_2S onto Co–Ni/ γ –Al₂O₃ and Cu–Zn–Ni/AC (adopted from [145]).

The source of the synergic effect of zinc and copper oxides (ZnO–CuO) supported onto activated carbon on the removal of H₂S from various gaseous streams at low temperature was also studied by de Falco et al. [146]. Commercial activated carbon was functionalized by impregnation using fixed total metal content and variable Zn:Cu ratio in order to prepare adsorbents for H₂S removal. H₂S (100–3000 ppmv in N₂) removal tests were run under dynamic conditions at 30 °C and compared through analysis of their breakthrough curves, adsorption rates, and values of adsorption capacity. Fresh and spent sorbents were characterized by various methods. Temperature programmed desorption/temperature programmed oxidation (TPO) trials testified, as in the former work, to the complexity of the surface reactions which heavily depended on the Zn:Cu ratio, the interactions between metal oxides and carbonaceous support, and the textural properties of the material.

Sorbents for low-temperature reactive adsorption were prepared and mixed with metal oxides (ZnO and CuO) and then supported on commercial activated carbon at fixed total metal loading and Cu:Zn atomic ratios from 0:1 to 1:1. H_2S removal tests were carried out under dynamic conditions at 30 °C. As a result of the high dispersion of the metal oxide phase and its propitious interaction with the carbonaceous support, the modified materials demonstrated a highly increased performance in terms of H_2S removal as compared to the raw activated carbon under dry conditions. On the other hand, the pore size distribution of the activated carbon support was affected due to high dispersion of the metal oxides. Moreover, the utilization factor of the active phase was enhanced along with the Cu content up to 76%, thereby showing a positive impact of Cu addition on the reactivity of ZnO, even at low Cu concentrations. TPD studies of H_2S from saturated adsorbents displayed that H_2S adsorption was combined with oxidation phenomena, resulting in the formation of metal sulfates except for metal sulfides and/or elemental sulfur [147].

Ferrous nanoparticles (Fe–NPs) were successfully loaded onto the carbon aerogel and employed as a sorbent for H₂S removal from hot coal gas [148]. This modified carbon aerogel, using 50%Fe/C700, was prepared as a precursor and demonstrated the highest performance at 600 °C (12.54 g S/100 g sorbent) probably owing to the larger specific area and pore volume of the sorbent at a higher temperature. This method was efficiently used to remove H₂S from hot coal gas, which provides new perspectives in hot coal gas desulfurization.

Microwaves were applied for the high-temperature removal of H_2S via Fe–based adsorbent supported on active coke (Fe₂O₃/AC) [149]. The determining effect of numerous operating parameters, such as the influence of loading content, adsorption temperature, and desulfurization method on the sulfidation properties of adsorbents was studied. N₂ adsorption, XRD, X–ray photoelectron spectroscopy (XPS), and scanning electron microscopy (SEM) techniques were employed to depict the structure of components before and after desulfurization. Study results demonstrated the high performance of the (Fe₂O₃/AC) sorbent, especially at high temperatures, as well as an increased number of oxygen and sulfide vacancies on the surface of the optimized desulfurizers. It was also reported in various studies that when iron oxide is exposed to temperatures above 500 °C, it forms iron carbide by excessive reduction and limited operating conditions due to decreasing H₂S adsorption reactivity [150].

A major drawback of this type of composite materials is the low probability of complete regeneration and reusability. This means that the disposal of the exhausted sorbents poses environmental and health–related challenges. For example, due to the pyrophobic nature of specific metal sulfides such as copper (II) or iron sulfide, acid gases may be released into the air. Furthermore, the dissolution of such gases in H₂O traps may not be an eco–friendly alternative. Therefore, efforts need to be made for controlling pollution due to the disposal of wastes by conversion of these unwanted wastes into utilizable raw materials for beneficial use. For example, some efficient techniques for the treatment of spent adsorbents involve regeneration, purging by inert gases, washing with water, and purging with steam [151]. However, these processes may lead to additional costs and thus represent an economically unviable solution.

2.4.3. Metal Hydroxide/Activated Carbon

The particles of metal hydroxides are inclined to be aggregated during the precipitation process, leading to the reduction of the active surface [152]. To overcome this drawback, support materials such as graphite, zeolite, and activated carbon have been applied. Activated carbons have been taken into account as the most preferable support due to their surface area, pore volume, and low cost.

Typically, zinc and iron hydroxide are regarded as the sorbents with the highest H_2S adsorption capacity [152–154]. Their capacity in trapping H_2S is largely reliant on the preparation method, for example, 47.2 mg S/g by the composite of zinc oxide and reduced graphene oxide [155], 49.0 mg H_2S /g by zinc hydroxide with graphene oxide [156], and 65 mg H_2S /g by iron–based adsorbent [157].

Bimetal hydroxide, by incorporating some other elements into iron hydroxide, seems to enhance the H_2S capture. The synergistic effect of bimetallic composites is due to the interaction of metal–metal or metal–oxygen–metal, which may influence both the physicochemical properties during the reaction [157].

Recently, bimetallic zinc–iron (Zn–Fe) hydroxides were fabricated by means of the co–precipitation method at room temperature and applied as a sorbent for the removal H₂S from mixed gas [158]. Adsorbent performance was characterized by altering several parameters at a time, such as the pH of the mixing solution of precipitating reagents, aging temperature (for adsorption capacity), and influence of Zn/Fe molar ratio, finalized to achieve optimal conditions. Ten percent powdered activated carbon (PAC) was used as the support material to ensure an active site on the modified materials. The modified sorbent exhibited maximum adsorption capacity of 143 mg H₂S/g, which was superior when evaluated against pure Fe hydroxide or Zn hydroxide. Following H₂S adsorption, scanning electron microscopy identified ZnS and FeS salts due to hydroxyl groups on the adsorbent surface. The study results verified that both the size and morphology of sorbents held a crucial role in improving the adsorption capacity of materials.

Nevertheless, few studies have been carried out on bimetallic hydroxides used as H_2S adsorbents [159] and further research is needed.

2.4.4. Supported Amines

Supported amine sorbents are usually categorized into three distinct classes. Class 1 adsorbents are based on porous supports impregnated with monomeric or polymeric amines which are physically loaded onto or into the support. This class of sorbents was first investigated by Song et al. in 2002 [160–165]. Class 2 adsorbents constitute adsorbents with a covalent bond between the solid support and the amine by means of silane chemistry or via polymeric supports with side chains that contain amines. The first class 2 amine adsorbents were reported by Tsuda et al. in 1992 [166,167];

noteworthy contributions on these materials were reported by the group of Sayari [168–175]. Class 3 adsorbents consist of porous supports through which aminopolymers are polymerized in situ. Materials in the class 3 category combine higher loadings of amines in comparison to materials of class 1 and improved stability in relation to materials of class 2. This is because of the development of amine–support covalent linkages [176].

Ma et al. [165] carried out an excellent study in which they reported a high degree of dependence between these sorbents and temperature for the competitive sorption of CO_2 and H_2S . With respect to the polyethyleneimine (PEI)/SBA–15 sorbents, at 75 °C they exhibited high capacity in trapping CO_2 (3.2 mmol/g, P = 0.15 atm). However, the kinetic barrier for H_2S was lower in comparison to CO_2 , which may be ascribed to the rapid transfer of protons during the reaction, leading to improved hydrogen sulfide breakthrough capacities at the low temperature of 22 °C. The authors proposed a two-stage sorption process with two sorption beds in series (Figure 6), using a model gas containing 0.40 v% H_2S , 2.40 v% CO_2 , and 20 v% H_2 in N_2 , with the first column being operated at 75 °C in order to remove CO_2 , and the second at 22 °C for H_2S removal.



Figure 6. Schematic diagram of a two-stage CO₂ and H₂S experimental setup (adopted from [165]).

Yoosuk et al. [177] also performed two–stage studies for polyethyleneimine which was loaded on fumed silica (fSi), focusing on regeneration carried out in multiple cycles. Results showed that the breakthrough capacities were improved for acid gases with single-component adsorption carried out at 30 and 80 °C, corroborating the studies carried out by Ma et al. [176]. However, for multi-component adsorption with a model gas containing 20% (v/v) CO₂, 0.36% (v/v) H₂S, and 74.8% (v/v) CH₄ balanced with N₂ with two sorption beds, the capacity for adsorption of carbon dioxide increased from 2.2 mmol/g to approximately 3.5 mmol/g. In contrast, the adsorption capacity of H₂S dropped from the anticipated 1.2 mmol/g to 0.045 mmol/g. The results obtained were somewhat different than those reported by Ma et al. [176], as adsorption at 22 °C for PEI/SBA–15 was significantly higher (the divergence observed at 30 °C for PEI/fSi was much lower). This can be probably explained by the fact that the gas mixture used by this group contained a much higher CO₂ concentration (20%) compared to H₂S (0.36%), while the model gas used by the group of Ma contained 0.40 v% H₂S and 2.40 v% CO₂. These deviations highlight the significance of choosing the appropriate process conditions in selecting candidate sorbents.

