Quantifying the effect of Si/Al ratio on proton solvation and water diffusion in H-FAU using reactive neural network potential

Indranil Saha, Andreas Erlebach, Petr Nachtigall, Christopher J. Heard, Lukáš Grajciar*

Department of Physical and Macromolecular Chemistry, Charles University, Hlavova

8, 12496 Prague 2, Czech Republic

*E-mail: lukas.grajciar@natur.cuni.cz

Abstract

Acidic zeolites are one of the most important catalysts. In many of their catalytic applications, the mode of interaction with water heavily influences their activity, efficiency, and durability as a catalyst. Despite the recent (first principles) computational efforts to understand the mechanistic underpinning of the water-zeolite interactions, it is still prohibitively expensive to carry out comprehensive studies employing realistic zeolitic models. Therefore, we used a recently developed reactive neural network-based potential for aluminosilicate zeolites in the protonic form including their interaction with the aqueous solution that has a capacity to accelerate simulation by orders of magnitude while retaining the reference level of accuracy. We used it to determine how multiple factors (aluminum content, water loading and temperature) influence the proton solvation and water dynamics in one of the industrially most important acidic zeolites, the faujasite (FAU). We found that Si/AI ratio is a significant determinant of the water diffusivity, water capacity to solvate protons in the nanopores, and the zeolite hydrolytic stability. We expect that many of these findings are readily extendable to other acidic zeolites in interaction with water.

Keywords: machine learning potentials, neural networks, acid zeolites, water, proton solvation, diffusion

1. Introduction

Zeolites are crystalline microporous aluminosilicate materials established for a long time in a wide range of applications in adsorption, gas separation and catalysis.¹ Recently, a lot of efforts aim to repurpose these well-known materials in sustainable applications such as biomass conversion, thermal energy storage or water purification.² In many of these "new" applications the multi-faceted interaction of zeolites with water in various states (e.g., as a pressurized hot liquid water) is at the core of the physical processes leveraged to achieve the application goals. This spurred a large interest aimed at understanding the hydrothermal stability of zeolites, water sorption properties or water dynamics inside the zeolitic nanopores.^{3,4}

A particularly interesting systems are the so-called acidic zeolites with a proton as chargecompensating cation, which are the main catalysts in fluid catalytical cracking process (zeolite FAU) in petroleum refineries,⁵ and have recently been also in the focus of the studies on how water clustering and creation of hydrated hydroxonium clusters inside the acid zeolite nanopores can enhance/influence the activity of the reacting species.^{6,7} Another interesting branch of research focused on how, typically acidic, zeolites effect the water mobility through the thin zeolite membranes.⁸ Both of these research branches stimulated a lot of computational efforts aimed at understanding the mechanism of proton solvation and/or the water dynamics in acidic zeolites, typically focused on MFI,^{9–11} BEA^{12,13} and FAU¹⁴ topologies. In particular the work by Grifoni *et al.*¹⁵ employing extensive biased *ab initio* molecular dynamics (AIMD) simulations for four topologies (GIS, FAU, MFI, CHA) seemed to settle the case about the thermodynamics of the proton solvation in high-silica zeolites showing that regardless of the zeolite topology/confinement not more than two to three waters are needed to solvate the Brønsted acid site (BAS) proton and that these protonated water clusters stay close to the BAS. However, the vast majority of previous *ab initio* quality studies focused on models (Si/Al ratio, topology, water content, *etc.*) that mostly mimicked the experimental set-up and allowed only for a very limited "through a keyhole" look at the problem in question. Even the work by Grifoni *et al.*, while rather comprehensive, is limited by the rather simple (but clearly important) problem of solvation of isolated BAS sites that still could be just barely tackled by *ab initio* calculations at present. Thus, looking for example at effects of increased aluminum content on proton solvation in a more comprehensive manner or carrying out numerous long equilibrium molecular dynamics (MD) runs to quantify water diffusion hindered by hydrated hydroxonium cluster, i.e., carrying 'higher' throughput studies that would be reactive (as protons solvation dynamics implies) and reliable (i.e., of ab initio quality) is beyond the reach at the moment.

