Preferred sites for the isomorphous substitution of boron in ZSM-5 zeolite structure*

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The semiempirical quantum chemical MNDO (modified neglect of diatomic overlap) technique is adopted to calculate the substitution energy for boron at different possible framework sites in the ZSM-5 zeolite structure. The topological analysis of the preferred boron substitution site indicates that boron is present in the 10-member ring of the straight and sinusoidal channel. The relative strengths of different acid sites in boron-substituted ZSM-5 are evaluated from the calculated proton affinity values. We have attempted to correlate the substitution energy and proton binding energy to acidic and catalytic properties observed for BZSM-5.

INTRODUCTION

The synthesis of boron-containing ZSM-5 was reported by Taramasso et al.[1] in 1980. Since then, there have been reports supporting the fact that the boron is incorporated in the framework using MAS ^{11}B n.m.r.[2-5] and i.r. studies,[4-7] X-ray studies,[8,9] and cation-exchange capacity measurements.[10] There are also patents[11,12] describing their application in new catalytic processes. Many authors have shown[6,7,13,14] that BZSM-5 had an attenuated acidity compared to AlZSM-5 due to the absence of strong acid sites from NH_3 t.p.d. studies. The weak acidic nature of BZSM-5[14,15] compared to AlZSM-5 has also been confirmed by the diminished activity of BZSM-5 for acid-catalyzed reactions.[10,16,17] However, the decreased acidity is also shown to be an advantage, since BZSM-5 retains its catalytic activity for the reactions such as disproportionation of ethylbenzene[16] and methanol to olefin conversions[17,18] longer than does the more acidic AlZSM-5 catalyst. The weakly acidic boron–pentasil zeolite has been shown to be useful for the synthesis of enol ethers from acetals.[19] This catalyst is superior to the conventional supported catalysts such as phosphates, sulfates, or carbonates in terms of lifetime and selectivity.

The presence of boron is also reported[8,9] to distort the framework and cause a decrease in the unit cell volume. As a consequence, synthesis of olefins from methanol has a different selectivity over BZSM-5

catalysts.[17,20-22] Hoelderich[23] has shown that BZSM-5 is more selective (although less active) in the conversion of 2-phenylpropanol to 1-phenylpropan-2-one than is FeZSM-5. The siting of boron and its influence on properties will provide valuable information for understanding the methods to tinker the zeolites for meeting the needs of catalytic applications. The site where boron is incorporated in the framework of ZSM-5 and its effect on the acidic property as well as the catalytic reactivity and selectivity are probed using cluster model calculations in the present study.

METHOD AND MODEL

The MNDO method[24] has been adopted for the calculation of the electronic structure of cluster models. We have followed a 'local' model approach to study the 'integral' structure and properties of ZSM-5, and the methodology is explained in detail elsewhere.[25] The cluster model chosen for the present study is $[(OH)_3B–O–Si(OH)_3]^{-1}$, a dimeric cluster defined by Fripiat et al.[26] The geometry of dimeric clusters and the numbering of T sites are as reported by Olson et al.[27] from the single crystal X-ray study of AlZSM-5. The cluster model represents a BO_4 group and an adjacent SiO_4 group sharing an oxygen atom. The terminal oxygen atoms were saturated by hydrogen atoms to maintain charge neutrality. The hydrogens are placed at the positions of nearest neighboring T sites.

RESULTS AND DISCUSSION

When boron is incorporated into the ZSM-5 framework, each BO_4 group will be bonded to four


Table 1 Substitution energy for boron at 12 sites of ZSM-5 structure and the calculated values of electron density for T–O–T atoms

Site for boron substitution	Sites for adjacent SiO₄ groups	Average substitution energy of boron[a] (kcal/mol)	Net electron density on		
			B^{3+}	O^{2-}	Si^{4+}
1	2, 4, 5, 10	47.56	0.36	−0.72	1.83
2	1, 3, 6, 8	44.97	0.45	−0.74	1.84
3	2, 4, 6, 12	29.63	0.44	−0.73	1.84
4	3, 1, 5, 7	45.83	0.41	−0.75	1.83
5	4, 1, 6, 11	50.79	0.37	−0.75	1.84
6	5, 2, 3, 9	38.69	0.39	−0.72	1.82
7	7, 4, 8, 11	37.24	0.39	−0.73	1.85
8	7, 2, 9, 12	36.43	0.39	−0.75	1.81
9	8, 9, 10, 6	52.81	0.33	−0.73	1.83
10	9, 10, 11, 1	37.70	0.36	−0.74	1.81
11	10, 5, 12, 7	30.21	0.39	−0.75	1.84
12	11, 3, 12, 8	34.24	0.39	−0.73	1.85