In a more recent study, Quan et al. [178], with a view to reducing the extra operational costs that a two-stage process require, employed a one-stage H₂S adsorption process using amine-coated (PEI, polyallylamine (PA) and tetramethyl hexanediamine (TMHDA)) mesoporous silica employed as molecular sieve for the selective removal of H₂S from biogas (CO₂ up to 40 % wt). In the case where the loading level for PA/SBA–15, PEI/SBA–15, and TMHDA/SBA–15 was fixed at 30 wt%, it was found that the breakthrough time for both PA/SBA–15 and PEI/SBA–15 dropped significantly in the presence of CO₂, while in contrast, the breakthrough time of TMHDA/SBA–15 remained nearly unchanged following CO₂ introduction in the mixture. Therefore, it can be concluded that introducing CO₂ into the feed gas affected the H₂S adsorption capacity of the sorbent using primary and secondary amines. Nevertheless, 90% of the capacity could be maintained with tertiary amine–based sorbent,

even at 40% CO₂. This work completes the previous two studies, and demonstrates the great potential of TMHDA/SBA–15 for selective H_2S removal from biogas. However, a small number of papers have focused on this matter; thus, further investigations are required to improve the H_2S sorption performance and understand the mechanism of H_2S sorption on the tertiary-amine-based "molecular basket" sorbent.

Although these sorbents are endowed with some interesting characteristics, the fact that ordered mesoporous silica is in powder form means that at high pressure drops, its direct exploitation in industrial scale is inhibited. In this context, it is worth mentioning that several studies devoted to porous silica supports for adsorption applications have been carried out, but they will not be further discussed in this review.

2.5. MOFs (Metal–Organic Frameworks)

MOFs can be considered as inorganic-organic hybrid materials that are crystalline in nature and are characterized by an open and porous framework [179]. They consist of metal ions or clusters of metal ions (inorganic secondary building units, ISBUs) linked together by polydentate organic linkers. The organic units, which are negatively charged molecules, are usually ditopic or polytopic organic carboxylates, which when linked to metal ions form nodes that bind the arms of the linkers, resulting in architecturally robust crystalline MOF structures. The possible use of MOFs as adsorbents for H₂S removal has been extensively examined mainly due to their high surface areas and porosity, the ability to vary their size and nature without changing their underlying topology, and the fact that they can be tailored in terms of chemical functionality. As discussed above, these characteristics have not been observed with other conventional adsorbents such as zeolites and activated carbons. The group of Hamon conducted the first experimental study of H₂S adsorption in MOFs. In particular, they studied small-pore (MIL-53(Al^{III}, Cr^{III}, Fe^{III}) and MIL-47(VIV)) and large-pore (MIL-100 (Cr) and MIL-101 (Cr)) Materials of Institute Lavoisier (MIL) frameworks. They found adsorption capacities ranging from 38.4 mmol·g⁻¹ at 2 MPa for MIL–101(Cr) to 8.53 mmol·g⁻¹ for MIL–53(Fe^{III}) at 1.6 MPa [180]. Following this work, several other studies have dealt with the adsorption of H₂S on pristine and functionalized MOF structures [181–183]. However, MOFs are yet to have a commercial impact, and concerns regarding their cost effectiveness and stability remain.

3. Conclusions

This work reviews the recent literature with regard to H_2S adsorption in an attempt to shed light on the most promising materials currently in development and use for this process. Bearing in mind the corrosive and highly toxic nature of H_2S and the fact that it is found at a wide range of concentrations in natural gas, syngas, biogas, and other industrial gases, the development of cost-efficient desulfurization materials is of paramount importance. The design of appropriate materials becomes more complicated by the presence of CO_2 , which usually co-exists in gas mixtures containing H_2S and is more acidic in comparison. Moreover, the presence of H_2O , another likely component of industrial gases, may have positive or negative implications on H_2S adsorption. In order to draw fair comparisons between the materials under consideration, precise operating conditions and clear definitions of breakthrough concentrations need to be established.

With respect to zeolites, further characterization of their metallic components will help to better understand their location, be it as active ion-exchange sites or simply as an extra framework. In turn, this would help to better elucidate the retention mechanism of this type of adsorbent. Moreover, as the majority of the published works focus their efforts in designing sorbents with improved adsorption capacity, there is a significant lack of studies in relation to the regeneration of adsorbents, adsorption at low temperatures, and the effect of thermal conductivities. Such efforts are necessary in order to create more efficient materials.

Although there is a general consensus that activated carbons can generally achieve higher adsorption capacities than zeolites and metal oxides, they exhibit poor regeneration potential. Future work should mainly focus on finding the optimum temperature, solvent concentration, and regeneration time in order to increase regeneration efficacy.

Metal oxides have also been extensively used as adsorbents for hydrogen sulfide capture. Among these materials those most studied are ZnO and Cu–Zn–O, as they seem to offer improved H_2S adsorption capacities. However, there is a clear lack of understanding in relation to the basic sulfidation mechanisms. The elucidation of these reaction mechanisms will be a toilsome but necessary undertaking in order to design materials with high regenerative capacity and structural reversibility.

Author Contributions: Conceptualization, A.G.G.; Data curation, A.G.G.; Formal analysis, A.G.G.; Funding acquisition, M.A.G.; Investigation, Methodology, M.A.G.; Project administration, M.A.G.; Resources, M.A.G.; Supervision, N.D.C.; Writing-original draft, A.G.G., N.D.C.; Writing-review and editing, N.D.C. 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.

References

- 1. De Crisci, A.G.; Moniri, A.; Xu, Y. Hydrogen from hydrogen sulfide: Towards a more sustainable hydrogen economy. *Int. J. Hydrog. Energy* **2019**, *44*, 1299–1327. [CrossRef]
- 2. Charisiou, N.D.; Siakavelas, G.; Papageridis, K.N.; Baklavaridis, A.; Tzounis, L.; Avraam, D.G.; Goula, M.A. Syngas production via the biogas dry reforming reaction over nickel supported on modified with CeO₂ and/or La₂O₃ alumina catalysts. *J. Nat. Gas Sci. Eng.* **2016**, *31*, 164–183. [CrossRef]
- Roberts, E.S.; Wong, V.A.; McManus, B.E.; Marshall, M.W.; Lancianese, S.; Dorman, D.C. Changes in intracellular pH play a secondary role in hydrogen sulfide-induced nasal cytotoxicity. *Inhal. Toxicol.* 2006, 15, 159–167. [CrossRef]
- Lindenmann, J.; Matzi, V.; Neuboeck, N.; Ratzenhofer-Komenda, B.; Maier, A.; Smolle-Juettner, F.M. Severe hydrogen sulphide poisoning treated with 4-dimethylaminophenol and hyperbaric oxygen. *Diving Hyperb. Med.* 2010, 40, 213–217.
- 5. Burnett, W.W.; King, E.G.; Grace, M.; Hall, W.F. Hydrogen sulfide poisoning: Review of 5 years' experience. *Can. Med. Assoc. J.* **1977**, 177, 1277–1280.
- 6. National Library of Medicine, National Center for Biotechnology Information. Available online: https://pubchem.ncbi.nlm.nih.gov/compound/Hydrogen-sulfide (accessed on 14 March 2020).
- Chen, Q.J.; Fan, F.C.; Long, D.H.; Liu, X.J.; Liang, X.Y.; Qiao, W.M.; Ling, L.C. Poly (ethyleneimine)-loaded silica monolith with a hierarchical pore structure for H₂S adsorptive removal. *Ind. Eng. Chem. Res.* 2010, 49, 11408–11414. [CrossRef]
- Charisiou, N.D.; Baklavaridis, A.; Papadakis, V.G.; Goula, M.A. Synthesis gas production via the biogas reforming reaction over Ni/MgO-Al₂O₃ and Ni/CaO-Al₂O₃ catalysts. *Waste Biomass Valorization* 2016, 7, 725–736. [CrossRef]
- 9. Barelli, L.; Bidini, G.; Micoli, L.; Sisani, E.; Turco, M. 13X Ex-Cu zeolite performance characterization towards H₂S removal for biogas use in molten carbonate fuel cells. *Energy* **2018**, *160*, 44–53. [CrossRef]
- 10. Hervya, M.; Minha, D.P.; Gérenteb, C.; Weiss-Hortalaa, E.; Nzihoua, A.; Villotb, A.; Le Coq, L. H₂S removal from syngas using wastes pyrolysis chars. *Chem. Eng. J.* **2018**, 334, 2179–2189. [CrossRef]
- 11. Vikrant, K.; Kailasa, S.K.; Tsang, D.C.W.; Lee, S.S.; Kumar, P.; Giri, B.S.; Singh, R.S.; Kim, K.H. Biofiltration of hydrogen sulfide: Trends and challenges. *J. Clean. Prod.* **2018**, *187*, 131–147. [CrossRef]
- 12. Carrera, L.; Springer, F.; Lipeme-Kouyi, G.; Buffiere, P. A review of sulfide emissions in sewer networks: Overall approach and systemic modelling. *Water Sci. Technol.* **2015**, *73*, 1231–1242. [CrossRef]
- 13. Bandosz, T.J. On the adsorption/oxidation of hydrogen sulfide on activated carbons at ambient temperatures. *J. Colloid Interface Sci.* **2002**, 246, 1–20. [CrossRef]
- Sisani, E.; Cinti, G.; Discepoli, G.; Penchini, D.; Desideri, U.; Marmottini, F. Adsorptive removal of H₂S in biogas conditions for high temperature fuel cell systems. *Int. J. Hydrog. Energy* 2014, *39*, 21753–21766. [CrossRef]

