

Molecular Simulation Study of the Competitive Adsorption of H₂O and CO₂ in Zeolite 13X

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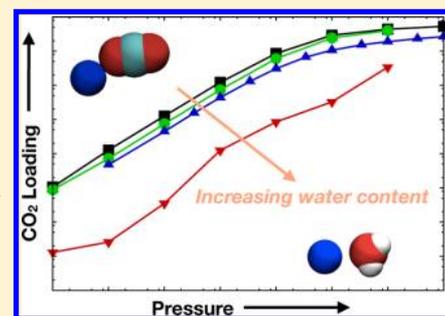
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S Supporting Information

ABSTRACT: The presence of H₂O in postcombustion gas streams is an important technical issue for deploying CO₂-selective adsorbents. Because of its permanent dipole, H₂O can interact strongly with materials where the selectivity for CO₂ is a consequence of its quadrupole interacting with charges in the material. We performed molecular simulations to model the adsorption of pure H₂O and CO₂ as well as H₂O/CO₂ mixtures in 13X, a popular zeolite for CO₂ capture processes that is commercially available. The simulations show that H₂O reduces the capacity of these materials for adsorbing CO₂ by an order of magnitude and that at the partial pressures of H₂O relevant for postcombustion capture, 13X will be essentially saturated with H₂O.



INTRODUCTION

Carbon capture and sequestration has been identified as a critical technology for reducing the impact of fossil fuel use on the concentration of CO₂ 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 CO₂ 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 CO₂ 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 CO₂ molecule, and CO₂/N₂ selectivities up to 300 are found in cation-exchanged zeolite frameworks.⁹

At the same time, these cations might interact strongly with water molecules^{9–11} 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 CO₂ adsorption is important because it could potentially reduce the capability of materials to selectively adsorb CO₂ efficiently enough for a practical process.

The adsorption of H₂O 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 H₂O and CO₂ on commercial 13X and 5A samples and noted that small amounts of water reduce the CO₂ capacity slightly. When water is adsorbed near its saturation loading, the CO₂ capacity is an order of magnitude lower than on the dry materials.^{15,16} Brandani and Ruthven studied the effect of water on CO₂ 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 CO₂.¹⁷ Finally, experiments by Ferreira et al.¹⁸ and Lee et al.¹⁹ also show that H₂O has a detrimental effect on the CO₂ 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 H₂O models in pure-silica zeolites and showed that the predicted isotherms were sensitive to the partial charges and crystal structure of the zeolite framework,²⁰ 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

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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 Bellat 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 adsorbs.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.^{30,31} Sodium atoms were placed randomly as counterions for the aluminum atoms 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 Bellat et al.^{24,25}

Figure 1 shows two views of the 13X framework through the 12-ring connecting the supercages (along the $\langle 111 \rangle$ 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, only showing the T-atom positions. The red circle in the center shows the center of one

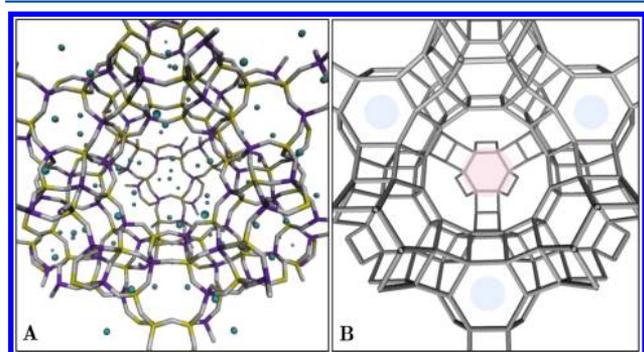


Figure 1. Views of the structure of 13X. (A) A view of the unit cell of 13X (NaFAU), Na positions taken from one configuration of a Monte Carlo simulation. Oxygen atoms are gray, silicon are yellow, aluminum are violet, and sodium are green. (B) Schematic representation of the FAU topology showing the connection between T-atom positions. The blue circles indicate the sodalite cages and the red one the center of the supercage.

