

Adsorption of H₂S from Hydrocarbon Gas Using Doped Bentonite: A Molecular Simulation Study

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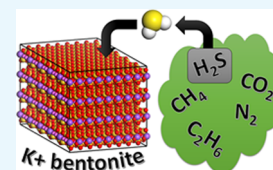


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ABSTRACT: Hydrogen sulfide is a commonly occurring impurity in hydrocarbon gases such as natural gas or landfill gas. Apart from its toxicity, H₂S can cause problems in downstream processing because of corrosion of piping in the presence of moisture. Removing this contaminant using a cost-effective and energy-efficient technique such as adsorption using commonly occurring adsorbents would be beneficial both for processing and refinement of hydrocarbon gases and for their use as an energy source. In this work, grand canonical Monte Carlo simulations were performed using an ab initio forcefield to predict adsorption isotherms for methane, hydrogen sulfide, and nitrogen in bentonite doped with K⁺, Li⁺, and Na⁺ cations with a view to aiding the development of low-cost pressure-swing adsorption systems for the targeted removal of H₂S from landfill gas or natural gas. Pure species simulations were done, in addition to considering mixtures at conditions approximating real-world natural gas fields. Highly selective targeted adsorption of hydrogen sulfide was achieved for all three doped bentonites, with the adsorbed phase consisting of almost pure H₂S, although the volume of gas adsorbed differed between adsorbents. The results suggest the following ranking for the three doped bentonite adsorbents in terms of their overall performance: K⁺ > Li⁺ > Na⁺. By considering both the composition of the adsorbed phase and the total quantity of adsorbed gas, there may be an interplay between the gas–gas and gas–solid interactions that becomes somewhat noticeable at low pressures.



1. INTRODUCTION

Natural or other gases containing significant quantities of hydrogen sulfide as an impurity are described as being “sour” gases, whereas gases that contain acidic gases such as carbon dioxide or hydrogen sulfide are described as “acid” gases. Hydrogen sulfide is especially problematic as it not only toxic, but in the presence of water, it can damage piping via sulfide stress cracking. This can of course add to maintenance costs in downstream processing or refinement of natural or landfill gas. Moreover, in cases where hydrocarbon gas is to be used as a fuel, it is undesirable for it to contain large quantities of sulfurous impurities.

Natural gas deposits naturally contain some hydrogen sulfide, with some wells producing gas with over 10 percent H₂S content.¹ Coal and biomass gasification to produce syngas also typically produces gases with substantial hydrogen sulfide content by way of sulfur content conversion. Treatment of syngas, natural gas, and landfill gas to remove hydrogen sulfide in particular is important for downstream processing, and this is typically achieved using either absorption, adsorption, cryogenic distillation, or membrane processes. The well-known amine and Claus processes are commonly used to sweeten sour gases in refineries, natural gas processing plants, or in gasification or syngas plants.

In terms of adsorption as an H₂S removal process, the solid adsorbent should be highly selective and have a high capacity in terms of the quantity of gas adsorbed per unit mass of the adsorbent.² In addition, the adsorbent should be stable under extreme acid gas environments so that it has a longer lifespan and thus reduce running costs. Metal oxides have been widely

used for removing sulfur from coal gas, syngas, and hydrogen fuel cell gas.³ For instance, doping zinc oxide with copper to enhance adsorption capacity has been studied previously.⁴

Although not directly important for separation processes, but relying on the same principles of adsorption, is the use of doped materials for the detection of noxious gases such as SO₂ and H₂S. In this case, adsorption on monolayer materials can be enhanced or modified through doping using specific metals such as Rh,⁵ Ni,^{6,7} or Pd.⁸ The inclusion of specific ions in these cases can lead to highly selective adsorption and hence yield targeted electrical responses for the detection of specific gas species. In both the present study and the aforementioned work on monolayer adsorbents, the underlying mechanisms are similar, as the cations can produce localized effects on the adsorption surface and thus alter the suitability of adsorption sites with respect to nonbonded interactions with specific gas molecules.

