H_2S Capture

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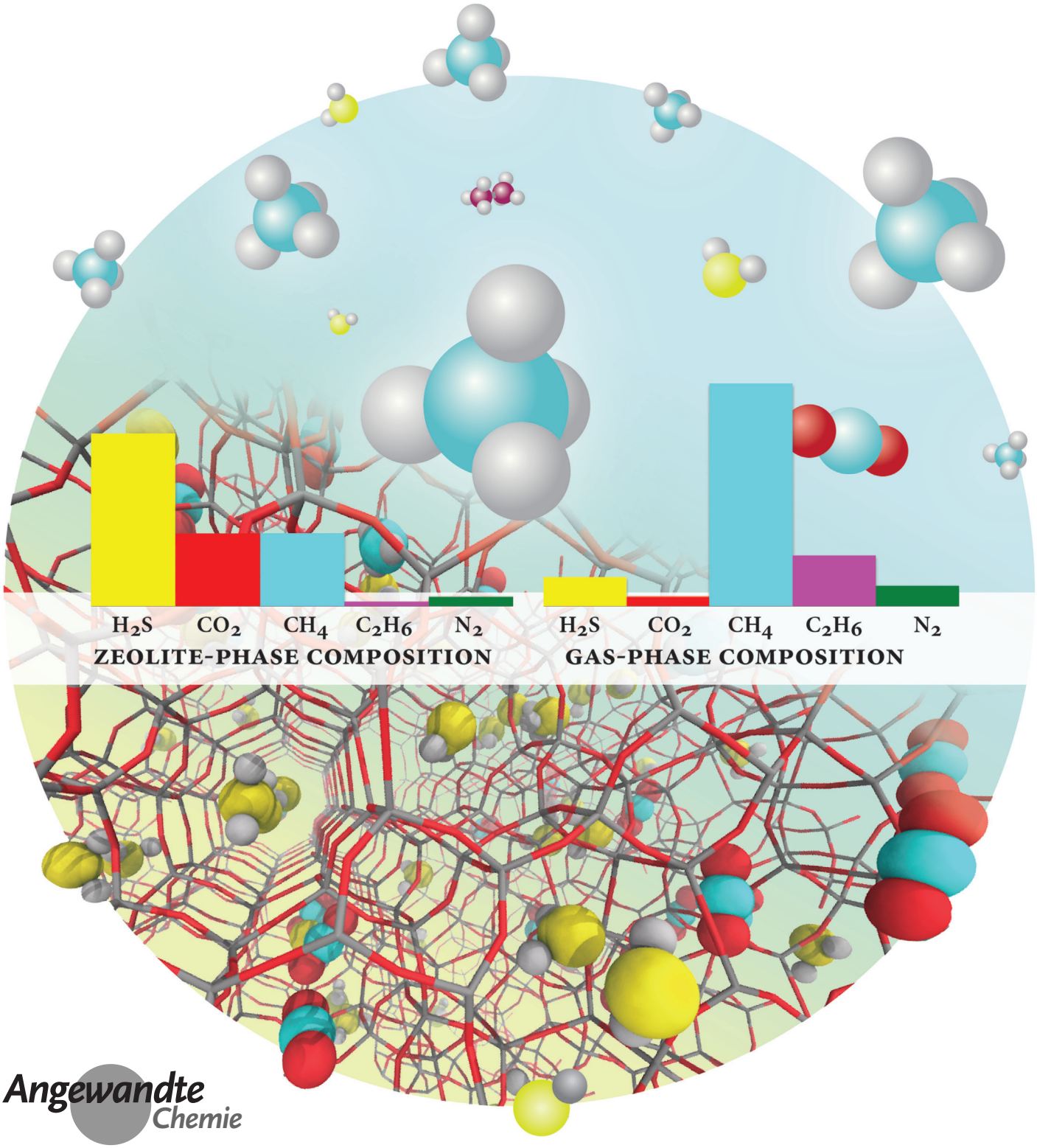
Identifying Optimal Zeolitic Sorbents for Sweetening of Highly Sour Natural Gas

