Modeling Adsorption and Self-Diffusion of Methane in LTA Zeolites: The Influence of Framework Flexibility

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The influence of framework flexibility on the adsorption and diffusion of methane in LTA zeolites was investigated by Monte Carlo and molecular dynamics simulations. In particular, we analyzed the framework flexibility of the pure silica structure (ITQ-29), the sodium form (LTA-4A), and the sodium/calcium form (LTA-5A). Simulations were performed at 500 K and over the full loading range. We found that the framework flexibility affects adsorption and diffusion of methane differently. The effect of flexibility on adsorption is small. However, the influence on diffusion seems to be much larger and strongly dependent on three factors: the density and type of the nonframework cations located in the LTA zeolite, the loading of methane in the structure, and, most importantly, the force field parameters used to model the framework.

Introduction

Zeolites are widely used as adsorbents, molecular sieves, ion exchangers, or catalysts in a number of important industrial processes. The performance of these processes is significantly influenced by the diffusion rates of the various guest molecules in the zeolite pores. Molecular simulation of diffusion has become a powerful tool to study the details of the diffusive processes of simple molecules adsorbed in the micropores of zeolites and is essential for understanding the role of the framework structure and dynamics of these complex systems. From a simulation point of view, computing diffusion coefficients is challenging, and several reviews on this topic have been published recently.1–3 The first simulation studies for diffusion in confined systems focused on self-diffusivities calculations for a single component using equilibrium molecular dynamics (MD) simulations.4 Most recently, the increase of computer power made it possible to extend those calculations for obtaining diffusivities over loading, providing insights into the mechanisms that control the molecular traffic along the zeolite pores.5–7 Earlier diffusion studies in zeolites date back to the 1970s,8 and they have been increasing in complexity over the years. In the 1990s, simulation methods were applied to compute molecular diffusion at infinite dilution in MFP9–11 and FAU12–14. These studies were later extended to other complex topologies, such as LTA, LTL, ERI, and CHA, not only for infinite dilution but also for low, medium, and high loadings.15–20

Most molecular simulation studies in zeolites are performed using the Kiselev-type potentials, where the zeolite atoms are held rigid at the crystallographic positions.21 However, some authors have also investigated the effect of flexibility, using a variety of potentials for the framework atoms22–25 and testing the accuracy and viability by comparison of the computed adsorption,26,27 diffusion,28,29 IR spectra,22,23,27 or structural parameters24,25 with experimental data.

Rigid-framework simulations provide predictions of equilibrium adsorption that are in good agreement with experimental data and show small differences from results obtained with flexible-framework models.30–36 However, diffusion coefficients are found to be strongly dependent on the flexibility of the framework.37–40 though, in some special cases, this influence seems to be canceled out by opposite effects induced by the model.38 Rigid-framework simulations have proved to be accurate for molecules smaller than the smallest pore aperture, though the assumption of a rigid framework can introduce significant errors when applied to molecules with diameters close to the size of the largest framework pore.22,41–44 In many cases, the flexible lattices can enhance the diffusion coefficients, but still, most simulations of diffusion are carried out using rigid frameworks.

Previous simulation studies on the influence of lattice flexibility in diffusion of hydrocarbons and other nonpolar molecules were performed in pure silica zeolites. Most of these studies used the model proposed by Demontis et al.,22,26,29 though several works suggested that, for diffusion of methane in MFI and cation-free LTA, there are substantial discrepancies depending on the flexibility model chosen.42

In this paper, we study the adsorption and self-diffusion of methane in Linde-type A zeolites. We have taken into account the flexibility of the framework structure to investigate the influence on diffusion in LTA, both with and without cations. To understand the flexible lattice influence, we have chosen the models of Nicholas et al.,23 and Hill and Sauer.25 We performed simulations using these flexible models as well as rigid frameworks for all zeolites studied. The structures chosen were LTA-4A, LTA-5A, ITQ-29, and hypothetical pure silica LTA (e.g., LTA-4A without ions and all aluminum replaced by silicon). We compare our simulations results with available experimental and simulation data from the literature. Experimental diffusivities of methane in LTA-5A at several temperatures were measured using the neutron spin echo (NSE) technique by Jobic et al.43 Heink et al. measured the self-diffusion of methane for LTA-5A with different calcium contents46,47 by pulse field gradient nuclear magnetic resonance...
spectroscopy. Most recently, Reyes et al.\textsuperscript{48} and Corma et al.\textsuperscript{49} used the same technique to obtain the self-diffusivity of methane in cation-free LTA.\textsuperscript{48} With the aid of molecular dynamics, Fritzsche et al. computed the self-diffusion of methane in a cation-free LTA, also taking into account the polarization interaction on exchangeable cations in the structure.\textsuperscript{30, 52} To our knowledge, the only values of the self-diffusivity of methane in flexible LTA were reported by Demontis et al.\textsuperscript{53} for the cation-free structure and by Fritzsche et al. for the influence of lattice vibrations on the diffusion of methane in a cation-free LTA zeolite.\textsuperscript{38}

In this work, we compare these values with the results obtained using more sophisticated flexible models, and we extend the study to structures with sodium and calcium cations. In addition, we performed molecular simulations of adsorption to prove the consistency of the results obtained with the flexible models chosen, comparing them to those obtained using a rigid framework structure.

