

Fe and B substitution in ZSM-5 zeolites: A quantum-mechanical study

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Abstract

Density functional theory has been used to study isomorphous substitution of Fe and B for Si in orthorhombic MFI type zeolite ZSM-5. Calculations were performed on monomer [T(OH)4], dimer [(OH)₃-Si-O-T-(OH)₃] and pentamer T(OSiO₃H₃)₄ cluster models where T = Fe or B. It has been experimentally observed that Brønsted acidity of substituted ZSM-5 increases in the order B-ZSM5 ≪ Fe-ZSM-5 ≪ Al-ZSM-5. Although change in acidic properties with substitution is known, the position of framework substitution with Fe and B in ZSM-5 has not yet been established. In the present work, we have done detailed density functional calculations to find out the site of framework substitution with Fe and B in ZSM-5. We have observed that the calculated properties display a substantial size dependence on the size of the model. Our calculations suggest that the preferable siting for Fe is 3 and 11 and for B it is 2 and 12 in ZSM-5 zeolite framework.

Keywords: Fe and B substitution; ZSM-5; Density functional theory (DFT)

1. Introduction

The main applications of ZSM-5 zeolite in the fields of fuel processing and synthesis of chemicals are based on the shape selective catalytic properties introduced by their structure [1,2]. ZSM-5 has the MFI framework topology, characterized by a three-dimensional pore system with straight and sinusoidal channels. The pore openings are defined by 10 member rings that are wide enough ($\sim 5.5 \text{ \AA}$) to allow passage of molecules as large as benzene. Among the twelve crystallographically distinct T sites, T4 and T10 sites occur in the ten member ring

which forms the straight channel. Similarly T8 and T11 sites never occur in the 10 member ring which forms the sinusoidal channel. Thus, there are eight T sites which are common to both straight and sinusoidal channels [3,4]. ZSM-5 contains Si and Al as T sites; a variety of trivalent atoms such as B and Fe can replace Si in the MFI structure [5,6]. Although some metals are present as extra framework material, experimental techniques as XRD, TPD, IR Mossbauer spectroscopy and NMR provide extensive evidence that trivalent metals are incorporated in the ZSM-5 framework [5,7,8]. The difference in catalytic and separation properties resulting from framework substitution offers the potential to design zeolites for new applications. B-substituted zeolite finds its application in the

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Assoreni process of methyl butyl ether conversion to methanol and isobutene. B–ZSM-5 has also been used in the xylene isomerization and ethylbenzene conversion process [9]. Fe–ZSM-5 has been shown to be an active catalyst for the production of methanol by the direct oxidation of methane [10]. Though the incorporation may be effectively assessed by using spectroscopic and crystallographic techniques, often the experimental data are inadequate to give univocal indications about the siting of the heteroatom. There comes the need to perform theoretical studies to locate the preferable site for isomorphous substitution.

There are a lot of studies of zeolite structure and reactivity using ab initio molecular orbital theory and density functional theory (DFT) [11–14]. The accuracy of ab initio methods strongly depends on the flexibility of the basis set and the level of electron correlation included in the calculation [15]. Density functional theory (DFT) provides an expedient, yet accurate, treatment of electron correlation. Another strength of the DFT methods is their ability to treat transition metal systems, which are difficult to describe by Hartree–Fock methods. We have performed a local density approximation calculation of the structure and acidity of the above mentioned molecules to predict the preferable siting for the substituents. We also present a detailed picture of the local environment of the substituents. This is the first high accuracy calculation of Fe and B substitution in ZSM-5 zeolite. We are also able to reproduce the experimental acidity trend.

