Hydrogen sulphide removal from biogas by zeolite adsorption
Part I. GCMC molecular simulations

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**Abstract**

In this work Grand Canonical Monte Carlo (GCMC) simulations have been used to study hydrogen sulfide (H₂S) removal from biogas streams by different zeolites such as FAU (Faujasite, NaX and NaY), LTA (zeolite A (Lynde division, Union Carbide)) and MFI (Zeolite Socony Mobil – five). Additionally, quantum mechanics (QM) molecular simulations have been performed to obtain structures and partial charges of some sorbates. The computational procedure adopted has been validated by comparison with experimental data available for H₂S removal in atmospheric environment by zeolite NaY. In order to obtain a priority list in terms of both H₂S isotherms and adsorption selectivity, adsorption simulations for pure H₂S at low pressures and for a prototype biogas mixture (i.e., CO₂, CH₄, and H₂S) have been performed and compared. The adsorption mechanisms and competition for accessible adsorption sites in terms of thermodynamic behavior have been also examined. Overall, the results obtained in this work could be routinely applied to different case studies, thus yielding deeper qualitative and quantitative insights into adsorption pollutant removal processes in environmental fields.

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1. Introduction

Pollutant removal from biogas is of crucial importance to guarantee better performances in biogas exploitation processes, and to reduce environmental impact of gaseous emissions. Biogas production and utilization is constantly increasing, as it represents a “green”, renewable energy, obtainable in a relatively economical way from anaerobic digestion [1–6]. Nevertheless, one of the most harmful pollutants, hydrogen sulfide (H₂S), is a biogas component, in a concentration range spanning from 10–30 to 1000–2000 ppm. Considering that exposure to a concentration of only 300 ppm for 30 min is enough to render a worker unconscious, it is clear that this fraction has to be dramatically reduced [1] to the lower toxic limit (i.e. at least 10 ppm [17]).

In some cases, aerobic biological processes, catalytic or oxidative processes can be used [8,9]: the use of adsorption processes, exploiting various types of adsorbents, is also widespread [10,11]. Zeolite materials are particularly suitable for adsorption removal processes [11–14], by virtue of their high selectivity and compatibility towards polar compounds, such as H₂S. Hydrophilic zeolites, with a high content of Al in their tetrahedral framework, are generally more appropriate for polar molecules adsorption, while hydrophobic zeolites are effective in the entrapment of apolar molecules [15]. In this work we investigated the potentialities of a series of zeolites for H₂S removal, using molecular simulation techniques such as Grand Canonical Monte Carlo (GCMC) [16], and ab initio quantum mechanics (QM).

Molecular simulations have become a powerful tool to explore both material science and life science fields; accordingly, we believe that these techniques have reached the stage to be successfully – and intensively – employed in environmental applications, determining a gain of time, money savings and the possibility to explore applications in an easier way [17]. Thus, in what follows we employed molecular simulations for ranking a list of selected zeolites in terms of selectivity and adsorption isotherms, giving also insights on adsorption mechanisms at atomistic level from a thermodynamic point of view. Relevant experimental data are scarce [12,18], and usually given in terms of pure contaminant adsorption isotherms. Nevertheless, some studies about H₂S vapor–liquid equilibria by means of molecular simulation techniques are available [19], or about vapor–liquid coexistence of H₂S in mixtures [20], these works are based upon the Gibbs Ensemble Monte Carlo Method [21].

Thus, in order to validate the computational procedure adopted we decided to compare our calculation with experimental adsorption isotherms of pure H₂S on zeolite NaY [12], and to examine

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the differences encountered in a realistic situation, when a biogas mixture of \( \text{CO}_2, \text{CH}_4 \), and \( \text{H}_2\text{S} \) at low pressures is considered. Finally, isosteric heats of adsorption, total energy contributions and energy densities were the selected quantities to investigate adsorption competition at different pressures, and zeolite selectivity \[22\].

2. Materials and methods

Simulations were carried out on an Intel bi-processor XEON 32bit workstation. We used Sorption and DMol3 software modules of Materials Studio \(\text{v. 4.0, Accelrys, San Diego, CA, USA}\), and in-house developed software. Stochastic methods have been described in our previous work \[23\] or elsewhere \[24,25\]; hence, here we will only briefly describe Metropolis \[16\] and Configurational Bias \[26\] methods.

