When less is more: more cations means more adsorption sites for toluene in zeolites?

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Abstract

The unique properties of zeolites makes them an interesting material to be used in separation processes. The possibility of tailoring some of their characteristics, like the Si/Al ratio, allows to optimize their synthesis for a given task. Concerning the adsorption of toluene by faujasites, an understanding of the effect of cations is necessary to foster the elaboration of new materials, which can capture molecules from humid environments with a high selectivity and sensibility. Undoubtedly, this knowledge is relevant for a wide range of applications going from the elaboration of technologies for improving the air-quality to the elaboration of diagnostic procedures to prevent health risks. Our simulations by Grand Canonical Monte Carlo elucidate the role of cations in the adsorption of toluene for faujasites with different Si/Al ratios. They detail how the location of the cations inhibits or enhances the adsorption. The cations located at site II are shown to be those enhancing the adsorption of toluene in faujasites. Interestingly, cations located at site III generate a hindrance at high loading. This becomes an impediment for the organization of toluene molecules the faujasite.

1 Introduction

Toluene is a well known aromatic compound used as a reagent in the synthesis of different chemicals and as a solvent in many industries. Together with benzene, ethyl-benzene, and xylene, toluene composes the so-called BTEX group of volatile organic compounds (VOC's). They are related to many health risks ranging from neurological disorders to cancer. These compounds act as pollutants because of their possible influence in chemical processes that occur at the troposphere.[?][?] These issues lead many regulations worldwide to control the level of toluene in different environments.[?][?] Henceforth, there is a need for developing strategies for separating or degrading toluene as adsorption or chemical conversion processes.[?] If we address the adsorption processes for capturing airborne toluene, many materials have been studied such as: activated carbon, metal-organic frameworks, clays, ionic liquids and zeolites.[?][?][?] Since zeolites present a low cost of production, they represent a promising alternative for the adsorption of toluene. Other interesting properties of this material are their high thermal stability and the possibility of tailoring them (c.f. modification of the Si/Al ratio and the chemical nature of exchanged cations). The faujasite structure is attractive because of the adequate size and geometry of the pore.

Molecular modeling of zeolites is interesting because it allows to study in detail the adsorption process and correlate them with the modifiable characteristics of the material. Namely, the comprehension of the effect of cations on the competing adsorption of water and toluene could be of great value for addressing an important technological challenge: the synthesis of a material which is capable of adsorbing toluene at environments with different levels of humidity.[?][?][?][?] Moreover, toluene can be seen as a bio-marker for lung cancer.[?] Thus, designing a material capable of detecting very-low quantities (some ppb) of toluene in a humid environment, such as the human breath, would open the possibility to use such systems in diagnostical procedures.[?]

While the research interest resides on improving either the sensibility or selectivity of the adsorbent, it is primordial to have a detailed picture of the cation effects on the adsorption

of aromatics.

In the experimental characterization of Fitch *et al.*, the authors identified preferable adsorption sites of benzene on the zeolite NaY.[?] They showed that, inside each super-cage, 4 benzene molecules are located near the cations at site II. In addition, other adsorption sites were identified near the center of the six-membered ring of the oxygen atoms (located at the windows connecting the supercages). Such results were also observed in early computational studies employing canonical Monte Carlo simulations of zeolites at a given loading condition.[? ?] Gonçalves *et al.* performed NMR experiments for elucidating the transport properties of adsorbed benzene molecules inside faujasites with Si/Al ratio of 2.65 (HY), 3.25 (USY) and 40 (NaY).[?] They showed that an increase in the number of cations in the zeolite reduced the mobility of the adsorbate (implying a decrease of the probability of site-hopping events). The authors argued that the lower mobility was due to the tightly interacting pairs benzene-cations at site II.

Interestingly, Auerbach and coworkers explained how the trend, mentioned in the last paragraph, is reversed if one compares NaY and NaX.[?] This was later verified also by Quasi-Elastic Neutron Scattering measurements.[?] The authors argued that the hopping movement is favored in NaX by the combination of different factors. First, the presence of cations at site III decreased the stability of the pair benzene-cation of site II. Second, the adsorption occurring near the cations at site III are more favorable than the adsorption around site II. Moreover, the aromatic compound is able to interact simultaneously with cations in both sites, which would be responsible for a competition in forming interaction pairs with the adsorbate. This would ultimately enhance the mobility of the adsorbates in zeolites with higher cation quantities.[?] This non-trivial behavior, that associates the location of cations and their interactions with aromatic compounds, plays a relevant role in the adsorption capacity and selectivity of such materials. For instance, the presence of a cation in NaY makes the adsorption of toluene energetically more favorable than in high-silica zeolites (*e.g, DaY*). This can be explained by evoking the occurrence of specific interactions between

the cations and the aromatic molecule.[?][?][?] This implies a different adsorption mechanism between the two materials. While the adsorption of benzene on NaY occurs near sites II, in DaY the sorbates are randomly distributed inside the structure. This has been reported in Grand Canonical Monte Carlo (GCMC) simulations.[?]

However, even if the adsorption of toluene in NaX is energetically more favorable than in NaY,[?] this is not necessary followed by a higher adsorption saturation value of toluene on NaX. In fact, Daems and coworkers[?] showed that, in the NaX at high loading, there would be the formation of interacting pairs between a benzene and a sodium located either at sites II or III. Which will create a degree of steric hindrance inside the super-cage. This can be associated to a change in the positions of adsorption of benzene molecules near the cage window. Given that in the NaY cations in sites III are absent, there will not be such effect. Hence, the system will show a higher adsorption capacity.[?] It is possible to argue that, since the high loading measurements are performed at the liquid phase of a mixture, these results could be driven by some competition between the aromatic compound and the solvent. Nonetheless, similar results have been reported for the adsorption of gaseous benzene in a temperature range of 100-180°C.[?]

Recently, González-Galán and coworkers derived a force field for simulating the adsorption of aromatics on faujasites. They fitted the parameters for reproducing experimental adsorption isotherms of benzene on DaY and NaY.[?] By combining *ab initio* calculations, classical simulations and experimental data, the authors explained how the presence of cation-π interaction pairs could explain why high-silica faujasites are less efficient for separating benzene and cyclohexane.

According to the studies mentioned above, there is a strong evidence of the decisive role of cations on the adsorption process on zeolites. Nevertheless, we have a lack of information about the role played by the amount and the location of the cations. Fulfilling this gap will be useful for designing task-specific zeolites. The work presented here is to report Grand Canonical Monte Carlo simulations for giving an atomistic point of view about the adsorption

processes of toluene in faujasites.

2   Computational details

A concomitant objective of this work is to pave the way to study the effect of the cation quantity on the competing adsorption of toluene and water in Na^+-exchanged faujasites. This paper reports a set of interaction parameters that are compatible with the force field developed by Buttefey *et al.*[?] and Di Lella *et al.*[?] for the interaction between water and faujasite. This force field has been shown to outperform the water adsorption on faujasites with different Si/Al ratio.[?]

2.1   Adsorbent structure

The spatial distribution of cations in a zeolite are not random and depending on the Si/Al ratio they tend to occupy different types of preferential sites (see Figure 1). The initial configurations presented in this study were obtained by modifying a NaX structure used in previous works.[?][?] This structure has 86 Na^+ per unit cell, which was the highest cation quantity considered in this work.

By generating other faujasites with higher Si/Al ratio than to the original one, it was possible to assure that some physico-chemistry characteristics of these materials were taken into account correctly. Namely, the Löwenstein rule is obeyed. Second, the relation between preferential site and number of cations is respected. That is to say, for a number of cations less than 32 per unit cell, the Na^+ occupy the so-called sites II. With a cationic quantity higher than 32, but lower than 65, the ions are distributed between the sites I and I'. Finally, for an even higher quantity of cations, the sites III and III' start to be occupied.[?][?] The sole approximation considered here is the indistinguishability of sites I and I' present in the original NaX structure.

This work considered 8 structures and they concern a faujasite framework with different
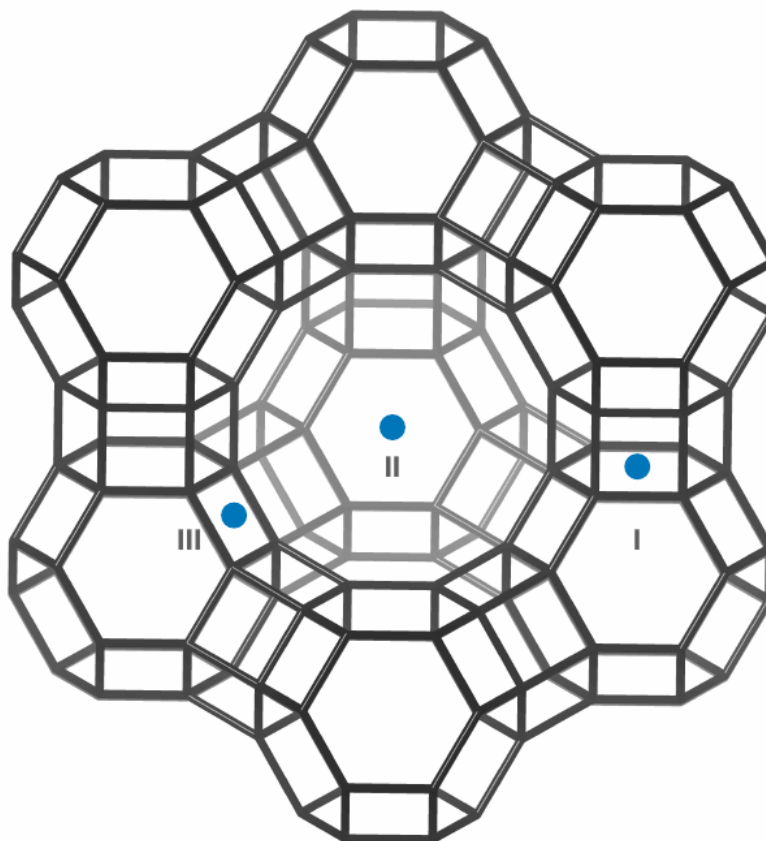
Figure 1: Location of cations at sites I, II and III for the Faujasite NaY and NaX.

number and location of cations. All the systems are listed in Table 1 with the unit cell composition and the population of cation occupying a given site type. The unit cells presented a cubic lattice parameter of 24.8536 Å and are replicated twice in each direction resulting in a 2x2x2 super-cell. Following the conventional nomenclature, faujasites with a Si/Al ratio higher than 1.8 are named NaY and NaX otherwise. The only exception is the system absent of cations, which is commonly denominated DaY as dealuminated Y zeolite.

