Molecular Dynamics Simulation of Water Diffusion in MFI-Type Zeolites

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Molecular dynamics simulation using COMPASS force field has been employed to understand the dynamics of water diffusion and structuring in silicalite-1 and Na-ZSM-5 (Si/Al = 95 and 191) samples at three different temperatures, 297, 354, and 393 K, at a water loading of 8 molecules per unit cell, in canonical ensemble. Diffusion coefficients were significantly reduced upon the introduction of aluminum atoms into the framework, together with charge balancing cations placed in their vicinity, since the ion-dipole interactions dominant in ZSM-5 samples are stronger than the H-bond interactions in silicalite-1. The activation energy of diffusion increased with decreasing Si/Al ratio. In the silicalite-1 and ZSM-5 samples, straight channels were observed to be preferred than the sinusoidal ones and the channel preference was not observed to be a strong function of either temperature or the Si/Al ratio. The ordered structures of the water molecules, forming clusters in the channels of silicalite-1 at low temperature was observed to be broken to some extent by increased temperatures, and decreased Si/Al ratio, resulting in less ordered structures. The positions of the water molecules in the straight and sinusoidal channels for the ZSM-5 samples were mainly determined by the location of the charge compensating cation(s) in the structure, as was shown by the concentration profiles.

Introduction

Zeolites are crystalline aluminosilicates having tetrahedrally bonded silica and alumina in their nanoporous framework structures with cations compensating the anionic charge associated with alumina in the crystal lattice. They have found widespread industrial application both as molecular sieves, due to their adsorption and diffusion properties, and as heterogeneous catalysts due to the porosity and Bronsted acidity of their structures.[1,2]

Synthesis of high-silica zeolites in 1970s from reaction mixtures containing organic structure-directing templates has opened a whole new series of application perspectives for zeolites. Silicalite-1[3] is an all-silica version of the MFI structure,[4] originally discovered as the zeolite ZSM-5.[5] It belongs to the family of pentasil zeolites as the framework is built up from five-membered rings. The framework structure of silicalite-1 comprises two different channel systems, each defined by ten-membered rings. Straight channels with an elliptical cross section of 5.7−5.8 Å × 5.1−5.2 Å are parallel to the crystallographic axis *b*, and sinusoidal channels with nearly circular cross section of 5.4 Å run along the crystallographic axis *a*. The resulting intersections are elongated cavities of up to 9 Å in diameter. The unit cell of silicalite-1 is composed of 96 SiO_2 units and has dimensions of $a = 20.06$ Å, $b = 19.8$ Å, and $c = 13.36$ Å. Because of the lack of aluminum atoms (and hence also the lack of charge-compensating extra-framework cations) in the structure, silicalite-1 has high thermal and chemical stability and is highly hydrophobic, rendering it especially suitable for some possible environmental applications for the removal and/or remediation of organics, such as chlorinated volatile organic compounds,[6] and MTBE[7] in water. Related to the importance of these application possibilities, the behavior of nanoconfined water within silicalite-1 has become a subject of great scientific and technological interest recently.[8−11] Because most synthesized samples of silicalite-1 contain traces of aluminum, it is also important to understand the effect of aluminum atoms and the associated cations on the behavior of water in high Si/Al ratio ZSM-5 structures.

Experimental[12,13] and theoretical[14−16] studies of diffusion of adsorbed water in silicalite-1 are rare. Experimental measurements are affected by uncertainties originating from the impurity of the aluminum contents of the real crystals or by the defects of the crystal lattice, which are almost never negligible.[13] Theoretical studies reveal interesting and unexpected complexities regarding the state of water at different temperatures.[15,16] At temperatures below 200−250 K, water appears to be mostly in form of amorphous solidlike clusters, giving rise to a single-file type diffusion. The diffusivities calculated by molecular dynamics simulations by employing the Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies (COMPASS) force field and microcanonical (*NVE*) ensemble in the temperature range of 250−600 K where the behavior of water is almost liquidlike were found to be about six times larger than the experimental values obtained by PFG-NMR technique.[16]

