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REGULAR ARTICLE

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# Lewis acid sites in boralites

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**Abstract** This work is aimed at modeling a framework L-site of a boralite using DFT and a cyclic cluster including one B and two Si atoms. A similar cluster was used earlier as a successful model for an L-site of a zeolite, which allows for the direct comparison of the properties of the two L-sites. It is shown that the boralitic L-site is rather weak. Unlike its zeolitic counterpart, it cannot bind a molecule of ethene or carbon monoxide. Only a base as strong as ammonia can form a stable 1:1 complex with the boralitic L-site. Water is found to bind to the boralitic L-site only if not less than two of its molecules are interacting with the model cluster. As water loading increases, the geometry of the $BO_3$ fragment undergoes gradual changes indicative of facile hydrolysis of the boralite lattice.

**Keywords** Zeolites · Boron substitution · Acidity · Adsorption · Density functional theory

## 1 Introduction

Zeolites are well known for their unique adsorption and catalytic properties. The most important zeolitic catalysts used in petrochemical processing and industry-scale organic synthesis are produced from H-zeolites, which are strong solid acids. Their acidity stems from defects in the crystal lattice. One kind of the catalytically active defects, known as the bridge OH group, possesses strong Brønsted acidity while another, the tricoordinated aluminum atom, is a Lewis acid. These framework defects are referred to as the H-site and L-site, respectively. L-sites are formed from H-sites during the activation of a zeolitic catalyst at elevated temperatures, which results in its partial dehydroxylation (see Fig. 1).

The catalytic role of framework L-sites in zeolites has been largely underestimated despite the evidence available since the early days of zeolite science [1]. Their very existence had been questioned [2] until it was shown experimentally that the strong Lewis acidity of zeolites, especially of high-silica ones, resulted from framework defects rather than from extra-lattice alumina debris [3]. Most of the doubt and uncertainty about zeolitic L-sites arises from the fact that these sites are very hard to investigate using the convenient methods of zeolite chemistry: X-ray structure analysis, IR and NMR spectroscopy. The major body of experimental data on L-sites has been obtained using the spectroscopic observation of test molecules adsorbed at the sites. Many of such results defy unambiguous interpretation at the molecular scale. Therefore quantum chemical modeling is crucial to the comprehensive understanding of the properties of zeolites.

A relatively recent advance in zeolite science is the chemical modification of the zeolitic framework aimed at “fine tuning” its properties. For instance, H-sites, as they appear in an unmodified zeolite, may be too strong for a particular catalytic reaction, leading to suboptimal selectivity of the catalyst. The strength of the H-sites can be attenuated in such cases by means of the isomorphous substitution of aluminum atoms in the zeolite framework by boron atoms [4]. A boralite is the ultimate product of such substitution, with no aluminum atoms left in its framework (see Fig. 1).

It is not unexpected that the isomorphous substitution affects the nature and properties of framework L-sites as well. It was found that, unlike in H-zeolites, L-sites would readily form in H-boralites at mild dehydration conditions [5,6]. In a dehydrated H-boralite framework, boron atoms are essentially tricoordinated [5,7] . These phenomena are accounted for by the rather low Lewis acidity of boron atoms not allowing them to form a close SiO(H)B bridge in the absence of solvating water molecules.

Consequently, boralitic L-sites, due to their significant concentration in a thermally activated sample, can play a role in catalysis over boron substituted zeolites. Notwithstanding, little interest has been paid so far to the adsorption properties of such L-sites. It might be partly due to the difficulties experimentalists have met with when studying the L-sites of conventional zeolites. Therefore quantum