Metal–organic frameworks are highly tunable materials that can be designed to target specific molecules for adsorption.⁹ A drawback for scenarios where volumetric economy is important is that they can be undesirable for the purposes of gas sweetening, such as in offshore gas exploitation.² Moreover, metal–organic frameworks are damaged at the conditions

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necessary for practical use, thus shortening their lifespan in an industrial setting.¹⁰

Zeolites are microporous crystalline aluminosilicate minerals that can accommodate cations such as Na⁺, K⁺, Ca⁺, and so on, and have a large variety of geometries and therefore a wide array of excellent sieving properties. A drawback of zeolites is that many natural gas fields contain CO₂, CO, and H₂O as impurities, which often compete with and may supersede H₂S adsorption into the solid.¹¹

Zeolitic imidazolate frameworks are a subclass of metal–organic frameworks consisting of silicon and aluminum atoms arranged according to a zeolite topology with organic linkers. They are a relatively new material that combine the best aspects of both metal–organic frameworks and zeolites: structural variability and stability.¹² Work on these materials is ongoing, and more work may be needed with regard to regeneration of the adsorbent in an industrial setting.²

This study focusses on adsorption as a sweetening and carbon dioxide removal method, and in particular, the use of bentonite doped with various cations is examined using Monte Carlo molecular simulation¹³ in the grand canonical ensemble.¹⁴ In terms of stability, bentonites may be resilient up to 900 °C, while exposure to highly acidic environments can increase the specific surface area but may reduce the temperature up to which the material remains stable.¹⁵ Recent work has focussed extensively on using bentonite to treat industrial wastewater,^{16–18} and some researchers have examined the use of bentonite to separate O₂/N₂ mixtures in the context of carbon molecular sieves,¹⁹ while others have studied its use to desulfurize oil.²⁰ The use of bentonite modified by the inclusion of copper and iron has also been studied within the context of mercaptan and hydrogen sulfide removal from industrial gas streams, for which it was found that bentonite was highly selective toward H₂S removal but was impeded by having a low total adsorption capacity.²¹

Adsorption of a natural gas mixture containing both CO₂ and H₂S onto bentonite doped with Li⁺, K⁺, and Na⁺ is considered in this study both by examining the adsorption isotherms of the pure species comprising the gas and adsorption of the gas mixture at both low and high pressures. The gas composition of interest to this study approximates real natural gas fields:^{22–24} 65 mol % methane, 15 mol % nitrogen, 10 mol % ethane, 5 mol % carbon dioxide, and the remainder hydrogen sulfide. Appropriate thermodynamic conditions are 343 K and 2000 kPa, with adsorption of the gas mixture also being considered at roughly ambient conditions (i.e., 100 kPa) for the purposes of understanding the behavior of the bentonite + gas system in a pressure swing adsorption apparatus.

A practical application of this study can be to aid in the development of a pressure-swing adsorption system along the lines of the aforementioned work on removing mercaptan and hydrogen sulfide from industrial gases using bentonite.²¹ Bentonite is a readily available adsorbent in some regions, and thus, such work may be useful for sweetening hydrocarbon gases such as natural gas or landfill gas. Older work on bentonite constituents found that upon saturation with small cations such as Li⁺, the material does not swell when exposed to moisture;²⁵ under stresses such as elevated temperatures, swelling can generally degrade materials structurally, thereby reducing the lifespan of the material in an industrial setting. Hence, this study focussed on the inclusion of Li⁺, Na⁺, and K⁺ in the bentonite lattice.

2. RESULTS AND DISCUSSION

2.1. Pure Species Adsorption Isotherms. Figure 1 shows the results of the molecular simulations for all pure species in the

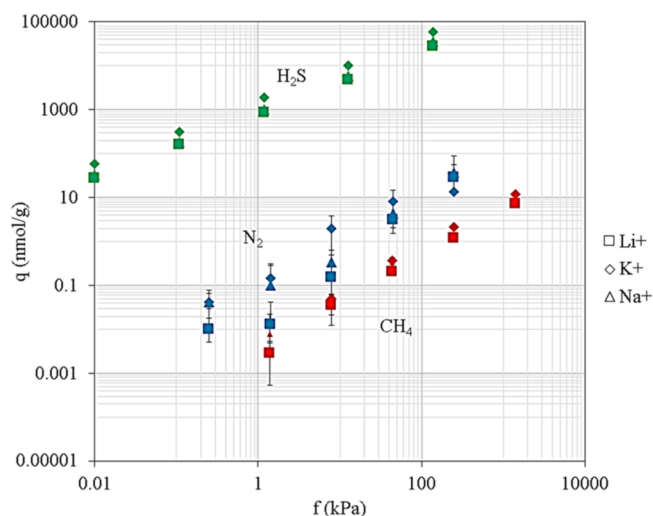


Figure 1. Adsorption isotherms at 343 K for all of the species of interest in this study. The quantity of gas adsorbed into the solid is q , and f is the gas fugacity. Both axes have been made logarithmic for clarity. Note that the absolute adsorption is shown.

