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Effects of Framework Flexibility on the Adsorption and Diffusion of Aromatics in MFI-Type Zeolites

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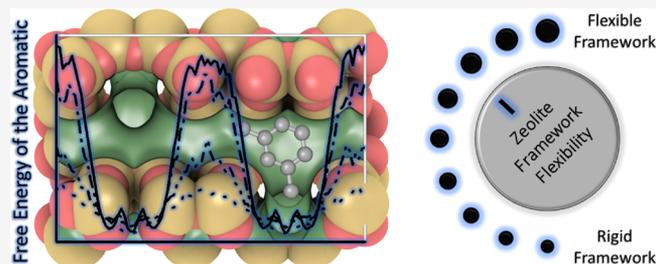
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ABSTRACT: We systematically study how the degree of framework flexibility affects the adsorption and diffusion of aromatics in MFI-type zeolites as computed by Monte Carlo simulations. It is observed that as the framework is more flexible, the zeolite structure is inherently changed. We have found that framework flexibility has a significant effect on the adsorption of aromatics in MFI-type zeolites, especially at high pressure. Framework flexibility allows the zeolite framework to accommodate to the presence of guest aromatic molecules. For very flexible zeolite frameworks, loadings up to two times larger than that in a rigid zeolite framework are obtained at a given pressure. We assessed the “flexible snapshot” method, which captures framework flexibility using independent snapshots of the framework. We have found that this method only works well when the loadings are low. This suggests that the effect of the guest molecules on the zeolite framework is important. Framework flexibility lowers the free-energy barriers between low energy states, increasing the rate of diffusion of aromatics in the straight channel of MFI-type zeolites for many orders of magnitude compared to a rigid zeolite framework. The simulations show that framework flexibility should not be neglected and that it significantly affects the diffusion and adsorption properties of aromatics in an MFI-type zeolite.



1. INTRODUCTION

The diversity of the application of zeolites is wide and ranges from being used as a catalyst for the petrochemical industry¹ to builder for laundry powders,² odor control agents,³ and many other applications.^{4–8} Many petrochemical processes strongly rely on the interaction and kinetic behavior of hydrocarbons inside a zeolite.^{9–13} For example, xylene molecules diffusing along the zeolite pores can undergo isomerization, disproportionation, and transalkylation reactions.¹⁴ Thus, knowledge of the adsorption and diffusion behavior of hydrocarbons in the pores of zeolites is important for the understanding of the catalytic activity of the zeolite.^{15–18}

The adsorption and diffusion of aromatics in MFI-type zeolites has been reported by several experimental studies.^{19–36} The interaction of an aromatic molecule within a zeolite framework is a complex process.³⁷ Factors such as molecules filling a new adsorption site,^{38,39} structural changes due to the number of adsorbed molecules,^{19,40,41} or structural changes due to a change of temperature^{42,43} may result in an inflection point in the adsorption isotherm. Talu et al.¹⁹ reported that with increasing temperature, the isotherm shape for benzene, toluene, and *p*-xylene changes from type IV to type I. The combination of such factors also leads to different phases of MFI-type zeolite structures. The all-silica form of the MFI-type zeolite is known to show a monoclinic or orthorhombic structure depending on the temperature and loadings.^{20,44} van Koningsveld et al.⁴⁵ identified three structures of the *p*-xylene/

silicalite system: Mono (monoclinic), Ortho (orthorhombic), and Para (also orthorhombic).

The adsorption and diffusion of aromatics in MFI-type zeolites has also been studied by molecular simulations.¹⁷ Commonly, Monte Carlo (MC) simulations in the grand-canonical ensemble are used to compute sorbate loadings as a function of temperature and pressure in a zeolite framework.^{46–48} Several studies where MC is used to study the adsorption of aromatics in MFI-type zeolites can be found in the literature.^{37,49–62} Zeolites are commonly considered as very rigid structures as their atomic bonds and angles are highly constrained.^{63,64} Computer simulations of the adsorption of hydrocarbons in zeolites are typically performed assuming that the zeolite framework taken from crystallographic data is a rigid structure.^{46,65,66} Nevertheless, Clark and Snurr⁶⁷ showed that the computed adsorption isotherms are sensitive to small differences in the atom positions of the zeolite. Framework flexibility is observed to play a role only if the adsorbate fits tightly in the zeolite pore.⁶⁷ Vlucht et al.^{65,68}

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reported the effect of framework flexibility in the adsorption of *n*-alkanes and cycloalkanes in MFI-type zeolites. It was found that for molecules with an inflection behavior in the isotherm, the influence of the flexibility seems to be larger than that for molecules without such inflection. Caro-Ortiz et al.³⁷ showed that the use of force fields for framework flexibility significantly affects the adsorption isotherm of xylene isomers and ethylbenzene in MFI-type zeolites. Such effect is related to intrinsic changes of the zeolite structure caused by the intraframework interactions of the force field for framework flexibility. Framework flexibility has also been studied in other porous materials such as metal–organic frameworks (MOFs) and zeolitic imidazolate frameworks.^{69–75} A recent review of the development of force fields for framework flexibility in MOFs by Heinen and Dubbeldam⁷⁶ shows that there is an urgent need for efficient sampling schemes that capture stimuli-driven phase transitions for these materials. This limits the predictive capacity of existing force fields for framework flexibility in MOFs.⁷⁶

Molecular dynamic studies have shown that accounting for framework flexibility considerably affects the diffusion coefficient of aromatics in zeolites.¹⁴ Forester et al.⁷⁷ reported that framework flexibility changes the diffusivity of aromatics in zeolites by an order of magnitude. Toda et al.¹⁴ assessed the performance of several force fields for framework flexibility by computing diffusion coefficients of *p*-xylene and *o*-xylene in 10-ring zeolites. It is observed that force fields for framework flexibility distort the structure and that the size and shape of the 10-rings act as bottlenecks for the diffusion.¹⁴ Kolokathis et al.⁷⁸ computed self-diffusion coefficients of *p*-xylene and benzene in silicalite-1 based on transition state theory (TST). It is found that *p*-xylene diffuses roughly 100 times faster than benzene when adsorbed at low occupancy in silicalite.

