Supporting Information:

Collective action of water molecules in zeolite dealumination

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S1 DFT-MD Computational Details

DFT-based molecular dynamics (DFT-MD) calculations were performed using the CP2K\textsuperscript{S1} programme. The Grimme DFT-D3 dispersion corrected\textsuperscript{S2,S3} revPBE exchange correlation functional\textsuperscript{S4} was applied using a combination of Gaussian and plane wave basis sets\textsuperscript{S5,S6} with kinetic energy cutoff at 350 Ry. GTH basis sets and pseudopotentials were utilized.\textsuperscript{S7} The simulations employed an integration timestep of 0.5 fs and a Nosé-Hoover thermostat\textsuperscript{S8,S9} with a chain length of 5 and a time constant of 100 fs. An MTK barostat\textsuperscript{S10} was used in the simulations at constant pressure and temperature (NPT) for unit cell equilibration.

The 36 T-site CHA unit cell was used with one substitution of Si with Al and addition of a proton. Umbrella sampling was performed in PLUMED\textsuperscript{S11} with CP2K as the MD engine. Each umbrella simulation has been run for 10 ps. If the sampling seemed incomplete after 10 ps, each umbrella was run for 10 additional ps. For every reaction 10–15 umbrellas were created evenly spaced across the entire CV region. The steepness of each umbrella was chosen so the umbrella potential was equal to $k_B T$ at the center of the neighboring umbrella, making sure of sufficient overlap. In a few cases where sampling was lacking in certain areas, extra umbrellas were added. Figure\textsuperscript{S1} shows a representative example of the resulting histograms for each umbrella simulation along the collective variable (Section S4) of a selected reaction step in the dealumination. The remaining simulations have similar overlap between the histograms. The free energy profiles were derived from the histograms and corresponding umbrella potentials using the Weighted Histogram Analysis Method (WHAM),\textsuperscript{S12,S13} at a temperature of 723 K. In this procedure every tenth entry of the histogram was used as input to WHAM, in order to avoid time correlations in the data.

Metadynamics (MTD) simulations were used to test different collective variables and finally create input structures for the umbrella sampling simulations, as the MTD simulations can be started with less computational cost than umbrella samplings. For the MTD simulations hills were spawned every 50 fs, initially at a height of 1.5 kJ/mol, and the hill height was
Figure S1: Histograms showing the sampling region of each umbrella simulation for step 1 (Scheme 1 of the main manuscript) in the single-water simulation series.

reduced by a factor of 2 after every time reaction had happened in the forward and reverse directions.

MTD simulations were not used to generate the final free energy profiles, for the following reason. In MTD the bias potential is determined by the full history of the simulation, and hence simulations have to be run in one long go. In umbrella sampling on the other hand, the bias potential is only a function of the collective variable, not the history, which offers the possibility of running many simulations in parallel.
**NPT Simulations**

NPT simulations were performed to obtain the unit cell parameters at the reaction temperature of 723 K, a pressure of 1 bar, and water loadings of 0-5 water molecules per unit cell. After an equilibration period of 5 ps, we performed production runs of at least 30 ps. In general, the volumes and other parameters were stable after 5 ps and 30 ps produced more than enough data to construct a trustworthy average.

The resulting time-averaged unit cell parameters are shown in table S1.

Table S1: Average unit cell parameters obtained from NPT simulations of the SSZ-13 unit cell with increasing water loading (numbers are water molecules per unit cell), at a temperature of 723 K, and a pressure of 1 bar.

