

H₂O-induced trigonal-to-tetrahedral transition in boron zeolites

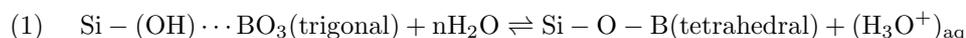
E. FOIS⁽¹⁾, A. GAMBA⁽¹⁾, F. TRUDU⁽¹⁾, G. TABACCHI⁽¹⁾

⁽¹⁾ *Dipartimento di Scienze Chimiche ed Ambientali, Universita' dell'Insubria, I-22100 Como*

Summary. — The behaviour of a protonated boron-containing zeolite at intermediate hydration degree has been investigated by means of periodic DFT approaches. Results of a combined room-temperature Car-Parrinello molecular dynamics blue-moon path sampling simulation indicate that, in line with experimental findings, the BO₃/Si-OH acid site typical of dry samples is converted to a hydrated H₃O⁺ hydrogen bonded to tetrahedral BO₄⁻ at moderate water content (four H₂O per B site) with an activation free barrier of the order of few kT.

1. – Introduction

Protonated boron zeolites [1] have attracted considerable attention in view of their moderate acidity, which is exploited in chemical reactions of industrial relevance requiring mild and shape-selective solid acid catalysts [2, 3]. Such a property arises from the peculiar structure of these materials, and, in particular, of the boron acid site. At variance with other framework cations, B is three-coordinated in a planar trigonal geometry in dry conditions and becomes tetracoordinated when contacted with water or other bases. A broad series of ¹¹B solid state NMR [4, 5, 6, 7] and IR experiments [8, 9, 10, 11, 12] indicate that the chemical behaviour of boronites is governed by the equilibrium:



It should be stressed that, in presence of proton acceptors such as water, not only a planar trigonal BO₃ unit is converted to a BO₄⁻ tetrahedron, but also that the silanol proton leaves the framework and becomes an extraframework species, namely a hydrated H₃O⁺ moiety. Such a reversible B-site structural transition has been detected only in proton-containing boronites, while with other extraframework cations (e.g. Na⁺) B is characterized by a stable tetrahedral geometry [7]. However, in spite of the number of investigations, the interconversion mechanism of the two possible structures of the B site (i.e. trigonal and tetrahedral) in the presence of water has not been clarified yet. These issues have been recently explored in a series of periodic DFT studies [13, 14] on

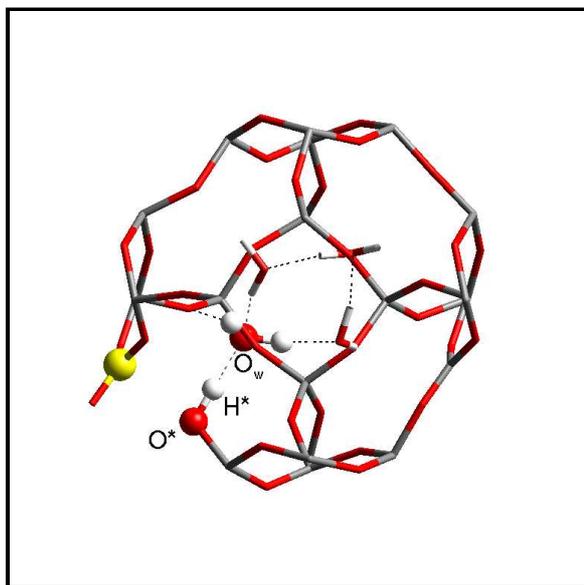


Fig. 1. – Schematic representation of the B-SOD-4W system with trigonal B and silanol. Labels refer to the atoms involved in the reaction coordinate Q for the bluemoon sampling. B: yellow; Si: grey; O: red; H: white

model B-zeolites characterized by different water content, where, on the basis of both geometry optimizations and first principles molecular dynamics simulations, a thorough picture of the physico-chemical properties of these materials was gained. In particular, it was evidenced that: i) in dry samples, the acid site is a silanol group Si-OH weakly interacting with a planar BO_3 unit; ii) the silanol-like character of the acid site is responsible of the lower acidity of boron zeolites and implies long range distortions of the framework structure; iii) the $\text{BO}_4^-/(\text{H}_3\text{O}^+)_{aq}$ arrangement becomes favored over the $\text{BO}_3/\text{Si-OH}$ form at moderate water content; iv) the tetrahedral B-site structure is further stabilized at high water loading.