2. Calculation methods and cluster models

Local density functional (LDF) calculations were performed by running the DMOL software package [16] on a Silicon Graphics Indigo II workstation. The localized cluster model approach to study the crystal lattice properties proposed by Fripiat et al. [17] has been used. Calculations were performed on monomer

[T(OH)₄], dimer [(OH)₃–Si–O–T–(OH)₃], and pentamer T(OSiO₃H₃)₄ cluster models where T = Fe or B and kept fixed throughout the calculations. The boundary oxygens are saturated by hydrogen atoms, with hydrogen atoms occupying the position of the nearest T-site. In the monomer cluster models the adjacent T sites are approximated by H atoms. The dimer cluster model consists of two TO₄ groups bridged by a commonly shared oxygen. The pentamer cluster model represents a TO₄ group which shares a corner with four adjacent TO₄ groups through the bridging oxygen atom. The boundary oxygens are saturated by hydrogen atoms, with hydrogen atoms occupying the position of the nearest T-site. Hydrogen atoms, necessary to maintain the cluster neutrality for a substituted situation, were located at 1 Å along the bond axes connecting with the bridging oxygen. The choice of cluster models involved in this calculation has been discussed elsewhere [18]. The cluster geometry was assumed according to the crystal structure of orthorhombic MFI type ZSM-5 [19]. A double numerical with polarization (DNP) basis with spin restricted energy calculations was performed with fine mesh grid and frozen core electrons. The LDF formalism in DMOL is based on the work of von Barth and Hedin [20]. The fine grid gives a reasonable compromise between accuracy and computational efficiency and was used for all calculations presented here. The approximation seems to be reasonable when considering the negligible contribution of the inner electrons to the chemical bonds. The self consistent field (SCF) tolerance was set to 10⁻⁴ and the gradient convergence to 10⁻³ ha/bohr.

3. Results and discussion

3.1. Geometric parameters

There are 12 distinct T sites in the unit cell of ZSM-5. Since it is not possible to distinguish Si from Al in X-ray crystallography, there is no

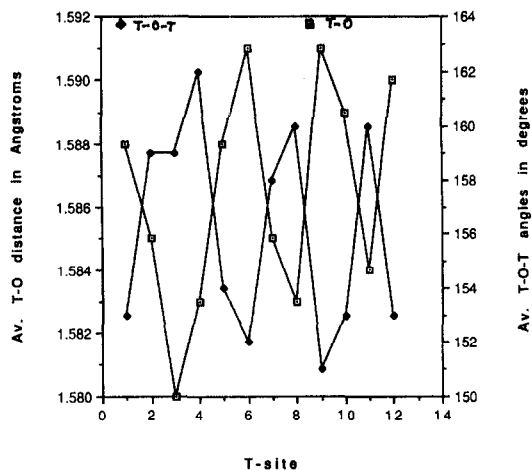


Fig. 1. Average T-O bond lengths and T-O-T bond angles as obtained from crystallographic data of van Koningsveld et al. [19].

direct evidence for the preferred sites of Al substitution. However, in our earlier study [18] it has been shown that Al in ZSM-5 favors longer bond lengths and smaller bond angles than Si. From Fig. 1 it is observed that larger bond lengths (T-O) are easily correlated with smaller bond angles (T-O-T). The figure indicates that substitution is preferable at the T9 site, with T6 and T12 being the other choices.

The internal co-ordinates of the all silicon and substituted ZSM-5 models show a dependence on the number of shells of atoms surrounding the central T-OH-Si bridge present in the protonated clusters. Fig. 2 shows the varia-

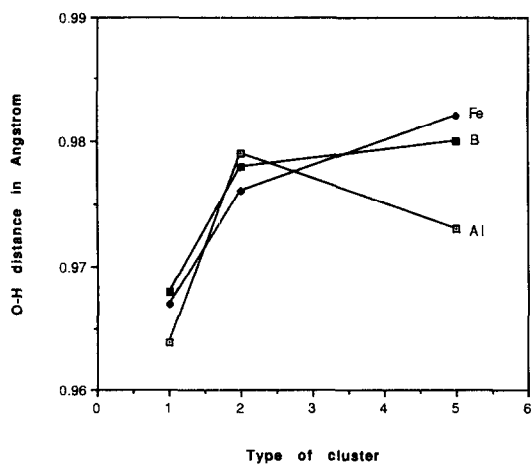


Fig. 2. O-H bond length variation with increasing cluster size.

