The Impact of Sodium Cations on the Adsorption of Carbon Dioxide in Zeolites

Meghan Thurlow and Daniela Kohen
Carleton College, Northfield, MN

Introduction
Separation of CO$_2$ from multi-species gas emissions such as those found in coal-fired power plants or cars, requires a filter that selects CO$_2$ strongly relative to other components which are not hazardous to the environment such as N$_2$ gas. Zeolites, crystal-structured aluminosilicates, are currently being investigated as promising materials for separation of CO$_2$ due to their structural diversity and stability.

Increasing the magnitude of the electric field found within zeolites may increase their selectivity. We are investigating the impact of the electric field by examining the effect of substituting Al for Si in three purely siliceous zeolites: silicalite, ITQ-3, and ITQ-7 (see figure 1.) Understanding adsorption of CO$_2$ at the atomic level guides engineers to better potential structures as they use zeolites to curb CO$_2$ emissions into the atmosphere.
Silicalite  
Composition: SiO$_2$  
Density: 1.79 g/cm$^3$  
void space: 0.08 cm$^3$/g  
pore diameter: $\sim$5 Å

ITQ-3  
Composition: SiO$_2$  
Density: 1.63 g/cm$^3$  
void space: 0.11 cm$^3$/g  
pore diameter: $\sim$4 Å

ITQ-7  
Composition: SiO$_2$  
Density: 1.54 g/cm$^3$  
void space: 0.15 cm$^3$/g  
pore diameter: $\sim$6 Å

Figure 1. Structural components of each zeolite that will be examined in this research.

This research focuses on the computer simulation of adsorption rather than experimental analysis. Note that the validity of the simulation has been verified through careful comparison to available experimental data$^1$. The benefits of simulation over experiment include the following ideas:
Extreme experimental conditions (such as high temperature and pressure) can be easily modeled.

Measurement adsorption in the lab is challenging, particularly in multi-component gas mixtures.

Changes can be readily made to adjust for mistakes that become apparent during the simulation.

Imaginary scenarios, such as the absence of Van der Waals interactions, can be modeled to determine the importance of isolated interactions.

Background Research
Past investigations studied the adsorption of pure CO$_2$ and N$_2$ gases over a range of pressures using a Grand Canonical Monte Carlo (GCMC) simulation of all three zeolites. The results of that experiment revealed that CO$_2$ absorbed strongly relative to N$_2$ when the pure gases were exposed to the zeolites separately. This trend was seen in all 3 zeolites, though ITQ-3 showed the highest adsorption. (See figure 2.) More importantly, however was the selectivity of adsorption when the gases were exposed to the zeolites in a mixture. Remarkably, the zeolites showed extremely high selectivity for CO$_2$. The results confirm that zeolites are promising materials for the separation of carbon monoxide, but do not expose the reason that certain zeolites adsorb more than others with the same chemical formula. Further analysis reveals that the distinction in adsorption cannot be easily attributed to the more obvious physical properties such as pore size, density, and void space.
Taking further advantage of simulation techniques, the study reevaluated the adsorption of carbon dioxide neglecting all coulombic interactions. (See figure 3.) This revealed the importance of the coulombic interactions in the amount of adsorption seen in each zeolite. The results suggest that ITQ3’s greater adsorption must be attributable to greater coulombic interactions and therefore, larger charge separations within the zeolite.¹ This observation provides the premise for our current research project. We hope to further evaluate the importance of charge separations in zeolites by examining the same 3 zeolite structures, but with greater charges within the zeolite framework.
In order to increase coulombic interactions within the siliceous zeolites examined, aluminum atoms replaced existing silicons into the zeolite framework. The resulting charge deficiency was remedied by also adding sodium cations. (See figure 4.)

**Figure 3.** Single-Component Isotherm of each zeolite without Coulombic Interactions

**Current Research**

In order to increase coulombic interactions within the siliceous zeolites examined, aluminum atoms replaced existing silicons into the zeolite framework. The resulting charge deficiency was remedied by also adding sodium cations. (See figure 4.)
Figure 4. The substitution of aluminum for silicon in the zeolite structure. This creates a charge deficiency which must be compensated for by a sodium cation. The combined effect is to increase the coulombic interactions of the zeolite with the adsorbate molecule.

Aluminum substitution within silicalite occurs in very specific sites in the framework which have been well characterized. There are 12 structurally unequal sites within the most basic repeated unit, the periodic building unit, of silicalite. Substitution is most favored at site 12, but at higher aluminum densities, also occurs at the 9th and 2nd sites (see figures 5 and 6).

Figure 5. The periodic building unit of silicalite. At low concentrations of aluminum, the substitution occurs at the T-12 site.
Aluminum substitution sites within the ITQ-3 and ITQ-7 have not been characterized as well as those in silicalite. Initially, substitution into those frameworks will be done randomly; however it will be useful to investigate these structures using GCMC simulation to find the preferred sites.

Additionally, the impact sodium cation’s presence within the channels and pores of the zeolite structure is a point of contention. First, the sodium cation may compete with adsorbate molecules effectively reducing adsorption in spite of the larger electric field. Alternatively, the sodium cation may be positioned in areas of the zeolite that are not occupied by adsorbate molecules, and adsorption would be increased because of the increased electric field.

**Figure 6.** The preferred substitution sites in silicalite seen from 2 perspectives.
Both results were observed in a study where propane was the adsorbate molecule rather than CO$_2$ in two different zeolite frameworks; one can conclude that which trend you see is largely determined by independent channel and pore structures.$^2$

**Figure 7.** Propane adsorption in 2 zeolite structures with aluminum and sodium cations$^2$

Currently, we are in the process of modifying a code to make it compatible with sodium cations and the zeolite silicalite. The first stage of this process is to ensure that modified version of the code produces results that compare favorably with available experimental results and other simulations.
Future Research
Eventually, we hope to modify the finished version of the silicalite code to make it ITQ-3 and ITQ-7 compatible. We will explore the adsorption of CO$_2$ in bulk-mixture in all three zeolites. Finally, we plan to use GCMC simulation to characterize preferred sites of aluminum substitution in ITQ-3 and ITQ-7.

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References