

Review

Review of Hydrogen Sulfide Removal from Various Industrial Gases by Zeolites

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Abstract: Hydrogen sulfide (H_2S) removal from various industrial gases is crucial because it can cause huge damage to humans, the environment, and industrial production. Zeolite possesses huge specific surface area and well-developed pore structure, making it a promising adsorbent for H_2S removal. This review attempts to comprehensively compile the current studies in the literature on H_2S removal in gas purification processes using zeolites, including experimental and simulation studies, mechanism theory, and practical applications. Si/Al ratio, cations of zeolite, industrial gas composition and operating conditions, and H_2S diffusion in zeolites affect desulfurization performance. However, further efforts are still needed to figure out the influence rules of the factors above and H_2S removal mechanisms. Based on an extensive compilation of literature, we attempt to shed light on new perspectives for further research in the future.

Keywords: hydrogen sulfide; adsorption; zeolite; mechanism



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1. Introduction

Hydrogen sulfide (H_2S) is a colorless, odorous, corrosive, and highly toxic impure gas that occurs in different industrial products, such as natural gas, biogas, syngas, and crude oil [1,2]. It is deadly for humans with a threshold limit value of 10 part per million (ppm) for 8-h exposure [3], immediate danger limit value of 20 ppm. H_2S paralyzes the sense of smell and irritates eyes and lungs when the concentration is greater than 100 ppm. At ~1000 ppm, breathing stops immediately [4]. The properties of H_2S are shown in Table 1 [5]. The acidity of H_2S makes it corrosive to industrial facilities and pipelines. In addition, the combustion of H_2S leads to the release of sulfur oxides, which is a main compound causing acid rain [6]. However, with the development of science and technology, more and more industrial processes prefer H_2S levels below 1 ppm. In particular, the concentration of H_2S in H_2 used for fuel cells is regulated below 0.004 ppm [7]. Therefore, H_2S removal, especially trace H_2S removal from industrial gases, is of vital importance and great significance for both humans and the environment.

Table 1. Summary of H_2S properties.

Property	Value
Molar mass	34.08 g/mol
Relative gas density	1.19
Odor threshold low	0.001 ppm
Triple point	187.6 K
Explosive range	4.5~46%
Kinetic diameter	0.36 nm
Dipole moment	0.97 D
Odor	Rotten eggs

In order to remove H_2S efficiently and economically, some technologies have been developed over the past decades, such as amine absorption [8], catalytic oxidation [9,10],

Claus process [11], biological desulfurization [12], and adsorption. Among these technologies, adsorption processes have attracted extensive attention since they are easy to operate and cost-effective, and achieved ultra-deep H_2S removal (below 1 ppm) [13]. Over the past decades, numerous studies have been carried out to develop high-performance adsorbents with high activity, sulfur capacity and selectivity, excellent thermal durability, and regeneration, including activated carbon, metal oxide [14,15], zeolite [16], mesoporous silica [17,18], and MOFs [19,20]. Zeolite is a promising adsorbent compared to others, as it has a wide range of sources and good thermal stability.

Zeolite is a class of three-dimensional ordered crystal material composed of SiO_4 or AlO_4 tetrahedra connected in a certain order by sharing oxygen atoms [21]. More than 250 zeolites have been discovered. Zeolite is widely used in adsorption, catalysis, and other fields as it has large specific surface area and molecular-level pores [22,23]. In addition, zeolites have many “cages” in their structure, which not only facilitate the diffusion of guest gas molecules inside the zeolite, but also provide space for accommodating other cations beneficial for subsequent further modification. Figure 1 shows the structure of several zeolites. So far, many zeolites have been studied as adsorbents for H_2S removal and some progress has been made. However, the differences in structure, composition, and chemical properties result in different H_2S adsorption mechanisms. Note that the pore size of zeolite is in the same order as the dynamic diameter of H_2S . This pore dimension leads to potential H_2S affinity as a result of physical confinement but also causes unavoidable diffusion barriers. These issues need to be taken into consideration when developing zeolite-based adsorbents for H_2S removal.

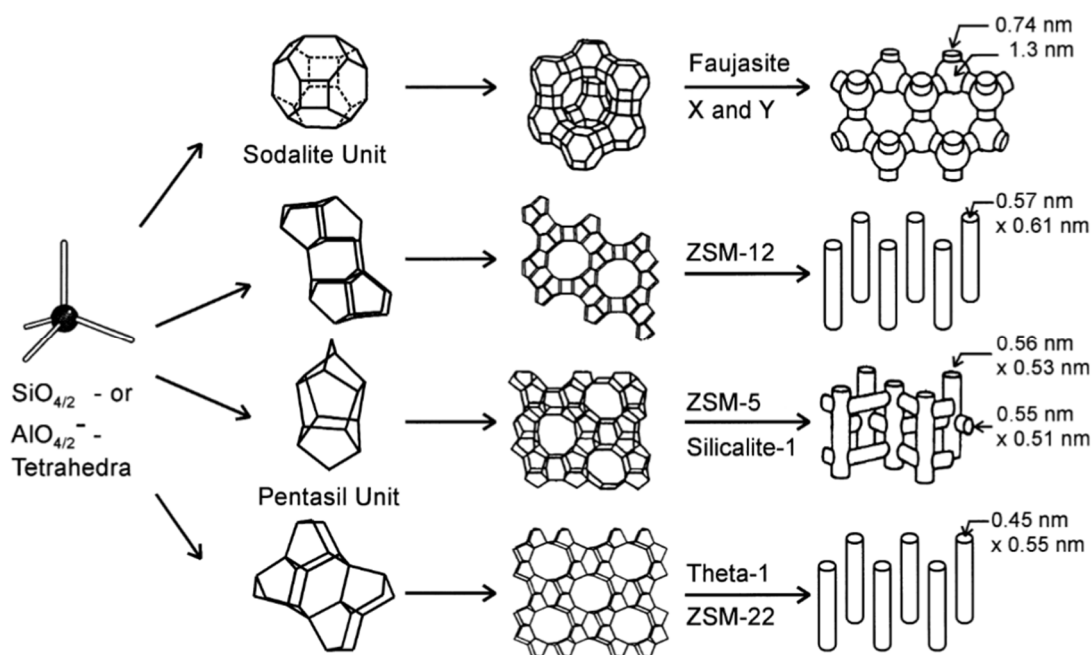


Figure 1. Structures of four selected zeolites (from top to bottom: faujasite or zeolites X, Y; zeolite ZSM-12; zeolite ZSM-5 or silicalite-1; zeolite Theta-1 or ZSM-22) and their micropore systems and dimensions. Reprinted with permission from Ref. [24]. 2000, Elsevier.

This paper reviews the current status and issues of zeolite-based adsorbents used to remove H_2S from industrial gases. Particular attention is paid to the adsorption mechanism and the measures as to how to enhance the adsorption performance. The results show that zeolites can remove H_2S through both physical and chemical mechanisms, and the desulfurization performance can be improved by various modification methods. Some components in the industrial gas, such as CO_2 and H_2O , make an impact on H_2S removal performance, and thus selectivity becomes a key parameter when assessing the adsorption

performance. In addition, the studies of hydrogen sulfide removal by molecular simulation are also reviewed here. Based on these studies, we attempt to shed light on new perspectives for the further research.

