ACS Catalysis
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Regioselectivity of Al–O Bond Hydrolysis during Zeolites Dealumination Unified by Brønsted–Evans–Polanyi Relationship

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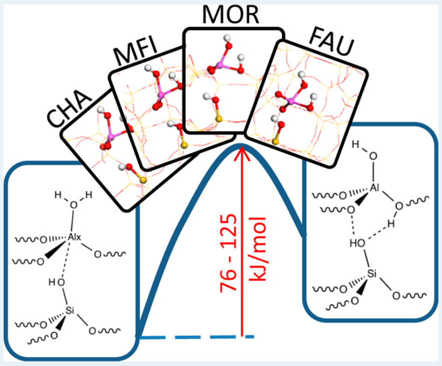
Supporting Information

ABSTRACT: We determine the mechanism of the initiation of Al–O(H) bond breaking for zeolitic structures mordenite (MOR), faujasite (FAU), MFI, and chabazite (CHA) with high Si/Al ratio occurring during dealumination. Periodic density functional theory calculations demonstrate that water adsorption on the Al atom takes place in anti position to the Brønsted acid site, via a penta- or tetra-coordinated Al species. A subsequent 1,2-dissociation of water on adjacent framework oxygen atoms leads to the first Al–O(H) bond breaking (with activation energies of ~76–125 kJ/mol). A Brønsted–Evans–Polanyi relationship to estimate transition states (TS) is established and opens the door to predictions of which crystallographic sites are able to initiate dealumination.



KEYWORDS: *zeolite, dealumination, water dissociation, Al–O bond activation, density functional theory, pentahedral aluminum*

Zeolites belong to crystalline alumino-silicate microporous materials and exhibit well-known strong acid properties, resulting from Lewis (LAS) and Brønsted acid sites (BAS), linked with thermal robustness and well-manageable pore sizes. This makes them suitable candidates for industrial catalysts[1] involved inter alia in fluid catalytic cracking, hydrocracking, isomerization, and alkylation of hydrocarbons. One major challenge in zeolite synthesis lies within the tailoring of the topology, the size, and the connectivity of intraframework channels,[2] tuning confinement effects[3] and diffusion limitations acting on the stability and residence time of reactants, intermediates, and products.[4] One possible way to introduce mesopores is water treatment under high temperature, called steaming, with a partial hydrolysis accompanied by demetalation (with Al–O and/or Si–O bond breaking) of the zeolite framework, leading to Extraframework aluminum (EFAL) species. The formation, structure, acidity, and catalytic behavior of these species have been the subject of numerous experimental studies.[5] Substantial progress has been made empirically on the optimization of postsynthetic treatments, with recent experimental insight on architecture-dependent mesopore distribution in H-ZSM5[5e] or in situ monitoring of site selectivity for dealumination in NH_4–Y,[5d] to name a few. However, on the molecular scale, crucial questions remain on the understanding of the demetalation mechanisms.[5j] With that respect, regarding theoretical investigations at the quantum level, efforts were primarily devoted to proposals for EFAL final structure.[5b,6] More recently, Swang et al. proposed the first ab initio study of the reaction mechanisms for the dealumination and desilication in two chabazite (CHA) frameworks.[7] Regarding the first Al–O bond breaking, they invoke as relevant intermediate a "vicinal disilanol" species, although it is obtained with a very high activation energy (E_A = 190 kJ/mol), where the T atom adopts a pentahedral coordination (Figure 1). In addition, the subsequent Al–O bond breaking requires an activation energy of E_A = 175 kJ/mol. Such a high activation barrier is very surprising and seems to be questioned by former experimental work in a different zeolite framework,[5d] revealing that moderate temperature is sufficient to activate the dealumination process. Thus, there are still many open questions related to the molecular scale mechanisms of the zeolite demetalation. Among them, we will address here the following ones: (i) What is the most probable elementary mechanism of the dealumination activation? (ii) Is this mechanism sensitive to the T site either in a given zeolitic framework or in various zeolitic frameworks? (iii) Is it possible to identify rational trends as a function of the zeolitic framework?