Generally speaking, during a sorption simulation the chemical potential \( \mu \) is kept fixed, creating a certain number of configurations of molecules to be adsorbed on a given framework. In the Grand Canonical ensemble, the chemical potentials of all components and the temperature are fixed as if the framework is in open contact with an infinite sorbate reservoir at a given temperature. The reservoir is completely described by temperature and fugacity of all components, and does not have to be simulated explicitly. Chemical potentials for each component are related to the fugacity (or partial pressure) \( f \) of the components; the reservoir, in this study, is always treated as an ideal-gas system, due to the low bulk pressures taken into account, thus, partial pressures have been considered.

Molecules can be created, translated, rotated or destroyed. Equilibrium is reached when temperature and chemical potential of the external reservoir (i.e., free gas outside the framework) and the framework are equal. The Metropolis sampling method generates chain of configurations with the ensemble probability. Transforming a configuration involves a random displacement of each atom in the system from its actual position; as in this case sorbates are flexible, trajectories are employed (see Additional Information). A trial move is accepted if it lowers the configuration energy of the system. If the configuration energy is increased, trials are accepted with a probability proportional to a Boltzmann factor: \( P = e^{-\Delta U/kT} \), where \( \Delta U \) is the configuration energy difference. Configurational bias (CBMC) methods are widely used to simulate adsorption of rather large and flexible molecules. In a CBMC sorption simulation, a bias is introduced towards high energy values, to avoid attempt of sampling configurations with low probabilities, which are likely to be rejected by the acceptance test \[26\].

In this work, adsorbed molecules are rather small if compared to all zeolite pore size; nevertheless, we decided to test both methods. Since the results for biogas adsorption isotherms in zeolites obtained with Metropolis Monte Carlo (MMC) and CBMC revealed negligible differences (see Supplementary material), we decided to adopt the MMC technique, being computationally faster than CBMC. \( \text{H}_2\text{S} \) molecular model has been built and optimized at QM density functional theory (DFT) \[27\] level with the DMol3 module, due to its flexibility and dipole moment; structures of the symmetrical \( \text{CH}_4 \) and symmetrical and linear \( \text{CO}_2 \) molecules have been minimized, and partial charges assigned by the selected Force Field, the cvff\text{aug} (consistence valence augmented force-field).

Four zeolites were considered: LTA, FAU NaX, FAU NaY, and MFI. The first three frameworks are hydrophilic, and already employed for \( \text{H}_2\text{S} \) adsorption \[12,28,29\]. The last one, MFI, is hydrophobic in nature, and has been taken into account to investigate adsorption differences between these categories. 3D molecular models of LTA (Si/Al = 1), NaX (Si/Al = 1), NaY (Si/Al = 2.5) and dealuminated MFI \[30\] were available in the structural database of Materials Studio. Aluminum substitutions have been performed by following Loewenstein’s rule \[31\], while Na\textsuperscript{+} ions position has been assigned by in-house developed software for identifying potential energy minima and, thus, most probable extra-framework cation positions.

An all-atom model has been chosen for calculation; the cvff\text{aug} was the potential energy expression of choice in all calculations \[32\]; a more detailed description of all molecule models is given in Additional Information. Electrostatic energy terms have been computed by the Ewald summation method. van der Waals interactions have been calculated with the classical Lennard–Jones function \[33\]; the cut off for van der Waals contribution, has been set to 8.5 Å, with an atom based calculations and cubic spline truncation; the cut-off distance should be less than a half of the minor cell side, so when necessary (zeolite MFI) we duplicated cells. The cubic spline truncation was set to 1 Å with a buffer of 0.5 Å; in this way, the van der Waals non-bond energy term is splined from its full value to zero within a radio of 1 Å. For electrostatic contributions, the accuracy of Ewald and group calculation was 0.001 kcal/mol with the same cut off and buffer. At least \( 1 \times 10^5 \) productive Monte Carlo steps (i.e. Monte Carlo trial moves), preceded by \( 1 \times 10^6 \) equilibration steps, have been performed under 3D periodic boundary conditions. Overall, we performed and compared MMC for pure \( \text{H}_2\text{S} \) adsorption (from 10 up to 1000 Pa), and competitive, simultaneous adsorption of \( \text{H}_2\text{S}, \text{CH}_4 \) and \( \text{CO}_2 \), with partial pressure in the range of a typical biogas (\( \text{CO}_2 \) and \( \text{CH}_4 \) with low concentrations of \( \text{H}_2\text{S} \)) and a bulk pressure \( P_{\text{total}} = 1 \text{ atm} \). The simulation temperature was fixed at 298 K, which is a realistic temperature for a biogas exiting from a mesophilic process \[1,2,6\].

