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Insights on the Anomalous Adsorption of Carbon Dioxide in LTA Zeolites

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Abstract

We use a combination of experiments and molecular simulations to address the discrepancies of the force fields available in the literature to accurately reproduce CO₂ adsorption in zeolites with high density of aluminum atoms and extra framework cations. We attribute these discrepancies to the fact that previous force fields are not parameterized to take into account the formation of carbonate-like complexes in these zeolites during CO₂ adsorption. Our data show that the formation of carbonate-like complexes has a marked effect on the accessible porous structure of the zeolite, and the strength is controlled by the density and nature of extra framework cations. Strong carbonate-like complexes are formed in zeolite topologies containing high density of sodium, whereas bivalent cations give rise to more labile complexes. We provide a new set of parameters capable to reproduce the experimental adsorption in these systems. Our approach consists on the modification of the partial charges of the atoms of the zeolite that are directly involved in the formation of the surface complexes (oxygen atoms and cations). The new set of charges combined with our previous transferable force field reproduces the experimental adsorption in structures containing carbon dioxide-cation complexes.

Keywords. Adsorption, carbon dioxide, carbonates, LTA, zeolites

Introduction

Carbon dioxide adsorption and separation over porous solids has received much attention in the last decades. In part this has been driven by the need to develop cost-efficient CO₂ capture technologies to mitigate the consequences of climate change, and the improvement of gas separation processes of industrial interest (i.e., natural gas cleaning, CO₂ separation in coal combustion processes). Among porous solids, different materials have been extensively investigated for the adsorption and selective separation of carbon dioxide, being activated carbons and zeolites the most effective structures due to their thermal stability and large surface areas.¹⁻³ Zeolites are molecular sieves formed by TO₄ tetrahedra (T can be either Si or Al) that are connected to each other generating 3D structures with different topologies. The charge imbalance due to the presence of aluminum in the framework is compensated by extra framework cations. The nature, number, and distribution of the extra framework cations affect the ion exchange properties of the zeolites, the basicity, and the electric field in the cavities of zeolites. These parameters tend to vary inversely with the Si/Al ratio of the framework. Besides other experimental conditions (such as pressure, temperature, and moisture), the topology, and composition of the zeolite govern the forces involved in the adsorption process and the overall adsorption efficiency. 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,⁴⁻⁵ whereas the pore shape and volume appear to control the adsorption capacity at high pressures.⁶ Molecular simulation is a powerful tool to accurately predict adsorption and diffusion processes in crystalline porous materials,⁷ and has been extensively used for predicting the adsorption of carbon dioxide in zeolites.^{5, 8-15} A number of force fields modeling the adsorption of carbon dioxide in zeolites can be found in literature, most of them only applicable to all-silica structures (Si/Al=∞)^{8, 11, 16-17} and fewer to structures containing aluminum and extra framework cations (mostly sodium). In a previous work we addressed the lack of transferability between the available force fields to different zeolite framework types and Si/Al ratios, providing a force field transferable to structures with Si/Al ratio ranging from 1 to ∞. This force field accurately

reproduces CO₂ adsorption in structures with different aluminum content (FAU, MFI and MOR) and sodium. However, some discrepancies with experimental data were found for LTA-type structures.¹⁶ With this information in mind, the following step is to understand the mechanism that governs CO₂ adsorption in zeolites with high aluminum content. Therefore the goal of this paper is to elucidate the factors that influence this adsorption behavior of carbon dioxide in zeolites with high aluminum content such as LTA and NaX, and to describe the methodology for the development of additional force field parameters for these structures based on the combination of simulation techniques and experimental data.

Methodology

This section describes the details of the experimental and computational techniques employed in this work.

Experimental details

Zeolites with faujasite, FAU, (NaY, NaX) and Linde Type A, LTA, (LTA4A, LTA5A) topology were purchased from Zeolyst Int. and Fluka, respectively. CO₂ adsorption isotherms at temperatures near ambient (i.e., 253-323 K) were performed in a volumetric analyzer (ASAP 2020, Micromeritics) in the pressure range from 10⁻² up to 120 kPa. The instrument was equipped with a turbo molecular vacuum pump and three pressure transducers (0.13, 1.33, and 133 kPa, uncertainty within 0.15% of each reading) to enhance the sensitivity in the low pressure range. Before the adsorption measurements, the zeolites were in situ degassed at 623 K (1K/min) under high vacuum (ca. 10⁻³ kPa) for 17 h to remove moisture. For the experiments carried out after exposure in carbon dioxide, the zeolites were degassed as indicated above and then put in contact with CO₂ at 298 K at 120 kPa for 24 h to allow the saturation of the zeolite with the gas and the formation of surface carbonates.¹⁸⁻¹⁹ Subsequently the samples were evacuated at 273 K for 2 hours under the turbomolecular pump vacuum and then hydrogen adsorption isotherms at 77 K were measured. This experimental protocol allowed assuring that the carbonate species formed during the saturation in CO₂ are not removed during the

subsequent physisorption measurements with H₂ at 77 K. By doing this, we can explore the effect of the carbonates formed on the porosity of the zeolites. The choice of hydrogen as the gas probe for the adsorption isotherms on the samples previously exposed to CO₂ was based on its accessibility to the porous structure of all studied zeolites at cryogenic temperatures (i.e., nitrogen or argon have kinetic restrictions to enter LTA4A at such low temperatures).²⁰⁻²² All of the isotherms were done in triplicate, and the data is reproducible with an error below 0.1%. The temperature of the isotherms was controlled using a liquid nitrogen bath (77 K) and a thermostatic circulating oil bath (253-323 K). Ultrahigh purity gases (i.e., 99.999 and 99.995 % for H₂ and CO₂, respectively) were supplied by Air Products.

