Influence of Organic Structure-Directing Agents on Fluoride Dynamics in As-Synthesized Silicalite-1

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Abstract

Silicalite-1, an all-silica zeolite having the MFI topology, can be synthesized in the presence of fluoride ions, which balance the charge of the cationic organic structure-directing agents (OSDAs, such as tetrapropylammonium). In as-synthesized Silicalite-1, the fluoride anions occupy well-defined positions in the $4^1 \cdot 5^2 \cdot 6^2$ cages, where they are covalently bonded to framework Si atoms. Previous experimental studies showed that the fluoride anions are dynamically disordered at room temperature. The dynamic disorder can be suppressed by cooling to cryogenic temperatures and also through a variation of the OSDA, pointing to an interplay between framework and extra-framework dynamics. In the present work, ab-initio molecular dynamics (AIMD) simulations in the framework of density functional theory (DFT) were employed to study the influence of the OSDA on the fluoride dynamics, comparing a total of eight alkylammonium OSDAs having either four alkyl chains of equal length (symmetric) or one short and three longer chains (asymmetric). In addition to time-averaged quantities, such as atomic root mean square displacements, the number of dynamic events in which fluoride ions "jump" from one Si atom to a neighboring one was analyzed. While the timescale accessible to the AIMD simulations was found to be too short to observe significant fluoride dynamic disorder at room temperature, it was clearly detectable when increasing the temperature to 373 K. For systems incorporating symmetric OSDAs, increasing OSDA size correlates with decreasing freedom of motion of the framework atoms. In line with previous experimental findings, a drastic reduction of the fluoride dynamic disorder was observed for systems containing tributylammonium-based OSDAs having one short (methyl or ethyl) chain. Besides reproducing the experimental observations, the computational approach also helped to explain this suppression of the dynamic disorder on the basis of the size and shape of the OSDA.

Introduction

The "classical" route of hydrothermal zeolite synthesis, pioneered by Barrer, Breck, and others, proceeds in hydroxide-containing media.¹ In addition to aluminosilicate zeolites, some all-silica zeolites like the prototypical Silicalite-1 (MFI framework type²) can also be synthesized via this route.³ During the synthesis of all-silica zeolites, the pure-SiO₂ framework is stabilized through the incorporation of organic structure-directing agents (OSDAs), which are mostly cationic.⁴ Due to the absence of a negative framework charge, the positive charge of the OSDA is balanced either through incorporation of hydroxyl ions⁵ or through structural defects (siloxo groups),⁶ often resulting in defect-rich crystals of limited size. An alternative to the synthesis in hydroxide media was proposed in 1978 by Flanigen and Patton, who synthesized Silicalite-1 via a hydrothermal route in the presence of fluoride anions.⁷ As the fluoride anions are incorporated into the structure of the as-synthesized material, there is no need to balance the OSDA charge through defects, and it has since been established that this "fluoride route" is well-suited to prepare large, defect-free crystals.^{8,9} Moreover, many of the more recently reported high-silica and all-silica zeolites are synthetically accessible only in the presence of fluoride.^{9,10}

Crystallographic investigations of fluoride-containing all-silica zeolites have delivered two typical fluoride environments:¹¹ In structures containing double four-ring cages ($d4r$, face symbol 4^6), the fluoride anions are located at the center of this highly symmetric cage. In frameworks that do not contain these $d4r$ units, they are incorporated in other small cages. They are covalently bonded to a silicon atom at one of the corners of the cage, forming (distorted) trigonal-bipyramidal SiO₄F⁻ units. An example for such an environment is shown in Figure 1, which visualizes the $4^1 \cdot 5^2 \cdot 6^2$ cage of a fluoride-containing sample of Silicalite-1, including the F positions determined using single-crystal X-ray diffraction (sc-XRD) by Aubert et al.¹² Like in many other fluoride-containing all-silica zeolites, the fluoride an-

ions are disordered over two equivalent positions within one cage. The frequent occurrence of disorder renders an accurate determination of the Si-F distances using crystallographic methods difficult, because the average long-range structure as "seen" by X-ray (or neutron) diffraction corresponds to an average over two different environments, SiO_4 tetrahedra and trigonal-bipyramidal SiO_4F^- units. Hence, uncorrected Si-F distances obtained with diffraction methods are always longer than $1.8 \text{ \AA}$,¹¹ whereas the sum of atomic (ionic or covalent) radii does not exceed $1.7 \text{ \AA}$.^{13,14} In contrast, solid-state NMR measurements, which are sensitive to the local environment, have delivered more realistic Si-F distances between 1.7 and $1.8 \text{ \AA}$ (in the absence of dynamic disorder).^{11,15} These values agree with predictions from density functional theory (DFT) calculations.^{16,17}

Figure 1: $4^1 \cdot 5^2 \cdot 6^2$ cage of fluoride-containing Silicalite-1 as determined from sc-XRD data by Aubert et al.¹² Color scheme: F = light blue, Si = yellow, O = red. The fluoride anion is disordered over two positions, which are symmetry-related by a mirror plane. As a consequence, the occupancy of the F position equals $1/2$. The double-headed arrow indicates that the fluoride anion moves back and forth between the equivalent positions (= dynamic disorder). The sc-XRD Si-F distance amounts to $1.92 \text{ \AA}$.