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

Table 1. Lennard-Jones Parameters Used in This Work^a

	ϵ/k_b		σ		
	K	Å	K	Å	
C _{CO₂} -C _{CO₂}	29.933	2.745	O _{spce} -O _{spce}	78.197	3.1656
C _{CO₂} -O _{CO₂}	50.640	2.880			
O _{CO₂} -C _{CO₂}	85.617	3.017			
C _{CO₂} -O _{13X}	37.595	3.511	O _{spce} -O _{13X}	85.152	3.723
O _{CO₂} -O _{13X}	78.980	3.237			
C _{CO₂} -Na	362.292	3.320	O _{spce} -Na	564.881	3.361
O _{CO₂} -Na	200.831	2.758			

^aH₂O-framework and H₂O-Na interactions were parametrized by multiplying the SPC/E H₂O-H₂O parameters by the ratio of CO₂-framework to CO₂-CO₂ interactions or CO₂-Na to CO₂-CO₂ interactions reported by García-Sánchez et al.³²

modeled using the SPC/E model.³³ Finally, H₂O-framework and H₂O-Na interactions were parametrized by multiplying the H₂O-H₂O parameters by the ratio of CO₂-framework to CO₂-CO₂ interactions or CO₂-Na to CO₂-CO₂ interactions respectively. In this scaling, it is important to account for the fact that for water there is only an interaction for O₂, while for CO_{H₂O}, there are interactions for both C_{CO₂} and O_{CO₂}.

To illustrate our reasoning, we elaborate the determination of $\epsilon_{O_{13X}-O_{spce}}$ as an example. First, two ratios r_{ϵ_C} and r_{ϵ_O} are computed, representing the ratio of CO₂-framework to CO₂-CO₂ interactions for both C and O

$$r_{\epsilon_O} = \frac{\epsilon_{O_{13X}-O_{CO_2}}}{\epsilon_{O_{CO_2}-O_{CO_2}}} \quad (1)$$

$$r_{\epsilon_C} = \frac{\epsilon_{O_{13X}-C_{CO_2}}}{\epsilon_{C_{CO_2}-C_{CO_2}}} \quad (2)$$

The resulting multiplication factor is the average of the r_{ϵ_C} and r_{ϵ_O} ratio, so for $\epsilon_{O_{13X}-O_{spce}}$ this would give

$$\epsilon_{O_{13X}-O_{spce}} = \frac{1}{2}(r_{\epsilon_O} + r_{\epsilon_C})\epsilon_{O_{spce}-O_{spce}} \quad (3)$$

A similar reasoning was applied for the unknown σ and ϵ parameters in Table 1. Although the σ parameters for the H₂O-framework and H₂O-Na interactions are relatively large, this force field seems to reproduce the adsorption isotherm for H₂O in 13X very well (see below). However, these parameters may not be transferrable

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

Table 2. Saturation Vapor Pressure of Water from the Antoine Equation³⁴

<i>T</i> (K)	<i>P</i> _{vap} (kPa)
273	3.14
323	12.25
373	100.78

for water at the temperatures where the isotherm was simulated.³⁴ 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.¹⁵ In the Supporting Information, we show that the results also agree well with experimental data from Ferreira et al.¹⁸ and furthermore, we provide the plots on a linear scale. Note that the experiments were conducted on pelletized zeolite samples, but we assume that the influence of the binder is minimal.

Our simulations reveal three distinct regions in the H₂O isotherm. The Henry's law regime is situated at partial pressures well below 1 Pa, that are very difficult to obtain with experiments, as loadings are lower than one water molecule per unit cell. Second, we observe a sharp rise in the loading of water over a narrow pressure range. This behavior can be understood by considering the desorption enthalpy in function of the H₂O loading in Figure 2b. At low loadings, H₂O molecules have high desorption enthalpies (up to 78 kJ/mol), so in this region there is a large thermodynamical driving force for H₂O molecules to adsorb in the framework. This large value then quickly drops as more water molecules are present in the pores, affecting the slope of the adsorption isotherm. Third, there is a plateau region where a significant increase in partial pressure has only a small influence on the water loading. For a postcombustion process around 323 K, the H₂O partial pressure is about 12 kPa (see Table 2), which would place the equilibrium loading within this plateau regime.

