

Transferable Force Field for Carbon Dioxide Adsorption in Zeolites

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We have developed a complete force field that accurately reproduces the adsorption properties of carbon dioxide in a variety of zeolites with different topologies and compositions. The force field parameters were obtained by fitting to our own experimental data and validated with available data taken from the literature. The novelty of this force field is that it is fully transferable between different zeolite framework types, and therefore, it is applicable to all possible Si/Al ratios (with sodium as extra-framework cation) and for the first time affording the prediction of topology-specific and chemical composition-specific adsorption properties.

Introduction

The prediction of carbon dioxide adsorption on porous materials is of crucial importance today for several reasons, from the need to develop cost-efficient CO₂ capture technologies that allow us to slow down the consequences of climate change to the improvement of gas separation processes of industrial interest (i.e., natural gas cleaning, CO₂ storage, separation from other gases generated in coal combustion, etc.). Carbon dioxide adsorption and separation using a variety of porous solids has received much attention in the last decades, the most common adsorbents being activated carbons and zeolites.

Among the porous materials, zeolites are considered as effective structures for the adsorption and selective separation of carbon dioxide. This is due to their thermal stability and their regular porous structure along with their large internal surface area.^{1–8} In addition to traditional adsorbents, recent novel porous adsorbents such as metal-organic frameworks (MOFs) are emerging as promising materials for carbon dioxide capture.^{9–16}

From an experimental point of view, the pressure, temperature, and moisture content seem to be the most important operating conditions that influence the adsorption of carbon dioxide.² As in most gas–solid systems, high gas phase pressures and low temperatures favor carbon dioxide adsorption on porous solids; however, the adsorption efficiency strongly depends on the zeolite type and composition.^{17–23} For instance, at low pressure, the amount of CO₂ adsorbed appears to be highly influenced by the nature and density of the cations inside the zeolite pores,^{5,24,25} whereas the pore shape and volume appear to control the adsorption capacity at high pressures.^{2,26} Zeolites are molecular sieves with a three-dimensional framework structure of alumina or silica tetrahedra whose negative charge is compensated by cations such as sodium to maintain electro-neutrality. The nature, number, and distribution of the extra-framework cations affects the basicity and electric field in the

cavities of zeolites. These properties tend to vary inversely with the Si/Al ratio of the framework. The charge imbalance due to the presence of aluminum in the framework determines the ion exchange properties of zeolites and induces potential acidic sites. As the Si/Al ratio increases, the cation content decreases, the thermal stability increases, the nature of the surface changes from hydrophilic to hydrophobic, and the zeolite loses its ion exchange or catalytic properties.

Molecular simulations are currently a powerful tool to accurately predict adsorption^{27–29} and diffusion³⁰ processes in zeolites, but efficient methods^{31–33} and good force fields capable of reproducing ideal experimental conditions for all zeolites^{5,26,34–36} are vital for this purpose. A variety of works reporting force fields for carbon dioxide in zeolites can be found in the literature, most of them only applicable to all-silica structures,^{37–40} i.e., with Si/Al = ∞. In contrast, there are only three sets of force field parameters available for CO₂ adsorption in zeolites containing aluminum atoms and sodium non-framework cations. Two of these sets were developed for the LTA4A zeolite,^{41,42} and the third set, for faujasites.⁴³ Unfortunately, it turns out that none of these force fields is transferable between different zeolite framework types and Si/Al ratios.

We have developed a new force field that (1) accurately reproduces carbon dioxide adsorption in zeolites, (2) is transferable to all zeolite structures, and (3) is applicable to Si/Al ratio that spans from unity (i.e., maximum aluminum substitution) to infinity (i.e., all-silica structure), using sodium atoms as extra-framework cation. In this paper, we first discuss the methodology for the development of the force field and, second, compare the results obtained using the new set of parameters with those obtained using previous sets reported in the literature.

Methodology

The development of our force field requires (1) models for adsorbents and adsorbates and interatomic potentials, (2) experimental isotherms for the fitting and a posteriori validation, and (3) an optimization of parameters using Monte Carlo simulations in combination with the Downhill Simplex Method.

Models and Simulation Techniques. Zeolites were built from silicon, aluminum, and oxygen atoms using their crystal-