<table>
<thead>
<tr>
<th>N H₂O</th>
<th>a [Å]</th>
<th>b [Å]</th>
<th>c [Å]</th>
<th>α [°]</th>
<th>β [°]</th>
<th>γ [°]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>13.79</td>
<td>13.74</td>
<td>14.93</td>
<td>90.09</td>
<td>89.94</td>
<td>120.12</td>
</tr>
<tr>
<td>1</td>
<td>13.79</td>
<td>13.77</td>
<td>14.90</td>
<td>89.94</td>
<td>90.03</td>
<td>120.18</td>
</tr>
<tr>
<td>2</td>
<td>13.80</td>
<td>13.76</td>
<td>14.89</td>
<td>89.94</td>
<td>90.05</td>
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<td>13.81</td>
<td>13.77</td>
<td>14.83</td>
<td>90.03</td>
<td>90.05</td>
<td>120.06</td>
</tr>
<tr>
<td>5</td>
<td>13.83</td>
<td>13.78</td>
<td>14.80</td>
<td>89.96</td>
<td>90.10</td>
<td>120.14</td>
</tr>
</tbody>
</table>

The resulting volume of the unit cell is plotted in Figure S2. The figure also includes the probability that the acid site is protonated, meaning that the acid proton is on the Brønsted acid site, contrary to being in solution due to the presence of water molecules. This is calculated as the fraction of the simulation time where a proton is less than 1.4 Å away from any of the oxygen atoms next to the aluminum atom.

These results show that the unit cell contracts slightly with increasing water loading. This effect is negligible compared to previous results on SAPO-34. The simulation with 3 water molecules per unit cell is an outlier due to a behavior where the unit cell periodically will contract substantially. As can be seen, the acid site is always protonated with a single water molecule in the cage, but with increasing water loading, the acid site is increasingly deprotonated.
Figure S2: The unit cell volume and probability that the proton is on the framework for NPT simulations of H-SSZ-13 at 723 K and 1 bar.

We conducted simulations with water loadings of one and four water molecule per unit cell, respectively. We chose a series starting with one water molecule and adding one for every step, as it will be consistent with previous static DFT calculations performed by us\textsuperscript{S17} and others.\textsuperscript{S18,S19} The second series of DFT-MD simulations start with four water molecules and maintains the number of atoms through all steps. This is to have the minimum amount of water molecules initially in the unit cell to simulate the full dealumination reaction while being close to the estimated water loading at realistic conditions of zeolite steaming (Section S3). This allows us to construct an overall energy diagram of the reaction with a realistic initial (reference) state, constituting a more rigorous approach to establishing the reference free energy than in our earlier work.\textsuperscript{S17}

In the further umbrella simulations the unit cell is kept fixed at the averaged geometry shown in Table S1 for 1 and 4 water molecules, respectively.

In the umbrella samplings it is necessary to keep track of the Brønsted proton (vide infra). As seen from Figure S2 the NPT simulations show that with one water molecule per unit
cell, the proton is always on the framework, and with four water molecules per unit cell, it is on the framework 50% of the simulation time.

S3 Grand Canonical Monte Carlo Simulations

To study the water loading in the zeolite, we used LAMMPS\cite{S20} and Grand Canonical Monte Carlo (GCMC)\cite{S21} to obtain chemical equilibrium between the zeolite and the surrounding steam. Similar studies have been performed by García-Pérez et al.,\cite{S22} but they used frameworks with no acid sites. Since our framework has aluminum sites, we used a recent ReaxFF force field for Si/Al/O/H fitted to DFT data and shown to give good agreement with experimental data on water adsorption/diffusion in zeolites.\cite{S23,S24} In conjunction with ReaxFF we used the charge equilibration method (QEq),\cite{S25,S26} where the electrostatic energy of the system is minimized by adjusting the charges of all atoms based on interactions with their neighbors. This means that atoms of the same element do not all have exactly the same partial charge, but one that is depending on the atom’s neighbors. QEq requires as input the electronegativity, the self-Coulomb potential and the valence orbital exponent for each element (here O, Si, Al and H), which are provided in the definition of the ReaxFF force field.

The simulation cell consisted of $3 \times 3 \times 3$ unit cells (2943 atoms). Such a large system was chosen to reduce finite size effects (system size is more than 3 times the force field cutoff), but still have reasonable computational efficiency. Steam at the conditions described in Section S2 has a low density and behaves like an ideal gas with a fugacity coefficient $\phi \approx 1.001$. This value was found by comparing ideal gas pressures with known pressures of steam at these conditions.\cite{S27} Assuming this, the chemical potential can be found from a fugacity corrected ideal gas.