The initial configurations were generated by randomly selecting some cations from the original structure to be preserved, while removing the others. In addition, the closest Al atom to the preserved cations is also kept. Notice that the random sampling of cations has been done by respecting the quantity/site population relation discussed previously.

Table 1: Faujasite structures considered in this work

Zeolite	Composition	N. of Cations	Sites I	Sites II	Sites III
DaY	$Si_{192}O_{384}$	0	0	0	0
NaY2	$Na_2(AlO_2)_2(SiO_2)_{190}$	2	0	2	0
NaY5	$Na_5(AlO_2)_5(SiO_2)_{187}$	5	0	5	0
NaY10	$Na_{10}(AlO_2)_{10}(SiO_2)_{182}$	10	0	10	0
NaY15	$Na_{15}(AlO_2)_{15}(SiO_2)_{177}$	15	0	15	0
NaY20	$Na_{20}(AlO_2)_{20}(SiO_2)_{172}$	20	0	20	0
NaY25	$Na_{25}(AlO_2)_{25}(SiO_2)_{167}$	25	0	25	0
NaY32	$Na_{32}(AlO_2)_{32}(SiO_2)_{160}$	32	0	32	0
NaY40	$Na_{40}(AlO_2)_{40}(SiO_2)_{152}$	40	8	32	0
NaY48	$Na_{48}(AlO_2)_{48}(SiO_2)_{136}$	48	16	32	0
NaY52	$Na_{52}(AlO_2)_{52}(SiO_2)_{140}$	52	20	32	0
NaY56	$Na_{56}(AlO_2)_{56}(SiO_2)_{136}$	56	24	32	0
NaY64	$Na_{64}(AlO_2)_{64}(SiO_2)_{128}$	64	32	32	0
NaX70	$Na_{70}(AlO_2)_{70}(SiO_2)_{122}$	70	32	32	6
NaX76	$Na_{76}(AlO_2)_{76}(SiO_2)_{116}$	76	32	32	12
NaX80	$Na_{80}(AlO_2)_{80}(SiO_2)_{112}$	80	32	32	16
NaX86	$Na_{86}(AlO_2)_{86}(SiO_2)_{106}$	86	32	32	22

2.2 Force field

2.2.1 Adsorbate-adsorbate interactions

The interactions between toluene molecules are described by using the 10-site model of the TRAPPE force field.[?] This model presents one positive charge at the center of the ring, and two negative charges located at the opposites planes of the ring. In this way, the model can account for the occurrence of cation-π interactions, that have been shown to be relevant for the description of the adsorption process of such compound on zeolites.[?]

Worthwhile to mention, that the partial charges of toluene presented in the original model greatly enhanced the attraction between the adsorbate and adsorbent containing high quantities of cations. This led to severe overestimation of the adsorption amount at lower pressures. Hence, this work opted to scale the partial charge values. Several scaling factors were tested for reproducing the experimental adsorption isotherm of toluene on NaY. By multiplying the toluene charges by a factor of 0.56, it was found a better agreement with

experiments. In addition, the molecule is treated as a rigid entity (no intramolecular degrees of freedom).

2.2.2 Adsorbent model

This work also considered the framework to be rigid. Although the flexibility might play a rule in the diffusion of the aromatic molecules, it has been shown that its omission do not have a significant effect on the adsorbed quantities.[?]

The partial charges were retrieved from the work of Buttefey *et al.*[?] and Di Lella *et al.*[?] The authors proposed a linear extrapolation procedure for estimating the partial charges as a function of the number of cations in the structure. The partial charge values for each atom, of the analyzed zeolites, can be found in Table 2. In addition, dispersion interactions involving the zeolite atoms are modeled only with pairs involving either the oxygen atom or the cation.

An important remark to make here is that the used model does not distinguish between the Si and Al atoms. That is to say, both atoms have the same charge value. Thus, the different heterogeneity is accounted by recalculating the average partial charge on oxygen atoms and tetrahedral centers (Si and Al) for each degree of cation exchange. This approximation has already gave satisfactory results.[? ? ?] However, there are other strategies for accounting for the different chemical environments, such as, for example, distinguishing oxygen atoms connected either to Si or Al. This last strategy was supposed to generate transferable models for zeolites with different degrees of cation exchange.[? ? ? ?] Unfortunately, this was proven to be difficult to verify for certain systems.[?]

Although the cation mobility is known to play an important role on the adsorption processes involving faujasites, an important first discussion concerning the effect of cation positions and quantity on such processes should be drawn. Thus, this work considered the cations to be fixed at the preferential sites.

Table 2: Partial charges of the zeolite atoms

Zeolite	q_O	$q_{Si/Al}$	q_{Na}
DaY	-0.8	1.6	-
NaY2	-0.800993	1.591576	0.999412
NaY5	-0.802483	1.578939	0.999412
NaY10	-0.804965	1.557878	0.999412
NaY15	-0.807448	1.536817	0.999412
NaY20	-0.809931	1.515756	0.999412
NaY25	-0.812414	1.494695	0.999412
NaY32	-0.815889	1.465210	0.999412
NaY40	-0.819862	1.431513	0.999412
NaY48	-0.823000	1.396000	1.00000
NaY52	-0.825000	1.379600	0.998400
NaY64	-0.831779	1.330420	0.999412
NaX70	-0.834758	1.305147	0.999412
NaX76	-0.838700	1.281700	0.999663
NaX80	-0.839723	1.263025	0.999412
NaX86	-0.843300	1.240000	0.997060

2.2.3 Adsorbate-adsorbent interactions

Here, we tested two sets of interactions parameters and the simulation results are compared with experimental data for the adsorption of toluene in DaY. The set presenting the best agreement with experimental result is then used to simulate the other faujsites.

The first set of parameters, called set A, was generated by applying the Lorentz-Berthelot mixing rule to the self-interaction parameters of the toluene atom types and of the oxygen atoms of the framework as reported by Di Lella *et al.*[?] The second set of parameters, called set B, is derived heuristically and is explained below.

The parameters developed by Dubbeldam *et al.*, for the interaction of n-alkanes and zeolite atoms have shown to reproduce experimental results for both the adsorption heat and isotherm of alkanes with different chain lengths on zeolites (and with different shapes and sizes).[?] Thus, it is reasonable to suppose that these parameters can accurately describe the dispersion interactions, since they largely depend on the volumes of the interacting species. For extracting a plausible value for the self-interaction parameter for the oxygen

of the zeolite, a linear regression was applied between σ_{i-i} and σ_{i-o} parameters for the different atom types reported by Dubbeldam *et al.*[?] By considering an arithmetic mean, the σ_{o-o} parameters are calculated as twice the value of the intercept obtained by this regression. Then, the arithmetic mean between this new value of σ_{o-o} and the σ_{i-i} given by the TRAPPE model was used to obtain the σ_{i-o}.

A different procedure was used for estimating ϵ_{o-o}. Given σ_{o-o}, σ_{i-i} and ϵ_{i-i}, different values for ϵ_{o-o} can be obtained by applying Equation 1,[?] where $i = CH_4, CH_3, CH_2, CH$ and C. The final estimate for ϵ_{o-o} is obtained by averaging the values obtained for the different pairs. The ϵ_{i-o} interaction parameters between the toluene atom types (given by the TRAPPE model) and the oxygen of the zeolite were obtained by applying the same mixing rule. This size-weighted mixing rule improves the accuracy of adsorption simulations.

$$\epsilon_{ij} = \frac{1}{2}\left(\frac{\sigma_i}{\sigma_j}\epsilon_i + \frac{\sigma_j}{\sigma_i}\epsilon_j\right) \tag{1}$$

The interactions between the cations and the atom of the toluene molecule have been modeled by using the Dang[?] (for Na^+) and the TRAPPE model (for the toluene molecule) and followed by the Lorentz-Berthelot mixing rule (Tables 3 and 4). A cut-off radius of 12 Å was applied to the pairwise interactions and periodic boundary conditions in the three directions. The Ewald sum is used for treating the long-range contributions to the electrostatic interactions.

2.3 Monte Carlo simulations

For calculating the adsorption isotherms, the GPU Optimized Monte Carlo (GOMC) code version 2.70[?] was used to carry on the simulations in the μVT ensemble and the Configurational-bias Monte Carlo method.[?] By imposing a chemical potential, the average number of adsorbed molecules is measured directly. The simulations are performed at 298.15 K and the fugacities range from 0.1 to 2500 Pa.

Table 3: Lennard-Jones Interaction Parameters

Atom type	Description	σ_{ii} (Å)	ϵ_{ii} (K)	q	Reference
CH_3	Methyl site	3.750	98.00	0.00	[?]
CH	Aromatic CH site	3.740	48.00	0.00	[?]
C	Aromatic C bonded to methyl site	3.880	21.00	0.00	[?]
CM	Charge site at the center of ring	-	-	1.3552	This work
M	Charge site on top and below ring	-	-	-0.6776	This work
Na^+	Sodium cation	2.584	50.27	Table 2	[?]
Si	Zeolite Silicon	-	-	Table 2	[? ?]
Al	Zeolite Aluminum	-	-	Table 2	[? ?]
O_A	Zeolite Oxygen (set A)	3.000	93.53	Table 2	[? ?]
O_B	Zeolite Oxygen (set B)	3.855	52.88	Table 2	This work

Table 4: Cross interaction Lennard-Jones Parameters

Interaction pair	Set A		Set B	
	σ_{ij} (Å)	ϵ_{ij} (K)	σ_{ij} (Å)	ϵ_{ij} (K)
CH3-O	3.375	95.74	3.480	93.00
CH-O	3.370	67.00	3.868	39.10
C-O	3.440	44.32	3.798	52.88

The proportion of Monte Carlo moves were: 0.1 translation; 0.1 rotation; 0.1 intrabox swaps; 0.7 insertion. Moreover, an exclusion distance of 0.5 Å was used to prevent the occurrence of nonphysical configurations. The simulation length is of 5×10^7 Monte Carlo steps for the zeolites having less than 70 cations. For the other systems (*e.g.*, $NaX_{(70-86)}$), 6×10^7 steps are used. In the simulations the last 1×10^7 iterations are used as production data. The input files were generated with the aid of the MoSDeF utilities[? ? ?] (see Supplementary Information).