In the present work, a model acid boron-zeolite containing four water molecules per acid site has been studied by DFT-based first principles molecular dynamics simulations with the aim of gathering both mechanistic and thermodynamical information on the water-induced trigonal-to-tetrahedral transition at the B site. In particular, by adopting a rare events sampling statistical technique, a reactive path for the reaction in Eq. 1 has been explored in order to gain an estimation of the energy barrier associated to this process.

2. – Computational section

Sodalite has been chosen as a case study system in view of its unit cell, which is composed by two cubo-octahedral β cages, the building blocks of many other zeolites, and whose size ($[\text{Si}_{12}\text{O}_{24}]$) is small enough for running accurate and extensive sets of simulations. Hydration effects on the B-site geometry were simulated in a model crystal containing one acid site, $\text{H}[\text{BSi}_{11}\text{O}_{24}]$ and four water molecules (B-SOD-4W). The cell

parameters here adopted are the same as in Refs. [13, 14] to which the reader is referred for further technical details.

First principles molecular dynamics (FPMD) simulations [15] were carried out by expanding Kohn-Sham orbitals in plane waves (PW) (Γ point only) up to a 70 Ry cutoff and using norm conserving semilocal Martins-Troullier pseudopotentials (with $l=2$ nonlocality) for the ionic cores-valence electrons interactions [16, 17]. The electronic structure was treated by means of a gradient-corrected DFT approximation, namely the Perdew-Burke-Ernzerhof (PBE) [18] functional. The validity of the present computational protocol in providing results in line with higher level of theory calculations and in convergence with respect to the kinetic energy cutoff has been previously reported [13, 14].

The trigonal to tetrahedral conversion at the B site was simulated by adopting the “bluemoon” ensemble approach [19]. In this statistical sampling technique, one has to define a *constraint* Q , related to the reaction coordinate, and an equilibrium configuration on the reactants side R characterized by a Q_R value. Q is stepwise modified from the starting point Q_R to a final value Q_P corresponding to the products side P . At each step in the bluemoon sampling, a constrained molecular dynamics is performed, by fixing the constraint at a given value Q_i and averaging the force $f(Q_i)$ needed to keep Q_i fixed. The free energy profile is calculated by integrating $f(Q)$ along the path from Q_R to Q_P , thus providing both activation and process free energies. Stationary points in the path are characterized by $f(Q)=0$, e.g. the equilibrium state of the reactants at $Q=Q_R$, the equilibrium at the products side $Q=Q_P$ and the transition state Q_{TS} .

In general the reaction coordinate Q is a geometrical parameter of the chemical system under study chosen in such a way that its variation is related to the simulated reactive process. In the present case, $Q=r(H^*-O^*)-r(H^*-O_w)$, i.e.: the reaction coordinate was defined as the distance between the H^* and O^* atoms of the silanol group ($r(H^*-O^*)$) minus the distance between H^* and the oxygen atom of the closest water molecule O_w ($r(H^*-O_w)$), as shown in Figure 1.

Simulations were performed at room temperature conditions in the NVT ensemble. Equilibration runs of 5 ps were performed by alternating 0.1 ps bins in the NVE ensemble by 0.1 ps bins with velocity rescaling. The Car Parrinello equations of motion [15] were integrated with a time step of 0.121 fs (5 a.u.). An inertia parameter of 500 a.u. was used for the electronic coefficients. Unconstrained FPMD trajectories were carried out for 20 ps elapsed time simulation each.

The bluemoon sampling of the reaction path corresponding to the trigonal-to-tetrahedral transition in B-SOD-4W was discretized in 10 steps. The starting value of the reaction coordinate Q_R (-1.0 a.u) was stepwise incremented by 0.25 a.u. until a stationary point at the products side was reached. Elapsed simulation times of the constrained simulations, ranging from 4 to 6 ps, depended on the $f(Q)$ convergence.

3. – Results and discussion

As mentioned in the Introduction, framework boron can be found either in a trigonal geometry loosely bound to a silanol ($BO_3/Si-OH$) or in a tetrahedral structure interacting with a solvated proton ($BO_4^-/(H_3O^+)_{aq}$) depending on the water loading.