In addition to allowing a determination of the Si-F equilibrium distance, solid-state NMR measurements can also provide insights into the nature of the fluoride anion disorder: While

tetrahedrally coordinated Si atoms give rise to signals in the range from -100 to -120 ppm in ^{29}Si NMR experiments (reference: tetramethylsilane), SiO_4F^- units are characterized by a sharp signal at about -145 ppm in the absence of dynamic disorder.^{18,19} Dynamic disorder of the fluoride anions gives rise to a broad signal centered at about -125 ppm. On the basis of this distinct difference, it was established that fluoride is dynamically disordered in as-synthesized Silicalite-1, ITQ-4 (IFR framework type), and SSZ-23 (STT) at room temperature (RT), and that the dynamic disorder can be frozen out by cooling to about 140 K.¹⁹ In contrast, no dynamic disorder has been found in Mu-26 (STF)²⁰ and nonasil (NON).¹⁸ A rather intriguing finding was reported in 2015 by Brace et al.: These authors showed that the fluoride dynamic disorder in Silicalite-1 is directly linked to the nature of the OSDA.²¹ Whereas samples containing tetrapropylammonium (TPA) cations exhibit the RT dynamic disorder that had already been established in Koller's earlier work,^{18,19} use of the methyltributylammonium (MTBA) cation as OSDA led to a suppression of the dynamic motion. Intermediate behavior was observed for some other asymmetric OSDAs (the term "asymmetric" is used here in a somewhat loose way to comprise alkylammonium OSDAs possessing chains of different length). The authors hypothesized that the presence of one short alkyl chain in MTBA leads to shorter average distance between the central N atom of the OSDA cation and the fluoride anion, enhancing electrostatic interactions and consequently reducing fluoride mobility. Very recently, it was also shown that the replacement of tetraethylammonium (TEA) by tetraethylphosphonium (TEP) slows down the fluoride motion.²²

Electronic structure calculations in the framework of DFT have been widely used to study zeolite structures and properties.²³ With regard to fluoride-containing zeolites, several authors have used DFT methods to investigate the local fluoride environment,^{16,17,24,25} to predict ^{19}F NMR shifts or vibrational spectra,²⁶⁻²⁹ and to study the stability of different possible fluoride positions.³⁰ Studies of fluoride dynamics using DFT-based ab-initio molecular

dynamics (AIMD) calculations are, however, so far rare, with the exception of one investigation of *d4r*-containing AST-type silicogermanates.²⁵ In the present work, an analogous methodological approach was used to address the following questions:

- Is it possible to reproduce the dynamic disorder of fluoride anions in MFI-type zeolites, at least qualitatively, using such simulations, which are limited to the picosecond timescale?
- Can the suppression of the dynamic disorder through variation of the OSDA be observed in the simulations?
- Is it possible to uncover and rationalize other relationships between the OSDA and fluoride dynamic disorder?

AIMD simulations were performed for MFI models containing eight different OSDAs (four symmetric, four asymmetric), and for OSDA-free Silicalite-1 as reference system, considering three different temperatures. The root mean square displacements (RMSDs) of different elements as well as selected radial distribution functions (RDFs) were computed from the AIMD trajectories. By analyzing the evolution of individual fluoride coordinates, the number of dynamic "events" occurring during the simulation time was determined, which was taken as an approximate measure of the extent of dynamic disorder. The qualitative differences between systems containing different OSDAs were then rationalized, providing deeper insights into the relationships between OSDA size/shape and fluoride anion mobility.

Models and Methods

Computational details

DFT structure optimizations and DFT-based AIMD simulations were carried out using the CP2K code (version 4.1 installed on HLRN-III "Konrad"), which uses a hybrid Gaussian and plane wave approach.^{31,32} All calculations used the PBE exchange-correlation functional³³ together with the "Grimme-type" D3 dispersion correction.³⁴ This dispersion-corrected DFT approach has been successfully employed in previous "benchmarking" work on all-silica zeolites³⁵ and in an AIMD study of fluoride-containing AST-type zeolites.²⁵ The CP2K calculations used a plane wave energy cutoff of 600 Ry, Goedecker-Teter-Hutter pseudopotentials devised by Krack,³⁶ and a double-zeta (DZVP-MOLOPT-SR) Gaussian basis set.³⁷ Due to the size of the MFI unit cell, only the Γ point was used to sample the first Brillouin zone. The structure optimizations used a BFGS optimization method. Atomic positions and unit cell parameters were optimized, but the unit cell was fixed to a monoclinic metric for guest-free MFI, and to an orthorhombic metric for all other systems. Calculations were considered converged when the magnitude of the geometry change from one step to the next was below 10^{-4} bohr, when the maximal residual force was smaller than $5 \cdot 10^{-6}$ Ha bohr⁻¹, and when the internal pressure was smaller than 0.01 GPa.

AIMD simulations were performed in the *NVT* (canonical) ensemble for temperatures of 298, 373, and 473 K. The calculations employed a Nosé-Hoover thermostat with a time step of 0.5 fs and a time constant of 50 fs. A time step of 0.5 fs is small enough to capture all atomic oscillations, including those of the hydrogen atoms, in sufficient detail, and it has been used in several AIMD studies of zeolites/zeotypes containing organic guests^{25,38,39} or adsorbed water molecules.^{40,41} The time constant was chosen because it provides a fast equilibration of the temperature without leading to excessive temperature fluctuations. Three independent trajectories were calculated for every system at each of the three temperatures considered,

with each trajectory consisting of an equilibration phase of 2.5 ps (5,000 steps) and a production phase of 7.5 ps (15,000 steps), i.e., the total simulation time from which the results were extracted for each system corresponds to 22.5 ps. Root mean square displacements of the constituent elements and selected radial distribution functions were calculated using the VMD code, version 1.9.3.⁴² All RMSDs and RDFs discussed in the following correspond to averages over three 7.5 ps trajectories.

