Review

Water–active site interactions in zeolites and their relevance in catalysis

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Zeolites are one of the most successful catalyst materials of the 20th century and are anticipated to be crucial in the coming decades to transition towards a more sustainable and circular society. Traditional zeolite-based catalytic processes, such as hydrocarbon cracking and transalkylation involving fossil-based resources, are usually performed in the absence of water. With the development of renewable processes based on agricultural and municipal waste, oxygen-rich molecules must be converted, which involves the presence of water. Hence, the impact of water on zeolite-based catalytic performance becomes crucial. In this review, we discuss the current understanding of the role of water during zeolite catalysis and provide insights into mechanistic aspects of water–zeolite interactions. Special attention is paid to molecular modeling approaches. A synergy between experimental and theoretical approaches represents another major challenge in modern catalysis science as it provides routes towards the design of novel and more stable zeolite catalysts.

Zeolites: general features and their applications

Since their introduction in the 1960s, **zeolites** (see Glossary) have taken an unquestionable place in the family of industrially important solid catalysts [1]. The large structural variability together with the unique catalytic activity and shape selectivity ensures that zeolites are often the most equipped catalysts for commercially important chemical processes, such as fluid catalytic cracking [2], hydrocracking [3], dewaxing [4], olefin oligomerization [5], alkylation [6], aromatization [7], and the methanol-to-olefin (MTO) conversion [8]. Current global environmental issues motivate to an extent the applicability of zeolites towards the production of renewable transportation fuels and important platform chemicals from alternative feedstocks such as biomass [9]. With new applications involving agricultural and municipal waste emerging, there is a powerful incentive to understand the fundamental aspects of zeolite chemistry that can aid in the rational design of future catalyst materials as well as in the optimization of current chemical processes.

Whether we consider already industrialized processes or novel zeolite applications, the zeolite-based catalyst is exposed to water at a certain point in its lifetime. Water plays a dual role as it can optimize catalytic reactions while, at the same time, it causes irreversible catalyst deactivation due to dealumination and/or desilication. Due to the rather complex nature of the whole catalytic system, these aspects are usually discussed separately, which does not reflect the behavior of a real catalytic system. The purpose of this review is to interpret the role of water during the catalytic cycle, based on the perspective of molecular-scale interactions between water and the zeolite. Since this topic covers rather a broad range of materials and conditions, we aim not to review entirely all of the available literature from the past years. Instead, we focus on the most important examples of how water alters the catalyst performance and link them with the underlying elementary processes.

The review is organized as follows. In the second section, we provide an overview of the role of water during the catalytic cycle from a macroscopic point of view, while in the third section we

Highlights

Water plays an important role during the utilization of zeolite catalysts for modern applications such as agricultural and municipal waste conversion.

Water has a divergent role in the catalytic cycle: it can cause irreversible catalyst deactivation as well as improve the catalytic activity.

The most important water–zeolite interactions occurring on the atomistic level include water adsorption to the active site, hydrolysis of zeolite framework bonds, and the formation of protonated water clusters and water–reactant complexes.

Atomistic modeling is indispensable tool in progressing the field of zeolite chemistry and catalyst design.

Efforts must be invested in the development of more realistic zeolite models and in situ characterization techniques.

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discuss current achievements in atomic-scale understanding of the underlying process and identify challenges in the pursuit of rational catalyst design. We end with concluding remarks and present our perspective on the development of future research.

Role of water during the zeolite lifetime

Zeolite synthesis

The distribution and nature of the acid sites across the zeolite framework crucially affect its catalytic properties as well as the hydrothermal stability [10–12]. Therefore, the synthesis of zeolites with a desired aluminum distribution is still an important topic of interest [13–15]. Recently, it has been proposed that water solvation can play a decisive role in the validity of **Löwenstein's rule** [16] (Box 1). Hence, the understanding of the role of water as a synthesis medium is crucial for the design of a functional zeolite-based catalyst and much work remains to be done to understand hydrothermal zeolite synthesis properly.

The concept of shape selectivity occurring in zeolites is attributed to their microporous structure with dimensions matching the size of small molecules. However, confinement of the pores often limits the catalytic performance by restricting the diffusion of reactants and reaction products within the zeolite network. The mass-transport limitations can be mitigated by introducing secondary pores (i.e., mesopores), as is done for **hierarchical zeolites** [17–19]. Mesopores can be formed either during zeolite synthesis using pore-directing agents, such as carbon, or by applying an additional treatment on already synthetized zeolites, including **zeolite steaming** and acid/base leaching [20,21]. During zeolite steaming at elevated temperatures (>673 K), water hydrolyses Si–O–Al bonds and removes aluminum atoms from the zeolite framework forming a defect site and extra-framework aluminum (EFAl) species [22]. The treatment is usually followed by a mild acid wash to remove amorphous debris from the zeolite pores. Zeolite steaming has been traditionally used in industry to control the Si:Al ratio as well as to tune to improve the catalyst stability and activity [17,18,23–25]. For example, Almutairi and colleagues studied the influence of steaming pretreatment on methanol and propane conversion reactions in zeolite HZSM-5. They found that under mild conditions the EFAls were inserted back into the framework at the defect site, while severe steaming resulted in a substantial decrease of acid sites. The latter pretreatment increased the conversion rate of methanol and reduced the coke formation rate [26]. A beneficial effect of steam pretreatment on catalyst performance was also observed for other processes, including ethanol dehydration and 1-butene cracking to propylene [27,28].