Water molecules were inserted with an H-O-H angle of 106°, the mean angle we measured
at these conditions with this potential. Since we insert and remove full water molecules, only regular GCMC steps (rotations and translations of the water molecules, keeping the molecules and the framework fixed) were performed to prevent hydrogen swaps and chemical reactions during equilibration.

GCMC drives the system towards chemical equilibrium by inserting, removing, translating and rotating water molecules following a Metropolis accept/reject step based in change in potential energy between water configurations. The atoms in the zeolite are kept fixed during the full simulation. 10 trial inserts/deletions were performed per monte carlo step whereas the number of translations/rotations were equal to the number of water molecules in the system as suggested by Frenkel and Smit. Since water molecules are expected to enter or leave the catalyst as full molecules, we also subtract the internal binding energy before performing the Metropolis step. This internal energy is almost constant since each water molecule is kept at a constant angle with no dynamics. A small error due to energy changes after charge equilibration is expected because of how GCMC is implemented in LAMMPS, but these are found to be negligible.

Simulations were conducted for a series of water steam pressures to obtain an isotherm. Each simulation reached equilibrium after around 1000 monte carlo steps. We then performed another 9000 steps to sample the distribution of water loadings. The resulting isotherm is shown in Figure S3. The error bars shown on the isotherm correspond to the observed distribution of water loadings in each simulation. This is illustrated for the simulation at 1.0 bar in Figure S4, the water loading in the unit cell is equal to 3.21 ± 0.19. Finally, in Figure S5 we see a snapshot of an equilibrium state with the water loading during 10000 monte carlo steps.
Figure S3: Isotherm of water adsorption in H-SSZ-13 zeolite at 723 K simulated with GCMC.

Figure S4: Histogram over number of water molecules per H-SSZ-13 unit cell obtained with GCMC at $T = 723$ K and $P = 1$ bar over 9000 monte carlo steps after the system reached equilibrium. Our simulation shows that the water loading is $3.21 \pm 0.19$ water molecules per unit cell.
Figure S5: Rendered image showing equilibrium water loading in the 27 unit cells of H-SSZ-13 zeolite at $T = 723$ K and $P = 1$ bar. In the insert, we see evolution of water molecule count per unit cell, skipping the initial steps to highlight the equilibrium range. Our simulation shows that the water loading is $3.21 \pm 0.19$ over 10000 steps.
S4  The Collective Variable in Umbrella Sampling

As other free energy sampling techniques, umbrella sampling relies on choosing one or more collective variables (CVs) describing the reaction of interest. In general, this choice relies on chemical sense, but Laio and Gervasio have provided guidelines for the CV(s): first, the CV(s) should clearly separate the initial, transition and final state of the reaction. Second, the CV(s) should describe all slow events relevant to the reaction. Third, there cannot be too many CVs, as it will be impractical to do the simulation.\textsuperscript{S28} A complete exploration of reaction coordinates for CV definition can be done using transition path sampling (TPS).\textsuperscript{S29} However, these simulations are extremely resource-demanding and have only been employed in rare cases in zeolite systems for exploring reaction paths.\textsuperscript{S30,S31} Even though exciting developments are undertaken to improve the TPS techniques for application to larger systems,\textsuperscript{S32,S34} they are still too resource-demanding to be within reach of the current work. We further note that commitor analysis\textsuperscript{S21} provides a formal way of checking whether the CV samples the reaction path. However, this technique too is extremely resource-demanding requiring hundreds or thousands of additional simulations, hampering its use in zeolite catalysis. Hence, we use MTD simulations to verify that the CVs connect reactants and products smoothly through a transition state region of the free energy surface. As such we check whether the CV represents the most critical changes, i.e. the ones leading to the largest free energy differences, during the reaction. Other parameters (bond lengths, angles etc.) that change during reaction, but that not require large free energy changes, will automatically be sampled as orthogonal degrees of freedom during the subsequent umbrella sampling simulations.