2. Physical Adsorption

Owing to huge specific surface area and molecular-level pore channels allowing diffusion of guest gaseous molecules through the structure easily, zeolite is an excellent physical adsorbent. Physical mechanisms of H₂S adsorption on faujasite-type (FAU) zeolite and Linde-Type-A (LTA) zeolite were studied [25,26]. When the partial pressure of H₂S was high (above ~2.5 kPa), H₂S molecules could coordinate with surface Na⁺ cations without dissociation.

Currently, pressure swing adsorption (PSA) is the most widely used technology for gas separation. Commonly used adsorbents in PSA processes include zeolites, activated carbon, silica, etc. Since these adsorbents are sensitive to water, and the adsorbent after water adsorption is hard to recover during PSA processes, water-free gases are preferred for the processes. At present, the performance evaluation standards for adsorbents have not been unified. However, compared to other adsorbents, zeolites have uniform pore structure with narrowly distributed channels and relatively good regeneration ability, thus they are preferred to be used in adsorption separation processes. For the demands on the process economic efficiency and product purity, excellent regeneration ability and selectivity of zeolites are required, and proper operation pressure and temperature are important as well. Since the 1970s, PSA technology with zeolite as adsorbents has been studied for separating and removing hydrogen sulfide from industrial gas streams. In 1978, a pioneering work was carried out by Karge and Rasko [25]. They investigated the desulfurization ability of FAU, focusing on the effect of different Si/Al ratios. The results indicated that NaY, which has a Si/Al ratio higher than 2.5, adsorbed H₂S reversibly, while zeolite with a lower Si/Al ratio, such as 13X, could be a catalyst for H₂S dissociation, leading to the formation of solid products, which result in poor regeneration performance. Similarly, Salman and Bishara [27] evaluated four types of zeolites as adsorbents for removing H₂S from H₂: 4A, 13X, NaY, and Y (rare earth). NaY zeolite had the highest sulfur capacity (80.5 mg/g zeolite) and adsorption efficiency among these four zeolites. As mentioned before, though zeolite 13X had relatively poor regeneration ability, it exhibited high adsorption capacity. Melo et al. [28] investigated the use of 13X for H₂S removal from CH₄. The results showed that a maximum adsorption capacity (52.7 mg/g) was obtained at 25 °C, 49 Pa. The best H₂S adsorption capacity using 13X was reported by Cruz et al. [29], it reached nearly 170 mg/g at partial pressure of 8 kPa, 25 °C. Moreover, 13X had a satisfying ability of selective removal of the trace H₂S from propane with a storage capacity of more than 62% (2500 kPa, 25 °C) [30].

H₂S adsorption by LTA zeolite was also studied. The separation of bulk quantities of H₂S from CO₂ was investigated through a series of pressure swing adsorption experiments utilizing zeolite 4A, 5A, and 13X by Tomadakis and co-workers [31]. The feed gas mixed with pure H₂S and CO₂ was supplied into the bed after the column was pressurized by nitrogen to the desired adsorption pressure. Gas samples were drawn regularly and analyzed by a gas chromatograph. According to the results, high selectivity for H₂S over CO₂ was encountered with all three types of adsorbents, reaching up to 11.9 for 13X at 84% H₂S concentration, 5.4 for 5A at 85% H₂S concentration, and 2 for 4A at 61% H₂S concentration. The best desorption recovery results obtained with 4A zeolites were between 76–91%. Furthermore, the group conducted another study to separate trace H₂S from equimolar mixtures of CO₂ and CH₄ [32]. The H₂S feed volume fraction was varied from 0.1% to 0.7% to determine the effect of H₂S concentration on PSA process efficiency. The results indicated that zeolite 13X and 5A were capable of producing high purity methane (up to 98%) of zero or nearly zero H₂S concentration in adsorption stage, and high purity carbon dioxide (up to 99.6%) in the desorption stage, H₂S was enriched in desorption product gas (0.04–5.6%). Zeolite 4A achieved the highest average H₂S desorption recovery efficiency and the most

pronounced improvement in H₂S concentration (in the collected desorption product vs. the feed), which was 72% and 2.9% vs. 0.3%, respectively. Furthermore, Wynnyk et al. [33] carried out a series of high pressure experiments to measure self-consistent adsorption isotherms and adsorption capacities for sour gas species (CO₂, COS, CH₄ and H₂S) on zeolite 4A with Si/Al ratios between 1.14 and 1.15 at different temperature (0, 25, 50 °C). Zeolite 4A was activated under ultra-high vacuum (10^{−8} kPa) up to 400 °C. The saturation adsorption capacities at 0 °C extrapolated from the fitted isotherm of CO₂, COS, CH₄, and H₂S were 7.25, 3.11, 9.16, and 5.87 mmol/g, respectively. The enthalpy of adsorption was also calculated using isotherms at different temperatures; at low loadings, the enthalpy value of CH₄ and COS was 20 kJ/mol, while CO₂ and H₂S was ~35 kJ/mol (near saturation loading). Such small enthalpy values cannot suggest a chemisorption behavior.

All pure-silica zeolites are free of aluminum, resulting in their extremely low polarity and strong hydrophobicity [34]. Maghsoudi et al. [35] investigated pure component adsorption of H₂S, CO₂, and CH₄ in an all-silica zeolite of chabazite (CHA) framework for the first time. Adsorption isotherms were measured over pressure range of 0–190 kPa and temperatures at 25, 50, and 75 °C. The results showed H₂S adsorption mechanism was physical and H₂S adsorption capacity was ~130 mg/g at 25 °C, 200 kPa.

Zeolites could be divided into synthetic zeolites and natural zeolites, and all the above mentioned were synthetic ones. However, there are many natural zeolites in nature. These zeolites have some advantages compared to synthetic ones, such as easy access and inexpensive. Yaşyerli et al. [36] investigated H₂S adsorption properties of Western Anatolian clinoptilolite in a fixed-bed system at different temperatures between 100 and 600 °C in atmosphere. The clinoptilolite H₂S capacity was found to decrease with the temperature increasing from 100 (92.4 mg/g) to 600 °C (31.9 mg/g). The results indicated that clinoptilolite could be used for H₂S removal at temperatures lower than 600 °C. However, natural zeolites have a certain amount of impurities in the pores, which limits their applications [37]. The drawback could be improved through different activation methods and chemical and thermal treatment are the most used ones [38–40]. Moldovan et al. [38] treated clinoptilolite by chemical (2M NaCl), thermal (150 °C for 24 h), and thermo-chemical (2M NaCl, 150 °C for 24 h) method and compared their ability to remove NH₄⁺ and H₂S simultaneously from drinking and waste water. The zeolite structure did not change significantly after activation. Adsorption results showed that thermally activated zeolite possessed the highest removal efficiency both for NH₄⁺ (77%, after 48 h) and H₂S (87%, after 72 h), and H₂S removal capacity was 0.87 mg/kg for drinking water (0.5 mg/L NH₄⁺ and 0.5 mg/L H₂S), 1.58 mg/kg for wastewater (3.2 mg/L NH₄⁺ and 2.5 mg/L H₂S). Alonso et al. [39] compared the behavior of zeolite 5A, 13X, and clinoptilolite for H₂S removal and upgrading of biogas. Prior to use, clinoptilolites were washed and calcinated to remove the soluble impurities and volatile compounds presented in their cavities or channels. Clinoptilolite washed at 40 °C and calcinated at 220 °C showed the H₂S breakthrough capacity of 1.39 mg/g at 1 cm/s biogas (CH₄/CO₂/H₂S) feeding velocity, 25 °C, 700 kPa, which was nearly 14 times higher than the original ones. Moreover, an unexpected behavior was observed for clinoptilolite because its H₂S adsorption capacity improved remarkably with the number of cycles and stabilized from cycle 4. The author believed this phenomenon might be related to chemical adsorption mechanism. Ion-exchange method could be another choice for natural zeolite activation. The sulfur capacity of clinoptilolite could be improved by ion-exchange treatment with some metal ions, such as Zn²⁺, Fe³⁺, Mn²⁺, Cu²⁺, and Ni²⁺. After activation, adsorption occurred through physisorption on Bronsted centers and chemisorption over cations [41], and sulfur compound could interact with cations through π -complexation which resulted in significant increment of adsorption capacity [42].