A possible solution to this problem is the adoption of the acceleration of the atomistic simulations offered by the advent of the machine learning potentials (MLPs).¹⁶ The MLPs can retain the *ab initio* quality of description, can be made reactive by construction and are orders of magnitude faster (after the subtraction of the time needed to generate reference database) than the typical workhorse of the first-principles calculations in materials, the density functional theory (DFT). Despite an exploding number of newly trained MLPs in the material science field,^{17,18} the field of zeolites mostly intact by this trend with the exception of our own recent work,¹⁹ in which we developed neural network based potential (NNP) for the purely silicious zeolites. In addition, most of the MLPs in the material science fields, in particular those for more complex systems such as solid-liquid interfaces, are aimed just for accelerating the dynamics for a particular thermodynamic state, rather than to deliver a globally optimal MLP²⁰ that could be used to "discover" a bit of a "new" chemistry covering a broader range of systems.

Therefore, in this work, we use a recently proposed neural network potential (NNP) for complex solid and solid-liquid interface, namely for the aluminosilicate zeolites in protonic form including their interaction with the aqueous solution. In particular, we employ it to determine how aluminum content, water loading and temperature influences the proton solvation and water dynamics in one of the industrially most important acidic zeolites, the faujasite (FAU). We also show that we are indeed able to "discover" new unexpected chemistry, namely how new peculiar hydroxonium species are being formed in our simulations and how low-silica FAU framework starts to amorphize.

2. Methods and Models

2.1. Simulation model detials

We used a general neural network potential (NNP) reported recently for protonic aluminosilicate zeolites, which is expected to cover all zeolite topologies at variable Si/Al ratios and water loadings. The NNP simulations were run using the Python packages SchNetPack²¹ and the atomic simulation environment (ASE)²².

2.2. FAU calculations

We employed a standard 576 atom cubic FAU unit cell $(UC)^{23}$ with a=24.345 Å for production runs and primitive cell for testing runs (see Section 3.1). We considered various aluminum contents ranging from purely silicious framework to the frameworks containing 4, 24, 48 and 96 aluminum atoms (corresponding to Si/Al ratios of 47, 7, 3 and 1, respectively). We also tested multiple water loadings in the FAU UC, namely 4, 8, 12, 16, 48, 96 and 192 waters (corresponding approx. to 0.6, 1.25, 1.9, 2.5, 7.5, 18, 33 wt %). The low water loadings (from 4-16) were considered only for high-silica FAU models. To quantify the mobility of the water molecules, the self-diffusion coefficient was calculated from by tracking the positions of the oxygen atom of each water, evaluating the mean square displacement (MSD), and using the Einstein formula for the linear part of the MSD vs. time dependence. The standard deviation of the total diffusion coefficient was approximated from the diffusion coefficients in the three cartesian directions (D_x , D_y and D_z). The BAS proton is considered solvated if its distance from the framework oxygen adjacent to aluminum is longer than 1.3Å. All calculations were run at least for 1 ns using the canonical (NVT) ensemble with a 0.5 fs time step and hydrogen being replaced by deuterium. We note that following the recent benchmark study of water diffusion in zeolites²⁴ we do not expect that obtaining diffusion coefficients from NVT rather than from NVE ensemble would have significant effects on our results.

3. Results and Discussion

3.1. Water diffusion

The water mobility, characterized by its self-diffusivity, appears to be significantly hindered in the (alumino)-silicate (H-)FAU zeolite models at 300 K (Figure 1). At low water loadings (below 16 waters per UC) we did not observe any diffusion in H-FAU(4AI) model during the ns-long trajectory with the water (cluster) staying close to the BAS. Even increasing the simulation temperature to 400 K did not result in at least temporary desorption of the water (cluster) from the BAS site over 1 ns. For purely silicious FAU model and low water loading of 4 waters per UC (Si-FAU/4w) we were unable to obtain a reliable statistic to use Einstein relation directly - rather we approximated self-diffusion coefficient using a simplified model of lattice/jump diffusion as we observed that isolated water molecules rapidly (within 100 ps) cluster to form a water tetramer, which then jumps twice from supercage to supercage (approx. 17 Å away) during the rest of the simulation (0.95 ns) (see Figure 2). Adopting this approximation, we estimate the self-diffusion coefficient reported²⁵ for purely silicious MFI zeolite (1.7 x 10^{-9} m² s⁻¹), albeit the water loading was somewhat higher in the experiment (corresponding to approx. 16 waters per FAU UC).