Models and Simulation Details

Adsorption isotherms and the self-diffusivity of methane were computed in rigid and flexible LTA-type zeolites containing 96 sodium cations per unit cell (LTA-4A), 32 sodium and 32 calcium cations per unit cell (LTA-5A), and all silica structures (ITQ-29 and LTAs). The adsorption isotherms were obtained from Monte Carlo (MC) simulations in the Grand Canonical ensemble (GCMC) where volume, temperature, and chemical potential were kept constant. The number of adsorbed molecules was changed during the simulation, and the total number of cations remains constant. To sample cation motions, we used displacements and insertions at new randomly selected positions that bypass energy barriers.\textsuperscript{30}

Self-diffusion coefficients were calculated using molecular dynamics (MD) simulations. In MD simulations, successive configurations of the system are generated by integrating Newton’s laws of motion, which then yields a trajectory that describes the positions, velocities, and accelerations of the particles as they vary with time. The equations of motion were integrated using the velocity-Verlet algorithm. For methane diffusion in rigid zeolite, we used an integration time step of 0.01 and 0.005 fs when we consider the flexible structures, to ensure satisfactory energy conservation during nanoseconds runs. Calculations were performed using an NVT ensemble for rigid and flexible structures at 500 K. The self-diffusion coefficients are computed by taking the slope of the mean-squared displacement at extended times.\textsuperscript{16, 61}

Zeolite LTA-4A, was synthesized for the first time by Breck et al.\textsuperscript{54} This zeolite presents a cubic crystal structure, space group \(Fm\bar{3}c\), and \(a = b = c = 24.555 \text{ Å}\). The unit cell composition is \(\text{Na}_96\text{Si}_{96}\text{Al}_{32}\text{O}_{384}\). The structure consists of an arrangement of sodalite units placed at the vertices of a simple cubic lattice and linked to each other by oxygen bridges. The central cavity formed by eight sodalite cages is called an \(\alpha\)-cage. This cage type is inaccessible to, for example, alkanes. Each \(\alpha\)-cage is connected to six other \(\alpha\)-cages in an octahedral way, forming what is called a \(\beta\)-cage, and the interconnection is via the eight-membered ring by windows of about 4.2 Å in diameter. One unit cell of this zeolite consists of eight \(\alpha\)-cages, and its diameter is about 11.4 Å. The unit cell of LTA-4A zeolite has three types of oxygen rings; eight-, six-, and four-membered rings. The charge compensating extra-framework sodium cations are distributed over the surface of the \(\alpha\)-cage. The cations occupy three distinct positions detected by X-ray diffraction.\textsuperscript{55} Eight of them are Na I type cations and are located at the center of the six-membered ring corresponding to the window between the sodalite cage and the \(\beta\)-cage. Three sodium cations are near the center of the eight-membered ring that constitutes the window between two \(\beta\)-cages; those cations are called Na type II. One Na III type cation is inside the cage in front of the four-membered connecting two sodalite cages. Cations on site Na II will partially block the aperture of the \(\beta\)-cage’s window, and the adsorbed molecules cannot easily diffuse into the interior of this zeolite.

Zeolite LTA-5A is obtained by replacing 64 sodium monovalent cations from the LTA 4A by 32 bivalent calcium ions in an exchange after synthesis. These cations are preferentially located in four crystallographic positions: in the window formed by an eight-membered ring, in the window of the six-membered ring, displaced inside an \(\alpha\)-cage, or in the sodalites displaced into the center of the six-membered ring. In this structure, there are no cations inside the windows of the eight-membered ring.\textsuperscript{56}

