Hydrogen sulfide removal from biogas by zeolite adsorption. Part II. MD simulations

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A B S T R A C T

Coupled Grand Canonical-Canonical Monte Carlo and molecular dynamics (MD) simulation techniques have been used to investigate in details the adsorption of low-pressure hydrogen sulfide \( (H_2S) \) in zeolites, and the selective adsorption behavior towards carbon dioxide and methane, the main biogas constituents. Results from Monte Carlo (MC) simulations indicated, among many others, zeolite NaY as the best option for \( H_2S \) removal. Afterwards, deterministic simulations have been performed to investigate hydrogen sulfide pathway inside NaY, with respect to other adsorbed molecules (methane and carbon dioxide), as a function of zeolite loading and \( H_2S \) partial pressure (i.e., biogas composition). Thermodynamic evaluations for 2D molecular dynamic simulations in terms of binding energy evolution vs. time confirm and reinforce the results obtained from Monte Carlo simulations, testifying the greater affinity for \( H_2S \) on NaY zeolite framework. Results give also new quantitative insights in terms of pathways, binding energies, and equilibration time inside zeolite pores for stabilization.

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1. Introduction

Nowadays biogas production and utilization is increasing, as it represents a renewable energy [1,2]. Nevertheless, there is a lot of interest for \( H_2S \) removal from biogas mixtures, as even low \( H_2S \) concentrations in atmosphere are harmful [1,3]; in fact, its concentration has to be dramatically reduced to the lower toxic limit (i.e., at least 10 ppm [1]). Among the possible solutions, one is the use of adsorption processes via hydrophilic, ion-rich zeolites [4–7]. Zeolite materials are particularly suitable for adsorption removal processes [8,9], by virtue of their high selectivity and compatibility towards polar compounds, such as \( H_2S \) [7,8].

The choice of the proper zeolite and the best operating adsorptive conditions can be refined by the helpful tool of molecular simulation techniques [10–12]. Grand Canonical Monte Carlo (GCMC) simulation techniques, such as those used in our recent publication [13], may give the possibility to choose the proper zeolite, and to evaluate its performances in terms of adsorption isotherms, both for \( H_2S \) only, and for \( H_2S \) in its biogas mixture (e.g., \( H_2S \), carbon dioxide \( (CO_2) \) and methane \( (CH_4) \), essentially). With this aim, in our previous work [13] we have performed GCMC simulations at 298 K, with an increasing \( H_2S \) partial pressure \( (P_{(H_2S)}) \) from 10 to 1000 Pa and at total pressure of 1 atm for both situations, being these compositions realistic for a biogas produced, for instance, by anaerobic digestion processes [1].

In this work we investigate in deeper details the results stemming from our previous GCMC simulations [13], which allowed us to choose the FAU NaY zeolite \( (Si/Al = 2.5) \) as the best one between NaY, NaX \( (Si/Al = 1) \), dealumined MFI and LTA \( (Si/Al = 1) \), in terms of \( H_2S \) removal. From these simulations it was clear that, increasing \( P_{(H_2S)} \), there is a competition for adsorption sites between \( CH_4 \) and \( H_2S \) in polar zeolites (especially in NaY). This results in a reduction of \( CH_4 \) adsorption, while the \( CO_2 \) adsorbed quantity remains substantially unvaried. Our idea is to use molecular mechanics and dynamics simulations (MM/MD) to give more insights to the swapping phenomenon, investigating the behavior of already adsorbed molecules when the ensemble (NaY and adsorbed molecules) is perturbed by a new \( H_2S \) molecule which approaches the zeolite external surface. We simulated this dynamic, swapping-like behavior both for different biogas compositions inside zeolite framework, and for different zeolite loadings. We aimed at explaining and confirm the general trend arising from GCMC simulations from a thermodynamic and deterministic point of view.