Adsorption thermodynamics were further investigated analyzing the values of the isosteric heat of adsorption, \( Q_h \), which is a measure of adsorption capabilities of a sorbate in an adsorbent framework. \( Q_h \) is defined as the difference between the partial molar enthalpy of the sorbate component in the external reservoir (i.e., free gas) and in the framework; accordingly, it is a measure of the enthalpy change involved in the transfer of a solute from the reference state to the adsorbed state at a constant solid phase concentration \[34\]:

\[
Q_h = h_R - h_F
\]

Evaluation of \( Q_h \) requires the application of Clausius–Clapeyron equation \[34\]:

\[
Q_h = \left( v_S - v_F \right) \left( \frac{dp}{d(ln\,T)} \right) = RT \left( \frac{d(ln\,p)}{d(ln\,T)} \right)
\]

where \( v_S \) and \( v_F \) are the sorbate partial molar volumes in the reservoir and in the framework, respectively, \( p \) the partial pressure, and \( T \) the temperature. In the right-hand side term of Eq. (2), the partial molar volume of the gas molecules in the framework is neglected with respect to that in the reservoir, and the gas behavior in the reservoir is assumed to be ideal. This leads to the expression of \( Q_{RF} \) in the Grand Canonical ensemble, where the free energy \( G \) can be calculated:

\[
Q_{RF} = RT - G
\]

A further criterion for investigating adsorption is given by the analysis of the total energy components of the system and the energy distributions. In the first case, the total energy \( E_M \) of a specific configuration of the simulation, \( M \), is given by the Coulomb (i.e., electrostatic) and van der Waals (i.e., dispersion) contributions:

\[
E_M = E_{\text{SSM}}^M + E_{\text{RF}}^M + U_M^M
\]

where \( E_{\text{SSM}}^M \) is the intermolecular energy between the sorbate molecules, \( E_{\text{RF}}^M \) is the interaction energy between the sorbate...
molecules and the framework, and $U_{SM}$ is the total intramolecular energy of the sorbate molecules, as a sum of intramolecular energies of all sorbates. The intramolecular energy of the framework is not included as the framework is fixed throughout the simulation. The energy distribution curves for each sorbate express sorbate-framework interactions over the entire cell volume; in this case, the interaction energy expressions take the form of Eq. (4) with the obvious exclusion of the last term $U_{SM}$. In the case of a mixture adsorption, the selectivity factor $S_{ij}$ can be also considered, as given by [35,36]:

$$S_{ij} = \left( \frac{x_i}{x_j} \right) \left( \frac{y_j}{y_i} \right)$$

where $x_i, x_j$ are the molar fractions of species $i$ and $j$ in the gas phase, while $y_i$ and $y_j$ are the molar fraction of species $i$ and $j$ adsorbed in the framework.

3. Results and discussion

Initially, we compared our simulated H$_2$S adsorption isotherms on zeolite NaY at 298 K with the corresponding, available experimental data [12]. As shown in Fig. 1, a good agreement is obtained. Small differences may be related, for instance, to the presence of impurities in original zeolite, and to the possibly different Si/Al ratio.

Simulation results for biogas purification are shown in Fig. 2. Considerably different behaviors for adsorption isotherms of pure
Table 1
Average values of $Q_{RF}$ for a biogas mixture adsorption process, and non-bond energy components relative to adsorption at $P_{H_2S} = 1000 \text{ Pa}$