Steaming can be used either to directly create mesopores in zeolites with a high Al concentration or in a tandem treatment prior to desilication to increase the Si:Al ratio and thus facilitate the subsequent dissolution of framework Si atoms [29,30]. In the latter case, dealumination has a decisive role in the efficiency of subsequent desilication treatment. Groen and colleagues showed that the resulting distribution of framework Al created during dealumination acts as a pore-directing agent [31]. The subsequent desilication is most efficient if the dealumination results in

Box 1. The validity of Löwenstein's rule

Based on theoretical calculations, Fletcher and colleagues proposed that in a bare protonated zeolite framework with a low Si:Al ratio, Löwenstein's rule is not obeyed, while in its sodium form it is [16]. Zeolites are usually synthesized in their sodium form and no direct zeolite synthesis method, which can directly produce the protonated form of zeolites, exists. Thus, it seems likely that non-Löwenstein's Al distribution can be generated only via post-synthetic treatment methods such as zeolite steaming, during which reorganization of the Al distribution occurs. However, recent first-principle modeling results suggest that in an aqueous environment the situation is different, and under hydrothermal conditions the formation of Al–O–Al linkages is avoided [105,106]. To date, there is no experimental evidence for violation of Löwenstein's rule in zeolites, although some exceptions have been found for other aluminosilicates with Si:Al ratio below 1 [107].

Glossary

Hierarchical zeolites: possess both micro- and mesoporosity. While micropores of diameter below 2 nm are needed to retain the shape-selective properties of zeolites, the introduction of meso- and macropores with dimensions between 2 and 50 nm ensures the optimal accessibility and transport of reactants and products by shortening the diffusion path length.

Hot liquid water: depending on the reaction conditions (i.e., temperature and pressure), water is either in a condensed or a gaseous phase. Hot liquid water refers to liquid-phase conditions with water heated above the boiling point (373–573 K), while steaming occurs at higher temperatures and lower pressures.

Hydrocarbon pool (HCP) mechanism: the most accepted mechanism for the MTO process. The active sites to produce hydrocarbons are a combination of BASs and a pool of both charged and neutral organic reaction intermediates trapped in the zeolite pores, which autocatalyze the methanol conversion. The exact reaction steps are still debated.

Löwenstein's rule: an empirical and generally accepted axiom of zeolite science, which forbids the occurrence of neighboring aluminium pairs in the zeolite framework.

Zeolite dealumination: during zeolite steaming, hydrolysis of Al–O bonds occurs leading to the selective removal of Al atoms from the framework (therefore the name 'dealumination'). While so-called severe steaming is often referred to as a treatment that causes a collapse of the crystal structure and irreversible catalyst deactivation, mild steaming mostly produces catalysts of higher activity. However, there is ambiguity in the literature about the exact conditions under which the treatment is performed [26,32,104].

Zeolite desilication: like water-induced dealumination, the zeolite framework structure is affected, but in this case the Si–O bond is broken, which is induced by dint of aqueous (basic) conditions. Desilication is conventionally used in a tandem reaction with dealumination treatment to create secondary mesopores.

Zeolites: crystalline aluminosilicate materials with a well-defined porous framework. The elementary building units of zeolites are TO_4 tetrahedra,

a homogeneous Al distribution, while an Al gradient across the crystals leads to too-large pores [30]. The tailoring role of dealumination pretreatment on mesoporosity generation has been recently confirmed by Yang and colleagues [29]. Using confocal fluorescence microscopy on single zeolite ZSM-5 crystals, Aramburo and colleagues showed that homogeneously distributed pores over the entire crystal are obtained after severe steaming at 973 K, while mild steaming generated only surface mesoporosity [32]. Karwacki and colleagues used focused ion beam (FIB) and scanning electron microscopy (SEM) tomography to characterize the distribution of pores within the same zeolite crystals. A nonuniform distribution of mesopores was observed, with more pores formed when sinusoidal pores were opened to the external surface [33]. Site specificity for Al removal during steaming was later confirmed both experimentally and theoretically as well as for other zeolite topologies [34,35], which suggests that post-synthetic zeolite treatment can be potentially used to tailor the Al distribution in zeolite materials.

Zeolite catalysis
Steering zeolite reactivity with water
While the effect of water in pretreatment can be great and is already better understood, the effect of water on catalytic reactions is often more controversial. Water can improve catalyst performance as well as cause catalyst deactivation. Corma and colleagues studied the steam catalytic cracking of naphtha over zeolite HZSM-5 at 923 K and observed intensive catalyst deactivation due to water-induced dealumination. At the same time, co-feeding with steam significantly decreased the formation of H_2, CH_4, and potential coke precursors [36]. Yang and colleagues applied steam during a catalytic fast pyrolysis of cellulose. The steam caused irreversible catalyst deactivation due to dealumination, resulting in lower yields of aromatics and coke precursors and higher yields of CO, methane, and other unidentified reaction products [37]. Catalyst deactivation due to **zeolite dealumination** was also observed during upgrading of the pyrolysis oil in zeolite HZSM-5 [38].