Computational details

Adsorption isotherms were obtained using Monte Carlo simulations in the Grand Canonical ensemble, where chemical potential, volume, and temperature are imposed. From the chemical potential we obtain the fugacity, and this is directly related to pressure by the fugacity coefficient. During the simulations, random moves were performed in cycles finding the most favorable energy configuration of the system and allowing one of the following trial moves in each cycle: rotation, translation, and reinsertion. To compare simulated and experimental isotherms, absolute adsorption is converted to excess adsorption.²³⁻²⁴ The excess adsorption (n_{exc}) is obtained by relation of the absolute adsorption (n_{abs}) with the pore volume of the adsorbent (V^E) and the molar density of the bulk gas phase (ρ^E), using the following expression:

$$n_{exc} = n_{abs} - V^E \rho^E$$

Isosteric heats of adsorption and Henry coefficients were calculated using Monte Carlo simulations in the canonical ensemble fixing the number of particles, the volume, and the temperature. The simulations were carried out in the limit of zero loading, providing important information about the strength of the interaction of the adsorbate with the structure. These energies were computed using the Widom test particle method.⁷ Simulations were performed with the *in-house* RASPA code developed by D. Dubbeldam, S. Calero, D. E. Ellis, and R. Q.

Snurr.²⁵ This code has been extensively tested and validated with a large number of experimental and simulation data.^{16, 26-28} Zeolites were modeled as rigid frameworks composed by silicon, aluminum, and oxygen atoms and using their crystallographic positions. 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 used in this work.^{6, 29} LTA and FAU zeolites have a cubic unit cell dimension of 24.555 Å and 25.028 Å, respectively.³⁰⁻³¹ They are formed by sodalite cages connected to each other by prisms that are hexagonal in FAU and cubic in LTA. In both structures sodalites describe supercages surrounded by 10 and 8 sodalites in FAU and LTA, respectively. FAU-type zeolites have been labeled either X or Y depending on their framework aluminum density. Zeolite X contains between 96 and 77 aluminum atoms per unit cell, whereas zeolite Y contains fewer than 77 aluminum atoms per unit cell. The initial distribution of the extra framework cations in the structure has an important role into the adsorption process.²⁹ Therefore for LTA we use the experimental position of the cations reported by Pluth and Smith for sodium³⁰ and by Firor and Seff for calcium.³² According to these works the cations from LTA4A are located in the supercages of the zeolite, coordinated by three types of aluminosilicate rings, and distributed among three different sites: a) at the center of the 6-member-rings of the sodalites, b) at the 8-member-rings windows between supercages, and c) opposite to the 4-member-rings of the cubic prisms. In the case of LTA5A the cations can be found either in the supercages or in the sodalites leading to four possible sites: a) at the 8-member-rings windows, b) at the center of the 6-member-rings of the sodalites, and two more sites resulting from the displacement of the latter to the supercages (c) or to the sodalites (d). However calcium cations are only coordinated to the 6-rings of the sodalites and not to the windows between supercages (8-member-rings). Regarding the extra framework cations distribution in FAU, their precise crystallographic location remains uncertain.^{31, 33-34} The distribution of these cations highly depends on different factors such as humidity or the nature of the adsorbate. Six sites have been identified for sodium cations: one site located at the center of the hexagonal prisms, two sites inside the sodalites, and other three sites inside the supercages of the structure. The sites inside the super cages are (1) at

the center of the hexagonal prisms but displaced into the supercage, (2) on a twofold axis opposing a 4-member-ring (from the hexagonal prism and the sodalite) between two 12-member-rings (window between supercages), and (3) at the center of the sodalite but displaced to the supercage. A representation of the positions of the cations in LTA and FAU zeolites is shown in Figure 1.