Next, we consider GCMC simulations that provide insight into the arrangement of the cations and the H₂O molecules at

different loadings. We did not use the concept of crystallographic cation positions to analyze and report these arrangements, because this approach assumes that the cations are frozen during the simulations and since we observe big displacements of the cations, the idea is only of limited usefulness.^{25,24} Instead, we opted to provide histograms that in 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.³⁵ 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.³⁶ Another paper from the same group reports the cation migration in NaX when methanol is absorbed.³⁷

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 LeVan¹⁵ 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.^{7,9,18} 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

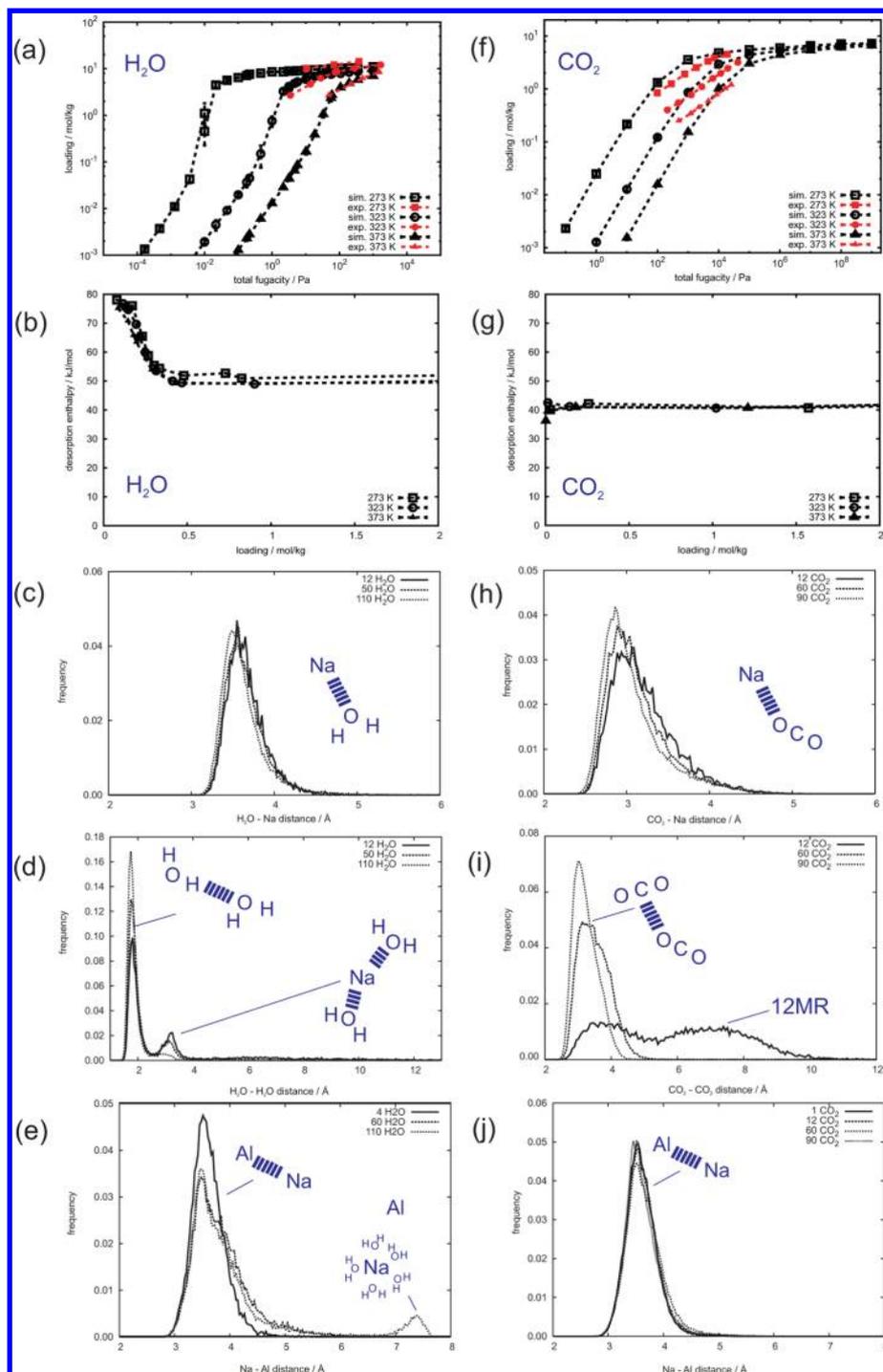


Figure 2. Pure component isotherms with experimental references¹⁵ (a,f), heats of desorption (b,g), and histograms providing an idea about the geometrical configurations (c–e,h–j) for H₂O and CO₂ adsorbing in zeolite 13X.

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 CO₂ at low loadings in our simulations. As the loading increases, the CO₂ molecules will be forced together and the interaction between CO₂ 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 CO₂ remains essentially the same. Compared to H₂O, CO₂ does not