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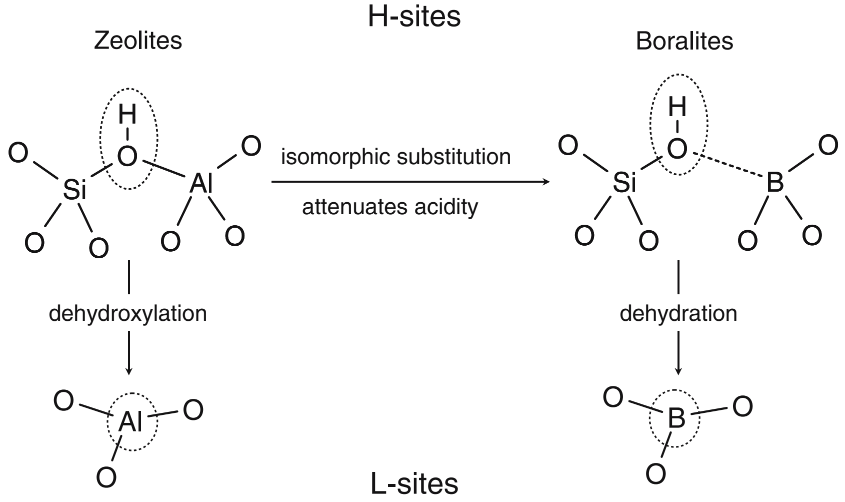

**Fig. 1** Interrelations between acid sites in zeolites and boralites

chemical modeling of boralitic L-sites and their complexes with test molecules can shed light on the molecular properties of these systems and provide valuable suggestions for further experimental research in this area.

## 2 Computational details

In the present work, all calculations were carried out using density functional theory (DFT) with the BLYP functional and 6-31G** basis set. This combination had previously been shown to perform well in modeling the L-sites of conventional zeolites and to give results in good agreement with ab initio methods, namely SCF and MP2 with the same basis set [8]. The *Jaguar* software suite [9] was used. Dissociation energies were not corrected for ZPE or BSSE. Vibration frequencies were not scaled. Atomic charges were calculated according to Mulliken.

This study adopted cluster approximation. A boralitic L-site was modeled with a small cyclic cluster denoted as “B3” (in order to distinguish it from its zeolitic counterpart “Z3” used in our earlier work [8], results from which we will use for comparison). See Fig. 2 for the structure of the B3 cluster. Such small cyclic clusters have proved particularly convenient for modeling L-sites in zeolites [8,11–13]. They reproduce the rigid structure inherent to zeolitic framework while staying compact enough to allow time-effective quantum chemical calculations involving full geometry relaxation.

**Note added in proof** In our recent studies of chemically modified zeolites, a more complex approach has been used: cluster models including eight T atoms, the cc-pVTZ basis set, and the Perdew–Burke–Ernzerhof functional as implemented in the *PRIRODA-04* software suite [10]. In particular, adsorption complexes analogous to those presented here were re-examined. Increasing the complexity of the approach was found to have no significant influence on the quantitative and qualitative results reported in this paper.

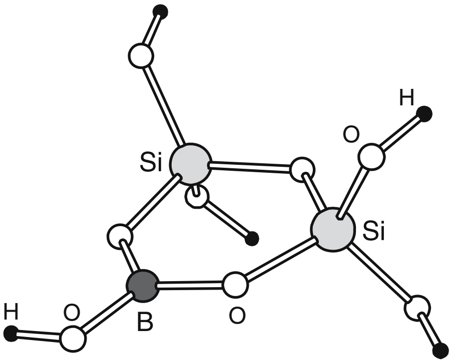

**Fig. 2** B3 cluster

## 3 Free cluster

In the B3 cluster, the $BO_3$ fragment is effectively planar. The OBO angles add up to 360° (see Table 1). This is the same as what was found for the $AlO_3$ fragment in the Z3 cluster. Of course, B–O bonds are shorter than Al–O bonds: the BO distances are 137–140 pm, as compared with AlO distances of 171–173 pm. The planar configuration of the $BO_3$ fragment is consistent with experimental data on the dominant presence of trigonal boron in dehydrated boralites [5,7].

While we are aware that Koopmans’ theorem does not hold for Kohn–Sham orbitals, the comparison of the HOMO and LUMO energies of the B3 and Z3 clusters within the same quantum chemical approximation may yield at least qualitative results. Indeed, the data from Table 2 show that B3 represents a weaker, yet harder, Lewis acid than Z3, which is in keeping with the chemical common sense.