2.4 Simulation analysis

In this work we compared the adsorption processes of the systems given in Table1 by analyzing: the adsorption isotherms, calorimetric heat of adsorption, radial distribution functions, occupancy maps and the total amount of interacting pairs formed between the toluene molecules and the cations. This last quantity was defined by the number of toluene molecules

for which the ring center are located below 3.3 Å from a cation. For the structural quantities, the VMD software[?] was used.

For extracting the adsorption isotherm, one has to calculate the average amount of adsorbed molecules at the production runs, and relate the fugacity of the adsorbate with the pressure for drawing the comparison with experimental results. Here, it was considered that the gas obeys the ideal gas law, which is a reasonable assumption at these conditions.

For calculating the calorimetric heat of adsorption, two approaches are used. One based on the fluctuations given by Equation 2. In this equation E_{tot} is the total energy of the system, N is the number of the toluene molecules of the system, T is the temperature, R is the universal gas constant and the brackets refer to the ensemble averages.

$$\Delta H_{ads} = RT - \frac{\langle E_{tot} N \rangle - \langle E_{tot} \rangle \langle N \rangle}{\langle N^2 \rangle - \langle N \rangle^2}. \tag{2}$$

Notice that this method may fail for poor statistics at low loadings. This can be overcomed by producing very long simulations to reduce the numerical noise and for having reliable averages. It has been reported that such procedure may be impractical at very low chemical potentials.[?] Hence, a second procedure has been employed based on the intermolecular energy (E_{inter}) given by:

$$E_{inter} = \frac{\langle E_{tot} \rangle - \langle E_{intra,tol} \rangle - E_{framework,t=0}}{N_{cells}}, \tag{3}$$

with $N_{cells}(=8)$ stands for the number of cells, $E_{intra,tol}$ is the intramolecular energy of the toluene molecules and $E_{framework,t=0}$ is the total energy of the empty framework at the beginning of the simulation. Given that, the cations were held fixed $E_{framework,t=0}$ is the intramolecular energy of the framework (that is constant for the entire simulation).

A molar potential energy of adsorption ($\Delta U_{mol,ads}$) can be defined as the derivative of $\langle E_{inter} \rangle$:

$$\Delta U_{mol,ads} = \frac{d\langle E_{inter} \rangle}{d\langle N_{(ad.U.C.)} \rangle}, \tag{4}$$

where $\langle N_{(ad.U.C.)} \rangle / \langle N/N_{cells} \rangle$. By assuming that the gas phase behaves as an ideal gas, it is possible to relate $\Delta U_{mol,ads}$ to the calorimetric heat using the relation:

$$\Delta H_{mol,ads} = \Delta U_{mol,ads} - RT. \tag{5}$$

3 Results and discussion

3.1 Model validation

Before discussing how the different amount of cations influence the adsorption, some comparisons with experimental results are given for justifying the parameters used. Figure 2 displays the accuracy of the sets given in Table 4 for reproducing the experimental results from Pujol *et al.*,[?] for the structure $Na_2(AlO_2)_2(SiO_2)_{190}$.

Clearly, set B outperforms set A. Not only the onset of the adsorption is closer to the experimental data for set B, but also set A seems to present a saturation plateau. This last is absent with set B which has an enhanced agreement with experimental results near the saturation pressure ($\approx$ 3800 Pa). This result suggests that the heuristics employed here to derive the σ_{o-o} and ϵ_{o-o} parameters is reasonable (see subsection 2.2.3). Its justification would reside in the use of cross-interaction parameters that present a good description of the dispersion interactions and the use of a mixing rule that describes better the interactions of atoms with a large difference on their sizes.

For completing the validation of our model, it was necessary to evaluate its accuracy for reproducing experimental results from cation-exchanged zeolites. Thereupon, the simulations are compared with experimental adsorption isotherms for toluene on NaY (composition $Na_{52}(AlO_{52})_2(SiO_2)_{138}$) at 298.15 K from Gregis *et al.*[?]

Figure 3 shows that by using the original partial charges of the toluene model the agreement is far from being satisfactory. Therefore, we opted for a scaling of the partial charges. In this way, the agreement was improved and the model continues to be compatible with the
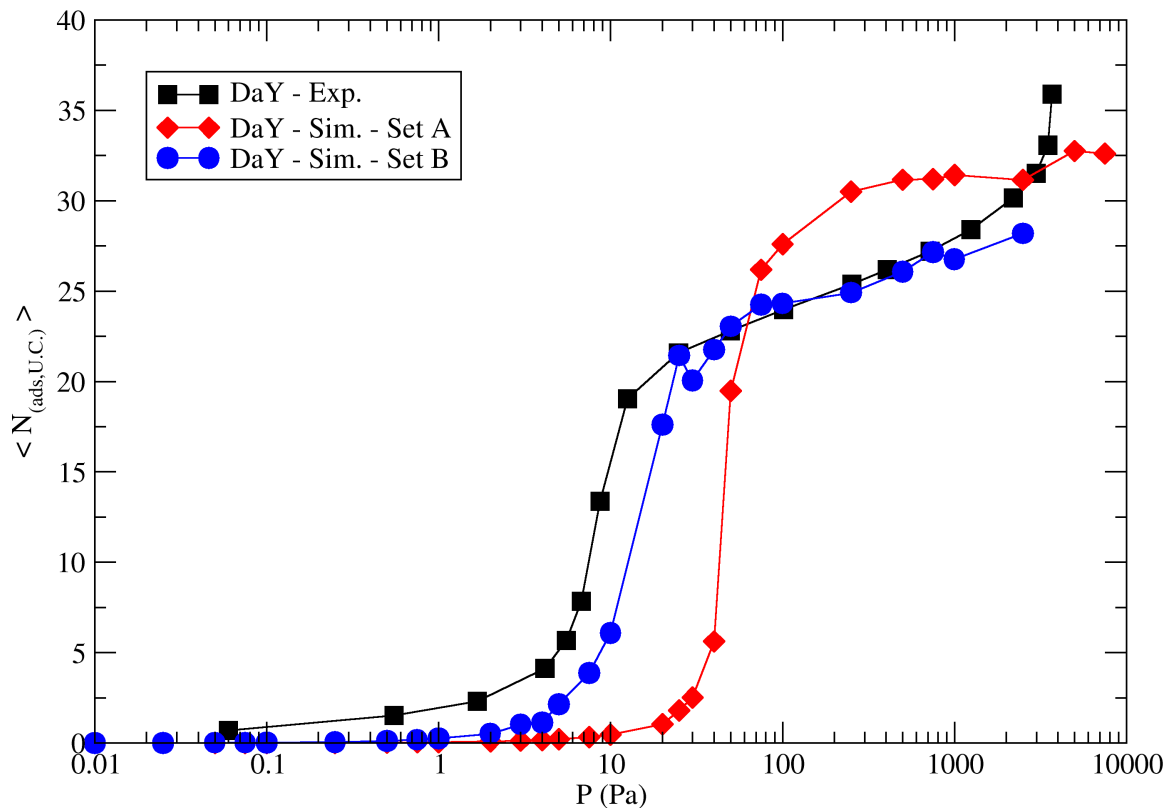
Figure 2: Comparison of the adsorption isotherm obtained with the parameters given in Table 4.

parameters of Buttefey *et al.*[?] and Di Lella *et al.*[?]

Different scaling factors were tested in a 1x1x1 cell and the best results are obtained with a factor of 0.56. Figure 3 shows the improved accuracy of the model for NaY52, while only having minor effects on the DaY-toluene systems. As a consequence, it is reasonable to assume that this charge scaling factor can be used with different degrees of cation exchange. Moreover, such results suggest that the adsorption of toluene on DaY is governed mainly by dispersion interactions.

Figure 4 gives the heat of adsorption for DaY, NaY56 and NaX86 by using Eq.2 and Eq.5,
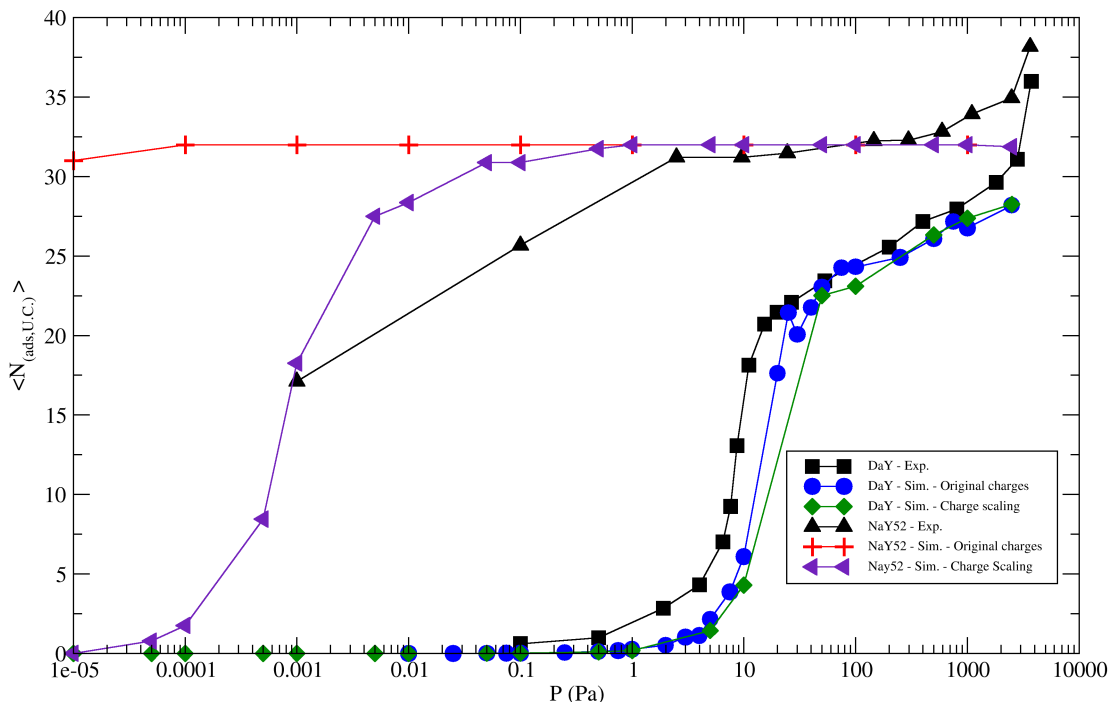
Figure 3: Comparison of the adsorption isotherms obtained with the original charges of the toluene model and with the charges scaled by 0.56. As can be seen the scaling does not change results for DaY, while it enhances the agreement with experiments for NaY52.

they show a good agreement with those reported by F. Benoit[?] and E. Pilverdier.[?] Although the values calculated with Eq.2 are in agreement within the experimental data for DaY, but it overestimates the heat of adsorption for NaY. Notice that, some of the experimental features are observed in the simulations as well. Namely, the increase of the heat of adsorption as a function of the adsorbed molecules for DaY. The pronounced decrease of heat of adsorption observed experimentally and by simulations may be associate to a condensation of molecules.

