First principles studies on boron sites

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Abstract

Results of periodic first-principles calculations on boron containing zeolites are presented. The boron site trigonal-to-tetrahedral transition is studied in model B-SOD and B-FER. We show how boron acid sites in different frameworks respond differently to bases.

Keywords: DFT calculations, boron zeolites, acid sites, silanols.

1. Introduction

Isomorphous substitution in zeolites [1] is a common procedure to obtain molecular sieves with tailored properties. As an example, zeolitic acid strength may be tuned by an appropriate choice of the trivalent cation replacing Si in tetrahedral sites. With the introduction of boron-substituted zeolites (boralites) [2,3], porous solid catalysts with moderate acidity became available to industries and research laboratories. Such catalysts are used when mild acid conditions are required, as in the case of e.g. Beckmann rearrangement of cycloexanone oxime [4], olefins isomerization [5] and MBTE cracking [2]. Boron-zeolites with different framework have been synthesized and characterized (see e.g. R. Millini et al., [6] and references therein). Besides their industrial relevance, boron containing zeolites have attracted attention in fundamental research due to the properties of boron sites to change coordination depending on the conditions. In particular, in the presence, as extraframework compensating charges, of metallic cations boron assumes a tetrahedral BO_4 structure, typical of zeolitic sites. On the other hand it is reported that in the presence of protons boron sites becomes tricoordinated, forming a planar trigonal BO_3 unit weakly interacting with a close silanol. Both experimental and theoretical studies have attributed the moderate acidity properties to the silanol character of the boron acid sites [7,8]). Such a structure is however unstable when the zeolite is loaded with e.g. water, and a reversible transformation to a tetrahedral BO_4 structure takes place [9]. Also, the trigonal-to-tetrahedral structural modification occurs when acid boralites are in contact with other bases like ammonia or pyridine [10,11].

In this work we present results of periodic DFT calculations on boron zeolites characterized by different framework structures (SOD, FER), charge balancing species (H^+, Na^+) and in the presence of different bases (H_2O, NH_3) at very low concentration, one molecule per acid site.

2. Method of Calculation

Calculations were carried out with the PBE gradient corrected density functional approximation [12] with periodic boundary conditions. The Kohn-Sham orbitals were expanded in plane waves up to a kinetic energy cut-off of 70 Ry. Non-local norm conserving pseudopotentials were used for the electron-ionic core interactions [13].

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Geometry optimizations were performed by a simulated annealing procedure via a Car Parrinello molecular dynamics [14] followed by a quasi-Newton method [15]. A time step of 5 a.u. and an inertia parameter of 500 a.u. were adopted for the integration of the equations of motion. A threshold of 1.0×10^{-4} a.u. was adopted as convergence criterion for the forces on atoms.

Model boron sodalite and ferrierite were built from the corresponding all silica structures, by replacing one Si atom with B. The cell parameters were calculated from the corresponding all silica values by using the Vegard rule and adopting the criteria as reported in G. Perego et al. [16] for the B-O to Si-O bond length ratio. Further computational details can be found in F. Trudu et al. [17]. The adopted B/(B+Si) ratio was 1/12 for boron sodalite (B-SOD) and 1/36 in the boron ferrierite model (B-FER). In order to balance the charge due to B/Si substitution one H or one Na were introduced, leading to acid models H-B-SOD and H-B-FER or Na-B-SOD and Na-B-FER respectively. In the B-SOD case, as all tetrahedral sites are equivalent, only one B-SOD structure is possible with the adopted B/(B+Si) ratio. On the other hand, in B-FER four different models can be obtained depending on the crystallographic site in which the B/Si substitution is made. We have therefore optimized the four possible Na-B-FER non equivalent structures. The more stable structure corresponded to boron located in the T3 position (sites nomenclature as in [18]). All of the calculations for dry H-B-FER and NH_3 loaded H-B-FER were performed by adopting the T3 site for boron location.

3. Results and Discussion

3.1. Dry samples

In both FER and SOD framework types, boron was found to be coordinated to four framework oxygens with a nearly tetrahedral geometry in the presence of Na. The average B-O bond distances are 1.482 Å and 1.484 Å in Na-B-SOD and Na-B-FER respectively. In contrast, the optimized structures of the acid models were characterized by a three-coordinated boron in a trigonal planar BO_3 unit. Specifically, in the H-B-SOD and H-B-FER structures, the average BO bond distances in the BO_3 structure are 1.367 Å and 1.365 Å respectively. The B atom was found to be separated by a distance of 2.574 and 2.718 Å from the silanol oxygen in H-B-SOD and H-B-FER. In H-B-FER the more stable structure was obtained when the proton was bound to O(7). As already reported in (F. Trudu et al., [17]), all of the dry acid boron structures are characterized by a significant framework distortion. The silanol character of a boron acid site is more pronounced than e.g. in the case of a gallium acid site (E. Fois et al., [19]) thus strengthening the hypothesis that, in zeolites, acidity decreases in progressively passing from a bridge acid site structure to a silanol-like one (C.T.W. Chu, [20]).