- Mescia, D.; Hernandez, S.P.; Conoci, A.; Russo, N. MSW landfill biogas desulfurization. *Int. J. Hydrog. Energy* 2011, 36, 7884–7890. [CrossRef]
- 16. Bamdad, H.; Hawboldt, K.; MacQuarrie, S. A review on common adsorbents for acid gases removal: Focus on biochar. *Renew. Sustain. Energy Rev.* **2018**, *81*, 1705–1720. [CrossRef]
- 17. Khabazipour, M.; Mansoor, A. Removal of hydrogen sulfide from gas streams using porous materials: A review. *Ind. Eng. Chem. Res.* **2019**, *58*, 22133–22164. [CrossRef]
- 18. Sing, K.S.W.; Rouquerol, J.; Rouquerol, F. *Adsorption by Powders and Porous Solids*; Academic Press: San Diego, CA, USA, 1998.
- 19. Dabrowski, A. Adsorption-from theory to practice. Adv. Colloid Interface Sci. 2001, 93, 135–224. [CrossRef]
- 20. Ozekmekci, M.; Salkic, G.; Fellah, M.F. Use of zeolites for the removal of H₂S: A mini-review. *Fuel Process. Technol.* **2015**, *139*, 49–60. [CrossRef]
- 21. Kerr, G.T.; Johnson, G.C. Catalytic oxidation of hydrogen sulfide to sulfur over a crystalline aluminosilicate. *J. Phys. Chem.* **1960**, *64*, 381–382. [CrossRef]
- Steijns, M.; Derks, F.; Verloop, A.; Mars, P. The mechanism of the catalytic oxidation of hydrogen sulfide. II. Kinetics and mechanism of hydrogen sulfide oxidation catalyzed by sulfur. *J. Catal.* 1976, 42, 87–95. [CrossRef]
- 23. Micoli, L.; Bagnasco, G.; Turco, M. H₂S removal from biogas for fuelling MCFCs: New adsorbing materials. *Int. J. Hydrog. Energy* **2014**, *39*, 1783–1787. [CrossRef]
- 24. Deo, A.V.; Dalla Lana, I.G.; Habgood, H.W. Infrared studies of the adsorption and surface reactions of hydrogen sulfide and sulfur dioxide on some aluminas and zeolites. *J. Catal.* **1971**, *21*, 270–281. [CrossRef]
- Sigot, L.; Ducom, G.; Germain, P. Adsorption of hydrogen sulfide (H₂S) on zeolite (Z): Retention Mechanism. *Chem. Eng. J.* 2016, 287, 47–53. [CrossRef]
- 26. Kumar, P.; Sung, C.; Muraza, O.; Cococcioni, M.; Al Hashimi, S.; McCormick, A.; Tsapatsis, M. H₂S adsorption by Ag and Cu ion exchanged faujasites. *Microporous Mesoporous Mater.* **2011**, *146*, 127–133. [CrossRef]
- 27. Mohammed, A.; Nassrullah, Z.K. Preparation and formation of zeolite 5A from local kaolin clay for drying and desulphurization of liquefied petroleum gas. *IJCPE* **2013**, *14*, 1–13.
- 28. Kikkinides, E.S.; Sikavitsas, V.I.; Yang, R.T. Natural gas desulfurization by adsorption: Feasibility and multiplicity of cyclic steady states. *Ind. Eng. Chem. Res.* **1995**, *34*, 255–262. [CrossRef]
- Bülow, M.; Lutz, W.; Suckow, M. The mutual transformation of hydrogen sulphide and carbonyl sulphide and its role for gas desulphurization processes with zeolitic molecular sieve sorbents. *Stud. Surf. Sci. Catal.* 1999, 120, 301–345.
- 30. Tomadakis, M.M.; Heck, H.H.; Jubran, M.J.; Al-Harthi, K. Pressure swing adsorption separation of H₂S from CO₂ with molecular sieves 4A, 5A and 13X. *Sep. Sci. Technol.* **2011**, *46*, 428–433. [CrossRef]
- 31. Wynnyk, K.G.; Hojjati, B.; Pirzadeh, P.; Marriott, R.A. High-pressure sour gas adsorption on zeolite 4A. *Adsorption* **2017**, *23*, 149–162. [CrossRef]
- Sigot, L.; Obis, M.F.; Benbelkacem, H.; Germain, P.; Ducom, G. Comparing the performance of a 13X zeolite and an impregnated activated carbon for H₂S removal from biogas to fuel an SOFC: Influence of water. *Int. J. Hydrog. Energy* 2016, 41, 18533–18541. [CrossRef]
- Xiao, Y.; Wang, S.; Wu, D.; Yuan, Q. Experimental and simulation study of hydrogen sulfide adsorption on impregnated activated carbon under anaerobic conditions. *J. Hazard Mater.* 2008, 153, 1193–1200. [CrossRef] [PubMed]
- 34. Alonso-Vicario, A.; Ochoa-Gomez, J.R.; Gil-Rıo, S.; Gomez-Jimenez-Aberasturi, O.; Ramırez-Lopez, C.A.; Torrecilla-Soria, J.; Domínguez, A. Purification and upgrading of biogas by pressure swing adsorption on synthetic and natural zeolites. *Microporous Mesoporous Mater.* **2010**, *134*, 100–107. [CrossRef]
- Melo, D.M.A.; De Souza, J.R.; Melo, M.A.F.; Martinelli, A.E.; Cachima, G.H.B.; Cunha, J.D. Evaluation of the zinox and zeolite materials as adsorbents to remove H₂S from natural gas. *Colloids Surf. A* 2006, 272, 32–36. [CrossRef]
- 36. Lee, S.K.; Jang, Y.N.; Bae, I.K.; Chae, S.C.; Ryu, K.W.; Kim, J.K. Adsorption of toxic gases iron-incorporated Na-A zeolites synthesized from melting slag. *Mater. Trans.* **2009**, *50*, 2476–2483. [CrossRef]
- Abdullah, A.H.; Mat, R.; Somderam, S.; Aziz, A.S.A.; Mohamed, A. Hydrogen sulfide adsorption by zinc oxide-impregnated zeolite (synthesized from Malaysian kaolin) for biogas desulfurization. *J. Ind. Eng. Chem.* 2018, 65, 334–342. [CrossRef]