three doped bentonite structures. Results are presented in terms of gas fugacity, which was estimated using the Peng–Robinson cubic equation of state.²⁶ Note that while the gas consists of methane, ethane, carbon dioxide, nitrogen, and hydrogen sulfide, only methane, hydrogen sulfide, and nitrogen actually adsorbed into the nanoporous bentonite crystal. It is apparent that hydrogen sulfide has a stronger affinity for all of the bentonite than either nitrogen or methane, by at least two orders of magnitude in terms of the quantity of adsorbed gas. This feature, coupled with the absence of carbon dioxide in the adsorbed phase suggests that doped bentonite may be suitable for sweetening sour gas but will not remove carbon dioxide, and hence, bentonite-based adsorption should be coupled with further processing in order to remove both of these undesirable constituents.

In terms of adsorption behavior, a good fit to the Freundlich adsorption isotherm model²⁷ was obtained for all systems, with a correlation coefficient of no less than 0.9277 in all cases. These results were obtained via least-squares fitting to the linearized form of the Freundlich model by considering $\log_{10}(q)$ as a function of $\log_{10}(P)$, where q is the quantity of gas adsorbed and P is the gas pressure. The Freundlich equation itself is given by

$$q = KP^{1/n} \quad (1)$$

where K and n are empirical parameters describing the adsorption capacity and the pressure-dependence, respectively. In this study, q was considered in terms of nmol/g and P was in kPa, and thus, K was in nmol/g kPa. The parameter n is in any case dimensionless. The close correlation between this simple adsorption isotherm model and the results shown in Figure 1 suggest that there may be a nonuniform distribution of adsorption heats and affinities over the heterogeneous adsorption surface.²⁸ Although it can be noted that the Freundlich model lacks a fundamental thermodynamic basis,²⁹ fitting according to the Langmuir adsorption isotherm model³⁰

yielded nonsensical parameters in some cases (such as a negative adsorption capacity for the case of methane + Li-doped bentonite), and so, there is strong evidence that the uniform adsorption surface of the Langmuir model is not present in the systems under consideration. Fitted adsorption isotherm parameters K and n are presented in Table 1, along with a

Table 1. Fitted Freundlich Adsorption Isotherm Model Parameters K and n , and the Correlation Coefficient ρ Associated with the Fit for H_2S , CH_4 , and N_2 in Bentonite Doped with Different Cations^a

		cations		
		K^+	Li^+	Na^+
H_2S	K	1.542×10^3	7.318×10^2	8.707×10^2
	n	1.419	1.425	1.410
	ρ	1.000	0.9998	0.9998
CH_4	K	8.179×10^{-3}	2.683×10^{-3}	6.295×10^{-3}
	N	1.037	0.9380	1.055
	ρ	1.000	1.000	0.9996
N_2	K	1.542×10^{-1}	2.027×10^{-2}	8.923×10^{-2}
	N	1.148	0.8386	1.038
	ρ	0.9277	0.9998	0.9976

^aNote that K and n are the parameters in eq 1, for which q is in nmol/g and P is in kPa, and hence, K is in nmol/g kPa and n is dimensionless.

measure of the quality of the fit (the correlation coefficient ρ), which was calculated as follows

$$\rho = \frac{\sum [(q_{\text{model}} - \bar{q}_{\text{model}})(q_{\text{sim}} - \bar{q}_{\text{sim}})]}{\sqrt{\sum (q_{\text{model}} - \bar{q}_{\text{model}})^2 \sum (q_{\text{sim}} - \bar{q}_{\text{sim}})^2}} \quad (2)$$

where q is the quantity of gas adsorbed onto the solid, the overbar represents the arithmetic mean, and the subscripts “model” and “sim” represent the fitted Freundlich model and the results of the simulations, respectively. The correlation coefficient is dimensionless, provided dimensional consistency is preserved for all values of q in this equation.