For verifying if the interactions between the aromatic ring and cations are well described, we calculated the radial distribution function, $g(r)$, between the center of the aromatic ring and the cations located at each site separately. Figure 5 gives the results for NaX86 (at 1000 Pa), we can observe the presence of a pronounced peak around 2.5Å involving the cation at site III. This value is in agreement with electronic structure calculations of cation-π complexes[?] and observed within the faujasite framework.[?]

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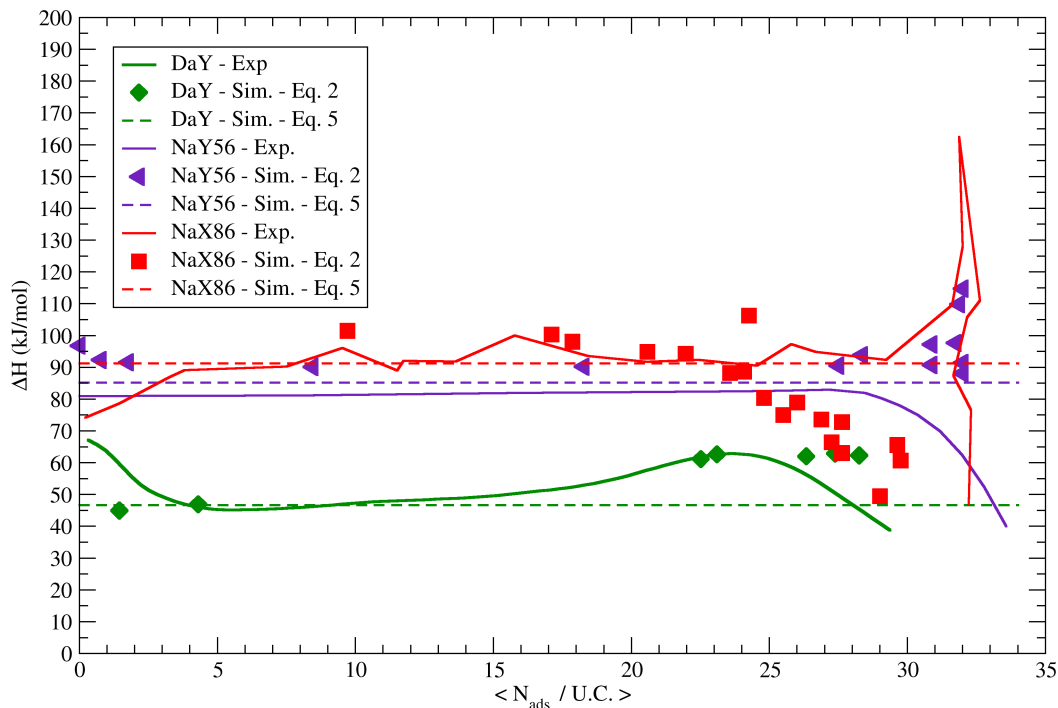
Figure 4: Comparison between experimental and calculated heats of adsorption by using Equations 2 and 5.

Another interesting aspect in Figure 5 is the smaller peak at 3.0Å involving cations located at site II. This suggests that either toluene molecules interacting with these cations are less tightly bonded or that cations at site III modulate such interactions. In addition, no interacting pairs are present between toluene and cations located at site I, which is related to the fact that such ions are less accessible.

3.2 The cumulative effect of cations in different sites

The comparison between the different cation-exchanged faujasites begins by analyzing zeolites without cations (DaY), with cations only on site II (NaY32), with cations on sites I and II (NaY64) and with cations on the three sites (NaX86). The obtained adsorption isotherms are displayed in Figure 6.

Our simulations show that cations increase the adsorption amount. It is interesting to ob-
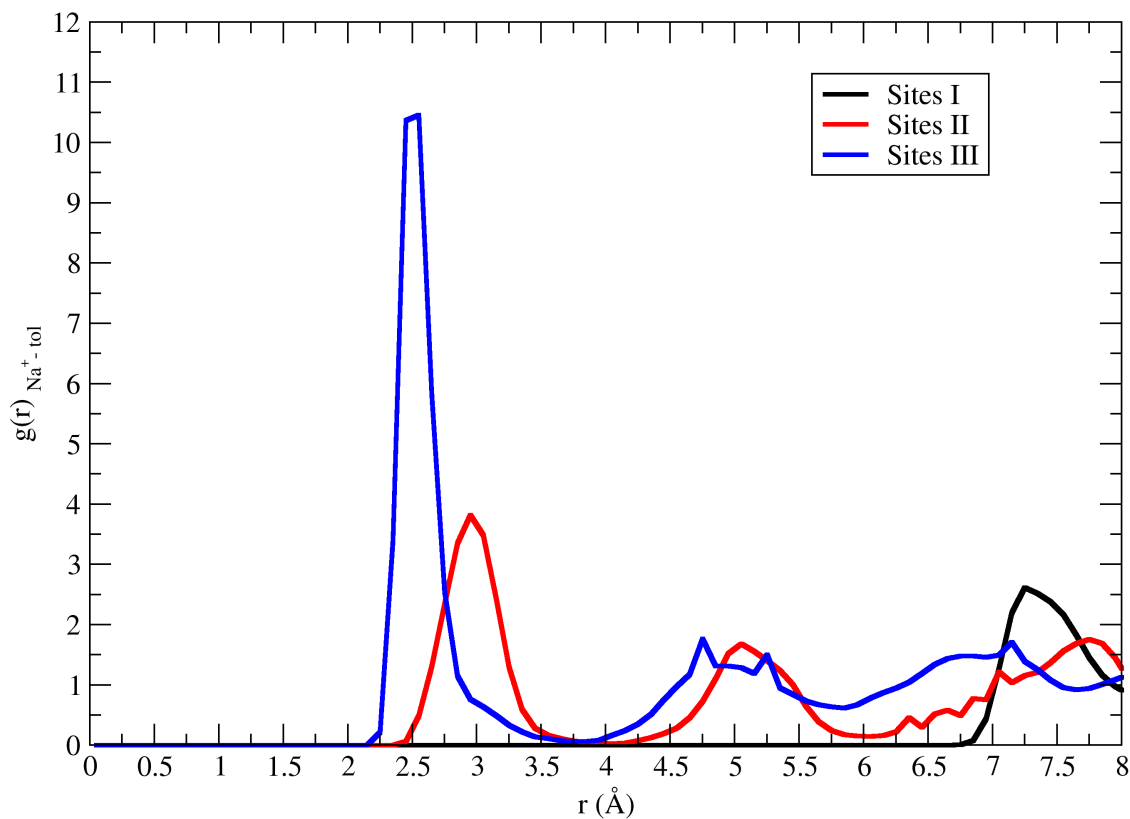
Figure 5: Pair distribution functions for toluene and Na^+ (NaX86 at 1000 Pa). The curve was calculated considering the center of the aromatic ring and the cations located at each site separately.

serve that NaY32 and NaY52 saturates both around 32 molecules per unit cell, while NaX86 does not seem to reach a saturation plateau. Notice that the NaX86 adsorbs more molecules at low pressures (< 0.004 Pa) than the NaY(32-52). However, as loading is increased this tendency is reversed. This last point is in agreement with reported experimental results for the adsorption of gaseous benzene[?] and for toluene diluted in octane *et al.*[?]

The isotherms for DaY and NaY32 show that the presence of cations in site II produce an increase of adsorption and for the structures NaY(32-52) we can say that cations on site I have a minor effect on the adsorption process.
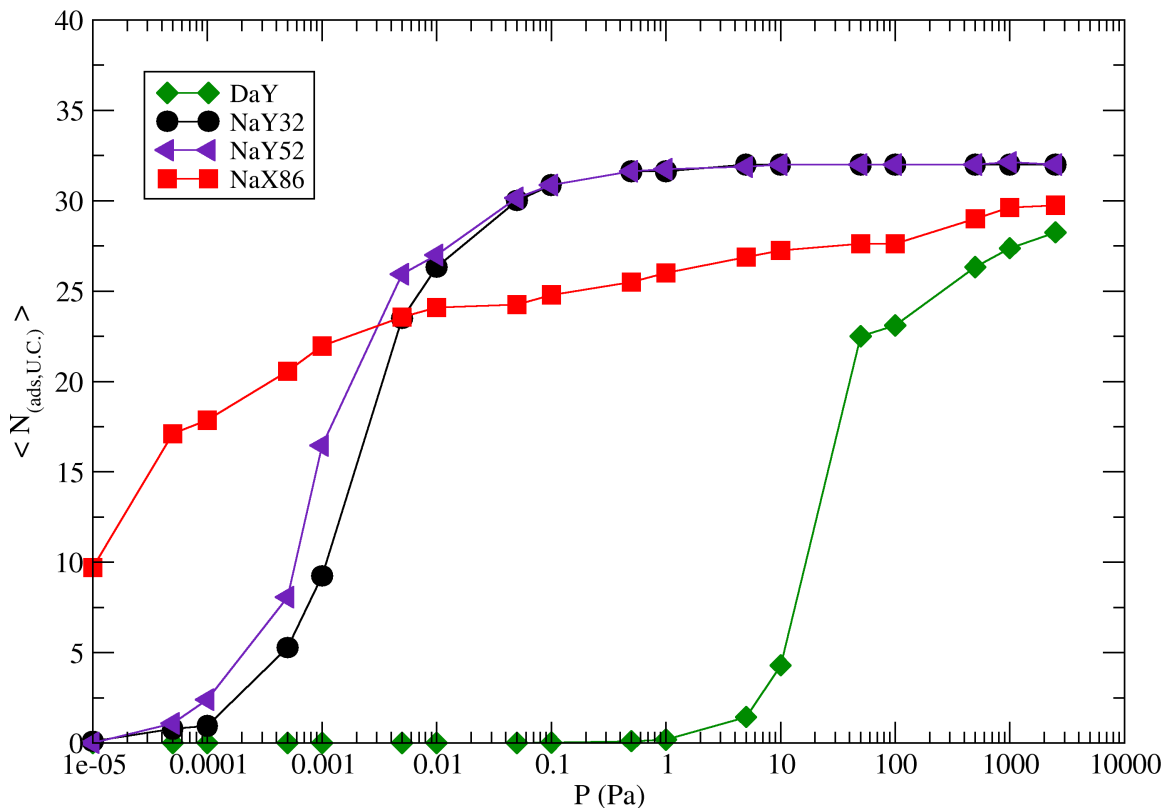
Figure 6: Adsorption isotherms for toluene on DaY, NaY32, NaY52 and NaX86.