We also performed simulations in two all-silica LTA-type structures, the hypothetical model obtained from the LTA-5A structure dealuminized, labeled as LTAs, in this work, and the silica stable form ITQ-29 obtained by Corma et al.\textsuperscript{57} The ITQ-29 topology is a simple cubic cell with space group \(Fm\bar{3}c\) and \(a = b = c = 11.867 \text{ Å}\). The crystallographic unit cell is 8 times smaller than LTA-5A, but with the same type of channels and cages. LTA-4A consists of a three-dimensional interconnected channel system. This structure has the eight large spherical \(\alpha\)-cages of approximately 11.4 Å interconnected via windows of about 4.2 Å in diameter and \(\beta\)-cages with an average diameter of 6.6 Å alternating with the \(\alpha\)-cages and separated by 2.2 Å openings. We use a single unit cell for the simulations in LTAs, LTA-4A, and LTA-5A and eight unit cells \((2 \times 2 \times 2)\) for ITQ-29. Note that the unit cell of ITQ-29 is a single cage. LTA-4A and LTA-5A have an alternating silicon and aluminum arrangement that can only be periodically described in terms of \(2 \times 2 \times 2\) \(\beta\)-cages. Without aluminum, the unit cell can be described as a single \(\alpha\)-cage.

The interactions between guest molecules (methylene and cations) with the zeolite host framework were modeled by Lennard-Jones and Coulombic potentials.\textsuperscript{30, 34} The Coulombic interactions in the system were calculated using Ewald summations. An “average” polarization was included implicitly in the parametrization by means of the polarization induced by the cation on the zeolite and by the cation on the methane.\textsuperscript{30} The Na–O and Ca–O interactions were calibrated to reproduce the experimentally known positions in LTA-4A and LTA-5A.\textsuperscript{30, 33} The charge distribution on the oxygen framework was considered to be static; that is, polarization of oxygen by nearby cations was neglected. The model used for the rigid frameworks explicitly distinguishes silicon from aluminum with a difference of 0.3e between \(q_{\text{Si}}\) and \(q_{\text{Al}}\).\textsuperscript{58} We consider different charges for oxygen atoms bridging two silicon atoms, \(q_{\text{OSi}}\), and oxygen atoms bridging one silicon and one aluminum atom, \(q_{\text{OAi}}\).\textsuperscript{30}

There are several force fields in the literature that describe the flexibility of the zeolite framework.\textsuperscript{4} Among them, we have focused on these reported by Nicholas et al.\textsuperscript{23} and Hill and Sauer.\textsuperscript{25} The reasons for choosing these two force fields are that they can be applied to pure silica structures and, using straightforward modifications, they can be easily extended to aluminosilicates with sodium and calcium cations. Following a previous work reported by Vlugt and Schenk,\textsuperscript{26} we additionally improved these models in such a way that the equilibrium distances are no longer constant but taken from the crystal structure.\textsuperscript{26} The flexible model of Nicholas et al. was developed for all-silica sodalite and contains terms that represent the valence and nonbonded interactions of the structure. This model
is able to reproduce the structure and dynamics of all-silica sodalite and is also transferable enough to reproduce the infrared spectrum of MFI. The Si–O–Si bond was modeled using a fourth-order polynomial; all other bends were harmonic in functional form. We extended this model with similar functions to describe the interaction with the aluminum, and we took into account contributions of dihedral-angle-dependent potential functions, Lennard-Jones interactions between nonbonded atoms, and Coulombic potentials. Detailed information of this model can be found in the original work of Nicholas et al.23 as well as in Table S1 of the Supporting Information (all additional implementations).

To check the consistency of flexible models, we also have used the model by Hill and Sauer.25 They developed a method to derive the parameters of a consistent force field type (CFF) from ab inito calculations that was first applied to aluminum-free zeolites24 and, afterward, to protonated aluminosilicates.25 The force field is defined by bonds, angles, torsions, out-of-plane, bond–angle, angle–bond, angle–torsion–angle, and nonbond energy expressions. Detailed information about this force field can be found in the original studies of Hill and Sauer24,25 and in Table S2 of the Supporting Information.