**Table 1** Properties of the B3 cluster and its complexes with molecules

| Species | $r_{BO}$(pm) | $\phi_{OBO}$(deg) | $E_{diss}$(kJ mol$^{-1}$) | Characteristic vibration frequencies and their shifts (cm$^{-1}$) |
|---|---|---|---|---|
| B3 | 140; 139; 137 | 123; 120; 117 | — | |
| B3–CO | 140; 139; 137 | 123; 120; 117 | 7 | $\nu$ CO, 2109 (+4) |
| B3–$C_2H_4$ | 140; 139; 137 | 123; 120; 117 | 7 | $\nu$ CC, 1653 (−3) |
| B3–$NH_3$ | 146; 146; 142 | 116; 114; 114 | 25 | $\delta_{as}$ NH, 1618, 1632 (−40, −25);<br>$\delta_s$ NH, 1271 (+178) |
| B3–$H_2O$ | 140; 139; 137 | 123; 123; 117 | 41 | |
| B3–2$H_2O$ | 147; 145; 141 | 116; 114; 115 | 96 | |
| B3–3$H_2O$ | 148; 147; 141 | 115; 113; 115 | 153 | |

**Table 2** HOMO and LUMO energies of the Z3 and B3 clusters

| Cluster | HOMO (eV) | LUMO (eV) | Gap (eV) |
|---|---|---|---|
| Z3 | −6.75 | −1.56 | 5.19 |
| B3 | −6.98 | −0.35 | 6.63 |

## 4 Carbon monoxide and ethene complexes

Earlier both CO and $C_2H_4$ molecules were shown to form stable complexes with a zeolitic L-site [8]. Indeed, CO is an important test molecule used to investigate acid sites in zeolites and other solids by means of IR and NMR spectroscopy. Our model of a zeolitic L-site was able to predict a shift of the CO IR band due to the "adsorption" of a CO molecule at the zeolitic L-site in agreement with the experimental data available [8].

At the same time, a boralitic L-site, as represented by the B3 cluster, appears too weak to bind a CO or $C_2H_4$ molecule. The B3–CO and B3–$C_2H_4$ complexes are characterized by rather low dissociation energy, ca. 7 kJ mol$^{-1}$. Their structures suggest that there is no immediate binding between the molecule and the boron atom: only weak VdW interaction occurs (see Fig. 3). The vibrational analysis of the complexes supports this opinion; the CO and CC band shifts due to the complexation are less than 5 cm$^{-1}$ (compare with shifts by +54 and −38 cm$^{-1}$ in Z3–CO and Z3–$C_2H_4$, respectively [8]). The $BO_3$ fragment of the cluster remains unperturbed; the sum of OBO angles still is 360° in either complex (see Table 1).

A conclusion can be drawn that weak bases are unsuitable spectroscopic tests for studying boralitic L-sites.

## 5 Ammonia complex

Ammonia is another test for acidity of solids widely used in such methods as calorimetry, temperature programmed desorption and IR spectroscopy. Earlier our model of a zeolitic L-site was able to predict important observable characteristics of the interaction between an ammonia molecule and the zeolitic L-site, namely the adsorption energy as high as 160 kJ mol$^{-1}$ and a considerable blue shift of the symmetric NH bending band $\delta_s$ by +185 cm$^{-1}$ [8].

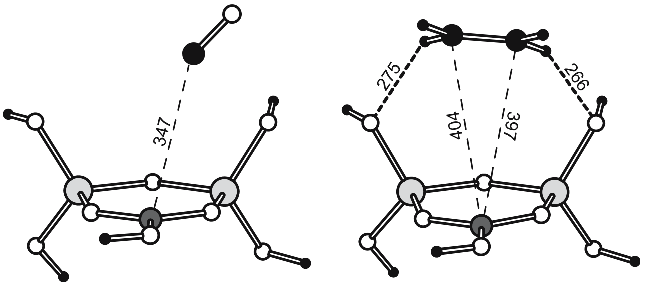

**Fig. 3** B3–CO (*left*) and B3–$C_2H_4$ (*right*) complexes (distances in pm)

Now let us consider our present model for an L-site in a boralite. Being a rather strong base, an ammonia molecule binds to such a site, thus forming an apparent N · · · B coordination bond (see Fig. 4). However, the dissociation energy of the complex to form, B3–$NH_3$, is considerably lower than that of Z3–$NH_3$, and amounts to as low as 25 kJ mol$^{-1}$. Nevertheless, the $\delta_s$ blue shift in B3–$NH_3$, +178 cm$^{-1}$, is just slightly less than that in Z3–$NH_3$. The $BO_3$ fragment loses its planar structure due to the complexation, the configuration of the boron atom becoming distorted tetrahedral. The sum of the OBO angles decreases to 345° while the B–O bonds elongate by 5–6 pm each (see Table 1).