In recent years, molecular simulations have become a powerful tool in material science to calculate material properties, predict material behavior, and validate experimental results. Applying these techniques can reduce the cost of experiments, improve safety, and enable difficult-to-perform experiments [43]. Cosoli et al. [44,45] carried out Grand Canonical Monte Carlo (GCMC) and ab initio quantum mechanics simulations for H₂S removal by

four different zeolites, including FAU (NaX, NaY), LTA, and MFI. The authors focused on the adsorption of pure H₂S at 25 °C (with pressures from 10 to 1000 Pa), as well as competitive adsorption of H₂S, CH₄, and CO₂ under typical biogas composition (CO₂ and CH₄ as bulk components, and H₂S present in trace), a total pressure of about 100 kPa, and temperature of 25 °C. The results indicated that hydrophilic zeolites were preferred for H₂S adsorption, mostly because of the higher calculated values of the isosteric heat of adsorption. Moreover, all hydrophilic zeolites showed higher selectivity of H₂S with respect to CH₄. A significant competitive adsorption by CO₂ and CH₄ was highlighted, especially in LTA and MFI frameworks, and these zeolites barely adsorbed H₂S when the typical biogas composition was considered in the calculations. Shah et al. [46] carried out Gibbs ensemble Monte Carlo simulations to investigate the adsorption behavior of seven silica zeolites (CHA, DDR, FER, IFR, MFI, MOR, and MWW) for H₂S and CH₄, both pure-component and mixture, over a wide range of temperatures (25, 70 °C), pressures (100–5000 kPa), and compositions. The simulation results were in good agreement with experimental data reported by Maghsoudi et al. [35]; the force field of H₂S and zeolite were verified at the same time [47,48]. The simulations demonstrated that selectivity increased with the increase of H₂S concentration. Due to the favorable interactions between H₂S and the zeolites, zeolite MOR and MFI exhibited the highest selectivity and the most favorable enthalpy of adsorption for H₂S at low H₂S concentration (below 10%) and high H₂S concentration, respectively. In subsequent research, Shah et al. [49] also carried out a vast computational study of the adsorption of binary H₂S/CH₄ and H₂S/C₂H₆ mixtures in the all-silica forms of 386 zeolitic frameworks. Figure 2 showed the performance of 62 adsorbents with the highest selectivities (the H₂S/CH₄ selectivity, S_{H_2S/CH_4} ; the H₂S/C₂H₆ selectivity, S_{H_2S/C_2H_6}). According to the binary adsorption selectivities and capacities, they selected 16 promising zeolites and investigated the adsorption performance for a five-component mixture involving H₂S, CO₂, CH₄, C₂H₆, and N₂ in a 25:10:50:10:5 mole ratio. It was found that different sorbents allow for optimal H₂S removal depending on the fractions of CH₄, C₂H₆, and CO₂. These studies provided the basis for the synthesis and application of all-silica zeolites in H₂S removal.

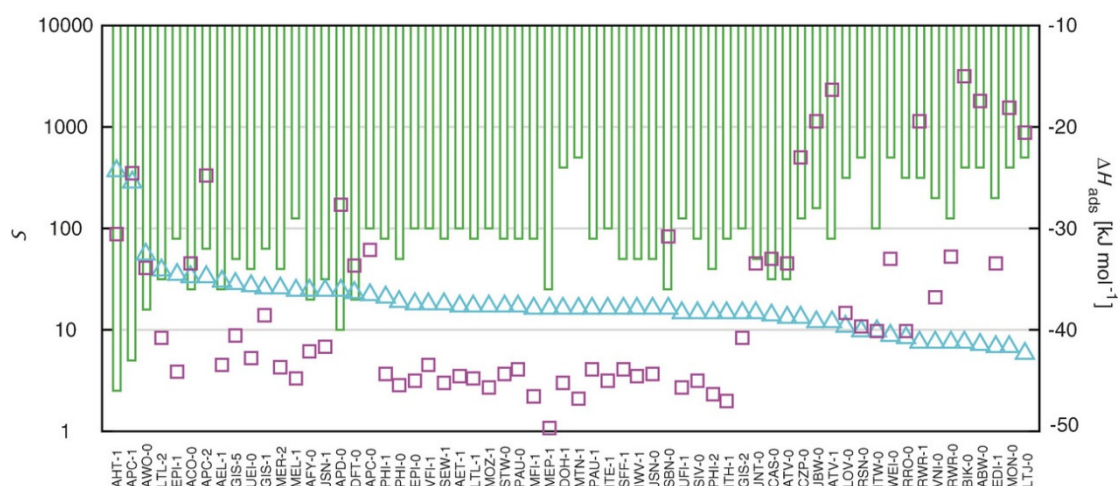


Figure 2. Selectivity (left axis) and ΔH_{ads} (right axis) in top-performing zeolite structures at $y_F = 0.50$, $T = 343$ K, and $p = 50$ bar. S_{H_2S/CH_4} cyan triangles, S_{H_2S/C_2H_6} magenta squares, and ΔH_{ads} (for the H₂S/CH₄ mixture) green bars. Reprinted with permission from Ref. [49]. 2016, Wiley.

Silicoaluminophosphate (SAPO) is an important class of microporous zeotype and has proven useful for industrial catalysis and separation. SAPO-43 is one of the SAPO zeolites, its structural information is shown in Figure 3. However, it is unsuitable for sour gas removal from other gases due to its low thermal stability. To improve the shortcoming, Hernandez-Maldonado et al. [50] calcined SAPO-43 partially and applied the treated samples to separate CO₂, H₂S, and H₂O from natural gas. Elemental analysis results and

CO_2 heats of adsorption pointed to the presence of amine-like compounds entrapped in the surface of SAPO-43. In general, it was found that H_2S adsorption capacity was 88 mg/g at 25 °C and atmospheric conditions. The authors proposed that regeneration using chemicals such as H_2O_2 might help remove H_2S thoroughly without the need to thermal regeneration.