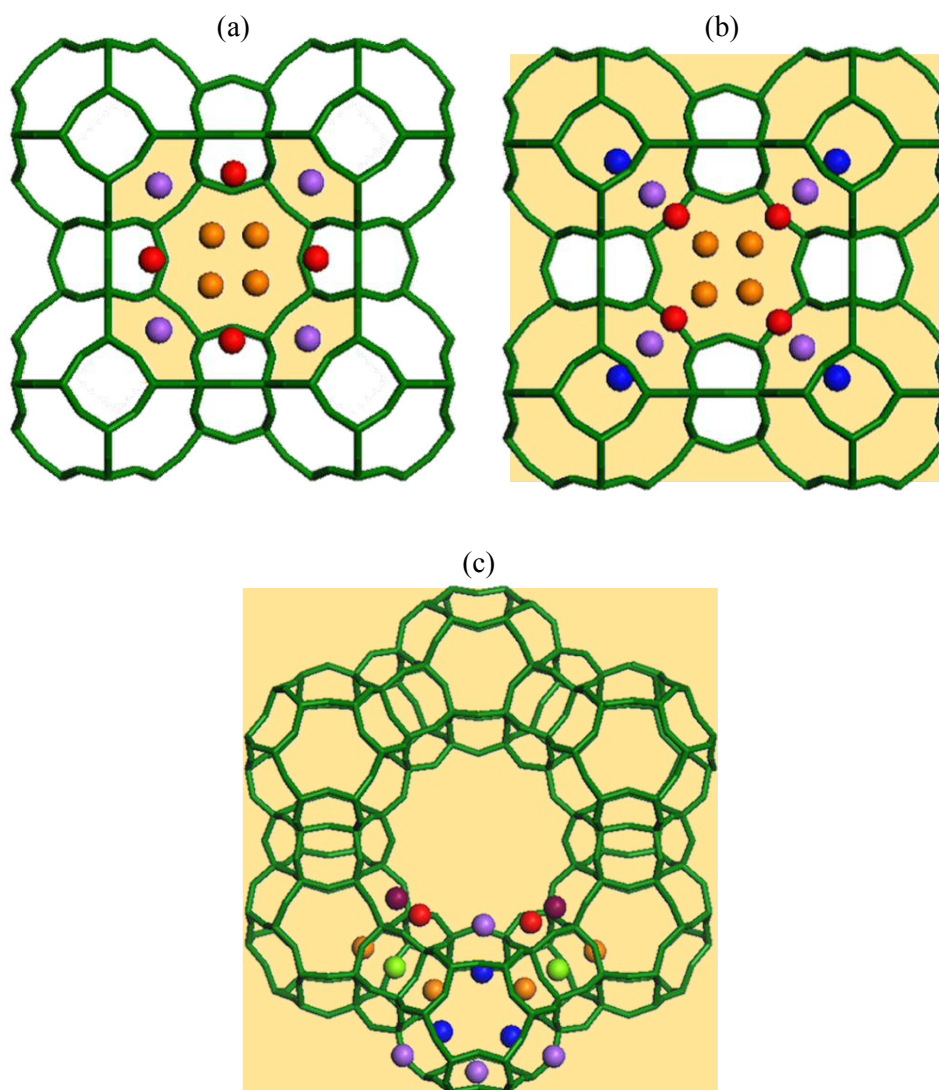


Figure 1: Positions of the cations in (a) LTA4A, (b) LTA5A, and (c) FAU. In LTA4A cations are located at the 6-rings of the sodalites (purple), at the 8-rings windows between supercages (orange), and opposite to 4-rings of the cubic prisms (red). In LTA5A cations can be found at the 8-rings windows between supercages (orange), at the 6-rings of the sodalities (purple), and the latter but displaced to the supercages (red) or to the sodalites (blue). In FAU cations are distributed at the center of the hexagonal prisms (green), inside the sodalites (orange and blue), and inside the supercages at the center of the hexagonal prisms but displaced into the supercage (red), on a twofold axis opposing a 4-ring between two 12-rings (purple), and at the center of the sodalite but displaced to the supercage (violet).

In order to ensure the influence of the alumina atoms and the cations distribution inside the structures we have studied the adsorption of carbon dioxide on NaY (with 54 Na⁺/u.c) in a variety of five different random configurations. The results obtained show that there are no differences on the adsorption values obtained. These results agree with previous studies on the adsorption of small gasses where the insensitiveness of NaY to the amount and positions of the alumina atom (and sodium cations) is studied.^{35,36} Carbon dioxide is modeled as a rigid molecule with three Lennard-Jones sites and point charges at each atom to reproduce the polarity of the molecule. The Lennard Jones parameters of the carbon and oxygen atoms were fitted to reproduce the experimental vapor-liquid phase equilibrium, while their combination (C-O) is obtained by Lorentz-Berthelot mixing rules.¹⁶ We use Lennard-Jones and Coulombic potentials to define the interactions of the structure with the extra framework cations, and with the adsorbates. These potentials are cut at 12 Å and shifted to zero. Coulombic interactions are computed with the Ewald summation method with a relative precision of 10⁻⁶. For adsorbate-adsorbent, adsorbate-sodium, and sodium-adsorbent, we use the set of parameters previously developed by Calero *et al.*, as this set is transferable for different zeolites.¹⁶ The interactions involving calcium as extra framework cations were obtained in this work. The Lennard-Jones parameters for all interactions used in this work are collected in Table 1.

Table 1: Lennard-Jones parameters used in this work.

Atom	Atom	σ/k _B (K)	ε (Å)
C_co2	C_co2	29.933	2.745
O_co2	O_co2	85.671	3.017
C_co2	O_zeo	37.595	3.511
O_co2	O_zeo	78.980	3.237
Na	O_zeo	23.0	3.4
Ca	O_zeo	18.0	3.45
C_co2	Na	362.292	3.320
O_co2	Na	200.831	2.758
C_co2	Ca	362.292	3.320
O_co2	Ca	200.831	2.758

