

Predicting Large CO₂ Adsorption in Aluminosilicate Zeolites for Postcombustion Carbon Dioxide Capture

Jihan Kim,^{†,⊥} Li-Chiang Lin,^{‡,⊥} Joseph A. Swisher,^{†,‡} Maciej Haranczyk,[§] and Berend Smit^{*,†,‡,||}

[†]Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States

[‡]Department of Chemical and Biomolecular Engineering, University of California, Berkeley, California 94720, United States

[§]Computational Research Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States

^{||}Department of Chemistry, University of California, Berkeley, California 94720, United States

Supporting Information

ABSTRACT: Large-scale simulations of aluminosilicate zeolites were conducted to identify structures that possess large CO₂ uptake for postcombustion carbon dioxide capture. In this study, we discovered that the aluminosilicate zeolite structures with the highest CO₂ uptake values have an idealized silica lattice with a large free volume and a framework topology that maximizes the regions with nearest-neighbor framework atom distances from 3 to 4.5 Å. These predictors extend well to different Si:Al ratios and for both Na⁺ and Ca²⁺ cations, demonstrating their universal applicability in identifying the best-performing aluminosilicate zeolite structures.

Porous materials such as zeolites and metal–organic frameworks are seen as promising candidates for carbon capture from postcombustion gas streams because of their selective CO₂ adsorption and large capacities.^{1–5} Specifically in aluminosilicate zeolites, the addition of cations changes the adsorption properties of the zeolite structure in two important ways: (1) it creates stronger adsorption sites as a result of the additional interactions between the CO₂ molecules and the cations, and (2) it decreases the saturation uptake of CO₂ because of the reduction in the free volume. In the adsorption isotherm, the modification is reflected as an increase in the CO₂ uptake at low pressures and a decrease in the uptake at high pressures. For the purpose of postcombustion CO₂/N₂ separation, these property changes can present an attractive tradeoff.

There have been many experiments conducted on aluminosilicate zeolites that have shown significant uptake enhancement relative to the pure-silica zeolites.^{6–9} Moreover, there has been simulation work that can reproduce the experimental data on a few selected International Zeolite Association (IZA) zeolites with different Si:Al ratios.^{3,10,11} However, to the best of our knowledge, there is not a theory available that can tell us which properties of the pure-silica zeolites can lead to the best aluminosilicate zeolite structures. When referring to the “best” structures in this work, we use the pure-component CO₂ uptake at 0.15 bar as the quantity to be maximized, as this is of interest to the postcombustion CO₂ separations community.

In our simulations, we utilized grand canonical Monte Carlo (GCMC) simulations to obtain the CO₂ uptake values at different pressures.^{12–14} The aluminosilicate zeolite structures were generated by randomly replacing Si atoms with Al while adhering to Löwenstein’s rule.¹⁵ For the Na⁺ cations, all of the Lennard-Jones interaction parameters and atomic charges were taken from the force field of García-Sánchez et al.,¹⁰ which has been shown to be transferrable to multiple aluminosilicate zeolites with varying Si:Al ratios. For Ca²⁺, the same Lennard-Jones force field of García-Sánchez et al. was used, but the charge was doubled. The positions of the cations were generated in two different ways: (1) fixed cations, where the cations were inserted one by one into the unit cell at the global minimum energy configuration, and (2) moving cations, where the cations were allowed to move during the GCMC simulations. Allowing the cations to move is computationally expensive, however, as it takes a very long time for the cations and adsorbates to equilibrate.^{16–18}

Initially, we checked the accuracy of our predictions on the zeolites NaX, CaX, NaA, and CaA by comparing the results with data from other simulations and experiments [see the Supporting Information (SI)]. Overall for NaX, there was good agreement between our moving-cations simulation data and other reported adsorption isotherm data under same conditions.^{10,19} The fixed-cations method generally under-predicted the CO₂ loading for most pressure values; however, there was good enough agreement that the method can be considered to provide a conservative estimate of the CO₂ uptake for our screening purposes. For CaA and CaX, there was reasonable agreement between the fixed-cations method and the experimental data of Bae et al.,⁹ although the simulation parameters for Ca²⁺ were not optimized.