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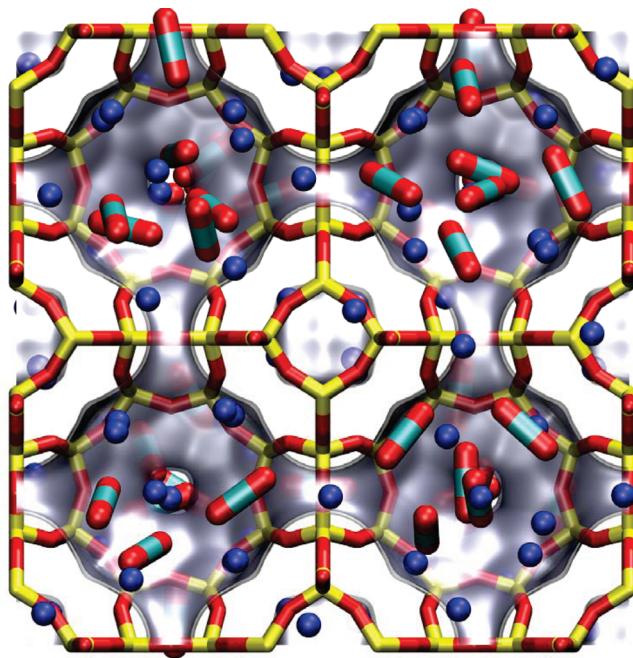


Figure 1. Snapshot showing the adsorption of carbon dioxide in LTA4A with 96 sodium cations per unit cell at 10^4 Pa and 298 K.

lographic positions. LTA4A ($\text{Na}_{96}\text{Al}_{96}\text{Si}_{96}\text{O}_{384}$) and FAU ($\text{Na}_x\text{Al}_x\text{Si}_{192-x}\text{O}_{384}$, $96 \geq x \geq 0$) have a cubic unit cell dimension of 24.555 and 25.028 Å, respectively.^{44,45} FAU-type zeolites have been labeled either X or Y, depending on their framework aluminum density. Zeolite X has a framework aluminum density between 96 and 77 aluminum atoms per unit cell, whereas zeolite Y contains fewer than 77 framework aluminum atoms per unit cell. The precise crystallographic location of some sodium cations remains uncertain for NaX and NaY.^{46,47} In contrast, there appears to be general agreement for LTA4A in which the sodium cations in the bare zeolite are distributed among three crystallographic sites: in the center of the six-membered ring (97.2% occupation), in the eight-membered ring windows (24.2% occupation), and opposite the four-membered rings (6.6% occupation).⁴⁴ The cation positions are modified with carbon dioxide adsorption as we show in the snapshots in Figure 1 for a pressure of 10^4 Pa and 298 K. MOR ($\text{Na}_x\text{Al}_x\text{Si}_{48-x}\text{O}_{96}$, $8 \geq x \geq 0$) and MFI ($\text{Na}_x\text{Al}_x\text{Si}_{96-x}\text{O}_{192}$, $0 \geq \text{Si}/\text{Al} \geq 8$) are structures consisting of interconnected channels. MOR is formed by channels parallel to the [001] direction that are connected with small side channels parallel to the [010] direction, with cross sections called side pockets.⁴⁸ On the other hand, MFI is formed by straight, parallel channels intersected by zigzag channels.⁴⁹ Four (MOR) and 12 (MFI) distinct crystallographic T sites ($T = \text{Si}, \text{Al}$) can be identified for these structures influencing the sodium cation distribution.

The zeolite structure is considered rigid, as previous studies demonstrated that flexibility of the framework has a minor effect on the adsorption of small molecules for the range of temperatures considered in this work.^{29,50} The structures with Si/Al ratio other than unity or infinity were obtained by randomly substituting aluminum with silicon, satisfying the Löwenstein rule. In this way, it is possible to reproduce a reasonable approximation of the framework aluminum distribution obtained by experimental methods.^{28,51–53} Our model explicitly distinguishes silicon from aluminum using different charges for oxygen atoms bridging two silicon atoms (q_{OSi}) and oxygen atoms bridging one silicon and one aluminum atom (q_{OAI}). The nonframework sodium cation density was adjusted to match the

framework aluminum density. Nonframework sodium cations can move freely, adjusting their position depending on their interactions with the framework atoms, other sodium cations, and the carbon dioxide molecules.³⁵

Our model for CO₂ has three Lennard-Jones sites with charges centered at each atom. The charge on the carbon and on the oxygen centers are +0.6512 and -0.3256 e⁻, respectively. The carbon–oxygen bonds are rigid and 1.149 Å long. The bond length and the assigned values for the point charges are taken from the model of Harris and Yung,⁵⁴ and the Lennard-Jones parameters were fitted using Gibbs ensemble Monte Carlo simulations to reproduce the vapor–liquid coexistence curves, using a Lennard-Jones 12-6 potential that is truncated at 12 Å and shifted so that the potential is zero at the cutoff. The Lennard-Jones interactions between CO₂ and the zeolite were modeled taking into account the interactions between carbon dioxide and the zeolite O atoms and Na cations, because they contribute most to the repulsive and dispersion forces; Lennard-Jones interactions between Si–CO₂ and Al–CO₂ were not taken into account. The Coulombic interactions in the system were calculated using the Ewald summation.⁵⁵