Results and Discussion

Figure 1 shows the computed absolute adsorption of methane in rigid ITQ-29, LTA-4A, and LTA-5A at 273 and 500 K. The adsorption of methane in LTA-type structures is determined by the number and distribution of cations in the structure. In particular, the effect of the number of cations in LTA structures is similar to that observed for FAU-type structures,30,61 where cations act as additional adsorption sites at low pressures while competing for the available free volume with methane at the highest pressures. However, an essential difference with FAU structures is that, in LTA zeolites, the computed adsorption for methane is insensitive to the initial set of positions of the cations. We can explain this finding based on the Si/Al ratios and symmetries of both structures. The composition of a single unit cell in FAU is Na$_x$Al$_x$Si$_{192-x}$O$_{384}$, where 96 $\leq x \leq 0$, with two types of oxygen atoms in the framework: oxygen atoms bridging two silicon atoms and oxygen atoms bridging one silicon and one aluminum atom. Because the cation interaction is stronger with the latter than with the former, the aluminum positions determine the cation distribution in FAU. LTA-type zeolites show Si/Al $\geq 1$ with alternating silicon and aluminum atoms in order to obey the Lowenstein rule. In these structures, all oxygen atoms are bridging one silicon and one aluminum atom, providing a symmetrical ion distribution that is independent of the positions of the cations selected as the starting configuration. Even though simulations for methane adsorption in LTA-type structures are not sensitive to the initial distribution of cations,34 the positions of these cations are of critical importance for adsorption kinetics in these structures. If the cations are located in the eight-ring windows, they obstruct diffusion. LTA-4A with 96 sodium cations would show a very high adsorption capacity, but experimentally, it has all the eight-ring windows blocked. The Ca/Na form LTA-5A used in this work contains 32 sodium and 32 calcium per unit cell, and none of the windows are blocked by the cations. This leads to diffusion values of methane similar to the ones obtained for the pure silica structure ITQ-29.

Figure 2 shows the self-diffusivity for methane in ITQ-29 and LTA-5A as a function of loading at 500 K. Diffusivities are very similar for both structures up to 9 molecules per cage (72 molecules of methane per unit cell) and decrease at a loading of 10 molecules and higher. Direct comparison between self-diffusivity values obtained for LTASi and LTA-5A shows that the methane–cation interaction dominates over the methane–zeolite interaction for methane loading up to 12 molecules per cage. However, at higher loadings, the effect of the cation is diluted by the increase of the molecule–molecule interactions available experimental data, as shown in previous studies. The adsorption of methane in LTA-type structures is determined by the number and distribution of cations in the structure. In particular, the effect of the number of cations in LTA structures is similar to that observed for FAU-type structures, where cations act as additional adsorption sites at low pressures while competing for the available free volume with methane at the highest pressures. However, an essential difference with FAU structures is that, in LTA zeolites, the computed adsorption for methane is insensitive to the initial set of positions of the cations.
as indicated by the similar values obtained for methane diffusivity in the structure with sodium and calcium cations and the hypothetical pure silica structure. To analyze the influence of host–guest, host–cation, and cation–guest interactions, we have additionally computed the self-diffusivity of methane as a function of loading in a hypothetical pure silica and cation-free structure labeled as LTASi. As mentioned in the previous section, this structure was obtained from the substitution of all aluminum atoms of LTA-5A by silicon. The obtained results are in qualitatively good agreement with the simulation data reported by Fritzsche et al., but quantitatively, they obtained higher values for self-diffusion (Figure 2) and consequently lower values for adsorption (Figure 3). These results support the finding that the diffusion coefficient depends sensitively on the choice of the Lennard-Jones parameters.51 The diffusion curve obtained for the structure with cations retains the overall shape as a function of loading, though it becomes lower than the one without cations (Figure 2). The former effect is due to the limited influence of the cations on the pore volume of the structure (see Figure 1a), whereas the latter effect can be attributed to the increased attraction with the cations.

Despite the fact that both LTASi and ITQ-29 have the same morphology, the computed self-diffusion is much higher for the hypothetical structure than for ITQ-29, independent of methane loading. However, differences in adsorption are less remarkable, as shown in Figure 3. The different behaviors in adsorption and diffusion can be explained from the window size and from the pore size distributions (PSDs) calculated with the method reported by Gelb and Gubbins.53 Figure 4 shows distributions of $V(r)$ and the PSD. The function $V(r)$ is the fraction of space “coverable” by spheres of radius $r$ or smaller; at $r = 0$, it corresponds to the void-fraction. $V(r)$ is a monotonically decreasing function. The derivative of this function is the PSD with peaks at around 10–11 Å for the size of the $\beta$-cage. The windows of ITQ-29 are slightly smaller than for LTASi, and the PSD distributions are narrower and have pore diameters slightly smaller for ITQ-29 than for LTASi. This suggests that the adsorption and self-diffusion values obtained for methane in LTASi could be probably analogous to those obtained for a flexible model of ITQ-29. To investigate the effect of framework flexibility in ITQ-29, we have computed the self-diffusivity of methane as a function of loading at 500 K (Figure 5) as well as the adsorption isotherm of methane at 500 K using both Nicholas et al.23 and Hill and Sauer25 models (Figure 6). Differences between the self-diffusivity values obtained for the rigid and the two flexible models are striking, but again, there seems to be hardly any influence of the framework flexibility on the adsorption isotherm.