Figure 1: Water self-diffusion coefficient of the water adsorbed in the FAU models as a function of: (a) aluminum content (different water loadings are depicted with colored lines), and (b) water loading (different aluminum contents are depicted with colored lines). '*' shows the approximated value of self-diffusion coefficient for Si-FAU/4w system (see the text) and '**' shows the approximated value of the self-diffusion coefficient for H-FAU(4Al)/4w system (see the text).



Figure 2: Unwrapped trajectory lines of four water molecules (colored in red, violet, green and orange) in the Si-FAU system during a one ns long simulation run at 300 K. The water molecules start as isolated monomers, cluster within approx. first 100 ps of the trajectory to form a tetramer that carries out two jumps between the FAU supercages in the rest of the trajectory. The FAU unit cell is depicted, and 'tm' marks the part of the trajectory lines in which each water is a part of the water tetramer.

For larger water loadings (48 waters and above) we did observe standard diffusion behavior (describable by Einstein relation), however, the *mean* (linear) displacement remained in low Ångstroms (per ns simulation), which translated into small self-diffusion coefficients ranging from 6 x 10^{-12} m² s⁻¹ to only 6 x 10^{-11} m² s⁻¹. Preliminary analysis shows that water molecules cluster heavily (containing also solvated protons) and are mostly immobilized in those very-slow moving clusters and only occasionally a water molecule jumps from one cluster to the neighboring cluster or at lower water loadings the whole cluster moves. Calculated values of self-diffusion coefficients are about an order of magnitude lower than the experimental values for sodium exchanged FAU (NaX and NaY) zeolites²⁶ or the recent analytical force field values for (H)-FAU models¹⁴ and are similar rather to

experimental self-diffusion coefficients reported for high-aluminum NaA zeolite²⁷ with much smaller cages than FAU. Considering the reasonable agreement with the experiment for Si-FAU model at low water loading it appears that the disagreement may originate in the tendency of water to over-structure at 300 K which can stifle its mobility - this has been reported at length in the literature^{28,29} and it was related to deficiencies of (meta)-GGA DFT functionals, including herein used reference DFT functional (SCAN), and to the lack to account for nuclear quantum effects. As a common pragmatic approach to alleviate these problems it was proposed to run liquid water simulations at increased temperatures. Obviously, running simulations at increased temperatures leads to increase in self-diffusion coefficients bringing them closer to the values reported in the literature (see Table 1). In particular, increasing temperature from 300 K to 400 K results in enhancement of the water self-diffusivity by approximately an order of magnitude, which is an increase similar to the one reported in the literature for H-MFI experimental samples³⁰ and for basically the same temperature jump.

Al content	Water content	Temperature [K]	D
[per UC]	[per UC]		[m ² s ⁻¹]
0	192	300	6.4±0.8 x 10 ⁻¹¹
		400	1.2±0.1 x 10 ⁻⁰⁹
6	48	300	3.9±0.8 x 10 ⁻¹¹
		400	1.1±0.2 x 10 ⁻¹⁰
		600	2.5±0.6 x 10 ⁻⁰⁹
24	48	300	1.2±0.1 x 10 ⁻¹¹
		400	1.6±0.3 x 10 ⁻¹⁰
24	192	300	9.0±0.9 x 10 ⁻¹²

Table 1: The effect of temperature on the self-diffusion coefficient of water in FAU models.

