Molecular Simulation Study of the Competitive Adsorption of H$_2$O and CO$_2$ in Zeolite 13X

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ABSTRACT: The presence of H$_2$O in postcombustion gas streams is an important technical issue for deploying CO$_2$-selective adsorbents. Because of its permanent dipole, H$_2$O can interact strongly with materials where the selectivity for CO$_2$ is a consequence of its quadrupole interacting with charges in the material. We performed molecular simulations to model the adsorption of pure H$_2$O and CO$_2$ as well as H$_2$O/CO$_2$ mixtures in 13X, a popular zeolite for CO$_2$ capture processes that is commercially available. The simulations show that H$_2$O reduces the capacity of these materials for adsorbing CO$_2$ by an order of magnitude and that at the partial pressures of H$_2$O relevant for postcombustion capture, 13X will be essentially saturated with H$_2$O.

INTRODUCTION

Carbon capture and sequestration has been identified as a critical technology for reducing the impact of fossil fuel use on the concentration of CO$_2$ in the atmosphere. Although switching to renewable energy sources would eliminate carbon emissions, no technology has been developed that could effectively scale to replace fossil fuels in the near future. Hence, any selection of technologies to reduce carbon emissions in the near term will have to include some form of carbon capture and sequestration.1−3 The standard industrial method for removing CO$_2$ from gas streams, known as scrubbing, involves contacting the gas stream with a concentrated solvent containing amines, typically monoethanolamine. However, the energy penalty for this process is high and a variety of alternative processes have been proposed, including membranes, advanced solvents, and adsorption.4−5

Zeolite 13X (NaFAU) has been used as a reference material for CO$_2$ adsorption due to its high selectivity and commercial availability on the tonne scale.6−8 Zeolites are porous aluminosilicate materials that have been used extensively in industrial adsorption processes, as the small pores and specific topology can sieve molecules based on their kinetic diameter. Moreover, the presence of aluminum gives these frameworks a net negative charge that is compensated by cations in the pore. These cations provide good adsorption sites for the quadrupolar CO$_2$ molecule, and CO$_2$/N$_2$ selectivities up to 300 are found in cation-exchanged zeolite frameworks.9

At the same time, these cations might interact strongly with water molecules9−11 that are present in large quantities in postcombustion gas streams (around 5−15 vol.%).12 In fact, 13X is marketed as a desiccant in some contexts and has been studied as a medium for storing solar thermal energy with water as the working fluid.13,14 Understanding the influence of water on CO$_2$ adsorption is important because it could potentially reduce the capability of materials to selectively adsorb CO$_2$ efficiently enough for a practical process.

The adsorption of H$_2$O on aluminosilicate zeolites has been studied by several groups. In an experimental study, Wang and LeVan determined both the pure component and mixture isotherms of H$_2$O and CO$_2$ on commercial 13X and 5A samples and noted that small amounts of water reduce the CO$_2$ capacity slightly. When water is adsorbed near its saturation loading, the CO$_2$ capacity is an order of magnitude lower than on the dry materials.15,16 Brandani and Ruthven studied the effect of water on CO$_2$ and propane adsorption at different water loadings on low-silica forms of X and CaX and correlated the water loading with an exponential decrease in the Henry’s law coefficient for CO$_2$.17 Finally, experiments by Ferreira et al.18 and Lee et al.19 also show that H$_2$O has a detrimental effect on the CO$_2$ adsorption capacity of X-type zeolites.

In addition to these experimental studies, there have been a variety of computer simulations performed on water in aluminosilicate zeolites. Castillo et al. compared different H$_2$O models in pure-silica zeolites and showed that the predicted isotherms were sensitive to the partial charges and crystal structure of the zeolite framework20 indicating the need for a well-designed forcefield. This is certainly true when considering water adsorption in frameworks with different Si/Al ratios, as was shown by Di Lella et al.21 Lee et al. and Faux et al. performed molecular dynamics (MD) simulations of
water and sodium molecules in zeolite 4A using a fixed and flexible zeolite framework respectively, indicating differences between these two approaches.22,23 Beauvais et al. simulated water in NaX and NaY (NaFAU at approximately 1.24 and 2.4 Si/Al, respectively) and observed that water can cause a rearrangement of the cations from their preferred sites in the dehydrated structure.24 These observations are supported by Bell et al., who demonstrated that there is a small amount of hysteresis at relatively low pressures in NaY, which they attribute to rearrangement of cations between the supercage and sodalite cages of FAU as water adsors.25 Moreover, Boddenburg et al. proposed that some Na cations would be coordinated by up to 6 water molecules near saturation.26 Finally, Hutson et al. showed that in LiLSX (low-silica X) even a small amount of adsorbed water caused a precipitous drop in the N2 adsorption capacity that required regeneration above 500 K to recover.27