Here, we report the results of molecular dynamics simulations of diffusion of water in silicalite-1 and ZSM-5 structures with different Si/Al ratios, carried out by using the COMPASS force field, employing canonical (*NVT*) ensemble at three different temperatures, 297, 354, and 393 K, at a water loading of 8 molecules per unit cell. The aim of this study is to understand the effects of the temperature and the presence of aluminum atoms in the framework on the dynamics of the water diffusion in MFI-type zeolites with high Si/Al ratio. The changes in the structures of the water clusters due to the introduction of ion−dipole interactions and changes in temperature were also studied by monitoring the radial distribution functions of the

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TABLE 1: Atomic Charges

atom	q (esu)
H-water	+0.410
O-water	−0.820
O-framework	−0.445
Si-framework	+0.890
Al-framework	+0.590
O-bonded to Al	−0.620
Na^+	+1.000

TABLE 2: Diffusion Coefficient Values of Water in Silicalite-1 at Different Temperatures

T(K)	$D \times 10^9$ m²/s				
	this work	ref 16	ref 15	ref 14	ref 13 (exp by PFG-NMR)
297	1.94	8.83	8.6	3.3	1.7
354	3.64	10			
393	6.00	10.55	10	6.7	1.5

water oxygens and the concentration profiles of water molecules and Na^+ ions.

Method

The quality of the description of both the system and properties being analyzed depends strongly on the choice of the force field. Since water−water interactions are stronger than the interactions of water molecules with the zeolite framework due to the hydrophobicity of the silicalite-1 structure, it is very important that H-bond and water−water interactions are well represented in the force field used. COMPASS, one of the well-validated force fields in the Discover module implemented in the Materials Studio 4.1 software,[17] was used throughout the calculations. All bonded and nonbonded interaction terms including H-bond and water−water interactions as well as the cross-coupled energy terms that describe the effects of internal energy components, for example, bond−bond, bond−angle, and bond−torsion terms are included in the force field.[18] The bonded terms describe intermolecular bond stretching, bending angles, torsion angles, and inversion angles. The cross-coupling effect is important for the description of vibrational frequencies and structural changes of the molecules. The nonbonded terms include a 6-9 Lennard-Jones potential with a cutoff radius of 9.5 Å for the van der Waals interactions, and a Coulomb potential for the electrostatic interactions. Self-diffusion coefficients were calculated from the Einstein relationship as follows

$$D_\alpha = \frac{1}{6N_\alpha}\lim_{t\to\infty}\frac{\mathrm{d}}{\mathrm{d}t}\sum_{i=1}^{N_\alpha}\langle |r_i(t) - r_i(0)|^2\rangle \qquad (1)$$

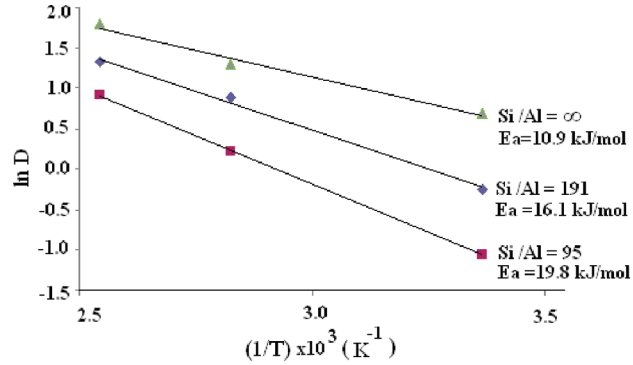

Figure 1. Arrhenius plot of the activation energies (E_a) for diffusion of water.

where N_α is the number of diffusing molecules of type α, $r_i(0)$ and $r_i(t)$ are the initial and final positions of the center of mass of molecule i over the time interval t, and $< |r_i(t) - r_i(0)|^2 >$ is the averaged mean-square displacement (MSD) of the ensemble.[19]

In the following generalized Einstein formula[15]

$$<r^2> = Ct^a \qquad (2)$$

C is a constant and a is also a constant obtained by computing the slope of the theoretically linear relationship ln (MSD) vs ln(t). If $a = 1$, the ideal Einstein relationship corresponding to the normal (Fickian) diffusion case can be used to estimate the diffusion coefficient. Within the temperature ranges employed in this study, normal diffusion of water molecules takes place,[16] allowing the ideal Einstein relationship to be satisfied.