To answer these questions, we focus on the initiation step (first Al–O(H) bond breaking) for dealumination of zeolites suspected to occur during steaming treatments, for four relevant frameworks: mordenite (MOR), faujasite (FAU), MFI, and chabazite (CHA). Using density functional theory (DFT), we determine the mechanism for this first Al–O(H)

Received: September 27, 2014
Revised: October 30, 2014
Published: November 10, 2014

dx.doi.org/10.1021/cs501474u | *ACS Catal.* 2015, 5, 11–15

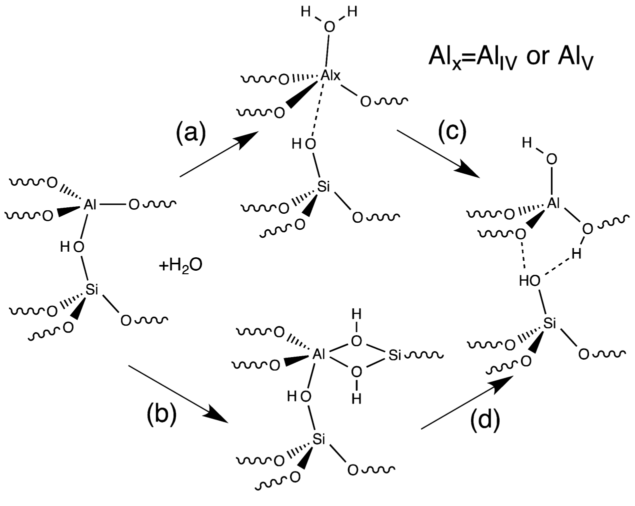


Figure 1. Thermodynamically most favorable intermediates and reaction products for an Al−O(H) bond breaking: (a) nondissociative water adsorption on Al in anti position to BAS, producing I0, (b) formation of vicinal disilanol, (c) 1,2-dissociation of water on adjacent framework oxygen with concomitant axial bond breaking, producing I2, (d) recombination of vicinal disilanol.

bond breaking. In particular, the initial water attack on framework Al atoms happens in anti position to the BAS. The subsequent 1,2-dissociation of the water molecule on an adjacent oxygen leads to partial removal of the Al atom from the framework. We identify a structural descriptor, which allows a preliminary estimation of transition state (TS) stabilities, depending on T site location. Additionally, an appealing Brønsted−Evans−Polanyi relationship is found.

To calculate electronic energy, we have used periodic DFT calculations as implemented in the VASP code[8] with a dispersion-corrected[9] Perdew−Burke−Erznerhof functional (PBE-D2).[10] Except cell relaxation, all calculations were performed at the Γ-point with a cutoff energy of 400 eV. For the localization of TS the Nudged Elastic Band method was employed.[11] The highest energy image (i.e. the supposed TS) was subjected to a quasi-newton algorithm and confirmed by vibrational analyses. Additionally, a hybrid QM/QM scheme (MP2:DFT+D2),[12] was applied, showing that PBE-D2 reproduces adsorption energies within 4 kJ/mol, and barriers within 9 kJ/mol (see Supporting Information). Note that our zeolitic systems contain a low BAS concentration (i.e., one Al atom per unit cell); however, the T site locations were chosen according to experimental data (see Supporting Information).

