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RESEARCH ARTICLE



Interaction of water with zeolites: a review

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ABSTRACT

Water is ubiquitous in many thermal treatments and reaction conditions involving zeolite catalysts, but the potential impacts are complex. The different types of water interaction with zeolites have profound consequences in the stability, structure/composition, and reactivity of these important catalysts. This review analyzes the current knowledge about the mechanistic aspects of water adsorption and nucleation on zeolites surfaces and the concomitant role of zeolite defects, cations and extra framework species. Examples of experimental and computational studies of water interaction with zeolites of varying Si/Al ratios, topologies, and level of silanol defects are reviewed and analyzed. The different steps associated with the process of steaming, including the Al-O-Si bond hydrolysis and subsequent structural modifications, such as dealumination, mesopore formation, and amorphization, are evaluated in light of recent DFT calculations, as well as SS NMR and other spectroscopic studies. Differences between the mechanisms of water attack of the zeolite in vapor or liquid phase are highlighted and explained, as well as the effect of hydrophobic/hydrophilic properties of the zeolite walls. In parallel, the various roles of water as modifier of reactivity are reviewed and discussed, both for plain zeolites as well as rare-earth or phosphorous-modified materials.

KEYWORDS

water-assisted reactions; water inhibition/promotion of catalytic activity; zeolite stability in water; hydrophobic/hydrophilic zeolites; interaction of water with zeolite cations

1. Water in zeolites

The interaction of water with acid zeolites has attracted the interest of researchers and technologists for many years as water can play a crucial role in both adsorptive and catalytic properties of zeolites. Early in the development of HY catalysts, interesting debates emerged about the effect of the water evolved during calcination on the structural stability of the zeolite [1,2]. It was already evident, in those early studies, that not only external conditions, such as water partial pressure and temperature, but also zeolite structure, chemical composition, and post-synthetic modifications could greatly influence zeolite stability and consequently catalytic performance. It is also clear that these modifications are dependent on what conditions water interacts with the solid zeolite. For instance, the interaction of vapor phase water at low temperatures

is simply limited to adsorption on zeolite sites. However, at higher temperatures the interaction may lead to structural and compositional changes (e.g. steaming). In turn, liquid water can cause (reversible) chemical changes at low temperatures, but more profound structural changes at high temperatures, which can lead to structural collapse. Therefore, when discussing water–zeolite interactions, it is crucially important to specify in which regime one is operating. In the following sections, we will discuss fundamental concepts of these interactions, starting with the adsorption phenomenon (in both vapor and liquid phases) and continuing with the mechanisms by which water can alter the structure and composition of zeolites during steaming and also during attack by hot liquid water.

1.1. Water adsorption

1.1.1. Purely siliceous zeolites

The analysis of all-silica zeolites is valuable for highlighting the role of the microporous topology in determining the water structure within the zeolite, before adding the complexity of the physical and chemical interactions with the Al^{3+} cations and protons present in aluminosilicate zeolites. For example, using classical molecular dynamics (MD) simulations, Zhou et al. [3] compared the interaction of liquid water with two different all-silica zeolites – FAU and MFI – and showed two distinct water microstructures as compared to that of bulk water. Figure 1 shows the geodesic paths (the shortest unbroken H-bonded chains between any pair of waters) in bulk liquid water and in

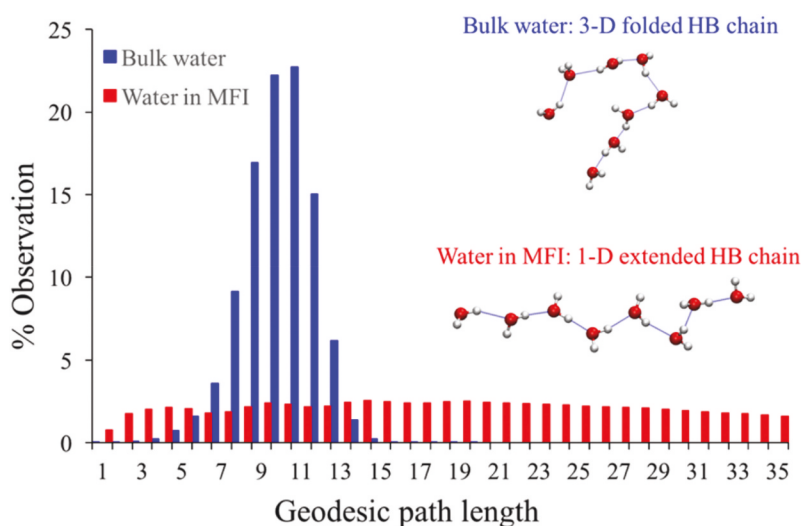


Figure 1. Distribution of geodesic path length of water in hydrophobic zeolite MFI as compared to bulk water. Reproduced from Ref. [3].

water confined within the MFI structure. These paths quantify the extension of the H-bonded network from any reference water molecule in the system. As illustrated in the figure, the distribution for bulk liquid water has a Gaussian shape centered at about 10–11 lengths; that is, each water is connected to other water within ~ 20 Å through 10–11 continuous H-bonds in a myriad of 3D configurations with an upper limit of only 15 hydrogen bonds (HB) (see [Figure 1](#)) [4]. By contrast, a completely modified structure is observed for water within MFI. In this case, any reference water can be connected to others that are far from it, through a long-range 1D chain, due to the constraints imposed by the framework topology. These authors further reported shortened lifetimes for HB in zeolites compared to those in the bulk liquid as well as a contrasting trend for the fluctuation of hydrogen bonds in the different systems. That is, for two given water molecules, the HB fluctuations increased in frequency for both FAU and MFI compared to the bulk. This trend is mostly determined by the geometry of the framework and partially by the water–zeolite interaction. Moreover, the higher fluctuation frequency found when confined in the microstructure of the zeolites was paralleled by a clear restriction in the reorientation of a given water molecule to switch H-bonded neighbors.

Computational studies also found that the structure of water and its dynamics inside the zeolite is very sensitive to the presence of structural defects. This is not so surprising since these defects may serve as nucleation centers for water molecules, which further affects the H-bonded water network. However, visualization of such an effect is a challenging task. Bukowski et al. have recently reported ab-initio molecular dynamics (AIMD) simulations of water clusters of different sizes in Beta zeolite [5]. They introduced different structural defects, such as a Sn dopant (tetravalent framework Sn), SnOH (trivalent framework Sn), and a hydrated Si defect (a silanol nest with four OH groups). By deriving the free energy and entropy changes as a function of water density in the BEA unit cell, they were able to show that, contrary to the case in defect-free Si beta zeolite, both Sn and SnOH can localize water clusters in their proximity through H-bonds, evidenced by a brighter color in the simulations that corresponds to a higher water density, as illustrated in [Figure 2](#). This kind of localization reduces the water entropy. At high water densities (23 in the unit cell), the water is more like liquid water and a H-bonded water network can be generated. Note the localized water clusters can still be preserved even as liquid-like water fills the pores. The Si(OH)₄ defects induce different behavior. Most likely due to the H bonding between the OH moieties in the silanol nests, the defect does not nucleate water molecules at low water densities (e.g., 8 water in [Figure 2g](#)), similar to Si-Beta ([Figure 2a](#)); instead, the silanol nest stabilizes more delocalized water networks in liquid water ([Figure 2h](#)), characterized by increased hydrophilicity. The role of defects in nucleating water was further supported by infrared

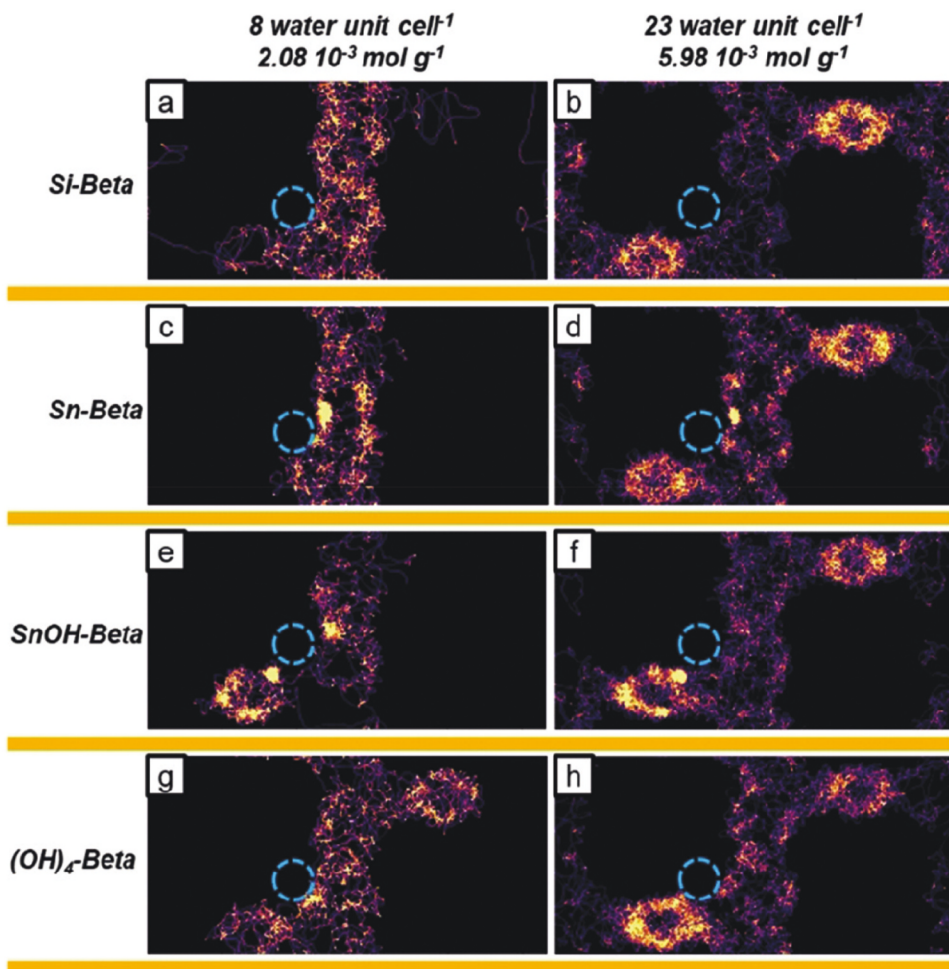


Figure 2. Time-averaged water density in each BEA model, as viewed along the [010] direction. The blue circles indicate the approximate locations where structural defects are incorporated for the c-h cases; there are no defects in those locations for the a-b cases. The bright points indicate the water density, and its correlation with the blue circles (defects) show the preferential nucleation of water near these defects in the c-h cases. Reproduced from Ref.[5].

spectra of water of varied pressures in low-defect and high-defect Si-beta, the latter of which has more silanol nests. By measuring the OH stretching frequencies, the authors showed H-bonded network in high-defect zeolite while low-defect sample adsorbs little water.

Fuchs et al. [6–14] have published extensively on water adsorption in Al-free zeolites, such as silicalite-1, and compared the behavior with that on the Al-containing NaX and NaY samples. Combining computational modeling with experimental adsorption isotherms and calorimetry they investigated the condensation transitions in these zeolites. Specifically, they simulated two different types of structural defects – one type weak, the other type strong.

The strength of these defects was adjusted with numerical values in the force field to tune the water–zeolite interaction. A strong defect means that the water–zeolite binding energy is stronger than the bulk water–water cohesive energy. Using this simplified model, they simulated the response of the framework from hydrophobic to hydrophilic; in the latter, gas-phase water was found to adsorb strongly, even at very low pressures [7]. These computational results were compared with experimental ones on defect-free silicalite, prepared via fluoride synthesis, representing the hydrophobic material and a commercial catalyst prepared via the hydroxide route, representing the hydrophilic one. Silicon Q3 sites (observed by MASSNMR) and representing internal silanols with or without associated cations were found responsible for controlling the adsorption of gas-phase water in hydrophilic samples and, ultimately, liquid nucleation through formation of water clusters [9].

More recently, as further discussed in [section 1.4](#), Zhang et al. [15] showed experimentally that a defect-free hydrophobic silicalite essentially maintained complete structural integrity in hot liquid water, while hydrophilic silicalite prepared via the standard hydroxide synthesis method, and containing internal silanol defects, lost all crystallinity under similar conditions. Thus, while the interior pore volume of a defect-free silicalite is essentially hydrophobic, the introduction of internal silanol defects leads to water cluster formation from the vapor phase and nucleation sites at lower P/P_0 values. Fuchs et al. further demonstrated that internal silanols containing a monovalent cation like Na^+ are more strongly hydrophilic than isolated silanols, and lead to formation of water hexamers in NaX and NaY structures [14] that were confirmed by neutron scattering studies (see [Figure 3](#)) of adsorption of vapor-phase water of different pressures [16]. An important conclusion from their work is that the distance between defect sites, or correlation length, controls water nucleation since the interior of a defect-free silicalite is mostly hydrophobic.

Some studies have indicated that when the sample is free of internal silanol groups, the Si/Al ratio may dictate the location of condensation of water from the vapor phase [17]. Moreover, it has been proposed that an acidic proton is more attractive to water than a silanol group. Olson reported the adsorption of vapor-phase water in ZSM-5 with varying Si/Al ratios and showed that at low pressure strong adsorption of water is directly dependent on the Si/Al ratio and that this strong adsorption of water is on acidic protons associated with framework Al atoms [18]. They further showed that at very low loadings of water, each proton in a high-silica ZSM-5 was solvated by four water molecules. Also, there has been discussion about changes in the number of compensated cations when varying the Si/Al ratio, which affected water adsorption. For example, Fuchs et al. have used Grand Canonical Monte Carlo (GCMC) simulations to illustrate the water physisorption in NaX with Si/Al ratios between 1.53 and 3. They found that the location of Na can change

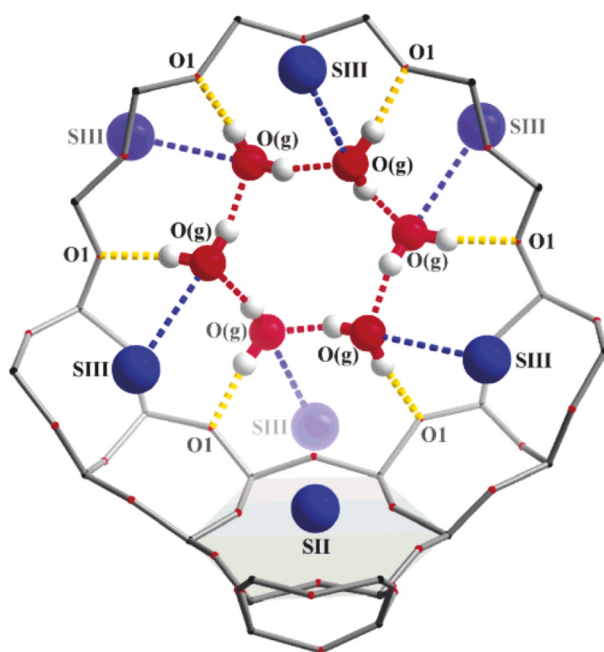


Figure 3. Location of water hexamer in structure NaX(72), where there are 72 water molecules in the unit cell. Reproduced from Ref. [16].

from site I in the hexagonal prisms to I' inside the sodalite cages, which is driven by water adsorption in the sodalite [14].

In addition to the Si/Al ratio, the nature of the compensating cations may also affect water adsorption. For example, XRD and NMR studies combined with water uptake measurements have shown that the cation type and charge can significantly influence the amount of adsorbed water; addition of Na^+ , Li^+ , and Mg^{2+} resulting in increasing amounts of water adsorbed in the same LTA or FAU structure, respectively, due to increased available microporous volume, which facilitate the water uptake [19].

MCM-41 is also a purely siliceous nanoporous material, albeit with ca. 2–3 nm channel diameters that are significantly larger than typical zeolite dimensions. Using NMR to detect water uptake versus time, Thomas et al. [20] observed more complex adsorption profiles than those shown above for faujasite. Initially, a rapid water vapor uptake occurs promoted by the presence of silanol groups on the MCM walls; this first uptake is followed by a slower uptake as larger water clusters and ultimately liquid water form. In each of the two regions of the isotherm, water uptake increases linearly with time. The presence of SiOH groups inside the confining solid, whether nanoporous or mesoporous, appears to be the determining factor for controlling water uptake, but it is reasonable to expect that adsorption enthalpies could also depend on the average diameter of the pore or channel in purely siliceous

materials. To our knowledge, a systematic study of water adsorption as a function of the characteristic size of the confining solid has not been yet reported.

While the main focus of this contribution is on water adsorption as it relates to catalysis in zeolites, siliceous zeolites are being increasingly used in membranes for separation processes. Clearly, development of efficient membranes also depends on a deep understanding of the relationship between water and the zeolite structure. For example, Wang et al. [21,22] have recently demonstrated that silanol defects inside MFI channels significantly impact water diffusion and overall permeability, both of which decrease by several orders of magnitude with increasing internal silanol defect density due to the strong interaction between the defects and adsorbed water. Therefore, this type of study not only impacts catalytic processes, but separation methods as well.