Models of zeolite structures

The monoclinic structure of OSDA-free (calcined) Silicalite-1 was taken from the sc-XRD study reported by van Koningsveld et al. (space group $P_{n}^{21}11$, note that an unusual a -unique setting is used to retain the axis orientations of the orthorhombic structure).⁴³ Even though a monoclinic-to-orthorhombic phase transition happens at about 350 K,⁴⁴ it was assumed for the purpose of the present work that the lattice dimensions do not change with temperature, an assumption that was made for all MFI models. Along with OSDA-free MFI, a variety of MFI models containing fluoride anions and different OSDA cations as listed in Table 1 were considered. They are designated as MFI_(X,F) throughout this work, where X represents the OSDA (because the OSDAs always appear in their cationic form, their positive charge is not indicated separately in the labels). The unit cell composition of the OSDA-containing models corresponds to $\text{Si}_{96}\text{O}_{192}\text{F}_4 \cdot \text{X}_4$. The starting model for all these systems was the sc-XRD structure of MFI_(TPA,F) determined by Aubert et al. (space group $Pnma$).¹² The disorder of propyl chains and fluoride anions was removed, leading to a reduction in symmetry to space group $P_{n}^{21}11$ (non-standard a -unique setting, as above). For the other models containing symmetric OSDAs (TMA, TEA, TBA), the optimized structure of MFI_(TPA,F) was taken as a starting point, and the length of the alkyl chains was modified accordingly. Hydrogen atoms were added using an automated placement procedure, and the OSDA coordinates were then pre-optimized using the DREIDING force field.⁴⁵ For

the case of MFI_(TBA,F), a simulated annealing procedure using this force field was used to obtain a realistic starting structure (a more detailed description of the DREIDING calculations is given in the Supporting Information). All structures were then optimized using the CP2K code as described in the preceding section. The resulting unit cell parameters are compiled in Table S1 of the Supporting Information and the optimized structures are visualized in Figures S1 to S5. It is worth noting that the unit cell volumes show a certain variation, from $\sim 5240 \text{ \AA}^3$ for MFI_(TMA,F) to $\sim 5450 \text{ \AA}^3$ for MFI_(TBA,F).

For MFI models with asymmetric OSDAs (MTBA, ETBA, PTBA, MTPA), four different starting structures in space group $Pn11$ were constructed. In each case, the DFT-optimized structures of the corresponding system with symmetric OSDAs (MFI_(TBA,F) and MFI_(TPA,F)) were taken as starting point, and the alkyl chains were modified to give different possible arrangements of shorter and longer chains. As solid-state NMR experiments have shown that the shorter chains of the OSDAs preferentially point into the straight channels,^{46,47} a trend that was confirmed in preliminary calculations, only such configurations were considered. The structures were then optimized using CP2K. The energetically most favorable structures are visualized in the Supporting Information, Figures S6 to S9. For MFI_(MTBA,F) and MFI_(ETBA,F), configurations in which each methyl/ethyl chain points towards a butyl chain of a neighboring OSDA cation are energetically favored. The reverse is true for MFI_(PTBA,F) and MFI_(MTPA,F), where the shorter chains of two neighboring OSDAs point into the same channel segment.

The majority, but not all of the OSDAs listed in Table 1 direct the formation of MFI-type structures. In the initial report of Silicalite-1, TPA was mentioned as one of several possible alkylammonium templates,³ and this OSDA has been used in many subsequent studies.^{12,18,19,21,48} TBA promotes the formation of an intergrowth of MFI-type Silicalite-1 and MEL-type Silicalite-2,⁴⁸ because the butyl chains fit less well into the channels of MFI.⁴⁹ While TEA cations, more typically used in the synthesis of zeolite beta, can also direct the

formation of MFI,^{22,50} the small TMA molecule does not act as an OSDA for MFI (it is, however, used in the synthesis of various clathrasils like AST-type octadecasil⁵¹). TMA was nevertheless included in the present study in order to study comprehensively the influence of the alkyl chain length on the fluoride dynamics. Among the asymmetric OSDAs, MTBA, ETBA, and MTPA were successfully employed to synthesize MFI-type zeolites by Brace et al., whereas attempts using PTBA delivered only amorphous phases.^{21,47}

Table 1: OSDA cations considered in this study.

Abbreviation	Complete name	Formula
Symmetric		
TMA	Tetramethylammonium	$(\text{CH}_3)_4\text{N}^+$
TEA	Tetraethylammonium	$(\text{C}_2\text{H}_5)_4\text{N}^+$
TPA	Tetrapropylammonium	$(\text{C}_3\text{H}_7)_4\text{N}^+$
TBA	Tetrabutylammonium	$(\text{C}_4\text{H}_9)_4\text{N}^+$
Asymmetric		
MTBA	Methyltributylammonium	$(\text{CH}_3)(\text{C}_4\text{H}_9)_3\text{N}^+$
ETBA	Ethyltributylammonium	$(\text{C}_2\text{H}_5)(\text{C}_4\text{H}_9)_3\text{N}^+$
PTBA	Propyltributylammonium	$(\text{C}_3\text{H}_7)(\text{C}_4\text{H}_9)_3\text{N}^+$
MTPA	Methyltripropylammonium	$(\text{CH}_3)(\text{C}_3\text{H}_7)_3\text{N}^+$

Results and Discussion

Calcined Silicalite-1

The RMSDs of the framework Si and O atoms of OSDA-free (calcined) Silicalite-1 were calculated from the AIMD trajectories. They are given in Table 2 (RMSDs and standard deviations for all systems are compiled in an EXCEL file supplied as Supporting Information). The RMSDs increase by approximately 25 % in the temperature range from 298 K to 473 K, and the standard deviations are typically in the range of 10 %. It should be noted that these error bars arise in part from the calculation of a single RMSD value for each

element. A more detailed analysis would probably reveal a certain spread of the individual RMSDs of non-equivalent atoms, however, this goes beyond the scope of the present work.

Table 2: AIMD-derived RMSD values for Silicalite-1 and MFI_(TPA,F).