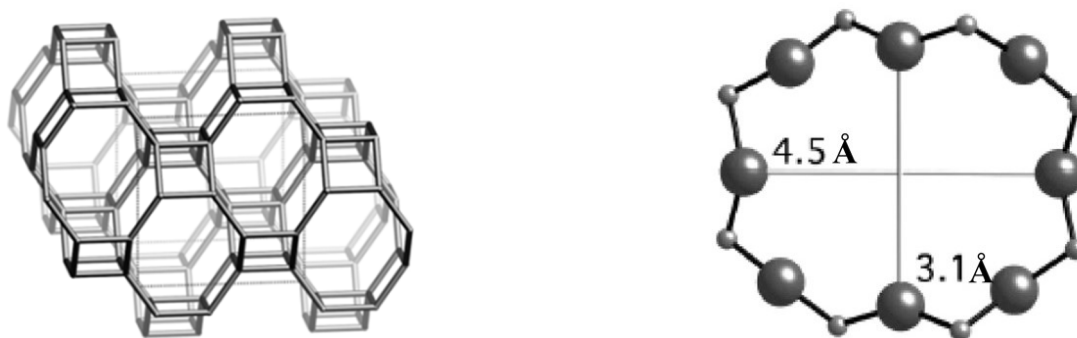


Figure 3. Structural schematic of SAPO-43 viewed along [100] (left) and 8-ring viewed along [100] (right). Source: Database of Zeolite Structure of the International Zeolite Association (IZA): https://asia.iza-structure.org/IZA-SC/ftc_table.php. (accessed on 23 June 2022).

3. Chemical Adsorption

Chemical adsorption (chemisorption) occurs when electrons are transferred, exchanged, or shared between the adsorbate and solid adsorbent surface atoms, or molecules, to form a covalent or ionic bond. Different from all silica zeolites, aluminosilicate zeolites framework is composed of SiO_4 and AlO_4 , which causes Bronsted acid sites and Lewis acid sites. In order to keep overall charge balance, aluminosilicate zeolites framework needs cations such as Na^+ , K^+ , Ca^{2+} , etc. [51], which allow the possibility of strong interactions with H_2S . Thus, in addition to physical adsorption, chemisorption also occurs during the adsorption processes. There are two mechanisms for H_2S chemisorption adsorption by bare zeolite: sulfide–zeolite π -complexation and sulfur–metal bond formation. Generally, in order to achieve better desulfurization performance, zeolite needs to be modified before use. However, different modification methods may lead to different desulfurization mechanisms. Relevant studies are reviewed by modification methods as follows.

3.1. Ion-Exchange Modification

Certain metal ions can be introduced to zeolites through ion-exchange modification that improves its activity and selectivity on H_2S removal. As zeolites contain Bronsted and Lewis acid sites, they can act as catalysts when an oxidant (such as SO_2) is present and the Claus reaction occurs [52–56]. In more cases, no oxidant is present in the gas composition. Kumar et al. [57] prepared silver and copper cations ion-exchange zeolites X and Y. Then, they studied the H_2S adsorption capacities of these zeolites for 10 ppm H_2S in He and N_2 in the absence and presence of CO_2 (20%), CO (2%), and H_2O (2%) in gas mixtures using a fixed-bed reactor (Figure 4).

The results showed that AgX possessed the highest H_2S adsorption capacity under different gas components at both room temperature and 150 °C, exceeding 40 mg/g. H_2S adsorption capacities reduced in the order of $\text{AgX} > \text{AgY} > \text{CuX} > \text{CuY} > \text{NaX}$ at room temperature. Interestingly, H_2S could not be removed by CuX and CuY in the presence of 2% CO . This was because the copper in these zeolites mainly existed in the form of Cu^+ , which adsorbed CO selectively. Similarly, Chen et al. [58] prepared Ag, Zn, and Co modified NaX zeolites by ion-exchange method and studied their adsorption performance of H_2S and COS removal from Claus tail gas at 25 °C. After modification, the microscopic properties of zeolites had been changed. The surface of zeolites became rougher, and some zeolite particles were broken. Due to the smaller ionic radius and higher valence of Zn^{2+} and Co^{2+} , ZnX and CoX had more inside vacant spaces than

NaX, resulting in larger specific area and pore volume. In this study, AgX also achieved the highest H₂S adsorption breakthrough capacity (52 mg/g) under normal pressure and temperature, and H₂S adsorption breakthrough capacities reduced in the order of AgX > ZnX > CoX > NaX. The authors also carried out regeneration experiments, the results showed that the adsorption capacity of used AgX reached up to 93.5% of the fresh one after treatment at 350 °C under air atmosphere. Furthermore, density functional theory (DFT) calculations were used to explore the adsorption mechanism. Figure 5 showed the adsorption configurations of H₂S on these zeolites cluster models. The study indicated that the S-M bond was formed between H₂S and metal ion, and Ag-sulfide bond was the strongest with the Mayer bond order at 0.639.

Similarly, Long et al. [59] synthesized ZnX, CuX, MnX, CaX, NiX, and CoX by ion-exchange method and investigated the adsorptive of H₂S at room temperature. The results showed that ZnX possessed the highest capacity of 23.5 mg/g. They proposed the mechanism of H₂S removal by ZnX: $\text{Zn}^{2+} + \text{H}_2\text{S} \rightarrow (\text{Zn}-\text{SH}_2)^{2+}\text{ads}$, $(\text{Zn}-\text{SH}_2)^{2+}\text{ads} \rightarrow \text{ZnS} + 2\text{H}^+$. Tran et al. [60] found that the desulfurization ability of NaX treated by Co²⁺ ion-exchange and heating was enhanced significantly due to the increase in the mesopore volume. They also proposed the chemisorption mechanism: $\text{H}_2\text{S} + [\text{Co}(\text{O}_x)_6]^{2+}\text{X}^{2-} \rightarrow \text{CoS} \downarrow + \text{H}_2\text{X} + \text{O}_x$. Another DFT study was conducted by Sung et al. [61] The authors investigated the capabilities of Cu-Y and Ag-Y zeolite for selective H₂S removal from Claus tail gas and compared their adsorption energies with Li-Y, Na-Y, and K-Y. According to the adsorption energies, Ag-Y had the best predicted selectivity for the adsorption of H₂S, while Cu-Y and alkali metal-exchanged Y zeolites tended to adsorb CO and H₂O strongly, respectively. Subsequently, the authors carried out further DFT research to compute the adsorption energies of H₂S and other Claus tail gas components (CO, H₂O, N₂, and CO₂) using zeolite cluster model to explore the potential use of Zn(II)Y, Ni(II)Y, and Ga(III)Y, as selective adsorbents for H₂S [62]. It was found that these zeolites were all favorable for strong adsorption of H₂O, and they proposed that using Cu(II)Y zeolites for H₂O removal, followed by H₂S removal using GaY, might be a useful strategy for adsorptive desulfurization. DFT calculations were also carried out to investigate natural gas compounds (H₂S, COS, CO₂, and CH₄) adsorption on FeY, CoY, NiY, CuY, and ZnY zeolite clusters [63]. H₂S, COS, and CO₂ adsorption on these zeolites were shown to be dominated by charge-transfer and polarization energy contributions, indicating the occurrence of a chemical reaction. Furthermore, H₂S adsorption energy on Co-Y and Ni-Y zeolite was −147.02 and −128.78 kJ/mol, respectively, which was at least 50% greater than that of CO₂, COS, and CH₄. Moreover, compared to CoY, NiY was more selective in H₂S adsorption due to its stronger interaction with H₂S than CH₄. These results demonstrated that Ni-Y zeolite was a promising selective adsorbent material for natural gas desulfurization. More recently, Bareschino et al. [56] studied and modeled H₂S adsorption from a synthetic biogas mixture by NaX in a fixed bed adsorption column and a one dimensional coupled heat and mass transfer model based on Linear Driving Force (LDF) was proposed. The parameters of the model were in good agreement with previous literature.