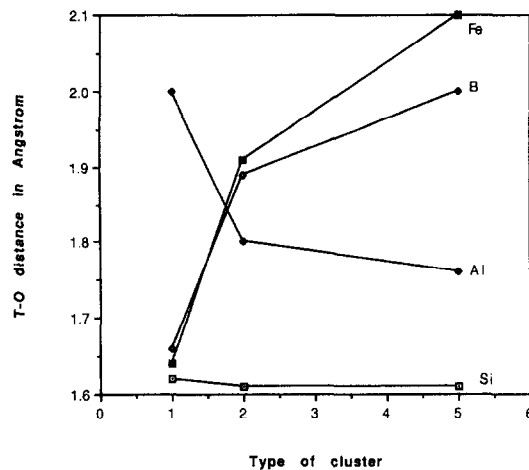


Fig. 3. T-O bond length variation with increasing cluster size.

tion of optimized O-H bond lengths in protonated models of increasing size from dimer to pentamer. The changes in bond-length are largely due to the change in electronic environment of the optimized atoms of the central bridge; in the dimer model T atoms are linked with OH groups. Further replacement of terminal hydroxyls by OSi(OH)₃ groups leads to a change in geometry, which leads to increase in the O-H bond lengths in case of B and Fe, and a decrease in case of Al. The T-O bond lengths behave in a more or less similar fashion as shown in Fig. 3. The T-O bond length in the all

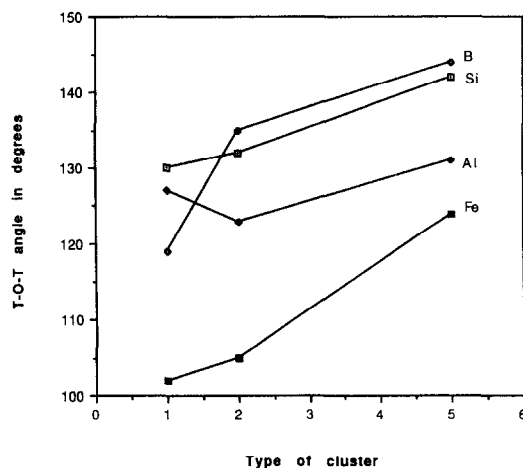


Fig. 4. Si-OH-T bond angle variation with increasing cluster size.

silicon model is relatively constant. The substituent atoms appear to cause significant changes in the zeolite geometry and are much more sensitive to model size. Fig. 4 shows the variation of T–OH–Si angles between the dimer and pentamer models. It is observed that for B and Fe the bond angles widen by $\sim 20^\circ$. The T–OH–T angles appear to converge slower with increasing model size. This is not very unexpected as a very small amount of energy is needed to vary the T–OH–T angles. The above data indicate that in order to get a reasonable optimization of the position of a particular atom within the zeolite, it is necessary to have at least the correct coordination of its nearest neighbors.

3.2. Classification of the T sites in the orthorhombic ZSM-5 framework

The energy calculations performed in the present investigation on the twelve monomeric $\text{Si}(\text{OH})_4$ clusters are reported in Table 1. Inspection of the relative energies, referred to the cluster T10, reveals that the energy differences are spread over 11 kcal/mol. It is observed that T2 and T12 are the most stable sites in the ZSM-5 framework.

The small energy differences resulting from the present investigation do not allow a clear distinction of the various sites. More definite evidence is expected from the study of pen-

Table 1
The total (E_T (a.u.)) and relative (ΔE (kcal/mol)) energies of monomeric $\text{Si}(\text{OH})_4$ clusters

Site	E_T (a.u.)	ΔE (kcal/mol)
T1	–579.53681	3.88
T2	–579.52859	9.03
T3	–579.53679	3.89
T4	–579.54084	1.34
T5	–579.52501	11.28
T6	–579.53205	6.64
T7	–579.53339	6.02
T8	–579.53676	3.91
T9	–579.52931	8.58
T10	–579.54298	0.0
T11	–579.53145	7.24
T12	–579.52742	9.76

Table 2

Total and relative energies of pentameric $\text{T}(\text{OSiO}_3\text{H}_3)_4$ clusters where T = Fe