	$T = 298$ K	$T = 373$ K	$T = 473$ K
	RMSD / Å	RMSD / Å	RMSD / Å
OSDA-free Silicalite-1			
Si	0.167±0.017	0.181±0.021	0.211±0.021
O	0.259±0.024	0.282±0.033	0.328±0.029
MFI_(TPA,F)			
Si	0.170±0.019	0.192±0.023	0.226±0.024
O	0.254±0.024	0.293±0.028	0.344±0.029
F	0.259±0.065	0.356±0.082	0.437±0.139
F _{noDE}	0.231±0.055	0.267±0.071	0.294±0.085
N	0.309±0.070	0.297±0.073	0.355±0.076
C	0.409±0.057	0.414±0.058	0.484±0.053
H	0.714±0.103	0.785±0.093	0.909±0.083

The RMSDs can be converted into isotropic displacement parameters U_{iso} using the equation $U_{iso} = \frac{1}{3}(RMSD)^2$.⁵² A plot of the U_{iso} values against temperature, shown in Figure 2a, gives a roughly linear relationship with an intercept close to zero, as expected for harmonic oscillators in the high-temperature limit.⁵³ The values obtained for 298 K can be directly compared to the experimental U_{eq} values reported in the sc-XRD study by van Koningsveld et al.⁴³ The theoretical values of $9.3 \cdot 10^{-3} \text{ Å}^2$ for Si and $22.4 \cdot 10^{-3} \text{ Å}^2$ for O agree reasonably well with the experimental values of $10.7 \cdot 10^{-3} \text{ Å}^2$ and $29.5 \cdot 10^{-3} \text{ Å}^2$, respectively (the experimental values quoted here were obtained by averaging over the individual U_{eq} values of the 24/48 non-equivalent Si/O atoms). The good quantitative agreement gives confidence in the ability of the AIMD calculations to predict realistic atomic oscillations, a crucial prerequisite for the subsequent investigations. Previous work on the hydrated aluminophosphate $\text{AlPO}_4\text{-H}_3$, which used an analogous computational approach, gave similarly good agreement between calculated and experimental displacement parameters of the framework atoms.⁴¹

Figure 2: Plot of AIMD-derived U_{iso} values against temperature for a) Silicalite-1 and b) MFI_(TPA,F). " F_{noDE} " = F excluding dynamic events (see text). The dashed lines represent linear regressions.

MFI_(TPA,F)

The RMSDs obtained from AIMD simulations of MFI_(TPA,F) are included in Table 2, and a plot of the derived U_{iso} values for Si, O, and F is shown in Figure 2b. The Si- and O-RMSDs of this system and their standard deviations are mostly somewhat larger than those of guest-free MFI, and the evolution of U_{iso} with temperature is essentially linear for these two elements, although there are more pronounced deviations from a zero intercept compared to OSDA-free MFI. Very different observations are made for the F-RMSDs: While

the value at 298 K is practically identical to the corresponding O-RMSD, the increase with temperature is much steeper. A plot of the derived U_{iso} values against temperature shows drastic deviations from a linear regression with intercept zero. This peculiar behavior of fluoride can be readily explained with the dynamic disorder: Occasionally, fluoride anions "jump" from one Si atom to a neighboring one, leading to a discontinuous change in the equilibrium position. As the RMSD of an atom is calculated with respect to its *average position*, such dynamic "events" will lead to an increase in the RMSD, consequently causing a deviation from the zero-intercept linear relationship between T and U_{iso} . Moreover, the fluoride location in the AIMD average structure will lie somewhere between the two Si atoms, and the Si-F distances will be longer than the DFT equilibrium bond length of approx. 1.78 Å. Therefore, an analysis of the F-RMSDs and of the Si-F bond distances in the AIMD average structures can give a qualitative idea of the occurrence of hopping events. To perform a more quantitative analysis, the atomic coordinates of each fluoride anion for which dynamic events were suspected were extracted from the production stage of the trajectory, and the number of events was determined on this basis. An instructive example is shown in Figure 3, which visualizes the evolution of the y coordinate of one particular fluoride anion in a 373 K trajectory. Apart from thermal oscillations, there are two pronounced and rapid changes of the coordinate after approx. 3 ps and approx. 5 ps. This corresponds to a jump of the fluoride anion from one Si atom to the adjacent one, and a subsequent jump back to its initial position. The time-averaged position of the fluoride anion is visualized on the right-hand side of Figure 3, showing that it lies between the two Si atoms, with both Si-F distances exceeding 2 Å.

Figure 3: Exemplary evolution of the Cartesian y coordinate of one fluoride anion in MFI_(TPA,F) during a 7.5 ps AIMD trajectory ($T = 373$ K), with two dynamic "events" occurring after about 3 and 5 ps. The insets show the approximate equilibrium position of the fluoride anion during the respective periods. On the right-hand side of the figure, the position of this fluoride anion in the AIMD average structure is shown.

Taking together the results from all nine trajectories computed for MFI_(TPA,F) (three temperatures, three trajectories of 7.5 ps for each temperature), there is only one dynamic event at 298 K, whereas there are six events at 373 K and nine events at 473 K, in line with the expected increase of dynamic disorder with increasing temperature. The frequency of dynamic events, and the possibility to calculate approximate "residence times" from them, will be discussed in more detail below. The identification of those fluoride anions which undergo dynamic events allows a recalculation of the F-RMSDs excluding these atoms. These values for the remaining F_{noDE} atoms (noDE = "no Dynamic Events") are also given in Table 2. A plot of the derived U_{iso} value against temperature for this subset, included in Figure 2b, gives the expected linear relationship with an intercept close to zero. Moreover, the values are very similar in magnitude to those of the framework oxygen atoms, as one would expect for atoms of similar mass in a similar bonding situation. As a last remark on the F-RMSDs, one may note the rather large standard deviations, which are often in the range of 20 % (Table 2). These large statistical uncertainties can be explained with differences

in the behavior of individual atoms on the one hand, and the fact that there are only four fluoride anions per unit cell on the other hand.

An alternative means to look at the fluoride anion dynamics in an averaged way is provided by the Si-F RDFs. The $g(r)$ curves for the three different temperatures are shown in Figure 4. The first maximum is centered at about 1.78 Å, which corresponds to the covalent Si-F bonds. The maximum of next-nearest neighbors starts at about 2.2 Å, and shows two peaks at about 2.6 and 3.1 Å corresponding to second- and third-nearest Si atoms. At 298 K, $g(r)$ values in the distance range between the first and second maximum, i.e., between 2.0 and 2.2 Å, are essentially zero. Si-F distances in this range hardly ever occur because most of the fluoride anions do not move away from the Si atom to which they are bonded (there is only one dynamic event over all three 7.5 ps trajectories). The increased number of dynamic events at higher temperatures leads to an increase of the $g(r)$ values in this distance range, which is clearly visible in the inset of Figure 4. The enhanced mobility of the fluoride ions also causes a shift of the left flank of the next-nearest neighbor maximum towards lower distances, and the separate peaks corresponding to second- and third-next neighbors disappear gradually, giving way to a broad maximum without apparent substructure at 473 K.