Experiments. Experimental carbon dioxide adsorption isotherms were performed in FAU and MFI zeolites at several temperatures ranging from 253 to 298 K. All silica MFI (Si/Al = ∞) was kindly supplied by ITQ (CSIC) and corresponds to a pure porous crystalline silicon dioxide. FAU with a Si/Al ratio 2.5 (54 Na⁺ per unit cell) was purchased from Zeolyst International SA. Prior to the adsorption measurements, the samples were *in situ* outgassed under primary vacuum ($\sim 1.33 \times 10^{-3}$ kPa) at 673 K overnight to remove any adsorbed impurities. The CO₂ adsorption isotherms were carried out in TriStar 3000 volumetric equipment from Micromeritics in the pressure range from 10^{-1} to 120 kPa. The instrument was equipped with a pressure transducer (0–133 kPa, uncertainty within 0.5% of reading) that guarantees an excellent sensitivity for carbon dioxide adsorption in the low pressure range, which is especially useful in adsorption studies on highly microporous materials. The temperature of the isotherms was controlled using a circulating thermostatic bath. Ultrahigh purity (i.e., 99.995%) carbon dioxide was purchased.

The experimental isotherms obtained in this way were used to fit, optimize, and validate our force field parameters. Consequently, to guarantee the accuracy of the experiments, all the isotherms were performed in triplicate, and the data is reproducible with an error below 0.1%.

Results and Discussion

Here, we present a force field obtained using Monte Carlo simulations of carbon dioxide in zeolites. In what follows, we describe the parameter optimization and the force field validation using faujasite with Si/Al ratio 2.5, the extension to other Si/Al ratio and other topologies and the improvement of this work compared to preceding models and force fields already available from the literature. Details on the partial charges and the other force field parameters used in this work are listed in Table 1.

A. Parameter Optimization and Force Field Validation. To construct a transferable force field for all frameworks, pressures, temperatures, and Si/Al ratios is a very complex task that requires the fitting of all force field parameters simultaneously. The zeolite framework charges and the adsorbate–adsorbent Lennard-Jones interaction parameters were fitted using the Downhill Simplex Method⁵⁶ and grand-canonical Monte Carlo simulations. We adjusted the force field parameters to obtain the excess adsorption that accurately reproduces our

TABLE 1

	this work	Akten et al. ⁴²	Jaramillo and Chandross ⁴¹	Maurin et al. ⁴³
a. Lennard-Jones Force Field ϵ/k_B [K] Parameter Used in This Work and in the Published Literature				
O _{co2} –O _{co2}	85.671	79.000	110.236	76.474
C _{co2} –C _{co2}	29.933	27.000	29.195	46.650
O _{co2} –C _{co2}	50.640	46.184	56.880	18.335
O _{co2} –O _{zeo}	78.980	41.689	118.793	69.743
C _{co2} –O _{zeo}	37.595	24.372	61.410	42.125
O _{co2} –Na	200.831	25.139	47.316	31.332
C _{co2} –Na	362.292	14.697	24.161	88.079
O _{zeo} –Na	23.000	13.266		
b. Lennard-Jones Force Field σ [\AA] Parameter Used in This Work and in the Published Literature				
O _{co2} –O _{co2}	3.017	3.050	3.470	3.360
C _{co2} –C _{co2}	2.745	2.800	2.753	3.830
O _{co2} –C _{co2}	2.880	2.925	3.112	3.310
O _{co2} –O _{zeo}	3.237	3.025	3.255	3.480
C _{co2} –O _{zeo}	3.511	2.900	2.897	3.900
O _{co2} –Na	2.758	2.950	3.335	2.950
C _{co2} –Na	3.320	2.825	2.977	3.350
O _{zeo} –Na	3.400	2.925		
c. Partial charges [e^-] and Carbon–Oxygen Bond Distance [\AA] Used in This Work and in the Published Literature				
q (O _{co2})	-0.325 60	-0.35	-0.40	-0.36
q (C _{co2})	0.651 20	0.70	0.80	0.72
q (Si)	0.785 98	0.80	3.70	2.40
q (Al)	0.485 98	1.42	2.775	1.70
q (O _{Si})	-0.392 99			-1.20
q (O _{Al})	-0.413 84	-0.74	-1.868 75	-1.20
q (Na)	0.383 40	0.74	1.00	0.70
d (C–O)	1.149	1.16	1.143	1.143

experimental isotherms at 273 K for FAU with a Si/Al ratio of 2.5 that corresponds to 54 aluminum atoms and 54 sodium cations per unit cell. We fit to the entire isotherm following the methodology reported by Dubbeldam et al.³² The main reasons to select Na–Y type zeolite for the fitting were that (1) it is a well-tested material with very low degree of defects; (2) it has been previously shown that the adsorption properties of small molecules on this material are insensitive to the aluminum distribution, whereas for other classes of structures, the distribution matters;²⁸ (3) in contrast to LTA4A, the Si/Al ratio can be easily varied; and (4) most experimental data on carbon dioxide adsorption are available for faujasites, providing a valuable number of isotherms from independent groups to the force field validation. Additional experimental isotherms at 253, 263, 283, 298, and 303 K were measured and subsequently used for the validation of the force field.