- 38. Liu, X.; Wang, R. Effective removal of hydrogen sulfide using 4A molecular sieve zeolites synthesized from attapulgite. *J. Hazard Mater.* **2017**, *326*, 157–164. [CrossRef]
- 39. Yokogawa, Y.; Sakanishi, M.; Morikawa, N.; Nakamura, A.; Kishida, I.; Varma, H.K. VSC adsorptive properties in ion exchanged zeolite materials in gaseous and aqueous medium. *Procedia Eng.* **2012**, *36*, 168–172. [CrossRef]
- 40. Karge, H.G.; Raskó, J. Hydrogen sulfide adsorption on faujasite-type zeolites with systematically caried Si-Al ratios. *J. Colloid Interface Sci.* **1978**, *64*, 522–532. [CrossRef]
- 41. De Oliveira, L.H.; Meneguin, J.G.; Pereira, M.V.; Da Silva, E.A.; Grava, W.M.; Do Nascimento, J.F.; Arroyo, P.A. H₂S adsorption on NaY zeolite. *Microporous Mesoporous Mater.* **2019**, *284*, 247–257. [CrossRef]
- 42. Ratnasamy, C.; Wagner, J.P.; Spivey, S.; Weston, E. Removal of sulfur compounds from natural gas for fuel cell applications using a sequential bed system. *Catal. Today* **2012**, *198*, 233–238. [CrossRef]
- 43. Rong, C.; Chu, D.; Hopkins, J. *Test and Characterization of Some Zeolite Supported Gas Phase Desulphurization Sorbents*; ARL-TR-4859; Army Research Laboratory: Adelphi, MD, USA, 2009.
- 44. Crespo, D.; Qi, G.; Wang, Y.; Yang, F.H.; Yang, R.T. Superior sorbent for natural gas desulfurization. *Ind. Eng. Chem. Res.* **2008**, *47*, 1238–1244. [CrossRef]
- 45. Hernández-Maldonado, A.J.; Yang, R.T.; Chinn, D.; Munson, C.L. Partially calcined gismondine type silicoaluminophosphate SAPO-43: Isopropylamine elimination and separation of carbon dioxide, hydrogen sulfide, and water. *Langmuir* **2003**, *19*, 2193–2200. [CrossRef]
- 46. Yasyerli, S.; Ar, I.; Dogu, G.; Dogu, T. Removal of hydrogen sulfide by clinoptilolite in a fixed bed adsorber. *Chem. Eng. Process.* **2002**, *41*, 785–792. [CrossRef]
- 47. Pourzolfaghar, H.; Ismail, M.H.S.; Izhar, S.; Maghareh Esfahan, Z. Review of H₂S sorbents at low-temperature desulfurization of biogas. *Int. J. Chem. Environ. Eng.* **2014**, *5*, 22–28.
- 48. Bashkova, S.; Baker, F.S.; Wu, X.; Armstrong, T.R.; Schwartz, V. Activated carbon catalyst for selective oxidation of hydrogen sulphide: On the influence of pore structure, surface characteristics, and catalytically-active nitrogen. *Carbon* **2007**, *45*, 1354–1363. [CrossRef]
- 49. Shanmugam, S.R.; Adhikari, S.; Wang, Z.; Shakya, R. Treatment of aqueous phase of bio-oil by granular activated carbon and evaluation of biogas production. *Bioresour. Technol.* **2017**, *223*, 115–120. [CrossRef]
- 50. Singhal, S.; Agarwal, S.; Arora, S.; Sharma, P.; Singhal, N. Upgrading techniques for transformation of biogas to bio-CNG: A review. *Int. J. Energy Res.* **2017**, *41*, 1657–1669. [CrossRef]
- 51. Figueiredo, J.L.; Pereira, M.F.R.; Freitas, M.M.A.; Orfao, J.J.M. Modification of the surface chemistry of activated carbons. *Carbon* **1999**, *37*, 1379–1389. [CrossRef]
- 52. Lippens, B.C.; De Boer, J.H.; De Boer, J.H. Studies on pore systems in catalysts: V. The T method. *J. Catal.* **1965**, *4*, 319–323. [CrossRef]
- 53. Bagreev, A.; Bandosz, T.J. A role of sodium hydroxide in the process of hydrogen sulfide adsorption/oxidation on caustic c-impregnated activated carbons. *Ind. Eng. Chem. Res.* **2002**, *41*, 672–679. [CrossRef]
- 54. Turk, A.; Sakalis, E.; Lessuck, J.; Karamitsos, H.; Rago, O. Ammonia injection enhances capacity of activated carbon for hydrogen sulfide and methyl mercaptan. *Environ. Sci. Technol.* **1989**, *23*, 1242–1245. [CrossRef]
- 55. Adib, F.; Bagreev, A.; Bandosz, T.J. Adsorption/oxidation of hydrogen sulfide on nitrogen-containing activated carbons. *Langmuir* **2000**, *16*, 1980–1986. [CrossRef]
- Tian, S.; Mo, H.; Zhang, R.; Ning, P.; Zhou, T. Enhanced removal of hydrogen sulfide from a gas stream by 3-aminopropyltriethoxysilane-surface-functionalized activated carbon. *Adsorption* 2009, 15, 477–488. [CrossRef]
- 57. Adib, F.; Bagreev, A.; Bandosz, T.J. Effect of surface characteristics of wood-based activated carbons on adsorption of hydrogen sulfide. *J. Colloid Interface Sci.* **1999**, *214*, 407–415. [CrossRef] [PubMed]
- Bagreev, A.; Adib, F.; Bandosz, T.J. Initial heats of H₂S adsorption on activated carbons: Effect of surface features. J. Colloid Interface Sci. 1999, 219, 327–332. [CrossRef]
- 59. Bandosz, T.J. Effect of pore structure and surface chemistry of virgin activated carbons on removal of hydrogen sulfide. *Carbon* **1999**, *37*, 483–491. [CrossRef]
- 60. Bagreev, A.; Rahman, H.; Bandosz, T.J. Study of H₂S adsorption and water regeneration of spent coconut-based activated carbon. *Environ. Sci. Technol.* **2000**, *34*, 4587–4592. [CrossRef]
- 61. Bagreev, A.; Rahman, H.; Bandosz, T.J. Thermal regeneration of a spent activated carbon previously used as hydrogen sulfide adsorbent. *Carbon* **2001**, *39*, 1319–1326. [CrossRef]