At intermediate hydration degree (i.e., four water molecule per B site) the $BO_3/Si-OH$ and $BO_4^-/(H_3O^+)_{aq}$ optimized structures were found to be separated by a very small energy difference [14]. In order to explore whether a barrierless trigonal to tetrahedral transition could take place, the room temperature behaviour of the two systems was investigated by FPMD.

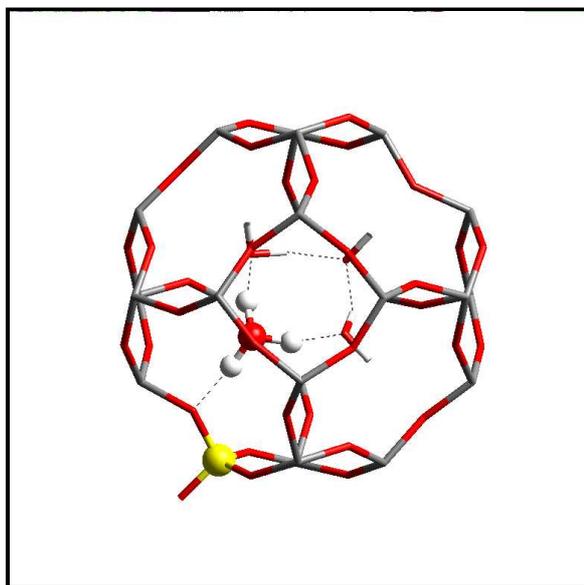


Fig. 2. – Schematic representation of the B-SOD-4W system with tetrahedral B and hydrated hydronium. Atoms color codes as in Figure 1.

In both simulations, no interconversion between the $\text{BO}_3/\text{Si-OH}$ and $\text{BO}_4^-/(\text{H}_3\text{O}^+)_{aq}$ forms was observed, suggesting an activation barrier higher than kT for the trigonal to tetrahedral B-site transition. Actually, the equilibrated structure resulting from each trajectory closely resembled the corresponding energy minimum. Specifically, in the $\text{BO}_3/\text{Si-OH}$ system the water molecules are arranged in a four-membered water ring (4WR), connected to the silanol group via a strong hydrogen bond involving O_w as proton acceptor (Figure 1), while the other molecules interact only transiently with framework oxygens. In the 4WR, each water molecule accepts a hydrogen bond from the neighboring one and such a feature is maintained along the simulation time. Interestingly, only a few rotation/translation events were detected. Such motions however did not lead to the breaking of the 4WR structure, indicating a substantial stability of this hydrogen bonding arrangement also at finite temperature. Therefore the signature of the $\text{BO}_3/\text{Si-OH}$ structure is a strong and stable hydrogen bond connecting the silanol proton and a solvating water molecule. In the $\text{BO}_4^-/(\text{H}_3\text{O}^+)_{aq}$ simulation, the hydronium was found to be hydrogen bonded to an oxygen atom of the BO_4^- unit (O^*) and two water molecules, like in the corresponding optimized structure. Moreover, the fourth water molecule remained hydrogen bonded as a double acceptor to the H_2O s solvating H_3O^+ , thus forming a tight protonated 4WR structure stable at room temperature (Figure 2). These equilibrated structures may be considered respectively as the initial and the final point of a reactive path leading from trigonal B plus silanol to tetrahedral BO_4^- plus hydrated hydronium. With the structures of both the reactants and products states available, a bluemoon path sampling could be performed starting from a well equilibrated configuration taken from the $\text{BO}_3/\text{Si-OH}$ simulation. On the basis of the analysis of the FPMD trajectories of the reactants and products states, the reaction coordinate

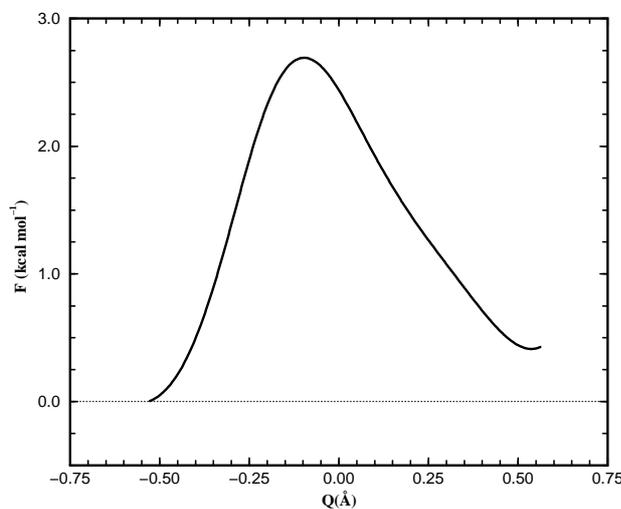


Fig. 3. – Calculated free energy profile for the $\text{BO}_3/\text{Si-OH} \rightarrow \text{BO}_4^-/(\text{H}_3\text{O}^+)_{aq}$ conversion