If the diffusion coefficient of a molecule in a zeolite framework is sufficiently high, molecular dynamic simulations can be directly used.¹⁷ Processes such as the separation of aromatic isomer mixtures in zeolites show self-diffusivity coefficients lower than $10^{-12} \text{ m}^2 \text{ s}^{-1}$.⁷⁹ As such, the diffusion behavior may occur outside the time scales accessible to molecular dynamics simulations.⁸⁰ The free-energy landscape of molecules within the pores of a zeolite shows the mobility of the molecules inside the zeolite and can be used in a more quantitative investigation of product shape selectivity of zeolite catalysts.⁸¹ Low diffusion coefficients are observed when the molecules are trapped in low free-energy sites in the zeolite framework and sporadically hop from one low energy site to another.¹⁷ TST methods can be used to estimate the diffusion coefficients in porous materials at slow diffusion time scales^{82–84} using the free-energy landscape.⁸⁵ Such methods have been used for the estimation of diffusion coefficients of aromatics in MFI-type zeolites.^{77,78,86–88} Caro-Ortiz et al.³⁷ showed that force fields for framework flexibility produce a zeolite structure that vibrates around a new equilibrium configuration with limited capacity to accommodate bulky guest molecules. To the best of our knowledge, molecular simulation studies where the effect of framework flexibility on the adsorption and diffusion of aromatics in zeolites is systematically studied are not available.

This article explores how the variation of framework flexibility in a model affects the adsorption and diffusion of aromatic hydrocarbons in MFI-type zeolites. Force fields for framework flexibility that include intraframework Lennard-

Jones (LJ) and electrostatic interactions induce small but important changes in the atom positions of the zeolite, affecting the adsorption isotherm.³⁷ The Demontis model⁸⁹ consists of modeling zeolite framework flexibility by a bond-stretching potential for the Si–O bond and a bond-stretching potential for oxygen atoms linked by a silicon atom, not including intraframework LJ and electrostatic interactions. The effect of framework flexibility on the adsorption and diffusion of C_8 aromatics in MFI-type zeolites is studied using a Demontis-like model in which the spring constants of such bond-stretching parameters are varied. MC simulations are used to compute adsorption of ethylbenzene and xylene isomers in an MFI-type zeolite structure when framework flexibility is varied. Also, free-energy profiles are used to obtain the self-diffusion coefficients of aromatics in the straight channel of the zeolite.

This article aims to study how variations of framework flexibility change the MFI-type zeolite framework and influence the interactions with guest molecules. The “flexible snapshot” method has been developed by Sholl et al.^{90–92} to capture the effect of framework flexibility on adsorption in nanoporous materials. In this method, snapshots are obtained using fully flexible MD simulation of an empty framework and have been used to study the selectivities of C_8 aromatics in multiple MOFs.⁹² In this work, the “flexible snapshot” method is used to see how the empty zeolite structure changes due to framework flexibility. The potential of this method to describe adsorption at high pressures is briefly assessed. The simulation procedure is explained in Section 2. The computed Henry coefficients, diffusion coefficients, and adsorption isotherms of C_8 aromatics in an MFI-type zeolite are reported and discussed in Section 3. It is shown that framework flexibility induces small but important changes in the atom positions of the zeolite and hence in the adsorption isotherm and the diffusion coefficient of aromatics in MFI-type zeolites. The concluding remarks regarding the effect of the framework flexibility on the interaction of aromatics within MFI-type zeolites are discussed in Section 4.

2. METHODS

The adsorption computations are performed using the Continuous Fractional Component Monte Carlo (CFCMC)^{93,94} algorithm in the grand-canonical ensemble. RASPA software^{95,96} is used for all simulations. Periodic boundary conditions are applied to a simulation box consisting of $2 \times 2 \times 3$ unit cells of the MFI-type zeolite Ortho structure described by van Koningsveld et al.⁹⁷ A cut off radius of 14 Å is applied for all LJ interactions, and analytic tail corrections are used.⁹⁸ The interactions between different atom types are obtained using Lorentz–Berthelot mixing rules.⁹⁹ MC simulations are performed in MC cycles. The number of trial moves per cycle equals the number of adsorbed molecules *N* with a minimum of 20. At each MC cycle, trial moves attempt to rotate, displace, randomly reinsert, and insert/remove adsorbates. In the CFCMC algorithm, the interactions of a fractional molecule are scaled by the λ parameter in the range 0–1 (0 for no interactions with surrounding molecules/framework and 1 for full interaction with surrounding molecules/framework). The so-called λ -trial moves scale the interactions of the fractional molecule via the CFCMC algorithm.^{93,94} The simulations use 10^5 MC cycles to initialize the system. The initialization run only allows translation, rotation, insertion/deletion, and reinsertion trial moves. After

initialization, a stage of 4×10^5 MC cycles are used to equilibrate the CFCMC biasing factors. All the considered types of trial moves are allowed, and the biasing factors for the λ -trial moves of the CFCMC algorithm are calculated. λ -trial moves are biased to obtain a flat λ probability distribution. The use of this trial move is advantageous as it enables an efficient insertion and deletion of sorbate molecules in the system.^{94,100,101} Ensemble averages are obtained in a 5×10^5 MC cycle production stage. The reported errors account for the 95% confidence interval calculated by dividing the production run into five parts and computing the standard deviation. An additional MC trial move is included to simulate a flexible zeolite framework, which attempts to give a random displacement to a randomly selected zeolite atom.⁶⁵ *p*-Xylene and benzene adsorption cause volume changes of the MFI-type framework smaller than 0.4%^{23,102} at high loadings (4 to 8 molec./u.c.). As such, the volume of the simulation box in this work is kept fixed.

The framework snapshots considered for the “flexible snapshot” method^{90–92} are obtained by performing simulations of an empty zeolite structure in the *NVT* ensemble. Random framework atom trial moves are allowed. A 10^5 MC cycle run is performed as initialization. After that, snapshots are produced every 10^4 MC cycles. The average properties for each snapshot are computed and then averaged.