1.1.2. Acidic zeolites

After discussing all-silica zeolites with and without structural defects, we focus here on aluminosilicates, where some of the T sites are occupied by Al instead of Si, with their deficient charge balanced by protons. These substitutional Al atoms are also hydrophilic defects, and they change the structure of water confined in the channels of zeolites significantly.

Relatively simple experiments can be used to illustrate the contributions from zeolite structure or composition on water adsorption. For example, Figure 4 shows gravimetric adsorption results for water vapor in the same zeolite structure, i.e. a commercial HZSM-5 catalyst from the MFI family of

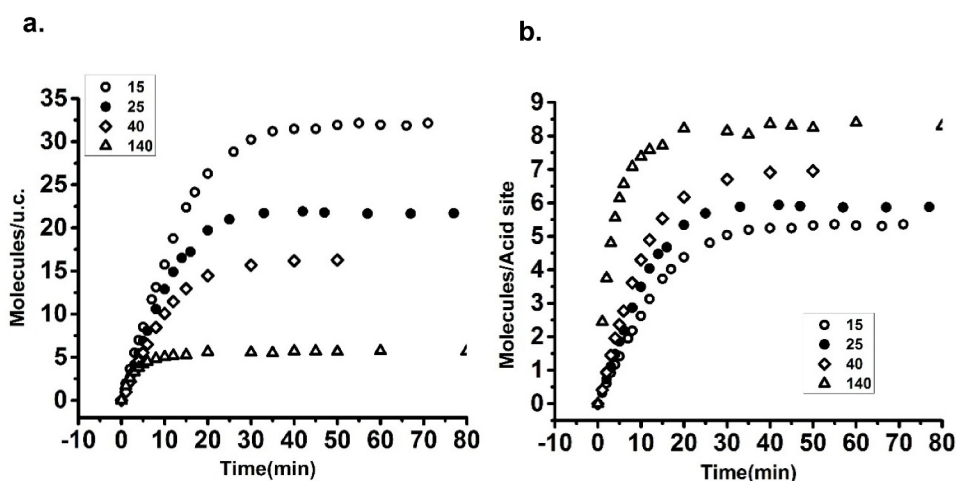


Figure 4. Gravimetrically determined water uptake rates and maximum loadings for dehydrated acidic HZSM-5 catalysts exposed to ambient moisture, plotted as a function of (a) number of water molecules per unit cell, and (b) number of water molecules per acid site. Different Si/Al ratios are identified in each legend. The catalyst particle bed thickness was 1–2 mm on average. Reproduced from Ref.[23].

zeolites, as a function of the Si/Al ratio in the zeolite framework and at ambient conditions [23]. Figure 4a indicates that water vapor adsorbs at individual framework Al sites and their associated acid site in the zeolite interior; the total water sorption increases with increasing Al content up to 32 molecules per unit cell for the highest Al content with detailed site specificity revealed by NMR measurements. The results from Figure 4b are somewhat less intuitive, as the data suggest that decreasing framework Al content is accompanied by an increase in the water molecule cluster size adsorbed at each acid site. However, even an Al-free silicalite MFI structure can adsorb water vapor, and the role of internal silanol defects and external hydroxyls on the crystallite surface can play a larger role at low framework Al content.

The simple experiment in Figure 4 inspires additional questions about the role of water's interaction with the surface of zeolite catalysts. For example, is the impact of water on catalyst activity and stability larger for high acid-density catalysts? What are the key factors governing nucleation of water molecules and subsequent condensation on or in zeolites? Can rational chemical modification of zeolite surfaces be used to control the impact of water in the vapor and liquid phases? Do only framework Al sites control water adsorption, or do non-framework sites contribute? Are adsorbed water molecules a potential proton source? Can water adsorption enhance reaction rates without ultimately leading to framework hydrolysis? These questions and related content will be addressed in the following sections. Additionally, deciphering the many recent reports regarding water in zeolites requires that one know whether adsorption involves liquid or vapor-phase water at the conditions discussed, and more fundamentally, if water remains adsorbed at the high-temperatures characteristic of many reactions. For example, in an early work Gorte showed that vapor-phase water underwent isotopic exchange with acidic protons in HZSM-5, and that at room temperature water adsorbed with a ΔH_{ads} equal to 12 kcal/mole at the acid site [24]. More recently, Chen et al. [25] showed that water underwent isotopic exchange with isobutane at room temperature, acting as a proton source in concert with the zeolite active site. However, the degree to which gas-phase water adsorption impacts proton transfer at elevated temperatures used for hydrocarbon conversions is uncertain. By contrast, water adsorption, condensation to form a liquid phase, and subsequent solvation of the reaction coordinate creates a complex reaction system, requiring the additional consideration of a transient catalyst structure resulting from framework hydrolysis.

Another intriguing factor upon water adsorption on protonic zeolite is the potential protonation of water, generating hydronium ions in zeolite. It is generally believed that a very low dose of water, such as a single water per bridging hydroxyl group, cannot lead to protonation of water [26–29]. Addition of a second water changes the energy difference between the neutral water adsorption and water protonation [30]; the protonation of water

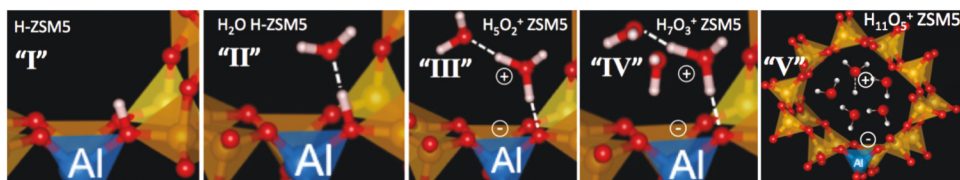


Figure 5. DFT-optimized structures illustrating the process of hydrating the zeolite with increasing numbers of water molecules. Reproduced from Ref. [26].

forming hydronium ions was favored (Figure 5), which was supported by more recent calculations and X-ray absorption near edge structure (XANES) spectra [26]. Sauer and coworkers [31] used density functional theory (DFT) calculations and Car-Parrinello MD simulations to show that proton affinity increased with increasing water cluster size. They find that water clusters involving four waters lead to proton transfer from the zeolite lattice forming the most stable protonated clusters in H-SSZ-13 and that, in the presence of three water molecules, proton transfer to the water is only short-lived at room temperature. Qualitatively, this is in agreement with earlier experimental ^{27}Al NMR work showing that on average, three water molecules per acid site are required to facilitate proton transfer from the lattice and generate a protonated water cluster [32]. Our previous DFT study showed that protonation of a single water can only happen when the two Al form a Al-O-Al pair, the latter of which is unlikely due to the restrictively small distance between the charges, which forms the basis for “Löwenstein’s rule” [33]. However, recent AIMD work on chabazite has demonstrated that non-Löwenstein Al-O-Al configurations are energetically preferred in the absence of water, while the presence of water molecule clusters/solvation leads to an Al distribution consistent with Löwenstein’s rule and active site best described as a protonated water cluster associated with the framework [34]. Clearly, the water-loading dependence of proton transfer as well as the dynamic nature of the structure of the framework BAS must be carefully considered. We further showed in AIMD simulations that the proton in the bridging hydroxyl group can become delocalized in the water cluster interacting with the acid sites and dynamically shuttling back and forth along a chain of water [35]. The solvation of the proton also depends on its location. For example, in the case of an Al-O-Al pair, solvating the proton between the two Al (Al-OH-Al) is unfavorable, while the terminal proton Al-OH-Al-OH is similar to an isolated Bronsted proton and its solvation by water is more favorable [33,34]. We also notice that when comparing the stability of Al pairs in the zeolite framework, semi-local functionals such as PBE tend to stabilize the Al-O-Al pairs while correction of the charge delocalization error using hybrid functionals suggest spaced acid sites are more thermodynamically favorable [33]. It is worth noting that the exact distribution of Al pairs is also determined by the kinetics in synthesis

rather than just the thermodynamic stability. This formation of hydronium ions upon water adsorption may have strong consequences on the catalytic activity of the acidic species as discussed later in this review.

1.1.3. Competitive adsorption of water and hydrocarbons

The impact of water on the kinetics of hydrocarbon reactions in zeolites is treated elsewhere in this review. In addition, water evolved during the course of a reaction, e.g., methanol conversion to hydrocarbons, has been discussed in recent literature [36]. An initial query into the role of water in zeolitic reactions requires evidence of differential or competitive adsorption of water versus hydrocarbons. Zeolite structure type, composition, and history will significantly influence experimental outcomes, but recent results demonstrate that experimental methods are available to probe water co-adsorption. For example, in-situ and variable pressure experiments for methanol and water co-adsorption in mordenite (MOR) revealed that methanol preferentially adsorbs at sites in the 12 MR channels, while water adsorbs at both 12 MR and 8 MR sites [37]. It is unclear from those reports whether such a distinction is important under reaction conditions, where it has been reported that reaction rates for carbonylation and cracking in MOR are site-dependent [38,39]. Water and toluene co-adsorption was compared on siliceous MFI versus Al-rich FAU zeolites; it was found that only in the latter, water was able to compete for adsorption in the catalyst interior, assisted by the high density of framework Al and silanol defect sites. In the former, toluene adsorption was independent of water's presence, while water adsorption occurred exclusively on the external surface of the crystallite [40]. A similar conclusion of competitive adsorption between benzene and water was drawn on several other zeolites [41]. Benzene is a good representative for a variety of hydrophobic substances and this conclusion may not be applied for water-miscible compounds such as alcohols. Indeed, in early work, Gorte showed that methanol preferentially adsorbs on HZSM-5 active sites, and it is able to displace pre-adsorbed water [24]. In contrast, water was not able to displace methanol.

1.2. Water-assisted chemical and structural modification of zeolites

1.2.1. Dealumination by steaming. Mechanistic aspects

Zeolite steaming is a post-synthesis thermal treatment extensively used by zeolite manufacturers when adjusting the structure and composition of the original microcrystalline material to the specific intended applications [42,43]. For example, the typical Si/Al ratio of as-synthesized faujasite Y is around 2.5, which is too low for utilization as the active component in fluid catalytic cracking (FCC) catalysts. Low Si/Al ratios result in exceedingly higher extent of coke formation and hydrogen transfer than those specified in the FCC operation. Also, the microporous diffusion path of as-prepared Y zeolite is

longer than that needed to optimize intracrystalline residence time of reactants, intermediates, and products. Thermal steaming causes an increase in Si/Al ratio (decrease in acid site density) by extracting Al ions from the framework and generates mesoporosity that modifies the topology of the crystallite and enhances the connectivity of intraframework channels. As a result, the rate of mass transfer within the crystallite is enhanced, coke formation is reduced, and hydrogen transfer can be controlled. In fact, the extent of dealumination is known to affect product distribution and intrinsic activity. It is known that the interaction of water with the zeolite framework results in hydrolysis of the Al–O and Si–O bonds and removal of Al from its tetrahedral position and creation of extra-framework Al (EFAl) species [44]. While this process has been empirically optimized and known by zeolite practitioners for a long time, the exact dealumination mechanism has been understood only recently.

1.2.2. How does water react with zeolites?

Recent solid-state NMR studies have shown that a chabazite (CHA) zeolite undergoes oxygen exchange when it is exposed to ^{17}O -enriched water, even for less than an hour at room temperature [45]. Triple-quantum NMR analysis (MQMAS) suggests that while isotopic exchange readily occurs on framework oxygen in both, Si–O–Si and Si–O–Al groups, the latter preferentially occurs during the first exposure, while the former takes a much longer time, reaching a constant ratio after more than 100 days. Moreover, despite a significant extent of oxygen exchange, the framework remains unaffected even after many days in the liquid bath (at room temperature). In fact, the ^{27}Al MAS NMR spectra show no formation of additional octahedral Al species after the treatment. Moreover, the line corresponding to the tetrahedral Al stayed very narrow before and after the treatment, indicating a very small quadrupolar coupling constant, which is consistent with a symmetric environment around the framework Al, unchanged by the exposure to liquid water. Another interesting observation was that when the enriched zeolite was exposed to wet air, i.e. ^{18}O -water vapor, the ^{17}O signal remained unchanged, which indicates that liquid water is needed to accomplish the isotopic exchange at room temperature. This is in contrast to zeotypes like silicoaluminophosphates, where it has been shown that vapor-phase water attack leading to acid-site framework hydrolysis occurs in SAPO-34 at room temperature [46].

Figure 6 shows a proposed mechanism for water attack at a framework Al site, as has been discussed in several reports involving both theory and experiment [47,48]. While the depicted scheme focuses on a sequential addition of individual water molecules, more likely framework hydrolysis occurs through cooperative water cluster solvation, as recently discussed [49]. In this aspect, theory is currently leading experimental work. For example, recent enhanced-sampling DFT-MD simulations indicate that the collective or

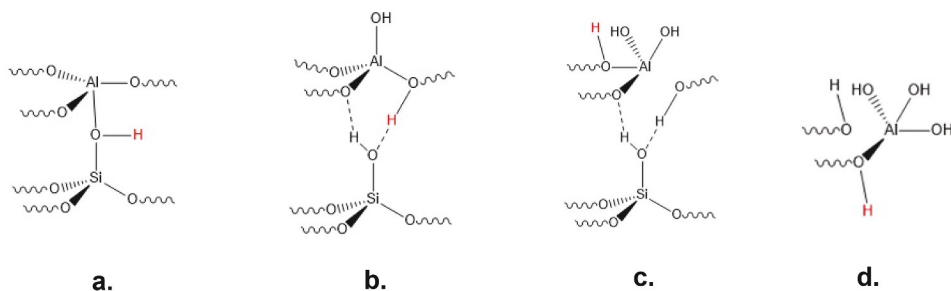


Figure 6. Schematics depicting (a) the well-known BAS in the zeolite lattice, and intermediate structures formed via attack of (b) one, (c) two, and (d) three water molecules at the BAS. The Al atoms in structures (b) and (c) give rise to the Al(IV)-2 species. Reproduced from Ref. [47].

cooperative action of water provides the lowest free energy for hydrolysis of Al-O bonds under steaming conditions [50]. While dealumination in zeolite catalysts probably represents the larger area of industrial relevance, desilication in SAPO materials is also relevant to methanol-to-hydrocarbon chemistries. Recent work, based on comparisons to the zeolite analogue SSZ-13, indicated that multiple water molecules could lead to reduced free energies of framework desilication in SAPO-34 through coordination with neighboring Al sites [51]. Based on the current literature, it appears likely that proton shuttling afforded by multiple waters is central to the mechanisms of framework hydrolysis.

We note that while the role of water molecules and clusters on Al-O and Si-O bond hydrolysis is an important emerging area, we are also learning that understanding these challenges is only one step in many that ultimately should explain the observed changes induced on zeolite structures by the high-temperature water treatments. As will be discussed in more detail later in this review, depending on the framework type, initial hydrolysis steps may be rather facile and not rate-determining when considering morphological changes. Instead, the role of water in not only hydrolyzing structures but also stabilizing extra lattice species in various forms is likely key to understanding the effects of water. In this sense, the presence of water, the location of T sites within a confined lattice, and the proximity to other charged species can all play a role in the rates and extents of desilication and dealumination.

In addition to the tetrahedral framework Al's that form bridging acid sites, often referred to as Al(IV)-1 BAS's, framework Al sites in zeolites can also exist as partially coordinated tetrahedral sites denoted Al(IV)-2 [47]. These sites are themselves a type of framework defect caused either by incomplete framework dehydration during crystallization, or as a result of partial hydrolysis of an Al(IV)-1 site, and are characterized by two hydroxyl groups attached to the Al atom. Previous work has shown that they contribute to catalyst reactivity, since reaction rate constants for low-temperature isotopic exchange reactions

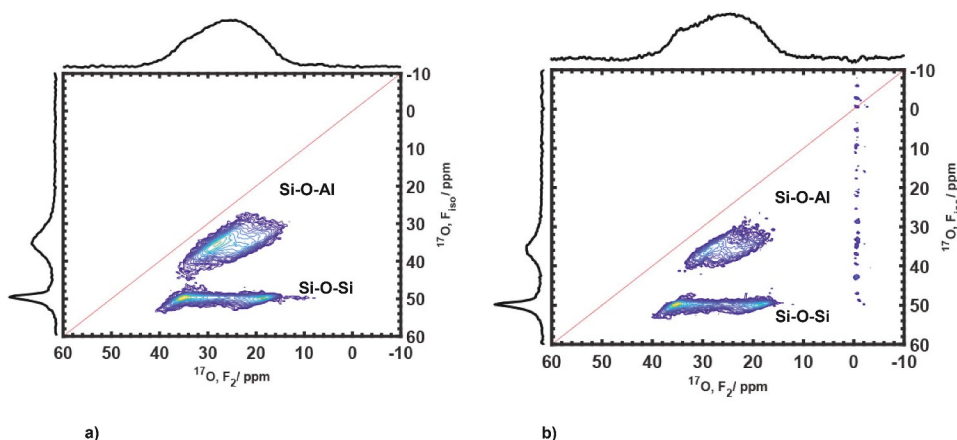


Figure 7. ^{17}O MQMAS NMR data showing overall reduction in Si- ^{17}O -Al incorporation of zeolite HZSM-5 framework from room-temperature exposure to H_2^{17}O liquid for a catalyst that was washed with ammonium hexafluorosilicate (AHFS) (b), relative to the starting HZSM-5 (a). AHFS removes the partially coordinated framework Al(IV)-2 sites, which along with fully coordinated Al(IV)-1, are framework acid sites. Unpublished work by J. White et al.

markedly decrease when Al(IV)-2 sites are absent. Figure 7 shows the results of ^{17}O MQMAS data acquired on zeolite HZSM-5 with (a) and without (b) Al(IV)-2 sites, following exposure to ^{17}O -labeled liquid water for similar time periods of several days. The reduced intensity of the framework Si- ^{17}O -Al correlation in (b) vs. (a), as well as the lower signal-to-noise of the projection on the horizontal axis, shows that Al(IV)-2 sites are also involved with oxygen exchange from liquid water.