The difference between structures NaY(32-52) and NaX86 is the presence of cations in site III for the latter structure. Figure 6 suggests that the presence of these cations enhance the adsorption at lower pressures but hinders it when the pores are already occupied.

The different amount of cations and their location gives rise to a different charge distribution for each faujasite and gives place to the formation of different kind of interacting pairs. These implies that the interaction energies and the spatial organization of the adsorbed molecules will be different.

Figure 7 gives $\langle E_{inter} \rangle$ as a function of the adsorbed molecules and presents a linear trend. The figure shows that DaY (without cations) has the less negative slope. The structures

NaY32 and NaY52 have a rather similar slope and the structures have cations on site II. This suggests that these last cations are energetically determinant for adsorption, even when sites III are energetically the most favorable as indicated by the deepest slope of the NaX86. The calculated attractive interactions in NaX86 might be associated to the formation of cation-π complexes and can explain its earlier onset of the adsorption.
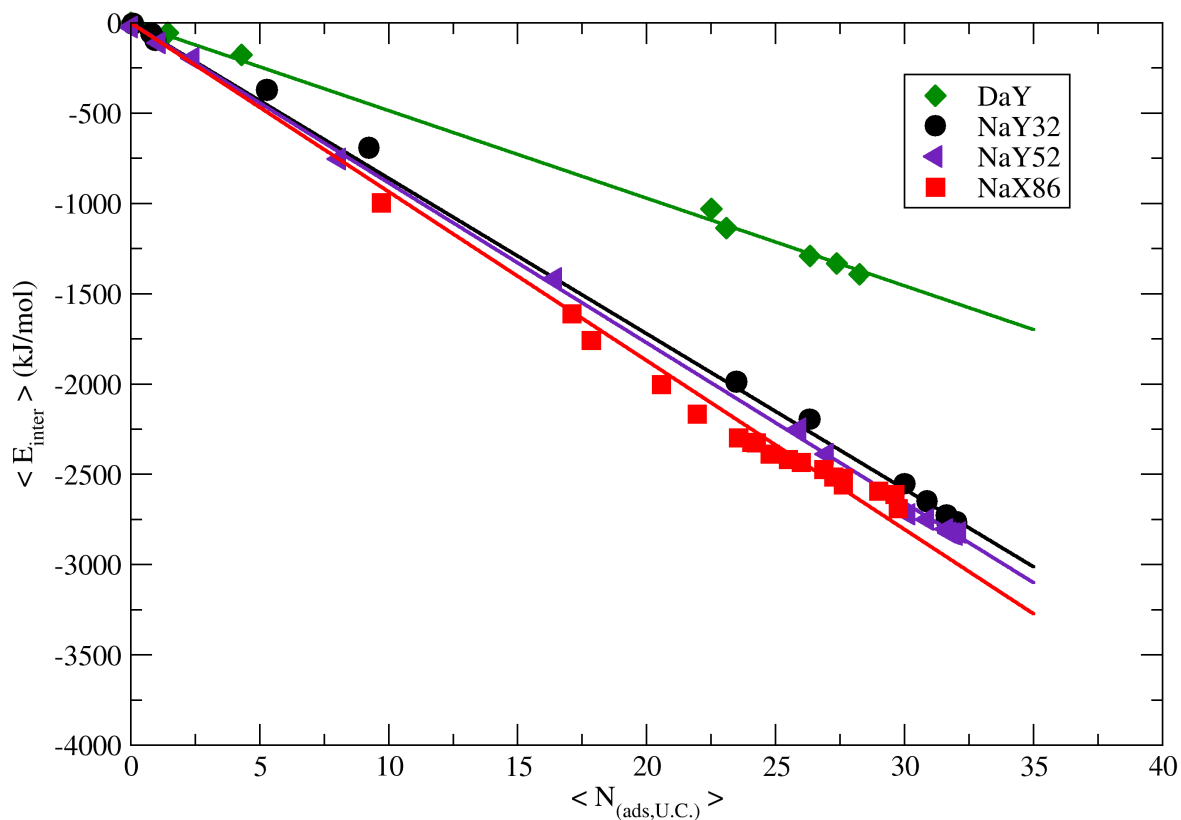
Figure 7: Internal energy (in kJ per mol) as a function of the number of adsorbed molecules of toluene on DaY, NaY32, NaY and NaX

3.3   The effect of increasing the number of cations at site II

Next, we proceed to analyze the effect of varying the number of cations at site II. According to the literature,[?][?] when the number of cations do not exceed 32 per unit cell, the ions would be located at site II. Figure 8 compares the adsorption isotherms of toluene on faujasites with a degree of cation exchange smaller than 32. A small number of cations, e.g., 2 or 5 per unit cell, is already enough to shift the adsorption curve towards lower pressures. In addition, there is a trend to increase the adsorption with the number of cations at site II. Moreover, as the number of cations is increased, the interaction energy between the framework and the adsorbate becomes more attractive. This is shown in Figure 9 that gives the molar internal energy of adsorption ΔU_{ads} as a function of the number of cations. By taking the derivative of the previous figure, it is easy to show that the highest variations will be between 0 to 32 cations (corresponding to the points with the higher steep).

Let us discuss more in detail the form of the adsorption curves in Figure 8. The change on the steepness of the curves can be explained by making use of the occuppation of cationic sites by toluene molecules. In the y-axis of Figure 10 is given the average fraction of adsorbed toluene molecules occupying a cationic site. This is calculated by taking the ensemble average of the ratio between the number of toluene molecules within a distance of 4Å from the cation and the total number of adsorbed toluene molecules ($\langle N_{(pairs,tol-cat)}/N_{(ads,U.C.)}\rangle$). The decreasing value of this ratio means that all the cationic sites are linked to an adsorbed molecule and subsequent molecules find their equilibrium positions in the free available space of the supercage. Intrigantly, the starting points of the decay in Figure 10 (*e.g.* in NaY15 the decay starts at $\langle N_{(ads,U.C.)}\rangle \approx 15$) coincides with the change of adsorption regime (Figure 8). Hence, we may conclude that adsorption begins by first saturating the cationic sites.
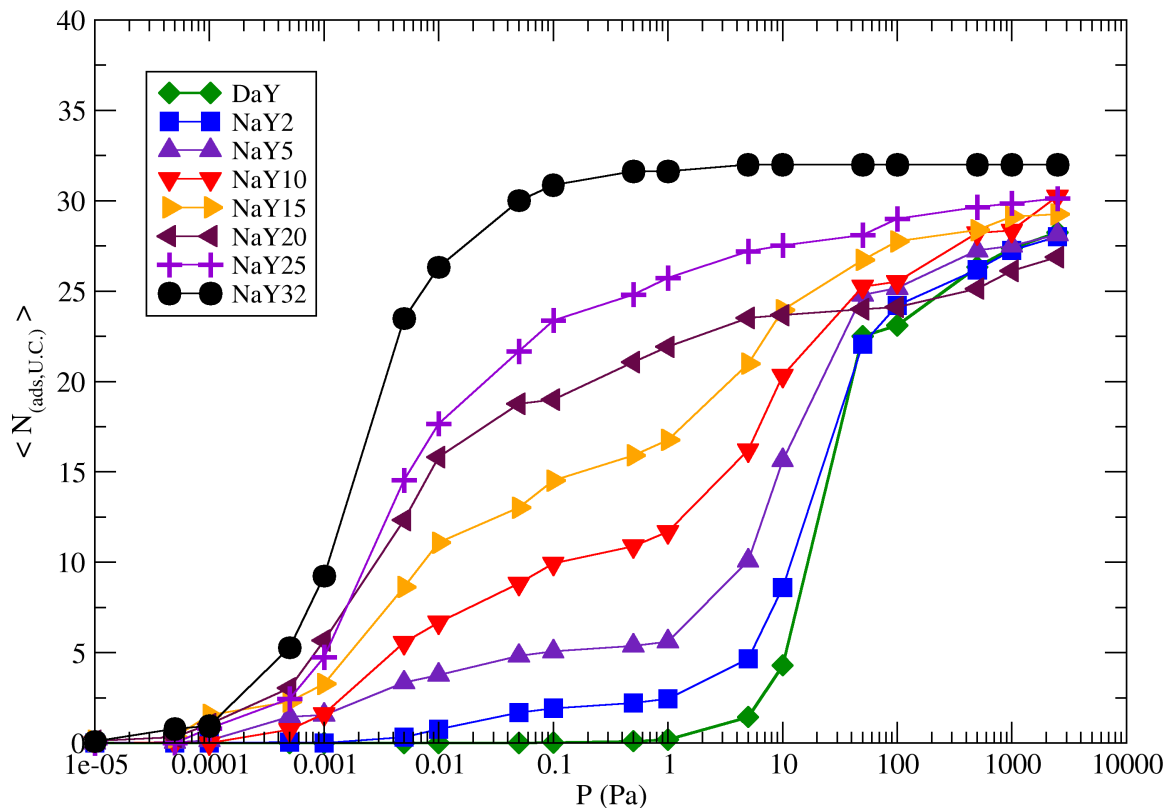
Figure 8: Adsorption isotherms of toluene on faujasites containing cations on site II.