Figure 2 shows an excellent agreement in all ranges of pressures and temperatures between our experimental and simulation data. These results are also in agreement with previous experimental isotherms, as shown in Figure 3, where our data (54 Na⁺/uc at 298 K) are compared with those from Pires et al.⁵⁷ (56 Na⁺/uc at 298 K), Walton et al.⁵⁸ (58 Na⁺/uc at 298 K), and Maurin et al.⁴³ (56 Na⁺/uc at 300 K). Our computed excess adsorption isotherms in faujasites with a Si/Al ratio other than 2.5 are also in very good agreement with experimental data taken from the literature. Figure 4 compares our computed isotherms with those of Pires et al.⁵⁷ for a Si/Al ratio of 4.8 (33 Na⁺/unit cell (uc)) at 298 K and with those of Dunne et al.¹⁹ for a Si/Al ratio of 1.2 (87 Na⁺/uc) at 305 K. For our simulations shown in Figure 4, we have adjusted both the temperature and the Si/Al ratio to that of the corresponding experiment available in the literature. In all cases, there is good agreement between our simulations and the experiments in the whole range of pressures analyzed. We have verified that the error in the computed loadings is smaller than the symbol size for all the figures shown in this work.

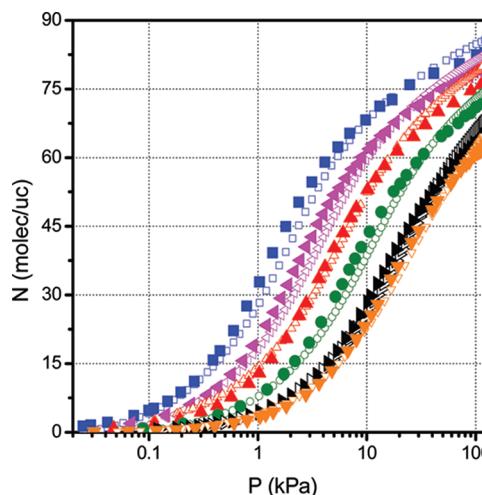


Figure 2. Comparison of computed (open symbols) and experimental (solid symbols) carbon dioxide adsorption isotherms in FAU with a Si/Al ratio of 2.5 (54 Na⁺/uc). The isotherms are obtained at 253 K (\square , ■), 263 K (left-pointing open and solid triangles), 273 K (\triangle , ▲), 283 K (\circ , ●), 298 K (right-pointing triangles), and 303 K (∇ , ▽).

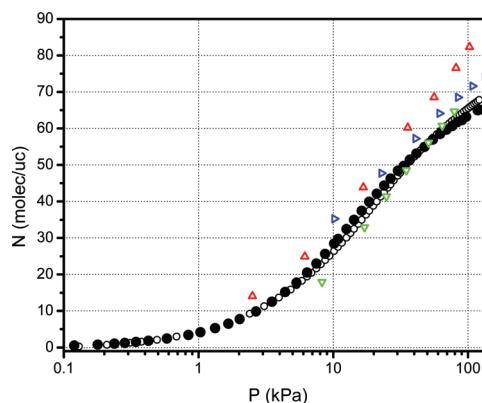


Figure 3. Carbon dioxide adsorption isotherms in faujasites with a Si/Al ratio around 2.5 (54–58 aluminum atoms and sodium cations per unit cell) at 298–300 K. Comparison of the experimental (\circ) and simulation (\bullet) data obtained in this work with previous experimental results from Maurin et al.⁴³ at 300 K (right-pointing open triangle), Pires et al.⁵⁷ at 298 K (\triangle) and Walton et al.⁵⁸ at 298 K (∇).

B. Extension to Other Topologies (MFI, MOR, and LTA).

To confirm that the new force field parameters are transferable to other structures (in addition to FAU), we have selected MFI, MOR, and LTA-type zeolites. Our simulated isotherms for pure silica MFI are compared with our experimental isotherms in Figure 5a and with other previous available experimental data in Figure 5b. Both figures show excellent agreement between simulation and experiments. Figure 6 compares our simulation results for MFI and MOR type structures with several Si/Al ratios. The isotherms for MFI were computed at 297 K and for Si/Al ratio 95 (1 Na⁺/uc) and 31 (3 Na⁺/uc) and compared with previous experimental data of Dunne et al.¹⁹ The isotherms for MOR were computed at 293 K for a Si/Al ratio 5.8 (7 Na⁺/uc) for direct comparison with the experimental values reported by Delgado et al.⁵⁹ The agreement is excellent for MFI in the entire range of pressures and at both Si/Al ratios, whereas for MOR, there is good agreement only at high pressures. At low pressures, our simulations underpredict the CO₂ adsorption behavior in MOR. For small, nonpolar hydrocarbons, these discrepancies have been attributed to differences in the aluminum distribution between the experimental and simulated structure.^{28,53} However, molecular simulations for carbon dioxide in MOR using