In this work we used knowledge of the chemical reaction as a starting point for defining a CV: the hydrolysis reactions take place by transfer of a proton from a water molecule to an oxygen bound to aluminum in the zeolite framework. Hence, the CV should describe coordination of protons from water with said oxygens. Different CVs were defined and tested in MTD
simulations as described in Section S1. It was found that we can use a simple CV defined by the number of coordinations between all hydrogen atoms in water molecules and the oxygen atoms on the framework bound to aluminium in Al-O-Si bonds. Note that in this definition of the CV there is no bias as to which proton of the water molecules is transferred. This turns out to be important in order to sample the proton-shuttling pathway, where multiple protons are close to the Al site (see Figure 1 of the main manuscript). Each coordination is described by a function defined as follows

\[ s(i, j) = \frac{1 - \left( \frac{r_{ij}}{r_0} \right)^n}{1 - \left( \frac{r_{ij}}{r_0} \right)^m} \]  

(S1)

where \( r_{ij} \) is the distance between atoms \( i \) and \( j \) and \( n = 6, m = 12 \) by default. The \( r_0 \) parameter has been set to 1.2 Å, which is in the high end of the length of OH-vibrations observed for the Brønsted proton when a water molecule is adsorbed on it (Figure S6).

Figure S6: histogram of the OH-length of the Brønsted proton to the framework oxygen, when a water molecule is adsorbed.

The oxygen atoms included have been highlighted in Figure S7 for each step. The CV does not include the oxygen where the Brønsted proton is bound, since with no bias the proton is able to be absorbed in a water cluster, as seen in the NPT simulations of section S2 and thereby confound the CV. For the same reason, we include a bias potential to keep the acid site protonated. The bias is included as a standard UPPER_WALLS in PLUMED S11. The same is done in steps 2 and 3 for the O-H groups on the zeolite framework, so they cannot
confound the CV by exchanging protons with the water molecules. The bias potentials are only effective at an OH-distance above $\sim 1.4$ Å, which is outside the region sampled by OH-vibrations at 723 K (Figure S6), and hence the wall will not be reached often in a simulation.

We note that sampling only states with the Brønsted site protonated does not significantly influence the free energy profiles extracted from the simulations. The reason is that even with four water molecules, the Brønsted site is protonated around 65% of the sampling time (Section S2). At a temperature of 723K this translates to a free energy difference in favor of the protonated state of 2 kJ/mol in step 1. In the following steps the water loading decreases and hence the protonated state is even more favored.

For steps 2 and 3, the energy diagram when using the standard coordination function in PLUMED (Eq. (S1) with $n = 6$ and $m = 12$), becomes extremely steep at low values of the CV. This is remedied by changing the coordination function so the values in the lower range of the CV correspond to longer O-H distances than by default, without changing $r_0$, since $r_0$ is where the coordination function is most steep, and should still be in the TS-region. This is specifically changed by setting $n$ to 8 and $m$ to 12 in Eq. (S1), essentially causing a less steep energy diagram. The standard coordination function along with the changed function used for step 2 and 3 are shown in Figure S8. The implication of changing the coordination function
Figure S8: The standard coordination function in PLUMED along with the changed coordination function used for step 2 and 3. A vertical line is added at the $r_0$ value of 1.2 Å.

Function is sketched in Figure S9. As seen in the figure, setting $n = 8$ causes a smoother energy profile which is much easier to sample, than having $n = 6$. This is obtained while keeping the transition state (energy maximum) at about the same CV-value.

Figure S9: Sketch of the implications on the free energy profile by changing the $n$-value of the coordination function for steps two and three. Here only the first part of the profile is illustrated, as this is where the changes are most significant.
S5  Comparison with Previous Static DFT Results

It is possible to compare the intrinsic free energy barriers obtained with only a single water molecule present in the reaction to the previous results from static DFT,$^\text{S17}$ albeit they were obtained with a different functional than used in this work. The barriers from this work along with the barriers found in Ref. $^\text{S17}$ are shown in Table $^\text{S2}$.