The pore size distribution (PSD) of an MFI-type structure is calculated geometrically with the method reported by Gelb and Gubbins.^{103,104} Henry coefficients and free-energy profiles of aromatics in the MFI-type zeolite structure are calculated via the Widom test-particle insertion method.¹⁰⁵ In this method, the average Boltzmann weight of a ghost molecule is calculated. Such ghost molecule perceives the same energy as a real particle. The other molecules in the system (zeolite framework in this case) do not feel the presence of the ghost particle.¹⁰⁶ The simulations are started with 10^5 MC cycles to initialize the system. The initialization run only allows framework atom moves. After that, the Henry coefficient and free-energy landscape are computed in a 10^5 MC cycle production run. The helium void fraction (HVF) is determined using iRASPA visualization software¹⁰⁷ by probing the framework with a non-adsorbing helium molecule using the Widom test-particle insertion method.¹⁰⁵

Force fields that model the flexibility of the zeolite framework are commonly based on the description of vibrational properties, such as the infrared spectra of the zeolite atoms^{108,109} and/or ab initio quantum chemical calculations.^{110,111} Several force fields for framework flexibility have been reported in the literature.^{63,89,110–117} Such force fields are typically used for the calculations of diffusion of aromatics in MFI-type zeolites by molecular dynamics simulations.^{14,118} In this work, the host–host interactions are modeled using a Demontis-like force field. The Demontis model^{89,113,114} consists of modeling zeolite framework flexibility by a bond-stretching potential for the Si–O bond and a bond-stretching potential for the oxygen atoms linked by a silicon atom. The bond-stretching potentials U are modeled using the expression: $U(r) = 0.5 \times k \times (r - r_0)^2$, where k is the spring constant and r_0 is the equilibrium bond length. The original values of the spring constants are $k_{\text{O}-(\text{Si})-\text{O}}/k_{\text{B}} = 51,831.61 \text{ K}\text{\AA}^{-2}$ and $k_{\text{Si}-\text{O}}/k_{\text{B}} = 251,778.07 \text{ K}\text{\AA}^{-2}$. To reduce the number of parameters, the ratio $k = k_{\text{O}-(\text{Si})-\text{O}} = 0.2 \times k_{\text{Si}-\text{O}}$ is kept fixed.⁶⁵ The original Demontis model⁸⁹ uses constant equilibrium bond lengths and angles. The so-called modified

form of this model takes the equilibrium bond lengths and bend-angles (in the Urey–Bradley term) directly from the crystallographic structure to which the model is applied.⁶⁵ This modification is used in this work, and it is used to avoid large deviations from the experimental crystal structure.³⁷ When this modification is in use, the minimum energy structure is exactly reproduced when $k \rightarrow \infty$ ⁶⁵ or for any value of the spring constant k when $T \rightarrow 0 \text{ K}$.

The interactions between the zeolite and guest hydrocarbons are modeled using the TraPPE-zeo model.¹¹⁹ In this force field, all oxygen and silicon atoms are modeled with LJ interactions and partial charges. The development of this force field was focused on transferability and variety of zeolite/guest systems.¹¹⁹ As such, it is fitted to match the experimental adsorption isotherms of *n*-heptane, propane, carbon dioxide, and ethanol in zeolites.

Molecular simulations of aromatics typically use force fields (guest–guest interactions) that model the vapor–liquid equilibrium (VLE) with LJ potentials or a combination of LJ and electrostatic interactions.^{120,121} In the case of aromatic species, a common practice in the development of these force fields is to fit the interaction parameters to reproduce the VLE of the pure components^{122–128} or by optimizing LJ interactions by a combination of ab initio quantum mechanical calculations and empirical methods.^{129–133} In this work, the guest–guest interactions are modeled using the TraPPE-UA¹³⁴ force field. The TraPPE-UA is a widely used force field that is designed to reproduce the VLE of alkylbenzenes and *n*-alkanes, among other chemical species. The united atom approach is used by merging a carbon atom and its bonded hydrogen atoms into a single uncharged interaction site representing each CH_x group in the aromatic species. Aromatics are modeled as rigid molecules, except ethylbenzene that includes a torsional potential in the $\text{CH}_3\text{--CH}_2\text{--CH}$ bend angle. Electrostatic interactions (guest–guest, guest–host, and host–host) are not considered in this work, as electrostatic interactions are not a part of the TraPPE-UA force field for xylenes.¹³⁴ Framework flexibility is also important for adsorption and diffusion in zeolites containing extra-framework cations. Studies exploring the effect of framework flexibility in such systems require models that include electrostatic interactions for the zeolite atoms and guest molecules. However, models for framework flexibility that include intraframework electrostatic interactions inherently change the zeolite structure, significantly affecting adsorption.³⁷ This suggests that to study the effect of framework flexibility in zeolites containing extra-framework cations, strategies different than those used in this work might be needed.

The reader is referred to ref 37 for details about the choice of force fields and the parameters used in this work.

3. RESULTS AND DISCUSSION

The Henry coefficients of ethylbenzene and xylene isomers (as single components) in an MFI-type zeolite at 353 K are computed using the flexible framework model and the “flexible snapshot” method, varying k . Five snapshots are used for the “flexible snapshot” method. The computed Henry coefficients as a function of the framework flexibility are shown in Figure 1. It is observed that for all aromatics considered in this study, the “flexible snapshot” method yields the same Henry coefficient as the simulations using a flexible framework.

Figure 1 shows that framework flexibility has a significant influence on the Henry coefficient of aromatics in the MFI-

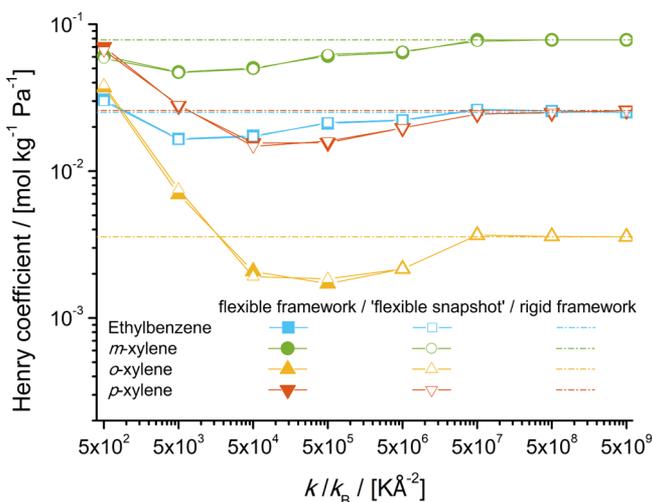


Figure 1. Henry coefficient of ethylbenzene and xylene isomers computed in an MFI-type zeolite at 353 K as a function of framework flexibility k . Closed symbols denote the computations using the flexible framework. Open symbols denote the computations using the “flexible snapshot” method.⁹⁰ Dashed lines denote the computations using the rigid framework.

type zeolite. When the framework is very flexible (i.e., $k/k_B = 500 \text{ KÅ}^{-2}$), the Henry coefficients of ethylbenzene, *p*-xylene, and *o*-xylene are higher than those computed for the structure with atom positions fixed to the crystallographic data (rigid framework). When $5 \times 10^4 \text{ KÅ}^{-2} \leq k/k_B \leq 5 \times 10^6 \text{ KÅ}^{-2}$, the Henry coefficients of ethylbenzene and xylene isomers are lower than that in the rigid zeolite framework.