These results suggest that ammonia can be a spectroscopic test for L-sites in boralites, but low stability of the surface complex should be taken into account while planning experiments.

## 6 Water complexes

Water plays a very important role in zeolite catalysis. It was shown by means of quantum chemical modeling that the binding of a water molecule by a zeolitic L-site leads to the formation of a strong Brønsted acid site able to "adsorb" additional water molecules [8,11,12], as well as other species [13].

Unlike a zeolitic L-site, a tricoordinated boron atom does not bind a single water molecule: a weak VdW complex is formed instead (see Fig. 4). Its dissociation energy, 41 kJ mol$^{-1}$, is not greater than the energy of two H-bonds found in the complex. (The dissociation energy of a free water dimer is 32 kJ mol$^{-1}$ at the BLYP/6-31G** level.) The $BO_3$ fragment

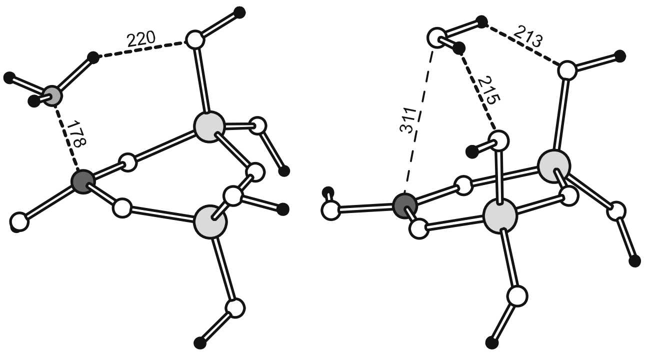

**Fig. 4** B3–$NH_3$ (*left*) and B3–$H_2O$ (*right*) complexes (distances in pm)

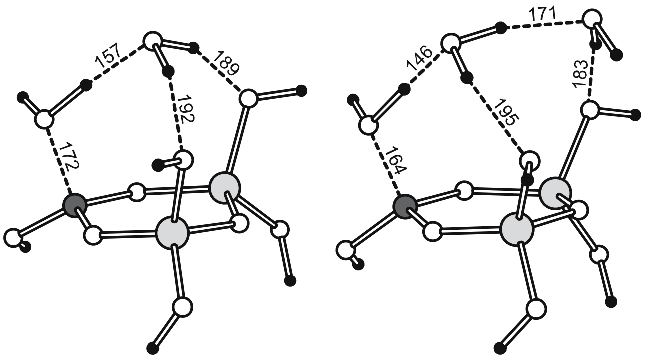

**Fig. 5** B3–$2H_2O$ (*left*) and B3–$3H_2O$ (*right*) complexes (distances in pm)

of the cluster is not remarkably affected by the complexation; the B–O bonds are not perturbed and the sum of the OBO angles remains at 360° (see Table 1).

As soon as water loading increases to two molecules per L-site, one of the water molecules becomes engaged in the interaction with the boron atom of the cluster (see Fig. 5). The corresponding $O \cdots B$ distance decreases to 172 pm, indicating the formation of a coordination bond between the two atoms. The $BO_3$ fragment of the cluster deforms as the boron atom leaves the plane; the sum of OBO angles decreases to 345°. This is concomitant with the B–O bonds of the cluster elongating by 4–7 pm each. The total dissociation energy of the B3–$2H_2O$ complex is 96 kJ mol$^{-1}$. Accordingly, the energy released upon binding the second water molecule amounts to 55 kJ mol$^{-1}$, which is even more than the dissociation energy of the complex involving a single water molecule. It can be clearly seen that addition of the second water molecule qualitatively affects the properties of the model adsorption system. A search for alternative structures resulting from the interaction of two water molecules with the B3 cluster has shown that the structure in Fig. 5 corresponds to the global minimum on the potential energy surface of the adsorption system under study.