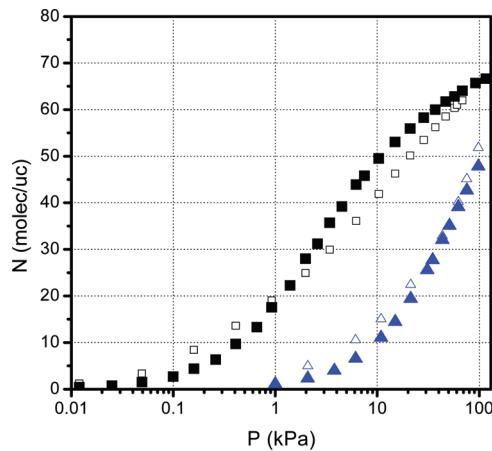


Figure 4. Comparison of computed (solid symbols) and previous experimental (open symbols) carbon dioxide adsorption isotherms in faujasites with a Si/Al ratio of 4.8 at 298 K (triangles) and Si/Al ratio 1.2 at 305 K (squares). Previous experimental data have been taken from Dunne et al.¹⁹ and Pires et al.⁵⁷

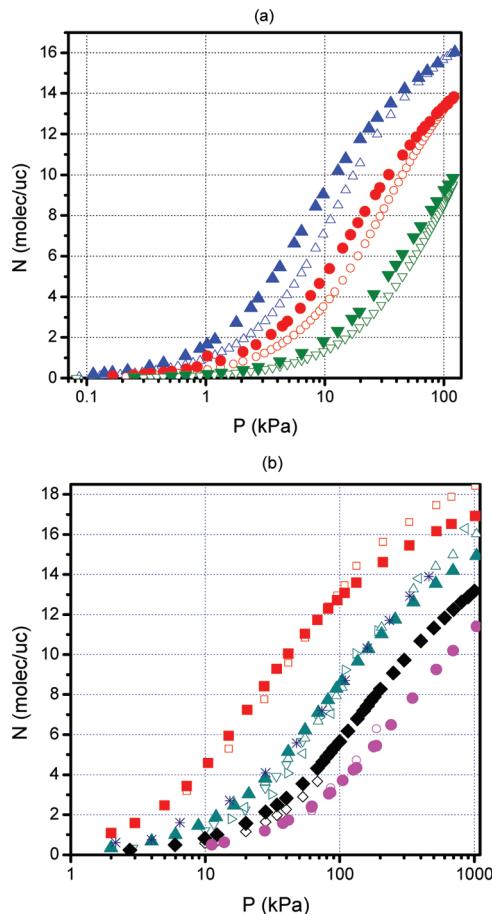


Figure 5. Comparison of computed (solid symbols) and experimental (open symbols) carbon dioxide adsorption isotherms in pure silica MFI zeolite. (a) Comparison with our own experimental data at 253 K (Δ , \blacktriangle), 273 K (\circ , \bullet), and 303 K (∇ , \blacktriangledown). (b) Comparison with previous experimental data taken from Sun et al.²³ at 277 K (\square , \blacksquare) and 308 K (\triangle , \blacktriangle); Hirotani et al.³⁹ at 303 K (∇), 305 K (left-pointing open triangle), and 330 K (\diamond , \blacklozenge); Choudhary et al.¹⁷ at 303 K (right-pointing open triangle) and 353 K (\circ , \bullet); and Li et al.⁴⁰ at 313 K (*).

structures in which the aluminum atoms are randomly distributed but keeping the preferential sites and the fraction of aluminum atoms at the four T-sites of MOR as reported by Meier⁴⁸

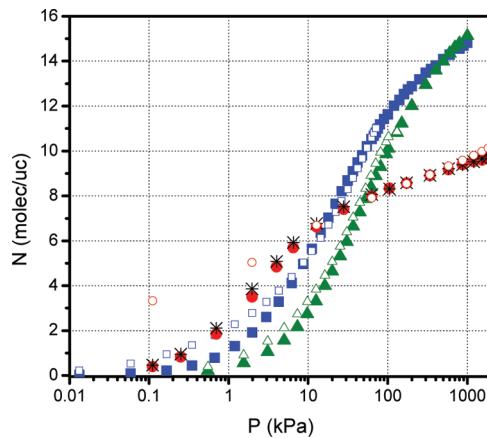


Figure 6. Comparison of computed (solid symbols) and experimental (open symbols) carbon dioxide adsorption isotherms in MFI- and MOR-type zeolites for several Si/Al ratios. The computed isotherms in MFI were compared with the experimental values of Dunne et al.¹⁹ at 297 K for the structures with a Si/Al ratio of 95 and 1 Na⁺/uc (\triangle , \blacktriangle) and a Si/Al ratio of 31 and 3 Na⁺/uc (\square , \blacksquare). The isotherms in MOR were obtained at 279 K for structures with a Si/Al ratio of 5.8, 7 Na⁺/uc and a random distribution for the aluminum atoms, but keeping the preferential sites and the fraction of aluminum atoms at the four T-sites in MOR as reported by Meier⁴⁸ (structure 1, \bullet) and by Alberti⁶⁰ (structure 2, *). The computed isotherms (\bullet , *) were compared with the experimental data of Delgado et al.⁵⁹ (\circ).