Results and Discussion

As mentioned above, the force field reported by Calero *et al.* accurately reproduces CO₂ adsorption in zeolites with different aluminum content (FAU, MFI, and MOR) and sodium cations. However, some discrepancies with experimental data were found for structures with high density of aluminium atoms and extra framework cations such as LTA4A and NaX.¹⁶ FAU and LTA type zeolites contain both silicon and aluminum atoms. The Si/Al ratio generates different FAU structures (zeolite X and Y for Si/Al ratio of 1-1.5 and >1.5, respectively),³⁷ while for LTA this ratio is always 1. Not only topological and composition differences but also the density and nature of the extra framework cations are important. While FAU structures (NaX and NaY) only have sodium as extra framework cation, LTA zeolites (4A and 5A) can combine both sodium and calcium. These differences result in the above-mentioned discrepancy in predicting carbon dioxide adsorption. According to the literature, the molecular mechanism that explains CO₂ adsorption in zeolites involves both physical and chemical adsorption, the latter through the interactions of carbon dioxide molecules with the extra framework cations and the oxygen of the zeolite. The formation of linear and/or bent configurations of bridged adsorption complexes has been reported for different alkali-metal cations, where the oxygen atoms of CO₂ interact with the cation sites.^{2, 38-42} For instance, carbonate-like species in various configurations have been reported for NaX zeolite^{43-44,45} and attributed to the basic character of the oxygen atoms of the structure. The phenomenon seems to be less perceptible in NaY zeolite, likely as a result of its lower but yet non negligible aluminum content.⁴⁶ The linear complexes Na-CO₂ formed in NaY are easily removed by degassing at room temperature. More recently Montanari and Busca^{2, 47} demonstrated the formation of CO₂-Na⁺ complexes in Na-LTA that induce a perturbation of the Si-O-Al bonds. They also reported that linear CO₂-complexes desorb completely by degassing at room temperature, while other carbonate species resist degassing at 420 K. A similar behavior has been observed for Ca, Na-LTA (LTA5A) but with less formation of carbonate species. Combining IR spectroscopy, gas adsorption, and theoretical approaches, Zukal *et al.*¹⁹ showed that interactions between CO₂ molecules and Na-LTA zeolite

depend on the gas loading. At low coverage carbon dioxide forms complexes by interaction with three sodium cations, whereas at higher loadings only two cations interact with each molecule of carbon dioxide. In this work we show that the formation of carbonate-like complexes during CO₂ adsorption has an effect on the porous structure of the zeolite and on the gas-host interactions. This effect is not taken into account in previous force fields, and therefore they are unable to predict the adsorption capacity of carbon dioxide in this type of structures.

To quantify the likely effect of the CO₂-complexes on the accessible pore void of the zeolites, physisorption measurements (hydrogen at 77 K) were performed on the samples previously exposed to CO₂. We have selected Na-X and LTA4A with 96 sodium cations per unit cell, Na-Y with 54 sodium cations per unit cell, and LTA5A with 32 sodium cations and 32 calcium cations per unit cell. This experimental approach was designed to assure the formation of carbonates and avoid their decomposition in the degassing step at 273 K preceding the measurements of the adsorption isotherms. Also, hydrogen was chosen as the gas probe due to its smaller molecular diameter compared to the usual gases employed for textural characterization (i.e., nitrogen or argon have kinetic restrictions to enter Na-LTA at cryogenic temperatures). Figure 2 shows the adsorption isotherms of hydrogen in FAU zeolites (NaY and NaX) at 77 K. For each structure we compare the results obtained in the bare structure and after saturation in CO₂ atmosphere. No differences are observed for NaY with the adsorption isotherms corresponding to the bare and CO₂-saturated structure completely overlapping in the whole range of pressure. This indicates that CO₂ adsorption does not alter the accessible pore volume of the zeolite, either because surface-complexes are not formed or are removed during the degassing step at low temperature before the measurements. For NaX the loading of hydrogen in the bare structure is significantly higher than that after exposure to carbon dioxide. This drop in the hydrogen uptake accounts for the amount of carbon dioxide that remains in the pores of the zeolite due to the formation of carbonate-like complex that are not easily removed. Several experimental evidences for the formation of these complexes in NaX and NaY structures have been reported.⁴³⁻⁴⁵ Our work supports these studies pointing out that the Si/Al

ratio regulates the strength of the complexes. In structures with low aluminum content (i.e., NaY, Si/Al >1.5), the complexes can be easily removed by degassing at low temperature, thus they cannot be quantified by physisorption measurements. Contrariwise for Si/Al=1 (NaX) the interactions of carbon dioxide with the cations are stronger, resisting higher degassing temperatures and allowing us to quantify a ca. 8 % drop in the accessible pore volume of the zeolite after CO₂ exposure, due to the formation of the carbonate-like complexes.

