Supporting Information:

Predicting Large CO_2 Adsorption in Aluminosilicate Zeolites for Post-combustion Carbon Dioxide Capture

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Section 1: Comparison between experimental[1,2,3,4] and simulated CO_2 uptake in the aluminosilicate zeolite structure.

Figure SI 1 shows the simulated results in NaX for both moving cations and fixed cations. Figure SI 2 illustrates that by using the non-optimized force field parameters of Ca^{2+}, there can be good agreement between experimental and simulation adsorption isotherm curves for CaA and CaX.

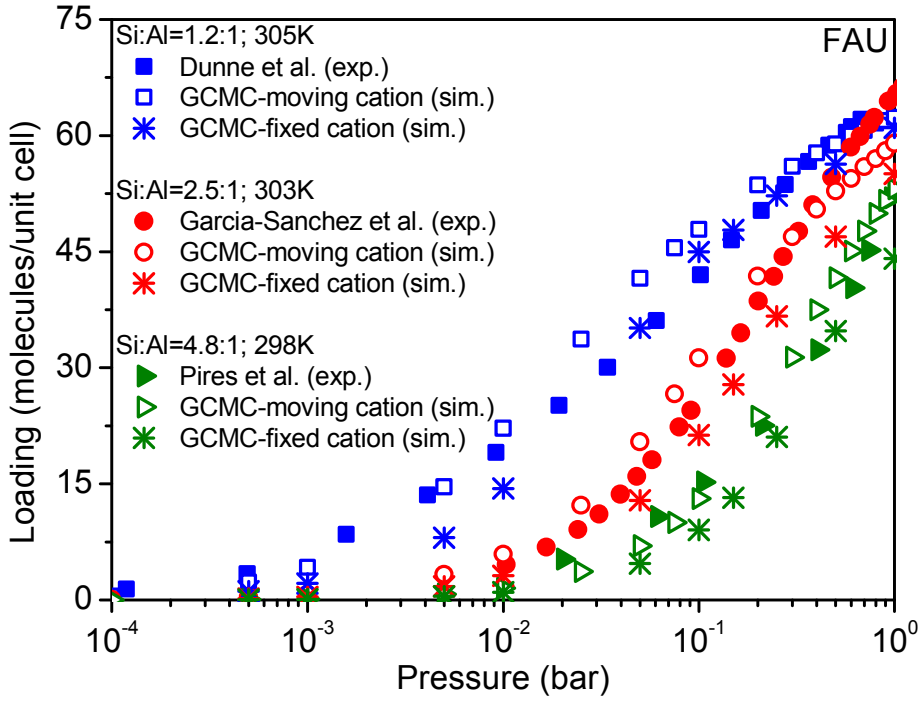

Figure SI 1: Comparison of the experimental and simulated isotherm in aluminosilicate zeolite (Na) FAU with different Si/Al ratio. Both simulated categories: moving and fixed cation show generally good agreement with the experiment data. [1,2,3] The result with fixed cation shows lower uptake than the moving one, which provides a conservative prediction of loading in our study.