Table S2: The free energy barriers for the three steps of the dealumination process derived in this work. Also shown are the free energy ($G_{\text{DFT}}$) and potential energy ($E_{\text{DFT}}$) barriers from static DFT.$^\text{S17}$

<table>
<thead>
<tr>
<th>Functional</th>
<th>DFT-MD w/ umbrella sampling</th>
<th>Static DFT</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>revPBE-D3</td>
<td>PBE-D2</td>
<td></td>
</tr>
<tr>
<td>Step</td>
<td>single-water (kJ/mol)</td>
<td>multi-water (kJ/mol)</td>
<td>$G_{\text{DFT}}$ (kJ/mol)</td>
</tr>
<tr>
<td>1</td>
<td>100</td>
<td>87</td>
<td>164</td>
</tr>
<tr>
<td>2</td>
<td>115</td>
<td>107</td>
<td>168</td>
</tr>
<tr>
<td>3</td>
<td>109</td>
<td>90</td>
<td>70</td>
</tr>
</tbody>
</table>

The barriers obtained in the multi-water simulation series can be collected into a full free energy diagram, as done in the main manuscript. Figure $^\text{S10}$ shows this next to static DFT results from Ref. $^\text{S17}$. The initial state in the DFT-MD results has been chosen to have the same energy as the 'initial 1' state of static DFT, since in the initial state of the DFT-MD simulations, a water molecule is adsorbed on the Brønsted site (Figure $^\text{S11}$), which is exactly what the 'initial 1' state represents.$^\text{S17}$

Comparing to the previous results from static DFT,$^\text{S17}$ it is clear that the free energy barriers for the first two steps are significantly lower when derived with DFT-MD. Looking at the potential energy barrier ($E_{\text{DFT}}$, in Table $^\text{S2}$) for step 2, the value is well in line with the single-water reaction of DFT-MD, while the free energy barrier from DFT ($G_{\text{DFT}}$) is about 50 kJ/mol too high. This suggests that using a harmonic vibrational analysis is at least problematic for this reaction, as an increase in the barrier for step 2 of about 45 kJ/mol just from vibrational contributions is unlikely to be accurate. For step 3 the barrier seems to be slightly lower using static DFT.

S-15
Figure S10: Free energy profile for dealumination obtained using DFT-MD with umbrella sampling and static DFT.

The fact that there is no general trend in differences between free energy barriers derived using the two methodologies, illustrates how challenging it is to model this reaction using static DFT and harmonic vibrational analysis.

Despite the different barrier heights, the free energy of activation for the complete reaction is similar. This is a remarkable result, since Nielsen et al. used a corrected reference state to obtain a free energy profile that matches the experimentally measured rate of dealumination. Thus, in this work we obtain results matching well with experiment without any corrections. In our previous work we made the correction by lowering the free energy of water reference state by an amount corresponding to about two translational degrees of freedom. Such reference state was hypothesized to represent water within the zeolite framework, corresponding to the initial state used in the DFT-MD simulations of this work. Hence, the present work supports the hypothesis and illustrates why it is important to know the loading of reactant molecules inside the framework when modeling reactions in zeolites.
S6 Water-Framework and Water-Water Interactions

The purpose of this section is to supplement the snapshots shown in the main manuscript with a quantitative analysis of central structural parameters describing interactions of water molecules with the framework as well as between each other.

In step 1, the water initially adsorbs on the Brønsted acid site. To quantify the time a water molecule spends at the Brønsted acid site, the distance from the Brønsted proton to the closest oxygen in a water molecule is measured. Figure S11 collects histograms of this distance in the initial state in the single- and multi-water simulation.