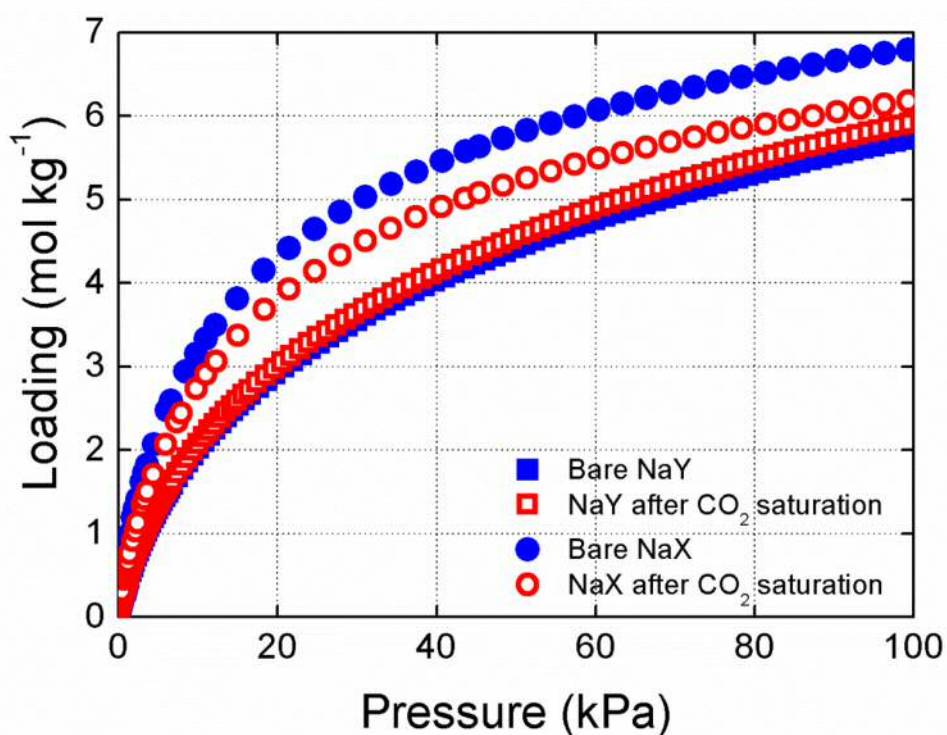


Figure 2: Adsorption isotherms of hydrogen in NaY with 54 Na⁺/u.c. (squares) and NaX with 96 Na⁺/u.c. (circles) at 77 K. The isotherms were measured in the bare structures (full symbols) and in the structures resulting from carbon dioxide saturation and degassing (empty symbols).

The adsorption isotherms of hydrogen in LTA structures (Figure 3) follow similar behavior than in NaX, with a fall in the gas uptake after CO₂ exposure that evidences the formation of strong carbonate-like complexes in both LTA4A and LTA5A zeolites. Interestingly, the decrease in the amount of hydrogen adsorbed in the bare and CO₂-exposed structures was larger for LTA4A (ca.18 %) than for LTA5A (ca.6 %). As both structures have the same Si/Al ratio (Si/Al=1), this finding confirms the outstanding influence of the amount and nature of the extra framework

cation. Due to the different polarity of sodium and calcium cations, the density of extra framework cations is higher in LTA4A (96 Na⁺/u.c.) than in LTA5A (64 cations per unit cell), therefore, the amount of carbonate-like complexes is expected to be larger in the former than the latter. This is in agreement with the different hydrogen uptake shown in Figure 3. Since differences between both LTA structures also concern the charge of the extra framework cations (LTA5A with 32 Na⁺/u.c. and 32 Ca²⁺/u.c.), it may be inferred that bivalent cations reduce the formation of carbonate-complexes and those formed are more labile, thus easily desorbed upon degassing.

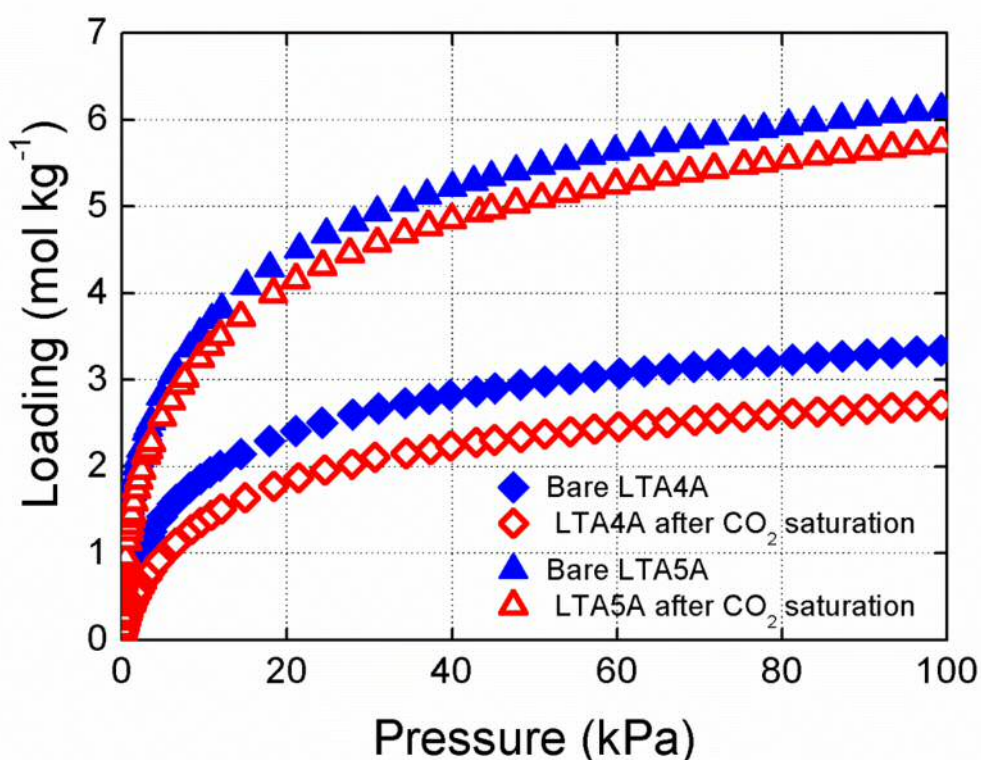


Figure 3: Adsorption isotherms of hydrogen in LTA4A with 96 Na⁺/u.c. (diamonds), and LTA5A with 32 Na⁺/u.c. and 32 Ca²⁺/u.c. (triangles) at 77 K. The isotherms were measured in the bare structures (full symbols) and in the structures resulting from carbon dioxide saturation and degassing (empty symbols).