1.3±0.1 x 10⁻¹⁰

Increasing aluminum (and proton) content leads almost invariably to sizable decrease in the water selfdiffusion coefficients (see Figure 1a), notwithstanding the water loading. The coefficients are highest for the purely silicious FAU, drop mildly (by not more than a half) for rather high-silica H-FAU (Si/Al=47 and 7) and then decrease significantly (three to ten-fold decrease compared to the pure silica model) for low-silica H-FAU model (Si/Al=3 and 1). In line with our results, mild (up to two-fold) drop in diffusivity going from purely silicious to high-silica acidic zeolites has been reported experimentally for (H)-MFI zeolite³⁰ and computationally for H-FAU.¹⁴ Next, with increased water loading in the FAU nanopores the aluminums (and the BAS sites) start to hinder the water motion more extensively - for 48 waters the diffusivity decreases only three-fold going from Si-FAU to HX (Si/Al=1) model but it decreases more than seven-fold when 192 waters are adsorbed in the FAU unit cell. Hence, our data suggest that water self-diffusivity can change by as much as an order of magnitude as a function of the aluminum content in the FAU framework, with the degree of change modulated by the water content.

400

For the water loadings above 48 water per UC (7.5% wt %) the water loading has typically only a minor effect on the self-diffusion coefficients (see Fig. 1b). For a particular Si/Al ratio, increasing the water loading all the way to 192 water per UC does not change the diffusion coefficients more than two-fold with the exception of H-FAU(48Al) for which a four-fold decrease was observed. For lower water loadings, as noted above, we can only approximate the diffusion coefficients that are expected to be either much larger (e.g., $1 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ for Si-FAU with four waters in UC) or much smaller (possibly in low $10^{-12} \text{ m}^2 \text{ s}^{-1}$ or less for H-FAU models) due to very strong interaction of water molecule with the BAS site³¹ that is not compensated by the sufficient water-water interactions. Hence, for all aluminum containing H-FAU samples, one could cautiously generalize that, irrespective of the aluminum content, the water self-diffusion coefficients initially increase significantly with increasing water loading in the nanopores and then mostly plateau or even decrease as one nears the water

adsorption saturation limit. Similar behavior has been reported for low-silica NaX and NaY zeolites both experimentally and computationally using analytical force fields.^{26,32}



Figure 3: (a) Ratio of solvated BAS protons as a function of water loading in the FAU UC (different aluminum contents are depicted with colored lines). (b) Average number of waters needed to solvate a BAS proton (different aluminum contents are depicted with colored lines). Dashed lines for H-FAU(24Al) models as well as empty markers show the water loadings at which all the BAS protons are solvated, i.e., at those water loadings the pore contains some excess water with respect to the amount necessary to solvate all BAS proton. '*' shows the approximated value for H-FAU(4Al) system (see the text).

3.2. Proton solvation

Leveraging the ability of our neural network potential to describe reactive interactions, we evaluated the amount of BAS that are deprotonated, i.e., how many protons are solvated in the FAU unit cell as a function of aluminum (Si/Al ratio) content and water loading (Figure 3). For high-silica H-FAU(4Al) model and low water loadings (from one to four waters per BAS site) we observe that two waters per BAS can partially solvate protons (50% of protons are solvated on average) while three waters are enough to completely solvate the BAS proton (Fig. 4a). Hence, one can approximate that on average 2.5 ± 0.5 waters are needed to solvate a BAS in high-silica FAU at 300K. This is in very good agreement with the biased AIMD (at PBE+D2 level) results by Grifoni et al.¹⁵ who reported that solvated and non-solvated state in FAU with two waters per BAS are basically isoenergetic with a very low (~ 5)

kJ/mol) barrier separating the two and that increasing the water count to three per BAS completely destabilizes the non-solvated BAS state. However, for low-silica models (48 and 96 Al) even with very high-water loading (as many as 192 waters per UC and water/BAS ratio as high as 4) one is unable to completely deprotonate the framework. This indicates that proton solvation capacity of water is significantly Si/Al-dependent. This is exemplified in Figure 3b which shows how many waters (on average) are needed to solvate a proton. For systems in which not all protons are solvated this number is rather constant for broad range of water loadings (from 48 waters to 192 waters) and depends on the Si/Al ration going from 2.9±0.3 to 4.7±0.4 to 12.3±0.4 for H-FAU(48Al), H-FAU(96Al), and H-FAU(24Al), respectively. It seems that increasing the proton charge density leads to significant jump in the number of waters needed to screen the solvated protons from the rest of the: i) BAS protons protruding to the supercage, and/or ii) the neighboring protonated water clusters. We hypothesize that the entropy gains¹⁵ from proton solvation may start to be offset by the internal energy losses due to electrostatic repulsion between the solvated and BAS (and solvated) protons. Hence, all this means, rather counterintuitively, that there will be less solvated protons per UC at very low Si/Al ratios compared to higher Si/Al ratios (e.g., Si/Al = 7) and that these very low-silica FAU samples can be considered as less acidic than higher silica ones (Figure 4).