2. Methods

All simulations have been carried out on an Intel bi-processor XEON 32bit workstation. We used Sorption, Forcite and DMol3
As can be seen, the best porous material for H2S removal is indeed zeolite NaY. The selectivity factor is defined as

\[ \frac{S_{ij}}{S_{H2S}} = \frac{x_i}{x_j} \times \frac{y_j}{y_i} \]  

where \(x_i, x_j\) are the molar fractions of species \(i\) and \(j\) adsorbed in the zeolite, while \(y_i\) and \(y_j\) are the molar fraction of species \(i\) and \(j\) in the gas phase.

In this paper our aim is to confirm and investigate in greater details these results by the use of MC/MD coupled techniques. Many studies have been performed about self or corrected diffusion [25,26], and about preferential pathways of small molecules in zeolite pores [22,27]. The application of these methods seems quite difficult for our complex systems, both in terms of equilibrium dynamics and computing times [28], as Kinetic Monte Carlo techniques have been often indicated as the techniques of election. Basing our simulation procedures on previous MD techniques for similar systems [21,19,22,23,25–28], we looked for a correlation between the evident, more favorable tendency of H2S to enter in NaY pores vs. the less favorable adsorption behavior exhibited by the other molecules, especially the less polar CH4.

To this purpose, we considered the behavior of an H2S molecule which is approaching the zeolite surface when the NaY cell is already filled with adsorbed molecules (H2S, CO2, CH4) at different loadings and at different \(P_{H2S}\). From previous MC adsorption isotherms calculations [13], we obtained the number of H2S molecules in the NaY pores using a group-based sum, while all other interactions are calculated using a Ewald sum.

Zeolite partial charges were assigned via the force field, while partial charges of molecules to be adsorbed have been taken from previous quantum-mechanics simulations (H2S), or assigned by the force field (CH4, CO2) [13]. From these simulations, we considered the lowest final energy frames for each system for further considerations.

The 3D periodic cubic cells (25.1 Å for each side) have then been transformed into 2D periodic cells with a (0 0 1) cut plane (normal to z-axis), and then a new H2S molecule has been inserted, as shown in Fig. 1. The molecule has been placed at the center of the cell length, at a distance of 2 Å from the NaY external surface. Although this is an arbitrary choice, the cell has a cubic symmetry, so the H2S positioning is not affected by the choice of the cut plane. In this way, adsorbed molecules are free to change adsorption sites or to move outside the zeolite if the non-bonded interactions are less favorable, due to the disequilibrium imposed by the new H2S molecule approach. The same H2S molecule is free to move and position inside the cell, or to escape from the zeolite. The zeolite framework for all MD was kept fixed, while Na\(^+\) ions and H2S, CO2 and CH4 molecules had no constraints.

### Table 1

<table>
<thead>
<tr>
<th>Non-bond terms</th>
<th>Type</th>
<th>Accuracy (kcal/mol)</th>
<th>Cut-off (Å)</th>
<th>Truncation</th>
<th>Spline width (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrostatic</td>
<td>Ewald and group</td>
<td>0.001</td>
<td>12.5</td>
<td>12.5</td>
<td>Cubic spline</td>
</tr>
<tr>
<td>van der Waals</td>
<td>Atom based</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>1</td>
</tr>
</tbody>
</table>

Software modules of Materials Studio (v. 4.0, Accelrys, San Diego, CA, USA).

Details of Metropolis GCMC methods [14] employed in our research have already been described in details in previous works [12,13], and in many other publications [15–20], both for single and for multiple mixtures. The same applies to MM/MD classical methods to evaluate diffusion or permeation phenomena [21,19,22,23]. Accordingly, we will only briefly summarize below the aims and novelties of the procedure.

Adsorption isotherms for both pure H2S and H2S in a biogas mixture (CH4, CO2, H2S) have been calculated for the following zeolites, in order to establish a list of priorities in terms of selectivity factor (CH4, CO2, H2S) have been calculated for the following zeolites, and the relevant selectivity curves in Fig. 5[13] are shown.