Figure 4 shows our experimental and computed adsorption isotherms of carbon dioxide in LTA4A at 273K. Available adsorption data were also added for comparison.¹⁹ Simulations were performed using our previous force field.¹⁶ This force field is expected to be transferable between zeolite topologies and can also be applied to all possible Si/Al ratios with sodium as

extra framework cations. However, as shown in Figure 4, it fails to reproduce the experimental adsorption isotherms of carbon dioxide in LTA4A in the whole range of pressure. Simulations underpredict experimental adsorption, especially at low pressure and at saturation. We attribute these discrepancies to the fact that the force field was not parameterized to take into account the formation of $\text{CO}_2\text{-Na}^+$ complexes in a zeolitic structure. The strong interaction of the carbonate-like complexes in NaX and LTA structures, confirmed by the need of high temperatures for their complete removal, could explain the higher carbon dioxide uptake and the need of lower values of pressure to adsorb a given amount of carbon dioxide in experiments.

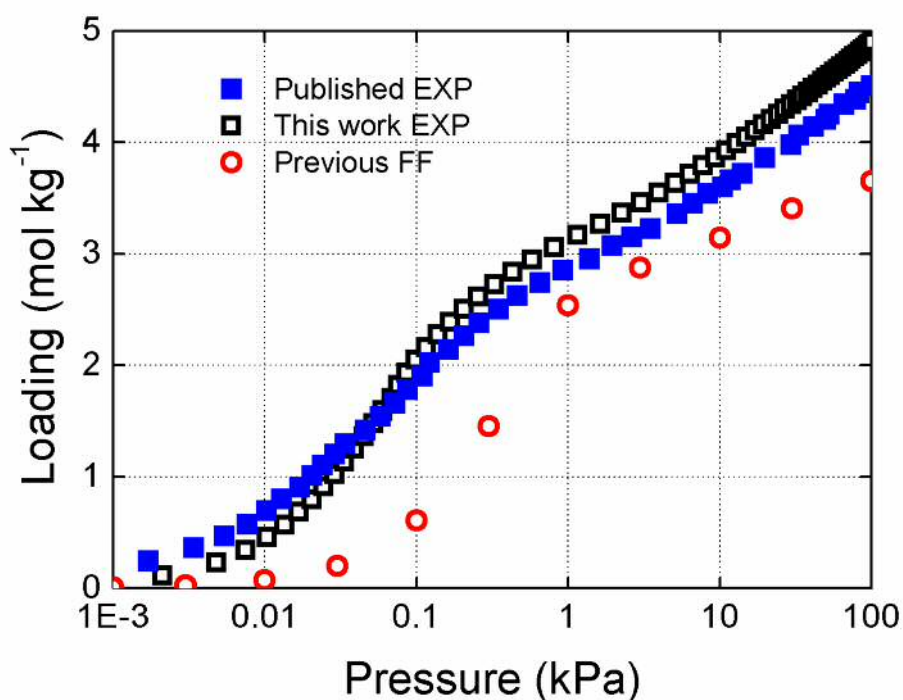


Figure 4: Experimental (squares) and simulated (circles) adsorption isotherms of CO_2 at 273 K in LTA4A (96 $\text{Na}^+/\text{u.c.}$). Simulations were performed using our previous force field.¹⁶ The results obtained in this work (empty symbols) are compared with experimental data taken from the literature for validation¹⁹ (full symbols).

According to literature, the strong interactions inside structures with $\text{Si}/\text{Al} = 1$ lead to variations in the polarity of the framework and to perturbations of the Si-O-Al bonds.^{2, 47} Thus, these variations need to be taken into account in order to reproduce the adsorption of carbon dioxide when complexes are formed. A straight-forward approach consists on the modification of the partial charges of the atoms of the adsorbent that are directly involved in the formation of the

complexes. Hence, the point charge of the oxygen atoms of the zeolite has been increased slightly (more negative), while increasing the point charge of the extra framework cations in order to compensate the negative net charge of the system (Table 2). As shown in Figure 5, the previous transferable force field with this new set of charges successfully reproduces experimental adsorption of carbon dioxide in LTA4A zeolite not only at 273 K but also at 298 K. In addition, the isosteric heat of adsorption of carbon dioxide in LTA4A computed with the new set of charges is 44.2 kJ/mol, in excellent agreement with the heat of adsorption that we obtained from experimental measurements (43.3 kJ/mol).

Table 2: Partial charges of the atoms used in this work when complexes are formed in presence of only Na^+ or Na^+ and Ca^{2+} cations. In absence of complexes we use the set of charges previously reported by Calero *et al.*¹⁶

Atom	Na-LTA	Ca, Na-LTA
	charge (e-)	charge (e-)
C_co2	0.6512	0.6512
O_co2	-0.3266	-0.3266
O_zeo	-0.4838	-0.4372
Al	0.4859	0.4859
Si	0.7859	0.7859
Na	0.6633	0.4767
Ca	-	0.9534

Figure 6 shows an Arrhenius plot of the dependence of Henry coefficients with temperature in LTA4A. The experimental and simulation data obtained in this work were compared with experimental values available in the literature.¹⁹ Considering the sensitiveness of the methods used for the obtainment of Henry coefficients, our simulation data are in reasonable agreement with our experimental data.