Figure 4: Total number of solvated BAS protons as a function of water loading in the FAU UC (different aluminum contents are depicted with colored lines). Dashed lines for H-FAU(24Al) models as well as empty markers show the water loadings at which all the BAS protons are solvated.

'Pinned' hydroxonium. During our simulations a peculiar hydroxonium species was formed in all the FAU models with at least 24 aluminum per UC (Si/Al \geq 7) and at least 48 waters per UC (Figure 5). The 'pinned' hydroxonium is predominantly formed over 6-rings of the sodalite cage (very intermittent formation over two neighboring 4-rings with abundant aluminum was also observed) and it is characterized by at least two but mostly three short H...O_f bonds (typically in the range of 1.4-1.8 Å) between hydrogens of the hydroxonium and the framework oxygens (typically the BAS oxygens in the crystallographic position O3²³). In addition, as the 'pinned' hydroxonium is saturated by the hydrogen bonds to the framework, it does not interact with the surrounding mostly protonated water molecules/clusters and consequently it is surrounded by a 2-3 Å wide void space. This also presumably leads to its long lifetime since once it is formed it typically survives until the end of simulation (i.e., few hundreds of ps) staying *pinned* by the hydrogen bonds to the 6-ring. However, it may temporarily deposit proton to the framework or be (even less frequently) perturbed by the incoming water that could lead to its demise. It appears that the necessary condition for formation of the 'pinned' hydroxonium is the presence of at least two aluminums in the 6-ring and since our H-FAU(24Al) model with Si/Al=7 does contain few 6-rings with two aluminums it forms already at this Si/Al ratio (Figure 6). Figure 6 shows that there does not seem to be a clear trend in frequency of 'pinned' hydroxonium occurrence as a function of aluminum content or water loading. However, the maximum occurrence seems to coincide with the water/BAS ratio of two for all aluminum contents, which may suggest that some trade-off is taking place, possibly between the tendency to solvate the 'pinned' hydroxonium and the ability of water to screen/stabilize the standard solvated hydroxonium. Importantly, the existence of '*pinned*' hydroxonium is supported by the neutron diffraction study³³ on hydrated H-Y sample (Si/Al=2.5 and approx. 15 waters) which reports on significantly elongated distance (2.04 Å) between hydrogen (deuterium) and the framework oxygen in the O3 crystallographic position, i.e., the framework oxygen position in the 6-ring to which our '*pinned*' hydroxonium is bound. The H(D)-O distances to other accessible crystallographic framework oxygens (O1 and O2) were on the other hand close to standard BAS values (0.97 and 1.14 Å).³³



Figure 5: The structure of the '*pinned*' hydroxonium species formed above the 6-ring of the sodalite cage (note two other '*pinned*' hydroxonium speceis are formed on the 6-ring faces of the sodalite cage in the background). The structure is a snapshot from the simulation with H-FAU(96AI)-192w at 300 K.



Figure 6: The total number of the *'pinned'* hydroxonium species formed in the FAU UC as a function of water loading in the FAU UC (different aluminum contents are depicted with colored lines).

Increasing simulation temperature to 400 K favors proton solvation for three systems tested (see Table 2), including formation of the increased quantities of the '*pinned' hydroxonium*. However, further

increase to 600 K diminishes proton solvation significantly as water tends to form shorter-living clusters and behave more like a free gas in the nanopores (compare diffusion coefficients in Table 1).

Al content	Water content	Temperature [K]	Number of solvated
[per UC]	[per UC]		protons
6	48	300	16.3±1.5
		400	18.7±2.0
		600	10.2±2.0
24	48	300	3.8±1.5
		400	8.4±2.0
24	192	300	15.4±0.9
		400	23.2±3.8

Table 2: The effect of temperature on the proton solvation in FAU models.