Addition of the third molecule of water to the system under study results in further changes in the system's parameters (see Fig. 5). Namely, the $O \cdots B$ coordination bond becomes as short as 164 pm; the B–O bonds of the cluster elongate slightly, by 1–2 pm each; the sum of the OBO angles in the cluster decreases by 3°. Such changes are less considerable than those to happen upon addition of the second water molecule. The energy released upon binding the third water molecule, 57 kJ mol$^{-1}$, still is not less than that for the second molecule. Therefore the water oligomer could grow larger in the field of a boralitic L-site if excess of water were present.

The growth of the water oligomer is accompanied by changes in its inner part due to solvation effects. Specifically, the H-bond between the first and second water molecules becomes shorter (see Fig. 5) while a positive charge on the bridge H atom increases from 0.35 to 0.38e. This can indicate the increase in proton acidic properties of the water molecule coordinated to the L-site. However, the said positive charge is not as great as that in the respective zeolitic complexes, namely 0.42e in Z3–$2H_2O$ and 0.46e in Z3–$3H_2O$. In agreement with the role of boron substitution to moderate acid sites, a boralitic L-site imparts lower acidity to a water molecule when compared with that imparted by a zeolitic L-site. Nevertheless, the effect of both sites on a water molecule is substantial.

The overall picture of water interacting with a trigonal boron atom within a boralite framework is in accord with the experimental observations discussed earlier. The Lewis acidity of such a boron atom is not high enough for it to bind a single water molecule. On the contrary, two or three water molecules at the boralitic L-site form a rather stable H-bonded complex that is linked to the boron atom through a coordination bond. Upon the formation of such a complex, the B–O framework bonds elongate considerably, which may represent the initial step in the removal of boron from the boralite framework due to its hydrolysis (see Table 1).

## 7 Conclusions

For the first time the adsorption properties of an L-site at a tricoordinated boron atom within a boralite framework were investigated quantum chemically, using DFT. The results obtained are in agreement with known phenomena, supporting the application of DFT to studies of boron substituted zeolites.

Weak basic test molecules, such as CO and $C_2H_4$, were shown to be unsuitable for the spectroscopic investigation of boralitic L-sites since the latter failed to bind weak bases or affect their observable properties noticeably. At the same time, a strong base as ammonia was found to form a stable coordination complex with a boralitic L-site. While the complex is less stable than that of ammonia and a zeolitic L-site, its properties should allow for distinguishing ammonia bound to boralitic L-sites by means of IR spectroscopy.

In our model, water starts to interact with a boralitic L-site at the loading of two molecules per site. This is in keeping with experimental observations on the changes to the local structure of boralites upon their dehydration and re-hydration. The interaction with water weakens the bonds between the boron atom and the surrounding framework.

Consequently, the removal of the boron atom could become more facile under hydrolysis conditions.

There still are interesting phenomena left beyond the scope of the present work. In particular, the synergy between aluminum based and boron based adsorption sites in partially substituted zeolites [14] remains largely uninvestigated at the molecular level. It is a challenging subject for future studies.

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## References

1. Lunsford JH (1968) J Phys Chem 72:4163–4168
2. Kühl GH (1977) J Phys Chem Solids 38:1259–1263
3. Kazansky VB (1988) Catal Today 3:367–372
4. Howden MG (1985) Zeolites 5:334–338
5. Wendlandt KP, Unger B, Becker K (1990) Appl Catal 66:111–122
6. Datka J, Kawałek M (1992) Collect Czech Chem Commun 57:745–749
7. Simon MW, Nam SS, Xu W et al (1992) J Phys Chem 96:6381–6388
8. Tikhii YV, Kubasov AA, Stepanov NF (2003) Russ J Phys Chem Eng Ed 77:1340–1343
9. Jaguar 3.5 (1998) Schrödinger, Inc, Portland
10. Laikov DN, Ustynyuk YuA (2005) Russ Chem Bull 54:820–826
11. Stepanov NF, Novakovskaya YV, Kubasov AA et al (1998) Internet J Chem 1:14
12. Domracheva TM, Novakovskaya YV, Kubasov AA, Stepanov NF (1999) Russ J Phys Chem Eng Ed 73:1115–1120
13. Tikhii YV, Kubasov AA, Stepanov NF (2003) Russ J Phys Chem Eng Ed 77:1455–1459
14. Xu WQ, Suib SL, O'Young CL (1993) J Catal 144:285–295