To gain a deeper understanding of the mechanism of H₂S adsorption by ion-exchanged zeolite, IR analysis was applied. According to IR results, the first H₂S molecule was adsorbed dissociatively on aluminum-rich FAU zeolite to produce OH groups [64], and at higher coverages, H₂S dissociated into HS[−] and H⁺, as shown in Figure 6. The type A zeolites were also investigated [65]. Upon adsorption of H₂S onto ZnNaA and MnNaA zeolites, a band at 2560 cm^{−1} was found in the result. It was concluded that the band was due to the product of both dissociative and non-dissociative adsorption. Water formation was observed on adsorption of H₂S onto MnNaA, ZnNaA, and CoNaA, which was in consistent with previous studies [55,66,67]. However, the source of O in H₂O remained unclear.

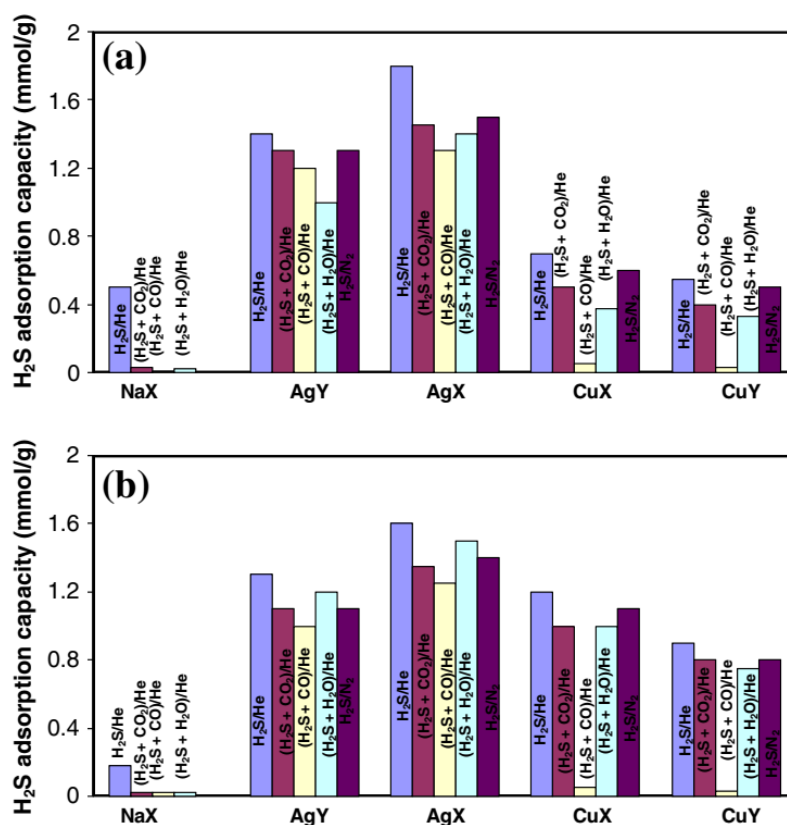


Figure 4. H₂S adsorption capacities of NaX, AgY, AgX, CuX, and CuY zeolites for 10 ppm H₂S in He and N₂ in the absence and presence of CO₂ (20%), CO (2%), and H₂O (2%) in the feed at (a) room temperature and (b) 150 °C. Reprinted with permission from Ref. [57]. 2011, Elsevier.

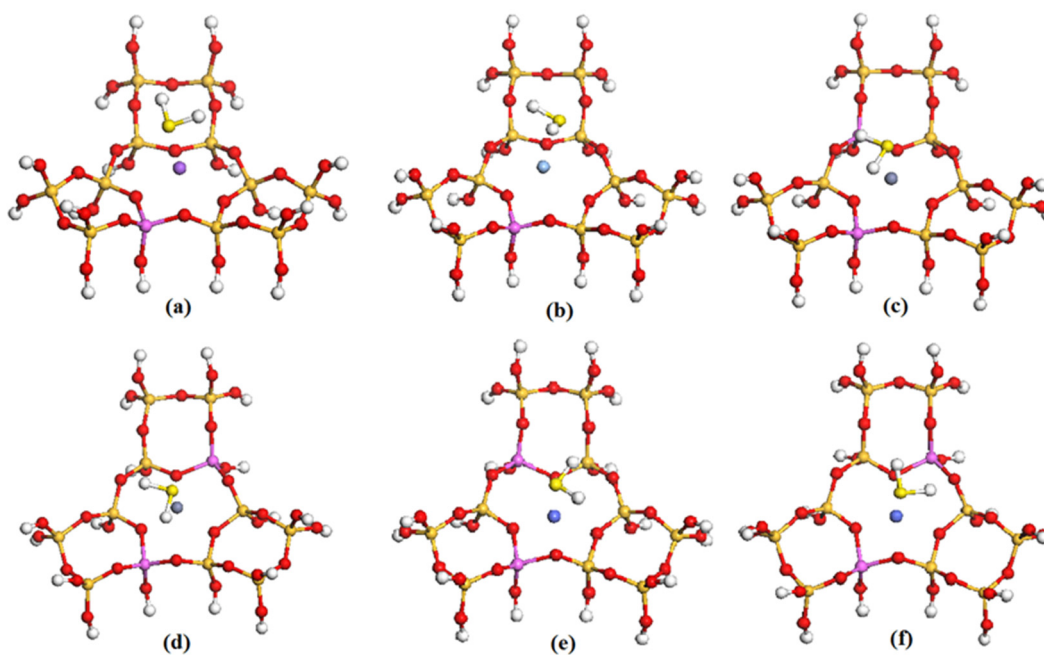


Figure 5. Adsorption configurations of H₂S on (a) NaX, (b) AgX, (c) ZnX(i), (d) ZnX(ii), (e) CoX(i), and (f) CoX(ii) cluster models. (Red: O, orange: Si, white: H, pink: Al, yellow: S, purple: Na, blue: Ag, grey: Zn, dark blue: Co.) Reprinted with permission from Ref. [58]. 2018, Elsevier.

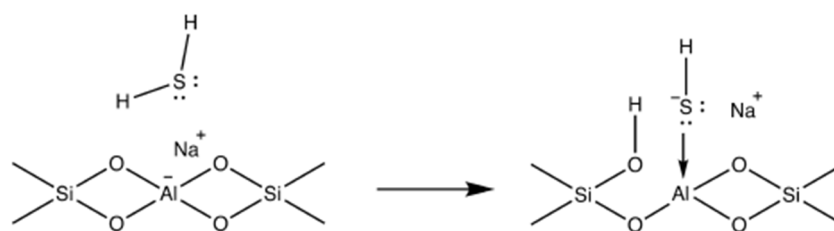


Figure 6. Diagram of dissociative H₂S adsorption on an aluminosilicate zeolite.

