

Supporting Information for

First Principles Derived, Transferable Force fields for CO₂ Adsorption in Na-Exchanged Cationic Zeolites

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DFT Calculation Details

Periodic DFT calculations were performed using VASP,^{1, 2} where electron-ion interactions were described with the projector augmented wave (PAW) formalism.^{3, 4} For valence electrons a plane wave basis set was applied with an energy cutoff of 400 eV. A single *k*-point centered at the Γ -point of the unit cell was used, and geometry optimizations were converged until forces were smaller than 0.03 eV/Å. The PBE-D2⁵ method was used for geometry optimizations and DDEC (density derived electrostatic and chemical) was used for charge calculations for Na-exchanged zeolites.⁶⁻⁹ For interaction energies between CO₂ and zeolites, both PBE-D2 and DFT/CC¹⁰ methods were used and compared with each other. The correction functions in the DFT/CC method are taken from previous calculations, which were developed specifically for CO₂ adsorption in zeolites.¹¹

GCMC Simulation Models and Methods

For LTA-4A, the XRD determined structure by Pluth and Smith was adopted in the GCMC simulations.¹² The zeolite model has a cubic crystal structure with lattice constants of 24.555 Å and composition Na₉₆Al₉₆Si₉₆O₃₈₄. The Si/Al ratio is 1, and the framework Si and Al atoms appear alternatively. There are 64 cations in the center of six-membered ring window, 24 cations in the eight-membered ring window, and 8 cations opposite the four-membered ring window.

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NaX and NaY both have the FAU topology but with different Si/Al ratios and Na contents. The Si/Al ratios we investigate are 1.23 for NaX and 2.37 for NaY, and the corresponding compositions for one unit cell are $\text{Na}_{86}\text{Al}_{86}\text{Si}_{106}\text{O}_{384}$ and $\text{Na}_{57}\text{Al}_{57}\text{Si}_{135}\text{O}_{384}$, respectively. Like previous study of alkane adsorption,¹³ the FAU-type framework structure was taken from the experimental X-ray diffraction study of NaX by Olson.¹⁴ The crystalline structure is described in the Fd3 space group and the cubic lattice parameter is 25.099 Å. Zeolite structures with lower framework aluminum densities were obtained by randomly substituting Al by Si. This procedure automatically obeys the Löwenstein rule.

For NaY structures, the initial sodium positions are taken from the XRD experiment by Eulenberger et al., i.e. 8 cations in site I, 19 in site I', and 30 in site II.¹⁵ For NaX structures, the initial sodium positions are determined based on the experimental¹⁴ and simulated^{16,17} results, i.e. 32 cations in site I', 32 in site II, and 22 in site III'. Because the exact distributions of Al atoms are unknown for both NaX and NaY, we generated three structures with different Al distributions for each material. The simulation results show that the CO₂ adsorption properties in these Na-exchanged FAU zeolites are not sensitive to the Al distribution, and this conclusion is consistent with studies of alkane adsorption.^{18,19} For simulated adsorption isotherms and heats of adsorption, we report average values with error bars (i.e., standard deviations) for three different Al distributions. The standard deviation is a measure of how widely values are dispersed from the average value and defined as

$$\sigma = \sqrt{\frac{\sum (x - \bar{x})^2}{n - 1}} \quad (1)$$

where x is loading or heat of adsorption, \bar{x} is the average value, and n is the number of the zeolite models.

The MUSIC code was employed for the GCMC simulations,²⁰ where vdW interactions were evaluated with the cutoff of 12 Å, and electrostatic energies were calculated using Wolf summation^{21,22} with a relative error of 10⁻⁶. It was reported that in zeolites and aluminosilicate nanotubes, Wolf method could give similar adsorption or diffusion results with respect to the conventional (but more computationally expensive) Ewald summation.^{23,24} Periodic boundary conditions were employed. 1×10⁷ steps were used to guarantee equilibration, and the following 1×10⁷ steps were used to sample the desired thermodynamics properties. During the simulations all framework atoms were fixed at their crystallographic positions while cations were allow to move. CO₂ molecules were not allowed to adsorb inside the sodalite cages of LTA and FAU zeolites in our simulations.

Isosteric heats of adsorption, Q_{st} , defined as the difference in the partial molar enthalpy of the adsorption between the gas phase and the adsorbed phase, were obtained during GCMC simulations using²⁵

$$Q_{st} = RT - \frac{\langle NV \rangle - \langle N \rangle \langle V \rangle}{\langle N^2 \rangle - \langle N \rangle^2} \quad (2)$$

where T is the temperature, R is the gas constant, $\langle \rangle$ denotes the ensemble average, N is the number of adsorbed molecules, and V is the sum of the interactions of all adsorbed molecules among themselves and with the zeolite.

Table S1 Force Field Parameters Derived Based on the 200 Randomly Generated CO₂ Configurations (R200) and 100, 200, 300 Configurations from GCMC Simulations (G100, G200, and G300).

Cross species	R200		R200 + G100		R200 + G200		R200 + G300	
	ϵ (K)	σ (Å)	ϵ (K)	σ (Å)	ϵ (K)	σ (Å)	ϵ (K)	σ (Å)
Na-C	44.41	2.948	57.86	2.880	66.30	2.841	66.78	2.827
Na-O	36.42	2.823	47.45	2.758	54.37	2.720	54.76	2.707
Al-C	21.42	3.510	27.91	3.429	31.98	3.382	32.21	3.366
Al-O	16.84	3.385	21.94	3.307	25.14	3.262	25.32	3.246
s_{12}	1.314		1.292		1.258		1.195	
s_6	0.307		0.347		0.366		0.358	
MD ^a	0.7		0.5		0.4		0.4	
MAD ^a	3.3		3.1		2.8		2.8	

^a Mean deviation (MD) and mean absolute deviation (MAD) are calculated by comparing the interaction energies from the fitted force fields and DFT/CC method, in kJ/mol.