Water and C1 compounds, such as CO_2 and methanol, are always side products during the catalytic upgrading of oxygen-abundant biomass feedstock. Thus, a further conversion of low-carbon compounds in the presence of water into valuable platform molecules, such as olefins or aromatics, is necessary for the successful optimization of the whole process. It was shown that co-feeding with water during zeolite-catalyzed methanol conversion improves the selectivity towards olefins and suppresses catalyst deactivation due to coking [39,40]. As a result, a prolonged catalyst lifetime and a decrease in the rate of coke deposition were observed [40,41]. Chen and colleagues studied the zeolite-catalyzed isobutane C–H bond activation and showed that the reaction can be both catalyzed and inhibited by water, depending on the water loading [42]. Similar behavior was observed by Wang and colleagues in the conversion of ethene into aromatics over zeolite HZSM-5. While under moderate reaction temperatures (573 K) water decreased the conversion of ethene and the yield of aromatics, at higher temperatures (623–773 K) the influence of water became beneficial due to suppressed coke formation [43].

Water as a reaction medium
Very different behavior is observed when zeolites are exposed to **hot liquid water**, as they are during biomass conversion in aqueous solution, including dehydration [44], hydroalkylation [45], and hydrodeoxygenation [45,46]. While water is an attractive solvent because it can solubilize oxygen-rich biomass compounds, zeolites provide a confinement [47]. However, a dramatic structural collapse of the zeolite even at temperatures as low as 473 K has been observed [48]. Hot liquid water attack occurs preferentially via hydrolysis of Si–O bonds [49], creating hydrophilic defects that propagate further degradation. Zhang and colleagues studied the stability of different zeolite samples of varying Si:Al ratio, density of silanol defects, and density of Brønsted acid sites

where each T-site can be occupied by either silicon or aluminium atoms. Neighboring tetrahedra are linked at their corners via shared oxygen atoms, producing a great variety of 3D porous structures with shape-selective properties. The inclusion of aluminum in the zeolite structure causes an increase of a local negative charge, which must be compensated by a cation to ensure the overall neutrality of the framework. The cationic sites are sources of Lewis and/or Brønsted acidity, giving zeolites their catalytic properties. Additionally, the Al atom makes the framework hydrophilic, while purely siliceous zeolites are considered hydrophobic.
Zeolite steaming: a post-synthetic zeolite treatment method in which the zeolite is exposed to water vapors in a controlled manner at temperatures higher than 673 K. For example, steaming of zeolite Y is a preferred industrial method to create ultrastable zeolite Y with superior hydrothermal stability [25].

(BASs) on exposure to liquid water at 473 K. They observed that MFI as well as FAU zeolites can be stable or unstable depending on the synthesis procedure and post-synthesis treatment, and samples dealuminated via steaming with a high density of defects suffered severe degradation [50]. The stability of zeolites in hot liquid water can be improved by silylation and carbonization of defects with organosilanes, underpinning the hypothesis that zeolite collapse is initialized at defect sites [44,50,51].

Zeolite regeneration

An essential part of the catalytic cycle, after deactivation by, for example, coke deposits, is zeolite regeneration, in which the catalytic activity of the spent catalyst material is restored. An unavoidable side-effect of the harsh regeneration conditions to which the catalyst is exposed during the regeneration step is the eventual collapse of the zeolite framework. Liopoulou and colleagues investigated the performance of zeolite Co-ZSM-5 during catalytic biomass pyrolysis in a pilot-scale fluidized bed reactor [52]. In another study, Vitolo and colleagues studied the behavior of zeolite HZSM-5 during the conversion of pyrolysis oil through multiple upgrading–regenerating cycles [53]. Catalyst deactivation was observed in both studies. Vitolo and colleagues concluded that the primary cause of the catalyst deactivation is the loss of acid sites, which were gradually removed during the regeneration cycles [53].

Irreversible catalyst deactivation due to dealumination during regeneration cycles is an issue for methanol conversion and traditional processes such as steam cracking or fluid catalytic cracking [2,54–56]. Considering rapid catalyst deactivation by coking, preservation of catalyst stability after many regeneration steps without significant irreversible deactivation is of the highest importance. The hydrothermal stability of zeolites is traditionally improved by an exchange with rare-earth ions (e.g., La^{3+}), but also the effect of other metals and phosphorus has been explored [57–60]. Nevertheless, the mechanism of how extra-framework cations prevent water-induced dealumination is still highly debated in the literature [61–64]. Recent density functional theory (DFT) results suggest that the introduction of extra-framework cations makes the kinetics of Al–O bond hydrolysis energetically more demanding [62,64].

## Molecular insights into water–zeolite interactions

All of the above studies point to various phenomena that occur in zeolites due to presence of water, such as dealumination or the attenuation of coke formation. In what follows, we discuss the current understanding of the underlying physicochemical processes at the atomic scale. The most important interactions occurring at the water–zeolite interface are summarized in Figure 1 (Key Figure).

Origin of zeolite acidity in the presence of water

Every chemical reaction with a solid catalyst material starts by the adsorption of a reactant. The preferred adsorption sites for water are the Al site with the BAS proton or defect sites, while Si domains are regarded as hydrophobic. It has been shown both theoretically and experimentally that water molecules inside the zeolite framework are heterogeneously distributed among Al sites [65–67]. De Wispelaere and colleagues studied the MTO process using molecular simulations combined with *in situ* microspectroscopy. They found that during the reaction water molecules compete with methanol molecules for adsorption on BASs, which results in the attenuation of all reaction steps including the reactions leading to the **hydrocarbon pool (HCP) mechanism**, responsible for coking (Figure 1A) [68]. Another explanation for the beneficial impact of water co-feeds has been proposed by Bollini and colleagues in which water catalyzes formaldehyde (an important MTO intermediate) hydrolysis, thereby causing attenuation of the reaction rates in the HCP mechanism [69].