To identify the key structural predictors responsible for large CO₂ uptake in aluminosilicate zeolite structures, we utilized Zeo++²⁰ to obtain the helium free volume (FV) and the largest included free-sphere diameter (*D*) for the 190 IZA structures and the predicted zeolite set (i.e., PCOD) of over 130 000 structures.²¹ In searching for the predictors, we used the PCOD set instead of the IZA set, as having a larger number of structures at our disposal was more useful in establishing correlations. From the PCOD set, 400 zeolites were randomly

Received: October 4, 2012

Published: November 8, 2012

selected from an FV bin size of 50 cm³/kg. For these structures, 1:0 Si:Al (pure silica) was used to generate 3:1 and 1:1 Si:Al configurations along with minimum-energy fixed-cation positions. In all of the structures, the adsorption properties were computed at 300 K.

Figure 1a shows the average CO₂ uptake as a function of FV. For all of the pure-silica zeolites, we found that the CO₂ uptake

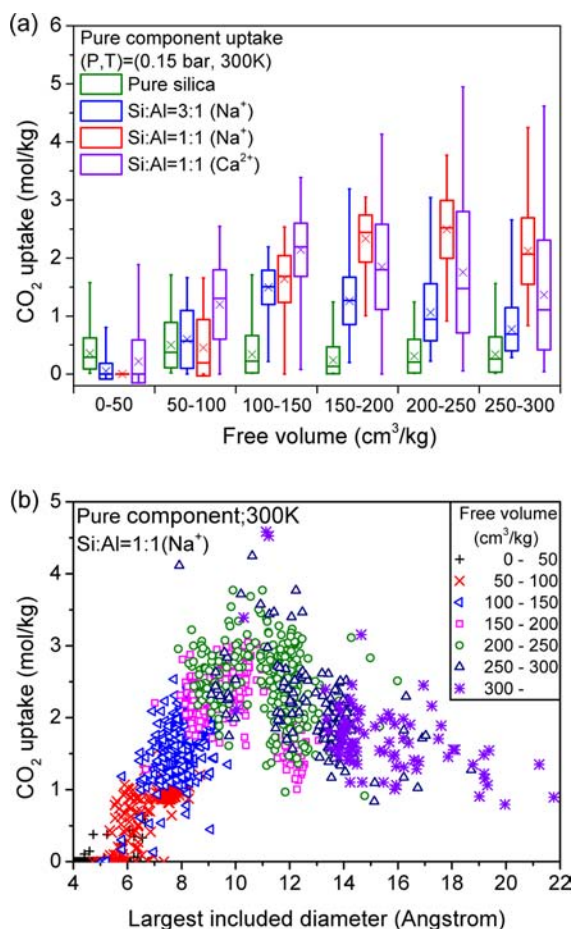


Figure 1. (a) Box plot of CO₂ uptake at 0.15 bar obtained from GCMC simulations for pure-silica (green), Si:Al = 3:1 (Na⁺) (blue), Si:Al = 1:1 (Na⁺) (red), and Si:Al = 1:1 (Ca²⁺) (purple) as a function of free volume for six FV intervals with 400 predicted zeolite structures per interval. Each box represents from lowest to highest the minimum, average minus one standard deviation, median, average plus one standard deviation, and maximum uptake. Cross symbols represent the average CO₂ uptake values. (b) CO₂ uptake as a function of D_i for the same set of predicted zeolite structures as in (a).

is nearly constant. On the other hand, for the 3:1 and 1:1 Si:Al aluminosilicate zeolite structures, the CO₂ uptake is close to zero for small FV, as the cations occupy all of the free space in the structure. For larger FVs, the stronger adsorption sites created by the addition of the cations coupled with the excess FV available for the CO₂ molecules enhance the CO₂ adsorption in these structures. However, when the FV becomes too large, only a small subset of the space is fully exploited, lowering the performance. Because there are more cations present in the 1:1 Si:Al Na⁺ materials than in 3:1 Si:Al Na⁺ materials, the CO₂ uptake for 1:1 Si:Al is higher for larger FVs and lower for smaller FVs. Comparison of Ca²⁺-exchanged zeolites and Na⁺ zeolites indicates that because of the larger

charge on the Ca²⁺ cations and the reduced number of cations, the CO₂ uptake is higher at smaller FVs for structures containing Ca²⁺.

The box plot in Figure 1a suggests that within the same FV bin, there are a large number of structures with similar uptake values and a few “outliers” that have significantly higher uptake. These outlier high-performing structures have higher FVs and specific topologies that allow for extraordinarily large CO₂ adsorptions. As such, these structures are not necessarily indicative of what is generally expected from the structures within the same FV bin. Overall, the CO₂ uptakes predicted for the best aluminosilicate zeolite structures are much higher than those for the best pure-silica idealized IZA zeolites.