For each gas species, differences in adsorption behavior for each doped bentonite may be related to combination of steric effects because of the sizes of the different cations (and the associated effects on the geometry of the adsorption surface), and the dispersive interactions between the cation-doped surfaces and the gas molecules. For each system, an additional simulation at fixed loading of 1 gas molecule was undertaken (see Section 4 for details on methodology). The mean (μ) and standard deviation (σ) of the van der Waals energy component of the energy of the system are shown in Table 2. For all gases, there are more attractive gas–solid interactions with bentonite doped with K^+ than with the other cations, with second most attractive interactions being with Na-doped bentonite in all cases. This trend is positively correlated with the molar mass of the cation, with approximate decreases in the dispersive van der Waals energy of 0.06, 0.05, and 0.04 kJ/mol per g/mol molar mass of the cation for H_2S , CH_4 , and N_2 , respectively.

A single factor analysis of variance was undertaken for each gas species to determine whether there were differences between the van der Waals energy of the simulation cell for the case of one gas molecule in each solid lattice. For each gas, this approach detected a statistically significant difference between the solids: $p_{\text{H}_2\text{S}} = 1.47 \times 10^{-7}$, $p_{\text{CH}_4} = 0.000$, and $p_{\text{N}_2} = 0.000$. Hence, even

Table 2. Values of the van der Waals Energy of the Simulation Cell for 1 Gas Molecule Adsorbed Into Each Cation-Doped Bentonite^a

		cations		
		K^+	Li^+	Na^+
H_2S	μ_{vdW} (kJ/mol)	−25.17	−23.22	−24.04
	σ_{vdW} (kJ/mol)	7.01	7.15	6.46
CH_4	μ_{vdW} (kJ/mol)	−10.45	−8.83	−9.16
	σ_{vdW} (kJ/mol)	2.92	3.01	2.86
N_2	μ_{vdW} (kJ/mol)	−21.89	−20.67	−21.00
	σ_{vdW} (kJ/mol)	0.51	0.48	0.47

^aThe mean (μ) and standard deviation (σ) are shown.

though in all cases the vast majority of potential gas–solid interaction sites remained the same regardless of which cation was included in the bentonite lattice, this key atom resulted in an effectively different solid from the point of view of intermolecular adsorbate–adsorbent interactions.

2.2. Sour Gas Adsorption. Because of the lack of adsorption of carbon dioxide in any of the doped bentonite structures, only sour gas sweetening (i.e., the removal of hydrogen sulfide from hydrocarbon gas mixtures) can be considered. To that end, adsorption of a mixture consisting of 65 mol % methane, 15 mol % nitrogen, 10 mol % ethane, 5 mol % carbon dioxide, and hydrogen sulfide at 343 K was considered at both gas field pressure (2000 kPa) and ambient pressure (100 kPa). For this investigation, the mole fraction of each species in the gas phase (y) was compared with its mole fraction in the adsorbed phase (x), which was calculated using the amount of each species adsorbed into the solid lattice q

$$x_i = \frac{q_i}{\sum_j q_j} \quad (3)$$

These results are shown in Tables 3 and 4, for 2000 and 100 kPa total pressure, respectively.

For all of the doped bentonites it is apparent that H_2S has a high affinity for the adsorbed phase as opposed to the gas phase, with $x_{\text{H}_2\text{S}}$ (see eq 3 for clarity) being approximately unity for all solids and both pressures. However, the mole fraction of hydrogen sulfide in the adsorbed phase in Na^+ bentonite may be slightly lower than for the other solids, although still well within the standard deviation. To examine differences between the adsorbents in greater detail, a pairwise single factor analysis of variance was undertaken for all three solids to determine if there were differences in terms of both $x_{\text{H}_2\text{S}}$ and $q_{\text{H}_2\text{S}}$. Figure 1 shows that there may be a ranking of the doped bentonite adsorbents in terms of hydrogen sulfide adsorption ($\text{K}^+ > \text{Li}^+ > \text{Na}^+$) and so it can be expected that for the gas mixtures, an analysis of variance may of course detect differences. The analysis of variance results is presented in Table 5.