- 62. Boudou, J.P.; Chehimi, M.; Broniek, E.; Siemieniewska, T.; Bimer, J. Adsorption of H₂S or SO₂ on an activated carbon cloth modified by ammonia treatment. *Carbon* **2003**, *41*, 1999–2007. [CrossRef]
- 63. Farooq, M.; Bell, A.H.; Almustapha, M.; Andresen, J.M. Bio-methane from anaerobic digestion using activated carbon adsorption. *Anaerobe* **2017**, *46*, 33–40. [CrossRef]
- Skouteris, G.; Saroj, D.; Melidis, P.; Hai, F.I.; Ouki, S. The effect of activated carbon addition on membrane bioreactor processes for wastewater treatment and reclamation—A critical review. *Bioresour. Technol.* 2015, *185*, 399–410. [CrossRef] [PubMed]
- 65. Huang, C.; Chen, C.; Chu, S. Effect of moisture on H₂S adsorption by copper impregnated activated carbon. *J. Hazard Mater.* **2006**, *136*, 866–873. [CrossRef]
- 66. Papurello, D.; Tomasi, L.; Silvestri, S.; Santarelli, M. Evaluation of the Wheeler-Jonas parameters for biogas trace compounds removal with activated carbons. *Fuel Process. Technol.* **2016**, *152*, 93–101. [CrossRef]
- Sitthikhankaew, R.; Chadwik, D.; Assabumrungrat, S.; Laosiripojana, N. Effects of humidity, O₂, and CO₂ on H₂S adsorption onto upgraded and KOH impregnated activated carbons. *Fuel Process. Technol.* 2014, 124, 249–257. [CrossRef]
- 68. Feng, W.; Kwon, S.; Borguet, E.; Vidic, R. Adsorption of hydrogen sulfide onto activated carbon fibers: Effect of pore structure and surface chemistry. *Environ. Sci. Technol.* **2005**, *39*, 9744–9749. [CrossRef] [PubMed]
- 69. Primavera, A.; Trovarelli, A.; Andreussi, P.; Dolcetti, G. The effect of water in the low-temperature catalytic oxidation of hydrogen sulphide to sulfur over activated carbon. *Appl. Catal. A Gen.* **1998**, 173, 185–192. [CrossRef]
- 70. Bagreev, A.; Bandosz, T.J. H₂S adsorption/oxidation on unmodified activated carbons: Importance of prehumidification. *Carbon* **2001**, *39*, 2303–2311. [CrossRef]
- 71. Le-Minh, N.; Sivret, E.C.; Shammay, A.; Stuetz, R.M. Factors affecting the adsorption of gaseous environmental odors by activated carbon: A critical review. *Crit. Rev. Environ. Sci. Technol.* **2018**, *48*, 341–375. [CrossRef]
- Papurello, D.; Gandiglio, M.; Lanzini, A. Experimental analysis and model validation on the performance of impregnated activated carbons for the removal of hydrogen sulfide (H₂S) from sewage biogas. *Processes* 2019, 7, 548. [CrossRef]
- 73. Ciahotny, K.; Kyselova, V. Hydrogen sulfide removal from biogas using carbon impregnated with oxidants. *Energy Fuels* **2019**, *33*, 5316–5321. [CrossRef]
- Barelli, L.; Bidini, G.; De Arespacochaga, N.; Perez, L.; Sisani, E. Biogas use in high temperature fuel cells: Enhancement of KOH-KI activated carbon performance toward H₂S removal. *Int. J. Hydrog. Energy* 2017, 42, 10341–10353. [CrossRef]
- 75. McIntyre, N.S.; Mount, G.R.; Lipson, T.C.; Humphrey, R.; Harrison, B.; Liang, S.; Pagotto, J. Surface and microanalytical studies of whetlerite charcoals: 1. Effects of aging. *Carbon* **1991**, *29*, 1071–1079. [CrossRef]
- Awe, O.W.; Minh, D.P.; Lyczkob, N.; Nzihoub, A.; Zhao, Y. Laboratory-scale investigation of the removal of hydrogen sulfide from biogas and air using industrial waste-based sorbents. *J. Environ. Chem. Eng.* 2017, 5, 1809–1820. [CrossRef]
- 77. Skerman, A.G.; Heubeck, S.; Batstone, D.J.; Tait, S. Low-cost filter media for removal of hydrogen sulphide from piggery biogas. *Process Saf. Environ.* **2017**, *105*, 117–126. [CrossRef]
- Rambabu, N.; Azargohar, R.; Dalai, A.K.; Adjaye, J. Evaluation and comparison of enrichment efficiency of physical/chemical activations and functionalized activated carbons derived from fluid petroleum coke for environmental applications. *Fuel Process. Technol.* 2013, *106*, 501–510. [CrossRef]
- 79. Mochizuki, T.; Kubota, M.; Matsuda, H.; D'Elia Camacho, L.F. Adsorption behaviors of ammonia and hydrogen sulfide on activated carbon prepared from petroleum coke by KOH chemical activation. *Fuel Process. Technol.* **2016**, *144*, 164–169. [CrossRef]
- Asaoka, S.; Okamura, H.; Morisawa, R.; Murakami, H.; Fukushi, K.; Okajima, T.; Katayama, M.; Inada, Y.; Yogi, C.; Ohta, T. Removal of hydrogen sulfide using carbonated steel slag. *Chem. Eng. J.* 2013, 228, 843–849.
 [CrossRef]
- 81. Kim, K.H.; Asaoka, S.; Yamamoto, T.; Hayakawa, S.; Takeda, K.; Katayama, M.; Onoue, T. Mechanisms of hydrogen sulfide removal with steel making slag. *Environ. Sci. Technol.* **2012**, *46*, 10169–10174. [CrossRef]
- 82. Asaoka, S.; Okamura, H.; Kim, K.; Hatanaka, Y.; Nakamoto, K.; Hino, K.; Oikawa, T.; Hayakawa, S.; Okuda, T. Optimum reaction ratio of coal fly ash to blast furnace cement for effective removal of hydrogen sulfide. *Chemosphere* **2017**, *168*, 384–389. [CrossRef]

- Asaoka, S.; Okamura, H.; Akita, Y.; Nakano, K.; Nakamoto, K.; Hino, K.; Saito, T.; Hayakawa, S.; Katayama, M.; Inada, Y. Regeneration of manganese oxide as adsorption sites for hydrogen sulfide on granulated coal ash. *Chem. Eng. J.* 2014, 254, 531–537. [CrossRef]
- 84. Bazan-Wozniak, A.; Nowicki, P.; Pietrzak, R. The influence of activation procedure on the physicochemical and sorption properties of activated carbons prepared from pistachio nutshells for removal of NO₂/H₂S gases and dyes. *J. Clean. Prod.* **2017**, *152*, 211–222. [CrossRef]
- Zulkefli, N.N.; Masdar, M.S.; Wan Isahak, W.N.R.; Md Jahim, J.; Md Rejab, S.A.; Lye, C.C. Removal of hydrogen sulfide from a biogas mimic by using impregnated activated carbon adsorbent. *PLoS ONE* 2019, 14, e0211713. [CrossRef] [PubMed]
- Nam, H.; Wang, S.; Jeong, H.R. TMA and H₂S gas removals using metal loaded on rice husk activated carbon for indoor air purification. *Fuel* 2018, *213*, 186–194. [CrossRef]
- Leboda, R.; Skubiszewska-Zieba, J.; Tomaszewski, W.; Gun'ko, V.M. Structural and adsorptive properties of activated carbons prepared by carbonization and activation of resins. *J. Colloid Interface Sci.* 2003, 263, 533–541. [CrossRef]
- Kazmierczak-Razna, J.; Gralak-Podemska, B.; Nowicki, P.; Pietrzak, R. The use of microwave radiation for obtaining activated carbons from sawdust and their potential application in removal of NO₂ and H₂S. *Chem. Eng. J.* 2015, 269, 352–358. [CrossRef]
- De Oliveira, L.H.; Meneguin, J.G.; Pereira, M.V.; Do Nascimento, J.F.; Arroyo, P.A. Adsorption of hydrogen sulfide; carbon dioxide; methane; and their mixtures on activated carbon. *Chem. Eng. Commun.* 2019, 206, 1533–1553. [CrossRef]
- Montes, D.; Tocuyo, E.; Gonzalez, E.; Rodriguez, D.; Solano, R.; Atencio, R.; Ramos, M.A.; Moronta, A. Reactive H₂S chemisorption on mesoporous silica molecular sieve-supported CuO or ZnO. *Microporous Mesoporous Mater.* 2013, 168, 111–120. [CrossRef]
- Charisiou, N.D.; Tzounis, L.; Sebastian, V.; Baker, M.A.; Hinder, S.J.; Polychronopoulou, K.; Goula, M.A. Investigating the correlation between deactivation and the carbon deposited on the surface of Ni/Al₂O₃ and Ni/La₂O₃-Al₂O₃ catalysts during the biogas reforming reaction. *Appl. Surf. Sci.* 2019, 474, 42–56. [CrossRef]
- 92. Gangwal, S.K.; Harkins, S.M.; Stogner, J.M.; Woods, M.C.; Rogers, T.N. *Bench Scale Testing of Novel High-Temperature Desulfurization Sorbents*; Final Report No. DOE/MC/23126–2662; NTIS/DE89000935; Research Triangle Institute: Research Triangle Park, NC, USA, 1988.
- 93. Garces, H.F.; Galindo, H.M.; Garces, L.J.; Hunt, J.; Morey, A.; Suib, S.L. Low temperature H₂S dry-desulfurization with zinc oxide. *Microporous Mesoporous Mater.* **2010**, 127, 190–197. [CrossRef]
- 94. Westmoreland, P.R.; Harrison, D.P. Evaluation of candidate solids for high-temperature desulfurization of low-Btu gases. *Environ. Sci. Technol.* **1976**, *10*, 659–661. [CrossRef]
- Portela, R.; Marcos, F.R.; Leret, P.; Fernández, J.F.; Bañares, M.A.; Ávila, P. Nanostructured ZnO/sepiolite monolithic sorbents for H₂S removal. *J. Mater. Chem. A* 2015, *3*, 1306–1316. [CrossRef]
- Samokhvalov, A.; Tatarchuk, B.J. Characterization of active sites, determination of mechanisms of H₂S, COS and CS₂ sorption and regeneration of ZnO low-temperature sorbents: Past current and perspectives. *Phys. Chem. Chem. Phys.* 2011, 13, 3197–3209. [CrossRef] [PubMed]
- 97. Jalan, V. High-temperature desulfurization of coal gases by regenerative sorption. In Proceedings of the 1981 International Gas Research Conference, Los Angeles, CA, USA, 28 September–1 October 1981; pp. 291–303.
- 98. Davidson, J.M.; Lawrie, C.H.; Sohail, K. Kinetics of the absorption of hydrogen sulfide by high purity and doped high surface area zinc oxide. *Ind. Eng. Chem. Res.* **1995**, *34*, 2981–2989. [CrossRef]
- 99. Sasaoka, E.; Hirano, S.; Kasasoka, S.; Sakata, Y. Characterization of reaction between zinc oxide and hydrogen sulfide. *Energy Fuels* **1994**, *8*, 1100–1105. [CrossRef]
- 100. Rodriguez, J.A.; Maiti, A. Adsorption and decomposition of H₂S on MgO(100), NiMgO(100), and ZnO(0001) surfaces: A first-principles density functional study. *J. Phys. Chem. B* **2000**, *104*, 3630–3638. [CrossRef]
- 101. Rodriguez, J.A.; Chaturvedi, S.; Kuhn, M.; Hrbek, J. Reaction of H₂S and S₂ with metal/oxide surfaces: Band-gap size and chemical reactivity. *J. Phys. Chem. B* **1998**, *102*, 5511–5519. [CrossRef]
- 102. Rodriguez, J.A.; Jirsak, T.; Chaturvedi, S. Reaction of H₂S with MgO (100) and Cu/MgO (100) surfaces: Band-gap size and chemical reactivity. *J. Chem. Phys.* **1999**, *111*, 8077–8087. [CrossRef]
- 103. Carnes, C.L.; Klabunde, K.J. Unique chemical reactivities of nanocrystalline metal oxides toward hydrogen sulfide. *Chem. Mater.* **2002**, *14*, 1806–1811. [CrossRef]