The CO₂ uptake values are plotted as a function of D_i in Figure 1b for the same selected subset of the PCOD zeolite structures. Although D_i and FV are correlated, they are not exactly the same, as one can observe structures with large FV yet relatively small D_i and vice versa. Figure 1b reveals that the optimal D_i values are generally found in the range of 8 < D_i < 13 Å. Accordingly, although the data from Figure 1a indicates that the best aluminosilicate zeolite structures are located in the bins that have the largest FV, there needs to be an upper limit restriction put on the FV in terms of D_i . In structures that possess very large D_i values, the proportion of the FV regarded as strong adsorption sites decreases, resulting in lower CO₂ uptake.

Although FV and D_i are useful predictors that reduce the search space for the best structures, there are still a large number of structures with similar FV and D_i values that have a wide range of CO₂ loading values. For example, Figure 1b indicates that there are many structures within the optimal range of 8 < D_i < 13 Å with very low CO₂ uptake values. Subsequently, we examined the localized geometric features of each pure-silica zeolite structure to filter out the unpromising structures. To help with the analysis, a three-dimensional distance grid was superimposed on top of the unit cell of the pure-silica zeolite structure, with each grid point storing the distance to the nearest-neighbor framework atom (i.e., Si or O). From these values, the normalized probability distribution of all of the nearest-neighbor distances was obtained. In our analysis, two pure-silica zeolite structures (i.e., PCOD8163185 and PCOD8200816) were chosen to illustrate cases where two structures have similar FV and D_i values but very dissimilar CO₂ uptake values (4.25 and 2.00 mol/kg, respectively) in the Na⁺-added 1:1 Si:Al aluminosilicate zeolites. The solid lines in Figure 2a demonstrate that compared with PCOD8200816, PCOD8163185 contains a proportionally larger volume fraction of nearest-neighbor distances within the 3–4.5 Å range. The picture that emerges suggests that materials need to have such region, which leads to strong CO₂ – cations interactions. This can be seen from the plots of the probability distributions after the placement of Na⁺ cations in the two pure-silica structures. The new distribution curves (Figure 2a, dashed lines) indicate that the disparity between the cation-added PCOD8163185 structure and the cation-added PCOD8200816 structure has now shifted toward the range between 2.25 and 3.25 Å, which is where the strongest interaction between the Na⁺ cation and the CO₂ molecule is found, as shown in the Figure 2a inset. This suggests that we can quantify the quality of the material by integrating the area under the curve in the range between 3 and 4.5 Å and assign the value to each structure in the zeolite set. Figure 2b indicates that the largest CO₂ uptake is observed in aluminosilicate