Recent periodic DFT calculations have been conducted to identify the elementary steps involved in dealumination, estimate the relative energy barriers for each step, and explore the role that the type of framework and nature of the specific T site involved may have. For example, Silaghi et al. [48] performed systematic DFT study of water interaction with FAU, MFI, MOR, and CHA to form EFAl species. They showed that while the exact rate-determining step in the multistep hydrolysis could differ among the different frameworks, the dealumination was always initiated by water adsorption on an Al cation in an anti-position to the proton in the BAS; this leads to the formation of a pentahedral (or distorted tetrahedral) Al species in the four different zeolites (see Figure 8). It is worth noting that similar partially hydrolyzed, distorted tetrahedral Al species were inferred from combined solid state NMR and first-principles calculations; these species exhibit an increased chemical shift and unique quadrupolar parameters relative to the BAS in the dehydrated state [47].

The intrinsic activation barriers for the hydrolysis steps vary quite a bit among the four different zeolites but they are all rather moderate, with the majority of them in the range 60–120 kJ/mol. The specific activation barriers

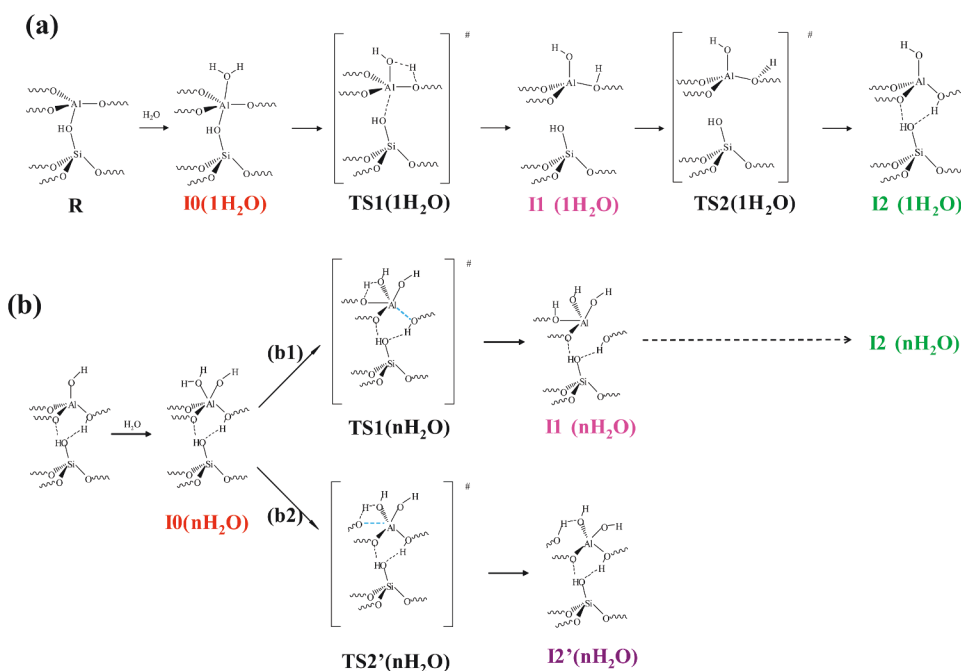


Figure 8. Schematics of the dealumination process. (a) Attack of the first water molecule ($n = 1$) on an Al atom in anti-position to the BAS ($I0(1H_2O)$) followed by a 1,2-dissociation giving rise to $I1(1 H_2O)$. The H-bond between the newly created BAS and a silanol leads to a more stable intermediate $I2(1 H_2O)$. (b) Attack of the second water molecule ($n = 2$) on the Al atom in anti-position to the BAS ($I0(nH_2O)$) followed by breaking of another Al-O bond. Reproduced from Ref. [48].

also depend on the location of the BAS within the same zeolite. In the case of faujasite, the Al corresponding to the T1O1 position was taken as starting point since this site is thought to be the one with the highest protons occupancy among the preferred proton positions [48]. The overall free energy change upon introducing four water molecules is uphill; in this process, each hydrolysis step has a comparable intrinsic barrier, while the overall reaction rate seems to be determined by the third hydrolysis step that creates an $Al(OH)_3$ species, still bonded to the framework. In FAU, comparing free energy profiles of hydrolyzing the T1O1 site in the sodalite cage and T1O3 in the super cage, the intermediate, partially hydrolyzed structures are more stable along the dealumination pathway of T1O3. The same trend holds true for HZSM5, where the overall rate is limited by the third hydrolysis step. The calculations also suggested that the intersection regions of ZSM-5 is the place where dealumination is favored both kinetically and thermodynamically over the sinusoidal and straight channels. Combining this favorable dealumination at the intersection and the reduced stability of the EFAl in the sinusoidal channel as compared to the linear one and the intersection, the authors suggested a favored formation of mesopores along the sinusoidal channels.

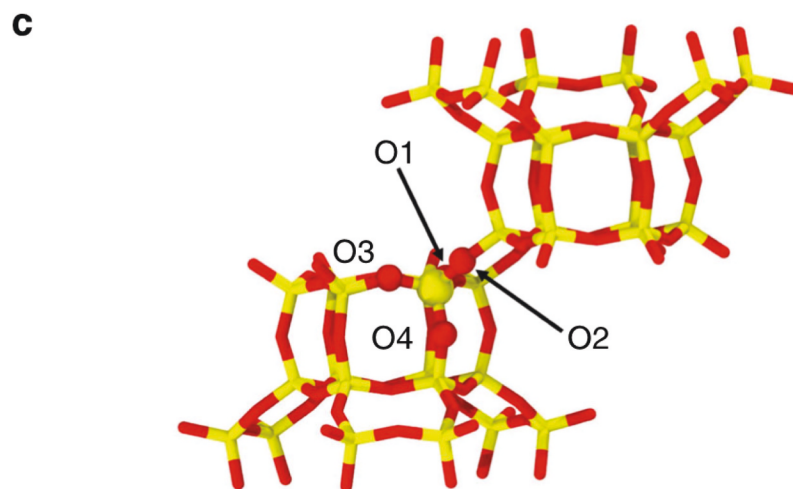
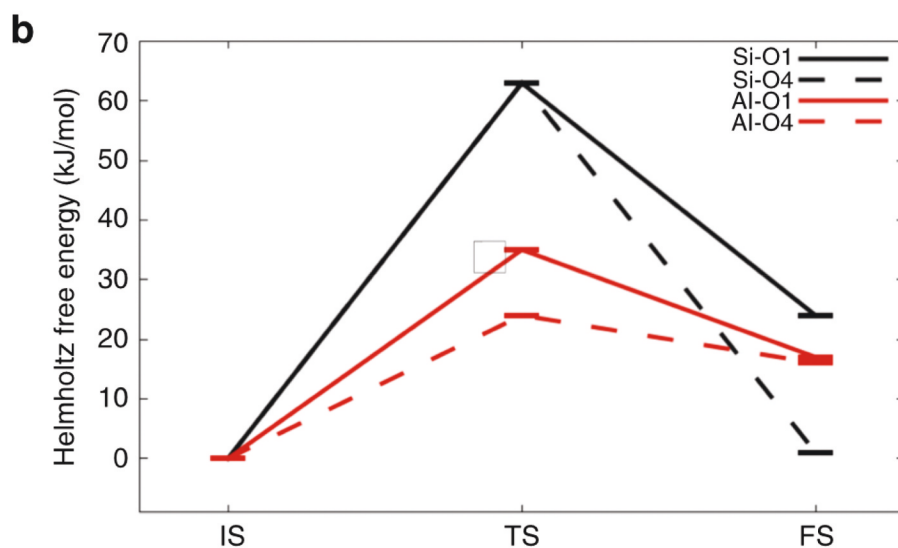
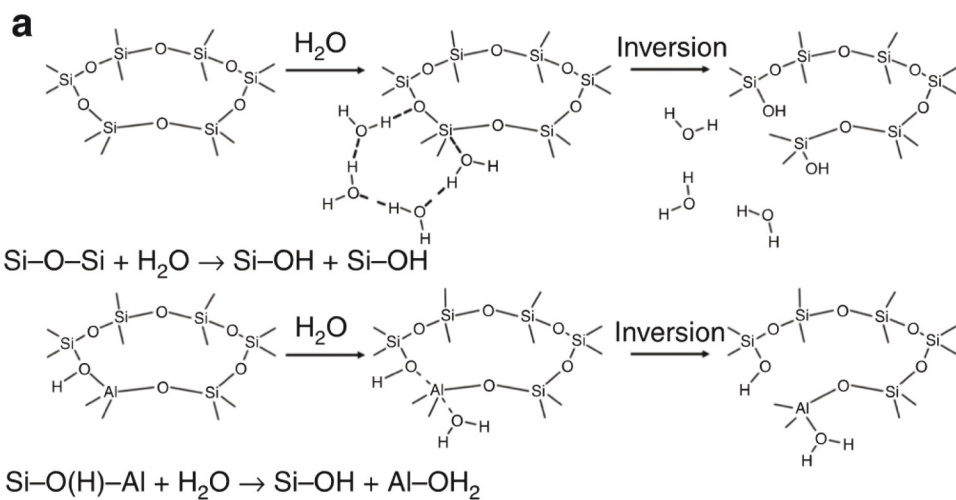


Figure 9. Mechanism and energetics for the hydrolysis of bonds in zeolites. (a) Both, the Si-O and Al-O bond breaking start with non-dissociative water adsorption. (b) The relative Helmholtz free

energies of initial compounds (IS), transition states (TS) and final products (FS) of the hydrolysis of Al–O and Si–O at O1 and O4 sites. (c) Schematic of the Si-only CHA cell showing the four crystallographically distinct oxygen atoms: yellow indicates the silicon atoms and red the oxygens. Reproduced from Ref. [54].

Overall, it is worth noting that the water adsorption and reaction on Al in an anti-position to BAS leads to lower activation barriers than other proposed mechanism. It is believed that dealumination is favored over desilication. For example, Malola et al. [52] performed DFT calculations for chabazite and showed that the effective barrier is about 40–50 kJ/mol lower for dealumination than desilication. The dealumination results in formation of $\text{Al}(\text{OH})_3(\text{H}_2\text{O})$ that is H-bonded with the zeolite framework. In this work and later by the same authors [51], water strongly adsorbs at the proton site. Indeed, Silaghi et al. [53] have shown that water adsorbing at the anti-position can further lower the activation barrier for dealumination.

More recently, Heard et al. [54] performed constrained ab initio MD simulations and compared the hydrolysis of the bond breaking of the first Si–O and Al–O bonds. They showed Si–O bond-breaking in silicious framework (such as silicalite) could proceed via non-dissociative water adsorption on Si, assisted by proton transfer via the Grotthuss [55] mechanism in liquid water (15 H_2O molecules per 36 T site supercell), and Si–O bond breaking in an anti-position to adsorbed water (Figure 9). The first water adsorbs on a Si site, creating a penta-coordinated Si. This adsorbed water and a framework O atom bonded to the same Si are bridged by a chain of solvent water molecules. The water dissociates to an OH forming a covalent bond with Si, while the proton is shuttled through this H-bonded water chain and attacks the axial framework O, breaking the Si–O bond at the site opposite to the initial water adsorption. This mechanism (water anti-position adsorption and proton shuttling) further lowers the free energy barrier to 63 kJ/mol for the first Si–O bond hydrolysis. The breaking the Al–O was shown to have an even lower barrier (around 20–30 kJ/mol); here, water adsorbs at the anti-position site, leading to the Al–O(H) bond dissociation.

This easier-than-expected cleavage of Al–O and Si–O bonds upon interaction with water was experimentally validated by observation of isotopic substitution of ^{17}O in the framework of a chabazite zeolite in less than one hour of contact with labeled water at room temperature. An important point to emphasize here is that this isotopic substitution was not accompanied by framework degradation as no significant octahedral Al moieties were produced during this treatment. It is therefore plausible that the low-temperature water activation of Al–O and Si–O bonds is reversible; only when the temperature is high enough to give the Al species mobility the process may become irreversible.

It is also interesting to note that Na-exchanged MOR without Brønsted acid protons shows similar oxygen exchange into the zeolite framework [45]. Pugh et al. [45] observed Si- ^{17}O -Al and Si- ^{17}O -Si in the ^{17}O MAS and MQMAS spectra of Na-MOR after leaving in $\text{H}_2^{17}\text{O}(\text{l})$ for 25 days. Some of Pugh's preliminary results also indicated that this ^{17}O enrichment is slower for Na-MOR with enrichment primarily of Si-O-Al species observed after 2 days. A systematic study of the role of proton in introducing O into the framework is still needed. It is worth noting that previous work has shown that the Brønsted acid protons may leave the framework oxygen and be solvated by water upon interaction with liquid water [26,35] as discussed above in Figure 5; it is thus not very surprising that both the Al-O bond dissociation and the formation of EFAL are rather independent of the cation.

Once EFAL species are created, the role of water at promoting their stability, mobility, and migration is equally important. As discussed in section 2.6, these extra lattice species can have profound influence on reactivity. Cationic species may serve to alter the environment surrounding an active site, with proposed shifts in adsorption enthalpies and entropies and transition state energetics. Excess mobility of extra lattice species will create alumina clusters, which tend to aggregate and serve as Lewis acids. The transition from tetrahedral to octahedral, and the role of both charge and water on the stability of these species was discussed by Ruiz et al. [56]. Through Hartree-Fock calculations, they investigated the importance of hydrogen bonding in an aqueous environment on the ultimate stability of penta- and hexacoordinated Al species. They proposed that these penta- and hexacoordinated species were greatly stabilized by the presence of second shell water molecules, indicating that water is not only involved in initial hydrolysis steps, but greatly influences the nature of

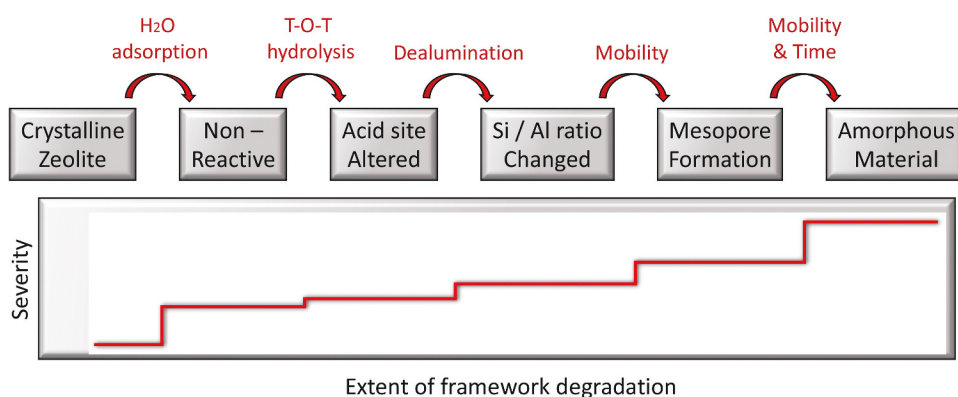


Figure 10. Schematic depiction of the process of dealumination by steaming. The initial steps including water adsorption and T-OT bond hydrolysis are reversible and with relatively low energy barriers. The subsequent steps that result in dealumination and mesopore formation are irreversible and require higher severity (H_2O concentration, temperature, time). They involve a higher energy barrier.

produced extra lattice species as well. Bhering et al. [57] used DFT calculations to show that the interaction between water and extra lattice Al species modifies both the resulting charge and the preferential location with respect to the framework. For example, they showed that a fully dehydroxylated Al^{3+} species reacts very exothermically with water to generate $\text{Al}(\text{OH})_2^{2+}$ species, but subsequent hydration to form monovalent cations or subsequently neutral species carries far lower enthalpic driving force. However, a monovalent AlO^+ or $\text{Al}(\text{OH})_2^+$ species tends to react with framework T sites as an exchangeable cation. Higher valent species tend to preferentially occupy spaces with higher T site density to balance the charge. While this may appear obvious, it implies that the ultimate migration of extra lattice species to preferentially titrate a single T site, occupy spaces with proximate sites, or exhibit less interaction with the framework and ultimately form larger alumina clusters will highly depend on the degree of hydration. Higher degrees of hydration form species that are likely to interact less strongly with the charged surface, which