- 104. Rosso, I.; Galletti, C.; Bizzi, M.; Saracco, G.; Specchia, V. Zinc oxide sorbents for the removal of hydrogen sulfide from syngas. *Ind. Eng. Chem. Res.* 2003, 42, 1688–1697. [CrossRef]
- 105. Neveux, L.; Chiche, D.; Perez-Pellitero, J.; Favergeon, L.; Gay, A.S.; Pijolat, M. New insight into the ZnO sulfidation reaction: Mechanism and kinetics modeling of the ZnS outward growth. *Phys. Chem. Chem. Phys.* 2013, 15, 1532–1545. [CrossRef]
- 106. Bezverkhyy, I.; Skrzypski, J.; Safonova, O.; Bellat, J.-P. Sulfidation mechanism of pure and Cu-doped ZnO nanoparticles at moderate temperature: TEM and in situ XRD studies. *J. Phys. Chem. C* 2012, *116*, 14423–14430. [CrossRef]
- 107. Patrick, V.; Gavalas, G.R.; Flytzani-Stephanophoulos, M.; Jothimurugesan, K. High-temperature sulfidation-regeneration of CuO-Al₂O₃ sorbents. *Ind. Eng. Chem. Res.* **1989**, *28*, 931–940. [CrossRef]
- 108. Tamhankar, S.S.; Bagajewicz, M.; Sharma, P.K.; Flytzani-Stephanopoulous, M.; Gavalas, G.R. Mixed oxide sorbents for high temperature removal hydrogen sulfide. *Ind. Eng. Chem. Process Des. Dev.* **1986**, 25, 429–437. [CrossRef]
- 109. Li, Z.; Flytzani-Stephanopoulous, M. Cu-Cr-O and Cu-Ce-O regenerable oxide sorbents for hot gas desulphurization. *Ind. Eng. Chem. Res.* **1997**, *36*, 187–196. [CrossRef]
- 110. Pola-Albores, F.; Zambrano–Solís, K.; Ríos–Valdovinos, E.; Conde-Díaz, J.; Vilchis–Bravo, H.; Reyes–Nava, J.A.; Pantoja-Enríquez, J.; Moreira–Acosta, J. ZnO and Cu-based adsorbents for biogas desulfurization at room temperature. J. Mater. Sci. Mater. Electron. 2018, 9, 15597–15603. [CrossRef]
- Xue, M.; Chitrakar, R.; Sakane, K.; Ooi, K. Screening of adsorbents for removal of H₂S at room temperature. *Green Chem.* 2003, *5*, 529–534. [CrossRef]
- 112. Skrzypski, J.; Bezverkhyy, I.; Heintz, O.; Bellat, J.P. Low temperature H₂S removal with metal-doped nanostructure ZnO sorbents: Study of the origin of enhanced reactivity in Cu-containing materials. *Ind. Eng. Chem. Res.* **2011**, *50*, 5714–5722. [CrossRef]
- 113. Elyassi, B.; Al Wahedi, Y.; Rajabbeigi, N.; Kumar, P.; Jeong, J.S.; Zhang, X.; Kumar, P.; Balasubramanian, V.V.; Katsiotis, M.S.; Mkhoyan, K.A.; et al. A high-performance adsorbent for hydrogen sulfide removal. *Microporous Mesoporous Mater.* 2014, 190, 152–155. [CrossRef]
- 114. Yang, H.; Tatarchuk, B. Novel-doped zinc oxide sorbents for low temperature regenerable desulfurization applications. *AIChE J.* **2010**, *56*, 2898–2904. [CrossRef]
- 115. Cimino, S.; Lisi, L.; De Falco, G.; Montagnaro, F.; Balsamo, M.; Erto, A. Highlighting the effect of the support during H₂S adsorption at low temperature over composite Zn-Cu sorbents. *Fuel* 2018, 221, 374–379. [CrossRef]
- Dhage, P.; Samokhvalov, A.; Repala, D.; Duin, C.E.; Bowman, M.; Tatarchuk, B.J. Copper promoted ZnO/SiO₂ regenerable sorbents for the room temperature removal of H₂S from reformate gas streams. *Ind. Eng. Chem. Res.* 2010, 49, 8388–8396. [CrossRef]
- 117. Wang, J.; Wang, L.; Fan, H.; Wang, H.; Hu, Y.; Wang, Z. Highly porous copper oxide sorbent for H₂S capture at ambient temperature. *Fuel* **2017**, *209*, 329–338. [CrossRef]
- 118. Jiang, D.; Su, L.; Ma, L.; Yao, N.; Xu, X.; Tang, H.; Li, X. Cu-Zn-Al mixed metal oxides derived from hydroxycarbonate precursors for H₂S removal at low temperature. *Appl. Surf. Sci.* 2010, 256, 3216–3223. [CrossRef]
- 119. Baird, T.; Denny, P.J.; Hoyle, R.; McMonagle, F.; Stirling, D.; Tweedy, J. Modified zinc oxide absorbents for low-temperature gas desulfurisation. *J. Chem. Soc. Faraday Trans.* **1992**, *88*, 3375–3382. [CrossRef]
- Baird, T.; Campbell, K.C.; Holliman, P.J.; Hoyle, R.; Stirling, D.; Williams, P.B. Mixed Co-Zn-al oxides as absorbents for low-temperature gas desulfurisation. *J. Chem. Soc. Faraday Trans.* 1995, *91*, 3219–3230. [CrossRef]
- Shah, M.S.; Tsapatsis, M.; Siepmann, J.I. Hydrogen sulfide capture: From absorption in polar liquids to oxide, zeolite, and metal-organic framework adsorbents and membranes. *Chem. Rev.* 2017, 117, 9755–9803. [CrossRef]
- 122. Polychronopoulou, K.; Fierro, J.L.G.; Efstathiou, A.M. Novel Zn-Ti-based mixed metal oxides for low-temperature adsorption of H₂S from industrial gas streams. *Appl. Catal. B Environ.* **2005**, *57*, 125–137. [CrossRef]
- 123. Liu, D.; Chen, S.; Fei, X.; Huang, C.; Zhang, Y. Regenerable CuO-based adsorbents for low temperature desulfurization application. *Ind. Eng. Chem. Res.* **2015**, *54*, 3556–3562. [CrossRef]
- 124. Jung, S.Y.; Lee, S.J.; Lee, T.J.; Ryu, C.K.; Kim, J.C. H₂S removal and regeneration properties of Zn-Al-based sorbents promoted with various promoters. *Catal. Today* **2006**, *111*, 217–222. [CrossRef]