Finally, we take a look at the RMSDs of the OSDA atoms, which are also listed in Table 2. The nitrogen atom constitutes the center of mass of the TPA cation. If the OSDA was subjected to significant movements as a whole, it would be expected that the RMSDs of the N atoms should be significantly larger than those of framework oxygen atoms. This is not the case, as N-RMSDs and O-RMSDs have a fairly similar magnitude at all three temperatures. This indicates that translations of the whole OSDA occur only to a very limited extent because the central area of the TPA cation is confined to the channel intersections. The alkyl chains, however, possess a certain freedom of motion, resulting in increased carbon RMSDs. The RMSDs of the hydrogen atoms are even larger, as these light atoms are moving considerably, for example, during rotations of the terminal CH₃ groups.

Figure 4: Si-F radial distribution function obtained for MFI_(TPA,F) from AIMD simulations performed for temperatures of 298 K (dark blue), 373 K (turquoise), and 473 K (orange). The inset shows the distance range between the first and second maximum.

MFI systems with other symmetric OSDAs

In addition to tetrapropylammonium, three other OSDAs having four alkyl chains of equal length were included (TMA, TEA, TBA). Figure 5 visualizes the RMSDs obtained for a temperature of 373 K. Starting with the OSDA atoms, it is noteworthy that there is a significant decrease of the N-, C-, and H-RMSDs with increasing OSDA size: For example, the RMSD of the nitrogen atoms decreases from 0.57 Å for MFI_(TMA,F) to 0.27 Å for MFI_(TBA,F), and the differences for carbon and hydrogen atoms are even more prominent. It is thus obvious that the freedom of motion of the OSDA varies massively as a function of its molecular dimensions: The TMA cation is small enough to move around within the channel intersections (large RMSD for N) and to rotate more or less freely (very large RMSDs for C and H). TEA still possesses a considerable freedom of motion, but the RMSDs are already significantly reduced because the rotation of the molecule is hindered by the longer ethyl chains. As discussed above for TPA, the movement of the larger TPA and TBA cations is heavily restricted due to the confinement of the alkyl chains to the channels of the MFI structure. Although their behavior is qualitatively similar, there is still a systematic decrease of the RMSDs when increasing the chain length from three to four carbon atoms.

Figure 5: AIMD-derived RMSD values obtained for MFI systems with symmetric OSDAs for a temperature of 373 K.

While the observations made in the preceding paragraph are not surprising, a rather unexpected trend is found when looking at the RMSDs of the framework atoms: As is visible in Figure 5, the Si-RMSDs decrease from 0.22 Å for MFI_(TMA,F) to 0.19 Å for MFI_(TBA,F), and the O-RMSDs decrease from 0.32 Å to 0.29 Å. As the standard deviations are in the range of 0.02 to 0.03 Å, the observed trend appears to be significant. In particular, it is worth noting that the framework RMSDs of MFI systems incorporating TMA and TEA are distinctly larger than those computed for guest-free Silicalite-1. This points to an interplay between the dynamics of the OSDA molecules and the framework, with the increased motion of small OSDAs entailing enhanced oscillations of the framework atoms. Correlations between framework and extra-framework dynamics have been observed previously, for example, for the case of organic dye molecules adsorbed in the channels of zeolite L.⁵⁴

As discussed above, the RMSDs of the fluoride anions are strongly affected by dynamic events. To study this further, the number of dynamic events occurring over the three trajectories was evaluated. It is visualized in Figure 6 for all systems and all temperatures considered. At 373 K, the number of dynamic events decreases from MFI_(TMA,F) (eight

events) to $\text{MFI}_{\text{-(TBA,F)}}$ (five events). As the total number of events is small, it has to be expected that somewhat different numbers would be obtained in some instances if three other, independent trajectories were computed for a given system and temperature. Nevertheless, the overall trend is too pronounced to be merely accidental: With increasing size of the OSDA, the number of fluoride hopping events at 373 K decreases. This appears plausible in the view of the coupling between OSDA and framework dynamics observed above. The picture is less clear at 298 K, as there are only very few dynamic events observed within 22.5 ps, indicating that much longer AIMD trajectories would be needed to draw any semi-quantitative conclusions for this temperature. At 473 K, the number of dynamic events increases further compared to 373 K, but the correlation with the OSDA size is no longer so apparent. Having identified the individual fluoride anions that undergo hopping events, the RMSDs of the remaining F_{noDE} atoms were calculated, and these values are included in Figure 5. The F_{noDE} -RMSDs mostly follow the trend seen above for Si and O atoms, as one should expect for those fluoride anions that undergo only local oscillations.

Figure 6: Number of dynamic events $N(\text{DE})$ observed during AIMD simulations in MFI systems with different OSDAs, including symmetric OSDAs (blue labels) and asymmetric OSDAs (dark red labels). For TBA, MTBA, ETBA, and MTPA, no dynamic events occurred for $T = 298$ K.

In order to gain deeper insights into the relationships between OSDA dynamics and fluoride anion disorder, the Si-F and N-F radial distribution functions were analyzed. The Si-F RDFs are shown in Figure 7a, including a zoom-in into the distance range between the first and second maximum. While the RDFs are generally very similar, the slightly elevated values for MFI_(TMA,F) and MFI_(TEA,F) at distances around 2 Å and between 2.2 and 2.35 Å can be seen as an indicator of the increased fluoride dynamics. In order to test whether the extent of dynamic disorder is correlated with the average N-F distance, as hypothesized previously,^{21,47} the N-F RDFs were computed, and they are shown in Figure 7b. The results for MFI_(TMA,F) and MFI_(TEA,F) on the one hand, and for MFI_(TPA,F) and MFI_(TBA,F) on the other hand, are fairly similar. The former two systems exhibit a broader first maximum centered at about 6.1 Å, whereas the maximum observed for the latter two systems is narrower, and centered at a larger distance of 6.4 Å. This, once again, reflects the higher mobility of the TMA and TEA molecules inside the channels: The smaller OSDAs are moving more vigorously, leading to broader maxima in the RDF, and they are able to approach the pore walls more closely, affording shorter N-F distances.