As in our previous paper, adsorbed molecules have been modeled by quantum-mechanics techniques, in the case of flexible H2S, to determine bond lengths and angles under dynamic conditions, and partial charges, while CH4 and CO2 have been taken and represented with an all-atom model, with partial charges obtained from the selected cvff, aug force field. Then, the same Lennard-Jones parameters used in the first paper have been employed in all structures. MC simulations have been performed with the cvff, aug force field, at 298 K and a total constant pressure of 1 atm, being \(P_{H2S}\) held as a variable. Validation of the procedure has been obtained against experimental data [13]. We refer to Fig. 2, as taken from our previous paper [13], where the adsorption isotherms of pure H2S and H2S in biogas mixtures for all considered zeolites, and the relevant selectivity curves in Fig. 5[13] are shown. As can be seen, the best sorbent material for H2S removal is indeed zeolite NaY. The selectivity factor \(S_{ij}\) defined as [16]

\[ S_{ij} = \frac{x_i}{x_j} \times \frac{y_j}{y_i} \]
Equilibration was performed with 20 ps of MD in the NVT ensemble, which allowed reaching sufficient energy stability in all simulations. NVT ensemble has been chosen for equilibration to preserve the cell morphology [29,30]. The last frames of NVT simulations have been used to start 500 ps of constant volume-constant energy (NVE) simulations, an ensemble which is usually more indicated to preserve the thermodynamics of the system [26,32–34], because if an external (artificial) thermostat is used, this will lead to an inevitable error of dynamics [35].

The details of NVT and NVE simulations are reported in Table 2; it should be noticed that the Ewald calculation method [31] was used for the calculation of the Coulomb energy component in the 2D periodic systems. The analysis of the MD simulations has been carried out considering:

- the number of molecules of each species escaping from the cell;
- the temporal evolution of molecules removal for each species;
- the binding energy evaluation for each species over time.

Binding energy analysis has been used in molecular simulation to evaluate thermodynamic behavior and stability of several complexes [36]. In a general case, given a complex of two generic molecules 1 and 2, the expression of the relevant energy of binding can be written as

$$E_{BIND(1,2)} = E_{1,2} - (E_1 + E_2)$$

(2)

where $E_1$, $E_2$ and $E_{1,2}$ are the total energies of the isolated molecules 1 and 2 and the complex, respectively. The calculation of $E_1$, $E_2$ is obtained by cancelling the other molecule(s) in a selected frame of MD. Given the method, the bond energy contributions cancel out in the difference (2), and only the non-bonded energy difference account for the binding energy term in physical complexes, as expected. If the value of $E_{BIND}$ is negative, the complex is supposed to be thermodynamically favored while, on the contrary, the separation will be favored [37–40].

We considered five different ensembles in our simulation cell: the whole system itself, the zeolite framework (including Na+ ions), and the adsorbed molecules (H₂S, CO₂, CH₄). In this way, the binding energies for H₂S, CO₂ and CH₄ have been calculated according to the following equation:

$$E_{BIND(ads, i)} = E_{TOTAL} - (E_{ads, i} + E_{ZEO})$$

(3)

where $E_{BIND(ads, i)}$ is the binding energy of the specific complex, $E_{TOTAL}$ is the total energy of the whole system, $E_{ads, i}$ is the total energy of the specific adsorbed group of molecules, and $E_{ZEO}$ is the total energy of the zeolite alone. Binding energies have been analyzed for each different adsorbate, at different time steps, and taking into account molecular escape events. Binding energies have been then normalized by dividing $E_{BIND(ads, i)}$ for the number of molecules of the considered species inserted in the framework at the beginning.

3. Results and discussion

It was clear, even from the beginning of the NVT MD equilibrations, that the CH₄ molecules have a major tendency to escape from the framework, a phenomenon clearly related to their less polar characteristics. This confirms also the fact that hydrophilic zeolites, such as NaY, exhibit higher affinity for polar molecules (or molecules with a quadrupole moment, like CO₂). For this reason, the perturbation of the equilibrium, reached in the lowest energy frame of NVT-MC simulation, by a new H₂S molecule insertion tends decidedly to mobilize CH₄ molecules. Regarding CO₂ behavior, although its selectivity and isosteric heat of adsorption given by GCMC simulations is lower than that calculated for H₂S [13], it is not severely influenced by the perturbation: CO₂ molecules generally oscillate next to their adsorption sites, and their escaping tendency is very low. This can be ascribed to the fact that the quadrupole moment contributes to CO₂ binding stability, and to the planar, linear CO₂ shape, which allows the molecules to align inside the straight pores of NaY.