*Mansi S. Shah, Michael Tsapatsis, and J. Ilja Siepmann**



Abstract: *Raw natural gas is a complex mixture comprising methane, ethane, other hydrocarbons, hydrogen sulfide, carbon dioxide, nitrogen, and water. For sour gas fields, selective and energy-efficient removal of H_2S is one of the crucial challenges facing the natural-gas industry. Separation using nanoporous materials, such as zeolites, can be an alternative to energy-intensive amine-based absorption processes. Herein, the adsorption of binary H_2S/CH_4 and H_2S/C_2H_6 mixtures in the all-silica forms of 386 zeolitic frameworks is investigated using Monte Carlo simulations. Adsorption of a five-component mixture is utilized to evaluate the performance of the 16 most promising materials under close-to-real conditions. It is found that depending on the fractions of CH_4, C_2H_6, and CO_2, different sorbents allow for optimal H_2S removal and hydrocarbon recovery.*

In recent years, discovery of shale gas and advancement in fracking technologies have led to a large increase in the North American natural gas production. However, even today, a significant fraction of the global gas reserves continues to remain untapped, and this is due to the sour nature of these reservoirs with H_2S concentrations high enough to deem the conventional amine-based absorptive separation followed by a Claus process as uneconomical.[1] Finding innovative and cost-effective solutions for sour-gas sweetening can have far-reaching environmental and economic implications. While there are several adsorbent materials available for H_2S removal under dilute conditions, the SPREX process[2] using cryogenic distillation is, at present, the only alternative to amines for bulk H_2S removal. For adsorptive separations, one of the main challenges for selective H_2S removal from sour gas is the presence of H_2O vapor because H_2O, with its higher dipole, has a higher affinity for strong adsorption sites. Selectivity can be achieved through a chemical reaction, but this leads to an inherently energy-intensive separation.[3–5] Siliceous zeolites (high Si/Al ratio) containing only minute quantities of polar cations and silanol defects are very hydrophobic,[6] and offer an opportunity to selectively capture H_2S from moist natural gas.[7–9]

In silico discovery of optimal porous materials for gas storage, separations, and catalysis has added a new scientific dimension by not only accelerating materials screening, but by also providing molecular insights for the rational design of such materials.[10–14] This approach becomes especially important for systems involving very hazardous chemicals, such as H_2S, where the costs and risks associated with experimental measurements for even a small number of materials are quite high. Advances in efficient Monte Carlo algorithms[15,16] and accurate force fields[17,18] have enabled predictive modeling of phase and sorption equilibria. Our goal herein is to assess zeolite-based adsorptive processes for sweetening of sour gas mixtures by a computational screening (see Supporting Information, for a detailed description) of all the 386 electrically neutral structures found in the IZA-SC database.[19]

Natural gas obtained at the well head varies considerably in composition, temperature, and pressure depending on the geographical location.[20] Sour gas mixtures may contain not only CH_4, H_2S, and CO_2, but also ethane (C_2H_6) and other light alkanes that are even more valuable as fuel and chemical feedstocks.[21] Previously, we have shown that depending upon the strengths of the sorbate–sorbate and sorbate–sorbent interactions, the H_2S/CH_4 selectivity, S_M, changes differently with feed composition for different frameworks.[9] Accordingly, herein, we evaluate performance at three different H_2S mole fractions in the feed ($y_F = 0.10$, 0.30, and 0.50) for binary H_2S/CH_4 and H_2S/C_2H_6 mixtures. This relatively large composition range reflects that the treatment may involve a multi-stage adsorption unit, and may also be applicable to ultra-sour natural-gas mixtures. We focus discussion on performance at $T = 343$ K and $p = 50$ bar, but we also carry out simulations at 298 K and 10 bar and find a very good correlation between the data at different state points (see Supporting Information).

Figure 1 shows binary H_2S/CH_4 and H_2S/C_2H_6 adsorption data for all the structures investigated in this work. We define the performance metric, P_{H_2S}, as the product of H_2S loading, Q_{H_2S}, and the logarithm of selectivity toward H_2S versus CH_4 or C_2H_6, $\ln S_M$ or $\ln S_E$. P_{H_2S} is intrinsic to the properties of a sorbent and is independent of any specific process design. We also define another performance metric which involves modeling of a breakthrough column, and y_F here refers to the inlet condition at the column. Estimates are made for the number of stages and the total mass of a particular zeolite framework, M_{zeo}, required to adsorb 10 mmol H_2S at ≥ 90 mol % in the sorbent ($x_T \geq 0.90$).