The relationship between the MSD and the diffusivity depends on the dimensionality of the system. For a three-dimensional system, this relation will be[16]

$$\langle r^2(t)\rangle = 6Dt \qquad (3)$$

Simulation

Silicalite-1 and ZSM-5 supercells, each composed of two unit cells adjacent in the c direction were generated. One and two Si atoms in the supercells were replaced with Al atoms to yield ZSM-5 structures with Si/Al ratios of 191 and 95, respectively. Although the energy difference between the least and most favorable T sites was reported[20] to be only 3 kcal/mol, a Si atom residing at a T9 site was first replaced with Al, since the T9 site located at the intersection of the linear and sinusoidal channels in the framework structure was reported[21] to be one of the energetically favorable sites (T6, T9, T12). For the simulations carried out on the ZSM-5 sample with a Si/Al ratio

TABLE 3: Variation of the Diffusion Coefficients ($\times 10^9$ m²·s⁻¹) of Water Molecules in Silicalite-1 and ZSM-5 (Si/Al = 191 and 95) Structures at Three Different Temperatures

Si/Al Ratio	T	D	D_x	D_y	D_z	D_x/D (%)	D_y/D (%)	D_z/D (%)
∞	297	1.94	0.69	1.24	0.00	36	64	0
∞	354	3.64	1.47	2.11	0.07	40	58	2
∞	393	6.00	2.06	3.53	0.40	34	59	7
191	297	0.78	0.17	0.59	0.03	21	76	3
191	354	2.42	0.63	1.70	0.09	26	70	4
191	393	3.75	1.31	2.24	0.20	35	60	5
95	297	0.35	0.14	0.20	0.02	39	56	5
95	354	1.25	0.34	0.81	0.10	27	65	8
95	393	2.66	1.12	1.34	0.20	42	50	8

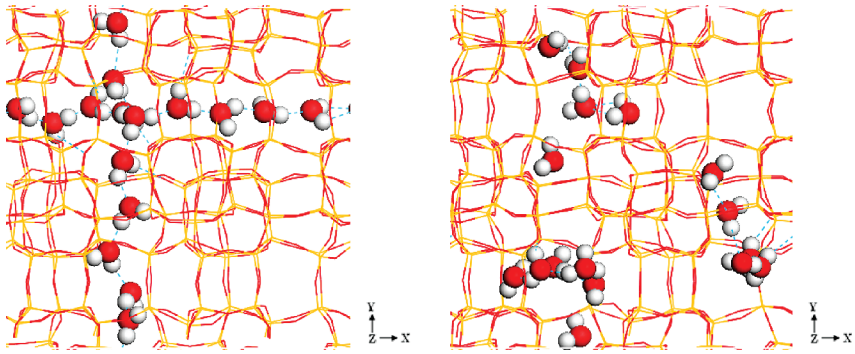

Figure 2. Snapshot pictures from the simulation box of silicalite-1-water system at two different temperatures, 297 K (left) and 393 K (right). Dotted lines show the hydrogen bonds. Water molecules and the framework atoms are shown with ball-and-stick and wire representations, respectively.

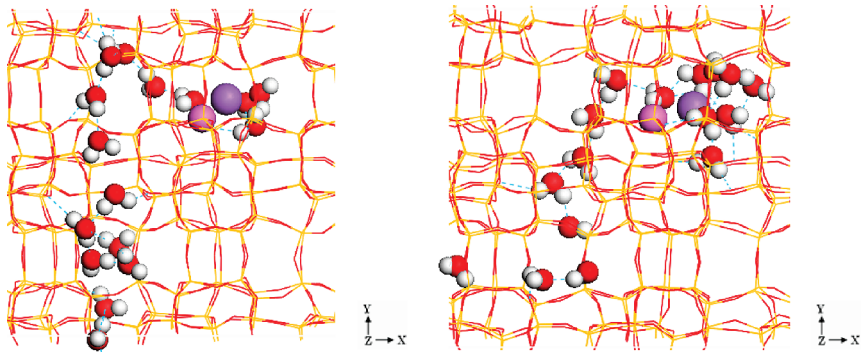

Figure 3. Snapshot pictures from the simulation box of ZSM-5 (Si/Al = 191)-water at two different temperatures, 297 K (left) and 393 K (right). Dotted lines show the hydrogen bonds. Water molecules and the framework atoms are shown with ball-and-stick and wire representations, respectively, where the sodium cation is shown in purple and aluminum in violet.