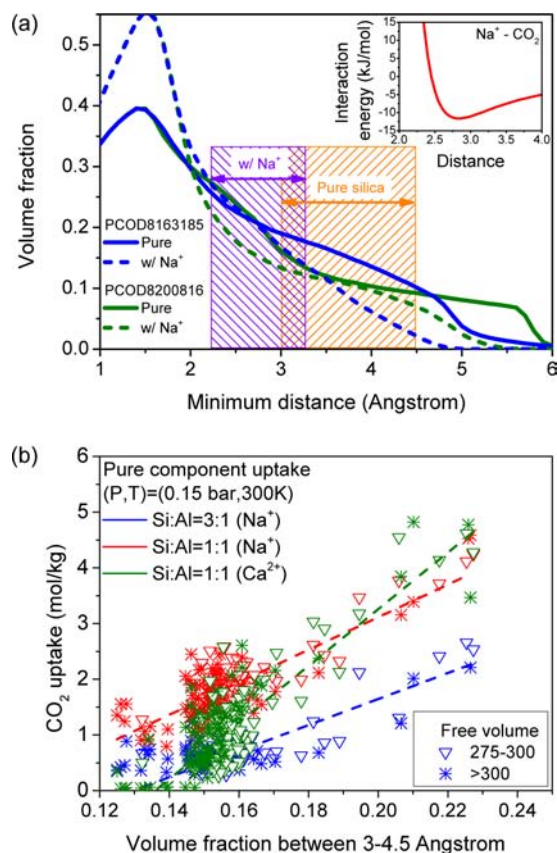


Figure 2. (a) Probability distribution of nearest-neighbor framework distances for the PCOD8163185 (blue) and PCOD8200816 (green) pure-silica zeolite structures (solid lines) and the structures with added Na⁺ cations (dashed lines). The relative fraction of the total volume between 3 and 4.5 Å is significantly larger for PCOD8163185, leading to higher uptake (4.25 mol/kg) relative to PCOD8200816 (2.00 mol/kg) in the aluminosilicate zeolite structures. The inset shows the Na⁺-CO₂ interaction energy (Lennard-Jones + Coulomb) as a function of the distance between Na⁺ and the closest O (CO₂) with the CO₂ and the Na⁺ aligned in a line. (b) CO₂ uptake as a function of the fraction of total volume between 3 and 4.5 Å for predicted zeolites with FV > 275 cm³/kg for Si:Al = 3:1 (Na⁺) (blue), Si:Al = 1:1 (Na⁺) (red), and Si:Al = 1:1 (Ca²⁺) (green). The three dashed lines show linear fits to the data sets presented here.

zeolite structures with high volume fractions between 3 and 4.5 Å in the pure-silica structures for both the 3:1 and 1:1 Si:Al structures with either Na⁺ or Ca²⁺ cations.

Utilizing the FV and the volume fraction between 3 and 4.5 Å in the pure-silica structure as predictors, we analyzed the IZA structures to study the use of our predictors for experimentally realized structures. According to Figure 3, we identified IZA structures such as SAO and RWY that may outperform more commonly studied structures such as FAU and LTA. To facilitate experimental efforts, we have summarized a list of promising IZA structures in the SI.

In conclusion, we have obtained simulated adsorption data for thousands of materials using an efficient algorithm that can quickly compute the adsorption properties of aluminosilicate zeolites. Our analysis indicates that the structures with the highest CO₂ uptake values possess both large free volumes and specific configurations of Si/O framework atoms that maximize the regions with nearest-neighbor distances between 3 and 4.5 Å. From the experimental and simulation points of view, this

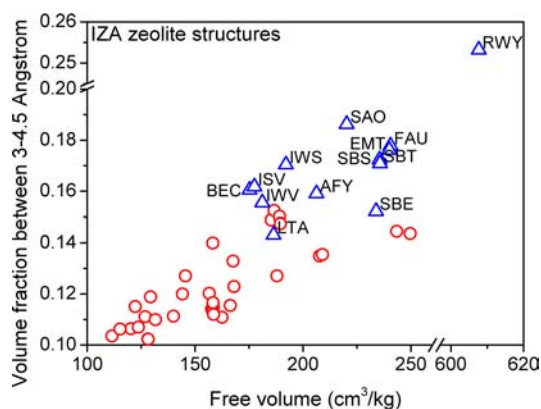


Figure 3. Fraction of total volume between 3 and 4.5 Å as a function of free volume for IZA structures with some highlighted structures in blue triangles.

finding significantly reduces the complexity in finding the most promising structures for CO₂ capture. Accordingly, we have discovered simple predictors that can allow us to determine a priori which pure-silica zeolite structures will provide the largest CO₂ uptake values for different Si:Al ratios and for different cation types. Our study has identified SAO and RWY as examples of promising IZA structures for aluminosilicate zeolites and has predicted that many other structures in the PCOD set potentially possess even higher CO₂ uptake abilities than any of the known zeolite structures. Our study allows us to rank all of the existing and hypothetical zeolite materials systematically. Of course, there are many factors (e.g., feasibility of forming aluminosilicate structures, cost, stability, diffusion coefficients, etc.) that determine whether a particular material will work in practice. Our ranking will be useful in guiding this selection process. In the future, we hope to extend this work by considering the presence of water, as it can influence the adsorption properties.

■ ASSOCIATED CONTENT

📄 Supporting Information

Experimental/simulation adsorption isotherm comparison, CO₂ uptake as a function of D_i for pure-silica and 3:1 Si:Al structures, correlation of loading between Ca and Na structures, tabulated predictor data for the promising IZA structures, and calculation of FV and D_i . This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

✉ Corresponding Author

Berend-Smit@berkeley.edu

✍ Author Contributions

[†]J.K. and L.-C.L. contributed equally.