3.4 The effect of increasing the number of cations at site III

The adsorption isotherms for structures with cations on site III are displayed in Figure 11. These cations imply a shift of the adsorption process at lower pressures. One may expect that by increasing the amount of cations on site III may induce an increase of the adsorbed molecules, since the molar internal energies of adsorption for these frameworks are the most favorable (Figure 9). However, Figure 11 shows that NaY64 (i.e.,cations on site I and II) adsorbs the most at higher pressures. This apparent contradiction, as it is discussed below, is due to the steric hindrance induced by cations on site III.

Given that, the hindering of adsorption at higher pressures occurs in faujasites containing
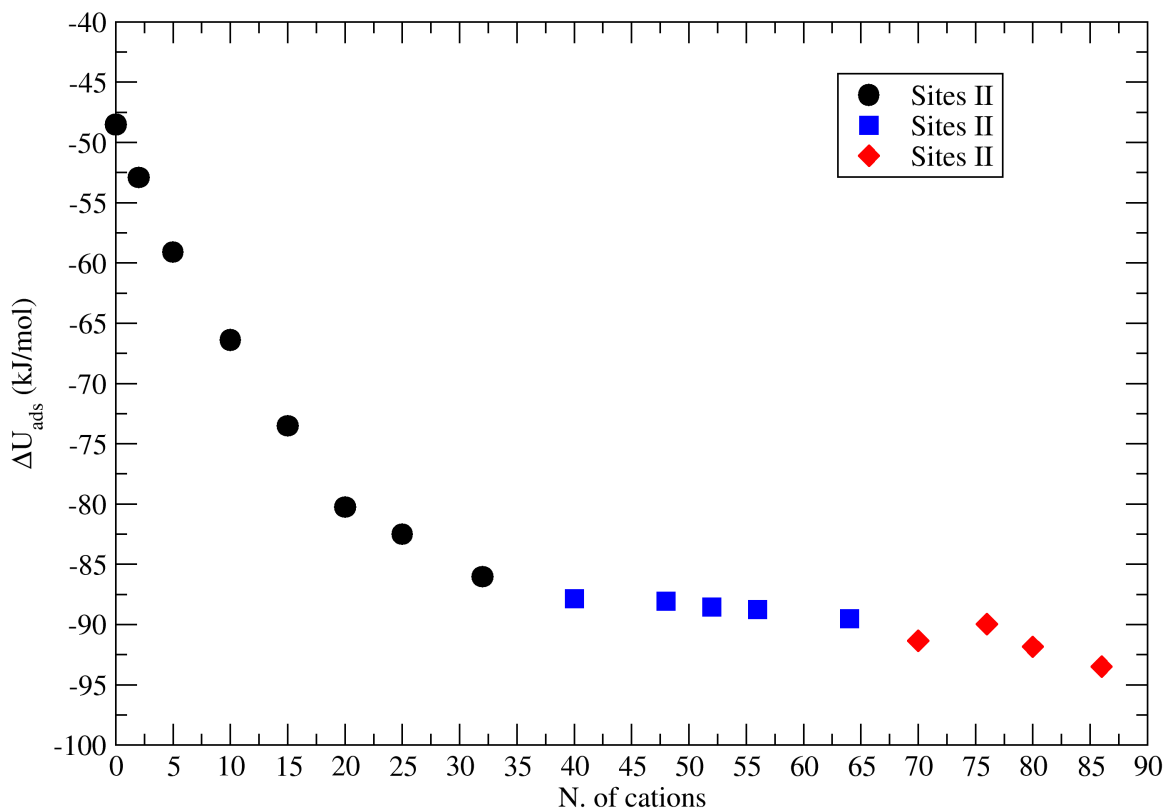
Figure 9: Internal energy of adsorption as a function of the number of cations for the faujasites analyzed.

cations at site III, specific interactions between the toluene and these cations might play a decisive role on the origin of the steric hindrance. In Figure 12 is given the comparison of the $g(r)$ involving center of the toluene rings and cations for different zeolites. The $g(r)$ for cations at site II present a peak at the same distance as for NaY64 (green solid line) and NaX86 (red solid line). This interaction produces an organized arrangement of toluene molecules (see inlets in Figure 12). The $g(r)$ for the cations at site III of the NaX86 is shifted to the left by 0.5Å. This implies that toluene molecules interact preferentially with cations on site III and they disturb the arrangement of the toluene molecules. More details can be
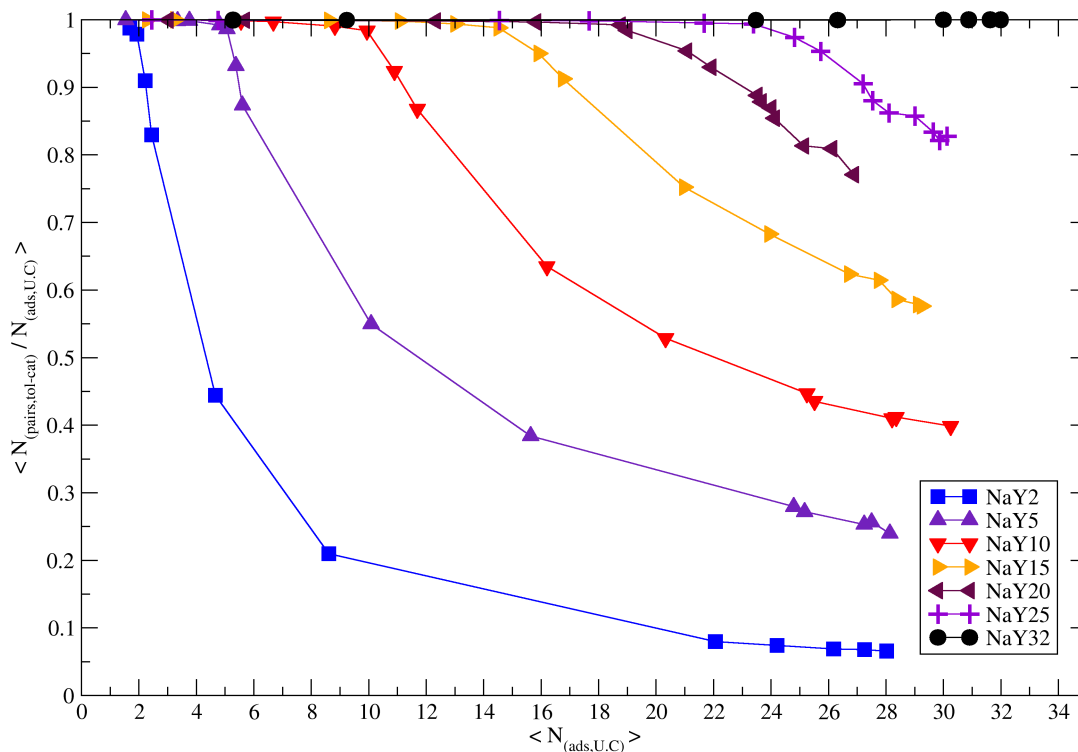
Figure 10: The fraction of toluene molecules interacting with a cation on site II for faujasites NaY2-32.

evoked to explain such results, by analyzing the fraction of toluene molecules occupying a given site, see Figure 13. At low loadings, the toluene molecules are preferentially attached to site III cations. This reflects the higher exposition of the adsorbate molecules to these sites and its high attractivity. As loading is increased, a competition of the two sites for adsorbing the aromatic molecules starts. The number of adsorbate molecules interacting with the site II cations increases and simultaneously decreases the fraction of aromatic molecules adsorbed near site III.

If one compares the NaY and NaX systems, for the latter the toluene molecules are less restraint to the cations on site II. This is probably due to the strong interactions between the adsorbate and cations at site III. This explanation is in agreement with the Vitale *et al.*[?] neutron diffraction experiments for NaX with a low coverage of benzene. The authors claimed that the presence of cations at site III changes the relative stability of other adsorption sites.
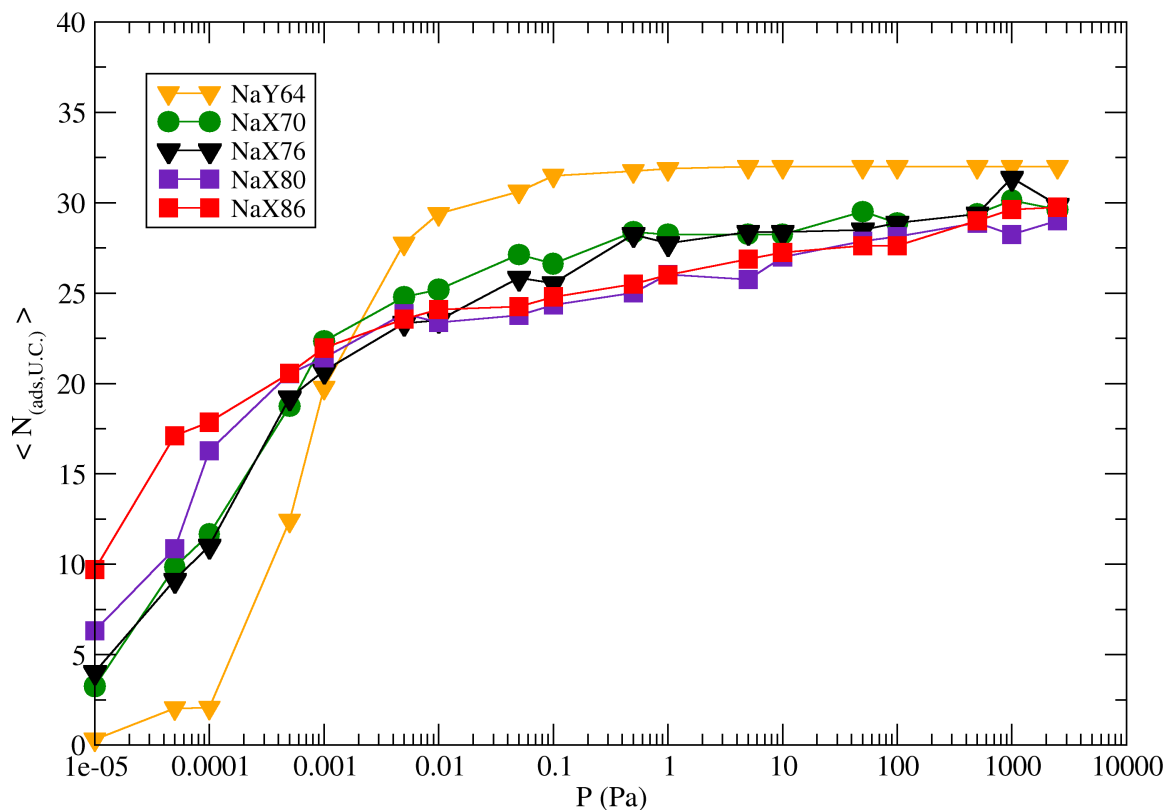
Figure 11: Adsorption isotherms of toluene on faujasites containing cations on sites I, II and III.