Quantitative results can be given both on terms of escaped molecules and in terms of binding energies. In Table 3 the list of total escaped molecules for each species is shown, while Fig. 2a–c shows escape events for each molecule in the NVE simulations. In this figure, each point represents escaping events at the given time step. It is important to note that we defined molecules as escaped when their center of mass is at a distance from the external zeolite surfaces greater than 12.5 Å. It may be observed that CH₄ molecules tend to exit rapidly from the cell along the z direction, as exemplified for example by the 3D visualizations of the 2D periodic simulation cell visualized in Fig. 3.

<table>
<thead>
<tr>
<th>Table 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Details of the 2D dynamic simulations</td>
</tr>
<tr>
<td>NVT</td>
</tr>
<tr>
<td>van der Waals</td>
</tr>
<tr>
<td>Coulomb</td>
</tr>
<tr>
<td>Thermostat algorithm</td>
</tr>
<tr>
<td>Time step</td>
</tr>
<tr>
<td>Simulation time</td>
</tr>
<tr>
<td>Temperature</td>
</tr>
<tr>
<td>Frame sampling</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Escaped molecules from NVT and NVE MD for different loading and different $P(H₂S)$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Molecules</th>
<th>Loading = 1/3</th>
<th>Loading = 2/3</th>
<th>Full loading</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P(H₂S) = 10$ Pa</td>
<td>$CH_4$</td>
<td>$CO_2$</td>
<td>$H_2S$</td>
</tr>
<tr>
<td>Initial number of molecules</td>
<td>3</td>
<td>19</td>
<td>0 (+1)</td>
</tr>
<tr>
<td>Escaped from NVT equilibration</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Escaped from NVE simulation</td>
<td>3</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$P(H₂S) = 50$ Pa</td>
<td>$CH_4$</td>
<td>$CO_2$</td>
<td>$H_2S$</td>
</tr>
<tr>
<td>Initial number of molecules</td>
<td>2</td>
<td>19</td>
<td>3 (+1)</td>
</tr>
<tr>
<td>Escaped from NVT equilibration</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Escaped from NVE simulation</td>
<td>2</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>$P(H₂S) = 1000$ Pa</td>
<td>$CH_4$</td>
<td>$CO_2$</td>
<td>$H_2S$</td>
</tr>
<tr>
<td>Initial number of molecules</td>
<td>1</td>
<td>18</td>
<td>4 (+1)</td>
</tr>
<tr>
<td>Escaped from NVT equilibration</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Escaped from NVE simulation</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>
The equilibrium condition is reached, in each case, well before 500 ps; only few H₂S and CO₂ molecules tend to escape. Generally, however, in correspondence of higher P(H₂S), and thus for higher H₂S fractions in the cell and for lower loadings (i.e., Fig. 2b and c), the equilibrium is reached more slowly. Although this behavior is difficult to explain, a tentative explanation might be related to the lower occupancy of free adsorption sites, especially for the few CH₄ molecules, which in these cases are allowed to cover longer pathways in relatively empty channels before finding the way to exit the framework.

It can also be noticed that, after molecule exits, the temperature of the system tends to increase (see additional information); this is reasonable, due to the acceleration of the escaping molecule. Both molecule pathways and temperature of the system always show stability within 350 ps, and none of the probe H₂S molecule inserted escapes from the cell.

Considering binding energies, we examined the binding energy behavior as a function of time (see Figs. 4–6). Each frame in these figures represents 0.5 ps of NVE MD simulation, and each binding energy value is averaged over the total number N of specific molecules inserted.