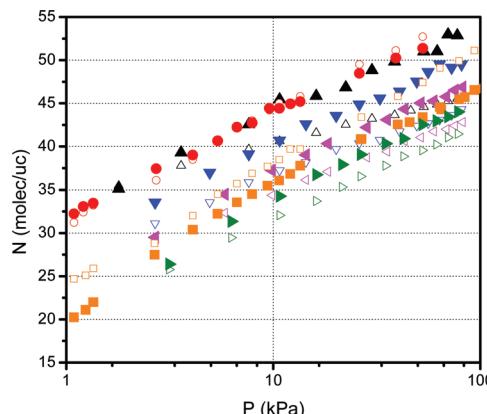


Figure 7. Comparison of computed (solid symbols) and experimental (open symbols) carbon dioxide adsorption isotherms in LTA4A. The computed isotherms were compared to the experimental isotherms of Ahn et al.⁶¹ at 273 K (\triangle , \blacktriangle), 283 K (∇ , \blacktriangledown), 293 K (left-pointing triangles), and 303 K (right-pointing triangles) and with the experimental values taken from ref 13 of Jaramillo and Chandross⁴¹ at 273 K (\circ , \bullet) and 298 K (\square , \blacksquare).

(structure 1) and by Alberti⁶⁰ (structure 2) show that this explanation is not applicable to carbon dioxide adsorption (Figure 6).

As shown in Figure 7, simulation obtained with our force field is also in good agreement with available experimental data for CO₂ adsorption in LTA4A (LTA-type zeolite with a Si/Al ratio of 1 and 96 sodium cations per unit cell) in the range of 273–303 K.^{41,61}

C. Comparing This Work and Preceding Models. To show the improvement of this work compared to previous force fields, we have performed simulations in LTA, FAU, MOR, and MFI zeolites using the new set of parameters and those from previous approaches. Previous force fields were developed to calculate adsorption of carbon dioxide in LTA4A (Jaramillo and Chandross⁴¹ and Atnen et al.⁴²) and in faujasites (Maurin et al.⁴³). All atomic charges and force field parameters for our and other force fields can be found in Table 1.

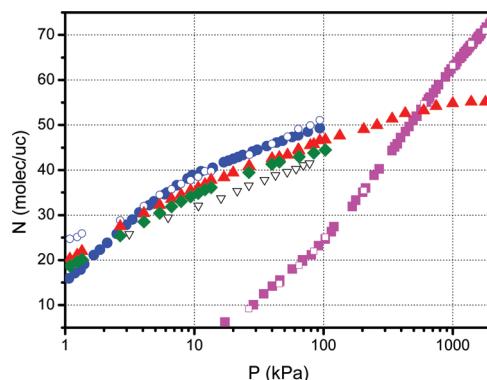


Figure 8. Comparison of computed (solid symbols) and experimental (open symbols) carbon dioxide adsorption isotherms in LTA4A at 298 K. The computed isotherms were obtained using the force fields from Jaramillo and Chandross⁴¹ (●), Akten et al.⁴² (■), Maurin et al.⁴³ (◆), and our new force field (▲). Experimental data for comparison were taken from Jaramillo and Chandross⁴¹ at 298 K (○), Ahn et al.⁶¹ at 303 K (▽), and Akten et al.⁴² at 298 K (□).

Jaramillo and Chandross⁴¹ and Akten et al.⁴² considered the same zeolite model and potential that was used by Faux and co-workers,⁶² but they differ in the CO₂ model: the former uses the model of Makrodimiris et al.³⁸ and the latter, the Trappe force field of Potoff and Siepmann.⁶³ The force field parameters of Jaramillo and Chandross⁴¹ were fitted to experimental isotherms at 298 K, and they completely disregard the mobility of the sodium cations. However, it is well-known that ignoring the mobility of the cations results in artifacts.³⁵ Akten et al.⁴² fitted the force field parameters to match their own experimental data at 298 K. They constrained the sodium cations associated with the six-membered oxygen rings, whereas cations associated with the eight- and four-membered rings were allowed to move. Maurin et al.⁴³ fitted the force field parameters to reproduce their experiments for faujasites with a Si/Al ratio of 1 and 2.4 that corresponds to 92 and 56 sodium cations, respectively. Similarly to the force field of Jaramillo and Chandross,⁴¹ the sodium cations were considered as an immobile part of the zeolitic framework, and therefore, they are restricted to their crystallographic positions during the simulations.