3.2. Effect of different bases on H-B-SOD

The effect of the Brønsted bases H_2O and NH_3 on the structure of acid sites in H-B-SOD was investigated by optimizing its structure in the presence of one water or one ammonia molecule. In the monohydrated H-B-SOD, boron site keeps its trigonal planar structure, with an average B-O bond length of 1.368 Å. The silanol proton is engaged in a strong hydrogen bond with water (silanol proton was 1.801 Å away from the water oxygen). The silanol oxygen was 2.588 Å away from boron, a distance slightly longer than in the dry model. The water molecule is close to the sodalite β-cage center, and its protons were not involved in hydrogen bonding. No other relative energy minima were found in H-B-SOD-H_2O structure. This picture changes in H-B-SOD-NH_3. Indeed two minima were detected in the optimizations: in the first, and more stable one, the planar trigonal structure of the boron site is conserved (see Figure 1).

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Here ammonia is engaged, as proton acceptor, in a very strong hydrogen bond with the silanol, (silanol proton 1.657 Å away from ammonia nitrogen). Ammonia is located close to the cage center, and does not form other hydrogen bonds. The boron-silanol oxygen separation (2.565 Å) is shorter than in the evacuated dry system, while the silanol O-H bond is significantly elongated (1.035 Å *vs* 0.974 Å). The average B-O bond length is 1.369 Å. A relative minimum was detected at 1.9 kcal/mol above the H-B-SOD-NH_3 structure: here, the acid proton is transferred to ammonia forming NH_4^+ and the boron site becomes tetrahedral, with an average B-O bond length of 1.484 Å. In such a (NH_4^+)-B-SOD structure, NH_4^+ forms a strong hydrogen bond with a Si-O-B bridge oxygen (1.549 Å) and causes a weakening of the involved Si-O-B bridge bonds. In particular such B-O bond, 1.558 Å, is 5% larger than the average. Also, the BO_4 structure deviates from the ideal tetrahedron geometry to a larger extent than in Na-B-SOD, due to the stronger interaction of the framework with NH_4^+ than with Na^+. In addition, the N-H bond (1.104 Å) in contact with the Si-O-B bridge is significantly longer than the other N-H bonds (7% larger than the average).

3.3. The ammonia H-B-FER interactions

In the case of H-B-FER, only structures characterized by the NH_4^+ cation in contact with tetrahedral BO_4 unit were found in the optimization processes. The most stable (NH_4^+)-B-FER structure, shown in Figure 1, presents the ammonium cation, located in an eight membered ring hydrogen bonded to the Si(3)-O(2)-B bridge (H-O(2) distance: 1.731 Å). Moreover, ammonium is also connected via hydrogen bond (1.741 Å) to O(6) belonging to an Si-O-Si bridge. The BO_4 tetrahedron shows a deviation from ideality less pronounced than in the case of the (NH_4^+)-B-SOD structure. Indeed, the B-O(2) bond is 1.520 Å, 3% longer than the average B-O bond distance (1.473 Å).

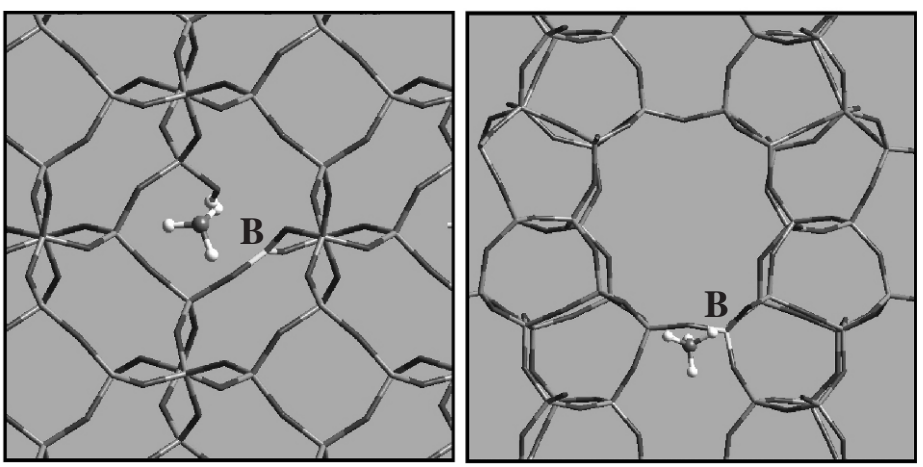

Figure 1. Left panel: Graphical representation of the minimum energy structure calculated for H-B-SOD-NH_3. The NH_3 atoms and the silanol proton are represented as spheres. Right panel: Graphical representation of the minimum energy structure calculated for (NH_4^+)-B-FER. The NH_4^+ atoms are represented as spheres.

4. Conclusion

In conclusion, the results here presented indicate that boralites acid strength depends on the framework structure. In H-B-SOD, a single base molecule is preferentially adsorbed

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on a silanol site weakly connected to planar BO_3. On the other hand, a single ammonia molecule is capable to deprotonate an acid boron site in ferrierite, leading to ammonium, and consequently inducing a trigonal-to-tetrahedral structural change at the boron site.

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