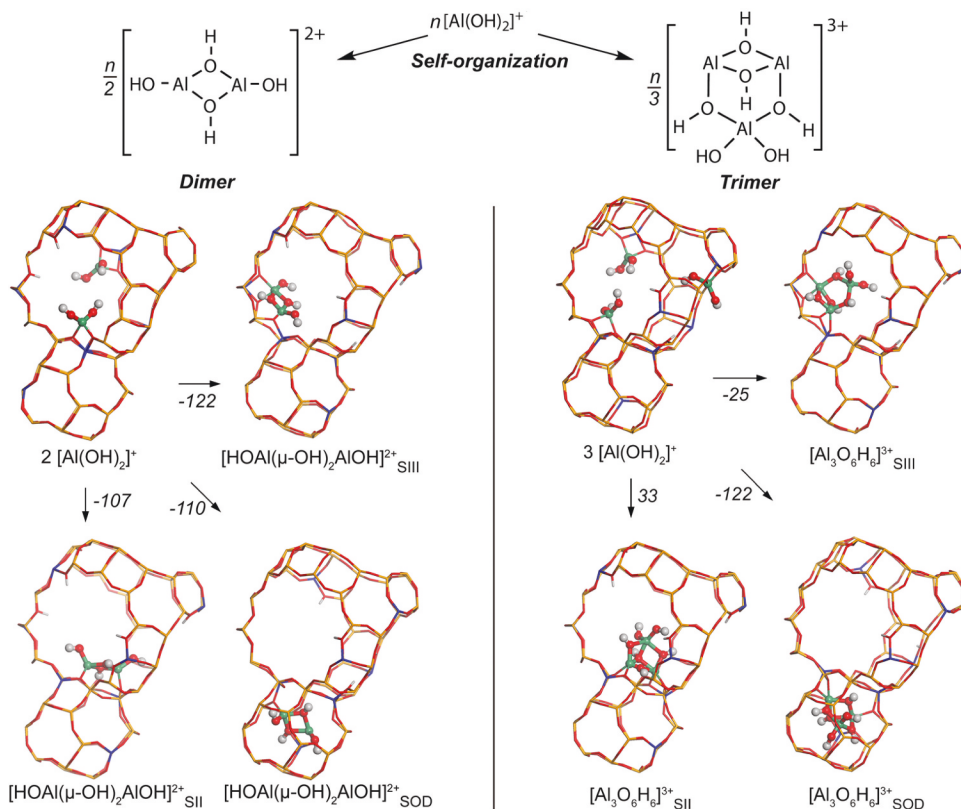


Figure 11. Optimized structures and relative stabilities of bi- and trinuclear EFAls formed by the self-organization of mononuclear $[\text{Al}(\text{OH})_2]^+$ cations in faujasite. The reaction energies in kJ/mol correspond to the differences in total energies of the faujasite models containing multinuclear EFAl products and the respective starting configurations containing two or three isolated $[\text{Al}(\text{OH})_2]^+$ located in a single faujasite unit cell. Reproduced from Ref. [60].

influences migration rates and ultimately impacts the nature of active sites as well as pore blocking and mesopore formation. This formation of hydronium ions upon water adsorption may have strong consequences on the catalytic activity of the acidic species as discussed later in this review.

Based on the observation of facile O-exchange between zeolite framework and liquid water without framework breakdown, combined with the reaction profile reported by Silaghi et al., it is unlikely that entire dealumination process, accompanied by the extraction of EFAl species and creation of mesopores, is limited by the first water attack or first Al-O bond hydrolysis; otherwise significant structural degradation and changes in ^{27}Al chemical shift should have been observed at low temperatures. Instead, we think it is likely that at low temperatures, the Al-O bond undergoes very dynamic changes upon interaction with water, forming partially hydrolyzed, distorted Al species, which may revert to the original BAS by dehydration. In these (reversible) fast hydrolysis and dehydration steps, the oxygen can thus be exchanged between the framework and the water solvent, without degrading the framework. Much higher severity – in terms of temperature, water partial pressure, and treatment time – is required to achieve the profound (irreversible) framework modifications obtained during the full steaming process. This important differentiation has been recently made by Heard et al. [58], who highlighted the different extents of framework degradation. The interaction of the zeolite with water starts with a non-reactive adsorption, it is followed by reversible hydrolysis of the T-O bond, mild zeolite dealumination (or desilication), mesopore formation, and total amorphization (see scheme in Figure 10).

By creating intracrystalline mesoporosity it is possible to break up the micropores facilitating the transport of large molecules in and out the zeolite framework channels. Since the mesopores are opened to the exterior of the zeolite, the generation of intracrystalline mesoporosity is equivalent to the expansion of the external surface area, thus reducing the diffusion path for reactants and products [59].

This profound irreversible framework modifications may be caused by zeolite dealumination as well as diffusion and nucleation of these extra framework species. Liu et al. [60] investigated the formation of cationic, multinuclear EFAl clusters. For example, as shown in Figure 11, formation of bi- and trinuclear EFAls is significantly favorable over two and three mononuclear EFAl species by over 100 kJ/mol. The trinuclear EFAls are particularly favored in the sodalite cage over the supercage where the narrower confinement in the sodalite stabilizes cationic species. This nucleation of multinuclear species must start with diffusion of EFAl. They calculated the diffusion of $[\text{Al}(\text{OH})_2]^+$ cation from its preferred position at a framework Al to the next Si-O-Si site and showed an activation barrier of 69 kJ/mol with a reaction energy of 51 kJ/mol. Further diffusion to the following Si-O-Si site needs to overcome an activation barrier of 46 kJ/mol with a reaction energy of 10 kJ/

mol. Considering the endothermic diffusion, we can calculate that the overall diffusion barrier from a framework to the second next Si-O-Si site may thus be 97 kJ/mol, which is considerably higher than the water-assisted cleavage of the Si-O-Al bond as shown in Figure 9. Thus, as discussed in Figure 10, these different elementary steps in framework degradation may happen at very different time scales and under very different experimental conditions.

1.3. Use of zeolite modifiers to prevent water vapor attack and stabilize the structure

1.3.1. Rare earths in faujasites

The hydrothermal stability of zeolite catalysts is especially important in FCC. During each regeneration cycle, the FCC catalyst is exposed to water vapor (steam) at temperatures exceeding 800°C. As a result, the so-called “equilibrium” catalyst ends up with a much lower activity than the fresh catalyst mostly due to dealumination of the framework. The proton-form zeolites present in the FCC catalyst tend to lose the tetrahedrally coordinated Al; without a stabilizer they would lose all the acidity. Specifically, it is well known that the incorporation of rare earths (such as La) in zeolite Y [61–64] and phosphorus in ZSM-5 [65,66] helps retain Al in the framework. In the

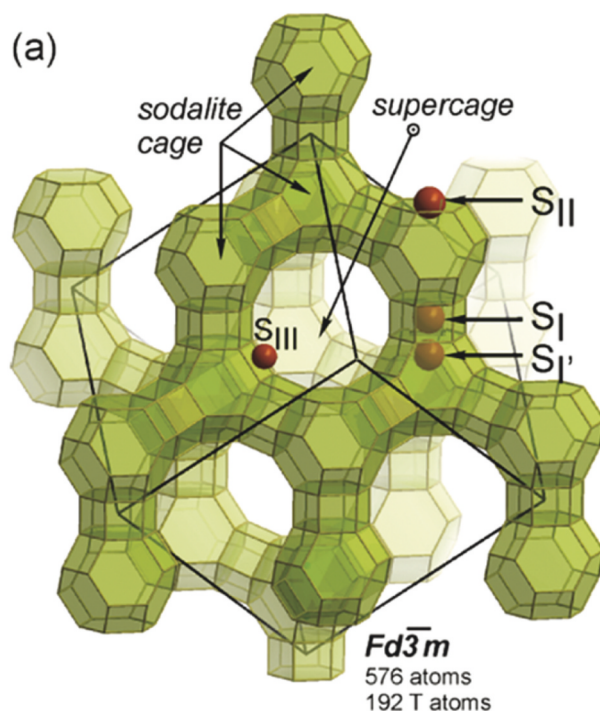


Figure 12. Diagram of the faujasite structure illustrating the cation site designations. Reproduced from Ref. [71].

following sections we analyze the different views proposed in the literature on how the nature and location of these zeolite-modifiers influence the thermal stability of the framework in the presence of water vapor.

In modern FCC catalysts, HY zeolite is usually the most active component, embedded in a porous silica–alumina active matrix and modified by the addition of several promoters. Among them, rare earth elements (RE) – mostly La – enhance catalyst activity and prevent the loss of acid sites during operation. The enhanced stability of RE-containing zeolites was recognized practically at the same time as the first introduction of faujasite Y in FCC catalysts [67]. Without these RE stabilization agents, the periodic regeneration steps, to which the zeolite is subjected inside the FCC unit, would cause severe dealumination. In the regenerator of the FCC unit, air is introduced to burn off the coke deposited during the reaction step. The steam produced by this combustion causes removal of Al cations from their tetrahedral positions in the framework, altering the acidic and structural characteristics of the zeolite; the presence of RE prevents this dealumination. While RE have been in practically every FCC catalyst since the 1960s, their exact role during the various thermal stages of the operation and their interaction with water have been a matter of discussion until today.

In most preparation methods, RE cations are incorporated onto the FCC catalysts by 3–4 ion exchange cycles with an aqueous solution of an appropriate La salt, such as lanthanum nitrate, and then calcined to a relatively high temperature [68,69]. An interesting cation migration occurs during this process. In aqueous solution, the La exists as $\text{La}[\text{H}_2\text{O}]_n^{3+}$; this hydrated cation is large enough to be sterically prevented for exchange in some cation positions of the zeolites [70]. That is, while the original Na of the faujasite (NaY) used as base material occupies all the cation positions associated with framework Al (see Figure 12), the Na cations that can be exchanged by $\text{La}[\text{H}_2\text{O}]_n^{3+}$ are only those in the pore openings and supercages (S_{III} sites in Figure 12), to which this hydrated cation can have access (<75% of the total) [72]. The remaining 25% of the sites are located in the sodalite cages (S_{I} sites) and hexagonal prisms (S_{II} sites) and are not accessible to the $\text{La}[\text{H}_2\text{O}]_n^{3+}$ hydrated cations.

By combining ^{23}Na Magic-angle spinning (MAS), double rotation (DOR), and two-dimensional nutation NMR and static ^{39}La NMR Klein et al. [72]

Table 1. Characteristics of USY-based catalysts.

No.	Catalyst	Total surface area (m^2g^{-1})	Zeolite surface area (m^2g^{-1})	Bronsted acid site density ($\mu\text{mol g}^{-1}$)	Lewis acid site density ($\mu\text{mol g}^{-1}$)	ucs (nm)	$\text{Al}_\text{f}^{\text{a}}/\text{uc}$	$\text{Si}/\text{Al}_\text{f}$
1	USY-C	668	583	662	105	2.4549	33.3	4.8
2	REUSY-C	593	513	484	171	2.4563		
4	REUSY-S1	438	375	172	227	2.4371		
5	USY-S1	418	327	53	159	2.4240	0.21	895

^aNumber of framework Al atoms per unit cell, ref. [32].

studied the location and migration of Na and La cations after exchange and subsequent calcination. They observed characteristic NMR signals corresponding to Na^+ in three locations: large cavities, sodalite cages, and hexagonal prisms. After La exchange, the signals corresponding to Na in hexagonal prisms and sodalite cages remained. However, upon calcination, La cations were seen to migrate from the large cavities into the sodalite cages. This La migration was coupled with a strain in the Si-O-T and Al-O-T angles estimated from Si and Al MAS NMR. Several authors have proposed that the alteration of the T-O-T angles by the La-induced causes an increase in the strength of the Brønsted acidity of the corresponding sites [72]–[74].

Migration upon calcination is helped by hydrolysis of the initially hydrated $\text{La}[\text{H}_2\text{O}]_n^{3+}$ cations. This hydrolysis not only allows for the partially dehydrated cation to become small enough to penetrate the sodalite window, but it also generates Brønsted acid sites according to the expression $\text{La}[\text{H}_2\text{O}]_n^{3+} = \text{La}(\text{OH})[\text{H}_2\text{O}]_{(n-1)}^{2+} + \text{H}^+$ as demonstrated by IR spectra that showed O–H stretching bands due to OH groups attached to both exchanged La cation and aluminosilicate framework [75].

Schussler et al. [71] have proposed that the stabilization of La cations within the sodalite cages of high Si/Al ratio faujasites (Si/Al = 4) involves the formation of multinuclear OH-bridged La clusters. These multinuclear aggregates also form within the small sodalites of low Si/Al ratio zeolites (Si/Al = 1.2); however, the La-La repulsion dominates in this case and it causes migration out of the sodalites to the supercage. In the first case, the low Al concentration inhibits the formation of larger aggregates. As the Al concentration increases, more La^{3+} cation aggregates can be formed; however, a more pronounced repulsion between them force them to become stabilized as individual cations in the supercage.

While the location of La cations inside the zeolite is an important research question, one that is more relevant to this review is the following: how does La prevent the loss of catalytic activity in the presence of water vapor? Does La create a new Brønsted acid site that is less susceptible to water than the traditional Al-O-Si bridge site? Alternatively, does it stabilize framework Al, thus preventing dealumination?

Sanchez-Castillo et al. [76] investigated a series of faujasite catalysts (see Table 1). They chose an ultrastable proton form of zeolite Y, calcined at 798 K for 2 h as a base catalyst (USY-C). The corresponding La-containing sample (REUSY-C) was prepared from the original USY and exchanged with lanthanum nitrate to obtain 7.9% wt. La. These samples were then steamed at 1060 K for 4 h (USY-S1 and REUSY-S1). While both USY and REUSY lost a significant fraction of BAS, the one containing RE retained a higher density of sites. That is, the presence of RE cations inhibits the loss of sites. An important analysis can be made on the variation of unit cell size (ucs) through this series of samples. It is well known that during dealumination by steam treatment the Al

cations removed from tetrahedral framework locations are replaced by Si cations (at least partially [77]), which leads to a decrease in the size of the unit cell [78].

As shown in Table 1, steaming causes a stronger decrease in the ucs of the USY sample than in the one containing RE. Indeed, the ucs of USY drops from 24.55 to 24.24 Å (i.e. 0.31 Å) upon steaming, while in the REUSY it only drops from 24.56 to 24.37 Å (i.e. 0.19 Å). This difference is consistent with the conclusion that the presence of La hinders the dealumination process. It is also known that the proton form of a zeolite is much more susceptible to dealumination than that exchanged with other cations [79–81]. Accordingly, it can be proposed that exchanging H^+ by La cations at the Al-O-Si sites would inhibit dealumination. However, if that were the case, the BAS would be lost unless there is a proton associated with the La species that resist dealumination.

In a solid-state MAS NMR investigation of HY and USY, van Bokhoven et al. [73] showed that significant lattice distortion occurred upon La^{3+} incorporation into HY or NaY catalysts, in a manner similar to that caused by EFAl species. Significant lattice polarization was revealed by large changes in quadrupolar NMR parameters for framework Al species and in the isotropic framework Si chemical shifts. Given that La^{3+} and Na^+ cations are of comparable size, it is reasonable that the increased charge density of the former leads to lattice distortion, and a modified Madelung potential for the lattice. However, as mentioned above, even if this modification affects the initial hydrolysis of the Al-O bond, it should not affect the overall framework tolerance to steaming since the hydrolysis step is not rate limiting.

1.3.2. Phosphorous in H-ZSM-5

Analogously to rare earths in faujasites, phosphorous in H-ZSM-5 enhances the tolerance to dealumination during vapor phase steaming. However, the first industrial interest in phosphatation of ZSM-5 was not due to its effects on hydrothermal stability but on the improved shape selectivity toward para-xylene during alkylation of toluene with methanol. In fact, the original composition-of-matter patents from Mobil [82] that described the phosphorus-containing zeolite and preparation methods, as well as the subsequent publications from the same lab [83,84] emphasized the changes in constraint index caused by the incorporation of P, which enhances the shape selectivity. Also, in addition to the controlled reduction of pore openings and channels, they point out another important role of the P species in ZSM-5; that is the deactivation of acid sites on the external surface, which inhibits the secondary isomerization to the other xylene isomers. In addition, those earlier studies showed that the addition of P converts strong Brønsted acid sites into weak ones [85,86]. More recently, it was noticed that these modifications have important benefits

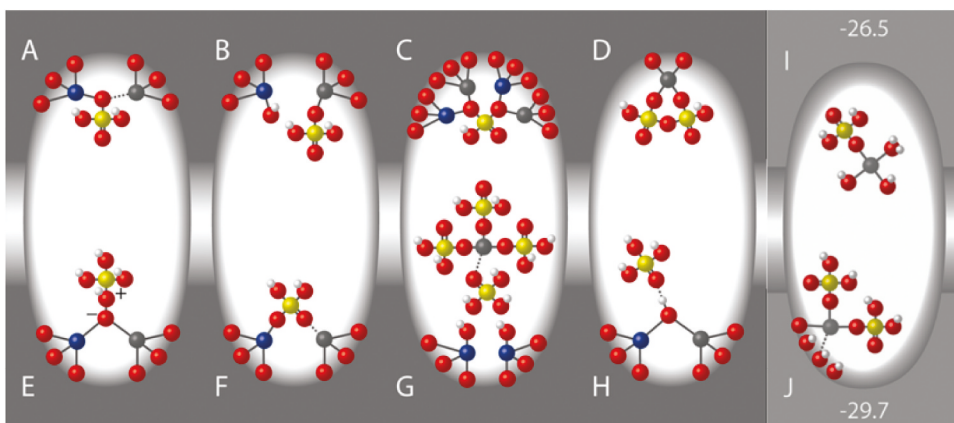


Figure 13. Different models proposed in the literature for the anchoring of phosphate groups in ZSM-5 zeolite, reproduced from ref. [91] O (red); Si (blue); Al (gray); P (yellow); H (white). Models: (A) from Ref., [87] (B) from Ref., [92] (C) from Ref., [93] (D) from Ref., [89] (E) from Ref. 59, (F) from Ref., [85] (G) from Ref., [94] (H) from Ref., [95] (I) and (H) from Ref.[91].

in the conversion of methanol to C2-C4 olefins, without further conversion to higher molecular weight olefins [87,88].