Figure 8 shows the computed carbon dioxide adsorption isotherms in LTA4A at 298 K using the three previous force fields, the experimental data that Jaramillo and Chandross⁴¹ and Akten et al.⁴² used for their fitting, and the adsorption isotherm at the 298 K using our new force field. It should be stressed further that although all isotherms were obtained at the same temperature and, in theory, for the same structure, discrepancies between the experimental sets used by the authors are large, leading to completely different carbon dioxide adsorption curves. Our results are in agreement with those of Jaramillo and Chandross⁴¹ as well as with the computed isotherms obtained using the force field of Maurin et al.⁴³ and the experimental data of Ahn et al. at 303 K,⁶¹ also included in Figure 8 for comparison. It is striking that experimental isotherms reported by Akten et al.⁴² do not match those reported by Jaramillo et al.⁴¹ and Ahn et al.⁶¹ On the basis of the experimental procedure described in the literature,^{64,65} this disagreement might be due to the low outgassing temperature (i.e., 25 °C) used in the preparation of the samples prior to running the isotherms. Coping with IUPAC recommendations, such experimental conditions do not guarantee the corrected evacuation of the zeolite,^{64,65} and therefore, those data from Akten et al. may be seriously affected by experimental errors. Thus, it appears that their force field parameters have been fitted using an incorrect experimental data set.

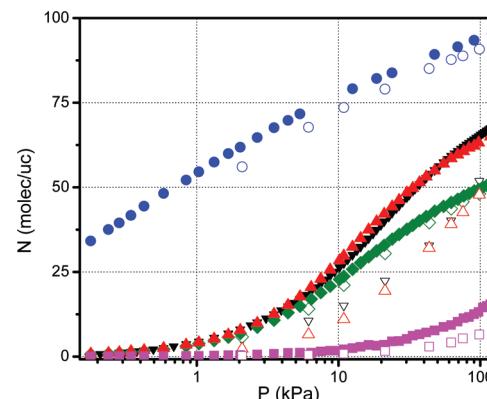


Figure 9. Comparison of computed and experimental carbon dioxide adsorption isotherms in faujasites with Si/Al ratio 2.5 (solid symbols) and 4.8 (open symbols) at 298 K. The computed isotherms were obtained using the force fields from Jaramillo and Chandross⁴¹ (●, ○), Akten et al.⁴² (■, □), Maurin et al.⁴³ (◆, △), and our new force field (▲, △). Experimental data for comparison were taken from this work for a Si/Al ratio of 2.5 at 298 K (▼) and Pires et al.⁵⁷ for a Si/Al ratio of 4.8 at 298 K (▽).

Figure 9 shows the computed and experimental adsorption isotherms of carbon dioxide in faujasites with a Si/Al ratio of 4.8 (33 Na⁺/uc) and 2.5 (54 Na⁺/uc) at 298 K. The computed isotherms were obtained using the four sets of force fields and compared with available experimental data for various Si/Al ratios: this work (Si/Al ratio 2.5) and Pires et al. (Si/Al ratio 4.8).⁵⁷ The isotherms obtained from our force field parameters reproduce the experimental data, regardless of the Si/Al ratio, as opposed to the simulations obtained using the force field parameters by Akten et al.,⁴² as well as those by Jaramillo and Chandross.⁴¹ The experimental values are underestimated using the parameters of Jaramillo and Chandross,⁴¹ and overestimated with those reported by Akten et al.⁴²

The isotherms obtained with the force field of Maurin et al.⁴³ show reasonable agreement with the experimental data, although they are almost insensitive to the aluminum density. The fact that our force field reproduces experimental adsorption isotherms for different aluminum framework densities in sharp contrast to previous force fields can be attributed to both the restrictions on cation mobility and the underestimations of the Na–CO₂ Lennard-Jones interactions in the latter. Taking into account the excellent agreement with experimental data using our force field parameters, it appears that this mobility becomes vital to accurately reproduce carbon dioxide adsorption in faujasites. The significant role of cation mobility has also been found to be an essential factor on the adsorption of alkanes in this type of structure.³⁵

Our force field clearly outperforms previous available approaches not only for LTA4A and faujasites but also for MOR- and MFI-type structures containing aluminum atoms, as shown in Figure 10a and b. In addition, our force field accurately reproduces pure silica MFI (Figure 11), whereas those from Jaramillo and Chandross⁴¹ and Akten et al.⁴² cannot be applied to all-silica structures (the electroneutrality of the framework is not preserved), and the force field from Maurin et al.⁴³ clearly overpredicts carbon dioxide adsorption at low pressures, whereas the adsorption at high pressures is underpredicted.

