Dealumination mechanisms of zeolites and extra-framework aluminum confinement

Marius-Christian Silaghi [a], Céline Chizallet [a,*], Joachim Sauer [b], Pascal Raybaud [a]

[a] IFP Energies nouvelles, Direction Catalyse et Séparation, Rond-point de l'échangeur de Solaize, BP3, 69360 Solaize, France
[b] Institute of Chemistry, Humboldt-Universität zu Berlin, Unter den Linden 6, 10099 Berlin, Germany

ARTICLE INFO

ABSTRACT

Dealumination of zeolites is a major issue in material science and catalysis for decades, with tremendous lack of knowledge about the molecular scale mechanisms involved. Considering four relevant zeolitic frameworks (MOR, FAU, MFI, CHA), we determine the formation mechanisms of extra-framework Al species (EFAL) $Al(OH)_3H_2O$ during dealumination, by using periodic density functional theory (DFT) calculations including dispersion corrections and free energy estimation. We identify a rather universal mechanism based on water adsorption on the Al atom in anti-position to the Brønsted acid site allowing successive Al–O bond hydrolyses until dislodgement of the framework Al to a non-framework position. The determination of Brønsted–Evans–Polanyi (BEP) relationships for the entire dealumination pathway was possible, despite degradation of the correlation with increasing number of hydrolyzed Al–O bonds. Moreover, we quantify the confinement effect acting on EFAL species within the zeolites cavities and show that this effect is also a thermodynamic driving force for the Al extraction.

© 2016 Elsevier Inc. All rights reserved.

1. Introduction

Zeolites, crystalline alumino-silicate microporous materials, possess interesting intrinsic and post-synthetic features, such as a strong acidity, resulting from Lewis-(LAS) and Brønsted-acid sites (BAS) [1,2]. Additionally their thermal robustness and well manageable pore sizes make them suitable candidates for industrial reactions such as fluid catalytic cracking, hydrocracking, isomerization and alkylation of various hydrocarbon molecules [3–7]. However, one major topic in zeolite synthesis lies within the tailoring of the shape, size and the connectivity of intra-framework channels [8–17] since confinement effects [18] and diffusion limitations can impose severe constraints on the reactants, intermediates and products [19]. Steam treatment of the zeolite is conducted to introduce mesopores [20,21], where partial hydrolysis of the framework leads to Al–O and Si–O bond breaking. The removal of a certain number of hydroxylated Al or Si species from the framework leads to the formation of a moiety called silanol nest with four hydroxyl groups surrounding the tetrahedral void

[22,23]. The lifetime of such species, also called hydrogarnet defect [24], has been questioned, however [25,26].

Apart from that, extra-framework aluminum (EFAL) and extra-framework silicon (EFSI) species, located within the cavities, are generated and studied extensively in the literature [20,27–38]. Several reports show that dealumination can be site specific [36,37,39]. In particular, NMR and FTIR analyses on steam treated H-Mordenite could reveal that Al is randomly distributed over 4 and 5 membered rings (MR) and that a favored dealumination of T3 and T4 sites, located in the 4MR, takes place [36,37]. At a mesoscopic scale, Weckhuysen et al. showed by focused ion beam (FIB) and scanning electron microscopy (SEM) that steam treatment of ZSM-5 zeolite generates either surface mesoporosity (mild treatment) or uniformly distributed mesopores (severe treatment) where sinusoidal channels are more susceptible to the dealumination and hence mesopore formation compared to straight channels [32,40]. On a steamed NH_4-Y Agostini et al. were able to show that, contrary to the general opinion, the dealumination is not a high-temperature process but takes already place at moderate temperatures (450–500 K). They also show the appearance of 30–35% of the total Al within the sodalite cage [28].

Considering the abovementioned experimental findings, one still misses *in situ* and *operando* approaches to reveal the atomic structure rearrangement occurring during the dealumination

---

processes [21]. To gain atomistic insight into the mechanism, some early theoretical calculations have been used to describe both, the structure and catalytic properties of dealuminated zeolites in presence of EFAL species. Ruiz and co-workers for instance examined the structure and energetics of aluminum complexes serving as models for Brønsted-acid sites, without any explicit simulation of the zeolite framework [41]. Their results obtained by Hartree–Fock (HF) and Moller–Plesset second order perturbation theory (MP2) show that a transition from tetrahedral to octahedral Al occurs when the net charge of the cluster is $q = +1$. The latter is 7 kJ/mol lower in energy. In order to analyze the structure and coordination of some EFAL species (e.g. Al^{3+}, $Al(OH)_2^+$, $Al(OH)_3$), Bhering et al. used density functional theory (DFT) calculations on zeolite Faujasite [30], modeled by a T_6 cluster, and showed that monovalent cations prefer a bi-coordination whereas di- and tri-valent cations are tetrahedrally coordinated with oxygen atoms near the framework aluminum. They also quantified the effect of EFAL on the Brønsted acidity [42]. Periodic DFT calculations were performed by Benco et al. [29]. By analyzing the dynamical behavior of the EFAL species ($Al(OH)_3(H_2O)_3$ and $Al(OH)_3(H_2O)$) in Gmelinite, they revealed a localization depending mobility of these aluminum–hydroxide clusters. In the main channel, both, the two non-coordinated H_2O molecules and the EFAL are mobile, whereas a network of hydrogen bonds suppresses its mobility within the cage and the EFAL occludes the pore. They also investigated the preferred location of the bare Al^{3+} ion as EFAL within a periodic Mordenite framework, and observed limited relaxation of the framework around this EFAL [43].