In this computational study, we aim to understand the adsorption of pure H2O and CO2 as well as H2O/CO2 mixtures in hydrophilic zeolites. Grand Canonical Monte Carlo (GCMC) simulations were used to predict adsorption isotherms and heats of adsorption and Canonical Monte Carlo (CMC) simulations were performed to study the average structure of sodium, H2O, and CO2 at different loadings.28

### METHODS

For our simulations in zeolite 13X, we used the faujasite topology reported by Olson.29 In the unit cell, aluminum atoms were randomly assigned to 86 T positions (Si/Al ratio of 1.24), respecting Löwenstein’s rule, an empirical rule that excludes aluminum atoms in adjacent T-sites. The positions of the framework atoms are kept fixed at all times, since earlier studies showed that this does not have a significant influence on the adsorption of small molecules such as CO2 and H2O.30 Sodium atoms were placed randomly as counterions for sodium and CO2 adsorption in the framework, and were equilibrated using canonical Monte Carlo moves. We allowed the sodium atoms to move during all simulations; for a good idea about the Na distribution in the framework, we refer to work of Beauvais et al. and Bell et al.24,25

Figure 1 shows two views of the 13X framework through the 12-rings connecting the supercages (along the (111) direction). On the left, the atomic structure of the material with the positions of the green extra-framework sodium atoms taken from a Monte Carlo simulation. On the right, a simplified view of the FAU topology showing the connection between T-atom positions. The red circle in the center shows the center of one supercage, which is connected to 4 other supercages by 12-rings of T-atoms, the blue circles indicate the sodalite or β-cages of the material. In our simulations, Na and H2O are allowed to enter both the supercages and sodalite cages, but CO2 can only access the supercages, not the sodalite cages.

Adsorbate molecules were allowed to make either translation, rotation, swap, and regrowth moves. Swap moves involve the insertion or deletion of a single molecule to or from the simulation box. The regrowth move involves taking an existing molecule in the simulation and placing it at another location in the box at random. Interactions between the framework, cations, and adsorbed molecules were modeled using a sum of a 12-6 Lennard-Jones (LJ) term (representing dispersive interactions) and a Coulombic term (including electrostatic interactions). The Ewald summation technique is used to compute the electrostatic contribution.

Lennard-Jones parameters and partial atomic charges for the CO2-framework, CO2–Na and CO2–CO2 interactions were taken from the force field developed by García-Sánchez et al.32 and values for σ and ε are printed in the left side of Table 1. H2O–H2O interactions were modeled using the SPC/E model.33 Finally, H2O-framework and H2O–Na interactions were parametrized by multiplying the SPC/E H2O–H2O parameters by the ratio of CO2-framework to CO2 interactions or CO2–Na to CO2–CO2 interactions reported by García-Sánchez et al.32

### Table 1. Lennard-Jones Parameters Used in This Work

<table>
<thead>
<tr>
<th></th>
<th>σ (Å)</th>
<th>ε/ε&lt;sub&gt;k&lt;/sub&gt;</th>
<th>σ (Å)</th>
<th>ε/ε&lt;sub&gt;k&lt;/sub&gt;</th>
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<tr>
<td>CO&lt;sub&gt;2&lt;/sub&gt;–CO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>2.745</td>
<td>29.933</td>
<td>2.751</td>
<td>78.197</td>
</tr>
<tr>
<td>CO&lt;sub&gt;2&lt;/sub&gt;–O&lt;sub&gt;spce&lt;/sub&gt;</td>
<td>3.237</td>
<td>50.640</td>
<td>2.880</td>
<td>159.152</td>
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<tr>
<td>O&lt;sub&gt;spce&lt;/sub&gt;–O&lt;sub&gt;spce&lt;/sub&gt;</td>
<td>3.017</td>
<td>85.617</td>
<td>2.745</td>
<td>362.292</td>
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<tr>
<td>CO&lt;sub&gt;2&lt;/sub&gt;–Na&lt;sup&gt;+&lt;/sup&gt;</td>
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<td>50.640</td>
<td>2.880</td>
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<td>3.320</td>
<td>200.831</td>
<td>2.758</td>
<td>78.197</td>
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</table>