The possible initiation steps of an Al−O/Si-O bond breaking including one water molecule were exhaustively analyzed for one T site within MOR (T4O4, part of the 12MR channel and located in a 4MR ring) and one T site within MFI (T10O2, located in the sinusoidal channel) (see Supporting Information). Figure 1 illustrates relevant intermediates initiating the first Al−O(H) bond breaking we identified. The first intermediate (I0, Figure 1) results from water adsorption on Al in anti position to the BAS leading to the formation of either a trigonal bipyramidal Al$_V$ or a distorted tetrahedral Al$_{IV}$ species, depending on the local configuration for the adsorbed water molecule. The adsorption energies are −67 kJ/mol and −59 kJ/mol for the T4O4 site in H-MOR and the T10O2 site in H-MFI, respectively. In the literature, a ^{27}Al NMR signal at about 30 ppm attributed to distorted tetrahedral or pentahedral Al species is reported, which could correspond to the present initial dislodgement of Al to extraframework positions.[5d] After water adsorption, the Al−O(H) distance increases from 1.90 to 2.12 Å for the T4O4 site in H-MOR and from 1.90 to 2.19 Å for the T10O2 site in H-MFI which can already be seen as the initiation of the bond breaking, with the formation of a pseudobridging silanol.[13]

The second possible intermediate (I2, Figure 1) results from the 1,2-dissociation of the water molecule on an adjacent framework oxygen atom with a concomitant axial substitution of the silanol group in anti position to the water attack. The formation of I2 is exothermic for T4O4 in H-MOR (−38 kJ/mol) and becomes endothermic in H-MFI (15 kJ/mol). In that case, the Al−O(H) distance is 3.34 and 3.39 Å for T4O4 in H-MOR and T10O2 in H-MFI, respectively. All attempts to stabilize a 1,2-dissociation of water with equatorial substitution, that is, the scission of one Al−O bond in the plane perpendicular to the newly formed water-Al bond, was unsuccessful.

Another intermediate invoked by Malola et al.[7a] is a vicinal disilanol (Figure 1), in which the formation is less exothermic than the 1,2-dissociation intermediate for the T4O4 site in H-

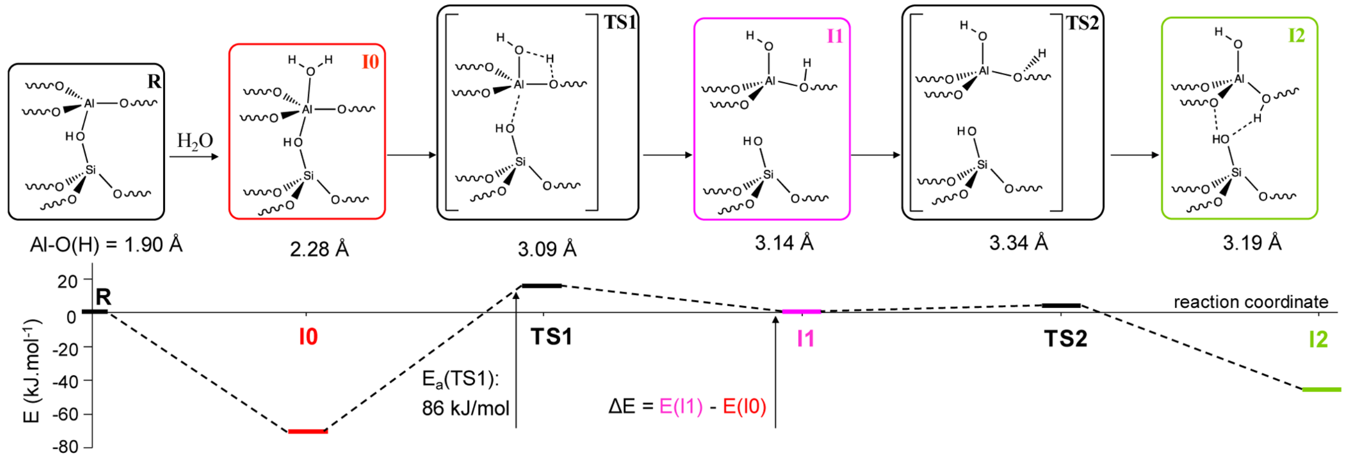


Figure 2. Reaction scheme and path of an Al−O(H) bond breaking at T3O4 in MFI via water adsorption on Al in anti position to BAS (I0, red), the TS1 leading to the 1,2-dissociation of the H_2O molecule (I1, pink) followed by a proton rotation (TS2), resulting in the most stable hydrolysis product (I2, green).