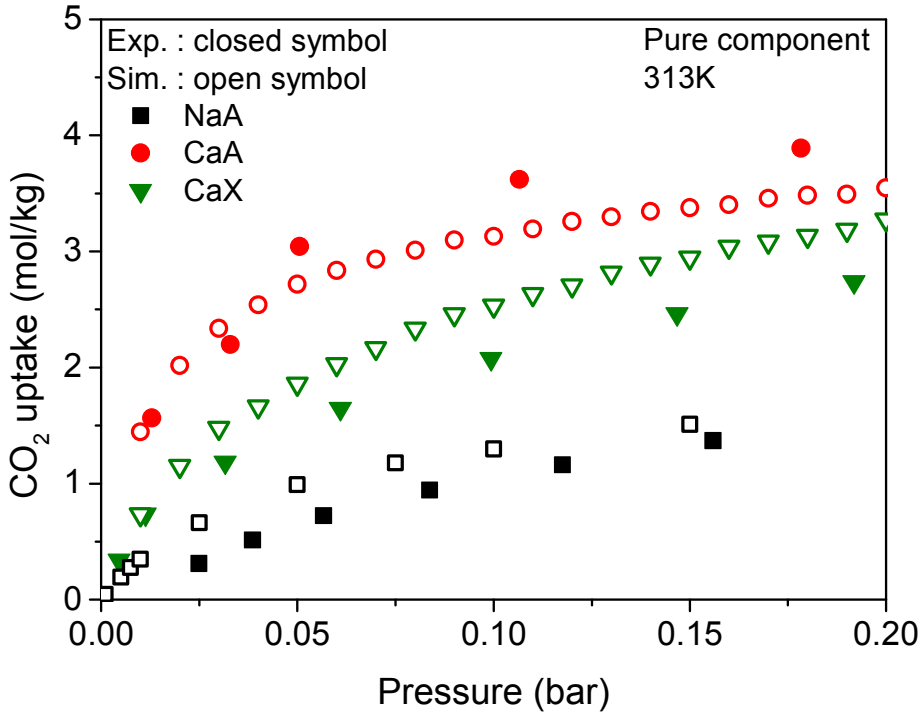

Figure SI 2: Comparison simulation isotherm with experimental data reported by Bae et al.[4] in NaA (black), CaA (LTA) (red), and CaX (FAU) (green). Calcium is further exchanged with the sodium in Si:Al=1:1 aluminosicliate zeolite structure to obtain CaA and CaX with the exchanged ratio to be 72% and 93%, respectively. The closed symbol represents the experimental data and the open symbol shows the simulated result.

Section 2: CO_2 uptake as a function of largest included diameter for different ratio of Si/Al.

The CO_2 uptake values as a function of the largest included diameter for Si/Al= 1 aluminosilicate structures has been provided in the manuscript. Here we provide similar data for pure silica structure and Si/Al=3 aluminosilicate structures (Na^+).

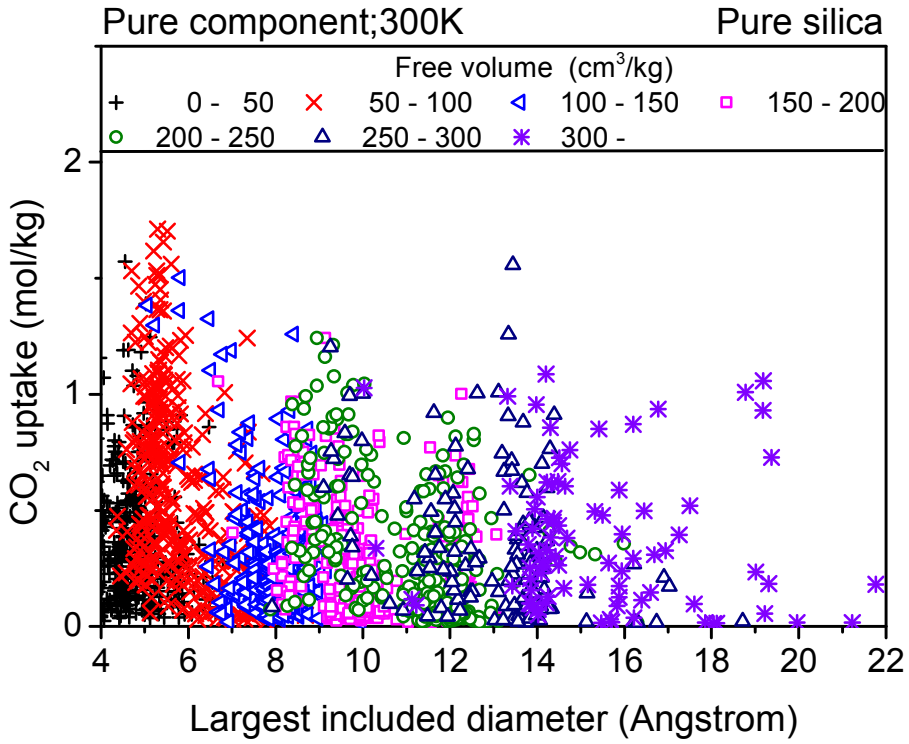

Figure SI 3: Pure component CO_2 uptake at 0.15 bar and 300K for pure silica zeolite as a function of largest included diameter grouped by similar free volume.