3.3. Defect formation

We detected spontaneous formation of the structural defects in the H-FAU(48Al) models (Si/Al=1) during our ns-long trajectories for the water loading of 48 waters per UC and above. The mechanism of the '*3-ring non-Löwenstein*' (3-RNL) defect formation (Figure 7) takes place in the 4-ring with two aluminum atoms and at least one Brønsted proton on the framework oxygen in the 4-ring. It can be characterized as a rotation of the two bonds (Si-O- and Si-OH-) of the Si(OH-)₁(O-)₃ tetrahedron that are in the 4-ring by approx. 90° around the axis that goes through Si atom and is perpendicular to the 4-ring. The resulting defect is a 3-ring with two neighboring aluminum atoms (i.e., violating the Löwenstein's rule³⁴) and a neighboring Q³ silicon, i.e., the silicon with one silanol group (Figure 8a). Once formed, it remains throughout the whole simulation. At 300 K, one to two such defects are formed per UC for three water loadings considered (48, 96 and 192 waters). At 400 K as much as six defects are formed with 48 waters per UC, however, with 192 waters per UC barely one defects forms which is fast healed. In the former simulation we even observe a propagation of the 3-RNL defect,

where two such defects are formed next to each other (Figure 8b). The hydrolytical instability of the H-FAU samples with Si/Al=1, i.e., of the HX zeolite, is well-known experimentally^{35,36} and our reactive simulations are in line with those observations providing the first mechanistic insight into this amorphization process at the atomistic level.



Figure 7: The scheme of the '*3-ring non-Löwenstein*' defect formation taking place in the 4-ring of the FAU models with Si/Al=1.



Figure 9: (a) The structure the '*3-ring non-Löwenstein*' (3-RNL) defect formed in all simulations with H-FAU models with Si/Al=1. (b) The structure of the *extended* 3-RNL defect, where two 3-RNL defects are formed in the neighboring 4-rings. Such extended 3-RNL defect was formed only during simulations with H-FAU(96Al)-48w system at 400 K.

4. Conclusions

In this work, we, for the first time, used the recently developed neural network potential (NNP) capable of describing reactive interactions of aluminosilicate zeolites in their protonic form and their reactive interaction with the water solution. We applied it to determine how aluminum content, water loading and temperature influences the proton solvation and water dynamics acidic form of zeolite faujasite (FAU). Our data show that water self-diffusivity can change by as much as an order of magnitude as a function of the aluminum content going from purely silicious FAU zeolite to FAU zeolite with Si/Al=1 (zeolite HX) and that it is only mildly modulated by the water content if the nanopores are at least moderately loaded with water (above 48 waters per UC, i.e., above approx. one fourth to one sixth of the water sorption capacity).

We observed, rather counterintuitively, that less protons are solvated in the extremely low-silica samples (Si/Al=1 and 3) compared to samples with higher Si/Al ratio (Si/Al = 7) and that these very low-silica FAU samples can be considered as less acidic than higher silica ones. An alternative view is that the number of waters needed to solvate a proton is Si/Al-dependent and rather insensitive to the total water loading in the nanopores. Indeed, we observe that while approx. three waters are needed to solvate proton for Si/Al=7, it increases to almost five for Si/Al=3 and goes all the way to twelve for Si/Al=1. We assume that this is a consequence of a tug-of war between entropy gains from proton solvation and the internal energy losses due to electrostatic repulsion between the solvated protons and BAS (and solvated) protons.

Supporting the claim about the ability of our NNP to discover a "new" chemistry and not only accelerate the costly *ab initio* calculations we: i) identified formation of a peculiar long-living "*pinned*" hydroxonium species formed over 6-ring faces of the sodalite unit that contains at least two aluminums and which is pinned to the 6-ring by three short hydrogen bonds shunning from the H-bond interaction with the surrounding waters, and ii) observed spontaneous formation of the silanols and 3-ring defects containing non-Löwenstein -Al-O-Al- bonds in the HX models. We assume that both observations are not limited to the very low-silica FAU zeolite but can be generalized to other very low-silica zeolites containing 4- and 6-rings.

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