When $k/k_B > 5 \times 10^7 \text{ KÅ}^{-2}$, the Henry coefficient of ethylbenzene and xylene isomers is in agreement with the Henry coefficient computed for the rigid structure. This suggests that when k is sufficiently high, framework flexibility does not affect the zeolite structure.

The Henry coefficients of aromatics in MFI-type zeolites computed with the “flexible snapshot” method are in excellent agreement with the values computed using the flexible framework for all k . This suggests that the snapshots can be used to describe the changes that framework flexibility induces on the empty zeolite structure. The mean displacement of the zeolite atoms compared to the rigid structure,⁹⁷ the HVF, and the PSD is computed for the five snapshots used in the “flexible snapshot” method. Figure 2 shows the mean displacement of the zeolite framework atoms compared to the rigid framework, the HVF, and the PSD, as a function of k , computed for five MFI-type zeolite snapshots. It is observed that as k is decreased, the mean displacement of the framework atoms increases. When $k/k_B = 5 \times 10^2 \text{ KÅ}^{-2}$, an average displacement of 0.95 Å is observed. For $k/k_B > 5 \times 10^7 \text{ KÅ}^{-2}$, the average displacement of framework atoms is close to zero. The HVF of the MFI-type zeolite structures is significantly influenced by framework flexibility. The highest HVF is observed when $k/k_B = 5 \times 10^2 \text{ KÅ}^{-2}$. For $5 \times 10^4 \text{ KÅ}^{-2} \leq k/k_B \leq 5 \times 10^5 \text{ KÅ}^{-2}$, the HVF of the MFI-type zeolite structure is lower than the HVF computed for the rigid framework. For $k/k_B > 5 \times 10^6 \text{ KÅ}^{-2}$, the HVF of the MFI-type zeolite structures is in good agreement with the HVF computed for the rigid zeolite structure. The influence of framework flexibility on the HVF shows that the accessible pore volume of the zeolite is directly related to the Henry coefficient of aromatics in MFI-type zeolites.

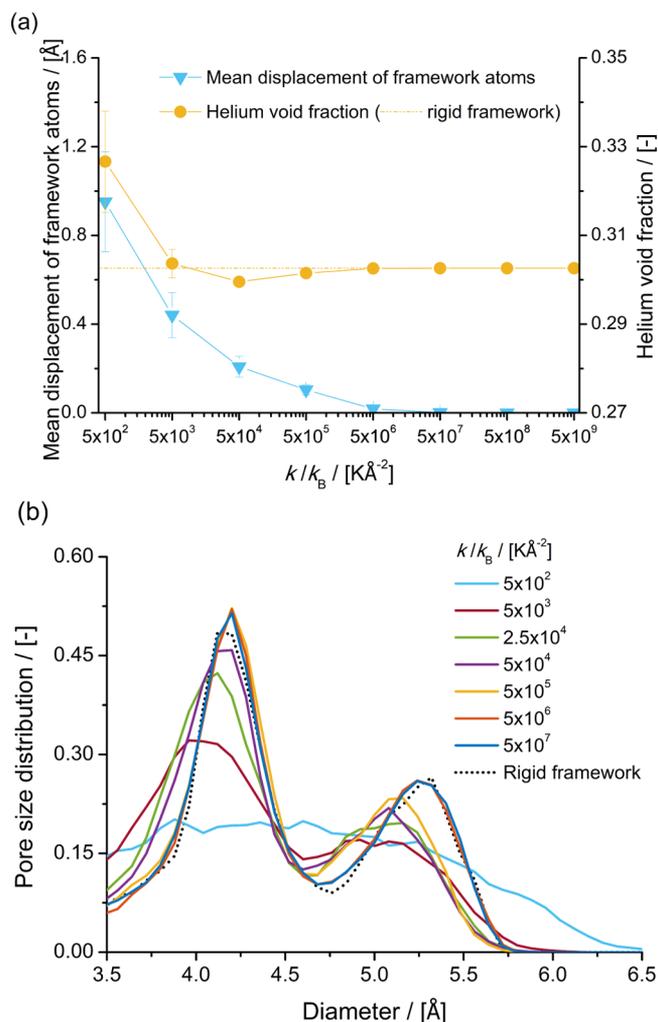


Figure 2. (a) Mean displacement of framework atoms compared to the rigid structure⁹⁷ and HVF and (b) PSD of the five empty MFI-type zeolite snapshots used for the “flexible snapshot” method⁹⁰ at 353 K as a function of framework flexibility k .

For the PSD of MFI-type zeolites, the peak centered at a diameter of approximately 4.3 Å corresponds to the zigzag and straight channels. The peak centered at a diameter of approximately 5.5 Å corresponds to the intersection of the channels. The PSD of the MFI-type zeolite snapshots shows the influence of framework flexibility on the zeolite pore sizes. It can be observed that as k is decreased, the peak that corresponds to the intersections is shifted to lower diameters. The peak that corresponds to the channels is shifted to lower diameters when $k/k_B \leq 5 \times 10^4 \text{ KÅ}^{-2}$.

The PSD of the MFI-type structures when $k/k_B = 5 \times 10^2 \text{ KÅ}^{-2}$ does not show a pore size peak distinction between channels and intersection. The maximum pore size observed is 6.5 Å , suggesting that for very high framework flexibility, the deformation of the zeolite void spaces is very large.

As framework flexibility changes the pore size of the zeolite intersections and channels, a decrease of the pore size of the intersection directly affects the adsorption of molecules, and Henry coefficients lower than that for the rigid framework are obtained. This suggests that the interaction of the aromatic molecules and the zeolite framework is highly influenced by changes on the pore sizes of the zeolite. Higher Henry coefficients of aromatic molecules than that in the rigid