- 125. Thanakunpaisit, N.; Jantarachat, N.; Onthong, U. Removal of hydrogen sulfide from biogas using laterite materials as an adsorbent. *Energy Procedia* **2017**, *138*, 1134–1139. [CrossRef]
- 126. Wang, Z.; Flytzani-Stephanopoulos, M. Cerium oxide-based sorbents for regenerative hot reformate gas desulfurization. *Energy Fuels* **2005**, *19*, 2089–2097. [CrossRef]
- Kobayashi, M.; Shirai, H.; Nunokawa, M. High-temperature sulfidation behavior of reduced zinc ferrite in simulated coal gas revealed by in situ X–ray diffraction analysis and mössbauer spectroscopy. *Energy Fuels* 2002, *16*, 601–607. [CrossRef]
- 128. Zhang, R.; Huang, J.; Zhao, J.; Sun, Z.; Wang, Y. Sol-Gel auto-combustion synthesis of zinc ferrite for moderate temperature desulfurization. *Energy Fuels* **2007**, *21*, 2682–2687. [CrossRef]
- Pahalagedara, L.R.; Poyraz, A.S.; Song, W.; Kuo, C.H.; Pahalagedara, M.N.; Meng, Y.T.; Suib, S.L. Low temperature desulfurization of H₂S: High sorption capacities by mesoporous cobalt oxide via increased H₂S diffusion. *Chem. Mater.* 2014, 26, 6613–6621. [CrossRef]
- 130. Van Nisselrooy, P.F.M.T.; Lagas, J.A. Superclaus reduces SO₂ emission by the use of a new selective oxidation catalyst. *Catal. Today* **1993**, *16*, 263–271. [CrossRef]
- DesMarias, T.L.; Costa, M. Mechanisms of chromium-induced toxicity. *Curr. Opin. Toxicol.* 2019, 14, 1–7. [CrossRef]
- 132. Barba, D.; Palma, V.; Ciambelli, P. Screening of catalysts for H₂S abatement from biogas to feed molten carbonate fuel cells. *Int. J. Hydrog. Energy* **2013**, *38*, 328–335. [CrossRef]
- Palma, V.; Barba, D. Vanadium-ceria catalysts for H₂S abatement from biogas to feed to MCFC. *Int. J. Hydrog. Energy* 2017, 42, 1891–1898. [CrossRef]
- 134. Fan, H.L.; Sun, T.; Zhao, Y.P.; Shangguan, J.; Lin, J.Y. Three dimensionally ordered macroporous iron oxide for removal of H₂S at medium temperatures. *Environ. Sci. Technol.* **2013**, 47, 4859–4865. [CrossRef]
- 135. Huang, G.; He, E.; Wang, Z.; Fan, H.; Shangguan, J.; Croiset, E.; Chen, Z. Synthesis and characterization of γ-Fe₂O₃ for H₂S removal at low temperature. *Ind. Eng. Chem. Res.* **2015**, *54*, 8469–8478. [CrossRef]
- 136. Wang, L.J.; Fan, H.L.; Shangguan, J.; Croiset, E.; Chen, Z.; Wang, H.; Mi, J. Design of a sorbent to enhance reactive adsorption of hydrogen sulfide. *Appl. Mater. Interfaces* **2014**, *6*, 21167–21177. [CrossRef] [PubMed]
- Wang, J.; Yang, C.; Zhao, Y.R.; Fan, H.L.; De Wang, Z.; Shangguan, J.; Mi, J. Synthesis of porous cobalt oxide and its performance for H₂S removal at room temperature. *Ind. Eng. Chem. Res.* 2017, *56*, 12621–12629. [CrossRef]
- 138. Wang, X.; Sun, T.; Yang, J.; Zhao, L.; Jia, J. Low-temperature H₂S removal from gas streams with SBA-15 supported ZnO nanoparticles. *Chem. Eng. J.* **2008**, *142*, 48–55. [CrossRef]
- 139. Wang, X.; Jia, J.; Zhao, L.; Sun, T. Mesoporous SBA-15 supported iron oxide: A potent catalyst for hydrogen sulfide removal. *Water Air Soil Pollut*. **2008**, *193*, 247–257. [CrossRef]
- Geng, Q.; Wang, L.J.; Yang, C.; Zhang, H.Y.; Zhao, Y.R.; Fan, H.L.; Huo, C. Room-temperature hydrogen sulfide removal with zinc oxide nanoparticle/molecular sieve prepared by melt infiltration. *Fuel Process. Technol.* 2019, 185, 26–37. [CrossRef]
- 141. Zeng, H.Z.; Qiu, K.Q.; Du, Y.Y.; Li, W.Z. A new way to synthesize ZnS nanoparticles. *Chin. Chem. Lett.* 2007, *18*, 483–486. [CrossRef]
- 142. Hussain, M.; Abbas, N.; Fino, D.; Russo, N. Novel mesoporous silica supported ZnO adsorbents for the desulphurization of biogas at low temperatures. *Chem. Eng. J.* **2012**, *188*, 222–232. [CrossRef]
- 143. Li, L.; Sun, T.H.; Shu, C.H.; Zhang, H.B. Low temperature H₂S removal with 3-D structural mesoporous molecular sieves supported ZnO from gas stream. *J. Hazard. Mater.* **2016**, *311*, 142–150. [CrossRef]
- 144. Hong, Y.S.; Sin, K.R.; Pak, J.S.; Kim, C.J.; Liu, B.S. Kinetic analysis of H₂S removal over mesoporous Cu-Mn mixed oxide/SBA-15 and La-Mn mixed oxide/KIT-6 sorbents during hot coal gas desulfurization using the deactivation kinetics model. *Energy Fuels* 2017, *31*, 9874–9880. [CrossRef]
- 145. Daneshyar, A.; Ghaedi, M.; Sabzehmeidani, M.M.; Daneshyar, A. H₂S adsorption onto Cu-Zn-Ni nanoparticles loaded activated carbon and Ni-Co nanoparticles loaded γ-Al₂O₃: Optimization and adsorption isotherms. *J. Colloid Interface Sci.* 2017, 490, 553–561. [CrossRef]
- 146. de Falco, G.; Montagnaro, F.; Balsamo, M.; Erto, A.; Deorsola, F.A.; Lisi, L.; Cimino, S. Synergic effect of Zn and Cu oxides dispersed on activated carbon during reactive adsorption of H₂S at room temperature. *Microporous Mesoporous Mater.* 2018, 257, 135–146. [CrossRef]
- 147. Balsamo, M.; Cimino, S.; De Falco, G.; Erto, A.; Lisi, L. ZnO-CuO supported on activated carbon for H₂S removal at room temperature. *Chem. Eng. J.* **2016**, *304*, 399–407. [CrossRef]