influence the positions of sodium atoms, indicating a weaker interaction between CO₂ and sodium. Although Plant et al. report in a theoretical study³⁸ that CO₂ 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 H₂O has a much stronger interaction with zeolite 13X than CO₂: 13X is more easily saturated with H₂O, the desorption enthalpies are significantly higher, and the H₂O 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 H₂O/CO₂ mixtures. Figure 3 shows the H₂O and CO₂ isotherms for a 1% H₂O in

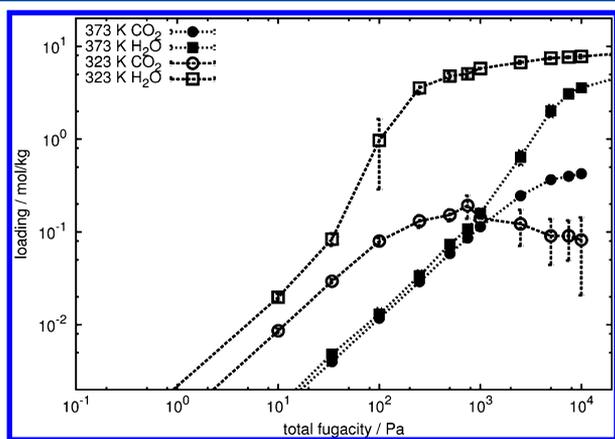


Figure 3. Mixture isotherms for a 99% CO₂, 1% H₂O mixture adsorbing in zeolite 13X at 323 and 373 K.

CO₂ 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 H₂O 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 CO₂ 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 CO₂ adsorption falls drastically.

To improve sampling of the CO₂ isotherms, we performed simulations where CO₂ was treated with GCMC moves and H₂O was treated with CMC moves. Figure 4 shows the adsorption isotherms for CO₂ at different total water loadings at 323 K. As expected, increasing the water loading reduces the equilibrium loading of CO₂ at all pressures. When 13X is near saturation loading (108 or 110 H₂O molecules per unit cell), the CO₂ uptake is more than an order of magnitude lower than for the pure CO₂ component. In the Supporting Information, the isotherms from Figure 4 are compared with experimental