The results presented in Table 5 demonstrate that there are no statistically significant differences in terms of the composition of the adsorbed phase at any conditions considered in this study. In terms of the amount of gas adsorbed, there were statistically significant differences except for the case of Li^+/Na^+ at 100 kPa, where there was no statistically significant difference at the 1% significance level (since in this case $p = 0.0102 > 0.01$). This observation, taken in conjunction with the pure species adsorption isotherms shown in Figure 1, suggests an interplay between the gas–gas and gas–solid interactions that becomes somewhat noticeable only at low pressures, although the

Table 3. Composition (in mole Fractions) of a Natural Gas Blend and the Adsorbed Gas Phase in Three Different Cation-Doped Bentonite Structures at 343 K and 2000 kPa

Species	gas phase	adsorbed phase		
		Li ⁺ bentonite	K ⁺ bentonite	Na ⁺ bentonite
CH ₄	0.65	1.778 ± 0.516 × 10 ⁻⁴	1.244 ± 0.272 × 10 ⁻⁴	1.496 ± 0.266 × 10 ⁻⁴
C ₂ H ₆	0.10	0.0	0.0	0.0
CO ₂	0.05	0.0	0.0	0.0
H ₂ S	0.05	9.998 ± 0.959 × 10 ⁻¹	9.999 ± 0.815 × 10 ⁻¹	9.979 ± 0.571 × 10 ⁻¹
N ₂	0.15	0.0	0.0	0.0

Table 4. Composition of a Natural Gas Blend and the Adsorbed Gas Phase in Three Different Cation-Doped Bentonite Structures at 343 K and 100 kPa

Species	gas phase	adsorbed phase		
		Li ⁺ bentonite	K ⁺ bentonite	Na ⁺ bentonite
CH ₄	0.65	1.133 ± 0.416 × 10 ⁻⁴	1.046 ± 0.533 × 10 ⁻⁴	1.842 ± 3.896 × 10 ⁻⁴
C ₂ H ₆	0.10	0.0	0.0	0.0
CO ₂	0.05	0.0	0.0	0.0
H ₂ S	0.05	9.999 ± 1.955 × 10 ⁻¹	9.999 ± 1.040 × 10 ⁻¹	9.973 ± 1.296 × 10 ⁻¹
N ₂	0.15	0.0	0.0	8.442 ± 18.88 × 10 ⁻³

Table 5. Analysis of Variance Results for Comparison of Adsorbent Performance in Removing Hydrogen Sulfide from a Gas Mixture in Terms of the Mole fraction of H₂S in the Adsorbed Phase (x_{H_2S}) and the Amount of Hydrogen Sulfide Adsorbed (q_{H_2S})

		P = 100 kPa		P = 2000 kPa	
		x_{H_2S}	q_{H_2S}	x_{H_2S}	q_{H_2S}
cations	K ⁺ /Li ⁺	p = 0.729	p = 1.40 × 10 ⁻⁵	p = 0.076	p = 1.071 × 10 ⁻⁶
	K ⁺ /Na ⁺	p = 0.168	p = 1.64 × 10 ⁻⁴	p = 0.149	p = 2.94 × 10 ⁻⁶
	Li ⁺ /Na ⁺	p = 0.169	p = 1.02 × 10 ⁻²	p = 0.159	p = 4.56 × 10 ⁻³

magnitude of this effect is rather small in absolute terms because $q_{H_2S}^{Li^+} = 2.473 \pm 0.484$ nmol/g and $q_{H_2S}^{Na^+} = 3.461 \pm 0.450$ nmol/g at 100 kPa.

In terms of overall performance, the results of both the pure species and mixture adsorption simulations suggest the following ranking for the three doped bentonite adsorbents: K⁺ > Li⁺ > Na⁺. This ranking may of course only hold over the pressure range of interest to this study, which covered a range from ambient pressure up to a higher value that mimicked natural gas fields. This constraint was in the interests of studying doped bentonite as a low cost adsorbent over a pressure range which would not require either an increase in pressure relative to the supply side (the natural gas field) or a decrease down to vacuum pressures, both of which would introduce additional energy costs. With regard to estimates of adsorbent requirements, the extreme high selectivity of all of the doped bentonites, a rough comparison in terms of performance can be undertaken by assuming that the adsorbed phase consists solely of adsorbent + H₂S. Using the Freundlich equation described by eq 1 together with the parameters presented in Table 1 in conjunction with a crude material balance at 2000 kPa (in which n is the number of moles, and W is the mass of adsorbent in g)

$$n_{H_2S}^{feed} = n_{H_2S}^{gas} + WKP^{1/n} \quad (4)$$

an approximation can be undertaken for discrete values of the adsorbent bed mass W . The degree of H₂S removal can then be estimated as

$$\% H_2S \text{ removal} = \frac{n_{H_2S}^{feed} - n_{H_2S}^{gas}}{n_{H_2S}^{feed}} \times 100 \% \quad (5)$$