- 148. Tian, H.; Wu, J.; Zhang, W.; Yang, S.; Li, F.; Qi, Y.; Zhou, R.; Qi, X.; Zhao, L.; Wang, X. High performance of Fe nanoparticles/carbon aerogel sorbents for H₂S Removal. *Chem. Eng. J.* **2017**, *313*, 1051–1060. [CrossRef]
- 149. Wu, M.; Su, Z.; Fan, H.; Mi, J. New way of removing hydrogen sulfide at a high temperature: Microwave desulfurization using an iron-based sorbent supported on active coke. *Energy Fuels* 2017, *31*, 4263–4272. [CrossRef]
- 150. Gupta, R.P.; Gangwal, S.K. Enhanced Durability of Desulfurization Sorbents for Fluidized-Bed Applications; Topical ReportUnder U.S. Department of Energy Contract No. DOE/MC/250063271; NTIS/DE9300247; Research Triangle Institute: Research Triangle Park, NC, USA, 1992.
- 151. UOPLLC. Handling of Zeolite Molecular Sieve Adsorbents in Process Units. *UOP5085*. Available online: https://www.uop.com/?document=uop-molsiv-handling-procedures-brochure&download=1 (accessed on 14 April 2009).
- 152. Lee, S.; Lee, T.; Kim, D. Adsorption of hydrogen sulfide from gas streams using the amorphous composite of α-FeOOH and activated carbon powder. *Ind. Eng. Chem. Res.* **2017**, *56*, 3116–3122. [CrossRef]
- 153. Jie, M.; Yongyan, Z.; Yongsheng, Z.; Ting, G.; Huiling, F. Semi-coke-supported mixed metal oxides for hydrogen sulfide removal at high temperatures. *Environ. Eng. Sci.* 2012, 29, 611–616. [CrossRef]
- 154. Ko, T.H. Removal of hydrogen sulfur from coal-derived gas by iron oxides in various oxisols. *Environ. Eng. Sci.* **2008**, *25*, 969–974. [CrossRef]
- 155. Song, H.S.; Park, M.G.; Kwon, S.J.; Yi, K.B.; Croiset, E.; Chen, Z.; Nam, S.C. Hydrogen sulfide adsorption on nano-sized zinc oxide/reduced graphite oxide composite at ambient condition. *Appl. Surf. Sci.* 2013, 276, 646–652. [CrossRef]
- 156. Seredych, M.; Mabayoje, O.; Bandosz, T.J. Visible-light-enhanced interactions of hydrogen sulfide with composites of zinc (oxy) hydroxide with graphite oxide and grapheme. *Langmuir* 2011, 28, 1337–1346. [CrossRef]
- 157. Mabayoje, O.; Seredych, M.; Bandosz, T.J. Enhanced adsorption of hydrogen sulfide on mixed zinc/cobalt hydroxides: Effect of morphology and an increased number of surface hydroxyl groups. *J. Colloid Interface Sci.* **2013**, 405, 218–225. [CrossRef]
- 158. Lee, S.; Kim, D. Enhanced adsorptive removal of hydrogen sulfide from gas stream with zinc iron hydroxide at room temperature. *Chem. Eng. J.* **2019**, *363*, 43–48. [CrossRef]
- Arcibar-Orozco, J.A.; Wallace, R.; Mitchell, J.K.; Bandosz, T.J. Role of surface chemistry and morphology in the reactive adsorption of H₂S on iron (HYDR) oxide/graphite oxide composites. *Langmuir* 2015, *31*, 2730–2742. [CrossRef] [PubMed]
- 160. Xu, X.C.; Song, C.S.; Andresen, J.M.; Miller, B.G.; Scaroni, A.W. Novel polyethylenimine-modified mesoporous molecular sieve of MCM-41 type as high-capacity adsorbent for CO₂ capture. *Energy Fuels* **2002**, *16*, 1463–1469. [CrossRef]
- Wang, X.X.; Schwartz, V.; Clark, J.C.; Ma, X.L.; Overbury, S.H.; Xu, X.C.; Song, C.S. Infrared study of CO₂ sorption over "molecular basket" sorbent consisting of polyethylenimine-modified mesoporous molecular sieve. J. Phys. Chem. C 2009, 113, 7260–7268. [CrossRef]
- 162. Xu, X.C.; Song, C.S.; Andresen, J.M.; Miller, B.G.; Scaroni, A.W. Preparation and characterization of novel CO₂ "molecular basket" adsorbents based on polymer-modified mesoporous molecular sieve MCM-41. *Microporous Mesoporous Mater.* 2003, 62, 29–45. [CrossRef]
- 163. Xu, X.C.; Song, C.S.; Miller, B.G.; Scaroni, A.W. Influence of moisture on CO₂ separation from gas mixture by a nanoporous adsorbent based on polyethylenimine-modified molecular sieve MCM-41. *Ind. Eng. Chem. Res.* 2005, 44, 8113–8119. [CrossRef]
- 164. Xu, X.C.; Song, C.S.; Miller, B.G.; Scaroni, A.W. Adsorption separation of carbon dioxide from flue gas of natural gas-fired boiler by a novel nanoporous "molecular basket" adsorbent. *Fuel Process. Technol.* 2005, *86*, 1457–1472. [CrossRef]
- 165. Ma, X.L.; Wang, X.X.; Song, C.S. "Molecular basket" sorbents for separation of CO₂ and H₂S from various gas streams. *J. Am. Chem. Soc.* **2009**, *131*, 5777–5783. [CrossRef]
- 166. Tsuda, T.; Fujiwara, T. Polyethyleneimine and macrocyclic polyamine silica gels acting as carbon dioxide absorbents. *J. Chem. Soc. Chem. Commun.* **1992**, 1659–1661. [CrossRef]
- 167. Tsuda, T.; Fujiwara, T.; Taketani, Y.; Saegusa, T. Amino silica gels acting as a carbon dioxide absorbent. *Chem. Lett.* **1992**, *21*, 2161–2164. [CrossRef]

- 168. Franchi, R.S.; Harlick, P.J.E.; Sayari, A. Applications of pore–expanded mesoporous silica. 2. Development of a high–capacity, water-tolerant adsorbent for CO₂. *Ind. Eng. Chem. Res.* **2005**, *44*, 8007–8013. [CrossRef]
- Harlick, P.J.E.; Sayari, A. Applications of pore-expanded mesoporous silica. 5. Triamine grafted material with exceptional CO₂ dynamic and equilibrium adsorption performance. *Ind. Eng. Chem. Res.* 2007, 46, 446–458. [CrossRef]
- 170. Harlick, P.J.E.; Sayari, A. Applications of pore-expanded mesoporous silicas. 3. Triamine silane grafting for enhanced CO₂ adsorption. *Ind. Eng. Chem. Res.* **2006**, *45*, 3248–3255. [CrossRef]
- 171. Harlick, P.J.E.; Sayari, A. Amine grafted; pore-expanded MCM-41 for acid gas removal: Effect of grafting temperature; water; and amine type on performance. *Stud. Surf. Sci. Catal.* **2005**, *158*, 987–994.
- 172. Serna-Guerrero, R.; Dana, E.; Sayari, A. New insights into the interactions of CO₂ with amine-functionalized silica. *Ind. Eng. Chem. Res.* **2008**, 47, 9406–9412. [CrossRef]
- 173. Belmabkhout, Y.; De Weireld, G.; Sayari, A. Amine-bearing mesoporous silica for CO₂ and H₂S removal from natural gas and biogas. *Langmuir* **2009**, *25*, 13275–13278. [CrossRef]
- 174. Belmabkhout, Y.; Sayari, A. Effect of pore expansion and amine functionalization of mesoporous silica on CO₂ adsorption over a wide range of conditions. *Adsorption* **2009**, *15*, 318–328. [CrossRef]
- Belmabkhout, Y.; Serna-Guerrero, R.; Sayari, A. Adsorption of CO₂-containing gas mixtures over amine-bearing pore-expanded MCM-41 silica: Application for gas purification. *Ind. Eng. Chem. Res.* 2010, 49, 359–365. [CrossRef]
- 176. Wang, X.; Ma, X.; Xu, X.; Sun, L.; Song, C. Mesoporous-molecular-sieve-supported polymer sorbents for removing H₂S from hydrogen gas streams. *Top. Catal.* **2008**, *49*, 108–117. [CrossRef]
- 177. Yoosuk, B.; Wongsanga, T.; Prasassarakich, P. CO₂ and H₂S binary sorption on polyamine modified fumed silica. *Fuel* **2016**, *168*, 47–53. [CrossRef]
- 178. Quan, W.; Wang, X.; Song, C. Selective removal of H₂S from biogas using solid amine-based "molecular basket" sorbent. *Energy Fuels* **2017**, *31*, 9517–9528. [CrossRef]
- 179. Deng, Y.; Vellingiri, K.; Kim, K.-H.; Boukhvalov, D.W.; Philip, L. Activation strategies of metal-organic frameworks for the sorption of reduced sulfur compounds. *Chem. Eng. J.* 2015, 350, 747–756. [CrossRef]
- 180. Hamon, L.; Serre, C.; Devic, T.; Loiseau, T.; Millange, F.; Férey, G.; Weireld, G.D. Comparative study of hydrogen sulfide adsorption in the MIL-53(Al, Cr, Fe), MIL-47(V), MIL-100(Cr), and MIL-101(Cr) metal-organic frameworks at room temperature. *J. Am. Chem. Soc.* 2009, 131, 8775–8777. [CrossRef] [PubMed]
- 181. Allan, P.K.; Wheatley, P.S.; Aldous, D.; Mohideen, M.I.; Tang, C.; Hriljac, J.A.; Megson, I.L.; Chapman, K.W.; De Weireld, G.; Vaesen, S.; et al. Metal–organic frameworks for the storage and delivery of biologically active hydrogen sulfide. *Dalton Trans.* 2012, 41, 4060–4066. [CrossRef]
- 182. Chavan, S.; Bonino, F.; Valenzano, L.; Civalleri, B.; Lamberti, C.; Acerbi, N.; Cavka, J.H.; Leistner, M.; Bordiga, S. Fundamental aspects of H₂S adsorption on CPO-27-Ni. *J. Phys. Chem. C* 2013, *117*, 15615–15622. [CrossRef]
- 183. Yang, Q.; Vaesen, S.; Vishnuvarthan, M.; Ragon, F.; Serre, C.; Vimont, A.; Daturi, M.; De Weireld, G.; Maurin, G. Probing the adsorption performance of the hybrid porous MIL-68(Al): A synergic combination of experimental and modelling tools. *J. Mater. Chem.* 2012, 22, 10210–10220. [CrossRef]



© 2020 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).