Figures 14a and b display the last configuration for zeolites NaY with cations on site II - only- and on sites I and II, respectively. They show an organization pattern of the toluene molecules. This pattern is formed by the aromatic ring located parallel to rings containing a cation at site II. A similar adsorption pattern has been observed experimentally by Fitch *et al.*[?] for the adsorption of benzene molecules. This molecular arrangement seems to be a robust result since it has been observed by other computational studies in all-silica faujasite and for HY zeolites.[?][?] Figures 14c and d correspond to faujasite NaX with an increasing number of cations on site III. They clearly show that the organized pattern is destroyed by
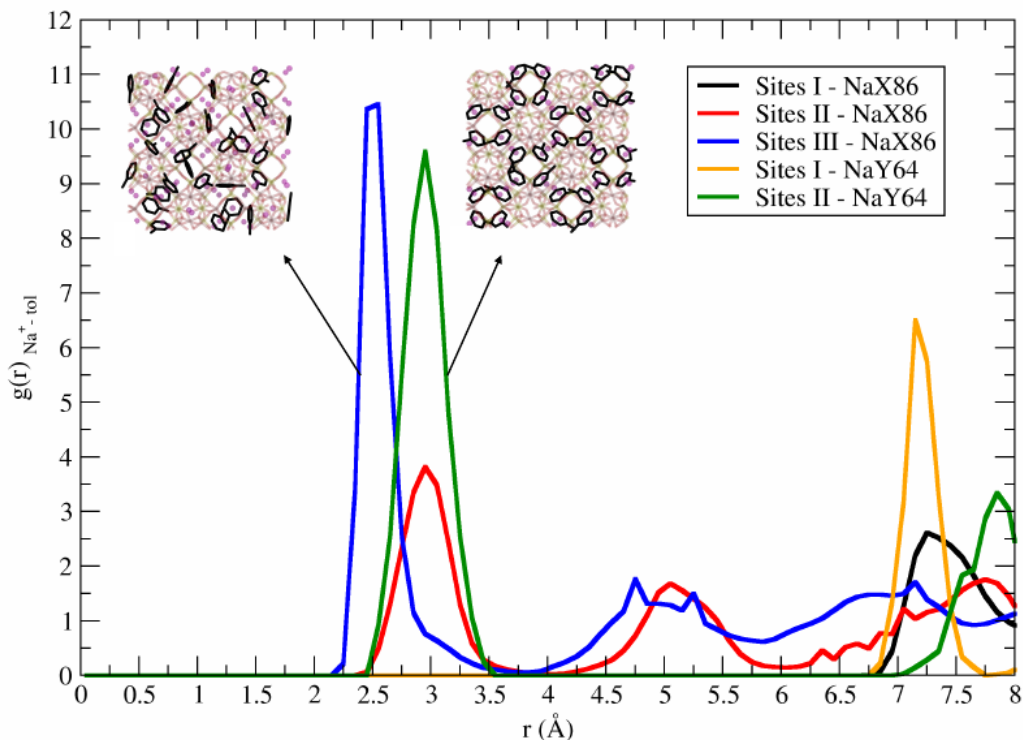
Figure 12: Radial distribution function between the center of the ring and the cations of each site.

the presence of these last cations.