To attain approximately 99% adsorption of H₂S would therefore require the following rough bed sizes (in kg/mol of feed gas) for Li⁺, K⁺, and Na⁺-doped bentonites, respectively: 2.7, 1.3, and 2.2. It may be noted that the extreme high affinity of H₂S to doped bentonite may result in highly segregated waste streams, such that potentially useful contaminants or impurities (such as carbon dioxide) may not require separation from a combined impurity stream. This observation is consistent with experimental measurements focussed on the removal of H₂S from refinery outlet gases using modified bentonite.²¹ Cement hydrate may be comparable in terms of the targeted removal of H₂S from natural gas and related hydrocarbon gas streams,^{31,32} but its production entails large carbon emissions, and so, bentonite may be a suitable alternative in potential sour gas sweetening processes.

3. CONCLUSIONS

Monte Carlo molecular simulations were performed in the grand canonical ensemble to predict adsorption of carbon dioxide, methane, ethane, hydrogen sulfide, and nitrogen on montmorillonite (the primary constituent of bentonite). These gas species are common to hydrocarbon gas streams such as landfill gas and natural gas. Adsorption isotherms were generated for pure species as well as a gas mixture comprising 65 mol % methane, 15 mol % nitrogen, 10 mol % ethane, 5 mol % carbon dioxide, and the remainder hydrogen sulfide, thereby emulating real natural gas fields. The conditions of interest for the gas mixture emulated real-world conditions in terms of temperature and pressure (i.e., 343 K and 2000 kPa), although additional simulations were performed at 100 kPa to assess performance

near ambient conditions for the purposes of designing potential pressure-swing adsorption systems.

In terms of overall performance, the results suggest the following ranking for the three doped bentonite adsorbents: $K^+ > Li^+ > Na^+$. There are no statistically significant differences in terms of the composition of the adsorbed phase at any conditions considered in this study, which consisted almost entirely H_2S . In terms of the amount of gas adsorbed, however, there were statistically significant differences except for the case of Li^+/Na^+ at 100 kPa, where there was no statistically significant difference at the 1% significance level. This suggests an interplay between the gas–gas and gas–solid interactions that becomes somewhat noticeable only at low pressures, although the magnitude of this effect is small in absolute terms.

This study demonstrated that bentonite doped with K^+ may be a viable adsorbent for the targeted removal of H_2S from hydrocarbon gas streams via pressure-swing adsorption. Specifically, this material may be used for the purification or sweetening of landfill gas or natural gas, although further work should be undertaken to assess its performance in an industrial setting and to analyze energy efficiency during the lifecycle of the system. In addition, any performance analysis should take be taken care to examine the degradation of the adsorbent over time under thermal stresses, which can inform the selection of operating conditions.

4. METHODOLOGY

4.1. Bentonite Structure. Bentonite is a clay mineral consisting predominantly of montmorillonite, which was employed as a proxy for bentonite in this study,³³ similar to recent studies that examined its use for wood gas upgrading³⁴ and humidity reduction.³⁵ A crystalline montmorillonite structure from the previous work concerning montmorillonite containing the Li^+ cation³⁶ was used as a basis for bentonite in this work (the postheat treatment structure was employed in this study to approximate a realistically modified adsorbent). In order to obtain bentonite with K^+ and Na^+ in this work, the Li^+ in the initial lattice was substituted. In the aforementioned literature, the two alkali cations considered were Li^+ and Cs^+ , for which it was observed that the lattice unit cells were approximately equal (the unit cell volumes were 0.565 nm^3 for Li^+ bentonite vs 0.564 nm^3 for Cs^+) following cation inclusion, which motivated for the use of a consistent lattice in this study.

The montmorillonite unit cell employed in this study is shown in Figure 2 for the case of the lattice containing the K^+ cation. The chemical formula of the unit cell is $O_{20}Mg_{0.28}Al_{1.72}Si_{7.80}X_{0.16}Fe_{0.20}$ (where X is the cation), and the lattice parameters are $a = 0.5171\text{ nm}$, $b = 0.8957\text{ nm}$, $c = 0.9740\text{ nm}$, $\alpha = \gamma = 90.0^\circ$, and $\beta = 96.1^\circ$. Note that this unit cell was repeated (as described in Section 4.2) to produce a sufficiently large simulation cell in order to obtain meaningful results.