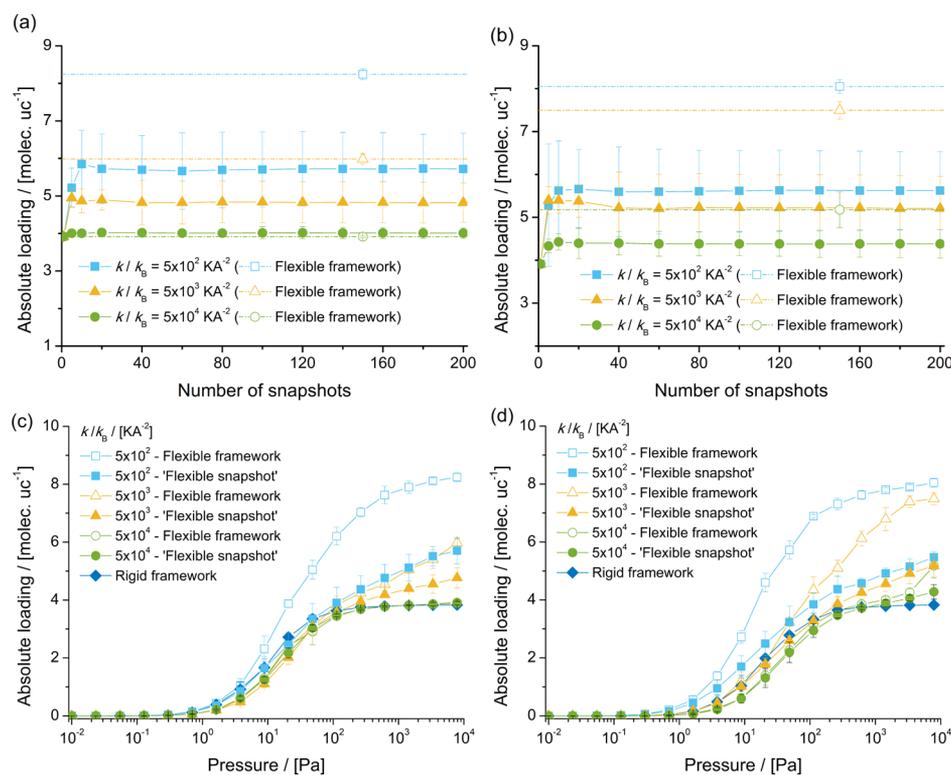


Figure 3. Absolute loadings of (a) ethylbenzene and (b) *p*-xylene at 7848 Pa in an MFI-type zeolite⁹⁷ at 353 K computed using the flexible framework and the “flexible snapshot” method, as a function of the number of snapshots considered in the “flexible snapshot” method, for different framework flexibility k . Adsorption isotherms of (c) ethylbenzene and (d) *p*-xylene in an MFI-type zeolite⁹⁷ at 353 K computed using the flexible framework and the “flexible snapshot” method using ten snapshots for different framework flexibility k .

framework when $k/k_B \leq 5 \times 10^3 \text{ K}\text{\AA}^{-2}$ can be related to an increase in the size of pores with a diameter of approximately 4.7 Å. The PSDs suggest that as k is decreased, the pore sizes of the channels and the intersections become uniform. When $k/k_B = 5 \times 10^6 \text{ K}\text{\AA}^{-2}$, a mean displacement of 0.018 Å of the zeolite atoms is enough to induce up to a 42% decrease of the Henry coefficient of *o*-xylene in MFI-type zeolites compared to the Henry coefficient computed in the rigid framework. With framework flexibility in the range of the original Demontis model (i.e., $k/k_B = 5 \times 10^4 \text{ K}\text{\AA}^{-2}$), Henry coefficients lower than that in the rigid framework are obtained. As the framework is more flexible, Henry coefficients higher than that in the rigid framework are obtained. This suggests that the interactions between the aromatic molecules and the zeolite framework are very susceptible to small displacements of the zeolite atoms and the geometry of the zeolite pores.

Knowledge regarding the effect of loading in the pores of the zeolite as a function of framework flexibility would be of interest. However, a characterization of a flexible framework as a function of loading is cumbersome. A given loading may have several adsorbate configurations in the framework. Sampling the effect of all these configurations in the framework for a given loading is computationally expensive. Therefore, the effect of framework flexibility on the zeolite framework was only estimated for an empty zeolite framework.

Since the snapshots are obtained from an empty zeolite structure, the capacity of the “flexible snapshot” method to describe the adsorption of aromatics outside the Henry regime is of interest. Simulations of adsorption of ethylbenzene and *p*-xylene in an MFI-type structure are computed at 7848 Pa, using different number of snapshots, for different k . Snapshot 1

corresponds to the crystal structure from experiments.⁹⁷ The loadings of ethylbenzene and *p*-xylene in MFI-type zeolite at 7848 Pa and 353 K as a function of the number of snapshots for different k are shown in Figure 3. The loadings computed using the “flexible snapshot” method are higher than the loadings computed in the rigid framework. The loadings computed with the “flexible snapshot” method are lower than the loadings obtained using a flexible framework. It can be observed that the loadings using the “flexible snapshot” method do not depend on the number of snapshots used if ten or more snapshots are used. Adsorption isotherms of ethylbenzene and *p*-xylene in an MFI-type zeolite at 353 K are computed using the flexible framework and the “flexible snapshot” method with ten snapshots are shown in Figure 3. The adsorption isotherms show the differences between the loadings computed with the flexible framework and the “flexible snapshot” method. In the “flexible snapshot” method, it is assumed that the adsorbate does not have a significant effect on the framework dynamics.⁹² This assumption has a significant effect on the computed loadings when framework flexibility is high (i.e., k is low). When $k/k_B = 5 \times 10^2 \text{ K}\text{\AA}^{-2}$, significant differences between the loadings of ethylbenzene and *p*-xylene in MFI-type zeolite computed with the flexible framework and the “flexible snapshot” method are observed for pressures higher than 10 Pa. For framework flexibility $k/k_B = 5 \times 10^3 \text{ K}\text{\AA}^{-2}$ and $k/k_B = 5 \times 10^4 \text{ K}\text{\AA}^{-2}$, the loading differences can be observed when the pressure is higher than 100 Pa, and loadings higher than 4 molec./u.c. are obtained. The “flexible snapshot” method can be used to understand the effect that bulky aromatic guest molecules produce on the zeolite framework. It can be observed that the loadings computed