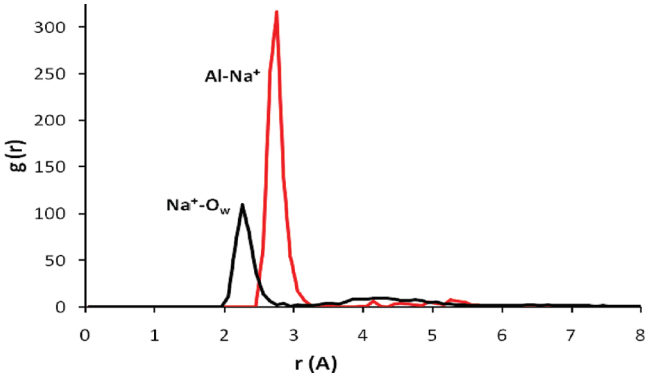

Figure 4. Pair correlation functions ($g(r)$) of Al−Na^+ and Na^+−O_w for ZSM-5 with the Si/Al ratio of 191 at 297 K.

of 95, the second silicon atom to be replaced with aluminum was chosen as one of those residing at the T10 sites, again at the intersections of the linear and sinusoidal channels. To maintain neutrality, Na^+ cations were placed in the close proximity of the Al atoms in the structure prior to equilibration.

Initially 16 water molecules (8 water molecules per unit cell) were placed inside randomly through a Monte Carlo simulation run. With sufficient simulation time, as reported previously,[16] the initial positions of water molecules did not affect the self-diffusion coefficients. COMPASS force field was used for the description of interatomic interactions, as mentioned above. The system was subjected to three-dimensional periodic boundary conditions and the nonbonded interactions were calculated by Ewald summation method.[22] The electrostatic charges of the atoms in water and the Si and O atoms of the framework were set to default force field values. The charge of the each framework Al atom and its four neighboring O atoms were assigned following the work of Beerdsen et at.[23] All charges are given in Table 1.

The zeolite framework was considered to be flexible in the simulations. The Verlet velocity algorithm with a time step of 0.5 fs was used for the numerical integration. The simulations were run in the *NVT* ensemble with the Nose thermostat applied. The MSD data were collected over 10 ns simulation time, and diffusivities were calculated from those regions of the MSD plots with slopes of 1.0, according to eq 2. This long simulation time was adopted to ensure that the diffusivities were truly Fickian.

Results and Discussion

Diffusion coefficient values of water in silicalite-1 obtained from the slopes of the mean square displacement (MSD) versus time plots at three different temperatures, 297, 354, and 393 K, are listed in Table 2, together with the values obtained previously by others via simulation[14−16] and experimental[13] studies. The values found in this study were in closer agreement with the experimental values reported in the literature, which were determined by PFG-NMR,[13] than those calculated previously in two simulation studies,[15,16] especially at lower temperatures, due to the differences in the ensembles, summation methods, and force fields used. Since the force field that we used was the same as in the work of Fleys et al.,[16] the differences between our results and theirs originate from the simulation parameters such as the differences in the summation methods and simulation times used in these two studies. Different from the atom-based summation method with 6 Å cutoff radius, used by Fleys et al.,[16] Ewald summation was employed here. The observation that the diffusion coefficient values approach each other at higher temperatures, where the diffusion is sufficiently rapid to make

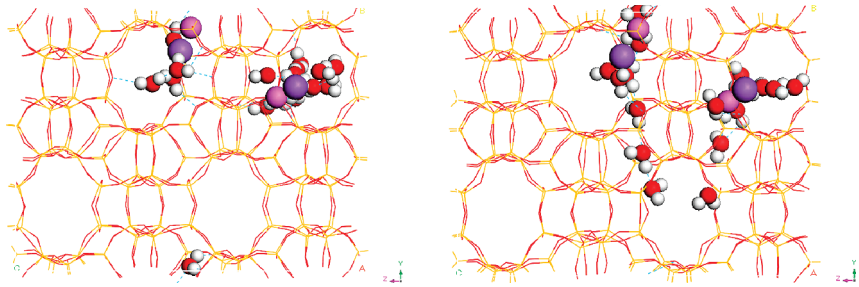

Figure 5. Snapshot pictures from the simulation box of ZSM-5 (Si/Al = 95)-water at two different temperatures, 297 K (left) and 393 K (right). Dotted lines show the hydrogen bonds. Water molecules and the framework atoms are shown with ball-and-stick and wire representations, respectively.