4.2. Simulation Details. Monte Carlo simulations following the Metropolis algorithm³⁷ (as implemented in version 2018 of the computer program Materials Studio³⁸) were used to simulate adsorption of all gas species in the crystalline montmorillonite lattice. This simulation scheme is a stochastic process that generates a set of configurations sampled from a selected ensemble, which can then be used to estimate averages of equilibrium properties. In this case, the grand canonical ensemble was the appropriate thermodynamic ensemble, for which the temperature, the simulation cell volume, and the adsorbate chemical potential were held constant. In the grand canonical ensemble, the simulation box has a fixed volume, and

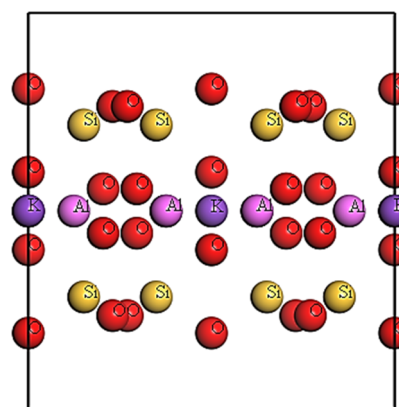


Figure 2. Ball model of the montmorillonite unit cell used in this work. Note the individually labelled atoms in the lattice. The Li^+ and Na^+ lattices were obtained by replacing K^+ with the aforementioned cations.

instead, the chemical potential of the fluid species is fixed, with particles being adsorbed/desorbed into/out of the simulation cell from an effectively infinite fluid reservoir. It can be noted that external equalization of pressure via a barostat is not needed for this thermodynamic ensemble. Conversion between the chemical potential and the pressure of the gas was undertaken using the Peng–Robinson cubic equation of state,²⁶ which is widely used in natural gas processing and is one of the leading two-constant cubic equations of state.³⁹ Random moves that mimic real-life behavior are applied to the system and are rejected or accepted on the basis of changes to the potential energy of the system. The details of the Metropolis scheme's approach to constructing Markov chains from which equilibrium properties are determined are described at length in the literature.⁴⁰ Moreover, recent work provides detailed discussions on the adsorption of methane in nanopores⁴¹ (describing both the excess and absolute adsorption for such systems) as well as morphology and its effects on physis- and chemisorption from the perspective of carbon dioxide and shale.⁴²

Following an equilibration period of 10^6 moves, 10^7 moves were used to generate results for each data point. For the pure species and mixture adsorption isotherms, the results were averaged arithmetically across five independent simulations, with the uncertainty being estimated as the standard deviation. The following moves were applied to the gas particles (with probabilities of occurrence in parentheses): creation (23%), deletion (23%), rotation (24%), translation (24%), and regrowth (6%). The first two moves mimic adsorption and desorption, respectively, while the remaining moves mimic thermal motion of the adsorbed molecules within the montmorillonite lattice. The atoms constituting the solid adsorbent were fixed in place because it is not a fluid material and serves as a rigid framework for the purposes of this work.

Figures 3–5 show the adsorption states for hydrogen sulfide at a fugacity of 50 kPa in montmorillonite doped with K^+ , Li^+ , and Na^+ , respectively. The gas adsorption sites are located primarily in narrow regions between oxygen atoms that lie on either side of the cavity and produce a narrow strip within the pore. The adsorption sites themselves are not completely identical of the probability of H_2S adsorption, although it is difficult to discern any regular pattern to the adsorption behavior. Hence, there may be some essentially random heterogeneity in terms of the distribution of the adsorption sites despite the ordered structure of the adsorbent.

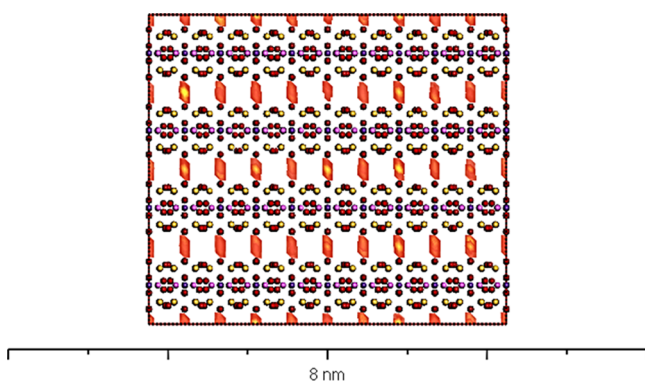


Figure 3. Adsorption state of hydrogen sulfide (density fields colored by intensity) in montmorillonite doped with K^+ (represented using a ball model). The colors of the atoms indicate the element: yellow = Si, red = O, pink = Al, purple = K.