The number of structures with $S_M \geq 10$ is significantly higher than those yielding $S_E \geq 10$. The critical temperatures of CH_4 and C_2H_6 are 0.51 and 0.82 times that of H_2S, respectively; thus, enthalpic contributions play a smaller role for S_E than for S_M. Moreover, P_{H_2S} generally increases from $y_F = 0.10$ to 0.50 because a higher fugacity of H_2S yields a higher Q_{H_2S}, and this enhances sorbate–sorbate interactions contributing to increased selectivity.[9] Nonetheless, the correlation between P_{H_2S} at low and high y_F is quite good for both H_2S/CH_4 and H_2S/C_2H_6 binary systems (see Supporting Information).

For a multi-stage adsorption process, the number of stages significantly impacts the operating as well as capital expenditure. Shown also in Figure 1 are data for those zeolites that can achieve x_T in at most two adsorption stages. For the H_2S/CH_4 mixture at $y_F = 0.50$, 222 zeolites can accomplish this task in a single stage, and another 148 require only two stages. For the H_2S/C_2H_6 mixture, these numbers are 84 and 36, respectively. The better performing zeolite structures for H_2S/C_2H_6 separation range from ones that perform very well to relatively poor for the H_2S/CH_4 mixture. Once again, the

[*] M. S. Shah, Prof. M. Tsapatsis
Department of Chemical Engineering and Materials Science
University of Minnesota
421 Washington Avenue SE, Minneapolis, MN 55455-0132 (USA)
Prof. J. I. Siepmann
Department of Chemistry and Chemical Theory Center
University of Minnesota
207 Pleasant Street SE, Minneapolis, MN 55455-0431 (USA)
E-mail: siepmann@umn.edu
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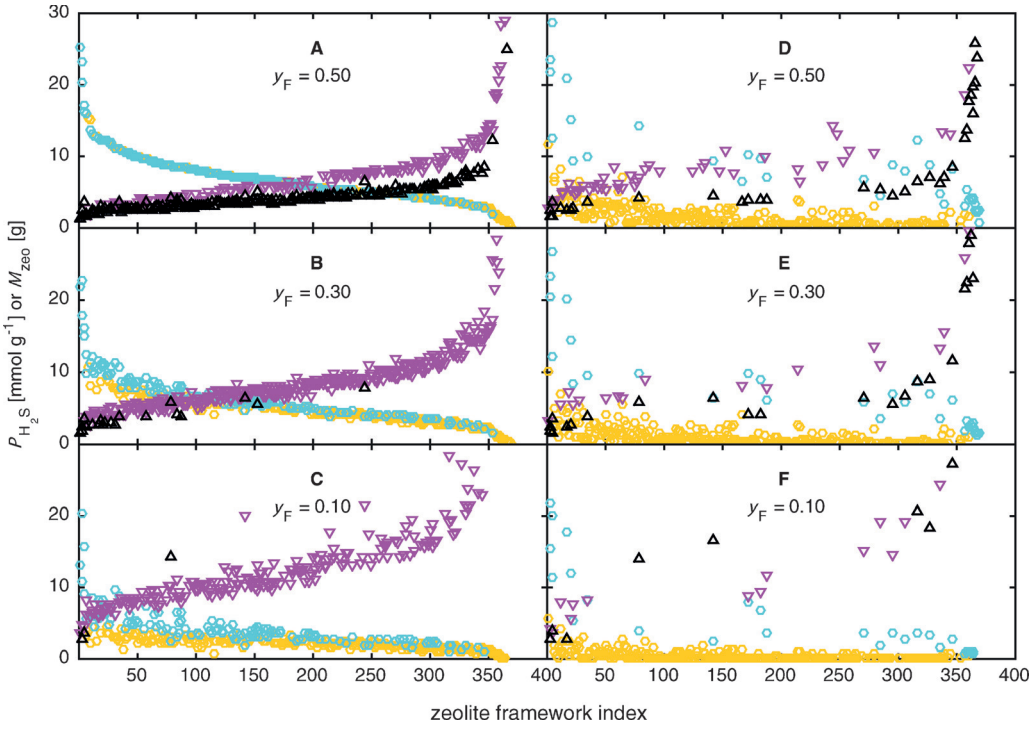