[a]Energy relative to the most stable cluster model, namely, $[(OH)_3B–O–Si(OH)_3]^{-1}$, connecting the 7–7 site

adjacent SiO₄ groups, provided there are no B–O–B linkages. B–O–B linkages are most unlikely at the low concentration (maximum of 4–5 B per unit cell containing 96 T sites) of boron in the framework.[9] Therefore, four clusters are studied wherein the geometry of the BO₄ group is the same but the geometries of adjacent SiO₄ are those of the four possible neighbors. The substitution energy of boron at a given site is calculated as the average of four cluster models.

Table 1 summarizes the results obtained from the above-mentioned calculations. The substitution site for boron and the four adjacent T (where T = Si) sites are tabulated. There are 12 crystallographically distinct sites in the ZSM-5 structure and, hence, 48 cluster models were studied to calculate the boron-substitution energy. The average energy for substitution of boron in each of these sites is given in *Table 1*. This approach has been successfully used earlier for the siting of Al in ZSM-5,[26] ZSM-11,[28] mordenite,[29] and Theta-1[30] as well as Fe in ZSM-5.[25] The process of substitution was considered as:

$$(OH)_3Si–O–Si(OH)_3 + [B(OH)_4]^{-1} \rightarrow [(OH)_3Si–O–B(OH)_3]^{-1} + Si(OH)_4$$
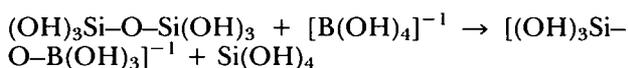
It was found that the most stable linkage was Si_7–O–B_7. The substitution energy values listed are relative to the most stable cluster, $[(OH)_3Si–O–B(OH)_3]^{-1}$, at T_7–T_7 linkage. The calculated substitution energy values indicate that the most favorable sites for the incorporation of boron shall be T_3 and T_{11}. The T_3 site occurs on the 10-member rings of the straight and sinusoidal channels, while the T_{11} site occurs only in the 10-member ring of the straight channel. These results show that the diameter of the straight and sinusoidal channels will decrease on boron substitution. Hence, a different pattern of product selectivity observed in methanol conversion reactions[17,20] over BZSM-5 is not surprising.

Substitution of boron is expected to cause a distortion in the ZSM-5 framework structure. The X-ray crystallographic technique cannot distinguish the isomorphously substituted atoms such as boron and

aluminum from silicon and, hence, the structure derived will be an average structure. It has been reported[8,9] that there is reduction in unit cell volume with increasing boron content in the framework. To study the extent of distortion, we tried the optimization of the geometry of BO₄ tetrahedron only with respect to the cluster energy of $[(OH)_3Si–O–B(OH)_3]^{-1}$. We were interested in the parameters such as B–O distance, O–B–O angle, and Si–O–B angle. In the starting geometry of the dimeric cluster model, these parameters are the Si–O distance, O–Si–O angle, and Si–O–Si angle as determined by X-ray analysis. After geometry optimization, for all the clusters, the O–B–O angles remain unchanged, while the values of the B–O distance and the Si–O–B angle uniformly approaches a value of ~ 1.45 Å and ~ 155°, respectively. The total energy values of all the optimized clusters were same with a variation of + 0.5 eV.

The above result indicates that the relative energy values for substitution of boron in the ZSM-5 framework is an indication of the distortion occurring in the framework due to "B" substitution and that the effect of geometry of the adjacent SiO₄ group is nominal. Thus, substitution of B at T_9 and T_5 sites is energetically unfavorable since the ZSM-5 structure has to undergo a drastic distortion. Boron prefers to become substituted where T–O distance is minimum and T–O–T angle is maximum.

A relation showing the contribution of each of these geometry parameters in deciding the hetero-atom substitution at a given site will be explained in a detailed report. Indeed, the nearness of the T atoms to the bridging oxygen control its electron charge density. In *Table 1*, we have included the net charge density values calculated for the bridging oxygen and its adjacent T sites. The negative charge on oxygen is the indication of its affinity to a proton and the extent of polarization of the O–H bond. The values do not differ much for different sites, showing that the acid strength will be the same for different boron-substitution sites.