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>$Q_{RF}$ (kcal/mol)</th>
<th>Total energy contributions ($P_{H_2S} = 1000 \text{ Pa}$) (kcal/mol)</th>
<th>van der Waals</th>
<th>Coulomb</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$H_2S$</td>
<td>$CO_2$</td>
<td>$CH_4$</td>
<td>$H_2S$</td>
</tr>
<tr>
<td>FAU NaY</td>
<td>17.9 (0.4)</td>
<td>11.4 (0.1)</td>
<td>7.2 (0.4)</td>
<td>$-300.3$ (9.4)</td>
</tr>
<tr>
<td>FAU NaX</td>
<td>15.6 (0.6)</td>
<td>12.3 (0.1)</td>
<td>9.7 (0.1)</td>
<td>$-302.3$ (8.6)</td>
</tr>
<tr>
<td>MFI</td>
<td>10.2 (0.4)</td>
<td>9.3 (0.3)</td>
<td>9.1 (0.2)</td>
<td>$-179.9$ (8.2)</td>
</tr>
<tr>
<td>LTA</td>
<td>14.5 (0.2)</td>
<td>14.6 (0.1)</td>
<td>9.3 (0.1)</td>
<td>$-389.7$ (9.5)</td>
</tr>
</tbody>
</table>

Standard deviations are reported in parenthesis.

H$_2$S and for the biogas mixture are obtained. These differences are qualitative, quantitative, and suggest a possible ranking of the zeolite performances. Due to the complexity of the systems and, sometimes, to the very low number of $H_2S$ molecules adsorbed, some difficulties in Monte Carlo samplings may arise; a consequence, isotherms are not always smooth, and the error bars for each point, resulting from running multiple simulations in the same conditions, are shown to quantify the variability of the predicted values. Nevertheless, as expected, the adsorption of $H_2S$ on the hydrophobic MFI network is always lower than all other zeolites; moreover, the considerable differences in loadings (1–4 orders of magnitude) allow a ranking among zeolites to be clearly established.

To complement the information on framework selectivity, it also instructive to examine the adsorption curves for $CH_4$ and $CO_2$ reported in Fig. 3. The isotherms of $H_2S$ are also shown for comparison.

As expected, in hydrophilic zeolites the amount of $H_2S$ adsorbed usually increases with increasing $H_2S$ partial pressure; the isotherms of $CH_4$ slightly decrease, whilst $CO_2$ adsorption curves remain stable. On the other hand, when considering the apolar MFI framework, the amount of adsorbed $H_2S$ is very low, even when considering pure component adsorption isotherms. During biogas adsorption simulations, however, the $CH_4$ loading remains stable, while $H_2S$ adsorption slightly increases at the expenses of $CO_2$.

The global results yielded by the MMC simulations are quite sensible. In fact, electrostatic interactions between the polar molecule $H_2S$ and the framework are more favorable in hydrophilic, ion-rich zeolites: at the same time, the increase of $H_2S$ partial pressure is detrimental to the adsorption of the less polar molecule, $CH_4$. The reverse is true when considering the hydrophobic MFI framework, onto which less polar compounds are more favorably attracted, as expected. Overall, the FAU NaY zeolite seems to be characterized by the highest selectivity towards $H_2S$, and MFI by the lowest one. The fact that NaY could be the framework of choice, and not the NaX counterpart, in spite of the higher Si/Al ratio, could be possibly rationalized by invoking greater steric hindrance imposed by the larger amount of sodium cations and, thus, lower pore dimensions available to $H_2S$ binding. Analogously, the different pore shape for LTA (with the consequent confinement effects), and the different charge distribution which influence sorbate-framework interac-

![Fig. 4. Energy density distributions for biogas mixture adsorption on NaY at $P_{H_2S} = 10 \text{ Pa}$ (a), NaY at $P_{H_2S} = 1000 \text{ Pa}$, MFI at $P_{H_2S} = 10 \text{ Pa}$ (c), and MFI at $P_{H_2S} = 1000 \text{ Pa}$ (d). Symbols legend: (····) $H_2S$; (–·–·) $CH_4$; (—) $CO_2$.](image-url)
tions can be the main reason for the lower H2S loading (with respect to NaX or NaY) when the mixture is taken into account.

Examining the simulation results from a thermodynamic standpoint we can confirm and further explain these tendencies. Table 1 list the calculated isosteric heats $Q_{RF}$ for each species, averaged over different H2S input pressures. Table 1 also reports the mean total non-bond energy components for the Metropolis Monte Carlo (MMC) sorption isotherm of the biogas mixture when $P_{H2S} = 1000$ Pa as an example. Utterly analogous results are obtained at different H2S partial pressures. Interestingly, the highly favorable values of the electrostatic components reveal that the different steric hindrance characterizing the three dimensional structure of the zeolite frameworks is not the only responsible for zeolite selectivity. In fact, given that the three gases do not differ very much in their molecular volumes ($V_{CO2} = 34.0 \, \text{Å}^3$, $V_{H2S} = 30.3 \, \text{Å}^3$, and $V_{CH4} = 28.20 \, \text{Å}^3$, respectively), all zeolite pore sizes are all rather large if compared to the mean radius of these molecules. Accordingly, the considered zeolites do not seem to behave predominantly as molecular sieves, but rather their selectivity appears be driven mainly by the electrostatic interactions in terms of total energy contributions.