Figure S11: Histograms showing the distance from the Brønsted proton to the closest oxygen atom in a water molecule in the initial state of step 1, for both the single- and multi-water simulation series.

As can be seen, in the single-water simulation the water molecule spends all the time coordinated to the Brønsted proton in the initial state of step 1. In the multi-water simulation, the proton-water distance is below 2 Å in 75 % of the time.

In steps 2 and 3, water spends most of the time coordinated directly to the aluminium in the initial states. Figure S12 shows the distance from the aluminium to the closest water oxygen for step 2, including the initial state of the single-water simulation and the initial and transition states of the multi-water simulation series. As can be seen, the closest water molecule spends all the time coordinated to the aluminium in the initial state of both the single- and multi-water simulations. For the transition state in the multi-water simulation,
Figure S12: Histograms showing the distance from the aluminium atom to the nearest oxygen atom in a water molecule in step 2.

there is no Al-water coordination, as the additional water most of the time participates in the proton-shuttling structure (see below). Data for the transition state in the single-water simulation are not shown, as the only water in the simulation is consumed in the hydrolysis reaction step.

Figure S13 shows the analogous data for step 3. The closest water molecule spends all the time coordinated to the aluminium in the initial state in both the single- and multi-water simulations. For the transition state in the multi-water pathway, the Al-water distance is 89% of the time below 2.5 Å.

Finally, we consider the proton shuttling transition states shown in Figure 1 of the main manuscript, which feature adjacent water molecules. This is quantified in Figure S14, which
shows the distance from the reacting water molecule to the closest atom of the remaining water molecules in the transition states of each step. This distance is measured as the lowest distance of any atom in the reacting water molecule to any atom in the remaining water molecules, in order to take into account that the reacting water can be both acceptor and donor in hydrogen bonding.

Figure S14: Histograms showing the minimum distance from any atom in the reacting water molecule to any atom in the surrounding water molecules, for the transition states of each hydrolysis step in the multi-water simulation series.

These results demonstrate that the structural snapshots of the transition states shown in the main manuscript are in fact representative; there are clear signs of a hydrogen bond interaction between the reacting water and an additional water molecule in the transition states of step 1 and 2, where the shortest water–water distance is below 2.0 Å at all times in the former and 63% of the time in the latter. If the simulation in the transition state region of step 2 were to be extended, we believe this number would increase, as we also observed proton-shuttling structures in adjacent regions of the transition state. As discussed in the main manuscript, in step 3 the additional water molecule is coordinated to Al in the transition state (Figure S13c) and hence not directly interacting with the reacting water molecule (see snapshots in Figures 1 and 2 of main manuscript), reflected in significantly longer water-water distances than in step 1 and 2 (Figure S14).
Free Energy Profiles of Single Hydrolysis Steps

The free energy profiles derived for each step in the dealumination reaction are shown in Figure S15. These are calculated using the WHAM routine at 723 K. In each of the simulations the standard deviation on a single point on the profile given by the WHAM routine is about 1 kJ/mol. The difference in the appearance of the reactant state for steps two and three is due to the slight change in collective variable, as described in Section S4.

Figure S15: Free energy profiles for each step of the dealumination reaction (Scheme 1 of main manuscript) derived using DFT-MD in the single- and multi-water simulation series.
S8 General Solvation

It is possible that a general solvation effect of the surrounding water molecules would lead to the lowering of the free energy barriers of the hydrolysis steps (cf. Figure 1 in the main manuscript). To determine if solvation influences the barrier by having a larger effect on the transition states than the initial states, the total dispersion energy (the DFT-D3 contribution) was averaged over the entire simulation of the transition state and the reactant state. For step one, the transition state did yield a higher average dispersion energy, but only by about 5 kJ/mol. For step two, the difference was about 1 kJ/mol, and for step three, the dispersion interaction was higher in the reactant state by about 8 kJ/mol. Since these differences are so low and do not exhibit a trend, general solvation is deemed unlikely to cause the observed free energy difference in the barriers of between the single- and multi-water simulation series.
References


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