MFI systems with asymmetric OSDAs

The RMSDs obtained for systems containing asymmetric tributylammonium-based OSDAs having one shorter alkyl chain are shown, and compared to MFI_(TBA,F), in Figure 8 ($T = 373$ K). The RMSDs of nitrogen, carbon, and hydrogen atoms are fairly similar for all four systems, with only a modest decrease with increasing OSDA size. Due to the presence of the three long butyl chains, the freedom of motion of the OSDAs is strongly restricted, and therefore largely independent of the length of the fourth chain. As the dynamic behavior of all OSDAs is similar, they do not influence the dynamics of the framework silicon and oxygen atoms, and there is no systematic variation in the Si- and O-RMSDs.

Figure 7: a) Si-F and b) N-F radial distribution functions obtained for MFI_(TMA,F) (red), MFI_(TEA,F) (yellow), MFI_(TPA,F) (turquoise), and MFI_(TBA,F) (blue) for a temperature of 373 K. The inset in the upper panel shows the distance range between the first and second maximum in the Si-F RDF. The top part of the lower panel shows the integrated N-F RDFs.

A different picture arises, however, when looking at the F-OSDAs. Here, the values obtained for the MTBA- and ETBA-containing systems are fairly close to the corresponding O-RMSDs, whereas those of MFI_(PTBA,F) and MFI_(TBA,F) are significantly larger. Indeed, the number of dynamic events varies considerably among these two groups of systems, with only two/one event(s) occurring in MFI_(MTBA,F)/MFI_(ETBA,F), compared to seven/five events in the PTBA-/TBA-containing systems (Figure 6). Interestingly, this

pronounced difference is visible only at 373 K. At 298 K, MFI_(PTBA,F) is the only system where fluoride hopping events occur, whereas the number of events at 473 K is similar for all four of them. As observed previously for MFI models with symmetric OSDAs, the exclusion of those fluoride anions that undergo dynamic events from the RMSD calculation leads to F_{noDE} -RMSDs that are similar to those of the framework oxygen atoms.

Figure 8: AIMD-derived RMSD values obtained for MFI systems with asymmetric tributylammonium-based OSDAs ($T = 373$ K). MFI_(TBA,F) is included for comparison.

The remarkable differences between the two groups of systems are also visible in the Si-F RDFs, which are shown in Figure 9a: While the Si-F RDFs of the MTBA- and ETBA-containing systems are close to zero at distances of about $2.1 \text{ \AA}$, the $g(r)$ values in this distance range are non-negligible for the other two models, where such distances occur during the hopping events of fluoride anions. In the N-F RDFs, shown in Figure 9b, there is a progressive shift of the first maximum in the RDF to higher distances from MFI_(MTBA,F) to MFI_(TBA,F). This shows that the asymmetric OSDAs with one short alkyl chain indeed allow for shorter N-F contacts, as hypothesized by Brace et al.²¹ The point whether this is the key factor in determining the influence of the OSDA on the fluoride dynamics will be analyzed in more depth in the Discussion section.

Figure 9: a) Si-F and b) N-F radial distribution functions obtained for MFI_(MTBA,F) (light green), MFI_(ETBA,F) (dark green), MFI_(PTBA,F) (light blue), and MFI_(TBA,F) (blue) for a temperature of 373 K. The inset in the upper panel shows the distance range between the first and second maximum in the Si-F RDF. The top part of the lower panel shows the integrated N-F RDFs.

An MFI sample containing a methyltripropylammonium (MTPA) OSDA was also included in the experimental NMR investigation by Brace et al.^{21,47} With four dynamic events at 373 K, the AIMD results for MFI_(MTPA,F) point to an intermediate behavior, between that of MFI_(TPA,F) (six events) and MFI_(MTBA,F) (two events). On the other hand, the Si-F and N-F RDFs of MFI_(MTPA,F) and MFI_(TPA,F), visualized in Figure S10, exhibit largely similar features, especially when contrasted with the pronounced differences observed among the RDFs of systems containing butylammonium-based OSDAs

(Figure 9). In the light of these inconclusive findings, it would probably be necessary to perform longer simulations to substantiate the reduced degree of fluoride dynamic disorder of MFI_(MTPA,F) in comparison to MFI_(TPA,F). In any event, it is clear that the replacement of one longer alkyl chain by a methyl chain has a much smaller effect on the fluoride dynamics for propylammonium-based OSDAs than for butylammonium-based OSDAs.

Discussion

The results for the series of MFI systems with symmetric OSDAs at 373 K have revealed a coupling between the dynamics of the OSDA and the zeolite framework. While it is straightforward to expect a decrease of the freedom of motion of the OSDA with increasing length of the alkyl chains, it is more surprising to see that it has also an effect on the RMSDs of the framework Si and O atoms, and on the dynamic disorder of the fluoride anions, with more dynamic events happening in the timespan covered by the AIMD simulations for systems with smaller OSDAs. This trend is not observed for systems with asymmetric OSDAs, where the dynamic disorder of fluoride anions is significantly reduced in MFI_(MTBA,F) and MFI_(ETBA,F). In their experimental studies, Brace et al. proposed that the presence of a short alkyl chain in MTBA affords short N-F distances, leading to stronger electrostatic interactions between OSDA cations and fluoride anions.^{21,47} However, a comparison of the N-F RDFs displayed in Figures 7 and 9 shows that even shorter N-F contacts than in MFI_(MTBA,F) are observed for the systems with the small, symmetric TMA and TEA OSDAs, where a much larger number of dynamic events occur. Thus, the previous explanation for the observed differences in fluoride dynamics appears to be too simple.

