

Inter-conversion of EFAL species and influence of alkaly cations in dealuminated zeolites

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Introduction

Industrial dealumination to improve stability and acidity of zeolites remains a permanent source of enthusiasm to search a mechanism which could explain the process. Various hypotheses have been discussed to provide a reasonable explanation of the acidity growing after steaming: (I) EFAL species reveal catalytic Lewis acid activity [1]; (II) stabilization of the negative charges on the lattice due to the EFAL species after the removal of acidic proton [2]; (III) synergism between Brønsted and Lewis type sites owing to a close location of both sites together [3]. During a long period the last idea met with a problem to find any experimental evidence of the spatial neighborhood of the Brønsted and Lewis sites. Such confirmation has been finally shown *via* combined ²⁷Al DQ- and TQ-MAS NMR studies and DFT computations which have approved spatial correlation between framework Si-O-Al species and EFAL moieties AlOH²⁺ and Al(OH)₂⁺ formed during consequent dealumination [4]. But the authors have not paid attention to the conversion between various EFAL forms which can be important for the NMR assignment. Another intriguing point is the old known fact about strong influence of residual alkali cations on the properties of dealuminated zeolites [5]. These non studied aspects of the EFAL behavior made us to start DFT modeling to check either possible relation the conversion between various EFAL forms and the Na⁺ influence takes place.

Computational details

The isolated cluster (8R, 6R+4R, 10T) approach was performed for the modeling of mordenite and Y zeolite structures using GAUSSIAN09 [7] at the B3LYP and MP2 levels using 6-31G*(Si, Al, O, H, Ca) basis set. At the periodic level (MOR type with neutral and charged cells), projected-augmented wave (PAW) method and the PBE functional were used with VASP5.2.12 code [8]. For calculating the minimum energy path between reagents and products, we used the climbing image nudged elastic band method [9].

Results and discussion

We have studied Na⁺ influence on the water dissociation reaction over both species AlOH²⁺ and Al(OH)₂⁺ in various positions. Similar barriers have been calculated in the 8R cluster and MOR (Fig. 1a-c) in which or Al(OH)₂⁺ species replace cationic species. For example, barrier and heat of the dissociation in 8R 0.34 and -0.12 eV become 0.51 and -0.20 eV (Fig. 1d-f), respectively, in the presence of Na⁺. Transition state frequency 1366.3i cm⁻¹ at the same MP2/6-31G* level without Na⁺ are close to 1211.4i cm⁻¹ in HMOR model using PBE/PAW (Fig. 1b).

Conclusions

The step of water dissociation can be indeed controlled by the Na⁺ influence but both increase (8R cluster) and decrease (6R+4R) of activation energy was obtained. Despite a slight variation between relative stabilities of hydrated AlOH²⁺ and Al(OH)₂⁺ species at the isolated cluster level and using periodic boundary conditions, activation energies remain similar being

around 0.3-0.7 eV. This shows relatively easy transformations between the AlOH^{2+} and $\text{Al}(\text{OH})_2^+$ species which can vary their AlO_X coordination between $X = 4$ and 5. The inclusion of the inter-conversion between EFAL species can be important for final NMR assignment.

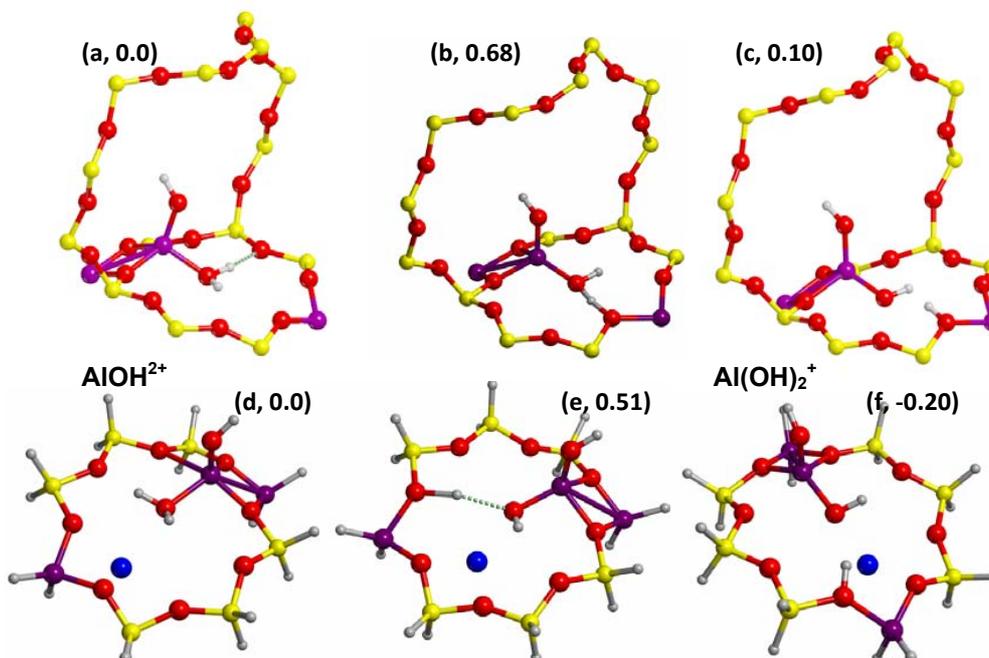


Fig. 1. The energies (eV) of reagents (a, d), transition states (b, e), and products (c, f) of the reaction $(\text{H}_2\text{O})\text{AlOH}^{2+} + \text{-Si-O-Al-} \rightarrow \text{Al}(\text{OH})_2^+ + \text{-Si-O-Al-}$ at the PBE/PAW level (a-c) in HMOR type and B3LYP/6-31G* level (d-f, together with Na^+) in 8R cluster. The Na, Al, Si, O, C, and H atoms are shown by blue, violet, yellow, red, brown, and gray colors.

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