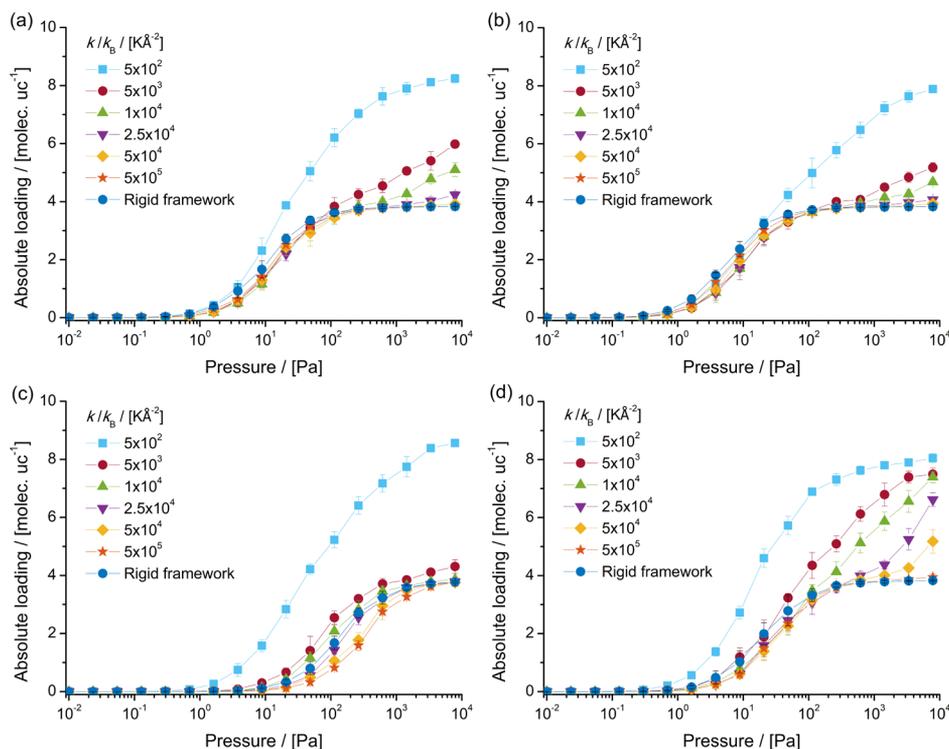


Figure 4. Adsorption isotherms for (a) ethylbenzene, (b) *m*-xylene, (c) *o*-xylene, and (d) *p*-xylene in an MFI-type zeolite⁹⁷ at 353 K, varying framework flexibility k .

using the “flexible snapshot” method account for the molecules that would fit in a new rigid framework with the new average configuration produced by a particular framework flexibility k . The difference between the loadings computed with the “flexible snapshot” method and the flexible framework correspond to the effect on the isotherm of how the framework accommodates to the guest molecules. The “flexible snapshot” method is useful for the description of the adsorption behavior at very low loadings/infinite dilution. For high pressures/loadings, the “flexible snapshot” method does not yield the same loading as when the flexible framework is used. This suggests that the effect of the guest aromatic molecules on the zeolite framework should not be neglected.

Adsorption isotherms of ethylbenzene and xylene isomers at 353 K in an MFI-type zeolite varying framework flexibility k are shown in Figure 4. Framework flexibility influences the adsorption isotherm of aromatics in MFI-type zeolite. In the low pressure regime (i.e., $P < 10^2$ Pa), the loadings of ethylbenzene are similar for $k/k_B \geq 5 \times 10^3 \text{ K}\text{\AA}^{-2}$. At higher pressures, the effect of framework flexibility is observed, yielding higher loadings as k is decreased. The highest loadings of ethylbenzene in the considered pressure range are obtained when $k/k_B = 5 \times 10^2 \text{ K}\text{\AA}^{-2}$, having up to 8.2 molec./u.c. at 7848 Pa.

At pressures lower than 20 Pa, framework flexibility does not play a role in the loadings of *m*-xylene. When $k/k_B = 5 \times 10^2 \text{ K}\text{\AA}^{-2}$, loadings of 7.8 molec./u.c. of *m*-xylene are observed at 7848 Pa. For $5 \times 10^3 \text{ K}\text{\AA}^{-2} \leq k/k_B \leq 10^4 \text{ K}\text{\AA}^{-2}$, framework flexibility influences adsorption only when the pressure is higher than 6×10^2 Pa. Figure 5 shows two typical snapshots of the simulation of adsorption of *m*-xylene in an MFI-type zeolite at 353 K and 7848 Pa, using a rigid zeolite framework (Figure 5a) and a flexible zeolite framework with $k/k_B = 5 \times 10^2 \text{ K}\text{\AA}^{-2}$ (Figure 5b). It can be observed that when using the

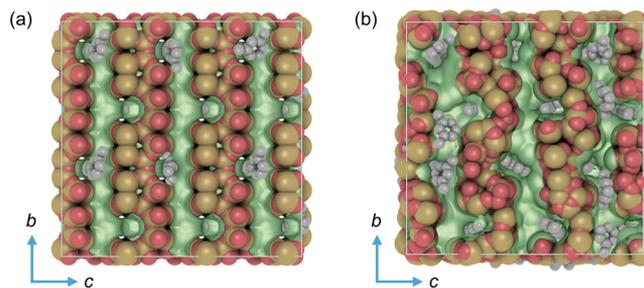


Figure 5. Typical snapshots of the simulations of adsorption of *m*-xylene in an MFI-type zeolite at 353 K and 7848 Pa. (a) Simulation using the rigid zeolite framework. (b) Simulations using framework flexibility $k/k_B = 5 \times 10^2 \text{ K}\text{\AA}^{-2}$. The green area denotes the adsorption surface computed with iRASPA.¹⁰⁷

rigid zeolite framework, *m*-xylene molecules are located exclusively in the intersection of the zigzag and the straight channel. When $k/k_B = 5 \times 10^2 \text{ K}\text{\AA}^{-2}$, *m*-xylene molecules are located in the intersections of the channels, as well as in the channels.

Unlike ethylbenzene and *m*-xylene, *o*-xylene adsorption is affected by framework flexibility already at very low pressures. The effects of framework flexibility are noticeable when the pressure is higher than 10 Pa. Framework flexibility has a significant influence on the Henry coefficient of *o*-xylene (Figure 1); the Henry coefficient of *o*-xylene is 1.9 times higher than that for the rigid structure when $k/k_B = 5 \times 10^3 \text{ K}\text{\AA}^{-2}$ and 0.48 times smaller than that for the rigid structure when $k/k_B = 5 \times 10^5 \text{ K}\text{\AA}^{-2}$. This suggests that the adsorption of *o*-xylene in MFI-type zeolite is sensitive to the changes of the zeolite structure caused by framework flexibility already at low loadings. When $k/k_B = 5 \times 10^2 \text{ K}\text{\AA}^{-2}$, *o*-xylene loadings of up to 8.5 molec./u.c. are obtained. For $k/k_B = 5 \times 10^3 \text{ K}\text{\AA}^{-2}$,