Table 1. Stability for the Species I0 and I2 and the Reaction Barrier E_a Leading to I1 along the Reaction Path of the Al−O Bond Breaking[a]

zeolite	T site	Al site	I0	E_a	I1	I2
FAU	T1O1	4MR	−63	98	29	−15
	T1O3	4MR	−54	83	21	−16
CHA	T1O3	4MR	−55	76	0	−35
MOR	T4O4	4MR	−67 (−63)[b]	100 (109)[b]	26	−38
MFI	T3O4 (inter.)	5MR	−70	86	0	−44
	T10O2 (sin.)	4MR	−59	120	60	24
	T11O3 (str.)	5MR	−68	101	34	19

[a] Values are given in kJ/mol, and referenced to R, see Figure 2. [b] Hybrid MP2:DFT+D result, see Supporting Information S6.

MOR (−18 kJ/mol) and more endothermic for the T10O2 site in H-MFI (46 kJ/mol). In any case, the formation of vicinal disilanol appears far less favorable than the molecular adsorption of water on the Al site. Note that among the several intermediates investigated, hydrogen-bond complexes that water (as an acceptor) forms with BAS (hydrogen-bond donor) are not stable for these two sites but can be very stable on other sites (not shown), as also reported in the past.[12a]

Mechanistic investigations for the Al−O(H) bond breaking were then undertaken on five additional T sites (including two additional zeolitic frameworks) in correlation with experimental data (see Supporting Information):

1. In FAU: T1O1 and T1O3
2. In MFI: T3O4 and T11O3 being located at the intersection of straight and sinusoidal channels and in the straight channels, respectively
3. In CHA: T1O3

In the case of CHA, Malola et al. found a prohibitive activation barrier (175 kJ/mol) for the first Al−O(H) bond breaking via vicinal disilanol intermediate.[7a] So in what follows, we investigate if an alternative pathway involving the anti adsorption of water is possible and if it exists, to which extent it is transferable to various zeolite frameworks. Because the dealumination of MFI has been the subject of many experimental studies, we give a detailed analysis of the mechanism on this zeolite, and we further show how it can be generalized. The corresponding reaction path, starting from the water adsorption on Al in anti position to the BAS followed by a 1,2-dissociation of water with axial substitution, is illustrated on the T3O4 site in MFI in Figure 2. Upon water adsorption on Al in anti position to BAS, a trigonal bipyramidal Al_V species (I0) is formed (−70 kJ/mol), and the Al−O(H) bond increases from 1.90 to 2.28 Å, which can be seen as the initiation of a bond breaking. Subsequently, one proton of the water molecule is transferred to an adjacent framework oxygen atom by surpassing a TS composed of a four-membered ring (TS1: E_a = 86 kJ/mol) and leading to the intermediate I1 (0 kJ/mol). Note that the Al−O(H) continues to increase. The last step is a proton rotation via TS2 resulting in a thermodynamically more stable product I2 (−44 kJ/mol). Compared to I1, I2 is stabilized by at least one additional hydrogen bond between the proton of the newly formed BAS and the oxygen of the silanol moiety.