Additional insights can be gained by looking at the DFT-computed electrostatic potential (ESP) for the butylammonium-based OSDAs. For these calculations, the OSDA molecules were placed in a box, using the configuration in which they are present in the zeolite (i.e., the OSDA geometries were not reoptimized). Figure 10 shows a projection of the ESP on

the $0.002 e \text{ bohr}^{-3}$ electron density isosurface. It is clearly visible that the short alkyl chains in MTBA and ETBA are strongly positively polarized. As visualized in Figure 11 for the case of MFI_(MTBA,F), the methyl moiety points towards a fluoride anion, and there is thus a fairly short contact between the positively polarized part of the OSDA and the anion. It can be expected that this short contact causes an enhanced electrostatic interaction, which explains the pronounced reduction of the dynamic disorder (if the electrostatic interaction is stronger, the energetic penalty for a movement of the fluoride anion to another Si atom increases). Since the propyl chain on the PTBA cation is much less strongly polarized, this electrostatic contribution becomes weaker, consequently, the dynamic disorder increases. Rather than explaining the suppression of dynamic disorder purely with the N-F distances, as done in the experimental works, the present study shows that the asymmetry of the OSDA plays a key role: On the one hand, long alkyl chains are needed to keep the central area of the OSDA confined to the channel intersections, rather than having the whole cation move around (as is the case for TMA and TEA). On the other hand, one short alkyl chain must be present, as this leads to a local accumulation of positive charge that is needed for an enhanced electrostatic interaction with the fluoride anions.

Figure 10: DFT-calculated electrostatic potential, plotted on the $0.002 e \text{ bohr}^{-3}$ electron density isosurface, for butylammonium-based OSDAs. Positively polarized areas are shown in blue, whereas neutral areas are shown in green. The volumetric visualization was prepared using VESTA.⁵⁵

The discussion in the preceding paragraphs focussed on the results obtained for 373 K. The calculations performed for 298 and 473 K are useful to confirm the overall trends regarding the thermal oscillations of framework and OSDA atoms. However, with regard to the fluoride dynamic disorder, AIMD simulations at both these temperatures are unable to capture the relationships discussed above: At 298 K, the number of dynamic events happening during the 22.5 ps covered by the simulations is simply too low to draw any conclusions. While much longer AIMD simulations could be useful, especially for better comparability with experiment (see below), the associated computational cost poses a serious restriction. Conversely, all systems exhibit a significant number of fluoride hopping events at 473 K (Figure 6). It can thus be concluded that the dynamic disorder of the anions becomes more or less independent of the OSDA at this temperature due to the overall increase of thermal motion.

Figure 11: Location of the MTBA cation in the pores of MFI_(MTBA,F) as obtained from the DFT structure optimization. Color scheme: F = light blue, Si = yellow, O = red, N = dark blue, C = grey, H = white, the methyl group is highlighted in orange. The distance between the methyl carbon atom and the fluoride anion amounts to 4.85 Å.

In this context, it has to be pointed out that the "manual" determination of the number of hopping events by analyzing the individual fluoride coordinates is a rather tedious procedure that would become impractical for larger datasets. While an automated identification of these events could be implemented, it is also interesting to evaluate to what extent the

number of hopping events is correlated to the integrated Si-F RDF in the distance range between the first and second maximum. For a preliminary analysis, the integrated RDFs obtained for an Si-F distance of 2.05 Å (lower boundary) were subtracted from those obtained for a distance of 2.25 Å (upper boundary), and the resulting values were plotted against the number of hopping events (Figure 12, note that the relationship shown in this figure is not particularly sensitive to small changes of the distance range). While a good correlation is observed for 298 and 373 K, it essentially breaks down at 473 K, presumably because there is a non-negligible contribution from vibrating Si-F bonds that are temporarily elongated without being broken. In any event, this indicates that the analysis of the Si-F RDFs in an appropriate distance range provides a useful means to estimate the degree of dynamic disorder.

Figure 12: Integrated Si-F RDF calculated for the distance range between 2.05 and 2.25 Å, plotted as a function of the number of dynamic events.

In principle, it is possible to derive approximate "residence times" of the fluoride anions at a given Si atom by multiplying the total simulation time (22.5 ps) by four (= number of fluoride anions per unit cell) and dividing this by the number of hopping events $N(\text{DE})$ shown in Figure 6. Clearly, this approach can only give a rather crude estimate due to the small number of events. Taking the series from MFI_(TMA,F) to MFI_(TBA,F) at 373 K

as an example, the residence time increases from 11 ps to 18 ps. These residence times in the range of tens of picoseconds are very short, shorter than the timescale on which dynamic disorder can be observed with NMR spectroscopic methods.⁵⁶ In addition, any significant fluoride anion mobility could only be obtained in simulations performed for elevated temperatures, whereas NMR experiments have mostly been performed at RT or lower temperatures. Therefore, any comparison of the AIMD results to experiment has to remain purely qualitative, focussing on the extent of dynamic disorder observed in different systems.

It has been established experimentally that MFI_(TEA,F) and MFI_(TPA,F) exhibit dynamic disorder of the fluoride anions at room temperature.^{19,21,22} Whereas the former system has not yet been investigated at cryogenic temperatures, the fluoride motion is frozen out at 140 K in MFI_(TPA,F).¹⁹ In contrast, MFI_(MTBA,F) shows only static disorder at room temperature, and at 233 and 323 K.^{21,47} MFI_(ETBA,F) exhibits dynamic disorder, but with an increased residence time of the fluoride anions compared to MFI_(TPA,F). Finally, the fluoride anions in MFI_(MTPA,F) are dynamically disordered at 298 K, but the disorder is frozen out at 233 K. There is a very good correspondence between the AIMD simulation results and these experimental findings: MFI_(TEA,F) and MFI_(TPA,F) show a high degree of dynamic disorder that is similar for both systems, whereas the fluoride mobility is reduced considerably in MFI_(MTBA,F) and MFI_(ETBA,F). The differences between the two latter systems cannot be resolved on the basis of the small number of hopping events observed, however, the different degree of positive polarization of the short alkyl chain that is visible in Figure 10 makes it plausible to expect a more effective suppression of the dynamic disorder by MTBA. The intermediate behavior of MFI_(MTPA,F) is also found in the simulations, although, as discussed above, one should probably avoid reading too much into the intricate differences between this system and MFI_(TPA,F).