Key Figure

Schematic representation of envisaged water–zeolite interactions
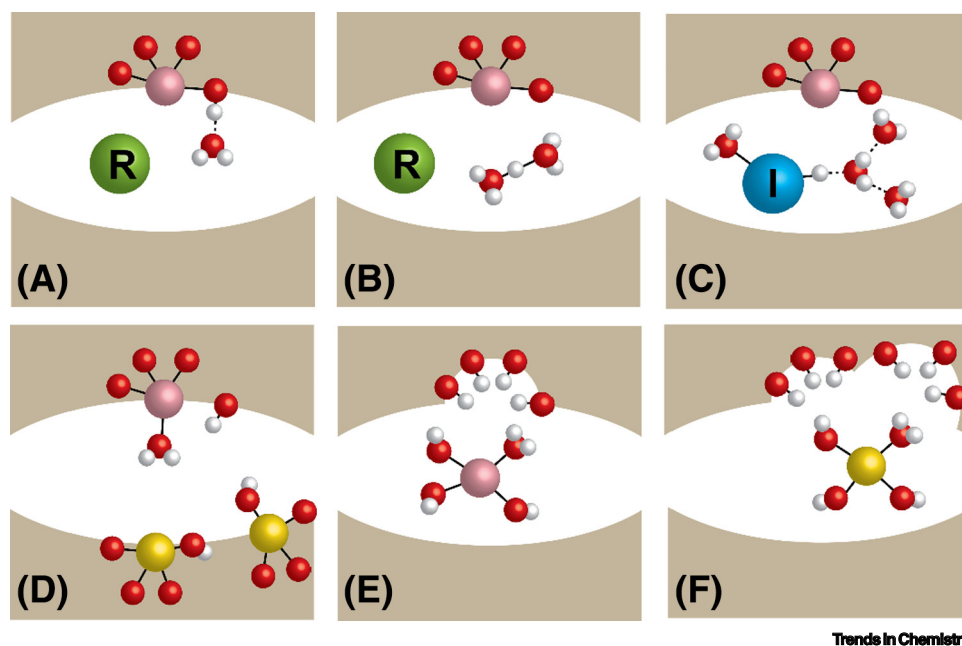
Trends in Chemistry

Figure 1. Water can (A) occupy the acidic proton and thus make it inaccessible for reactants, (B) form protonated clusters that act as mobile Brønsted acid sites (BASs), (C) alter catalyst selectivity and (de)stabilize reaction intermediates by the formation of water–intermediate clusters, or (D) attack the zeolite structure and cause reversible (E) or irreversible hydrolysis of the framework bonds [i.e., dealumination (F) or desilication], which is preferentially initiated from defect sites. Oxygen atoms are displayed in red, silica atoms in yellow, the aluminium atom in pink, and hydrogen in white color. R, reactant molecule (e.g., methanol, propanol); I, arbitrary intermediate during the catalytic conversion.

The chemical transformations of BAS protons (e.g., proton hopping) in the presence of water can be tracked using spectroscopic techniques or by molecular modeling methods. In recent work, Joshi and colleagues used reactive molecular dynamics (RMD) to probe the dynamics of water inside zeolite HZSM-5 and observed a depletion of acid sites due to frequent proton exchange between water molecules and the zeolite framework [70]. Vener and colleagues have used *ab initio* MD simulations to study the structure and dynamics of BAS protons in the H-form of the CHA framework structure under various water loadings. The authors observed the formation of protonated water clusters of various sizes depending on the water loading [66]. Although the size of protonated clusters remains highly debated in the literature, there is a general agreement that the smallest protonated stable water cluster contains at least two water molecules [70,71]. In an aqueous phase, all BASs are turned into solvated hydronium ions that provide protons for catalysis [72,73] (Figure 1B). The proton affinity of hydronium ions differs from that of the zeolite framework; thus, a change in the catalytic activity of the zeolite can be observed. Liu and colleagues combined ^{27}Al MAS NMR and ^{13}C NMR spectroscopy with DFT to follow the dehydration of cyclohexanol (a model molecule in the conversion of biomass towards unsaturated hydrocarbons) confined in zeolite H-BEA. The authors found that water enhances the zeolite activity by facilitating a proton transfer between hydronium ion–water clusters and cyclohexanol [74]. Eckstein and colleagues measured the adsorption properties of cyclohexane under varying

presence of hydronium ions. The authors showed that protonated water clusters of up to eight water molecules form a polar domain within the hydrophobic walls of the zeolite and impair the affinity of organic molecules for the zeolite framework, as shown in Figure 2 [71].

Recent mechanistic investigations on propanol dehydration in the presence of water suggest that water can impair the reaction rate by the formation of protonated water and water–propanol clusters of extraordinary stability (Figure 1C) [75,76]. Bates and colleagues have combined *in situ* IR spectroscopy with DFT calculations to resolve the structure of water–ethanol clusters in zeolite H-BEA during ethanol dehydration to form diethyl ether. At high water pressures (>10 kPa) extended hydrogen-bonded water networks were formed, which are disrupted more by interacting with transition states than with reactive intermediates. As a result, the catalytic process of ethanol dehydration is about three orders of magnitude inhibited compared with the reaction with no water co-feed [77]. Chen and colleagues studied benzene conversion in a dry and water co-fed zeolite H-ZSM-5 and observed that water's enhancement of the catalytic activity does not depend only on the reaction conditions, but also on other factors, such as the Si:Al ratio. The improvement of catalytic activity was observed only for the zeolites with a high density of acid sites (low Si:Al ratio) that allow 'vehicle-hopping' proton transfer, in which individual water molecules/hydronium ions act as a proton carrier between the acid sites [78]. Thus, one of the first steps towards control over the water effect on the catalytic reaction should be to relate the reaction conditions and system specificity (i.e., the Si:Al ratio and defect concentrations) with the structure and dynamics of water and BAS protons in a systematic manner.