*H2O-framework and H2O–Na interactions were parametrized by multiplying the SPC/E H2O–H2O parameters by the ratio of CO2-framework to CO2 interactions or CO2–Na to CO2–CO2 interactions reported by García-Sánchez et al.*32

To illustrate our reasoning, we elaborate the determination of ε<sub>Na–CO2</sub> as an example. First, two ratios r<sub>G</sub> and r<sub>C</sub> are computed, representing the ratio of CO2-framework to CO2–CO2 interactions for both C and O.

\[
\begin{align*}
\frac{\varepsilon_{Na-CO2}}{\varepsilon_{CO2-CO2}} &= \frac{\varepsilon_{Ospce-Ospce}}{\varepsilon_{CO2-CO2}} \\
\frac{\varepsilon_{Na-CO2}}{\varepsilon_{CO2-CO2}} &= \frac{\varepsilon_{Ospce-Ospce}}{\varepsilon_{CO2-CO2}} \\
\frac{\varepsilon_{Na-CO2}}{\varepsilon_{CO2-CO2}} &= \frac{\varepsilon_{Ospce-Ospce}}{\varepsilon_{CO2-CO2}}
\end{align*}
\]

The resulting multiplication factor is the average of the r<sub>G</sub> and r<sub>C</sub> ratio, so for ε<sub>Na–CO2</sub>–O<sub>spce</sub>, this would give

\[
\varepsilon_{Na-CO2-Ospce} = \frac{1}{2}(r_G + r_C) \varepsilon_{Na-CO2-Ospce}
\]
to other frameworks or systems and a more detailed analysis of the force field was out of the scope of this work.

Although CO₂ could react with water, we assume that no carbonic acid is formed during adsorption because the force field we used cannot describe this reaction. Moreover, we expect that water interacts more strongly with the Na cations than with CO₂ and that therefore the reaction to HCO₃⁻ would be slow.

From a practical point of view, it is useful to consider the predicted loadings when a gas stream would be saturated with water. This is the case when the postcombustion gas stream had been subjected to desulfurization processes. Table 2 shows the saturation vapor pressures for water at the temperatures where the isotherm was simulated. Finally, we mention that all loadings are displayed in mol/kg, that is, mol adsorbent per kilogram zeolite, in order to be easily compared with experiments. Note that 1 mol/kg corresponds to 11.434 molecules per unit cell, or that one molecule per unit cell corresponds with 0.088 mol/kg.

## RESULTS AND DISCUSSION

In this section, we will first discuss the pure components, CO₂ and H₂O, their isotherms, as well as the adsorption energy as a function of the loading and the arrangement of the adsorbed molecules inside the framework. All information is assembled in Figure 2 in order to provide a clear overview and an easy comparison between CO₂ and H₂O. After the analysis of the pure component systems, we will consider CO₂/H₂O mixtures and assess the influence of both components on the isotherm and the adsorbate arrangement.

First of all, Figure 2a shows a good agreement between the water isotherms obtained from our GCMC simulations and experimental data reported in Wang and LeVan. In the Supporting Information, we show that the results also agree well with experimental data from Ferreira et al. and furthermore, we provide the plots on a linear scale. Note that the experiments were conducted on pelletized zeolite samples, whereas our view give similar information more elegantly. Figure 2c shows histograms of the distances between sodium atoms and the oxygen atom in H₂O. The average distance is about 3.5 Å and the peak shifts to slightly smaller distances as the H₂O loading increases. This average distance is larger than the 2.76 Å distance reported for the coordination of sodium cations by water in aqueous solution. The discrepancy between these values will be partly due to the different environment but can also stem from the relatively large value of σ used for the Na–H₂O interaction in this work (see Table 1).

The interaction between the adsorbing water molecules is illustrated with Figure 2d, where the nearest distances between the oxygen and hydrogen atoms on different water molecules is plotted. The peak at shorter distances (1.7–1.9 Å) represents the interaction of hydrogen bonded molecules, while the peak around 3.2 Å is indicating two water molecules coordinated to the same sodium. As the water loading increases, the density of the latter disappears while the former increases. The stabilization of the water molecules hence shifts from the interaction with the Na cations to the formation of a hydrogen bond network.