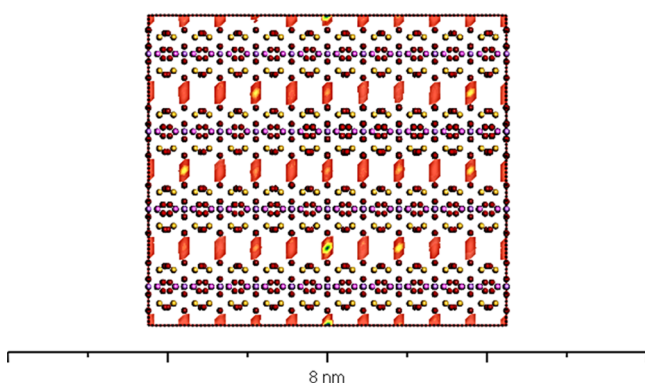


Figure 4. Adsorption state of hydrogen sulfide (density fields colored by intensity) in montmorillonite doped with Li^+ (represented using a ball model). The colors of the atoms indicate the element: yellow = Si, red = O, pink = Al, purple = Li.

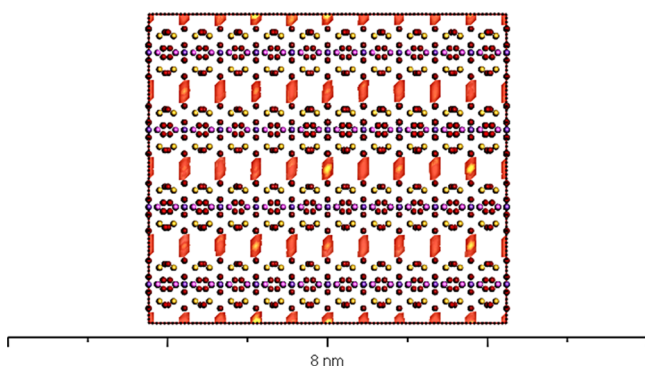


Figure 5. Adsorption state of hydrogen sulfide (density fields colored by intensity) in montmorillonite doped with Na^+ (represented using a ball model). The colors of the atoms indicate the element: yellow = Si, red = O, pink = Al, purple = Na.

All interactions were described using version 2.8 of the fully atomistic Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies (COMPASS) force field.⁴³ This set of interparticle potentials accounts for bonds, bond angles, dihedral angles, out-of-plane angles, van der Waals interactions, and electrostatic interactions. A cut-off radius of 1.85 nm with an analytical tail correction was used for the dispersive van der Waals interactions, and the Ewald summation technique was employed for the electrostatic interactions.⁴⁴ It may be noted

that this technique, while highly accurate, can consume up to 90% of the computational effort required for molecular simulations.⁴⁵ The van der Waals interactions were described using a 9–6 Lennard-Jones pair potential⁴⁶ in conjunction with the Waldman–Hagler⁴⁷ combining rules for unlike interactions. In order to avoid artificial periodicity errors,⁴⁸ the minimum length of each side of the simulation cell should be twice the cut-off radius. Hence, the simulation in all cases consisted of $8 \times 5 \times 4$ unit cells (i.e. 160 unit cells), yielding the following lattice parameters: $a = 4.3680$ nm, $b = 4.4785$ nm, $c = 3.8960$ nm, $\alpha = \gamma = 90.0^\circ$, and $\beta = 96.1^\circ$. The corresponding chemical formula of the lattice was $O_{3200}Mg_{44.80}Al_{275.20}Si_{1247.98}X_{25.60}Fe_{32}$, where X is the cation of interest.

Alternative force fields to COMPASS that are also fully atomistic include PCFF⁴⁹ and DREIDING.⁵⁰ Both COMPASS and PCFF are consistent force fields, although the latter is older, and recent work³² showed good agreement between experimental measurements and simulations with regard to adsorption of natural gas constituents (including H_2S) on cement hydrate, another silicate compound. Hence, COMPASS was seen as suitable for the purposes of this study.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.0c02934>.

Results of each molecular simulation run are included in the supporting information, along with the sampled results of the single adsorbate simulations (PDF)

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Notes

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