📄 Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

J.K. and M.H. were supported by the Director, Office of Science, Advanced Scientific Computing Research, U.S. Department of Energy (DOE) under Contract DE-AC02-05CH11231 and, during the final stage of this work, by DOE under Contract DE-AC02-05CH11231 through the Carbon Capture Simulation Initiative (CCSI). M.H. was supported jointly by the DOE Office of Basic Energy Sciences (BES) and

the Office of Advanced Scientific Computing Research through SciDAC Project CSNEW918 entitled “Knowledge Guided Screening Tools for Identification of Porous Materials for CO₂ Separations”. L.-C.L. was supported by the Deutsche Forschungsgemeinschaft (DFG) Priority Program SPP 1570. J.A.S. was supported by the DOE Advanced Research Projects Agency—Energy (ARPA-E). B.S. was supported as part of the Center for Gas Separations Relevant to Clean Energy Technologies, an Energy Frontier Research Center funded by DOE BES under Award DE-SC0001015. This research used resources of the National Energy Research Scientific Computing Center, which is supported by the DOE Office of Science under Contract DE-AC02-05CH11231.

■ REFERENCES

- (1) Yaghi, O. M.; Keeffe, M.; Ockwig, N.; Hee, C.; Eddaoudi, M.; Kim, J. *Nature* **2003**, *423*, 708.
- (2) D'Alessandro, D. M.; Smit, B.; Long, J. *Angew. Chem., Int. Ed.* **2010**, *49*, 6058.
- (3) Lin, L.-C.; Berger, A.; Martin, R.; Kim, J.; Swisher, J.; Jariwala, K.; Rycroft, C.; Bhowan, A.; Deem, M.; Haranczyk, M.; Smit, B. *Nat. Mater.* **2012**, *11*, 633.
- (4) Krishna, R.; Van Baten, J. M. *Phys. Chem. Chem. Phys.* **2011**, *13*, 10593.
- (5) Düren, T.; Bae, Y.-S.; Snurr, R. Q. *Chem. Soc. Rev.* **2009**, *38*, 1237.
- (6) Hudson, M.; Queen, W.; Mason, J.; Fickel, D.; Lobo, R.; Brown, C. *J. Am. Chem. Soc.* **2012**, *134*, 1970.
- (7) Zhang, J.; Singh, R.; Webley, P. *Microporous Mesoporous Mater.* **2008**, *111*, 478.
- (8) Pires, J.; de Carvalho, M. B.; Ribeiro, F. R.; Derouane, E. G. *J. Mol. Catal.* **1993**, *85*, 295.
- (9) Bae, T.-H.; Hudson, M. R.; Mason, J. A.; Queen, W. L.; Dutton, J. J.; Sumida, K.; Micklash, K. J.; Kaye, S. S.; Brown, C. M.; Long, J. R. *Energy Environ. Sci.* **2012**, DOI: 10.1039/C2EE23337A.
- (10) García-Sánchez, A.; Ania, C. O.; Parra, J. B.; Dubbeldam, D.; Vlucht, T. J. H.; Krishna, R.; Calero, S. *J. Phys. Chem. C* **2009**, *113*, 8814.
- (11) García-Sánchez, A.; van den Bergh, J.; Castillo, J. M.; Calero, S.; Kapteijn, F.; Vlucht, T. J. H. *Microporous Mesoporous Mater.* **2012**, *158*, 64.
- (12) Kim, J.; Martin, R. L.; Rubel, O.; Haranczyk, M.; Smit, B. *J. Chem. Theory Comput.* **2012**, *8*, 1684.
- (13) Smit, B.; Maesen, T. *Chem. Rev.* **2008**, *108*, 4125.
- (14) Smit, B.; Frenkel, D. *Understanding Molecular Simulations: From Algorithms to Applications*, 2nd ed.; Academic Press: San Diego, 2002.
- (15) Löwenstein, W. *Am. Mineral.* **1954**, *39*, 92.
- (16) Mellot-Draznieks, C.; Buttefey, S.; Boutin, A.; Fuchs, A. H. *Chem. Commun.* **2001**, 2200.
- (17) Buttefey, S.; Boutin, A.; Mellot-Draznieks, C.; Fuchs, A. H. *J. Phys. Chem. B* **2001**, *105*, 9569.
- (18) García-Pérez, E.; Dubbeldam, D.; Liu, B.; Smit, B.; Calero, S. *Angew. Chem., Int. Ed.* **2007**, *46*, 276.
- (19) Dunne, J. A.; Rao, M.; Sircar, S.; Gorte, R. J.; Myers, A. L. *Langmuir* **1996**, *12*, 5896.
- (20) Wilems, T. F.; Rycroft, C. H.; Kazi, M.; Meza, J. C.; Haranczyk, M. *Microporous Mesoporous Mater.* **2012**, *149*, 134.
- (21) Pophale, R.; Deem, M. W.; Cheeseman, P. A. *Phys. Chem. Chem. Phys.* **2011**, *13*, 12407.