Figure 1. Binary H_2S/CH_4 (**A**,**B**,**C**) and H_2S/C_2H_6 (**D**,**E**,**F**) adsorption at different feed concentrations of H_2S: $y_F = 0.50$ (**A**,**D**), 0.30 (**B**,**E**), and 0.10 (**C**,**F**) at $T = 343$ K and $p = 50$ bar. Circles represent P_{H_2S} values, and the zeolite frameworks are ordered by P_{H_2S} at $y_F = 0.50$ in a mixture with CH_4. Cyan circles show data points with $S \geq 10$ and yellow circles show data points with $S < 10$. Black up triangles show M_{zeo} for structures that can achieve x_T in one stage, magenta down triangles show M_{zeo} for structures that can achieve x_T in two stages.

number of zeolites that can reach x_T drops significantly at lower feed compositions. This is due to a decrease in S at lower y_F, as well as an increase in the enrichment required to achieve the same target from lower y_F.

An adsorbent can have several attributes and depending on the application, one attribute may be more important than the other. For instance, for gas-storage applications, the capacity of the adsorbent is a major factor determining the best adsorbent, but for separation applications, selectivity towards the molecule of interest is more critical as long as a reasonable capacity is reached. In Figure 2, we show the performance of the top 62 adsorbents selected for $S_M \geq 15$ (44 sorbents) or $S_E \geq 10$ (29 sorbents). There are 11 structures that satisfy both criteria: AHT-1, APC-1, AWO-0, ACO-0, APC-2, GIS-1, APD-0, DFT-0, APC-0, SBN-0, JNT-0 (here, XYZ-0 represents a framework in its idealized all-silica form and energy-optimized to avoid an unreasonably high-energy structure, while XYZ-*i* ($i = 1$–6) correspond to the experimental structures[19] that are taken as is but placing Si at all tetrahedral sites.) Also shown are data for the partial molar adsorption enthalpies of H_2S in the mixture with CH_4, ΔH_{ads}, that vary widely between 23–46 kJ mol^{-1}. Although DOH-1 and MTN-1 yield only moderate S_M, these frameworks have very low $|\Delta H_{ads}|$. In contrast, AHT-1 and APC-1 possess a very high S_M and S_E but also show high $|\Delta H_{ads}|$. This suggests that beyond high selectivity and reasonable Q_{H_2S}, sorbent selection can gain robustness by also including the regeneration costs contingent on ΔH_{ads}.

For the H_2S/CH_4 separation, S_M values of top-performing frameworks fall below 60 with the exception of AHT-1 and APC-1 with $S_M > 300$. These two structures are found experimentally as hydrated aluminophosphates, and solvent removal for this study resulted in very favorable pockets for H_2S adsorption (as indicated by the high $|\Delta H_{ads}|$). However, APC-0 and APC-2, which is a dehydrated experimental structure, also belong to the set of top structures from this screening study. It should be noted that the loading for APC-1, APC-2, and APC-0 are 4.0, 2.3, and 2.1 mmol g^{-1}, respectively, suggesting partial framework shrinkage on dehydration. For the top-performing experimentally hydrated structures (AHT-1, APC-1, LTL-2, EPI-1, GIS-5, GIS-1, PHI-1, VFI-1, LTL-1, PAU-1, PHI-2, GIS-2, EDI-1), our inference is that these will indeed be good structures for sour-gas sweetening if their energy-minimized analogues also offer similar P_{H_2S} and M_{zeo}, that is, it is the physical framework that enhances separation, rather than favorable pockets formed by water removal.