However, one of the most important effects of *P* – and of highest relevance to this review – is the enhanced stability of phosphated H-ZSM-5 catalysts compared to non-phosphated ones. While the exact mechanism of stability promotion is still a matter of discussion, there is plenty of experimental evidence for the improved retention of acid sites (and cracking activity) after steaming on the *P*-modified H-ZSM-5 compared to the plain H-ZSM-5. Van der Bij et al. [89] have explained the enhanced stability in terms of the formation of local framework silico-aluminophosphate (SAPO) interfaces, which are less affected by steaming and can hold the Al cations in the zeolite lattice, preserving the micro-structure. They also proposed the reversible transformation of tetrahedral framework Al to an octahedral position, forced by phosphate, which also remain stationary in the framework under steaming. Later, Danisi et al. [90] made a distinction on the species formed at different P loadings. That is, when $P/Al \leq 1$ the steaming process would cause bond cleavage in the Si–OH–Al bridging groups and partial dealumination, with most of the tetrahedral Al in a distorted environment affected by the presence of phosphorus, different from conventional Si–OH–Al sites. In turn, from the P side, it was proposed the formation of silico-aluminophosphate (SAPO) domains with acid sites attributed to *P*–OH groups. As the P loading increases, with $P/Al \geq 1$, formation of a crystalline silicon orthophosphate phase was observed, some of them located inside the zeolite pores causing enhanced crystal strain.

In a more recent study, Louwen et al. [91] combined synchrotron XRD and neutron diffraction, with pair distribution function analysis and quantum-

mechanical modeling to further investigate the nature of the phosphate groups. They emphasized the important role of the hydrolysis as a prerequisite for the phosphatation of the framework; that is, the crucial step is the reaction of the phosphate with a partially dislocated Al species that are still tethered to their original framework position. This concept is reminiscent of the dealumination mechanism described above in [Figure 10](#), analyzed in terms of reversible and irreversible steps. These authors have made a comparison of the various models discussed in the literature, as illustrated in [Figure 13](#).

While most investigations on *P*-modified ZSM-5 support the conclusion that P helps retaining framework Al upon high temperature steaming, the various proposed explanations differ in the specific details of the stabilization mechanism. In one of the early studies of this material, Kaeding and Butter [87] proposed that phosphate is coordinated to the Al-O-Si site via one of the P – OH groups (see model A in [Figure 13](#)); similar interactions are considered in other models, such as that of Xue et al. [93] (see model C), which involves two separate Si–OH–Al BAS in a bidentate coordination of phosphate. By contrast, other authors have proposed the protonation of the phosphate by the BAS (see model E) [65] or the replacement of the OH from the BAS and formation of Si–O – P – O– Al bonds (see model F) [85]. Disruption of the BAS has also been suggested by other authors (see model B) [92], while others have evoked the participation of dislodged Al cations in the anchoring of the phosphate group (see model G) [94]. The most recent models (see models D–J) propose that a prerequisite for the attachment of the phosphate group is the partial dislodging of the Al cation from the framework caused by steaming; these species are responsible for the strong interaction with phosphate groups. All previous models assumed a direct interaction with the BAS, without a hydrolysis step that opens the site. The work by Lowen et al. [91] suggests that phosphate species are tethered to partially dislodged framework Al cations, with two bonds lost and two remaining, providing acidity to the stabilized P– OH groups.

1.4. Liquid water as an agent of zeolite structure modification

1.4.1. Liquid water and zeolites

It is worth noting that the analysis of the structure of liquid water itself is already a complicated topic [96,97]. It is well accepted that liquid water is well-structured due to its characteristic extended hydrogen bonded network. The model of liquid water normally exhibits on the average 1.8 hydrogen bonds (HB) per water molecule at ambient condition [96,98]. X-ray emission spectroscopy and X-ray Raman scattering data suggest that the liquid water has inhomogeneous local structures, one is a strong near-tetrahedral structure that minimizes enthalpy, and the other is a distorted asymmetrical configuration

with non-directional H-bonds [99]. Both the number of HB per water and their local configuration are sensitive to temperature [100,101] and it is possible that the structured water can be strongly perturbed by the local environment. For example, in the presence of an extended hydrophobic surface, MD simulations show that water at the interface is re-orientated in a way characterized by “dangling” hydrogen bonds to balance between the number of hydrogen bonds and the packing density of the molecules [102]. Also, when confined in a zeolite, water shows structural properties distinct from those of bulk water. This difference in atomic structures is caused by both the geometric restriction offered by the zeolite topology and the dynamic water-zeolite interaction. This dynamic water-zeolite adsorption is further controlled by the number of Brønsted acid sites present in the framework of the zeolite. Previously, both grand canonical Monte Carlo and Car-Parrinello MD simulations were used to suggest that water in an all-silica hydrophobic zeolite behaves as a nanodroplet with an internal hydrogen-bonding network closed on itself, while weak hydrogen bonds form between the water clusters and framework oxygens in hydrophilic zeolites [11].

1.4.2. Structural collapse of zeolites in hot liquid water

While zeolites contain strong Si-O and Al-O bonds and crystalize in well-defined structures, which are stable under relatively harsh gas-phase environments, they can be severely modified in liquid media, particularly aqueous solutions. In fact, zeolites are synthesized under hydrothermal conditions in aqueous solutions that contain Si and Al precursors, which initially aggregate into amorphous domains and then, through a series of kinetically controlled nucleation and growth steps, crystallize into metastable configurations.

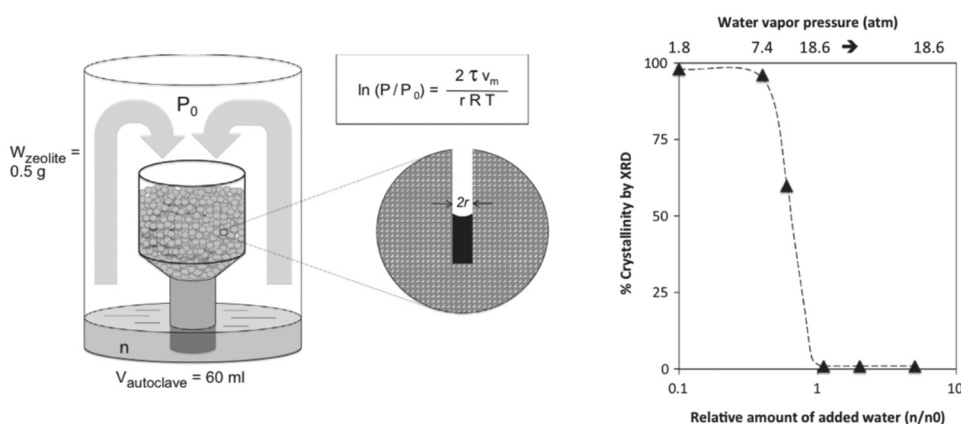


Figure 14. Left: Apparatus used to study the exposure of H-USY zeolite to water vapor at increasing partial pressures. Right: Percent crystallinity retained in an untreated H-USY zeolite after 6-h exposure at 200°C as a function to the amount of water added to the autoclave relative to that required to start condensation on a flat surface (n_0) from Refs.[110,111].

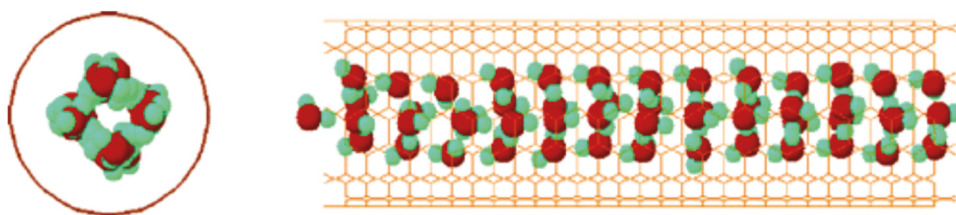


Figure 15. Simulation snapshots for H₂O confined in a CNT. Parallel (left) and perpendicular (right) views. O atoms shown in red; H atoms shown in light green. Note H-bonding among water molecules, but no interaction with hydrophobic walls. From Ref.110.

Depending on the conditions and chemical composition, these steps can be reversed to different extents and it is even possible to transform the structure of a given zeolite crystal into another structure [103,104]. Therefore, it is conceivable that when a metastable crystal as that of a zeolite is placed back in aqueous solution under hydrothermal conditions, it can be modified or attacked, causing partial or total collapse of its crystalline structure. Some of the characteristics of the aqueous solution (composition, pH, ionic strength, temperature, state of aggregation) as well as the characteristics of the zeolite (Si/Al ratio, topology, crystallite size, hydrophilicity/hydrophobicity, density of defects) can drastically change the extent and manner the zeolite structure responds to the presence of the medium.

The high susceptibility of zeolites to acidic solutions has been known for long time, with the extent of attack increasing with the acid concentration of the solution and the density of Al sites in the zeolite; this is because Al-O-Si linkages are more susceptible to attack in acid media than the Si-O-Si ones [105,106]. By contrast, when an alkaline aqueous solution is used, the latter are cleaved instead of the former. In fact, zeolites with a low Si/Al ratio are relatively inert to attack by high pH solutions and require higher concentrations of alkali or longer treatments. At the other extreme, zeolites with very high Si/Al ratios are susceptible to desilication, resulting in high mesoporosity [107]. The following scheme illustrates the effect of the Si/Al ratio on the resulting desilication in the presence of high-pH solutions. That is, in zeolites with $\text{Si/Al} < 25$, formation of mesoporosity is hindered; in $\text{Si/Al} > 50$, large pores are created with excessive dissolution and even structural collapse; in the intermediate region $25 < \text{Si/Al} < 50$ a controlled design of mesoporosity is possible, in which suitable crystallinity and acid density can be obtained [108].

Even neutral water, at high enough temperatures, is known to attack the structure of zeolites. For example, between 150°C and 200°C, the entire microporous structure of faujasite was found to collapse after a few hours in contact with liquid water [109]. Interestingly, if the amount of water present in the autoclave is lower than that required to reach the saturation vapor pressure at the given temperature (n_0), no collapse occurs, since no liquid phase is

present. Therefore, in stability studies, it is important to know the overhead volume, amount of liquid and saturation vapor pressure under hydrothermal conditions to determine whether the zeolite is exposed to liquid or vapor.

As illustrated in [Figure 14](#), water vapor does not cause structural collapse in this temperature range ($<200^{\circ}\text{C}$); when the partial pressure of water in the system was below n_0 the crystallinity loss was negligible, even after a 6 h-treatment [111]. When the amount of water exceeded $n/n_0 = 1$, even by a small amount, the zeolite became essentially amorphous (i.e., no diffraction peaks in XRD). Partial crystallinity losses started when the amount of water in the system approached n_0 . From the Kelvin equation, one can calculate what would be the mesopore diameter needed to begin having liquid water under these conditions. With a value of 0.042 N/m for the surface free energy of water at 200°C and a molar volume of 18 cc/mol, the corresponding diameter for capillary condensation would be around 1.5 nm. Therefore, one can envision that condensation might begin in very small defect pockets in the zeolite crystal, which would be the location of the initial water attack.

Different factors in the zeolite composition and topology may affect their susceptibility to hot liquid water. Among the possible characteristics of the zeolites that have been proposed to play a crucial role in the susceptibility to structural collapse, the following have been identified in different studies: (a) Brønsted acid site (BAS) density or Si/Al ratio, (b) Si–O–Si bonds, (c) zeolite framework type, (d) extra framework Al ions and (e) silanol defects. Latest studies give ample evidence that the presence of silanol defects is the most crucial factor that determines the instability of zeolites in hot liquid water [15,110–113]. There have been reports claiming that certain zeolite types have particular tolerance to hot liquid water [114]. However, these studies have not quantified the level of silanol defects in each sample. Moreover, without a proper analysis of vapor-liquid equilibrium – as that shown above that calculates the n/n_0 ratio – one cannot know whether under the hydrothermal conditions investigated the zeolite is exposed to hot liquid water or only to water vapor. First, Zapata et al. [110,111] and more recently Prodingier et al. [115,116] have greatly improved the stability of zeolites in hot liquid water by titrating the silanol defects with organosilanes that form a hydrophobic barrier and heal the hydrophilic defects. IR and ^{29}Si MAS NMR spectroscopies give ample evidence for the elimination of the silanol defects.

1.4.3. Hydrophobicity and water penetration

One important aspect to discuss is how the hydrophobicity of a microporous material affects the accessibility of water. Clearly, hydrophobicity affects the wettability of the walls and inhibits nucleation and formation of a surface film. However, water molecules from the vapor phase can still diffuse into the pores, whether their walls are hydrophobic or hydrophilic. Indeed, as illustrated in [Figure 15](#), MD simulations of water molecules confined in an infinitely long

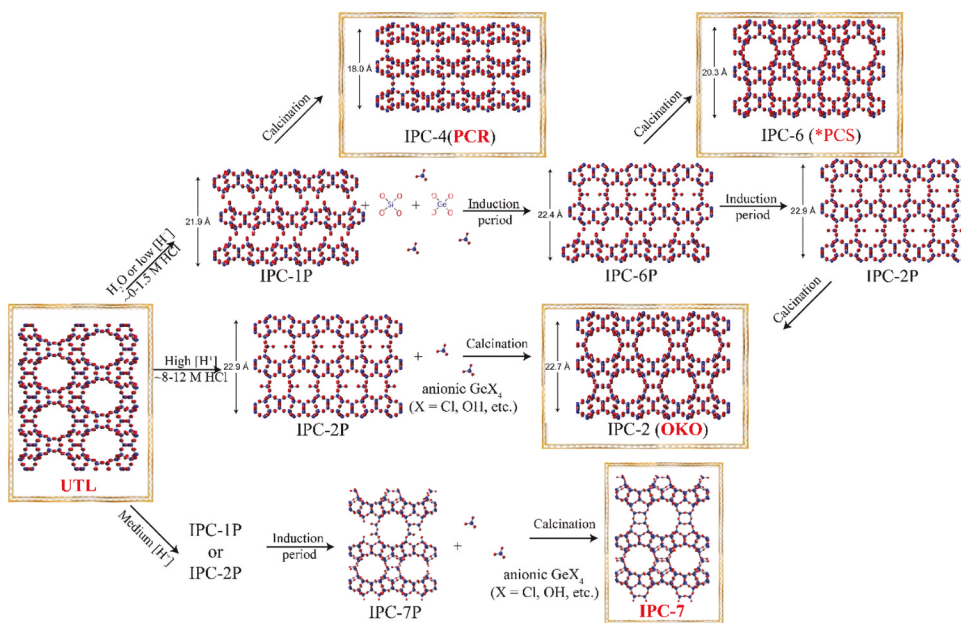


Figure 16. Utilization of liquid water attack to convert a UTL zeolite to different intermediate layered precursors and final zeolite topologies after calcination. From Ref.[125].

carbon nanotube with a smooth hydrophobic wall show that their diffuse is fast and ballistic [117,118].

These simulations have shown that the formation of long-lasting H bonds promote the ballistic diffusion mode of water clusters. In agreement with the simulations, experimental measurements have also given evidence for the fast diffusion of water inside hydrophobic nanotubes [119]. On the other hand, penetration of liquid water into hydrophobic enclosures requires exceedingly high pressures. For example, intrusion of liquid water in hydrophobized porous silica requires pressures above 500 bar [120]. Interestingly, MD simulations also show that when the hydrophobic enclosure contains hydrophilic patches that can be wetted by water, they act as nucleation sites for water condensation, which can reach them by diffusion from the bulk water. In fact, parallel plates of hydrophobic silica patterned with hydrophilic silanol (Si –OH) patches result in interesting dynamics, in which water molecules are seen to condense around the silanol islands and remain connected to bulk water through a chain of molecules spanning through the hydrophobic region. The walls in that region are not wetted by water, but they do wet the hydrophilic islands [121].

Specific examples exist on hydrophobized zeolites, which demonstrate the same principles. For example, it has been found that the amount of water adsorbed within an MFI zeolite with internal silanol defects is almost an order of magnitude higher than that in a defect-free hydrophobic MFI zeolite [21].