Mechanism of reversible and irreversible deactivation

While protonation of water molecules in the acidic zeolite is a reversible process, water can also attack the zeolite and cause structural modifications of the framework. In this context two processes are relevant: zeolite dealumination and **zeolite desilication** (Figure 1D–F). In the past
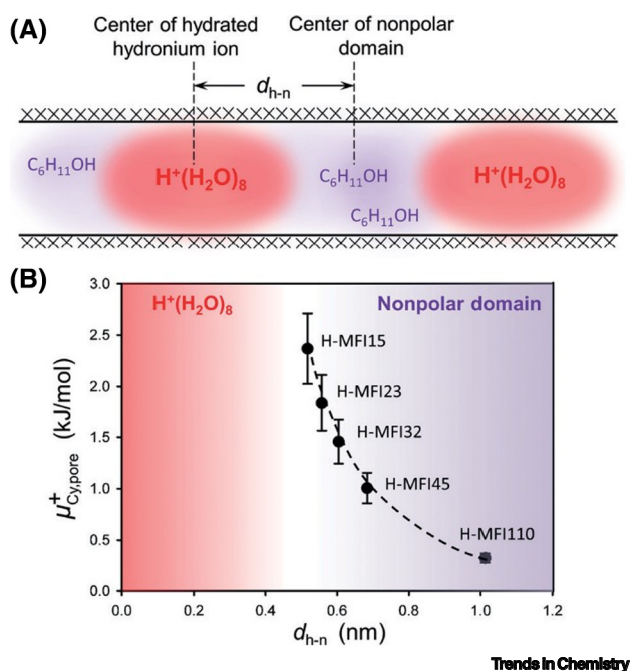
Figure 2. Formation of protonated water clusters in the zeolite channels and its effect on the adsorption of cyclohexanol. (A) Schematic illustration of polar and nonpolar domains in the micropore channels of zeolite H-MFI on the adsorption of aqueous cyclohexanol. Polar domains are made of solvated hydronium ions H_3O^+. (B) Chemical potential increment of adsorbed cyclohexanol as a function of the interdomain distance d_{h-n}. When domains are very close to each other, cyclohexanol is strongly destabilized. Extracted, with permission, from [71].

few years, computational simulations – especially DFT-based methods – have proved to be an essential tool to probe the mechanisms of catalyst deactivation [79,80].