A large fraction of the high-performing structures contain periodic building units that can be constructed from either a zigzag chain, a saw chain, or a crankshaft chain.[19] For H_2S/CH_4 separation, about 75% of the top selectivity structures contain a crankshaft chain and, conversely, about 60% of all frameworks having a crankshaft chain yield $S_M \geq 15$. These selective structures allow for Q_{H_2S} between 1.5–6.5 mmol g^{-1}. Most structures with $S_M < 15$ but $S_E \geq 40$ contain either a zigzag or a saw channel, but exhibit a relatively lower Q_{H_2S} of 0.5–2.5 mmol g^{-1}. Most of the top-performing structures (APC, AWO, ACO, GIS, APD, DFT, SBN, JNT) contain eight-membered rings as the limiting pore diameter. While treating the zeolite as rigid is a good assumption in most cases, framework flexibility is likely to influence the dynamic accessibility for molecules with dimensions comparable to the limiting pore diameter.[22] A concerted response involving the local zeolite structure and the sorbate conformation may play a role in adsorption kinetics and accessibility of selective adsorption sites.

From the set of 62 top structures shown in Figure 2, we select 16 structures to probe their performance for a five-

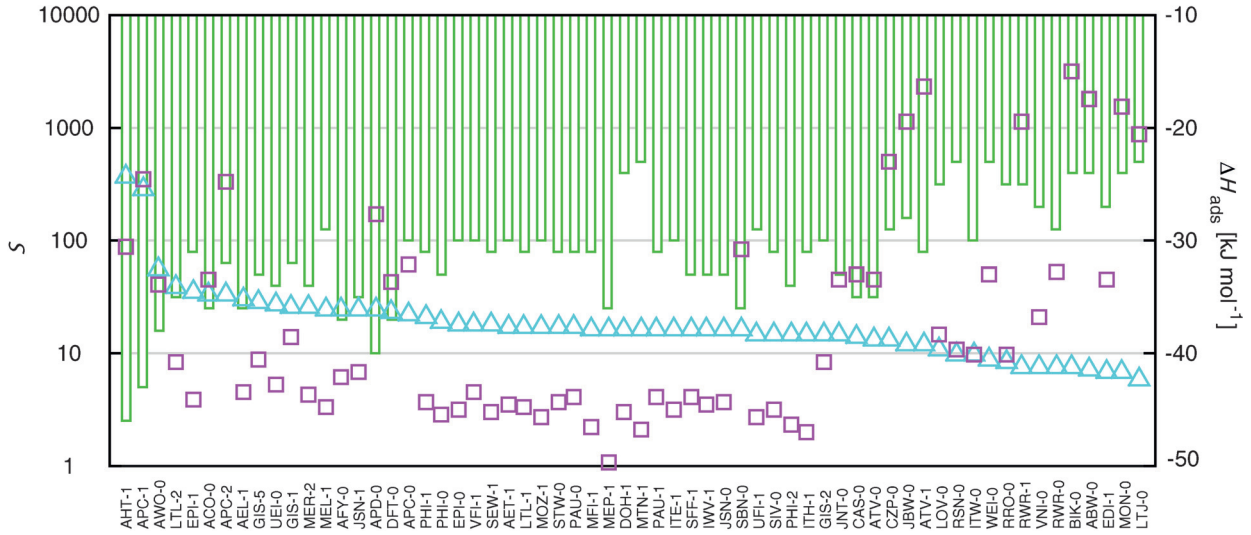

Figure 2. Selectivity (left axis) and ΔH_{ads} (right axis) in top-performing zeolite structures at $y_F = 0.50$, $T = 343$ K, and $p = 50$ bar. S_M cyan triangles, S_E magenta squares, and ΔH_{ads} (for the H_2S/CH_4 mixture) green bars.