Our results suggest that the formation of organized patterns depends on; the spatial and orientational freedom of the toluene molecules in the vicinity of site II. By being less restraint to the sites II (*i.e.*, inclusion of cations on site III), the toluene molecules may be subject to higher steric hindrance inside the cage, which, according to Daems and coworkers? will reduce the adsorption of molecules. This is shown by the average occupations maps in Figure 15. The depicted black surfaces correspond to the average spatial occupation of toluenes obtained from the total number of configurations. In faujasites having cations on site II and III (Figures 15c,d), the toluene molecules spread out a larger occupation area than in NaY32 and NaY64 (Figures 15a,b that do not contain cations on site III). This is translated as an impediment for the optimum packing of adsorbate molecules inside the cage.
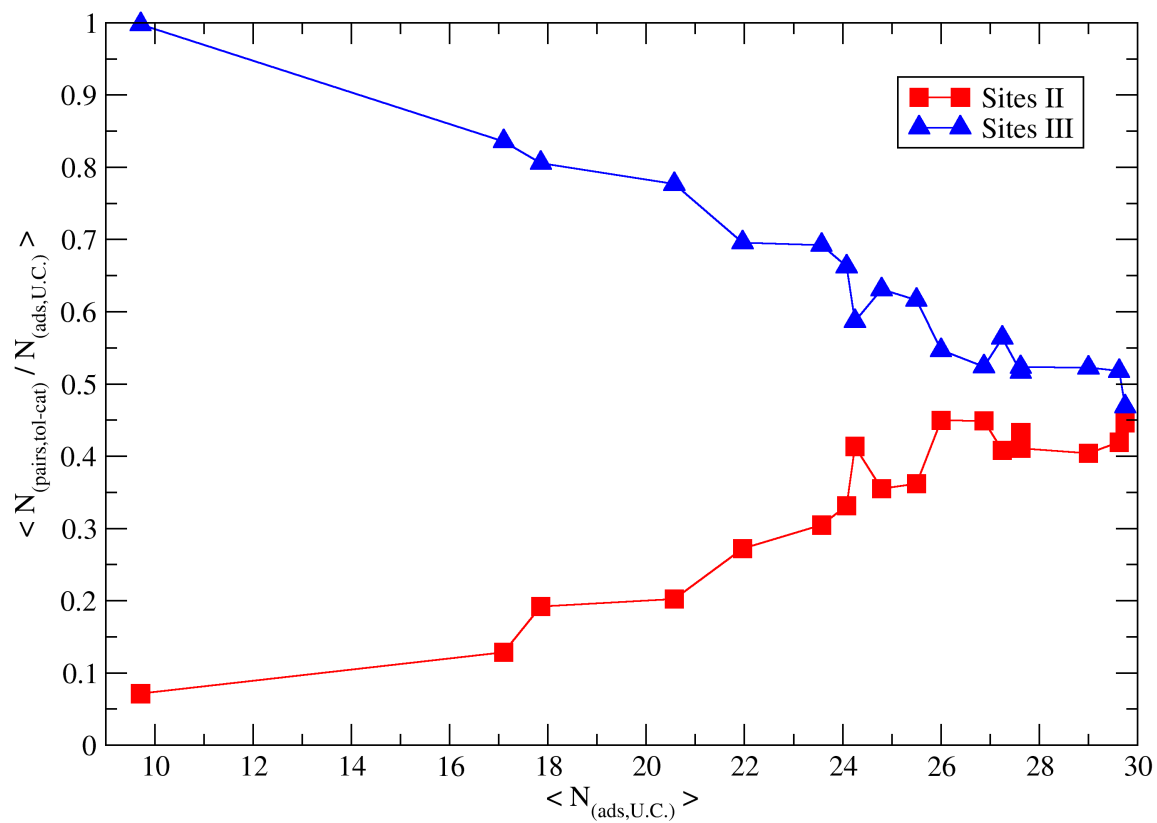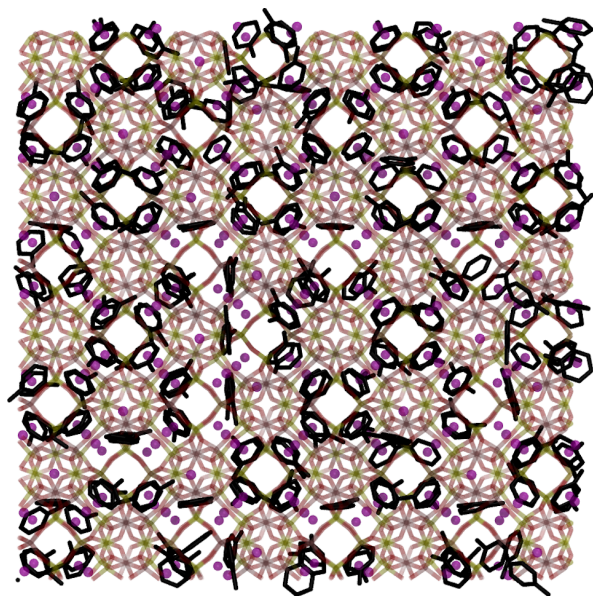
Figure 13: The fraction of toluene molecules interacting with a cation on site II (red squares) and with a cation on site III (blue triangles) for NaX86 at 1000Pa.
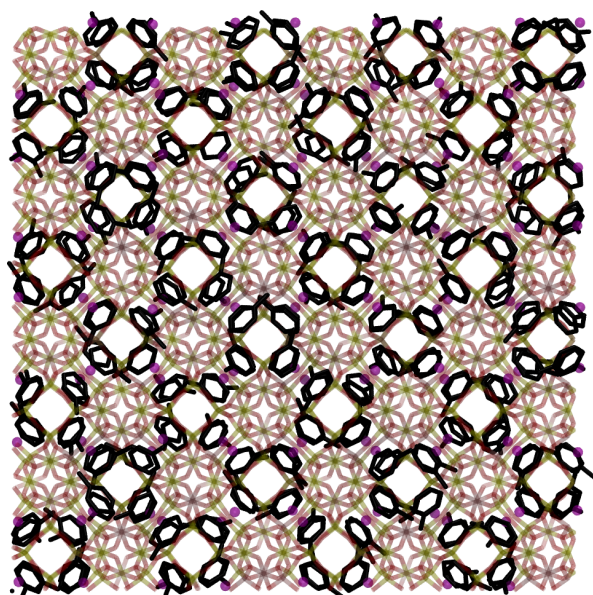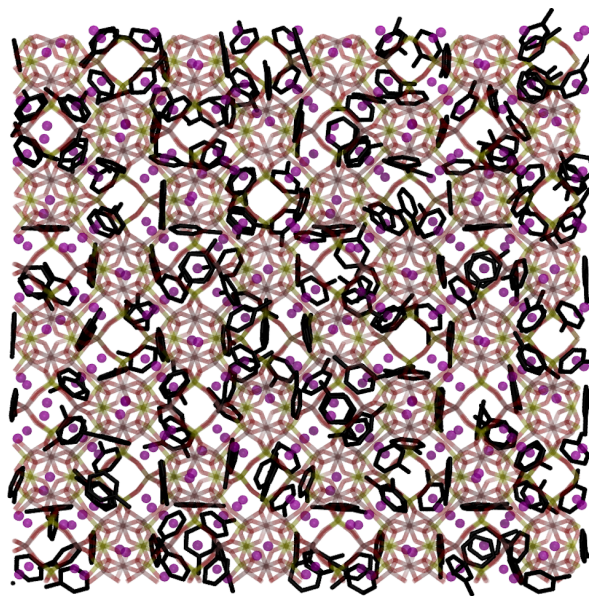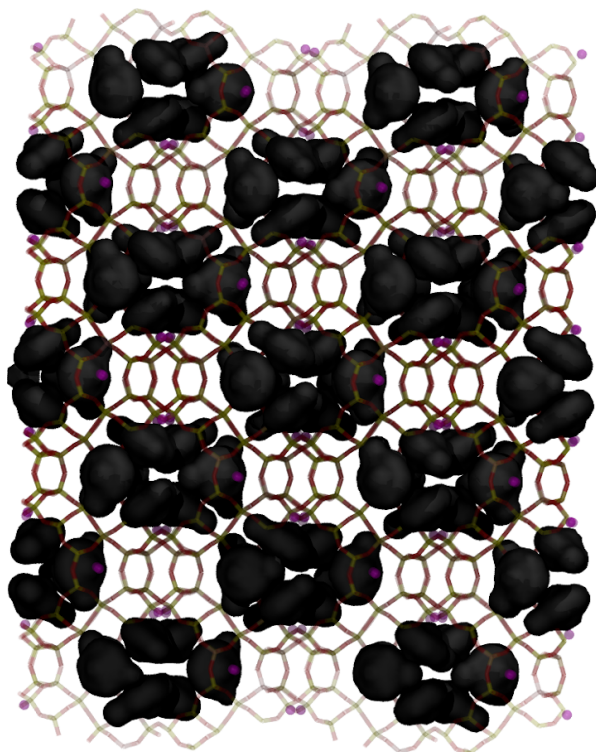
(a) NaY32
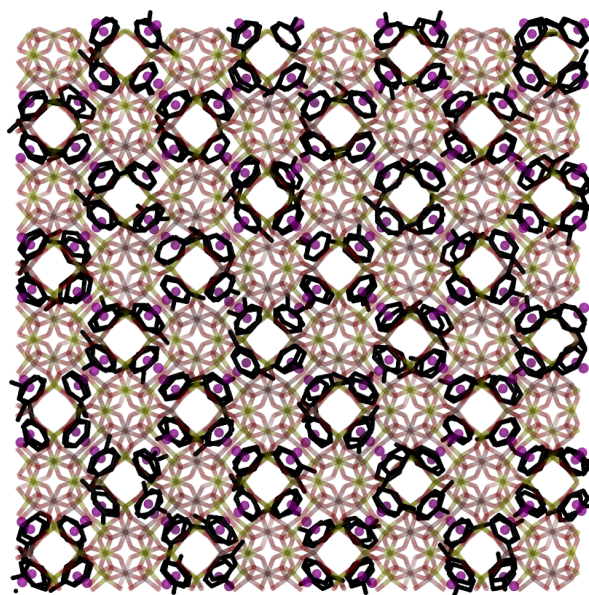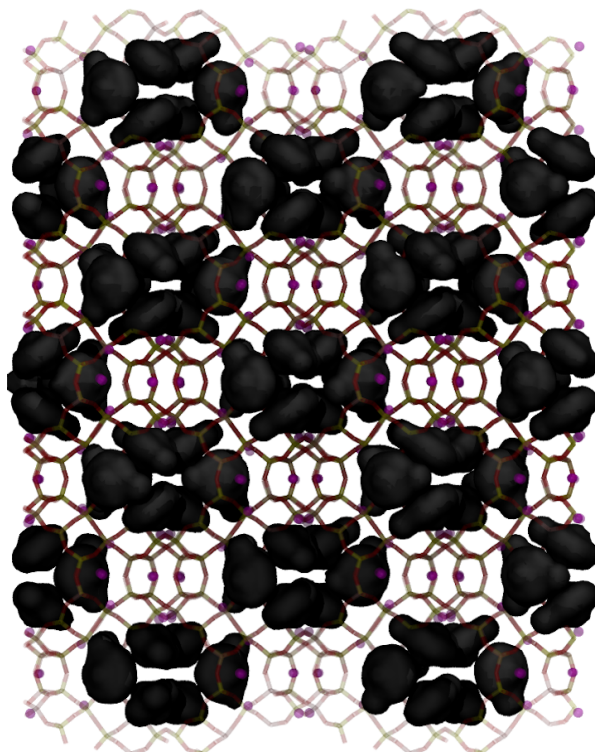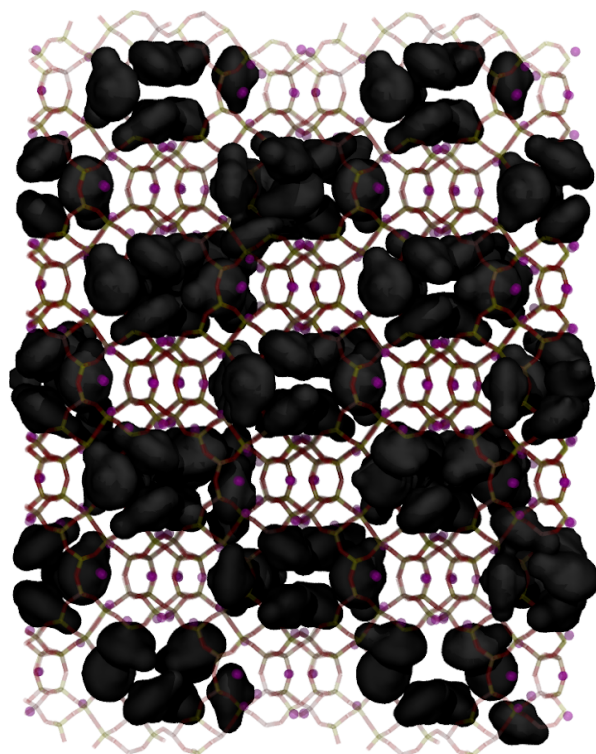
(b) NaY64

(c) NaX70

(d) NaX86

Figure 14: Configuration snapshots of adsorbed toluene molecules for (a) NaY32, (b) NaY64, (c) NaX70 and (d) NaX86.
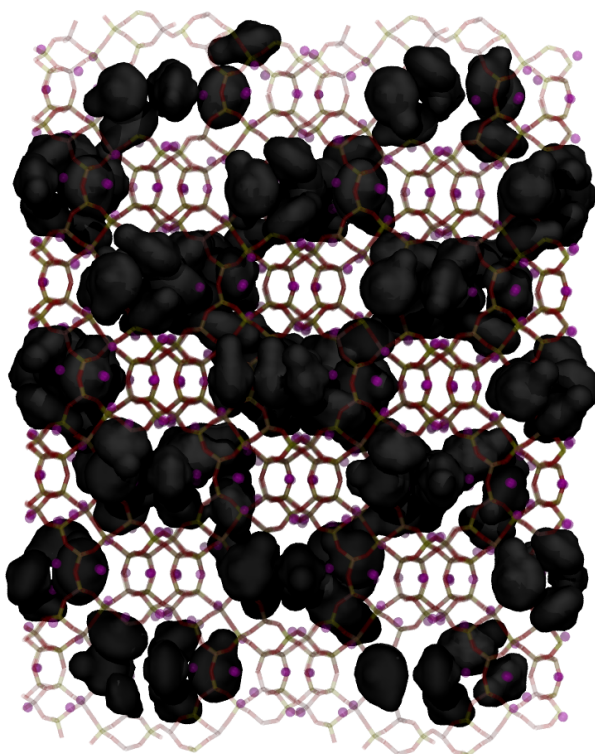
(a) NaY32

(b) NaY64

(c) NaX70

(d) NaX86

Figure 15: Average spatial occupations maps of toluene molecules for (a) NaY32, (b) NaY64, (c) NaX70 and (d) NaX86.

4 Conclusions

The cations inside a zeolite according to their quantity and location generate specific interactions, that will govern the adsorption processes, their understanding is undoubtedly necessary for engineering novel devices (e.g., captors).

The studies reported here give a set of interaction parameters for describing the interaction of toluene with faujasites with a variable Si/Al ratio. They are compatible with an already published model for the adsorption of water in faujasites.

The model revealed some interesting features. As more cations occupy site II, the lower are the pressures for initiating the adsorption process. These cations are responsible for making the interaction energy between the toluene and the framework more attractive. The cations on sites I do not shown a significant influence on the adsorption process. The cations on site III are responsible for increasing the adsorption at low pressures but as loading is increased they render it more difficult. This last is due to the fact that these cations produce a steric hindrance. We observed that the toluene molecules interact differently with cations on sites II and III. In consequence, there will be a competition between those sites for forming interaction pairs with the adsorbate. Our simulations show that such competition enhances the steric hindrance and damages the toluene organization (induced by sites II) inside the cages.

The Si/Al ratio is related to the hydrophobicity of the zeolite. Higher ratios (less cations) represent frameworks less prone to adsorb water molecules. However, such systems do not present a sensibility towards toluene. Thus, a perspective work would consist of performing computational studies to understand the competitive adsorption between toluene and water on faujasites. This would enable, for instance, finding an optimum Si/Al ratio that could adsorb the aromatic compound with high sensibility, while preserving its selectivity in relation to water. This last could be of practical use in applications ranging from pollution control to cancer diagnostic procedures.

5   Acknowledgments:

References

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TOC Graphic