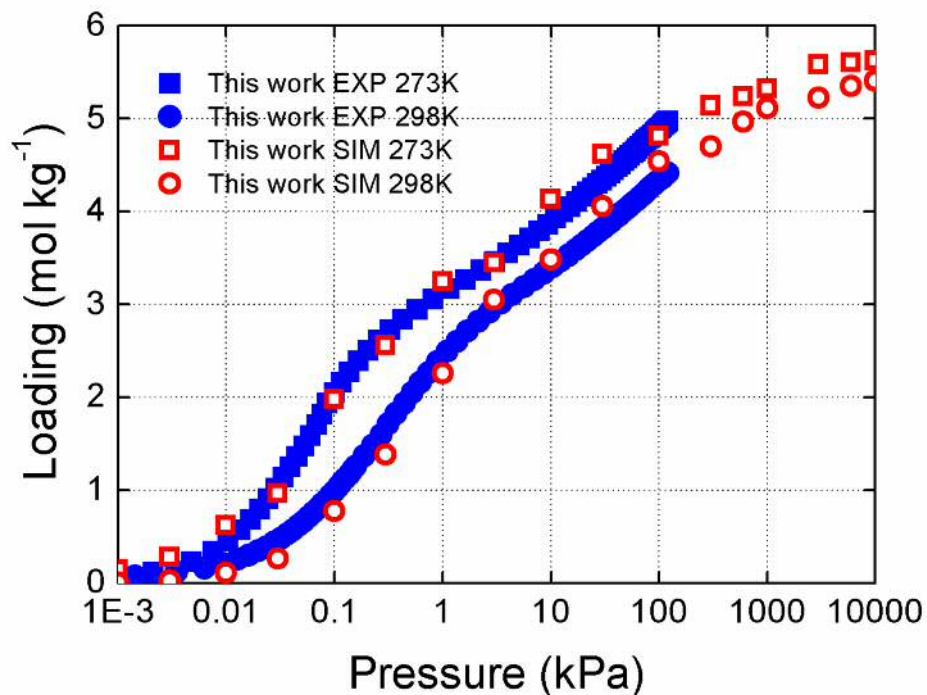


Figure 5: Experimental (full symbols) and computed (empty symbols) adsorption isotherms of carbon dioxide at 273 K (squares) and 298K (circles) in LTA4A (with 96 Na⁺).

However, both sets of data (experiment and simulation) are one order of magnitude higher than these previously reported.¹⁹ A possible explanation to these discrepancies could be that the authors evaluated the Henry coefficients on the isotherms measured after saturation in CO₂ and degassing at 293K. Under these conditions carbonate-like structures are already formed and the calculated Henry coefficients account just for the physisorbed gas. In this work Henry coefficients were obtained from the bare structures (evacuated at high temperature), thus they also account for the gas-framework interactions at low coverage where carbon dioxide chemisorption occurs. Consequently, our experimental values are consistently higher than those of Zúcal *et al.*¹⁹

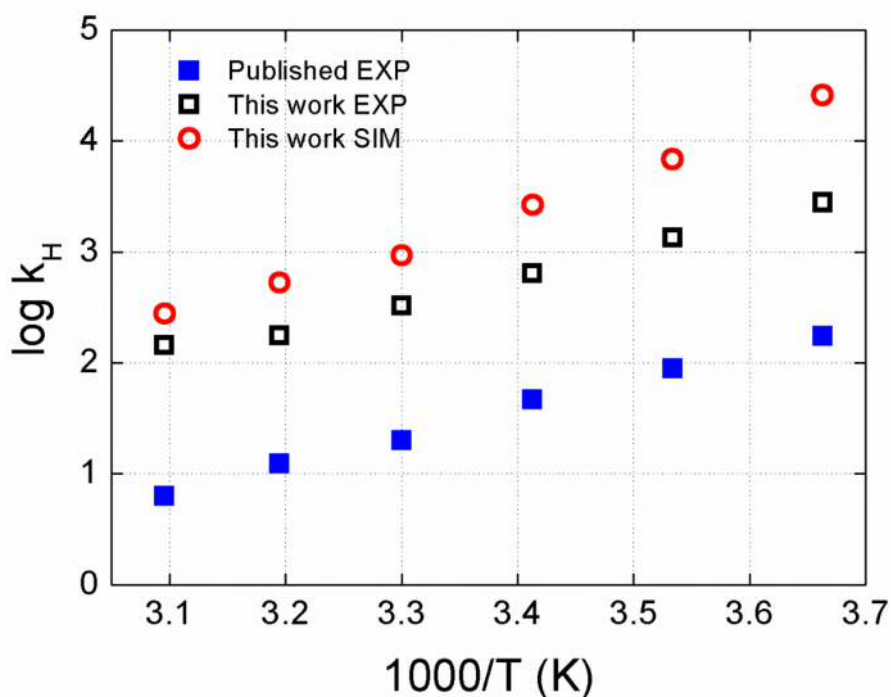


Figure 6: Henry coefficients of carbon dioxide as a function of temperature in LTA4A zeolite. The experimental and simulation values obtained in this work (empty squares and circles, respectively) are compared with previous experiments¹⁹ (full squares).