The applicability of the new set of charges developed for the zeolite framework and the sodium cations is by no means limited to carbon dioxide adsorption, for it also successfully reproduces the adsorption of alkanes in zeolitic structures. Figure 12 shows the computed adsorption isotherms for methane in a

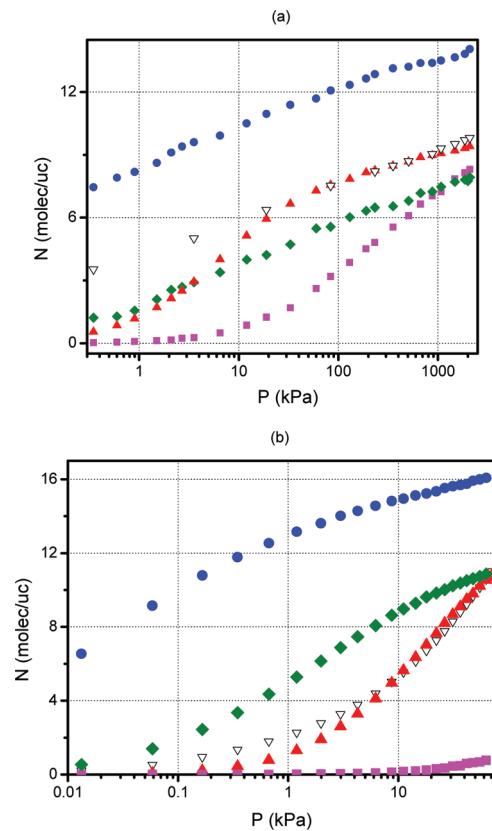


Figure 10. Comparison of computed (solid symbols) and experimental (open symbols) carbon dioxide adsorption isotherms in (a) MOR with a Si/Al ratio of 5.8 at 293 K and (b) MFI with a Si/Al ratio of 31 at 297 K. The computed isotherms were obtained using the force fields from Jaramillo and Chandross⁴¹ (●), Akten et al.⁴² (■), Maurin et al.⁴³ (◆), and our new force field in structure 1 (▲). Experimental data for comparison (▽) were taken from Delgado et al.⁵⁹ in MOR and from Dunne et al.¹⁹ in MFI.

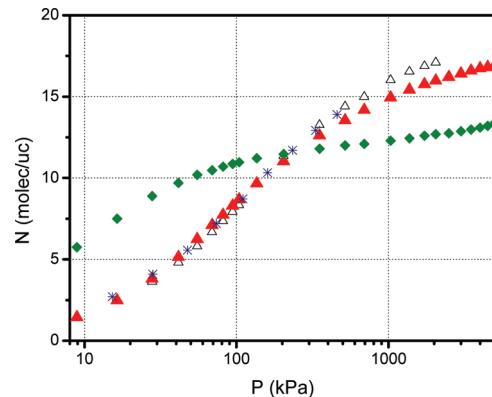


Figure 11. Comparison of computed (solid symbols) and experimental (open symbols) carbon dioxide adsorption isotherms in pure silica MFI at 308 K. The computed isotherms were obtained using the force fields from Maurin et al.⁴³ (◆) and our new force field (▲). Experimental data for comparison were taken from Sun et al.²³ at 308 K (△) and Li et al.⁴⁰ at 313 K (*).

faujasite structure with 48 aluminum atoms per unit cell at 323 K and for ethane in a MFI structure with three aluminum atoms per unit cell at 296 K. The isotherms were obtained using a combination of our previously reported models and Lennard-Jones parameters for alkanes^{34,35} and the new set of charges presented in this work, showing very good agreement with available experimental data.^{19,66} This additional feature of the force field set of charges is of particular interest for studying

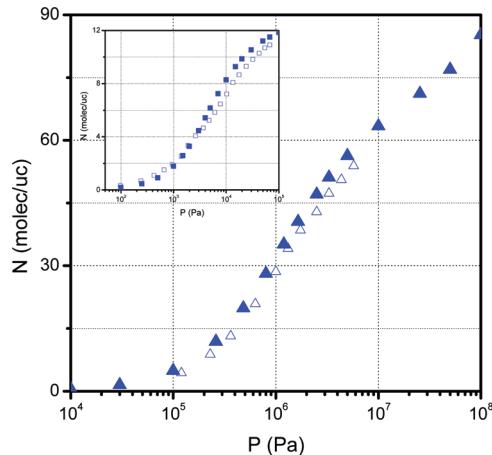


Figure 12. Comparison of computed (solid symbols) and previous experimental^{19,66} adsorption isotherms (open symbols) of methane in faujasite with a Si/Al ratio of 3 at 323 K (▲, □) and ethane (inset) in MFI with a Si/Al ratio of 31 at 296 K (■, △).

processes of industrial interest, such as those related to natural gas separation and purification.

Conclusions

We have developed a general force field for the adsorption of carbon dioxide in zeolites using Monte Carlo simulations and fitting to our own experimental data. Validation was carried out using both our experiments and available experimental data from the literature. The force field clearly outperforms previous force fields because it is more accurate, transferable between zeolite structures, and applicable to all Si/Al ratios. The work reported here can be expected to help the development of CO₂ separation and sequestration technologies by providing vastly improved molecular simulation data inputs.

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