The first Al−O(H) bond is now definitively broken, and the aluminum is partially dislodged from the framework, adopting a tetrahedral environment. This structure represents an internal silanol bond between the SiO_4 and the AlO_4 tetrahedron. Internal silanols are well-known defects in zeolites that are typically found between two SiO_4 tetrahedra.[14] We then examined this mechanism to the five other zeolite sites described above and found that this pathway is still valid. Table 1 summarizes the thermodynamic and kinetic data of the seven T sites studied here. Activation energies for the first Al−O(H) bond breaking are between 76 and 120 kJ/mol, thus significantly lower than the activation energies previously reported by Malola et al. In particular for CHA, our activation energy is about 90 kJ/mol lower than the one involving a vicinal disilanol intermediate.[7a]

This makes our alternative pathway through antiadsorption and 1,2-dissociation of water far more plausible than the one involving such a constrained 2MR vicinal disilanol. In the case of FAU, activation energies are 83 and 98 kJ/mol, which are also reasonable values compatible with experimental observations that the dealumination is already activated at moderate temperature.[5d] This would not be the case with a reaction pathway involving vicinal disilanol intermediate. Note that the occurrence of dealumination at moderate temperature is also linked with the compensation of energy gain afforded by antiadsorption by the entropy loss of gaseous water (typically at room temperature). Moreover, the local structure of the intermediates I0, I1, and I2 (involving distorted Al_{IV} species) are all compatible with the NMR analysis made by Agostini et al.[5d]

As a consequence, the activation energy depends on the zeolite framework type. However, it also depends on the T site within a given zeolite. According to our results, this is particularly true for MFI where the three investigated sites exhibit three distinct activation energies (Table 1). Experimentally, it was shown that steamed H-ZSM-5 zeolite displays an architecture-dependent mesopore formation,[5e] sinusoidal channels being more susceptible toward the dealumination compared to straight channels. Our findings confirm a local dependency for the initiation of the dealumination, though from a thermodynamic and kinetic analysis of three T sites within MFI, we identified the site located at the intersection region between straight and sinusoidal channels to be preferentially the initiation point for the dealumination (Table 1). Thus, we suggest that at the atomic scale, the initiation step of the first Al−O(H) bond scission would preferentially take place at these intersection regions, whereas the propagation steps of mesopores would occur in the sinusoidal rather than in the straight channels as observed experimentally.

Due to this heterogeneity of activation barriers, and because calculating activation barriers needs important computation time, we investigate if quantitative structure activity relationships may exist. This would allow us to determine susceptible T sites for the initiation of the dealumination without explicitly evaluating TS. Figure S7 (see Supporting Information) shows the Al−O(H) bond elongation (ΔAl−O(H)), being the difference in the bond length before (R) and after water adsorption on Al in anti position (I0), as a function of the TS1 stability (E(TS1)). Thus, calculating R and I0 allows a first estimate to determine the appertaining activation barrier for the Al−O(H) bond breaking. However, this correlation serves only as an approximate estimation, due to local effects affecting the stability of TS1, as for instance the T10O2 site in MFI (see Supporting Information). At this stage, it is important to underline the role of such hydrogen bonding in the stabilizing effect of all intermediates, which makes difficult to identify one single structural descriptor.

Despite this structural complexity, we were able to determine a Brønsted−Evans−Polanyi (BEP) relationship[15] for the initiation of an Al−O(H) bond breaking and thus be able to determine fragile T sites within the framework where EFAL formation is initiated. Such a relationship establishes the link between kinetics (activation energies) and thermodynamics (reaction energies) and thus allows to estimate in a rapid but accurate way activation barriers without identifying TS whose determination requires intensive quantum chemical calculations. Figure 3 reports the plot of the activation energy (E_a) as a function of the water dissociation energy ($\Delta E = E(I1) - E(I0)$) for the seven investigated T sites which shows a linear correlation. Note that this correlation is only valid between the state where a water molecule is adsorbed on Al (I0) and the intermediate product before rotation (I1) due to their geometrical similarity, and not between I0 and the final product after proton rotation (I2). In the latter case, an additional hydrogen bond between the new BAS and the silanol moiety stabilizes I2. This BEP relationship is thus able to unify the behavior of different T sites within the same zeolite or in various zeolites.