From a broader perspective, it is worth exploring to what extent a comparable computational approach could be employed to explain, or even predict, observations that are directly

relevant to the synthesis of zeolites in fluoride-containing media. DFT calculations have been previously used to rationalize experimental observations regarding the relative stability of competing zeolite phases. In particular, Zicovich-Wilson employed dispersion-corrected DFT calculations to rationalize the thermodynamically driven transformation from all-silica TON to all-silica ITW.¹⁷ In the guest-free form, TON was found to be thermodynamically favored over ITW due to its higher density. However, when OSDA cations and fluoride anions were included in the calculations, the energetic ordering changed for the following reasons: First, the OSDAs fill the voids of ITW more efficiently than in TON, enhancing attractive dispersion interactions. Second, the fluoride anions also have a different environment: While they participate in covalent Si-F bonds in TON, they occupy the center of $d4r$ cages in ITW, stabilizing these (otherwise strained) building units through electrostatic interactions. Altogether, these calculations demonstrated that both OSDA cations and fluoride anions contribute to the stabilization of ITW over TON, in other words, that both species exert a structure-directing effect.

A possible extension of the present work in this direction would be to use an AIMD-based approach to study competing zeolite phases in their as-synthesized form from a dynamic perspective. As discussed above, the interaction between OSDA cations and fluoride anions in MFI-type zeolites is not negligible, significantly affecting the dynamic behavior. In fluoride-containing phase systems where two (or more) competing phases exist, their relative stability may – in part – depend on the fluoride disorder: For example, the ability to form shorter contacts between the positively polarized part of the OSDA and the fluoride anions might favor one framework at lower temperatures, but this stabilization might disappear at higher temperatures, where fluoride is dynamically disordered due to increased thermal motion. To investigate this further, it would first be necessary to identify cases where more than one framework can be synthesized with the same OSDA in fluoride media at different temperatures. In the next step, AIMD simulations, possibly in conjunction with NMR ex-

periments, could show whether there is an appreciable difference in the dynamic disorder, and help to rationalize the stability trend through an analysis of host-guest interactions. As a final word of caution, however, it has to be conceded that a variety of thermodynamic and kinetic factors will determine the synthesis outcome, so it may be difficult to separate the effect of fluoride dynamic disorder from other contributions.

Conclusions

First of all, the present study convincingly shows that the AIMD simulations are able to reproduce the dynamic disorder of fluoride anions in MFI-type zeolites on a qualitative level. Whereas dynamic disorder has mostly been studied at RT in experimental investigations, a modest increase in temperature is necessary to make it visible on the timescale that is accessible with the simulations. The calculations comparing models with symmetric OSDAs of different size reveal a rather surprising effect: OSDAs with short chains (TMA, TEA) do not only have larger freedom of motion than those with longer chains (TPA, TBA), but they also cause stronger oscillations of the framework atoms. This coupling between OSDA and framework dynamics manifests in an increase of the number of fluoride hopping events with decreasing OSDA size, and in increased Si- and O-RMSDs in comparison to OSDA-free Silicalite-1. While it would be interesting to verify this relationship experimentally, one should bear in mind that the variations predicted by the calculations are rather intricate and might be difficult to observe with NMR and/or diffraction methods. Possibly, these methods could be combined with vibrational spectroscopy in order to further elucidate the relationships between OSDA size/shape and dynamic behavior of framework atoms and extra-framework species. There are several examples of a joint use of different experimental methods (possibly augmented by calculations) in in-depth investigations of the interaction between zeolites and OSDAs or other occluded organic species.^{50,57,58}

For systems containing MTBA and ETBA OSDAs, the calculations predict a drastic reduction of the number of dynamic events, but no complete suppression of the dynamic disorder. This agrees with the "slow" dynamic disorder found experimentally for MFI_(ETBA,F). In contrast, a completely static behavior has been observed for MFI_(MTBA,F), at least on the timescale on which dynamic disorder is observable with NMR experiments. Despite this qualitative difference, AIMD simulations and NMR experiments agree that there is no sharp boundary between static and dynamic disorder, but, instead, a gradual evolution that depends on both temperature and OSDA. The reduction of the fluoride dynamics in the MTBA- and ETBA-containing systems can be explained as being due to a combination of a) positive polarization of the short chain of the OSDA cation, leading to strong electrostatic interactions with the anion, and b) strongly restricted motion of the OSDA as a whole due to the presence of three long chains. In other words, both OSDA asymmetry and OSDA size play a role. The same effect appears to be present, but much less pronounced, in MFI_(MTPA,F).

While the present work addressed a series of MFI-type systems with OSDAs having a rather similar molecular structure, it would be interesting to extend this approach to other organic cations, ideally in conjunction with NMR experiments. For example, as mentioned in the introduction, it has been observed that the use of tetraethylphosphonium, rather than tetraethylammonium, as OSDA reduces fluoride mobility.²² Calculations could be used to develop an atomic-level explanation of the central atom's role. In addition, future work will look at other fluoride-containing all-silica zeolites for which either static or dynamic disorder of the anions has been reported. These investigations will aim to establish structural criteria for the occurrence/absence of dynamic disorder, both with regard to the local environment of the anions and the molecular structure of the OSDA.

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Supporting Information Available

Details of DREIDING calculations, figures and CIF files of DFT-optimized MFI models, RDFs of MFI_(TPA,F) and MFI_(MTPA,F), sample input files for CP2K calculations, EXCEL spreadsheet containing RMSDs and RDFs

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