A possible reaction mechanism for dealumination was first suggested by Lisboa and colleagues based on purely thermodynamic considerations [81]. However, the first information about reaction kinetics was obtained by Malola and colleagues, who studied both water-induced dealumination and desilication in zeolite SSZ-13 using static DFT [82]. For both processes, the authors proposed a stepwise reaction mechanism that proceeds via the formation of vicinal di-silanol that was previously identified as one of the stable defect species in zeolites [82,83]. The mechanism was later used to model desilication in silico-aluminophosphate zeolites (SAPO-34), which is a process analogous to zeolite dealumination [84]. However, a more plausible reaction mechanism, schematically shown in Figure 3, with lower activation energies was suggested by Silaghi and colleagues [35]. The viability of the proposed pathway was later confirmed by several computational studies using both static [85,86] and dynamic [87] DFT methods, for various zeolite topologies [62,88,89] as well as in the presence of different charge-compensating cations [61,62,89]. Based on these studies, our atomistic understanding of the dealumination can be generalized as follows. (i) Al–O bond breaking is always associated with the adsorption of at least one water molecule on the Al atom, and the stability of this adsorption state is lower than that of water adsorption on BAS protons or the formation of protonated water clusters [85]. (ii) A complete dealumination pathway to the formation of Al(OH)$_3$H$_2$O EFAl species requires at least four steps, of which three are the water-dissociation and subsequent proton-transfer steps and an additional step in which Al–O(H) bond breaking is induced by non-dissociative water adsorption. (iii) The reaction is facilitated by the presence of multiple water molecules that enhance the proton-transfer reactions [85,87]. Moreover, it has been shown that under sufficient water pressures non-dissociative water adsorption on the Al atom can partially dislodge Al from the framework, leading to a product with extraordinary stability of Al bonded to three framework oxygen atoms and water (Figure 1D) [85]. The process is fully reversible, and the existence of partially dislodged Al was confirmed using 3Q MAS NMR ^{17}O spectroscopy for zeolites that were in contact with liquid water at ambient temperature [90,105]. Recently, it has also been
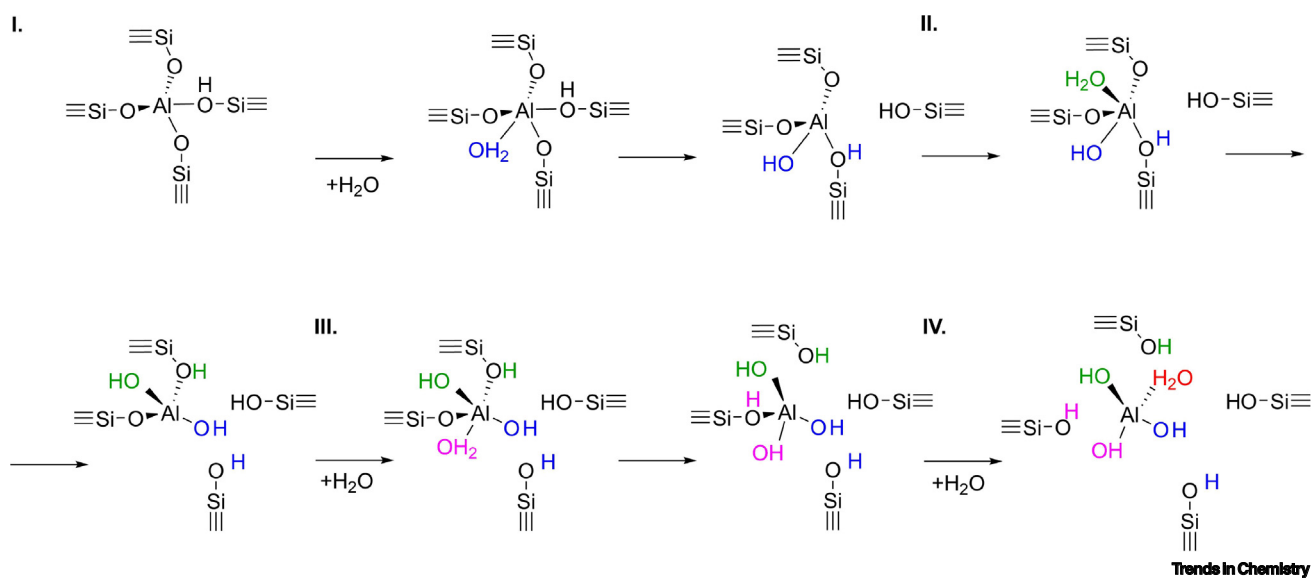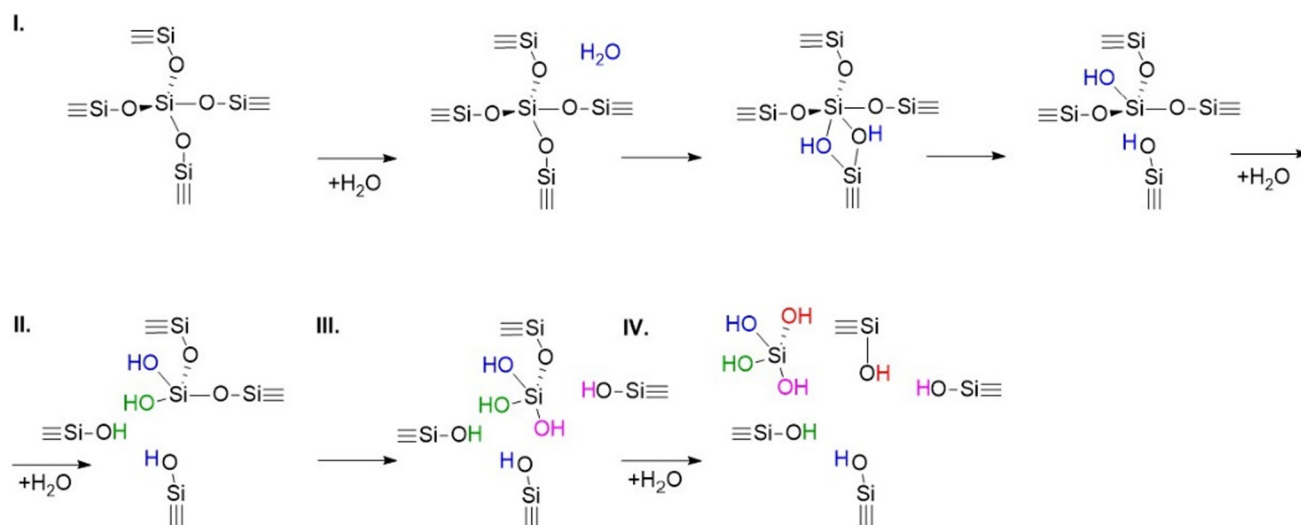

Figure 3. The envisaged mechanism for water-induced zeolite dealumination as proposed by Silaghi and colleagues [35].

shown that water adsorbed on the Al atom is an important surface site with mild Brønsted acidity [91]. The Al susceptibility towards partial or complete bond breaking is determined by zeolite topology as well as the accessibility of the active site [33–35,85], which suggests that the Al distribution can be tuned during post-synthetic zeolite treatment [85]. However, this hypothesis must be confirmed.

All of the abovementioned studies consider the presence of a single Al atom in the siliceous zeolite framework. However, the Al distribution – likewise, the Si:Al ratio – in zeolites can dramatically change their performance in catalytic reactions as well as the zeolites' susceptibility towards dealumination [10,33,34,92–94]. The 3D distribution of individual Al atoms in the zeolite framework depends on the exact conditions of zeolite synthesis [10]; thus, thermodynamics do not determine the structure of the zeolites and the calculation of the relative stability of Al atoms in the individual framework T-sites cannot be employed for the prediction of Al distribution.

An alternative approach has been recently taken by Louwen and colleagues, who used simulated annealing to create a periodic structure model of zeolite Y with a realistic Si:Al ratio that reproduces the experimental NMR data [61]. A promising methodology to partially resolve Al distribution is the direct coupling of DFT methods with experimental measurements such as extended X-ray absorption fine structure (EXAFS) analysis and ^{27}Al magic-angle spinning (MAS) NMR spectroscopy that, if combined with DFT modeling, are able to provide information about the relative occupancy of crystallographic sites (T-sites) [95]. The major (and currently impossible) challenge of this approach remains the upscaling of the procedure in a way that allows routine characterization of such zeolite-based samples.