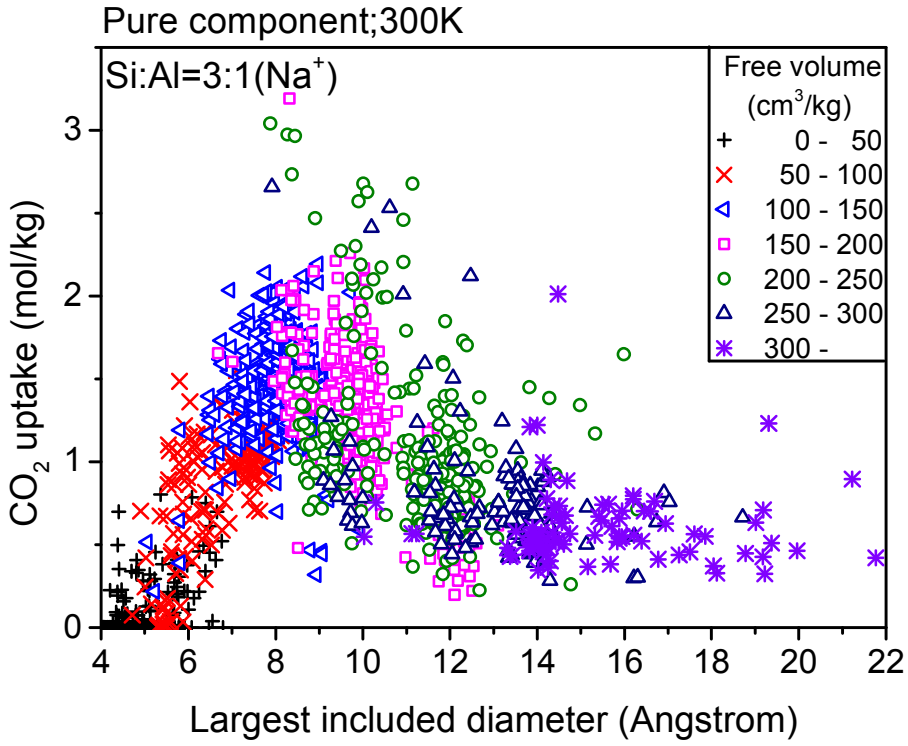

Figure SI 4: Pure component CO_2 uptake at 0.15 bar and 300K for aluminosilicate zeolite (Na^+) with Si:Al=3:1 as a function of largest included diameter grouped by similar free volume.

Section 3: Correlation between the CO_2 uptake for Ca^{2+}- and Na^{+}- aluminosilicate structures.

Figure SI 5 shows the correlation between the ratio of CO_2 uptake of Ca^{2+} to Na^{+} structures and the free volume. The Figure indicates that the Ca^{2+}-exchanged structures generally tend to have higher (lower) uptake compared to the Na^{+} structures for the structures with smaller (larger) free volume. However, even at higher free volume, the top Ca^{2+} structures still can outperform the top Na^{+} structures as shown in Figure SI 6.

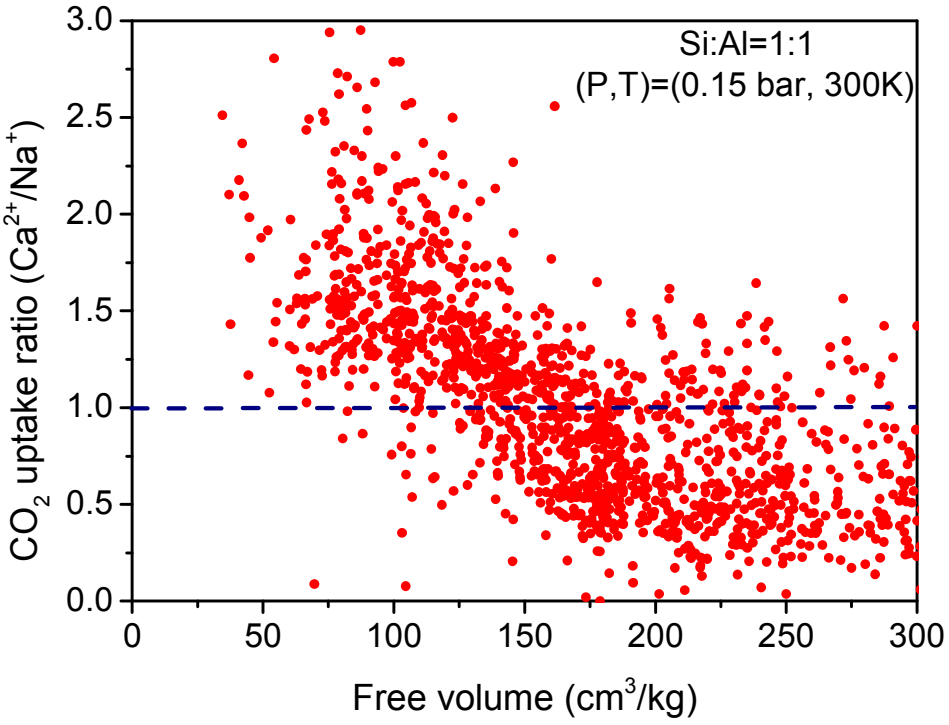

Figure SI 5: Ratio of CO_2 uptake at 0.15 bar and 300K for Ca- and Na- aluminosilicate zeolites with Si:Al=1:1 as a function of the free volume. The blue dashed line represents the points in which loading are the same in both type of structures.