Recently, Sigot et al. [68,69] investigated the effect of moisture on the H₂S removal performance of zeolite and proposed an adsorption-oxidation mechanism for H₂S adsorption by 13X at the presence of H₂O. The mechanism involved five stages: H₂S adsorption on the surface of zeolite ($\text{H}_2\text{S}_{(\text{g})} \rightarrow \text{H}_2\text{S}_{(\text{ads})}$), dissolution of H₂S in water film deposited on the surface ($\text{H}_2\text{S}_{(\text{ads})} \rightarrow \text{H}_2\text{S}_{(\text{aq})}$), dissociation of H₂S ($\text{H}_2\text{S}_{(\text{aq})} + \text{H}_2\text{O}_{(\text{l})} \rightarrow \text{HS}^-_{(\text{aq})} + \text{H}_3\text{O}^+_{(\text{aq})}$), oxidation of HS[−] by adsorbed oxygen to form element sulfur ($\text{HS}^-_{(\text{aq})} + \text{O}_{(\text{ads})} \rightarrow \text{S}_{(\text{ads})} + \text{OH}^-_{(\text{aq})}$), and conversion of element sulfur to stable sulfur polymers ($x\text{S}_{(\text{ads})} \rightarrow \text{S}_{x(\text{ads})}$). The formation of stable sulfur polymers comprised the thermal regeneration of 13X. Thus, the other regeneration methods were proposed by the authors, such as high temperature desorption at 500–600 °C in inert atmosphere, desorption–oxidation in air at a temperature <400 °C, desorption under reduced pressure and chemical dissolution with organic solvents.

When CO₂ exists in feed gas, in addition to the competitive adsorption, it also reacts with H₂S. The reaction $\text{H}_2\text{S} + \text{CO}_2 \rightleftharpoons \text{COS} + \text{H}_2\text{O}$ was reported on reactive adsorption of H₂S and CO₂ on cation-exchanged LTA and FAU zeolites in several studies [70–72]. As we know, zeolites were favorable for H₂O adsorption, resulting in the above reaction moving to the right. The results showed that H₂S conversion on LTA reached up to 50% for a Si/Al ratio of 1, and nearly zero for a Si/Al ratio of 3 [70]. These studies inspired us to focus on the COS breakthrough when investigating H₂S breakthrough behavior on cationic zeolites in the presence of CO₂.

Titanosilicates were a class of microporous zeolites that were obtained in 1989 for the first time [73,74]. Rezaei et al. [75] investigated low temperature reactive H₂S removal using different copper-exchanged Engelhard titanosilicates, named ETS-2, ETS-4, and ETS-10. The copper loading of Cu-ETS-2, Cu-ETS-4, and Cu-ETS-10 were 12.5%, 4.8%, and 8.4%, respectively. The adsorption results showed that Cu-ETS-2, activated at 100 °C, had the highest H₂S breakthrough capacity of 47 mg/g with the copper utilization of 71%. It was capable of maintaining a column outlet concentration of H₂S of less than 0.5 ppm for ~27 h, which was superior to commercial adsorbents. The H₂S adsorption behavior of Cu-ETS-2 at high temperature was also studied to explain whether the structural changes due to high temperature (>500 °C) affected the H₂S capacity of the adsorbent [76]. Below 750 °C, the adsorbent could remove 99% of H₂S from the feed gas (500 ppm H₂S in He) and achieve the breakthrough capacity of more than 50 mg/g. Above this temperature, H₂S adsorption capacity reduced due to the reduction of Cu²⁺ in the presence of H₂ generated from thermally dissociated H₂S. Furthermore, the authors prepared Ag, Ca, Cu, and Zn ion-exchanged ETS-2 and investigated their desulfurization performance of 10 ppm H₂S in He at room temperature [77]. Breakthrough experimental results showed that Cu-ETS-2 had the highest sulfur adsorption capacity of 29.7 mg/g, even higher than that of commercial samples (R3-11G, 36 wt% CuO, BASF). Recently, Cu-ETS-2, Cu-Cr-ETS-2, and Ce-ETS-2 were prepared by ion-exchange method and tested for their H₂S removal performance in the temperature range of 75–950 °C under hydrogen-rich and water-rich atmospheres [78]. The gas mixture was composed of He (69%), H₂ (14% or 28%), H₂O (17% or 3%), and 500 ppm H₂S. Cu-ETS-2, Cu-Cr-ETS-2, and Ce-ETS-2 exhibited H₂S capacities of 41 mg/g at 350 °C, 20 mg/g at 75 °C, and 3 mg/g at 250 °C, respectively. It was found that the adsorption of H₂S by the adsorbents was promoted in the presence of water. As for Cu-Cr-ETS-2, the presence of chromium effectively stabilized the copper against reduction to metallic copper up to 950 °C [79]. The H₂S capacity remained ~61mg/g from 350 °C to 950 °C.

3.2. Metal Oxide Loading

In 1970s, Westmoreland and Harrison [80] concluded that oxides of Zn, Cu, Fe, Mn, Co, Mo, Ca, V, Sr, Ba, and W had the potential for high-temperature desulfurization by using free energy minimization method, and metal oxide desulfurizers quickly became a research hotspot. However, bulk metal oxides have limited desulfurization kinetics and active component utilization due to their low specific surface areas, insufficient porosity and poor dispersion [81]. In order to improve these disadvantages, loading metal oxide particles on porous supports is an effective method [82–86]. Since zeolites have regular channels and high hydrothermal stability, they become good adsorbent carriers. Loading active metal oxides onto zeolites can compensate for the shortcomings of bulk metal oxides and obtain high-performance desulfurization adsorbents.

Pi et al. [87] prepared a series of NaX-WO₃ by a mechanical mixing method using NaX powder and WO₃ powder. The desulfurization test was carried out in a fixed bed with the composition of feed gas: 2% H₂S, 1% of O₂, 10% H₂O and N₂. Because of the stronger adsorption of H₂O on NaX, the presence of H₂O significantly decreased the activity of NaX. The authors confirmed that the addition of WO₃ caused either a decrease of the strong adsorption of water vapor on the zeolite NaX or an increase of the reducibility of WO₃ by some interactions between zeolite NaX and WO₃. Lee et al. [88] synthesized NaA zeolites from smelting slag and prepared iron-incorporated NaA zeolite. They found that the maximum concentration of iron that can be accommodated into the NaA zeolite was 78 mM, and the highest H₂S adsorption capacity at 30 °C, 101 kPa was 15 mg/g which was higher than commercial zeolites such as 4A and 13X. Liu et al. [89] synthesized a novel regenerable hybrid TiO₂/zeolite composite with double advantages of zeolite adsorption and TiO₂ photocatalysis. The materials showed an excellent performance in selective H₂S removal and simultaneously SO₂ emission reduction in biogas purification process. They also built a setup for biogas purification: a UV-light was placed in the center of the columns to supply irradiation (3 mW/cm², 365 nm), and a compound parabolic concentrator was used for providing irradiation in the back of the columns. Simulated biogases with different compositions were passed through the columns and the concentrations of H₂S and SO₂ in the outlet gas were measured. The results showed that the hybrid TiO₂/zeolite composite possessed the highest H₂S capacity (4.4 mg/g) compared to that of the bare zeolite (1.7 mg/g) and TiO₂ (2.4 mg/g) and released the lowest SO₂ at the same time.