At the same time, the measured water diffusivity is twice as high in the hydrophobic zeolite than in the one with silanol defects. These results further support the concept that while liquid water does not wet the surface of hydrophobic pores and consequently liquid intrusion is much less favorable, water vapor can diffuse easily and find hydrophilic sites if they are present, as was shown by ^1H solid-state NMR studies [23]. Therefore, it is incorrect to claim that water effects in hydrophobic zeolites can be explained by the inability of water molecules to access specific sites inside the zeolite.

1.4.4. Utilizing liquid water attack of zeolites to create new topologies

It is worth noting that, as a positive aspect of liquid water attack, hydrolysis by liquid water can be used to modify the zeolite structure intentionally and prepare new materials that may not otherwise be attainable through conventional hydrothermal crystallization [122]. This has been demonstrated for the case of germanosilicates, in which Ge atoms are incorporated in the zeolite framework, occupying T-sites. For example, the UTL zeolite contains Ge preferentially located at the double-four-ring units (D4Rs) [123,124]. The Si-O-Ge and Ge-O-Ge bonds can be selectively hydrolyzed in liquid water and acid solutions. Particularly, when the concentration of framework Ge is low, partial hydrolysis can be achieved, leading to the formation of two-dimensional layered materials, which can be organized (for example by intercalation of an organizing agent) and reassembled into a new topology by calcination, as illustrated in Figure 16. This is the so-called ADOR process (assembly-disassembly-organization-reassembly). The same approach has been applied to prepare UOV-derived zeolites [126] and IWW-derived zeolites [127]. The success of the ADOR approach leverages the selective water attack to the Ge-containing units in certain frameworks, providing an alternate route for synthesizing zeolites with controllable topology.

2. The influence of water on reaction rates

Water plays a variety of intriguing roles on catalytic reaction rates. In this section, we first discuss the direct interactions that water may have on catalytic reactions themselves, both in the liquid and vapor phases. We then discuss catalytic consequences of structural changes induced by water, as discussed in section 1.

2.1. Competitive adsorption

Water can interact with Brønsted acid sites to modify observed reactivity through a variety of means. The most common effect of water in heterogeneous catalysis is the competitive adsorption on active sites. Due to the protic nature of water, however, simple site competition is not as straightforward as it

may be with other aprotic adsorbates. As will be discussed in [section 2.3–2.5](#), water's interaction with a framework Brønsted site can lead to proton delocalization, modifying both the acid strength and confining environment. Further, water can form clusters around a traditional site, with the resulting influence on acidity correlated to the cluster size. With these possibilities noted, water does strongly bind to Brønsted sites. This can limit direct interaction of reactants with the catalyst surface and decrease the population of reactive intermediates in direct contact with a framework acid site.

The binding affinity of water on a Brønsted site has been estimated to be approximately 50 kJ/mol over MFI framework zeolites at water loadings of less than 1 water molecule per Brønsted site. At higher water loadings, small clusters can form around Brønsted sites, although with lower adsorption enthalpies. The average adsorption enthalpy at a loading of two water molecules per Brønsted sites has estimated to decrease to 34 kJ/mol, which is significantly greater than values reported over the same Al-free framework. This indicates that small water clusters will form, with decreasing enthalpies associated with subsequent water addition [24], as supported by the earlier work that estimated stable cluster sizes of approximately 4 water molecules per framework Al atom [128].

An important element to keep in mind with respect to water's impact on kinetic modeling is the fact that this impact can differ depending on the partial pressure of water, even when introduced in the gas phase. If temperature is lowered and/or the concentration is increased, condensation of a liquid water phase may occur; and this can both compete for active sites and modify the local structure of the framework bound proton. In a condensed liquid or in the presence of water clusters, the acidic proton will be delocalized, and as a result the proton-reactant interaction will be influenced. While it is important to note that the specific interaction between a proton and the reactant involves the combination of deprotonation energy of the zeolite, confinement within the pore, and interaction energy between the proton and reactant at the transition state, one must also consider the delocalized nature of the proton and the energetic modifications to both the adsorbed species and transition states, created by the solvating environment. It should also be noted that the delocalized nature of a proton resulting from proximate water cluster formation can modify reactivity, changing what is often termed acid strength.

When water molecules encounter a framework Brønsted acid site in the gas phase, clusters may form below the saturation point. Depending on the reactant and transition state to be stabilized, the proton's environment will be altered, thereby modifying the ability to protonate certain reactants or key intermediates. This can manifest itself as an inhibition in rate that can be interpreted as a reduced adsorption constant due to site competition. Competition for adsorption sites has been proposed for water on Brønsted acid sites for some time. Site competition has been used to explain both

decreased olefin surface coverage and oligomerization [129] as well as a shift to more primary conversion reactions with limited rates of secondary cracking for hydrocracking reactions [130,131]. Competition for active sites has been used to explain shifts in product evolution in methanol conversion reactions as well, altering both the product selectivity and total turnovers achieved. For example, modifications to rates have been proposed as due to preferential adsorption and blocking of stronger Brønsted sites within HSAPO catalysts [132]. Competitive adsorption due to water is of course present in Lewis cation exchanged zeolites as well where more traditional adsorption competition takes place. Competition and changes in local structure induced by water have been used to explain decreases in glucose reactivity [133], i.e., resulting from different concentrations within zeolite pores. Lercher et al. [134] similarly expressed the negative dependence or competition of water on alkylation rates, included in the denominator of a Langmuir-Hinshelwood-type rate expression, as a result of competitive rehydration of reactive intermediates to lower their concentration. Similarly, in the case of methanol to gasoline, Bollini et al. [135] correlated rates and total turnovers with the population of surface formaldehyde species, which undergo hydrolysis in the presence of water, thereby altering the rate of reaction.

Upon studying the rate of alcohol dehydration over unconfined polyoxometallates, Macht et al. [136] also found an inhibition in the dehydration rate consistent with competitive adsorption. This inhibition was present even at low alcohol and water coverages, implying that site blocking was not responsible. They proposed an alternative explanation through which water formed more stable dimers that were less prone to elimination and formation of the final products. These stable dimers exhibit lower rates of conversion, but by forming stable intermediate species rather than by competing for adsorption sites.

In addition to traditional site competition, condensed liquid water may induce a diffusion barrier. Protons, even in the form of hydronium ions, tend to be localized in the vicinity of the surface Al species. If capillary condensation occurs within the zeolite micropores [15], this could alter diffusion coefficients to and from the active site, with corresponding implications on reaction rates.

In summary, water does adsorb on Brønsted sites and may compete with reactants for these sites, but in a more complicated manner than most species. Not only can water compete for adsorption sites, but it can also react with some kinetically relevant intermediates, leading to delocalized hydronium ions, and changing the overall environment within pores. While these features may ultimately be expressed as an inhibition term in a Langmuir isotherm, the underlying cause of changes in reactivity may be more complex. If one is fitting the role of water on reactivity for a Brønsted catalyzed reaction, an inhibition in rate over a specific range of operating conditions may be

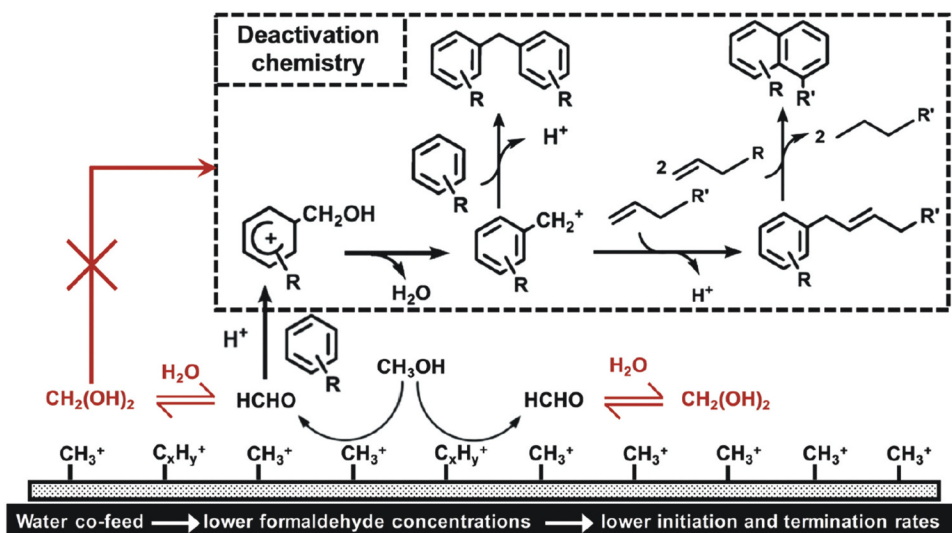


Figure 17. Pictorial depiction of the mechanistic basis for the effect of water co-feeds on chain initiation and termination rates: formaldehyde, formed in the transfer dehydrogenation of methanol with alkoxides, reacts with water to form methanediol. Unlike formaldehyde, methanediol does not participate in chain initiation and termination events. From Ref.[135].

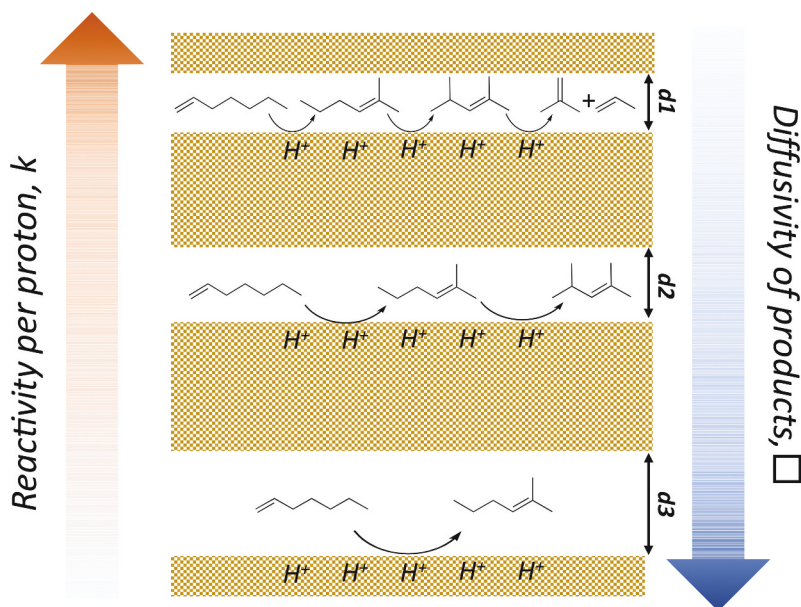


Figure 18. Schematic depiction of tradeoff between reactivity and diffusivity on product distribution within zeolite pores. Reproduced from Ref.[137].

adequately fit to a model expressing a competing adsorption constant for some reactions. However, it should be noted that this adsorption constant will vary as a function of water partial pressure, as clusters begin to form with more

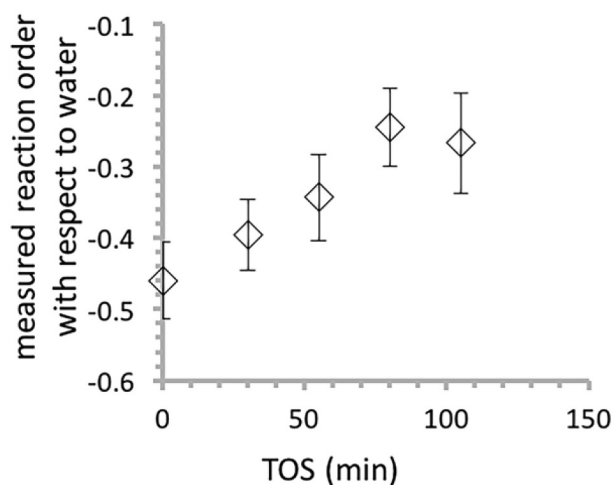


Figure 19. Order of reaction rate with respect to water as measured at varying TOS values. Conditions are vs. water concentration over CBV8014 at 300 °C, 0.025 g catalyst, with initial rates extrapolated to 0 min TOS. Error bars represent ± 1 standard error value of the reaction order coefficient. Adapted from Ref.[139].

than one water molecule interacting with a typical Brønsted site. Further, the local solvating environment created by a hydronium ion within a water cluster can alter rates of reactions in a variety of ways beyond simple competition for sites.

2.2. Product re-adsorption and deactivation

As discussed in the previous section, it has long been noted that water adsorption can hinder olefin adsorption on Brønsted sites [129], limiting oligomerization that would otherwise occur at room temperature. The resulting effects on deactivation or rate are only apparent when the delocalized proton that forms due to water adsorption is not sufficient to activate the species and carry out the chemistry in question, e.g., oligomerization. While we have previously pointed out that product inhibition can be confused with a shift in population of reactive surface species, the fact that water can limit coke formation rates by lowering the concentration (or readsorption of) coke-forming surface species remains.

This should be kept in mind as one considers enhancements in rates of reactions due to the presence of water. Oftentimes increased rates, especially in the case of batch systems, are confused with prolonged catalyst lifetimes due to diminished deactivation. A common example is methanol to gasoline (MTG) chemistry (see Figure 17), where water may influence the number of formaldehyde species on the surface and therefore modify rates, but comparison of

product yields as a function of the total turnovers reveals that the surface chemistry is unaltered [135].

Further, bulky product molecules generally diffuse more slowly through the zeolite pores. This leads to many instances where appropriate tests confirm that measured rates of reaction are not influenced by internal or external diffusion to the active site, but yet diffusion still strongly influences the product distribution as well as rates of deactivation [137,138] as shown schematically in Figure 18. In these cases, water may favorably compete for adsorption sites and effectively limit product readsorption.

Improper accounting for deactivation and decoupling its effects on measured rates can easily lead to incorrect conclusions regarding the role of water on a reaction. As an example, Figure 19 shows the order of the reaction that would be observed with respect to the partial pressure of co-fed water for the ketonic decarboxylation of acetic acid to form acetone over H-ZSM-5 [139]. This is an intriguing reaction due to the fact that a key surface intermediate involved is an acyl species on the surface resulting from the dehydration of acetic acid [140]. In a similar light to the concentration of formaldehyde species in methanol to gasoline chemistry, the equilibrium constant associated with the concentration of surface acyl species, and the corresponding acylium ion transition states, is inhibited by co-fed water. This inhibition results in diminished kinetic rates when water is co-fed. Further, water may compete with acetic acid for adsorption sites, further diminishing reaction rates. However, two key parallel reactions that influence deactivation, aldol condensation of the formed acetone to form more bulky products as well as desorption of surface acyl species as coke precursor ketenes, are detrimentally influenced by water. For this reason, if the reaction is carried out in a batch reactor, or a flow reactor at longer time on stream, one may observe that the positive consequences of co-fed water may counterbalance or outweigh the true negative influence on reaction rate. In the case described above, while extrapolating to initial time on stream to account for deactivation an -0.5 order with respect to water is observed. If one were to base the order on data points acquired at later time on stream, the order with respect to water would be much more positive. Water interaction with relevant species further impacts deactivation; this is quite a general phenomenon in zeolite catalysis, especially when polar or protic surface species are involved.

Other potential positive impacts of water involve the cleaning of the catalyst surface under reaction conditions, which may be influenced by a variety of mechanisms. For example, it is well known that at elevated temperatures water may react with surface species to carry out gasification reactions and remove carbonaceous deposits. This chemistry occurs at elevated temperatures where the stability of the zeolite would likely be modified by the presence of water as well. At more modest conditions, water may interact with adsorbed species in the vapor or liquid phases to either facilitate desorption or diminish

subsequent reaction rates. This can occur generally through three parallel pathways. The first is simple inhibition of active sites through adsorption competition to limit sequential reactions. Coke formation reactions generally proceed through the creation of several intermediates that are both more reactive and of higher molecular weight than the parent reactants, often resulting in diminished diffusion rates out of the zeolite pores. In these instances, the number of active sites that any reactant faces as it diffuses away from the active site can influence the rate of deactivation. Even if the rate of reaction is not influenced by reactant flux to the active site, the rate of reaction vs. diffusion of products out of the pores can be. Simple sequential reactions to form additional products, or ultimately coke, can lead many to make erroneous claims pertaining to acid strength of a catalyst [138,141]. If water adsorption influences product readsorption this can lead to similar effects, and diminished rates of subsequent reactions within pores can lead to prolonged catalyst lifetimes and improved selectivities to primary products.

The second common role of water is to react with adsorbed or gas phase species. Water has been proposed to react with surface intermediates, as in the cases of MTG, acylation, ketonization [139,142], and alkylation reactions [134]. As noted earlier, it may not react to form a new observable gas phase product, but may simply form a more stable intermediate with altered decomposition kinetics [136].