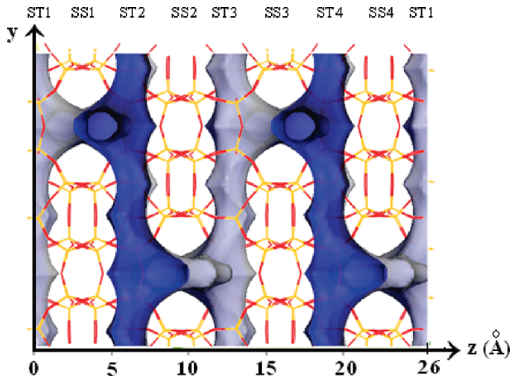

Figure 6. Projection on the *yz*-plane of straight (ST) and sinusoidal (SS) channels in MFI-type zeolites.

the long-range interactions less important, is thus understandable. The fact that the effect of simulation time on calculated diffusivity becomes more important at low temperatures, might also have played a role. On the other hand, our results are very similar to those found by Bussai et al.,[14] which were obtained as a result of an ab initio generated force field in combination with simulation in NVT ensemble.

Influence of Alumina Content on the Self-Diffusion Coefficient. Silicalite-1 is an all-silica version of the MFI structure, originally discovered as the zeolite ZSM-5. ZSM-5 is a zeolite with high silicon to aluminum ratio. The negative charge introduced into the framework when one of the silicon atoms is replaced with an aluminum atom is balanced by a positively charged ion to ensure electrical neutrality. The introduction of aluminum and the associated cation into the framework leads to strong ion−dipole interactions, resulting in a more polar and less hydrophobic zeolite structure. This was reflected in the changes observed regarding the structure and dynamics of water molecules within the channels.

Diffusion coefficients and their components along three axes for all of the systems at all temperatures are listed in Table 3, where the diffusivities and all of their axial components are seen to increase with temperature as expected. The variation of the diffusivities with temperature for the silicalite-1 and ZSM-5 structures is also shown in Figure 1. From the figure, the activation energy values, calculated by using the Arrhenius equation, are seen to increase with decreasing Si/Al ratio, and the diffusivities are seen to get closer to one another at higher temperatures. The activation energy obtained for silicalite-1 is higher than those computed previously for the same temperature range.[15,16] However, the observation that the activation energy values computed in this study for the ZSM-5 structures compare fairly well with the experimental value,[24] shows that our results are quite dependable.

From the D_y/D values given in Table 3, the straight channels are seen to be preferred for all structures and at all temperatures. However, for silicalite-1 and for the ZSM-5 structure with a Si/Al ratio of 191, the channel preference is seen to slightly shift in favor of the sinusoidal channels and intersections as the temperature is increased, as can be seen, respectively, from the D_x/D and D_z/D values listed in the table. A similar tendency was not clear for the ZSM-5 structure with a Si/Al ratio of 95. The observation that the straight channels were preferred when compared to the sinusoidal channels is understandable since the latter are energetically less favorable. D_z values, which are an indication of transport between straight and sinusoidal channels, were almost negligible at low temperature and increased slightly at higher temperatures. Figure 2 shows two snapshot pictures of the silicalite-1-water system, taken from the simulation box, at two different temperatures where water oxygens are shown as red balls.

Two unit cells of silicalite-1 contain 192 Si atoms. When the hydrophobicity was decreased by replacing one of these silicon atoms with an aluminum atom (ZSM-5, Si/Al = 191) and a charge compensating cation, Na^+, was introduced in its proximity, the diffusion coefficient was found to decrease significantly when compared to its value in silicalite-1 under the same conditions. Water molecules were seen to be located in the vicinity of the cation and the ion−dipole interactions became very strong depending on the equilibration temperature, resulting in clustering of the water molecules around the ionic center. This was reflected in the water oxygen O_w-Na^+ distances. At higher temperatures the increased kinetic energies of the diffusing molecules resulted in increased O_w-Na^+ and O_w-O_w distances. This behavior can be seen in Figure 3 for two different temperatures. The diffusion coefficient values for this sample with a Si/Al ratio of 191 were thus significantly reduced with respect to the corresponding values for silicalite-1 at all temperatures as can be seen clearly from Table 3. The $Al-Na^+$ distance, which was initially about 2.5 Å, slightly increased to about 2.8 Å (Figure 4) after equilibration at all temperatures indicating that the ion coordination to $Al(O_4)^-$ site is strong. The pair correlation function between the Na^+ ion and the water oxygens, given also in Figure 4, showed that the first and second solvation shells are formed at distances of about 2.3 and 4.3 Å, respectively.