Although the adsorption of water is stabilized by the ability to form a hydrogen bond network, water is still interacting strongly with the cations in the zeolite pores. This is clear from Figure 2e, showing the distribution of nearest distances between sodium cations and the aluminum in the framework at different water loadings and 323 K. At low water loading, there is a single peak at short distances, indicating that the sodium cation tends to stay close to the balancing negatively charged aluminum sites. At intermediate water loading, the height of this peak is smaller and there is a longer tail in the distribution because water can stabilize Na further away from the aluminum sites. At the highest water loading, a small second peak appears around 7.4 Å, showing that some of the sodium atoms can be “dissolved” from the surface of the zeolite pore and can be completely coordinated by H₂O in the pore. This is only the case for the sodium cations in the supercages. Water molecules do not enter the sodalite cages (although they were not excluded from it in our calculations) and hence do not alter the positions of the cations that are present there. A similar behavior was observed in a molecular dynamics study on Na-mordenite: water extracts the cations in the main channels and leaves the cations in the smaller channels untouched. Another paper from the same group reports the cation migration in NaX when methanol is absorbed.

The results of the GCMC simulations for the second pure component, CO₂, are presented in the right-hand column of Figure 2, so they can be easily related to those of H₂O. First, in Figure 2f the simulated CO₂ isotherm is compared with the previously mentioned experiments from Wang and LeVan and again shows fair agreement. In the Supporting Information, more experimental isotherms are considered, all of which show good agreement between theory and experiment, both on a log–log scale and on a linear scale. As opposed to the H₂O isotherm, the CO₂ isotherm does not reveal a steep region at lower fugacities. Moreover, the desorption enthalpy shows virtually no dependence on the loading (Figure 2g). This

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Table 2. Saturation Vapor Pressure of Water from the Antoine Equation

<table>
<thead>
<tr>
<th>T (K)</th>
<th>P_vap (kPa)</th>
</tr>
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<tbody>
<tr>
<td>273</td>
<td>3.14</td>
</tr>
<tr>
<td>323</td>
<td>12.55</td>
</tr>
<tr>
<td>373</td>
<td>100.78</td>
</tr>
</tbody>
</table>

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strengthens our previous conclusion that the shape of the isotherm is related to the evolution of the desorption enthalpies in function of the loading. Note that in typical exhaust gas conditions (325 K and CO₂ partial pressures around 15 kPa, that is, 15% CO₂ at 1 bar) the framework would not be saturated with CO₂, in sharp contrast to water.

CMC simulations at 323 K and at different total loadings of CO₂ provide more information about the average geometry. First, Figure 2h shows histograms of the distribution of Na–O.CO₂ distances. As the loading of CO₂ increases, the shape of the distribution stays essentially the same, and the peak value shifts to slightly lower distances as the higher density forces the CO₂ molecules together.

Next, Figure 2i presents the distributions of the distance between the O atom in one CO₂ molecule and the C atom in the closest neighboring CO₂ molecule. At low loadings, there are two broad peaks. The first one at distances around 4 Å is associated with CO₂ molecules that are stabilizing each other at a relatively close distance. The second peak between 6 and 8 Å corresponds to the distance between two CO₂ molecules that are sitting in neighboring 12-membered rings, which was...
identified as the preferred adsorption site for CO$_2$ at low loadings in our simulations. As the loading increases, the CO$_2$ molecules will be forced together and the interaction between CO$_2$ molecules becomes more important, resulting in only one peak that is shifted to lower distances.

Finally, Figure 2j shows that the histograms of the distances between sodium and aluminum atoms in the framework in the presence of different loadings of CO$_2$ remains essentially the same. Compared to H$_2$O, CO$_2$ does not influence the positions of sodium atoms, indicating a weaker interaction between CO$_2$ and sodium. Although Plant et al. report in a theoretical study that CO$_2$ can cause the migration of a sodium cation, no such effect was observed in our simulations.

As an intermediary conclusion, it is clear from the pure component simulations that H$_2$O has a much stronger interaction with zeolite 13X than CO$_2$: 13X is more easily saturated with H$_2$O, the desorption enthalpies are significantly higher, and the H$_2$O molecules have an influence on the position of the sodium cations.