The influence of water on altering reaction rates is also a function of the amount of water present and the local confining volume within the zeolite. For example, the dehydration of methanol to form dimethyl ether also can be expressed with a negative dependence on the partial pressure of water analogous to a Langmuir isotherm. Alternatively, Gounder et al. explained this phenomenon as the result of displacement of a water molecule within a water cluster surrounding a Brønsted site. At higher water loadings, however, larger water clusters are formed and the size of the confining void influences the reaction rates. This is due to the different energetics associated

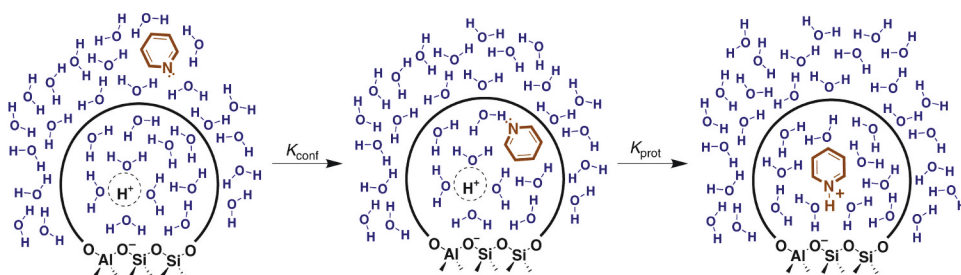


Figure 20. Pyridine enters the catalyst pore with an equilibrium constant of K_{conf} before being protonated by the BAS with an equilibrium constant of K_{prot} . Solid and dashed curved lines indicate zeolite pores walls and the BAS solvation sphere, respectively. Adapted from Ref.[144].

with solvent reorganization within the various confining voids within the zeolite pores [143].

A third form of altering rates of sequential reactions in continuous condensed solvent phase is through the modified solvation of products. While the coverage of a reactant on the surface is a function of chemical potential, which is in equilibrium with the gas phase chemical potential, the presence of a liquid solvent can influence the energetics of adsorbed species, surface transition states, and solvated molecules in the liquid. The polarity and protic nature of a solvent can alter the equilibrium constant associated with protonation of a molecule [144], especially if the reaction is influenced by mass transfer. This can also alter reaction rates within pores and consequentially influence deactivation.

2.3. Water as a stabilizer of TS with differential reactant and rate enhancements

The presence of water clusters within the pores of a zeolite can potentially influence both the solvation energy of a reactive intermediate and the energy of a transition state. When one considers the solvation energetics of each of these species, one must both consider the new stabilization environment created by the water cluster, as well as any entropic consequences. While a transition state itself will likely gain entropy in an aqueous solvated environment [145,146], water molecule restructuring within the solvent has also been proposed to explain entropy losses upon accommodation of the transition state [147]. The net changes in entropy from an adsorbed to transition state are not always trivial and require careful consideration. The relative changes in entropy and enthalpy associated with a transition state, compared to the parent adsorbed species, typically depend on the early or late nature of the transition state in question. The addition of a solvent amplifies this phenomenon.

Other features influence the relative stabilization of adsorbed and transition states within an aqueous solvent or cluster as well. Figure 20 depicts the role of water on the delocalization of a proton as well as subsequent interaction with a base in a confined aqueous environment. Even if one ignores the differing nature of a framework proton and a solvated hydronium ion, the interaction of a reactant in the presence of a condensed aqueous environment can be altered as well. For example, Gould et al.[144] reported a shift in adsorption constants when contrasting adsorption isotherms in water vs. adsorption directly from the vapor phase. In order to account for this, one must consider the enthalpy of solvation when the base is dissolved into the aqueous environment that is referenced. This creates a more stable intermediate solvated species, with a lower relative change in energy between the adsorbed state and solvated state than would be observed in the absence of a solvent. One must also

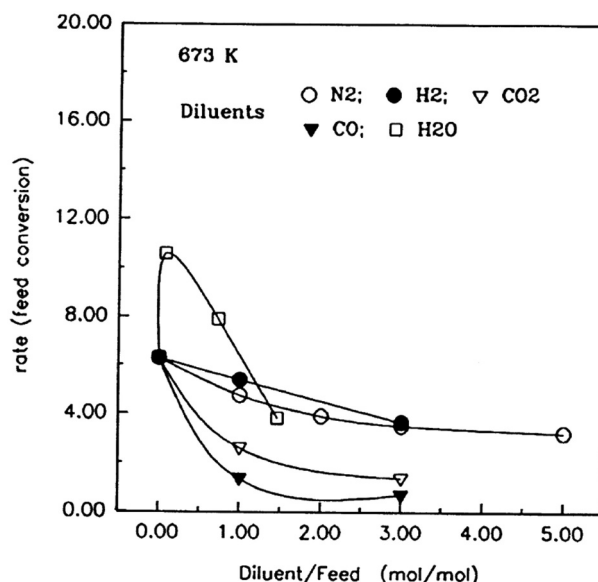


Figure 21. Rate of 2-methylpentane conversion vs. ration of diluent to feed at 400°C over Ultrastable Y zeolite. From Ref.[151].

consider the energetics associated with the removal of water molecules within the confined pores of the zeolite to accommodate the adsorbate. This manifests itself in more facile removal of species from zeolite pores to the more stable environment that the solvent creates, and altered adsorption constants when contrasting vapor vs. liquid phase interaction of molecules with Brønsted sites within a zeolite.

2.4. Transition state stabilization within confined voids of zeolites

Aqueous phase dehydration rates have been reported to increase within zeolite cavities when contrasted with rates obtained in the presence of homogeneous acids. Lercher et al. [148,149] have published a series of recent papers on this topic evaluating rates of alcohol dehydration. Interestingly, the authors claim shifts in activation enthalpy when contrasting a proton from a framework acid site within a zeolite with a free proton in solution due to the presence of phosphoric acid. Upon contrasting cyclohexanol dehydration rates within the confines of zeolite pores, the authors reported enhancements in large pore zeolites BEA and FAU as due to increased entropy within the pores rather than enthalpic stabilization, although rates were not directly contrasted with those in an aprotic solvent. Counter to this argument, the reverse argument is made for the smaller pored MFI catalyst, where the authors claim rate enhancements are due to enthalpic stabilization, while activation entropies are comparable with homogeneous phosphoric acid catalysis. Mei and Lercher [150] later

carried out a theoretical study illustrating the differing nature of protons as a function of water loading. Protons become delocalized as a hydronium ion upon the addition of two or more water molecules per proton. In all cases, the addition of water lowers the activity when compared with a traditional gas phase proton.

Examples of enhancements in rate which are not simple manifestations of improved catalyst stability have been reported as well, although our ability to understand these effects is continuously evolving. One of the most fascinating early examples of the role of water on potential enhancement of intrinsic reaction rates is the case reported by Wojciechowski et al. In this case, for the conversion of 2-methylpentane over USHY they observed a difference in diluent behavior for water in comparison with other inert species. Further, this enhancement was more pronounced at lower reaction temperatures. At very low water to feed ratios, they observed significant enhancements in 2-methylpentane conversion as shown in [Figure 21](#), but this effect was neglected at higher water partial pressures as the inhibition of reactants began to dominate. While we must point out that HY zeolites, especially pre-steamed derivatives, generally carry a high number of acid sites in close proximity, as well as several extra-lattice Al species. The roles of extra lattice aluminum species and paired sites will be discussed in more detail in [section 2.6](#). The intriguing behavior of this reaction relates to the significant lowering in activation energy for 2-methylpentane cracking [151], as well as a shift in selectivity. The addition of small amounts of co-fed water result in enhancements in C6 isomerization rates but did not significantly alter the rates of sequential cracking reactions. The same authors subsequently reported that water may serve to extend kinetic chain lengths, shifting the olefin to paraffin ratio at low dilution levels, although the only rates that are enhanced are those associated with isomerization [152].

Enhancements in rates of alkane conversion in the presence of water at elevated temperatures carries great consequences industrially, as steam is the commonly used diluent in fluid catalytic cracking processes. Corma et al. [153] carried out a follow-up study to investigate this effect and interrogate the potential mechanistic role of water during cracking of the heavier molecule n-hexadecane. The authors reported interactions between water and bridging acid sites at lower temperatures based on IR analysis, but they did not report consequences on activity at higher reaction temperatures. They ultimately concluded that the only role of water was to serve as a diluent during the reaction, similar to what would be achieved with nitrogen. An important differentiating factor, however, is that these conclusions were derived while operating under more severe conditions to mimic an industrial catalytic cracking system, with a linear alkane, higher operating temperatures, and much higher steam to feed ratios. It is notable to also mention that surface modifications to the catalyst are also more likely under these more severe

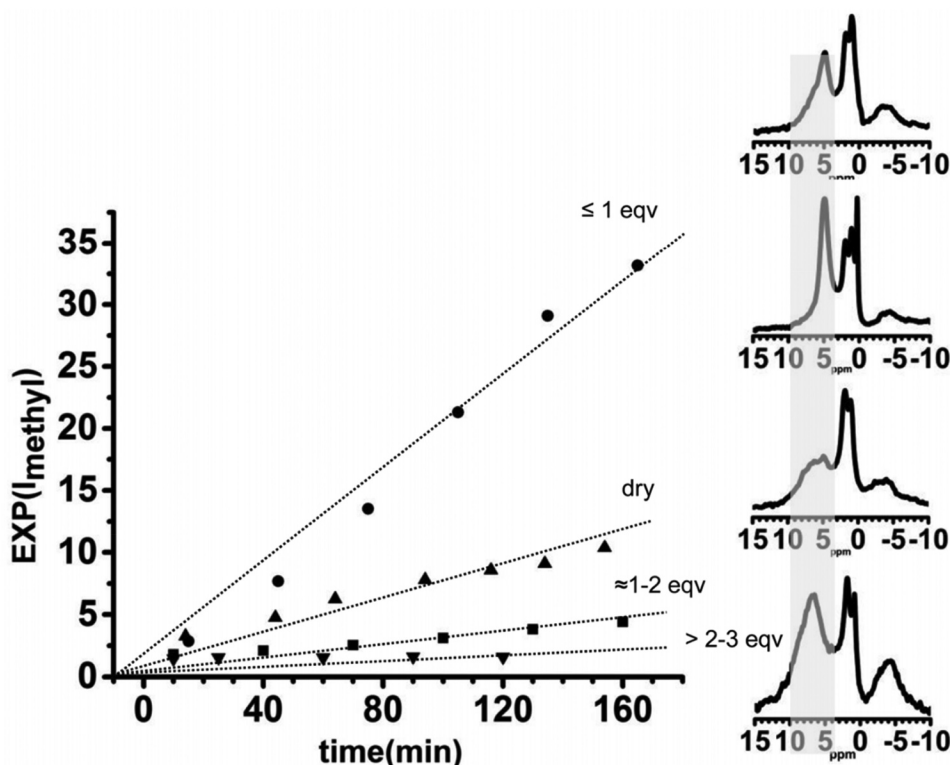


Figure 22. Linearized single-exponential growth plots of the isobutane CH_3 peak area in the ^1H MAS exchange spectra as a function of reaction time, for four different water loadings in equivalents. The dashed lines are simply drawn as guides to the eye through the raw data points. The corresponding spectra for the first time point in the exchange series are shown near their trend line, ordered from top to bottom. Note that the ca. ≤ 1 eqv loading corresponds to a spectrum with clear acid site peak but no obvious water peak (shaded box inset), the ca. 2 eqv loading corresponds to a spectrum with neither a well-defined water nor acid peak due to proton exchange in the intermediate time scale regime, and the ca. 2 – 3 eqv loading spectrum has a well-defined water peak but no acid site peak. From Ref. [154].

conditions. The role of water on positive enhancements is clearly not a general phenomenon, but highly dependent on the reaction conditions of interest.

Under mild conditions, Chen et al. [154] have reported enhanced rates of C-H bond activation through H/D exchange rates. Rate enhancements were only observed at sub-stoichiometric water loadings relative to the number of active sites. Higher water loadings water suppresses H/D exchange rates with the catalyst surface, as explained by the higher proton affinity of water than the corresponding alkanes. This illustrates the differing nature of water species bound to framework Brønsted sites as water loading increases and delocalized hydronium clusters begin to form.

Similar experiments with benzene H/D exchange rates reveal that the enhancement in low temperature exchange rates is also a strong function of the Si/Al ratio in the zeolite, implying that site proximity plays a role in the

ability of water to accelerate reaction rates within zeolite catalysts. These additional positive consequences of delocalized protons and the role of site proximity on reactivity will be discussed in more detail in the next section, as exemplified by the data shown in [Figure 22](#).

2.5. Remote polarization and proton hopping

The mechanism of rate enhancement in the presence of water is an emerging area of research. The general role of water to promote long-range interactions in heterogeneous metal, acid, and base catalysts has been recently reviewed by Li et al. [35]. Here, we focus on examples pertinent to the confined acid sites within zeolites. The ability of water to delocalize protons present in zeolites as discussed in [sections 2.3](#) and [2.4](#) can have a variety of consequences on reaction rates, with important distinctions in rate when active sites are located in close proximity. For example, Chen et al. [155] have attributed proton hopping as the most likely factor for enhanced H/D exchange rates over MFI zeolites with high Al density, while rate enhancements were not observed in samples of low Al density. Zeets et al. [33] illustrated how water can interact with two bridging acid sites if their proximity is close enough. Similarly, Ryder et al. [156] reported how low levels of water can facilitate proton hopping among the four O atoms surrounding an Al T site, shifting the barrier required for proton hopping from 28 kcal/mol to near barrierless, 4 kcal/mol. While our traditional view of a catalytic process involves a static active site interacting with mobile reactants, recent developments where low barriers associated with active site transformations within zeolites are increasing our awareness of the potential role of active site modifications participating in a single turnover [157]. While we have recently learned much about the role of Grotthuss hopping in metal catalysis, and water shuttling to selectively activate specific bonds over metal catalysis [158], similar analogs exist within acid base catalysis as well. For example, recent reports by Li et al. [159,160] illustrate how remote polarization of an adsorbed intermediate through a water bridge can influence transition state energetics. This behavior is likely more pronounced with more polar and protic reactants and intermediates, but we anticipate our understanding of the role of remote polarization and proton hopping will continue to advance over the next decade.

We may further consider other effects water can have on acid-catalyzed reactions. In instances where polar molecules are involved, e.g., dehydration reactions [161], water is often a product of the reaction and negative consequences on observed rates may arise due to reaction thermodynamics, as opposed to modification of the true kinetic constant. These should be considered along with the modification of the acid site as described in the prior section, as well as enhanced stability of catalysts before true kinetics effects may be proposed. The modification of a transition state in an acid catalyzed

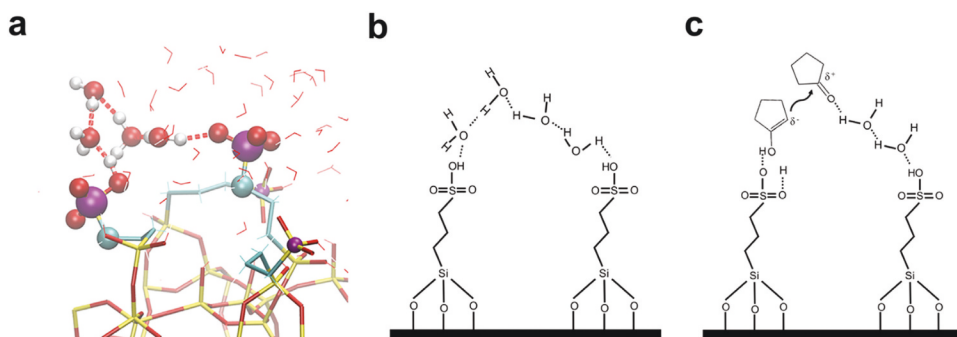


Figure 23. Optimized structure of water molecules interacting with a SO₃H-functionalized amorphous SiO₂ surface: a) the AIMD simulations of interaction between water and SO₃H groups; b) schematic illustration of AIMD simulations; c) proposed mechanism of C-C coupling in the presence of water. From Ref.[164].

reaction through interaction with a delocalized hydronium ion from a neighboring framework acid site may not enthalpically stabilize a transition state that likely already is positively charged. Rather, an additional water bridge may further separate a transition state from the surface, leading to an entropic contribution to increased rates for some reactions due to the additional entropy of the transition state. In many ways, this would echo what others have observed with high site density for activation of alkanes, where rate enhancements are often proposed as driven by entropy, not enthalpy [162]. One could infer that the extended range that water imparts to an acid site could modify a variety of reactions in a similar way. We caution readers, however, that this effect will not be universal for all reactions or reaction conditions. We use another example to illustrate these effects. For the reaction of propylene oligomerization, Bell et al. [163] reported shifts in oligomerization rates with site proximity due not to interaction of molecules with the sites themselves, but interaction of transition states with the oligomeric species that accumulate. Modification of the local confining environment around the transition state can also have consequences on rates which should be considered. In these examples, the role of water to shuttle protons could both influence the entropy of a transition state, but in some instances where water modifies the presence of local surface species enthalpies may also be influenced.