In Table 3, the diffusion coefficient values are seen to further decrease for the ZSM-5 structure with a Si/Al ratio of 95, due to the presence of two ions in the framework. Water clusters have formed around both ionic centers in this ZSM-5 structure, as can be seen clearly from Figure 5. As expected, no change was observed in the $Al-Na^+$ distances with the introduction of the second Al atom, and the corresponding Na^+ ion. The Na^+-O_w pair correlation function also remained unchanged due to the initial choice of the Al sites (T9 and T10) in the framework. The impact of introducing a second Al atom and

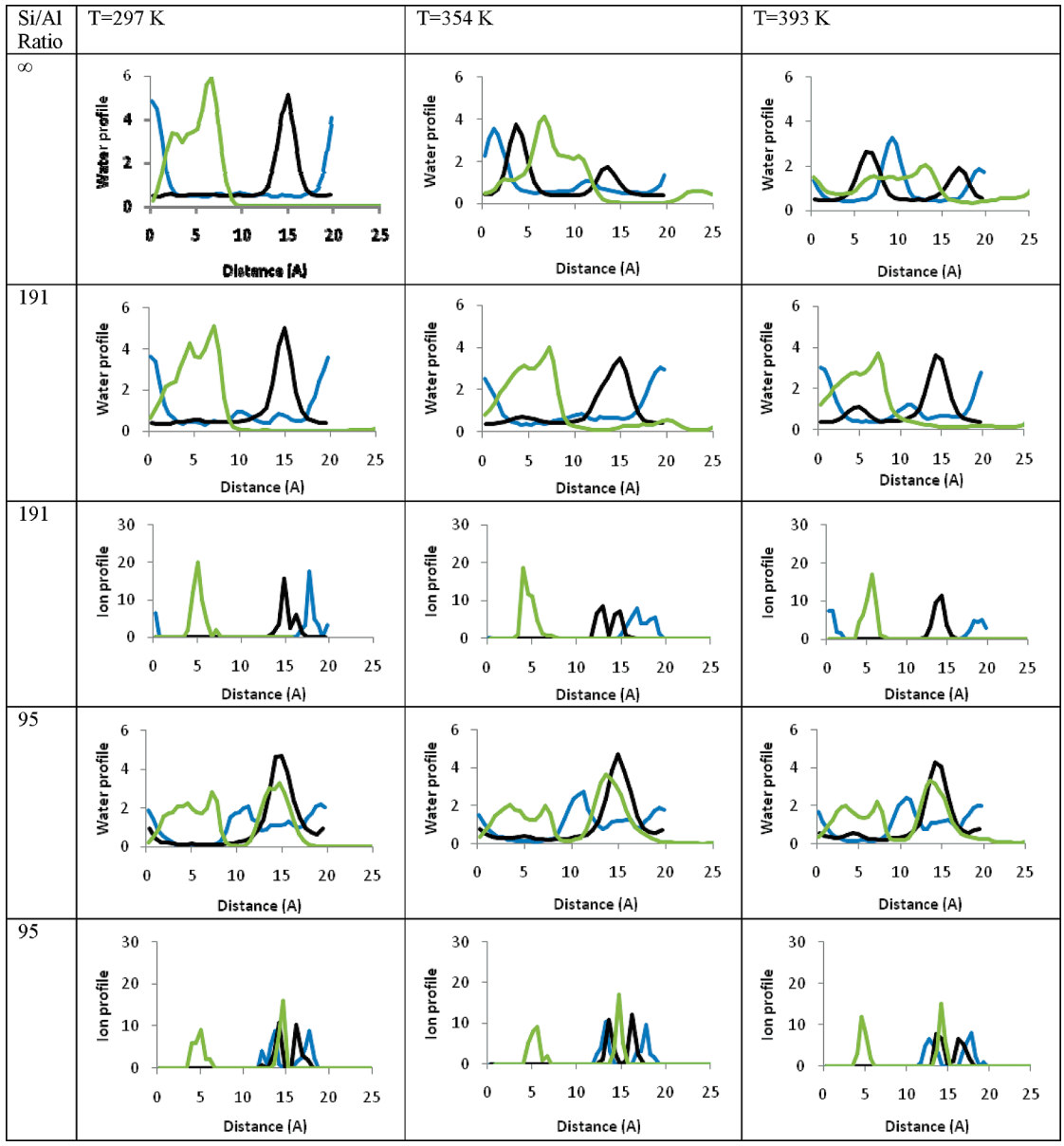

Figure 7. Concentration profiles of water and cation(s) in the studied structures along three crystallographic axes: *x*-axis (black), *y*-axis (blue), and *z*-axis (green).