ZnO is a promising H₂S adsorbent because of the low cost and high desulfurization precision. ZnO (10–30 wt% loading) impregnated on NaA zeolite was prepared by Abdullah et al. [90]. The adsorption of H₂S from biogas was also investigated in a fixed bed reactor. According to the results, dispersion of ZnO took place at the surface and internal pores of NaA zeolite, which resulted in the reduction of micropore surface area and micropore volume of NaA zeolite. Furthermore, ZnO loading concentration needed to be controlled at less than the critical dispersion capacity to avoid forming bulk zinc oxide. NaA zeolite with 20 wt% ZnO loading achieved the highest capacity of 15.75 mg/g. The authors further used Response Surface Methodology (RSM) and Box–Behnken experimental design to study the effects of adsorption variables (reaction temperature, inlet H₂S concentration, inlet flow rate), on the adsorbent adsorption capacity. The results showed that all three variables had significant effects on adsorption breakthrough capacity. The highest adsorption capacity of 33 mg/g was obtained at optimum conditions: reaction temperature 28 °C, inlet flow rate 22 mL/min, and inlet H₂S concentration 111 ppm.

Silicoaluminophosphate zeolites loaded with metal oxides were also studied. In order to figure out the effect of different incorporation methods on H₂S adsorption, Elmutasim et al. [91] prepared copper modified AlPO₄-5 and SAPO-5 via isomorphic substitution, liquid ion exchange (LIE), vapor phase ion exchange (VIE), and nanoparticles inclusion during hydrothermal synthesis. The adsorption experiments were conducted in a fixed bed reactor, where the feed gas was comprised of 100 ppm H₂S and balance N₂. The parent AlPO₄-5 showed the lowest sulfur capacity among these samples, attributed to the lack of acid sites coupled with the weak interaction of H₂S with its surface. AlPO₄-5

modified by isomorphic substitution had almost no desulfurization ability due to the strong interaction between Cu and $\text{AlPO}_4\text{-5}$ lattice thus hindering its reactivity. The highest sulfur removal capacity at $150\text{ }^\circ\text{C}$ was obtained over the CuO nanoparticles supported in $\text{AlPO}_4\text{-5}$ (10% CuO/ $\text{AlPO}_4\text{-5}$), followed by a sample prepared by VIE (Cu-VIE-0.2), accounting for H_2S breakthrough capacities of 10.5 and 5.8 mg/g, respectively. Liu et al. [92] carried out a pilot study to synthesize SAPO-34@as-prepared SBA-15 (SS) as a support. The support was used for Zn-based spinel loading (Figure 7). The results showed that ZnCo_2O_4 spinel loaded onto SS exhibited an outstanding desulfurization behavior and higher breakthrough capacity (138.08 mg/g) for simulate coal gas at $550\text{ }^\circ\text{C}$ compared to other sorbents whose partial Co was substituted by Mn or Fe in spinel B-site. This was because the formation of $\text{Mn}_3(\text{PO}_4)_2$ or $\text{Fe}_3(\text{PO}_4)_2$ exacerbates the instability of spinel nano-crystallites. According to the desulfurization-regeneration cycles test, the breakthrough capacity of ZnCo_2/SS declined during the successive recycles, which was related with the evaporative Zn substance, the remains of high stable sulfides and the partial sintering of ZnCo_2/SS . This study also verified the action of phosphate ions with H_2S during desulfurization.

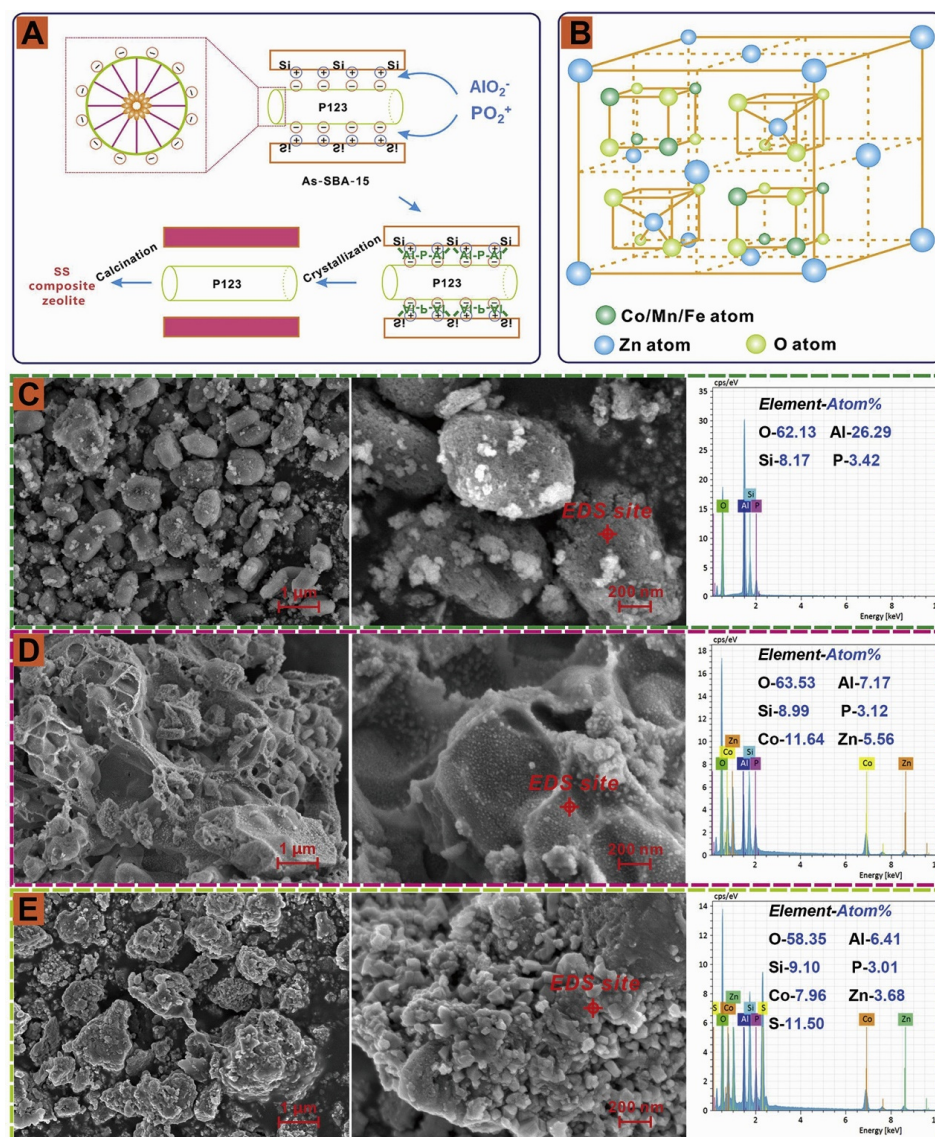


Figure 7. Schematic diagrams of (A) synthetic SS composite and (B) ZnCo_2O_4 structure. SEM photographs and EDS spectra of (C) SS, (D) ZnCo_2/SS and (E) S- ZnCo_2/SS . Reprinted with permission from Ref. [92]. 2020, Elsevier.