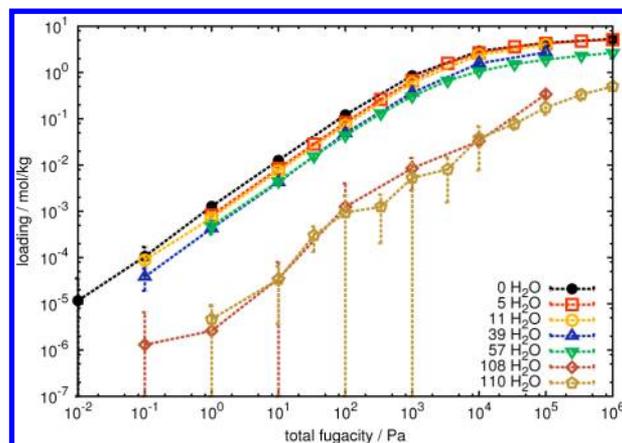


Figure 4. Adsorption isotherms for CO₂ in 13X with fixed loadings of water at 323 K. Water loadings are reported in molecules per unit cell. As the concentration of water in the material increases, the equilibrium CO₂ loading is reduced due to the occupation of pore volume and competition for coordination sites at the sodium cations.

isotherms measured by Wang et al.³⁹ There is a fair agreement at low water loadings, but a large discrepancy for the isotherm at 108 H₂O molecules per unit cell, which we were not able to explain.

To more effectively study the structure of the adsorbed solution of CO₂ and H₂O, NVT simulations were performed at different numbers of CO₂ and H₂O molecules. Figure 5 shows

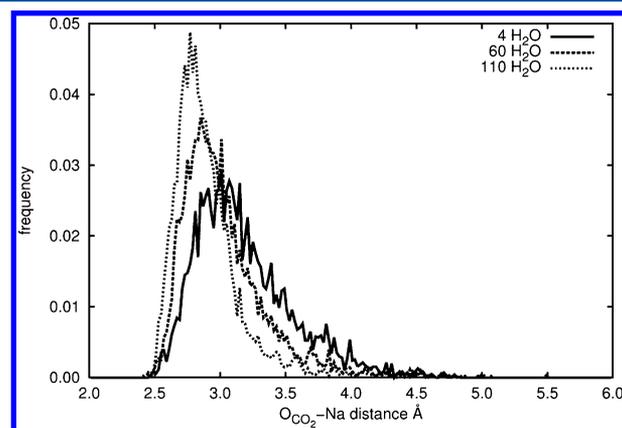


Figure 5. Histograms of O_{CO₂}-Na distances with different constant loadings of H₂O and 8 CO₂ per unit cell at 323 K.

the distribution of Na-O_{CO₂} distances at different H₂O loadings. The CO₂ loading was fixed at 8 molecules per unit cell. As with pure CO₂, the average distance between Na and the oxygen atom in CO₂ decreases. At the highest water loading, the most likely distance is smaller than for the pure CO₂ case (2.8 Å vs 3 Å). As the water hydrogen bonding network becomes more extensive, it is more favorable to force the CO₂ 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 CO₂ molecules per unit cell. The previously mentioned trend that it becomes more likely to find the H₂O molecules within hydrogen bond distance as the loading increases, does not seem to be disrupted by the presence of CO₂ molecules. The formation of a hydrogen bond

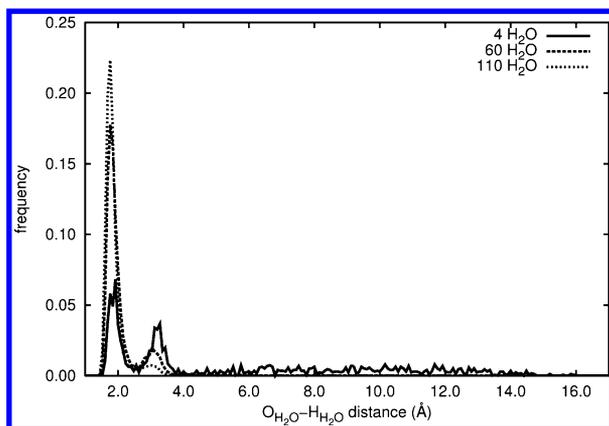


Figure 6. H₂O–H₂O distance histograms at different loadings of H₂O and 8 CO₂ per unit cell at 323 K.

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 adsorbs, H₂O dominates and adsorbs 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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Notes

The authors declare no competing financial interest.

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