To analyze the effect exerted by the nature of the extra framework cation, we have computed the adsorption isotherms of carbon dioxide in LTA5A (Figure 7). To our knowledge there is a lack of force field parameters defining the specific interactions for calcium cations with carbon dioxide in zeolites. Previous works used generic mixing rules⁴⁸ of individual Lennard-Jones parameters reported for calcium cations in clays and carbon slits⁴⁹ and carbon dioxide.⁵⁰ As shown in Figure 7 the experimental results are overestimated with this set of parameters. Our approach assumes that sodium and calcium are chemically similar, and then we used for calcium-carbon dioxide interactions the same Lennard-Jones parameters that we developed for sodium-carbon dioxide interaction (Table 1). However, as shown in Figure 7 the set of charges used for LTA4A overestimates the experimental results obtained for LTA5A, probably due to the lower amount of complexes formed in structures containing calcium as well as to the higher mobility of calcium.⁵¹ Assuming that the formation of carbonates is mainly dominated by the

amount of extra framework sodium cations and as this is three times lower in LTA5A than in LTA4A (96 Na^+ /u.c. LTA4A; 32 Na^+ /u.c. and 32 Ca^{2+} /u.c. LTA5A), we have performed additional simulations reducing the partial charges of the atoms involved into the complex formation by 2/3 respect to the previous increase needed for LTA4A zeolite (Table 2). As shown in Figure 7, the computed adsorption isotherm using this set of charges reproduces the experimental curve obtained at low pressure and up to 10 kPa, but underestimates the amount adsorbed at saturation. This is most likely attributed to the mobility of the cations at saturation conditions in the simulations. It should be recalled that from an experimental point of view, the mobility of the cations is hindered by the CO_2 -complexes formed and the molecules of carbon dioxide already physisorbed in the structure. Indeed, as seen in Figure 7 this effect can be reproduced, at high pressure, by molecular simulation keeping the cations fixed.

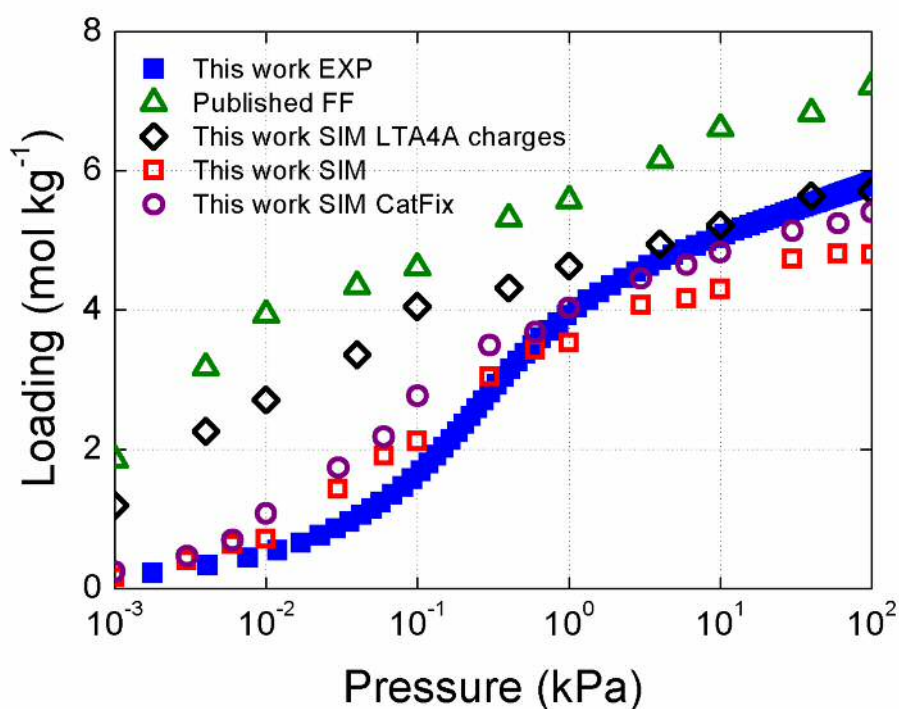


Figure 7: Experimental (full symbols) and computed (empty symbols) adsorption isotherms of carbon dioxide at 273 K in LTA5A (with 32 Na^+ /u.c. and 32 Ca^{2+} /u.c.). Simulations were performed using the set of charges developed for LTA4A (black prisms) and that for LTA5A zeolites (red squares). Simulations with the latter set of charges but keeping fixed the extra framework cations are also added for comparison (purple circles). Additionally we compare with the results obtained with the previously published parameters for calcium⁴⁹ (green triangles).

Finally, we want to emphasize that the new set of parameters developed in this work is a first approach to consider the presence of complexes in zeolites. Since there are no evidences about the number or position of the complexes formed on each system, our approach averages the effect of the complexes in the whole structure. In order to predict the irreversible behavior of the hysteresis, future experimental and theoretical work needs to be performed.

Conclusions

We have explored the mechanisms governing the CO₂ adsorption in zeolites with different aluminum content and density and nature of extra framework cations. We have shown that the accessible pore volume of the zeolite is affected by the amount and strength of carbonate-like complexes formed upon carbon dioxide adsorption; both aspects depend on the Si/Al ratio of the zeolite, as well as the nature and mobility of the extra framework cations. The strong interaction of carbonate-like complexes in zeolite structures with high amount of cations (NaX and LTA4A) explains the limitations of our previous force field to reproduce CO₂ adsorption in such structures. The experimental findings were validated with molecular simulation using transferable force fields to reproduce the adsorption of carbon dioxide in structures with high Si/Al ratio. We also provide new set of charges that accurately reproduces the experimental adsorption in structures containing carbon dioxide-cation complexes, reinforcing our previous force field.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. All authors contributed equally.

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