Mixture adsorption isotherms were simulated to quantify the influence of water in the adsorption of H$_2$O/CO$_2$ mixtures. Figure 3 shows the H$_2$O and CO$_2$ isotherms for a 1% H$_2$O in CO$_2$ mixture at 323 and 373 K. At low pressures, the two components appear to adsorb independently, which is not surprising as the loadings in this regime are as low as 0.1 mol/kg, or less than 1 molecule per unit cell. The inflection point in the H$_2$O isotherm is around 100 Pa at 323 K and 3400 Pa at 373 K, corresponding to water partial fugacities of about 1 and 34 Pa, respectively. Once the water isotherms pass the inflection point and enter the plateau regime, the corresponding CO$_2$ isotherms pass through a maximum and begin to decrease even as the total fugacity continues to increase. Overall, water adsorbs close to its pure component loading, while the capacity for CO$_2$ adsorption falls drastically.

To improve sampling of the CO$_2$ isotherms, we performed simulations where CO$_2$ was treated with GCMC moves and H$_2$O was treated with CMC moves. Figure 4 shows the adsorption isotherms for CO$_2$ at different total water loadings at 323 K. As expected, increasing the water loading reduces the equilibrium loading of CO$_2$ at all pressures. When 13X is near saturation loading (108 or 110 H$_2$O molecules per unit cell), the CO$_2$ uptake is more than an order of magnitude lower than for the pure CO$_2$ component. In the Supporting Information, the isotherms from Figure 4 are compared with experimental isotherms measured by Wang et al.\textsuperscript{39} There is a fair agreement at low water loadings, but a large discrepancy for the isotherm at 108 H$_2$O molecules per unit cell, which we were not able to explain.

To more effectively study the structure of the adsorbed solution of CO$_2$ and H$_2$O, NVT simulations were performed at different numbers of CO$_2$ and H$_2$O molecules. Figure 5 shows the distribution of Na–O$_{CO2}$ distances at different H$_2$O loadings. The CO$_2$ loading was fixed at 8 molecules per unit cell. As with pure CO$_2$, the average distance between Na and the oxygen atom in CO$_2$ decreases. At the highest water loading, the most likely distance is smaller than for the pure CO$_2$ case (2.8 Å vs 3 Å). As the water hydrogen bonding network becomes more extensive, it is more favorable to force the CO$_2$ molecule closer to the Na cations than to disrupt the network. Next, Figure 6 shows the distribution of O–H distances between different water molecules as the water loading increases with 8 CO$_2$ molecules per unit cell. The previously mentioned trend that it becomes more likely to find the H$_2$O molecules within hydrogen bond distance as the loading increases, does not seem to be disrupted by the presence of CO$_2$ molecules. The formation of a hydrogen bond...
network will also tend to exclude CO₂ since a CO₂ molecule is easily replaced by another water molecule.

In this study, we only considered the isotherms of CO₂ and H₂O, but a typical flue gas contains around 80% of N₂. Although we don’t expect a significant influence, this is certainly worth a thorough investigation. Moreover, it would be interesting to investigate the influence of the Si/Al ratio of the framework, for instance, by considering low silica X or zeolite Y.

## CONCLUSIONS

We have performed a molecular simulation study of H₂O and CO₂ adsorption in zeolite 13X, a prototypical aluminosilicate zeolite that is commercially available. Our model is able to reproduce the trends in experimental isotherms for H₂O and CO₂ at different temperatures. Moreover, we were able to ascribe the steep rise in the H₂O isotherm to the relatively high desorption enthalpy at low loadings. Generally, H₂O tends to form an extensive hydrogen bond network and is even able to dislodge sodium cations from the zeolite framework surface and stabilize it in the center of the pore. CO₂ on the other hand does not have a large influence on the sodium cations but is also shows good structuring near saturation loading.

When a mixture of H₂O and CO₂ adsors, H₂O dominates and adsors near its pure component isotherm, which dramatically reduces the available adsorption sites for CO₂. At flue gas conditions, with a CO₂ and H₂O partial pressures of about 15 and 12 kPa respectively, water will likely be adsorbed near its saturation loading, and the CO₂ loading will be reduced by an order of magnitude.

In conclusion, this behavior dramatically reduces the utility of these materials for postcombustion capture and expensive drying operations may be required to allow 13X to provide sufficient CO₂ adsorption capacity.

## ASSOCIATED CONTENT

* Supporting Information Additional information and figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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**Author Contributions**

L.J. and J.A.S. contributed equally to this work.

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**Notes**

The authors declare no competing financial interest.

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## REFERENCES