component mixture involving H_2S, CO_2, CH_4, C_2H_6, and N_2 in a 25:10:50:10:5 mole ratio (see Figure 3). The equilibrium composition attained in such a (virtual) system depends on the initial feed composition and the mole (or weight) ratio of zeolite sorbent contacted with the gas mixture (see Supporting Information for details). A larger amount of sorbent would further reduce the mole fraction of H_2S in the gas phase at the expense of decreased hydrocarbon recovery. Additionally, we also investigate a four-component mixture (H_2S:CO_2:CH_4:C_2H_6 with a molar ratio of 16:10:70:4, see Figure S3 in the Supporting Information) representative of the Lacq gas,[23] that has a H_2S:CH_4 ratio more than two-times smaller than the five-component mixture. We find that S_M and S_E values are very similar for the binary and four- and five-component mixtures (see Figure S4); this indicates that binary mixtures can be used for screening purposes. Ranking the performance of zeolite structures by the ratio of the percentage of H_2S removed over the percentage of carbon lost due to adsorption yields a very high correlation for these complex four- and five-component mixtures ($R^2 = 0.98$, see Figure S5). The AHT-1 and APC-1 structures with their very high S_M and high S_E values adsorb the least amount of hydrocarbons. However, these structures differ in H_2S/CO_2 selectivity resulting in APC-1 removing more H_2S but less CO_2. This is further accentuated by comparing AWO-0 and BIK-0; AWO-0 is very selective for H_2S over CO_2 and yields the highest x_{H_2S}, whereas BIK-0 is very selective for CO_2 and adsorbs the least combined amount of these acid gases so that it does not significantly lower the H_2S concentration in the gas mixture.

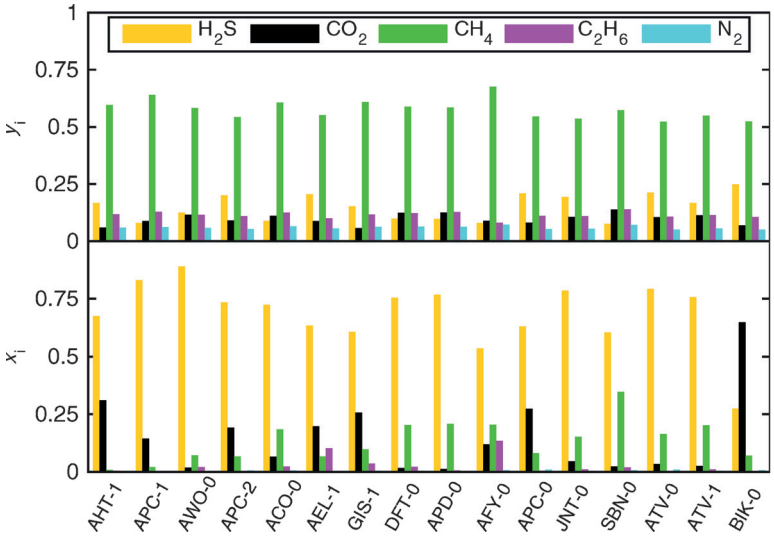

Figure 3. Five-component adsorption at $T = 343$ K and $p = 50$ bar using a H_2S:CO_2:CH_4:C_2H_6:N_2 feed composition with molar ratio of 25:10:50:10:5. Equilibrium mole fractions in the gas phase (top) and in the adsorbed phase (bottom) for 16 high-performing zeolite structures.

Of all the top-performing structures presented in Figure 2, CAS, DOH, ITE, ITH, ITW, MEL, MEP, MFI, MTN, RRO, RWR, and SFF frameworks have been synthesized in all-silica form, IWV with a Si/Al ratio of 29, SEW with a Si/B ratio of 13, and ABW, BIK, EDI, EPI, GIS, JBW, LTJ, LTL, MER, MON, MOZ, PAU, PHI, and UFI with a low to moderate Si/Al ratio[19] and their high-silica defect-free analogues can be interesting synthesis targets for the sour-gas sweetening application. Selecting from the already-synthesized zeolites, MEL and RWR are the best candidates for gas feeds lean and rich, respectively, in ethane and other light alkanes.

In conclusion, we identified zeolitic sorbents that can enable selective removal of H_2S from CH_4 and C_2H_6. A good correlation is found for the performance of these zeolites when applied to four- and five-component mixtures representing highly sour and ultra-sour gas reservoirs. However, the choice of optimal sorbent for sour-gas sweetening will

depend on the relative importance of CO_2 removal and the desire to reduce losses of C_2H_6 and other light alkanes. This computational study shows promise for (ultra) highly sour natural-gas sweeting with hydrophobic zeolites and opens avenues for experimental studies and process optimization.

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Keywords: hydrogen sulfide · Monte Carlo simulations · natural gas · zeolite

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