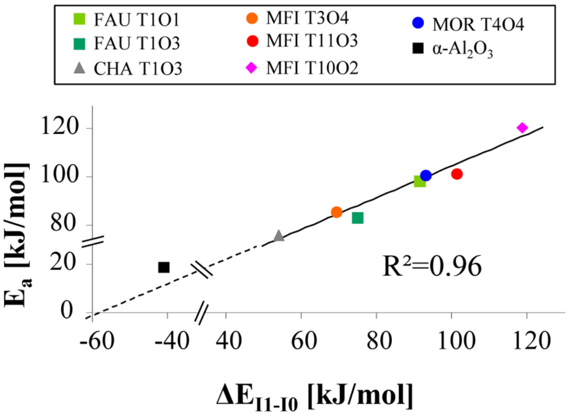


Figure 3. Brønsted−Evans−Polanyi relationship for the first Al−O(H) bond breaking; $E_a = 0.67\ \Delta E_{I1\text{-}I0} + 37.3$; α-Al_2O_3 extracted from ref 16 (not included for the BEP linear relation and R^2 evaluation).

Analyzing the hydrolysis of an Al−O bond on an α-alumina surface, Schneider et al. found a structurally related TS and intermediate.[16] Interestingly, the corresponding activation energy (18 kJ/mol) was significantly lower than the one reported here, which highlights that alumina is more easily dealuminated by water than alumino-silicate like zeolite. In addition, because their proposed TS consists also of a four-membered ring very similar as TS1 (Figure 2), we included their thermodynamic and kinetic data in our BEP correlation and found that this system also follows the BEP rule. This result allows us to go further in that sense, that such a BEP correlation seems to be also transposable to various alumino-silicates and aluminum-oxides in general.

As a preliminary attempt to decrease the Si/Al ratio, we undertook similar TS search for a low-silica X model (Si/Al = 1). We found a similar mechanism (see Supporting Information) with a barrier E_a= 125 kJ mol^{-1}. The dense hydrogen bond network in this framework, due to the huge proton content, makes the structure and stability of intermediates and TS more complex to anticipate. This suggests that even for high Si/Al frameworks, the propagation of Al−O bond breaking as silanol content increases may follow different trends than the very first Al−O bond breaking. Further works deserve to be devoted to the mechanism of the EFAL formation, as well as the impact of the presence of an ensemble of water molecules.

In summary, we have identified a general and relevant mechanism for the activation step of zeolite dealumination, e.g. the first Al−O(H) bond breaking. The key intermediate formed before the Al−O(H) bond breaking is a water adsorption on Al in anti position to the BAS resulting in either an Al_V or distorted tetrahedral Al_{IV}. The subsequent 1,2-dissociation of the water molecule on adjacent framework oxygen atom with a concomitant axial substitution of the silanol group in anti position to the water attack leads to a partial dislodgement of the Al from the zeolitic framework. This mechanism seems far more plausible than the previous one reported in the literature due to the lower activation energy. In a subsequent analysis, a Brønsted−Evans−Polanyi relationship was established against seven zeolite sites. We also attempted to highlight the compatibility with some relevant experimental observations. However, this parallel remains still challenging due to the very few experimental data available at a molecular scale level.[5j] In addition, to reinforce this comparison, we plan in the near future to extend our theoretical approach to the complete dealumination pathway leading to the EFAL species. This will be important to determine the nature of the dealumination limiting step. Awaiting this, we hope that the present work already helps for a better molecular scale's understanding of the hydrolysis−dealumination process of alumino-silicates and aluminum oxides.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The following file is available free of charge on the ACS Publications website at DOI: 10.1021/cs501474u.

Computational details, structural and energetic data (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

M.-C.S. acknowledges IFPEN for his PhD grant. J.S. acknowledges support from German Research Foundation (DFG) within CRC1109 "Metal Oxide/Water Systems". This work was performed using HPC resources from IFPEN (ENER110) and from GENCI-CINES (Grant No. 2014-x2014086134).

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