was defined as $Q=r(\text{H}^*-\text{O}^*)-r(\text{H}^*-\text{O}_w)$. Such a quantity is negative when the system is in the $\text{BO}_3/\text{Si-OH}$ arrangement and should become positive once the conversion to the $\text{BO}_4^-/(\text{H}_3\text{O}^+)_{aq}$ form is accomplished.

At the starting point of the bluemoon sampling $r(\text{H}^*-\text{O}^*)$ corresponded to the room-temperature equilibrium bond distance of the silanol hydroxyl group, which forms a hydrogen bond of length $r(\text{H}^*-\text{O}_w)$ with the closest water molecule in the four membered ring (Figure 1). With the chosen reaction coordinate, the end of the simulated reactive path should correspond to a system where H^* has been transferred to water, thus forming a solvated hydronium characterized by a $r(\text{H}^*-\text{O}_w)$ bond length and hydrogen bonded to the framework oxygen O^* at a $r(\text{H}^*-\text{O}^*)$ distance, as indicated in Figure 2. It is to be pointed out that, since no constraint has been applied to the B- O^* separation, the trigonal-to-tetrahedral transition at the B site is not forced by the adopted approach, but should rather be a result of the calculations.

Remarkably, the simulated reactive path resulted in a B-SOD-4W system characterized by a $\text{BO}_4^-/(\text{H}_3\text{O}^+)_{aq}$ arrangement similar to the equilibrium structure of the product states (Figure 2). The free energy profile obtained from the constrained simulations, reported in Figure 3, indicates that the $\text{BO}_3/\text{Si-OH} \rightarrow \text{BO}_4^-/(\text{H}_3\text{O}^+)_{aq}$ conversion proceeds without stable intermediates and is characterized by an energy barrier of 2.7 kcal/mol. Therefore, as predicted on the basis of FPMD results, the water-induced trigonal-to-tetrahedral structural transition in B-zeolites is an activated process, whose barrier is however small enough to be easily bypassed at room temperature conditions. The process appears to be slightly endoergonic (0.36 kcal/mol), however, since such a small value of the free energy difference is within the precision of the method, reactants and products states could be considered nearly iso-energetic.

It is worthy analyzing in detail how the structure of the B site evolves along the reactive path. The B-O radial distribution functions ($g(r)$) obtained from selected trajectories of the calculated bluemoon sampling are reported in Figure 4. For $Q=-0.53 \text{ \AA}$, i.e. at the

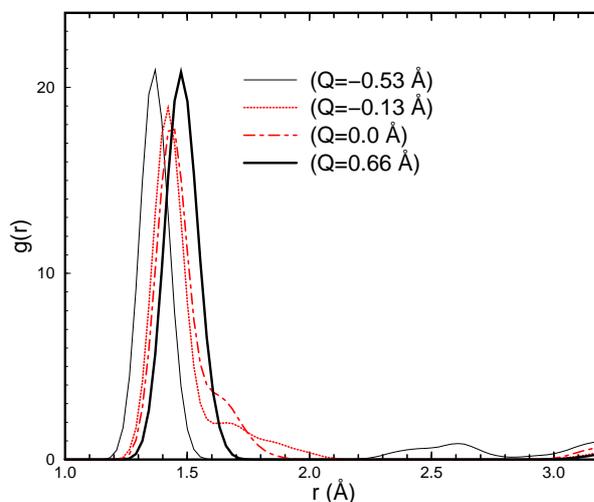


Fig. 4. – B-O radial distribution functions $g(r)$ calculated at different points of the bluemoon sampling: at the reactants side (negative Q values), at the transition state ($Q=0.0$ Å) and at the products side (positive Q values).