As well evident from Table 1, $Q_{RF}$ for H2S is always higher than the corresponding values for CO2 and CH4 when the adsorption takes place on polar frameworks; interestingly, however these differences flatten for the adsorption process onto the apolar zeolite. This can be taken as a further piece of evidence that H2S adsorption on FAU (NaY and NaX), and LTA is favored, and increases with increasing $P_{H2S}$.

The density distribution curves for the total energy confirm the same trend, as the H2S curves show the most mean negative values in all zeolites except MFI, where this tendency is inverted. Fig. 4 illustrates this behavior in the cases of NaY and MFI at $P_{H2S} = 10$ and 1000 Pa, respectively, as selected examples.

Fig. 4 shows different peaks for both NaY–H2S and NaY–CH4 energy distributions, a trend confirmed for the other hydrophilic zeolites in the entire H2S partial pressure range. CO2 curves, on the contrary, exhibit an invariant behavior characterized by a Gaussian distribution. As a rationale, we can say than CH4 and H2S are able to occupy more that one site, or position, in the framework with different probability, so that adsorption sites can be interchanged as $P_{H2S}$ increases. MFI curves have only one peak for each gas, and each peak is close to each other showing no appreciable differences.
in E values. Accordingly, sorption site interchange is more difficult in the MFI apolar framework. To consider more details of adsorption selectivity, we mapped H$_2$S selectivity with respect to CH$_4$ and CO$_2$ in Fig. 5.

Selectivity factors are generally very high in hydrophilic zeolites; again, according to our simulations, the best results are achieved with NaY. To find a rationale for these selectivity curves is less straightforward. As a general observation, they tend to decrease quickly for NaY and LTA; accordingly, selectivity is generally higher at low H$_2$S partial pressures, which indicates that sorption selectivity mechanism seems to work better in the typical low range of biogas H$_2$S content. Lower selectivity for NaY and LTA may be explained by the fact that, when $P_{H_2S}$ increases, H$_2$S gains new adsorption sites, for which H$_2$S is favored over CH$_4$ and CO$_2$, but not as well as for old adsorption sites, at lower $P_{H_2S}$. Selectivity for NaX shows less variation, probably because selectivity values at low H$_2$S pressures are already quite low. This, in turn, could be due to the higher steric hindrance exerted by the higher number of cations characterizing this framework. Once again, MFI does not show selectivity for H$_2$S.

We also investigated the density fields in the pores of the zeolite 3D periodic structures (Fig. 6). Although for low $P_{H_2S}$ in some cases, distributions are not symmetrical, it is qualitatively evident how H$_2$S prevalently substitutes CH$_4$ in sorption sites (especially in larger pores). Zeolites NaX and LTA show similar behaviors, while MFI adsorption site substitutions are much less evident, if at all.

4. Conclusions

The main results of this work confirm that hydrophilic zeolites are more indicated for H$_2$S adsorption. Differences arise, as evidences by both pure H$_2$S and biogas mixture adsorption simulations, from adsorption site competition.

Adsorption isotherms, isosteric heats of adsorption and energy distributions confirm specific trends and explain adsorption behaviors. Results are of remarkable practical use if considered in terms of selectivity, according to which a ranking for the considered zeolites towards H$_2$S can be formulated: the FAU NaY framework appears the best choice, being favored over NaX, which has essentially the same structure but a different Si/Al ratio, ultimately resulting in more sterical hindered pores. In this way, a reasonable ranking for the best zeolite choice has been determined. It should be noticed that for some kinds of zeolites, as LTA or MFI, H$_2$S is scarcely adsorbed when mixture are considered, this affects the shape of adsorption isotherms and, probably, the accuracy of Monte Carlo sampling. In these cases, further analysis may be performed to obtain much quantitative results. This can be obviously done by speeding up calculations or applying new, more efficient sampling methods, which is out of the scope of the present work.

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Appendix A. Supplementary data


References