It is interesting to speculate about the reasons if and why flexibility is essential to computing methane self-diffusivities but needless for adsorption. These reasons are probably very much related with the LTA topology that consists of cubically arranged cages of about 10 Å in size. The cages are connected by narrow windows in such a way that the windows form entropic barriers.64 In these structures, the diffusion is an activated process where the molecules of methane hop from one cage to the next and the crossing time is negligible compared to the time a particle spends inside the cage.16 These hops can easily be disturbed by small variations of the bond length...
between the silicon and oxygen atoms of the framework. The silicon–oxygen bond lengths for ITQ-29 and LTA-5A are around 1.57–1.61 Å and 1.59–1.60 Å, respectively. However, the aluminum–oxygen bond lengths for LTA-5A are around 1.72–1.74 Å. Because the hypothetical LTASi was built from direct substitution of the 96 aluminum atoms of the structure by silicon, without any posterior minimization of the bond lengths, 50% of its silicon–oxygen bond lengths are around 0.13–0.14 Å larger than the average silicon–oxygen bond lengths. This results in slightly wider pores for the rigid structure and, additionally, an abnormal deformation in its flexible models, as can be deduced from the significantly higher values on self-diffusivities of methane that we show in Figure 7. This anomalous deformation—also reported by Demontis and Suffritti using a more simplistic flexible model—does not affect methane adsorption in LTASi as this molecule has most of its distinct adsorption sites in the cage and only one in the window regions. The adsorption behavior is shown in Figure 8, which compares the computed adsorption isotherms obtained using the rigid structure, the flexible model of Nicholas et al., and the flexible model of Hill and Sauer.

For LTA-4A and LTA-5A structures, we found the same effect; the influence of framework flexibility is large for diffusion and almost negligible for adsorption. In Figure 9, we show that the adsorption isotherms almost overlap using rigid and flexible models, with only slight differences at the highest pressures. However, the computed data for the self-diffusivity of methane prove to be different for different models. According to the computed values depicted in Figure 10, up to five molecules per cage, we obtain analogous diffusion using both the rigid structure and the flexible model of Hill and Sauer. However, more than five molecules of methane per cage enhances the flexibility effect at the windows, as inferred from the higher self-diffusion obtained with the flexible model. It is interesting to note that the flexible model of Nicholas et al. provides a reverse behavior than the model of Hill and Sauer. Here, self-diffusion is higher than for the rigid structure up to nine molecules of methane per cage, becoming similar and even

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**Figure 7.** Computed self-diffusion for methane as a function of loading in LTA$_{5s}$ at 500 K using a rigid structure (squares), flexibility with the model of Nicholas et al. (circles), and flexibility with the model of Hill and Sauer (triangles). Simulations from Demontis et al. using a simplistic flexible model for LTAS$_{5s}$ at 359 K are also included (asterisks).

**Figure 8.** Computed adsorption isotherms for methane in LTAS$_{5s}$ at 500 K using a rigid structure (squares) and flexible models of Nicholas et al. (circles) and Hill and Sauer (triangles).

**Figure 9.** Computed adsorption isotherms for methane at 500 K using a rigid structure (squares) and flexible models of Nicholas et al. (circles) and Hill and Sauer (triangles) in (a) LTA-4A and (b) LTA-5A.

**Figure 10.** Computed self-diffusion for methane as a function of loading in LTA-5A at 500 K using a rigid structure (squares), flexibility with the model of Nicholas et al. (circles), and flexibility with the model of Hill and Sauer (triangles).
lower for the highest loadings. The fact that the two flexible models only show differences in diffusion for the LTA-5A structure leads us to conclude that the reverse behavior is essentially attributed to the interactions between the zeolite framework and the sodium and calcium cations. These interactions are probably overestimated in the model of Hill and Sauer, leading to a self-diffusivity value of $3.7 \times 10^{-10}$ m$^2$/s at 500 K when one single methane is located in the cage. At the same conditions, the self-diffusivity value obtained for the model of Nicholas et al. is $1.1 \times 10^{-9}$ m$^2$/s, in reasonable agreement with the experimental data provided by Jobic et al.\(^4^9\) ($1.0 \times 10^{-9}$ m$^2$/s at 475 K) and Corma et al.\(^4^9\) ($3 \times 10^{-9}$ m$^2$/s at 500 K).

We conclude this section by addressing the question of whether flexible models provide better predictions of the self-diffusion than rigid models. One could argue that a flexible model is, in principle, a more realistic description of the LTA zeolite. There is a wide agreement in the literature that flexibility is included depend very much on the model used. If there are no structural changes of the framework, then the rigid models would also allow reliable computations of both adsorption and diffusion.

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**Supporting Information Available:** Tables of energy potentials and force field parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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**References and Notes**

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