thus a second cation into the framework is more evident in the concentration profiles, which will be discussed later.

A previous PFG-NMR study[24] on water diffusion in MFI type zeolites of varying Si/Al ratios, have also observed a decrease in molecular mobility of water with increasing cation content, which was attributed to the substantial interaction of the cations with the water molecules. The absolute values reported in the same study for the intracrystalline self-diffusion coefficient of water in a NaHZSM-5 sample with a Si/Al ratio of 40 for the temperature range of 297−400 K varied between about 0.7−3.8 $\times 10^{-9}$ m^2/s. Our values can be considered to be in reasonable agreement, when the experimental errors that may be involved in determining the Si/Al ratios in the lattice and the effects of the presence of charge balancing hydrogens in the structure are taken into account.

There are four of each of straight (ST) and sinusoidal (SS) channels in the silicalite-1 supercell as shown in Figure 6. Concentration profiles of the three systems at 297, 359, and 393 K are given in Figure 7. The corresponding ion profiles for the Al-containing structures are also shown in the same figure. It can be seen from the figure that water molecules in silicalite-1 populate almost exclusively only one straight (ST2) and one sinusoidal (SS1) channel that are connected via an intersection. As the temperature increases, water molecules start to appear in a second set of channels as well. With the addition of the first Al atom and the corresponding Na^+ ion into the framework (Si/Al = 191), this partitioning to a second set of channels of water molecules at high temperature is hindered by the existence of the cation. Water molecules in this case, are seen to be present in the set of channels connected by the intersection where the cation is located. The peak positions in the concentration profiles for straight and sinusoidal channels are seen to shift according to the ion position in the structure, which are also shown in the same figure. For the structure with Si/Al = 95, two sets of straight and sinusoidal channels, connected by the two intersections where the cations are located, were populated with water molecules, even at the low temperature of 297 K, and this situation was not influenced by temperature. The locations of the concentration peaks for water were strongly determined by the positions of the two cations.