The synergetic effect of mixed metal oxides was investigated by Gasper-Galvin et al. [93]. The authors prepared oxides of Cu-, Mo-, and Mn-supported SP-115 zeolite and investigated their hot gas desulfurization performance at 871 °C and 205 kPa. The copper oxide was the main active component to react with H₂S, while Mo and Mn oxides acted as catalysts/promoters to enhance the initial desulfurization activity and the crush strength, respectively. The as-prepared materials maintained their reactivity and stability during successive multicycle sulfidation/regeneration.

4. Zeolite Membrane

Over the past three decades, membrane processes have received a lot of attention for gas separations due to their intrinsic properties such as low carbon footprint, good selectivity, and no phase change during operation. These factors lead to the reduction costs of construction and operation [94–96]. Due to the uniform pore texture, zeolite membranes have high selectivity and stability. Separation of CO₂ and hydrocarbons using zeolite membranes have been reported by several studies [97,98]. However, there are few studies focusing on the removal of H₂S using zeolite membranes.

Maghsoudi and Soltanieh [99] prepared high silica (Si/Al~5) CHA type zeolite membranes and studied the H₂S removal ability of these materials from ternary (H₂S-CO₂-CH₄) gas mixture. The 20 µm-thick zeolite was synthesized by in situ crystallization method on a plate-like α-alumina support, as shown in Figure 8. A good separation ability of H₂S and CH₄ was achieved because H₂S was adsorbed physically on the zeolite. The authors carried out an experiment at 25 °C and 400 kPa pressure difference to evaluate the membrane separation performance. A ternary gas mixture with the composition CO₂: 2.13 mol%, H₂S: 0.3 mol%, and CH₄: 97.57 mol%, was used. The results demonstrated that the as-prepared materials were able to separate H₂S from CH₄, with the H₂S permeance of 1.70×10^{-8} mol/m²s Pa and H₂S/CH₄ selectivity of 3.24. The results showed the potential of zeolite membranes for desulfurization in industry.

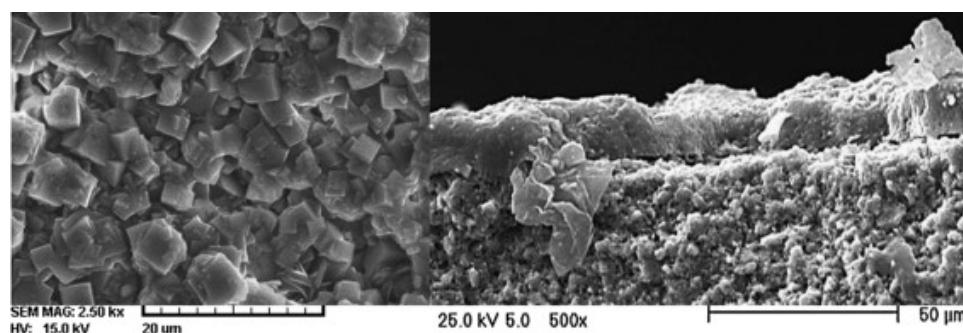


Figure 8. SEM photographs taken from surface and cross section of the membrane. Reprinted with permission from Ref. [99]. 2014, Elsevier.

5. Intracrystalline Diffusion of H₂S

Molecular diffusion, a basic form of mass transfer, is caused by irregular particle movement. Since the pore diameter of zeolite is similar to the gas molecular diameter, diffusion resistance is inevitable when gas molecules diffuse through the zeolite. However, the diffusion of gas molecules confined in zeolite is essential for adsorption (especially chemisorption), catalytic reaction rate etc. [100]. There are several factors affecting gas molecules diffusion behavior in zeolites, such as the topological structure of zeolite, temperature, and concentrations. Research on the intracrystalline diffusion of hydrocarbons in different zeolites has been carried out extensively [101–103], but similar studies on H₂S are very limited.

Sun and Han [104] carried out a systematic study on the diffusion behavior of H₂S, SO₂, N₂, and O₂ in zeolites MFI and 4A by molecular dynamics simulations under different temperature and loading. The results showed that higher temperature was favored for gas

molecules diffusion in zeolite, and the gas self-diffusivity value decreased in the order of $O_2 > N_2 > H_2S > SO_2$ at high loadings and temperatures in both two zeolites. However, the gas diffusion order was different in the two zeolites at lower loadings because of the different topological structure of MFI (straight channels) and 4A (α -cages). Interestingly, the diffusion coefficients of guest molecules in the two zeolites showed different trends with the increase of loadings: decrease in MFI and increase in 4A, which was because the relatively lower saturation level of guest molecules in 4A. The authors also calculated the center of mass (COM) probability densities to give insight into molecular-level diffusion process. The authors believed that the reason why probability density values of H_2S were lower than that of SO_2 was that the formation of H-bond between H_2S and zeolite framework decrease the probability density values of H_2S in MFI and 4A.

6. Conclusions and Perspectives

Removal of H_2S from various industrial gases is critical because of its highly toxic and corrosive nature. In this review, recent experimental and simulation progress in H_2S removal using zeolites has been summarized briefly according to different mechanisms. Zeolite possesses huge specific area and ordered pore structure. Different types of zeolites have different mechanisms for hydrogen sulfide adsorption due to different pore size, Si/Al ratios, cation species, and active components loading, which can be divided into physical adsorption and chemical adsorption. The adsorption process is not only affected by the properties of the zeolite itself, but also by the composition of the feed gas and the desulfurization conditions. Some impurities in industrial gas, especially H_2O and CO_2 , have competitive adsorption with H_2S ; moreover, CO_2 may react with H_2S under the catalysis of certain zeolites to produce COS, affecting the desulfurization efficiency. The H_2S removal efficiency also varies with temperature and pressure. Unfortunately, H_2S removal mechanism by zeolite and the influence rules of various external factors have not been clarified, and further research is needed.

Based on the review, suitable zeolites should be chosen according to different gas compositions and desulfurization conditions in actual industrial production. Furthermore, as some industrial processes require higher gas purity, hydrogen sulfide needs to be removed to an extremely low level (ppb level). Therefore, in future research, we not only need to focus on improving the selectivity of zeolite adsorption, but also develop a novel type of zeolite used for trace H_2S removal. At present, some progress has been made in improving desulfurization of zeolite treated by means of ion exchange, metal oxide loading, etc., but the desulfurization mechanism theories are still needed to be developed. Meanwhile, the study on the intracrystalline diffusion of H_2S in zeolites is still insufficient, which is essential for zeolite applications and needs to be taken seriously. In particular, experimental and simulation calculations of diffusivities of zeolites with intracrystalline defects, as well as reactions need to be done for further research. In this aspect, molecular simulations and artificial intelligence can also be used to help us screen materials or guide the synthesis of proper materials. In addition, zeolite membrane occupies advantages in both zeolite adsorption and membrane separation, which has a potential industrial application and becomes another important research highlight for the future.

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