MINDO/3 cluster calculations by Pelmentschikov et

Table 2 The calculated values of proton affinity and the geometry parameters for the 12 sites of ZSM-5 structure where boron is substituted

Site	Average T–O distance (Å)	Average T–O–T angle (degrees)	Average values of proton affinity of oxygen atoms of BO_4 (eV)
1	1.60	150.7	12.66
2	1.62	156.4	12.95
3	1.59	159.8	12.95
4	1.58	159.4	12.35
5	1.58	156.4	12.52
6	1.58	155.1	12.36
7	1.60	152.9	12.56
8	1.56	160.6	12.42
9	1.60	150.4	12.74
10	1.58	154.2	12.37
11	1.58	158.7	12.21
12	1.63	151.6	12.36

al.[31] showed that BO_4 is more stable than are AlO_4 fragments and the stability of planer BO_3 is higher than that of BO_4 tetrahedron. Hence, the incorporation of boron in the framework involves the energy-intensive process of conversion of trigonal boron (BO_3) to tetrahedral boron (BO_4) and results in a strained framework. These results are in agreement with the earlier reports[14,22] of the unstable BZSM-5 framework. As mentioned earlier, a maximum of four to five boron atoms are incorporated[9] in a unit cell containing 96 T sites, and the question arises whether the small amounts of boron can cause such large variation in selectivity.[17] Indeed, the boron substitution does cause changes in acidic properties. These changes in acidic properties can also alter selectivity; e.g., the aromatization reaction that needs strong acidic sites cannot occur over BZSM-5, thus leading to low selectivity for aromatics.

In *Table 2*, the geometry parameters, namely T–O distances and T–O–T angles,[27] for the 12 sites are included. The proton affinity is calculated according to the following process:

$$(OH)_3B-OH-Si(OH)_3 \rightarrow H^+ + [(OH)_3B-O-Si(OH)_3]^{-1}$$
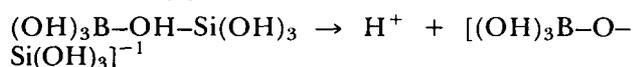
The proton affinity values are calculated as an average of four values when proton is bonded to four possible bridging oxygens of each B site and are reported in *Table 2*. The proton affinity is a measure of acid strength,[32] and these values are higher than those calculated for the AlZSM-5 system. Hence, BZSM-5 is expected to be less acidic than is AlZSM-5 based on these results. The electronegativity of boron (2.0) is higher than that of aluminum (1.6), and, hence, boron substitution decreases the electron density over bridging oxygen compared to Al substitution,[33] thus decreasing the Brönsted acidity. The disappearance of the 723–773 K peak in the t.p.d. study[13] of NH_3 may be attributed to the above reason. The O–H stretching vibrational frequency of the bridging oxygens calculated by the *ab initio* technique[34] and determined by the *FT*i.r. technique[7]

showed that the Brönsted acidity is decreasing in the order Si–OH–Al < Si–OH–B < Si–OH(terminal). The band gap picture observed from the present calculations for BZSM-5 is the same as for SiZSM-5,[25] but the occupancy of the HOMO band is low in the case of BZSM-5. Hence, Lewis acidity (ability to accept electrons) of BZSM-5 is expected to be enhanced, which may be the reason for the new peak in the t.p.d. study[13] of ammonia in the temperature range 573–623 K.

CONCLUSIONS

This work has shown the value of electronic structure calculations to understand the factors governing the heteroatom substitution. Three factors, namely, crystal radius, electronegativity, and the quantity, as well as quality of the electrons in the heteroatoms are crucial. The relative contribution of each of these factors can be determined with more refined techniques and larger cluster models. Several conclusions arise from the present study that can be summarized as follows:

1. When the crystal radii of the heteroatom is smaller than that of silicon, their site preferences are totally different from the site preferences of heteroatoms with larger crystal radii. Boron substitution occurs in both straight and sinusoidal channels, thus decreasing their diameters.

2. There is large strain in the framework due to B incorporation that leads to instability, thus making high-B/Si-ratio samples nonexistent.

3. The calculations predict that BZSM-5 has weak Brönsted acid sites and strong Lewis acid sites compared to AlZSM-5.

4. The strength of acid sites are almost uniform in BZSM-5 no matter which site is being occupied by boron.

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