From Table S1, it can be seen that a total of 300 CO₂ configurations from GCMC simulations plus the original 200 random configurations give converged force field parameters. More specifically, the changes of ϵ_{ij} and σ_{ij} values are within 1%, and the predicted isotherms and heats of adsorption are not influenced significantly by the change of these parameters.

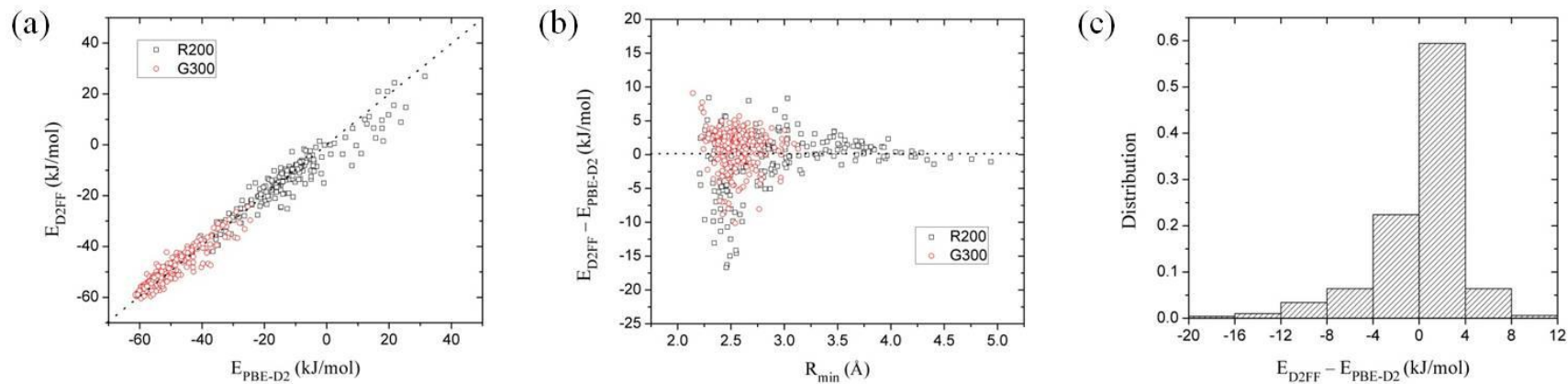


Figure S1. (a) Comparison of the interaction energies of CO₂ in LTA-4A zeolite for the D2FF and PBE-D2, (b) the difference in interaction energies ($E_{D2FF} - E_{PBE-D2}$) as a function of the nearest interatomic distance between CO₂ and LTA-4A, and (c) distribution of ($E_{D2FF} - E_{PBE-D2}$) for all 500 CO₂-zeolite configurations. The black squares are the 200 randomly generated CO₂ configurations (R200) and the red circles are the 300 CO₂ configurations from GCMC simulations (G300).

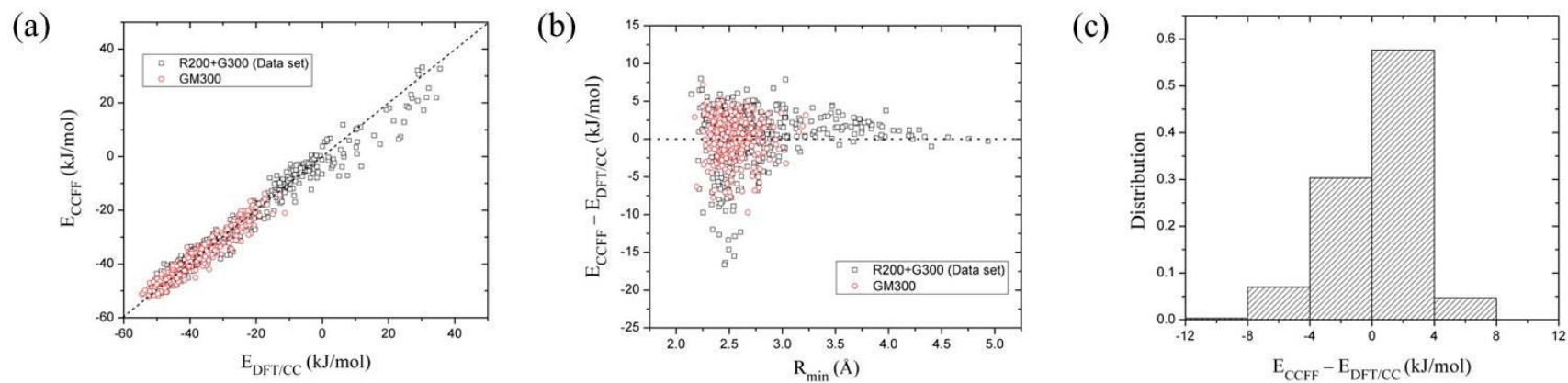


Figure S2. Validation of the CCFF for 300 CO_2 configurations from GCMC simulations where cations are allowed to move (GM300, red circles), (a) comparison of the interaction energies of CO_2 in LTA-4A zeolite for the DFT/CC and CCFF force field, (b) the difference in interaction energies ($E_{\text{CCFF}} - E_{\text{DFT/CC}}$) as a function of the nearest interatomic distance between CO_2 and LTA-4A, and (c) distribution of ($E_{\text{CCFF}} - E_{\text{DFT/CC}}$) for the GM300 configurations. It should be noted that the GM300 configurations are not included in the data set (R200 + G300, black squares) used for force field fitting.

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