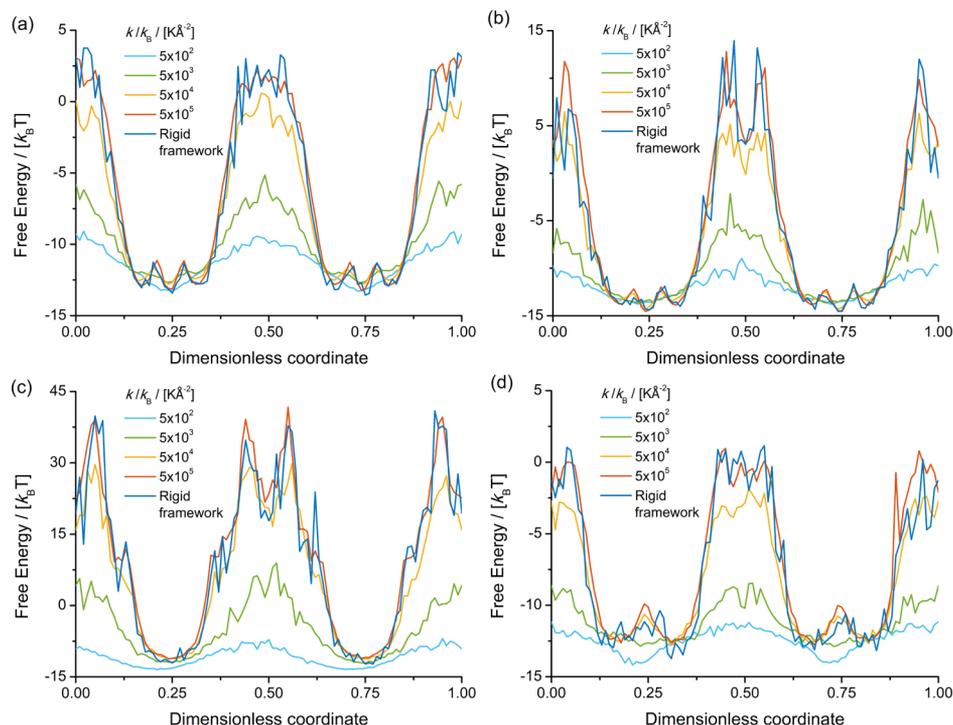


Figure 6. Free-energy profiles in the *b*-crystallographic axis (parallel to the straight channel) for (a) ethylbenzene, (b) *m*-xylene, (c) *o*-xylene, and (d) *p*-xylene at infinite dilution in an MFI-type zeolite⁹⁷ at 353 K, varying framework flexibility *k*. The dimensionless coordinate correspond to the dimensionless position across the *b*-crystallographic axis of the MFI-type zeolite unit cell.

the maximum loading obtained is 4.3 molec./u.c. As $k/k_B \geq 10^4 \text{ K}\text{\AA}^{-2}$, maximum loadings of approximately 3.8 molec./u.c. are obtained. *p*-Xylene adsorption is highly affected by framework flexibility, especially at high pressures. The maximum loading of *p*-xylene (8.1 molec./u.c.) is obtained for $k/k_B = 5 \times 10^2 \text{ K}\text{\AA}^{-2}$. Only when $k/k_B \geq 5 \times 10^5 \text{ K}\text{\AA}^{-2}$, the loadings obtained with the flexible framework are the same as the loadings obtained in the rigid framework. In the case of C_8 aromatics, inflection point in the isotherm can be an indication of the occupancy of new adsorption sites,³⁸ such as the zigzag and straight channels. For adsorption of aromatics in MFI-type zeolites, when the loadings are lower than 4 molec./u.c., the molecules occupy the intersection of the channels. At higher loadings, the molecules occupy the void spaces in the channels. It can be observed that as *k* is decreased to $k/k_B = 5 \times 10^2 \text{ K}\text{\AA}^{-2}$, the shape of the isotherms for ethylbenzene and xylene isomers changes from type IV to type I. The PSD of the empty zeolite structure for $k/k_B = 5 \times 10^2 \text{ K}\text{\AA}^{-2}$ (Figure 2b) shows the absence of a pore size peak distinction between the channels and the intersections. This suggests that the changes that framework flexibility induces in the zeolite structure can change the shape of the adsorption isotherm of aromatics in MFI-type zeolites. To determine optimal values of framework flexibility *k*, comparison with appropriate experimental data for all the sorbates considered is needed. However, experimental data of adsorption of aromatics in MFI-type zeolites is scarce and not always consistent under the same temperature/pressure conditions.³⁷ Therefore, the optimal framework flexibility *k* was not determined in this work.

The free-energy profiles of ethylbenzene and xylene isomers in an MFI-type zeolite as a function of framework flexibility are shown in Figure 6. The dimensionless coordinate correspond to the dimensionless position across the *b*-crystallographic axis of the MFI-type zeolite unit cell. The free-energy profiles

suggest that framework flexibility significantly influences the free-energy barrier between the low energy states (intersections). As *k* is decreased, the free-energy barrier between the intersections of the channels is decreased. This suggests that the pore size changes that framework flexibility induces on the zeolite framework have an important effect on the free-energy of aromatic molecules in MFI-type zeolites.

The free-energy profiles are used to compute the hopping rate $k_{A \rightarrow B}^{\text{TST}}$ and the self-diffusion coefficient (*D*) at infinite dilution of aromatics in the straight channel of an MFI-type zeolite framework using TST. Estimations of the self-diffusion coefficients of aromatics at high loadings or for the zigzag channel of MFI-type zeolite are not computed in this work. In TST, it is assumed that all particles that reach the free-energy barrier from a low energy site A to a low energy site B eventually end up in B.⁸⁰ In reality, not all the molecules at the dividing surface actually diffuse through the pores.⁸³ A dynamical correction can be computed to account for this factor.^{83,84} To study the effect of framework flexibility on the diffusion of aromatics in MFI-type zeolites, only an estimation of the diffusion coefficient is used. The dynamical correction was not included in this work as it is computationally expensive to determine. The hopping rates $k_{A \rightarrow B}^{\text{TST}}$ are obtained by computing the relative probability to find a molecule on top of the free-energy barrier, and the velocity of the molecule is given by a Maxwell distribution corresponding to the temperature of the system.¹⁷ The hopping distance $\lambda_{A \rightarrow B}$ is the distance between A and B. At infinite dilution, the self-diffusion coefficient is calculated using the expression $D = k_{A \rightarrow B}^{\text{TST}} \cdot \lambda_{A \rightarrow B}^2$. The reader is referred to refs^{17,80,83,84} for details about the calculation of diffusion coefficients from TST. The self-diffusion coefficients of ethylbenzene and xylene isomers in the straight channel of MFI-type zeolite at 353 K are shown in Figure 7. It can be observed that framework flexibility has an