Similarities may be drawn between framework Brønsted site density and grafted functional group density on mesoporous structures, with such effects potentially more profound in bifunctional chemistry. As an example, water has been shown to shift reaction mechanisms responsible for condensation of cyclic ketones, with the influence a strong function of acid site density. At high density of acid sites, in this case tethered sulfonic groups, the aldol condensation reaction proceeds through a Langmuir-Hinshelwood dual site

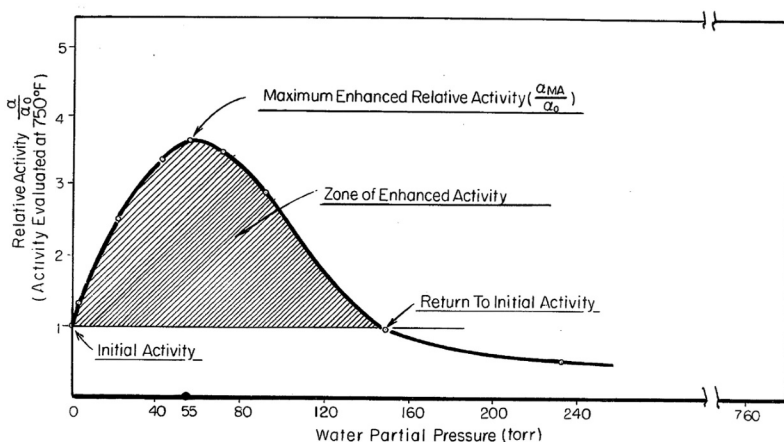


Figure 24. Dependence of activity enhancement during n-hexane cracking at 750°F on water partial present during calcination pretreatment. From Ref. [165].

mechanism. On the contrary, with a low site concentration the reaction behaves like a bimolecular, single-site mechanism due to the inability of a second site to polarize the second ketone. The presence of water serves to extend this effect, shifting catalysts that previously behaved as isolated sites to a dual-site mechanism due to presence of a water bridge as depicted in Figure 23. These effects will undoubtedly be present in reactions catalyzed by protons in zeolite pores as well [164].

When discussing the role of water pertinent to vehicle hopping or Grotthuss mechanisms to either protonate polar species or remotely polarize molecules, one must clarify that the polarity of a surface is not a prerequisite to water inclusion within the pores. It is often understood that higher Al and defect concentrations make the internal pores of a zeolite more polar, and that more polar microporous environments make liquid water accumulation more favorable. A common misconception regarding the role of water in zeolite catalysis is that it does not play a significant role on catalytic chemistry unless the pores are sufficiently polar to allow water to enter the channels. This is true with bulk liquid water, but not with water vapor. Water generally can penetrate by diffusion in all zeolite pores, regardless of the Al or defect content present, but the ability to form bridges necessary for two sites to influence a single adsorbate will undoubtedly depend on the T site location and proximity.

2.6. Role of EFAL and partially coordinated framework sites on reactivity

In addition to the modified environment surrounding a framework acid site, and the potential for water to form bridges to remotely protonate or polarize molecules, water also causes several modifications to a zeolite's structure that can influence reactivity. While much attention has been made regarding

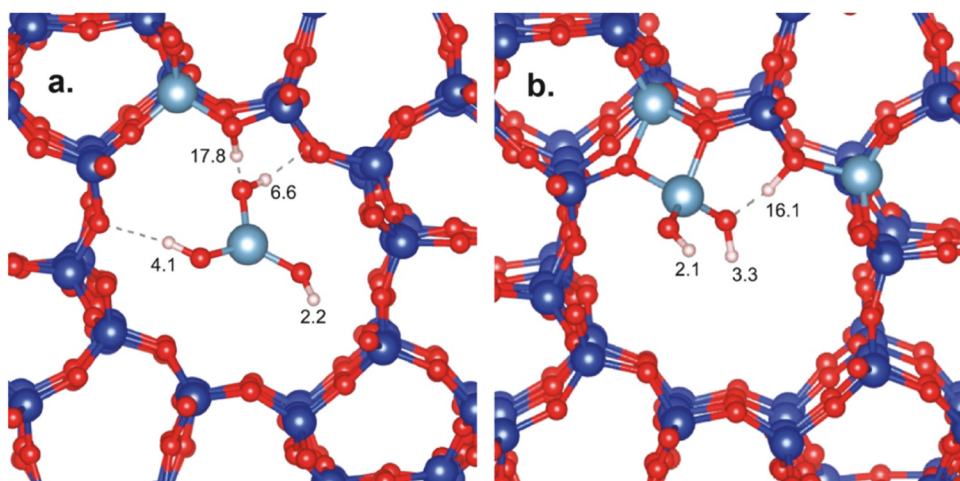


Figure 25. DFT-calculated HZSM-5 framework and extra-framework structures for a) an isolated and b) a paired framework acid site arising from next-nearest neighbor lattice Al atoms. Calculated ^1H chemical shift values are shown next to each protonic species, including the $\text{Al}(\text{OH})_3$ and $\text{Al}(\text{OH})^{2+}$ species in a and b, respectively. From Ref.[25].

structural modifications leading to loss of crystallinity and pore collapse, the more minor alterations to Al sites can lead to enhancements in activity. Haag recognized this enhanced activity for n-hexane cracking as a function of water partial pressure as can be shown in Figure 24 [165]. In this case, the rate passes through a maximum after exposure to moisture at modest temperature during catalyst calcination. Further increases in water pressure diminish rates, as subsequent attack by water leads to more severe removal of Al from the lattice and crystal collapse. This large range of treatment conditions that result in higher rates per gram of catalyst reveal that structure modifications are responsible for the observed conversion enhancement.

Water interaction with framework acid sites may influence reactivity in a variety of ways. As mentioned in section 1.2.2., Silaghi [48] and others have revealed that the initial attack of a zeolite by water is not necessarily rate determining [166–168]. We note that some of these features, such as the partially coordinated sites recently revealed by Chen et al. [47] do appear to be related to high temperature conditions. This implies that some correlation may exist between features observed under mild conditions and high-temperature reactivity. For example, these partially coordinated species may be more prone to fully leave the lattice and create sites we typically attribute as responsible for high temperature zeolite cracking. Aluminol species alone have been shown to themselves be active for low temperature H/D exchange reactions, but not necessarily for more demanding reactions such as cracking; but when these species are in proximity to additional framework sites, many consequences on the catalytic chemistry observed over these sites may result.

Extra framework or “non-crystalline” framework Al, i.e., defect sites of incomplete coordination, species create very different reaction environments when one considers the density of framework species. Figure 25 reveals the different form that an extra lattice hydrated Al species will take if interacting with a single framework atom vs. two framework acid sites in proximity [25]. Upon considering the n-hexane cracking rates over a MFI catalyst with a framework Si/Al ratio of 15, mild ammonium hexafluorosilicate (AHFS) washing to remove the extra lattice species, while not significantly modifying the framework sites nor the number of BAS's sites in close proximity, reveal that the high temperature cracking reactivity was correlated to the presence of extra-lattice or non-crystalline species, with a near factor of 4 loss in rate upon their removal by mild AHFS washing. Indeed, that same study showed that in “clean” catalysts containing only crystalline framework BAS's, the addition of sub-stoichiometric water did not increase H/D exchange rates as it did in catalysts prior to AHFS-washing, i.e., rates decreased, suggesting that the function of adsorbed gas-phase water at an isolated framework BAS does not lead to enhancements via a transition-state stabilization route in the absence of other proximate Al species. However, in-situ NMR revealed that water, the BAS, and both the CH and CH₃ groups of isobutane were involved in proton exchange via the expected carbenium ion mechanism, with exchange occurring first at the CH group.

Extra lattice species can induce reactivity in three general ways. Extra lattice aluminum cationic species may serve as Lewis acids, and when hydrated form aluminol species they are themselves mildly acidic. The ability of isolated cationic species to facilitate reactions, however, is quite limited. The most profound alterations in reaction rates have been attributed cationic species in the proximity of framework protons [169–171].

Even given this narrow depiction of the active site, several explanations have been presented to explain the enhanced activity observed when extra lattice Al species are in proximity to framework protons, ranging from increased acid strength [169], enhanced heats of adsorption of reaction intermediates [170] and the polarization of alkane molecules by Lewis acidic sites [171].

Stronger acidity is most commonly evidenced by two general shifts in behavior. The proposed mechanism for such a shift in acidity is ascribed to a partial electron transfer from the OH bond in the bridging acid site to the EFAL species, effectively modifying the deprotonation energy. The first is the shift in wavenumber of proton NMR spectra, where the presence of an extra lattice aluminol, similar to what is depicted in Figure 25b, is shifted to the 12–15ppm range. It should be noted, however, that many factors can contribute to shifts in a ¹H NMR spectrum, and these shifts do not necessarily correlate with deprotonation energy [172,173]. Further, it is common to attribute activity enhancements to increased acid strength based on the temperature by which a base such as NH₃ or pyridine desorbs from a catalyst surface [169,174].

However, the NH_3 desorption temperature is dependent on many factors, including the number of sites, the diffusion path length, presence of constrictions, and a variety of other factors. It should not be used as a metric to measure the strength of acid sites [141]. In summary, while deprotonation energies may be influenced by the presence of a neighboring species that modifies the local charge surrounding a proton, these techniques alone do not suffice to make such claims.

Results from van Bokhoven et al. [170] suggest that the enhancement in activity upon steaming is due to increased adsorption enthalpies that result from the coupled presence of extra lattice species and framework protons. They combined adsorption enthalpy and cracking kinetics analysis to conclude that the modest shift observed in apparent barrier can be ascribed to a slight increase in adsorption enthalpy caused by steaming. In agreement with this proposal, calorimetry experiments reveal a $\sim 5\text{--}10$ kJ/mol difference in adsorption enthalpy at low coverages on steamed samples. With identical intrinsic activation enthalpies, apparent enthalpies of activation will be slightly reduced, leading to rate enhancements, only when activation entropies are not greatly affected.

Modification of active sites by polarization of transition state due to the presence of extra lattice species has also been proposed. Zholobenko et al. [171] suggested that, contrary to other opinions, the steaming of HZSM-5 catalysts results in weaker, rather than stronger, Brønsted sites, ascribed to weakly acidic aluminol species generated by the steaming. Nonetheless, they noted an activity enhancement, ascribed to the polarization of adsorbed molecules that lead to higher rate constants for n-hexane cracking. The authors supported this claim by pointing to a band shift observed for methane adsorption at 2860 cm^{-1} .

An alternative explanation has been made by Gounder et al. [168] regarding the role of the remaining void size surrounding a framework proton when extra lattice species are present. They argued that the enhancements in activity

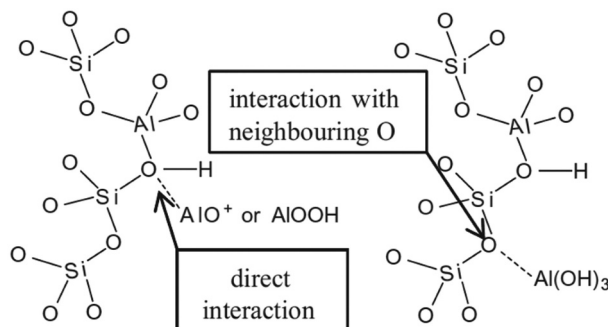


Figure 26. Interpretations of extra lattice Al species interacting with an isolated Al site. From Ref. [178].

observed in the presence of extra lattice Al species were simply due to a more confined environment that these species create. Observed enhanced rates for specific reactions in well-defined void spaces of different size can be used to infer reactivity of extra lattice species as well. To support their claims, they report isobutane cracking and dehydration rates per accessible proton, which are not altered when various amounts of Na are exchanged within the zeolite. They used this result to argue that a minority of sites with a higher affinity for Na^+ exchange could not be responsible for the observed enhancement in reaction rates, and enhancement is rather likely to be due to changes in confining environment. We note that others have observed the opposite effect, with selective removal of enhanced activity with small amounts of Na addition [175–177].

Lercher et al. [178] have suggested yet another explanation for the enhanced activity resulting from the presence of extra lattice species. They propose that this is not due to shifts in adsorption enthalpy nor in intrinsic enthalpy of activation, but to modifications of the entropy of adsorbed species and transition states. The authors note that rates for pentane cracking were more active over MFI catalysts with a higher density of active sites, speculating that the cause of this activity is due to a Brønsted site in proximity to an extra lattice Al site, with variants depicted in Figure 26. Removal of extra lattice Al by AHFS washing, again reduce the TOF to the rate per proton comparable to that measured over a low site density catalyst. Contrasting van Bokhoven's claims, they adsorbed n-pentane and did not observe measurable differences in adsorption enthalpy, leading them to conclude that higher surface coverages or stronger adsorption were not the cause of the observed rate enhancements. Cracking rates were higher over the high site density catalysts with extra lattice species, nonetheless, but activation enthalpies were not reduced. Instead, they were comparable or marginally higher over the more active catalysts. They ascribed the enhanced activity to a higher transition entropy that results when an extra lattice species is interacting with the transition state to provide more degrees of freedom.

The debate regarding the number of sites potentially created and responsible for the increases in activity is an important one. Haag et al. suggested that the activity enhancements in MFI samples upon steam treatment result in a great minority, 1–5% of the active sites, that are highly active [179]. Similarly, Fritz and Lunsford arrived at a similar conclusion based on the degree of cracking activity lost based on small levels of Na titration [176]. These claims have been debated, and are a very challenging proposal to prove or disprove, as these features may be so small that they are challenging to or sometimes impossible to measure. This concept has been rebutted by others [170] who have noted shifts within experimental uncertainty of activation energy and claim this as evidence that a minority of sites are not responsible for increased

rates. Nevertheless, this is an important area for future study as our ability to measure species that are in lower abundance improves.

In addition, while the argument that confinement is an important factor that must be considered when evaluating reactivity, we must acknowledge that to truly test if extra lattice species influence an active site, the location of these species with respect to that site is important. As a simple example, Hensen et al. [180] attempted impregnation of Y zeolites with various loadings of extra lattice Al species and were not able to replicate the activity enhancements that one observed upon steaming the zeolite. They attributed this to the cationic nature of species that are generated in-situ during steaming, and the importance of both their nature and location on creating more active sites. This result coupled with Lercher's observations as well as our own of enhancement in the presence of both extra lattice species and high framework site density implies that predicting the nature of these highly active sites is more complicated than some theories would suggest. Both the location of the active sites as well as the form and location of extra lattice species all appear to contribute to this enhanced activity observed.

3. Outlook

We have summarized a variety of elements by which water can affect structure/composition of zeolites and consequently manipulate activity. It is clear that these structural and compositional modifications not only depend on the original characteristics of the zeolite (framework, Si/Al ratios, defect density, presence of promoters, etc.) but also crucially depend on the conditions of the interaction with water (vapor or liquid; low or high temperatures). We draw attention to the important consideration regarding framework modification that is often overlooked, which is the rate-determining nature of each hydrolysis step. Framework stability or extra framework generation is often linked to the initial hydrolysis step, while in many cases these initial hydrolysis steps are facile and not kinetically relevant. Further studies to understand the intrinsic phenomena occurring during the different regimes are encouraged.

Similarly, additional experimental and computational work is needed to investigate structure-properties aspects such as:

- The exact mechanism of thermal stabilization of zeolites by the presence of rare earths (in FAU) and phosphorous (in MFI). While significant advances have been made in recent years regarding the location and migration of these cations in and out of FAU sodalite and supercages, more details on how they prevent dealumination under steaming conditions are still needed. Similarly, while the benefits of P on catalytic performance are clear, their exact mode of promotion is still a matter of discussion.

- The dynamics of tetrahedral framework Al interconversion with partially coordinated framework Al species in the presence of liquid and vapor-phase water, and concomitant impacts on the reaction rates.
- The transition between low-temperature and high-temperature regimes in both liquid phase and vapor phase that dramatically alter the effects of water on zeolite structures, from reversible hydrolysis that can only be demonstrated by isotopic labeling to irreversible dealumination and mesoporous formation to total collapse of the zeolite structure.

An interesting approach that may generate further applications is the utilization of controlled hydrolysis to prepare zeolite precursors, which subsequently can produce novel zeolite topologies. This top-down approach has been clearly demonstrated on various zeolites substituted with Ge and subsequently hydrolyzed in liquid water. This is an approach that might be expanded to other systems and it is, therefore, worth investigating further.

We have also analyzed the multiple ways by which water can affect catalytic activity, another area of recent interest that also requires further investigation. While the conflicting reports often observed regarding enhancement or inhibition of activity upon introduction of water can lead one to believe that there are no unifying concepts, we are beginning to realize that this is simply a result of erroneous attempts to over-generalize findings. Reactions often invoked to study the role of water such as H/D exchange, methyl isomerization, alcohol dehydration, and alkane cracking vary widely in terms of the activation barriers required. In addition to the range of stability of kinetically relevant intermediates and transition states, the conditions used to study these reactions vary widely as well. Some reactions may be influenced by water partial pressure in-situ, but to date water-induced enhancements have only been observed over a narrow window of partial pressure where significant water accumulation does not occur. In this sense, evaluating the enhancements in methyl shift results at low partial pressures invoked by Wojciechowski [151,152] are not necessarily contradictory to the results of large alkane cracking with very high partial pressures of water reported by Corma [153]. The partial pressures involved as well as the nature of reactions studies are not comparable. Further, we know that many reactions are sensitive to the nature of active sites as well. We have recently learned that catalysts with a higher framework site density are also more susceptible to form partially hydrolyzed species that appear to contribute to chemistry that occurs under mild conditions while also correlating with increased rates observed under high-temperature conditions [47]. Further, these sites may serve as precursors to other active sites after high temperature treatments, both of which depend not only on the Si/Al ratio, nor the total amount of extra framework species, but rather the proximity of sites and the nature of these extra framework species in proximity to them. As our abilities to systematically modify site location, extra

lattice type, and characterize the resulting sites created, these unifying concepts will continue to emerge.

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