Quantum mechanics/molecular modeling (QM/MM) calculations were performed to quantify the reaction energies for hydrolysis reactions in the surrounding of T sites substituted by various heteroatoms [44,45], but it is only very recently that full mechanisms were proposed from *ab initio* calculations to quantify both the thermodynamics and kinetics of zeolite hydrolysis reactions. The first periodic DFT calculations including thermodynamic and kinetic data and giving a first insight in the dealumination and desilication mechanism were indeed reported by Swang et al. [46,47] Employing H-Chabazite (SSZ-13) as zeolitic model, they simulated the subsequent addition of four water molecules leading to the formation of a silanol nest and a an EFAL being $Al(OH)_3H_2O$. In the same spirit they analyzed the creation of an EFSI species $Si(OH)_4$. Their first step, water adsorption on the proton of a Brønsted site, is followed by the formation of a vicinal disilanol (Si_V species) with a relatively high energy barrier, $E^{\ddagger} = 175$ kJ/mol for the desilication, and $E^{\ddagger} = 190$ kJ/mol for the dealumination. The origin of the strong energy cost might result from the strain in the 2MR cycle of vicinal disilanols. Subsequently, without addition of water, they suggested an inversion of the molecular environment around this penta-coordinated Si species leading to the first Al–O–Si bridge breaking. Again, this reaction exhibits an energy barrier of $E^{\ddagger} = 150$ kJ/mol and $E^{\ddagger} = 175$ kJ/mol for the desilication and dealumination, respectively. Subsequent hydrolysis steps by the successive addition of one water molecule at each step finally lead to the formation of an EFAL or EFSI and silanol nest.

Inspired by these pioneering DFT studies, recently we examined the reactivity of several T sites belonging to various zeolitic frameworks, i.e. MOR, FAU, MFI and CHA, by periodic calculations based on density functional theory (DFT) augmented with a dispersion term [48] (DFT + D2) which were supported by hybrid MP2:DFT + D2 calculations [49]. We found a general pathway for the initiation of dealumination (first Al–O bond breaking, Fig. 1a), which consists in the following:
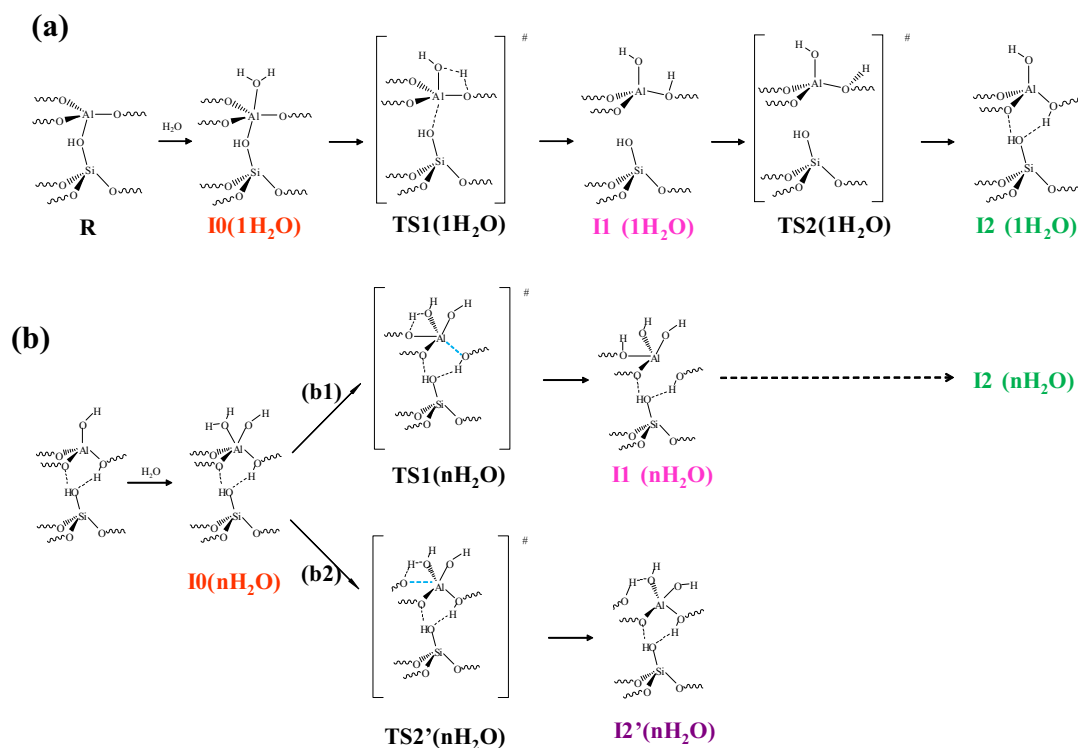

Fig. 1. (a) Attack of the first water molecule ($n = 1$) on an Al atom in anti-position to the BAS ($I0(1H_2O)$) followed by a 1,2-dissociation with axial substitution via a transition structure, $TS1(1H_2O)$, composed of a four membered ring giving rise to $I1(1H_2O)$. Establishing a hydrogen bond between the newly created BAS and a silanol, via a proton rotation ($TS2(1H_2O)$), leads to a more stable intermediate $I2(1H_2O)$. (b) Anti attack of the second water molecule ($n = 2$) on an Al atom in anti position to the BAS ($I0(nH_2O)$) followed by: (b1) a 1,2-dissociation with axial substitution via a transition structure composed of a four membered ring ($TS1(nH_2O)$) leading to $I1(2H_2O)$, (b2) 1,2-dissociation with equatorial substitution via a transition structure composed of a four membered ring ($TS2'(2H_2O)$) leading to $I'2(2H_2O)$. The difference between the (b1) and (b2) routes is the nature of the Al–O bond broken, depicted in light blue in the transition structures.