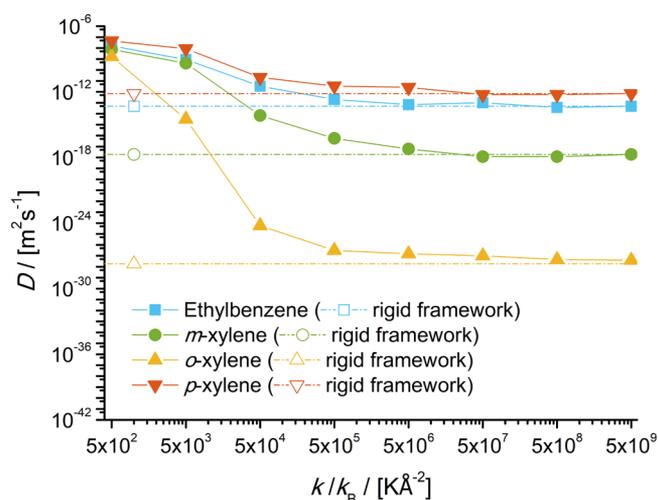


Figure 7. Self-diffusion coefficient D computed using TST for ethylbenzene and xylene isomers in the straight channel of an MFI-type zeolite⁹⁷ at 353 K, varying framework flexibility k .

important effect on the self-diffusion coefficient of aromatics in MFI-type zeolites. The highest self-diffusivity coefficients D are obtained when $k/k_B = 5 \times 10^2 \text{ KÅ}^{-2}$ for all aromatics considered. As k is increased, the computed D is in agreement with the self-diffusion coefficient computed in the rigid framework. For all values of k considered (and the rigid structures), $D_{p\text{-xylene}} > D_{\text{ethylbenzene}} > D_{m\text{-xylene}} > D_{o\text{-xylene}}$. Comparing the self-diffusion coefficients obtained when $k/k_B = 5 \times 10^2 \text{ KÅ}^{-2}$ and D obtained in the rigid structure, framework flexibility affects the diffusion of aromatic molecules in an MFI-type zeolite differently: $D_{\text{ethylbenzene}}$ increased from 4.7×10^{-14} to $1.5 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}$; $D_{m\text{-xylene}}$ increased from 1.9×10^{-18} to $7.6 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$; $D_{o\text{-xylene}}$ increased from 1.9×10^{-28} to $1.6 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$; and $D_{p\text{-xylene}}$ increased from 6.8×10^{-13} to $4.5 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}$. Framework flexibility significantly changes D when $k/k_B \leq 5 \times 10^6 \text{ KÅ}^{-2}$. This suggests that the changes that framework flexibility induces on the pore sizes of the channels of the zeolite framework notably influence the estimation of D .

4. CONCLUSIONS

The influence of framework flexibility on the adsorption and diffusion behavior of C_8 aromatics in an MFI-type zeolite has been investigated using molecular simulations. It has been observed that—regardless of taking the bond lengths and angles from the crystallographic data—framework flexibility induces changes on the average zeolite structure. As the framework is more flexible, it is difficult to discriminate the channels and the intersections based on pore sizes. This has a significant effect on the Henry coefficient and the adsorption isotherms of aromatics in MFI-type zeolites. The Henry coefficient of aromatics in MFI-type zeolites is significantly affected by framework flexibility. With framework flexibility in the range of the original Demontis model (i.e., $k/k_B = 5 \times 10^4 \text{ KÅ}^{-2}$), computed Henry coefficients of aromatics in MFI-type zeolites are lower than that in the rigid framework. As the framework is more flexible, Henry coefficients are higher than that in the rigid framework. When $k/k_B = 5 \times 10^6 \text{ KÅ}^{-2}$, a mean displacement of the zeolite atoms of 0.018 Å is enough to induce a significant change in the Henry coefficient of aromatics in MFI-type zeolites. This suggests that the

interactions between the aromatic molecules and the zeolite framework are very susceptible to small displacements of the zeolite atoms and changes of the geometry of the zeolite pores. The “flexible snapshot” method is useful for the description of the adsorption behavior at very low loadings/infinite dilution. For high pressures/loadings, the “flexible snapshot” method does not yield the same loading as when the flexible framework is used. This suggests that the effect of the guest molecules on the zeolite framework should not be neglected. For using the “flexible snapshot” method at high loadings, a loaded framework could be considered to create snapshots that yield estimation of the loadings closer to simulations using a fully flexible framework. However, the computational cost of creating such snapshots with energy equilibrated adsorbates is equivalent to the simulation of a loaded fully flexible framework, and hence the “flexible snapshot” method is not considered further. The adsorption isotherms are affected by framework flexibility. At low loadings, the influence of the framework flexibility on the adsorption is small. When the loadings are higher than 4 molec./u.c., lower framework flexibility k yields higher loadings than that in the rigid framework. For the pressure range considered, the maximum loadings of aromatics in MFI-type zeolites computed depend on the framework flexibility. Higher maximum loadings are obtained when the framework is more flexible (i.e., $k/k_B = 5 \times 10^2 \text{ KÅ}^{-2}$). For ethylbenzene, m -xylene, and p -xylene, framework flexibility plays an important role when the loadings are higher than 4 molec./u.c. For o -xylene, framework flexibility plays a role when the loadings are lower than 4 molec./u.c. The changes that framework flexibility induces in the zeolite structure can change the shape of the adsorption isotherm of aromatics in MFI-type zeolites for very flexible zeolite frameworks. Framework flexibility significantly decreases the free-energy barriers of aromatics between the low energy sites of the zeolite framework. As the zeolite framework is more flexible, the self-diffusion coefficient is significantly increased. Framework flexibility has a remarkable effect on the adsorption and diffusion of aromatics in MFI-type zeolites. The simulations from this work suggest that framework flexibility is important for systems with molecules fitting tightly in nonporous materials. Similar effects of framework flexibility may be found for other classes of porous materials, and studies addressing this topic are encouraged. However, materials such as MOFs can have large-scale structural rearrangements that may need different approaches. In the future, the development of force fields for zeolite framework flexibility should have a special focus on the interactions of bulky aromatic guest molecules with and within a zeolite framework.

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Notes

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