The process of zeolite desilication in the presence of hot liquid water is much less understood. The only complete zeolite desilication pathway was proposed by Malola and colleagues, who followed a reaction route similar to that which the authors proposed for zeolite dealumination (Figure 4). However, in this mechanism, the formation of extra-framework silica (EFSi) [Si(OH)$_4$] requires the adsorption and dissociation of four water molecules instead of three dissociation steps and one non-dissociative adsorption [82]. The first Si–O bond breaking in a simplified silica model (i.e., dimeric hydridosilsesquioxane) was studied by Hühn and colleagues using a highly

Figure 4. The envisaged mechanism for water-induced zeolite desilication as proposed by Malola and colleagues [82].

(A)

Si–O–Si + H$_2$O → Si–OH + Si–OH

Si–O(H)–Al + H$_2$O → Si–OH + Al–OH$_2$

(B)

(C)
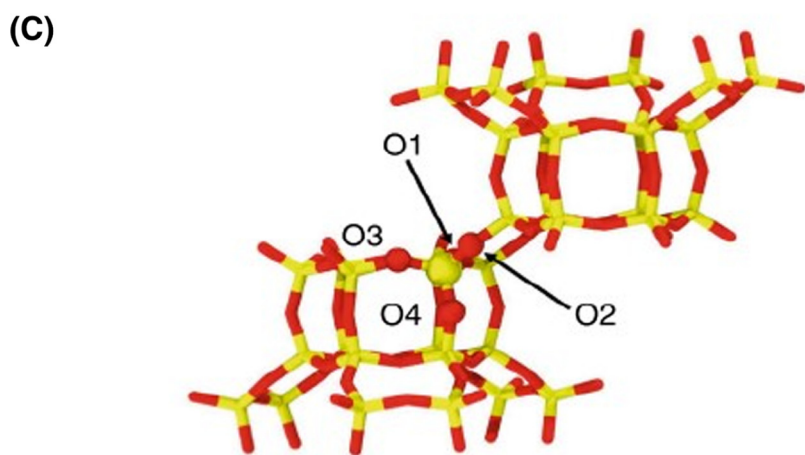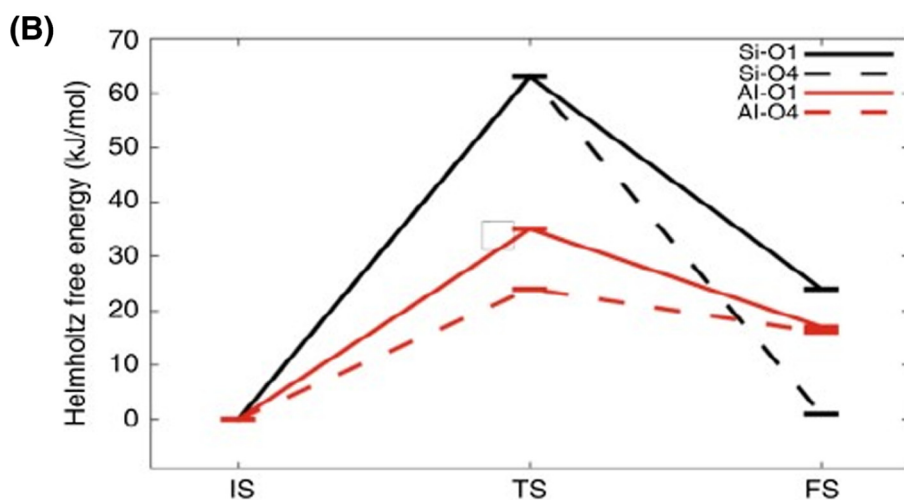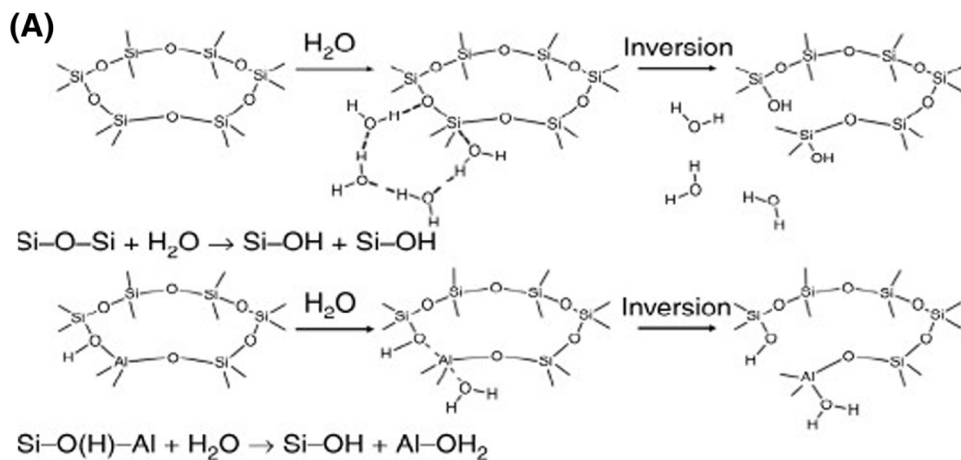
Figure 5. Water attack on the zeolite framework can cause the hydrolysis of Al–O and Si–O zeolite bonds. Extracted, with permission, from [73]. (A) The mechanism of reversible Si and Al dislodgement on water attack in zeolite H-SSZ-13. Si–O bond breaking is facilitated by a proton transfer via the Grotthuss mechanism across the chain