beginning of the reaction, the $g(r)$ shows a sharp peak at 1.37 Å and a broader second peak centered at 2.6 Å. The two peaks, which integrate to three and one, correspond to the three B-O bond distances in the trigonal BO_3 unit and to the loose contact between B and the silanol oxygen O^* respectively. For $Q=0.66$ Å, i.e., when the products are formed, the B-O $g(r)$ shows only one sharp peak, integrating to four and centered at 1.48 Å. This peak corresponds to the four B-O bonds of the BO_4^- tetrahedron. On the reactants side of the process, close to the transition state ($Q=-0.13$ Å), the $g(r)$ is characterized by a peak at 1.42 Å with a broad shoulder centered at 1.70 Å and tailing up to 2.1 Å. Such a drastic change in the $g(r)$ profile indicates that, while the H^* atom is being transferred from O^* to the water oxygen, the O^* atom is approaching the B nucleus. Actually, inspection of the corresponding trajectory indicated that, for this value of the reaction coordinate, the B site starts to switch from a trigonal structure to a distorted tetrahedral geometry, characterized by large values of the B- O^* contact (1.7 - 1.8 Å). At the same time, the water molecules forming the 4MR structure are involved in rotational and translational motions leading to rearrangements of the hydrogen bonding network. Both features become more pronounced at the transition state ($Q=0$ Å), where the $g(r)$, peaked at 1.43 Å, presents a shoulder at 1.65 Å and goes to zero beyond 1.80 Å, indicating that the tetrahedral form of the B site starts to become predominant.

A snapshot extracted from the bluemoon trajectory corresponding to $Q=0$ Å is reported in Figure 5. Here it is possible to recognize a structure where the H^* proton is shared between the water structure and the zeolite framework, moreover at this point of the reaction path a tetrahedral B site is present. It is to notice that the hydrogen bonding network has changed with respect to the reactant side of the path: here the water accepting the proton H^* from the zeolite silanol donates two hydrogen bonds to the two closest water molecules, while the remaining water molecule, far away from the protonated one, acts as a double-acceptor of hydrogen bonds. Such an arrangement is very similar to that found for the products state. This restructuring of the hydrogen

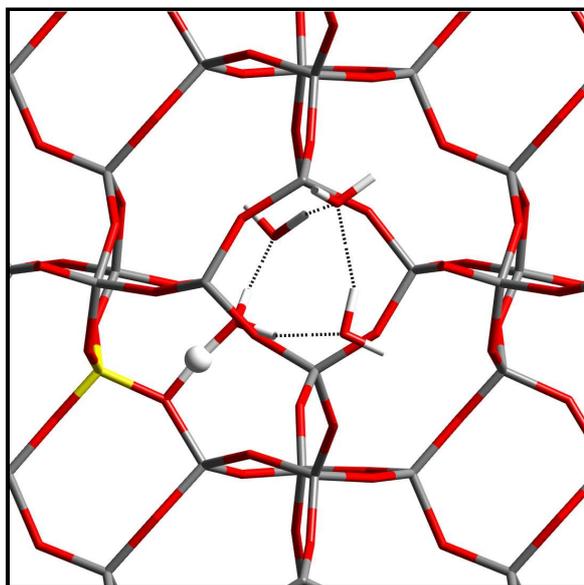


Fig. 5. – Snapshot from the bluemoon simulation with $Q=0.0 \text{ \AA}$, corresponding to the transition state. The H^* atom (represented as a sphere) is shared between the silanol oxygen O^* and the water oxygen O_w . Atoms color codes as in Figure 1.

bonding network occurs in correspondence of the maximum of the free energy path, indicating that, besides the trigonal to tetrahedral structural modification at the B site, also the hydrogen bonding network modifications contribute to determine the free energy barrier of the process.

4. – Conclusions

In this work we have presented a combined first principles molecular dynamics blue-moon sampling approach aimed at investigating the boron-site trigonal-to-tetrahedral structure modification induced by water in B-zeolites. The study has been performed with a loading of four water molecules per B site, a hydration degree where the trigonal and the tetrahedral structures are very close in energy.

The BO_3 -to- BO_4^- transformation occurs along with a global restructuring of the hydrogen bonding network of the caged water molecules. Such a hydrogen bonding rearrangement plays a key role in the transfer of a zeolitic silanol proton to the water system with the formation of a hydrated H_3O^+ moiety.

The adopted simulation technique allowed us, besides gathering detailed mechanistic information, to obtain an estimation of the free energy barrier of the process (2.7 kcal/mol), corresponding to a rate constant of $6.7 \times 10^{10} \text{ s}^{-1}$.

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