Dynamic anions in small cages

Dynamics of fluoride anions in all-silica and silicogermanate zeolites

M. Fischer, R. X. Fischer, Crystallography group, Department of Geosciences, University of Bremen

In Short

• *ab-initio* Molecular Dynamics calculations are used to study the dynamic behaviour of fluoride anions confined to small cages in zeolite structures.

• A published study has addressed the local environment and dynamic behaviour of fluoride anions in AST-type silicogermanates. Further work on these systems will look at different framework compositions and different organic cations.

• Ongoing work investigates the influence of the organic cation on the dynamic disorder of fluoride anions in MFI-type Silicalite-1.

• A comparison of all-silica zeolites with various topologies will allow to elucidate the impact of the local environment on the dynamic disorder.

Zeolites are a class of inorganic porous materials with important applications in ion exchange, gas and liquid separation, and catalysis. Zeolite structures consist of a three-dimensional framework of tetrahedrally coordinated T atoms connected by oxygen atoms. Prototypical zeolites, such as naturally occurring zeolite minerals, possess a negatively charged aluminosilicate framework whose charge is balanced by extra-framework cations. However, the development of sophisticated synthesis routes has led to the discovery of zeolite-like materials having a neutral framework, among them all-silica zeolites (composition SiO$_2$), germanates (GeO$_2$), silicogermanates (Si$_x$Ge$_{1-x}$O$_2$), aluminophosphates (AlPO$_4$), and gallophosphates (GaPO$_4$). The synthesis in the presence of fluoride anions ("fluoride route") is a particularly successful strategy to obtain neutral-framework zeotypes with very open frameworks and low defect concentrations. Various zeolites and zeotypes with unprecedented framework topologies can be synthesised via this route, many of which have (so far) not been obtained in the absence of fluoride.

In the as-synthesised zeolites, the fluoride anions occupy well-defined positions in the crystal structure, balancing the charge of the organic cations that are used to direct the formation of a particular structure type (organic structure directing agent = OSDA). In zeolites having double four-ring (d4r) cages, the fluoride anions occupy the centre of this cage. This is shown for the example of octadecasil (AST topology) on the right-hand side of Figure 1.

In one part of this project, *ab-initio* Molecular Dynamics (AIMD) calculations based on density-functional theory (DFT) are used to study the local environment and the dynamic behaviour of fluoride anions in zeolites containing d4r cages, focussing on the AST framework type as a prototypical example. Such a DFT-based AIMD approach allows to obtain a first-principles perspective of the zeolite’s dynamic behaviour on the timescale of picoseconds. A comprehensive AIMD study investigated the local environment and dynamic behaviour of fluoride anions confined to d4r cages of AST-type silicogermanates. While the fluoride anions occupy the centre of the cage in the pure end members, SiO$_2$-AST and GeO$_2$-AST, they are displaced towards a Ge atom, forming a partly covalent Ge-F bond, in many silicogermanates, as shown exemplarily in Figure 2. A systematic comparison of different Si,Ge arrangements for a given composition shows that arrangements which maximise the number of Ge-O-Ge linkages are energetically favoured. The AIMD calculations revealed that the dynamic behaviour is also strongly influenced by the local environment: In systems where no localised Ge-F bonds are present, the fluoride anions exhibit a much larger freedom of motion than in systems containing such bonds (RMSD values in Figure 2). Having successfully completed the work on silicogermanates, future calculations planned for AST-type systems will look at other framework compositions (alumino- and gallophosphates) and at the influence of the OSDA.
RMSD(F) = 0.28 Å RMSD(F) = 0.36 Å RMSD(F) = 0.22 Å

SiO₂-AST GeO₂-AST AST_(7Si,1Ge)

(F)MSD is a measure of the freedom of motion, with larger RMSD values corresponding to a more dynamic behaviour.

In structures without d4r units, fluoride anions also tend to occupy small cages. However, rather than being located at the cage centre, they are covalently bonded to a single silicon atom, forming trigonal-bipyramidal SiO₄F⁻ units. Frequently, the fluoride anions are disordered over two or more positions within one cage, as shown exemplarily for the case of MFI-type Silicalite-1 in Figure 1. It has been shown that the fluoride disorder in Silicalite-1 is of a dynamic nature at room temperature. This means that the anions “jump” between different positions on a very short timescale that is accessible with nuclear magnetic resonance (NMR) experiments. Upon cooling to cryogenic temperatures, characteristic changes in the NMR spectra show that the dynamic motion is frozen out.[5] Moreover, the extent of the dynamic disorder at room temperature depends on the organic cation.[6] MFI-type zeolites are particularly interesting due to their large relevance for applications (catalysis, separation). DFT-based AIMD calculations for Silicalite-1 incorporating tetrapropylammonium (TPA⁺) cations revealed that the dynamic disorder of the fluoride anions at room temperature is difficult to resolve computationally due to the short timescale that is accessible with the calculations. However, an increase of the simulation temperature to 100 or 200 °C permitted a semi-quantitative analysis, delivering approximate “residence times”, i.e., the average amount of time that passes between two “jumps” of a fluoride anion. A comparison of Silicalite-1 models incorporating OSDAs having alkyl chains of different length (TXA⁺ with X = methyl, ethyl, propyl) showed that the dynamic disorder is most pronounced in the system containing the smallest OSDA. Interestingly, the average distance between the fluoride anions and the nitrogen atoms of the positively charged OSDAs is shortest in this system, contradicting the previously published hypothesis that shorter N-F distances lead to a suppression of dynamic disorder.[5] Future AIMD calculations will look at OSDAs with longer chains and asymmetric OSDAs having chains of different length. The latter group is particularly interesting because it has been shown experimentally that the replacement of TPA⁺ cations by methyltributylammonium (MTBA⁺) cations suppresses the dynamic disorder at room temperature.[6] Such a systematic comparison of OSDAs will help to elucidate the relationships between the molecular structure of the organic cation and the dynamic disorder of fluoride anions.

Looking beyond Silicalite-1, other all-silica zeolites containing SiO₄F⁻ units show a varying degree of dynamic fluoride disorder at room temperature. For example, the fluoride anions in ITQ-4 (IFR topology) are dynamically disordered,[7] whereas those in STF-type zeolites show no disorder, despite the similar local environment in the two structures.[8] In order to investigate the microscopic origins of the differences in the dynamic behaviour, AIMD calculations will be performed for a total of six zeolites containing fluoride in different cages.

Figure 2: Fluoride-containing double-four-ring (d4r) cages in AST-type zeolites as obtained from DFT optimisations. Selected T-F distances are given in Å. The root mean square displacement (RMSD) is a measure of the freedom of motion, with larger RMSD values corresponding to a more dynamic behaviour.

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More Information


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