(Figure legend continued at the bottom of the next page.)

accurate multiscale QM/QM approach. In this mechanism, water is incorporated into the zeolite framework and the framework Si–O bond is replaced by two terminal silanol groups (Figure 1D). The reaction requires an activation energy of 163 kJ/mol [96]. Heard and colleagues showed that this reaction is reversible and can be catalyzed by the active participation of multiple water molecules that assist in a proton transfer via Grotthuss shuttling (Figure 5) [73]. A different hypothesis was put forward by Ravenelle and colleagues, who suggest that Si–O–Si bond hydrolysis is a hydroxide-catalyzed process instead of a proton-catalyzed process [48]. By contrast, Prodinger and colleagues attributed the collapse of the Al-rich frameworks (Si:Al = 50) to the attack of hydronium ions originating from the interaction of BAS protons and water [97]. Although zeolite stability in the presence of hot liquid water has been linked to the concentration of defect sites [50,97,98], little is currently known about the structure of the zeolite defects [83] and so far no reaction mechanism starting at the defective site has been proposed. Moreover, most of the reported mechanistic studies consider the interaction of water with the zeolite framework structure under conditions that are representative of steaming. A more realistic model should consider water as an aqueous solution with large amounts of water confined in the zeolite's pores.

During zeolite degradation, various extra-framework species (i.e., EFAl and EFSi) are formed. The EFAls can act as Lewis acid sites and thus influence the catalytic reactions [99]. Recently, Chen and colleagues showed that EFAl hydroxyl groups possess reactive protons that can react with hydrocarbon probe molecules such as alkanes [100]. This raises questions on the structure of stable EFAl species as it was not previously believed that EFAls can possess Brønsted acidity. It has been suggested that the clustering of EFAls and the confinement effect imposed by the zeolite framework can be a source of Al susceptibility towards dealumination [88] as well as it playing an important role in mesopore generation in a subsequent desilication treatment, as we discussed in the second section. Therefore, more efforts should be devoted to the study of structure of extra-framework species and their influence on catalyst performance [101].

Concluding remarks

Zeolite based-catalysis has been successfully explored for its use in sustainable manufacturing processes for transportation fuels and chemicals, which are not based on fossil-based resources but on renewable alternatives, including biomass. Nonetheless, new catalytic reactions starting from different oxygen-rich molecules comes with new scientific and technological challenges (see Outstanding questions). High-temperature conversion of oxygen-rich molecules such as methanol involves water formation, while the conversion of biomass-derived poly-alcohols, including sugar alcohols, into chemicals often requires an aqueous environment. By interaction with zeolite-based BASs and feedstock, water alters both the intrinsic catalytic activity and the selectivity of a chemical process. Furthermore, water vapors can induce hydrolysis of the Al–O bonds, while a dramatic collapse of the zeolite framework due to desilication occurs in the presence of hot liquid water. A solution can be a guided synthesis of new framework structures with optimized hydrothermal stability and catalytic activity, which cannot be achieved without a better understanding of zeolite synthesis, traditionally harnessed in a solution.

The rationalization of the role of water during zeolite synthesis and the conversion of biomass-derived molecules requires improvement of our knowledge about the elementary reaction

Outstanding questions

Can we control the Al distribution during post-synthetic zeolite treatment using steaming?

What is the mechanism of mesopore formation during zeolite steaming on the (semi)macroscopic level?

How does the mechanism of zeolite degradation in hot liquid water differ from the steaming conditions and how can we prevent it?

of water molecules. The Al–O bond breaking occurs on non-dissociative water adsorption on Al in the *anti*-position to a Brønsted acid site (BAS) and compared with Si–O bond breaking is less energetically demanding, as shown in (B). (B) Energy profiles of reversible Al and Si dislodgment caused by the water attack. Red and black colors correspond to Al–O and Si–O bond-breaking profiles, respectively, and are computed for two different protonation sites (O1 and O4). (C) A visualization of different protonation sites that were used as a model system to compute the energy profiles of reversible water-induced Al–O and Si–O bond breaking.

steps involved. In that respect, *in situ* and *operando* analytical methods, applicable in aqueous media or in the presence of steam, are of a great help [102], as has been recently demonstrated in, for example, the MTO reaction over HSAPO-34 when co-feeding water with *in situ* UV-Vis microspectroscopy and confocal fluorescence microscopy [68] and the oligomerization of furfuryl alcohol over HZSM-5 with single-molecule fluorescence microscopy [103].

In the past years, much atomic-scale information has also been gained from molecular modeling. Although molecular simulations are very effective, a remaining challenge is to create a zeolite model that reflects all of the relevant characteristics of the real zeolite system; that is, realistic Al distribution, acidity, and heterogeneities of the zeolite frameworks, including Al and/or Si zoning, as well as the presence of multiple species during catalytic reactions. An open question remains about how to connect our atomistic knowledge about elementary processes with macroscopic properties. Clearly, the mechanism of mesopore formation or catalytic biomass conversion is a multiscale problem that cannot be tackled using only the atomic scale. Therefore, we expect that in the coming years a joint multiscale modeling approach combined with state-of-the-art *in situ* or *operando* techniques will be at the center of research for rational zeolite design.

Declaration of interests

No interests are declared.

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