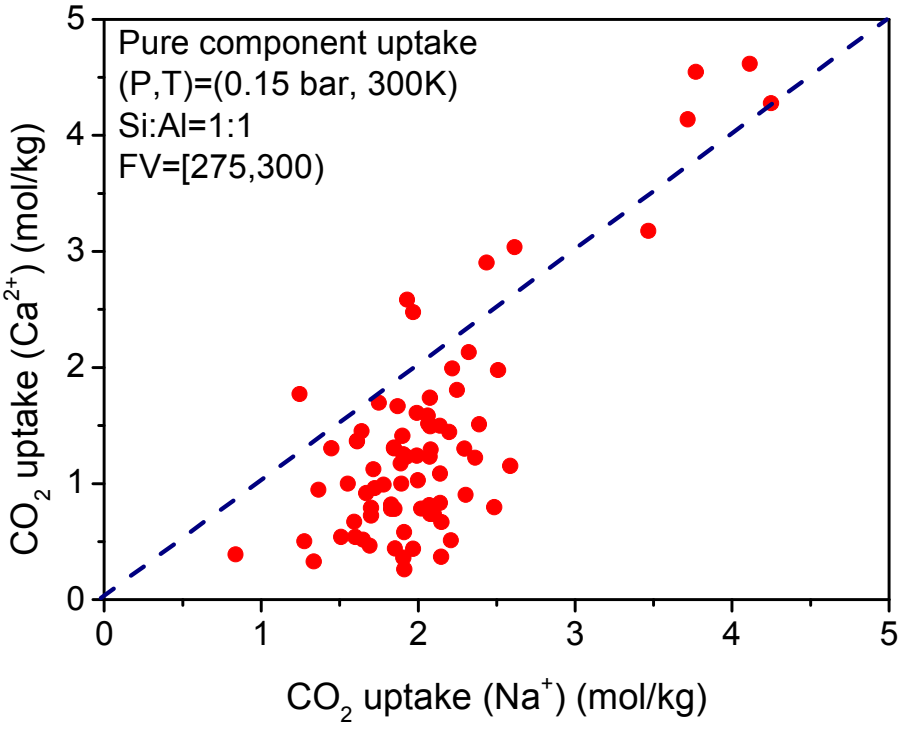

Figure SI 6: CO_2 uptake of Ca- vs. Na- aluminosilicate zeolite structures with Si:Al =1:1 at 0.15 bar and 300K. All of the structures present here have free volume be in the range of 275 to 300 cm^3/kg. The blue dashed line represents the points where loading are the same in both type of structures.

Section 4: Summary of promising IZA structures.

Within all the known zeolite structures (IZA), we listed the top 20 free volume structures with their corresponding value of the fraction of the total volume between 3.0 and 4.5 Angstroms. In order to facilitate the experimental efforts, these structures are recommended to be examined with higher priority.

Table 1: Top 20 free volume IZA structures and their fraction of the total volume with the min. distance from the framework atoms between 3.0 and 4.5 Angstrom.

Structure	Free volume (cm^3/kg)	Fraction of total volume between 3.0 and 4.5 Angstrom
BEC	175.3	0.161
ISV	177.5	0.162
IWV	181.1	0.156
DFO	185.3	0.149
LTA	186.4	0.143
MEI	186.7	0.152
RHO	188.0	0.127
AFS	189.1	0.150
BPH	189.5	0.147
IWS	192.1	0.170
AFY	206.7	0.159
VFI	207.7	0.135
OSO	209.0	0.136
SAO	220.2	0.187
SBE	233.8	0.153
SBS	235.5	0.173
SBT	235.7	0.171
EMT	240.0	0.176
FAU	240.5	0.178
OBW	243.4	0.145
TSC	249.6	0.144
RWY	607.7	0.253

Section 5: Calculations of free volume (FV) and largest included free-sphere diameter (D_i).

Calculation of the employed descriptors of the void space, D_i and FV, is based on our algorithms implemented in Zeo++ package.[5] Our tools are based on the Voronoi decomposition, which for a given arrangement of atoms in a periodic domain provides a graphic representation of the void space. When performing a Voronoi decomposition, the space surrounding n points is divided into n polyhedral cells such that each of their faces lies on the plane equidistant from the two points sharing the face. Edges of such cells overlap with lines equidistant to neighboring points (three points in a general asymmetric case), whereas vertices of cells, the Voronoi nodes, are equidistant from neighboring points (four points in a general asymmetric case). The Voronoi network, built of such nodes and edges, maps the void space surrounding the points. Analysis of such a network is fairly straightforward and can provide detailed information about void space geometry and topology. The largest included sphere (D_i) for a given structure is simply the largest distance assigned to the Voronoi nodes. The algorithm iterates over all Voronoi nodes in a periodic unit cell of a structure and finds the node with the largest distance to a neighboring atom. Accessibility of nodes in the Voronoi network is also determined for a given guest molecule (helium probe, radius of 1.2 Angstroms) and the resulting information is later used in Monte Carlo sampling of accessible free volume. Please refer to the reference 5 for more detailed explanation of the calculation.

Reference

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