Although an attempt of fitting these curves is rather difficult or even impossible, these charts are helpful to explain adsorbed molecules behavior obtained by MD simulations. Binding energy evolutions are obviously influenced by molecule exit events; for instance, by considering the MD trajectory of the case shown in Fig. 4b, one CH₄ molecule escapes at frame 66, comes back at frame 80, and then leaves the zeolite again at frame 148. As can be seen from Fig. 4b, the corresponding binding energy trend clearly reflects this behavior. In general, all trends dramatically confirm the high speed with which methane tend to move out from the zeolite. Only when P(H₂S) = 10 Pa, and thus the number of H₂S molecules is low, some CH₄ molecules remain in the zeolite framework, but generally they all escape before 300 ps. Indeed, values of E BIND = 0 kcal mol⁻¹ N⁻¹ mean that all CH₄ molecules are dispersed outside the cell at a distance higher than imposed cut-offs. Generally, it appears that H₂S binding energies per molecule are considerably higher than those of CH₄; CO₂, on the other hand, shows the most stable behavior and, generally, is characterized by the most favorable binding energy.

This analysis contributes to explain also the adsorption behavior at different H₂S pressures [13]: when P(H₂S) is increased, an adsorption competition process takes place, resulting in a swap of adsorption sites between H₂S and CH₄ molecules; accordingly, the H₂S adsorption increases. Nevertheless, selectivity S(H₂S,CH₄) is much more enhanced at low H₂S pressures (i.e., lower loadings) due to the fact that more energetically suitable and free pores are available for H₂S. Thus, examining local binding energy evolution, e.g. immediately before and after CH₄ molecules leave the framework, an interesting behavior can be noticed (see Table 4). We considered only...
Fig. 4. Binding energies as a function of time frames for NVE MD simulations at $P(H_2S) = 10$ Pa: (a) 1/3 loading, (b) 2/3 loading, (c) full loading; ($\bullet$) H$_2$S, ($\blacksquare$) CO$_2$, ($\triangle$) CH$_4$.

events of CH$_4$ exiting, in the absence of other event which might influence this process (e.g. simultaneous exiting of more than one molecule or different molecules). Thus we could calculate the binding energy differences (BED) for all considered exiting events, as

$$\text{BED} = E_{\text{BIND}, \text{after}} - E_{\text{BIND}, \text{before}}$$

where $E_{\text{BIND}, \text{after}}$ and $E_{\text{BIND}, \text{before}}$ are the binding energies for CH$_4$ or H$_2$S, calculated immediately after (when CH$_4$ molecules are far from zeolite boundaries more than 12.5 Å) and before (when CH$_4$ molecules are still crossing zeolite boundaries) the CH$_4$ exit.

Although variations are quite high, due to the complexity of the system and the different composition and loading for each set of simulation, there is a clear trend in binding energy modifications after CH$_4$ exits. After each escape event, as expected, CH$_4$ binding energy decreases as absolute value, but this phenomenon involves also a decrease in H$_2$S binding energy, even though the phenomenon is limited in time. This is probably due to the re-equilibration of the NVE system after a few ps. The behavior testifies that CH$_4$ molecules tend to exit because of the lower intermolecular attractive forces with the rest of the system; moreover, CH$_4$ exits seem also to favor the re-allocation of H$_2$S molecules in adsorption sites, contributing to improve their stability in the framework immediately after each CH$_4$ exit event.

Table 4

<table>
<thead>
<tr>
<th>Molecule</th>
<th>BED (kcal/mol)</th>
<th>Standard deviation (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_4$</td>
<td>2.816</td>
<td>0.889</td>
</tr>
<tr>
<td>H$_2$S</td>
<td>-2.051</td>
<td>1.950</td>
</tr>
</tbody>
</table>
behavior of the system explains results arisen from GCMC simulations, where adsorption of H$_2$S is favored over CH$_4$ when $P_{[H_2S]}$ is increasing.

Appendix A. Supplementary data


References


Fig. 6. Binding energies as a function of time frames for NVE MD simulations at $P_{[H_2S]} = 100$ Pa; (a) 1/3 loading, (b) 2/3 loading, (c) full loading; (●) H$_2$S; (■) CO$_2$; (▲) CH$_4$.