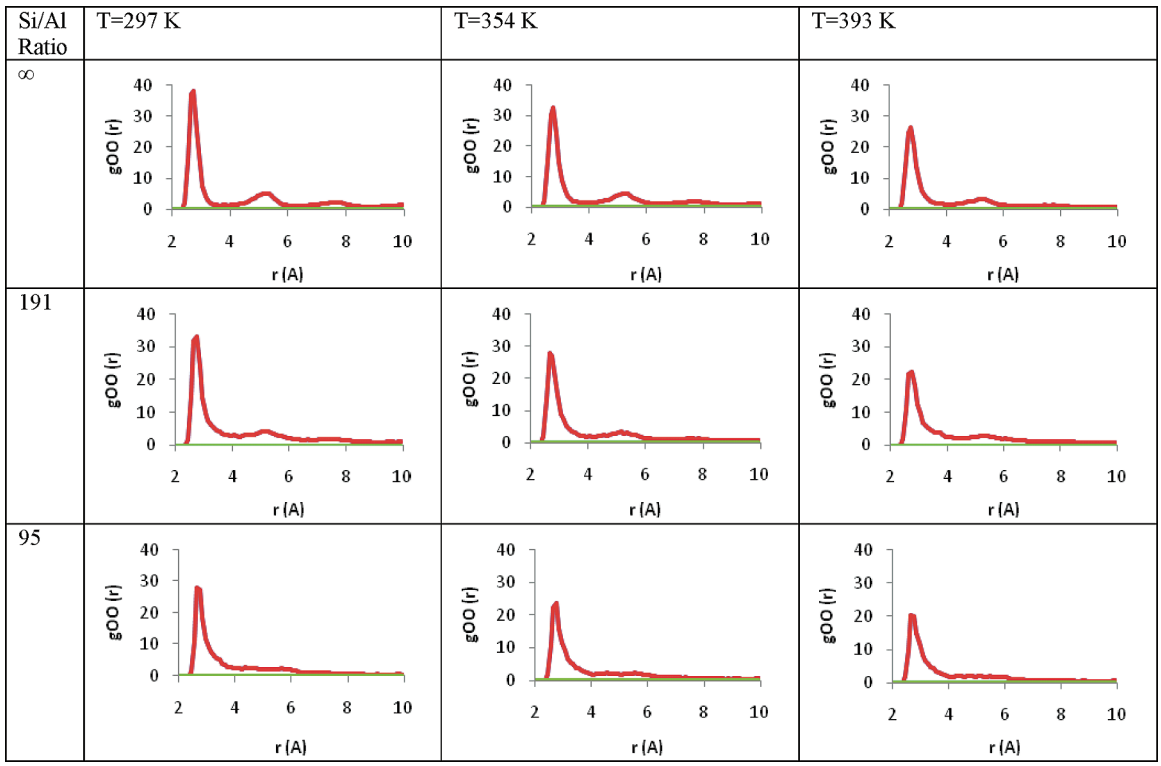

Figure 8. Change in the RDFs with temperature and alumina content (Si/Al Ratio).

When combined with the information provided with the concentration profiles shown in Figure 7, the radial distribution functions (RDFs) are very useful since they give insights into the water structures obtained. The RDFs of water oxygens (g_{OO}) for all samples studied here are given in Figure 8. The structural information obtained for the case of silicalite-1 at $T = 297$ K is that the majority of the oxygen atoms are present at around 2.7 Å distances from each other, and the radii of the second and third nearest-neighbors are found at around 5.2 and 7.5 Å, respectively, implying an ordered structure in which the water molecules form stable clusters, which is in agreement with the simulation results for silicalite-1 in literature.[16] From the intensity of the third peak, it is understood that only a few water molecules are present at about 7.5 Å. As the temperature is increased, the first two peaks are reduced significantly in intensity and are broadened, while the third peak almost disappears. This implies that the ordered structures formed by the water molecules are broken at higher temperatures, indicating a transition to a less ordered structure. Upon insertion of Al atoms into the framework, that is, with decreasing Si/Al ratio, the first peak was obtained at the same r_{OO} distance with decreased intensity; however, the ordered structure of the water molecules gradually disappeared. Consequently, the second and third nearest-neighbor peaks and the ordered structure of water molecules observed for the silicalite-1 sample were almost nonexistent in ZSM-5 structures, especially in the one with the Si/Al ratio of 95. As the temperature was raised, only one broad but much less intense peak remained in the RDFs due to increased mobility of water molecules around the ionic centers.

Conclusions

Molecular dynamics simulations of water diffusion in the all-silica zeolite, silicalite-1, and its Al-containing analogue, ZSM-5 (Si/Al = 95 and 191) were carried out at three different temperatures, 297, 354, and 393 K, at a constant water loading of 8 molecules per unit cell, using COMPASS forcefield in the canonical ensemble.

Water diffusion in silicalite-1 was controlled by the H-bond interactions, whereas in the ZSM-5 samples, ion-dipole interactions were stronger than the H-bond interactions, and they became the dominating factor in determining the overall dynamics of the water molecules in the channels and thus the diffusivity. Diffusion coefficients obtained from the slopes of the MSD versus time plots increased with temperature, as expected, and were significantly reduced with increasing alumina content. The activation energy of diffusion decreased with the Si/Al ratio, too. Straight channels were preferred in all structures at all temperatures and the channel preference was not observed to be a strong function of either temperature or the Si/Al ratio. The lowest diffusion coefficients were obtained for the z direction, which is a combination of the sinusoidal and straight channels, although the D_z values also increased somewhat with temperature.

Water molecules were seen to form clusters in the vicinity of the cation(s) and the ion-dipole interactions became very strong depending on the temperature in the ZSM-5 samples. The ordered structures of the water molecules, forming clusters in the channels of silicalite-1 at low temperature, were observed to be broken by increased temperatures and decreased Si/Al ratios, resulting in less ordered structures. The positions of the water molecules in the straight and sinusoidal channels for the ZSM-5 samples were mainly determined by the location of the charge-compensating cation(s) in the structure, as was shown by the concentration profiles.

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