Site	T = Si		T = Fe	
	E_T (a.u.)	ΔE (kcal/mol)	E_T (a.u.)	ΔE (kcal/mol)
T1	–2644.8091	19.26	–3203.0500	8.28
T2	–2644.8286	7.01	–3203.0224	24.47
T3	–2644.8271	7.94	–3203.0614	0
T4	–2644.8346	3.28	–3203.0561	4.45
T5	–2644.8398	0	–3203.0620	0.75
T6	–2644.8221	11.12	–3203.0445	11.73
T7	–2644.8036	22.72	–3203.0287	21.65
T8	–2644.8211	11.71	–3203.0427	12.86
T9	–2644.8358	2.46	–3203.0601	1.94
T10	–2644.8024	23.45	–3203.0281	22.02
T11	–2644.8100	18.72	–3203.0382	14.55
T12	–2644.7938	28.87	–3203.0198	26.10

tameric clusters. Total and relative energies, with respect to site T5 taken as a reference, of the twelve pentameric $\text{Si}(\text{OSiO}_3\text{H}_3)_4$ clusters are reported in Table 2. From these data the following conclusions can be drawn:

1. the relative energies are spread over about 30 kcal/mol, which allows a reasonable classification of the T sites;
2. T5, T9, and T4 sites are the most stable in the ZSM-5 framework;
3. T12, T10, T7, T1 and T11 are the less stable T sites, in which defects will be most likely localized.

3.3. Preferential substitution sites for Fe and B incorporation

The results of energy calculations performed on the $\text{Fe}(\text{OSiO}_3\text{H}_3)_4$ and $\text{B}(\text{OSiO}_3\text{H}_3)_4$ clusters, with the geometry of the twelve independent crystallographic sites of the ZSM-5 framework, are reported in Tables 2 and 3, respectively. The relative energies are spread about 27 kcal/mol for Fe clusters and about 34 kcal/mol for B substituted pentameric clusters. In our earlier study [18] we have shown that the rank ordering of energies of clusters representing various crystallographic sites is the same for all silicon and Al-containing clusters as long as the

Table 3

Total and relative energies of pentameric $T(\text{OSiO}_3\text{H}_3)_4$ clusters where $T = \text{B}$

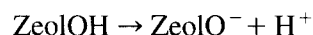
Site	T = Si		T = B	
	E_T (a.u.)	ΔE (kcal/mol)	E_T (a.u.)	ΔE (kcal/mol)
T1	-2644.8091	19.26	-3198.0532	11.48
T2	-2644.8286	7.01	-3198.0715	0
T3	-2644.8271	7.94	-3198.0195	32.63
T4	-2644.8346	3.28	-3198.0541	10.91
T5	-2644.8398	0	-3198.0626	5.96
T6	-2644.8221	11.12	-3198.0440	17.26
T7	-2644.8036	22.72	-3198.0278	27.42
T8	-2644.8211	11.71	-3198.0428	18.01
T9	-2644.8358	2.46	-3198.0604	6.96
T10	-2644.8024	23.45	-3198.0234	30.18
T11	-2644.8100	18.72	-3198.0542	10.85
T12	-2644.7938	28.87	-3198.0178	33.69

size of the cluster is same. Previously [21], it was observed that a pentamer cluster model was needed to satisfactorily predict the rank ordering of aluminum substitution energy at the twelve sites. The results show that the preferable site for Fe substitution is T3 and T11 and for B the preferred sites are T2 and T12 in the ZSM-5 zeolite framework. The calculation on the pentameric cluster model has demonstrated the importance of including distant oxygen shells, which again reinforces the role of calculations in attempting to determine the local structural effects of substitution in host materials. The geometric properties shown in the previous section very well matches with the energetics and the acidity trend as discussed in the following section, and also demonstrate the ability of the method.

The tendency of the trivalent T atoms to adopt trigonal coordination in the lattice is largely due to the dimension of the atoms. In

Table 4 the optimized T–O bond lengths for the molecule $T-(\text{OH})_3$ ($T = \text{B}$ and Fe, planar geometry) were compared with average values of the bond between the T site and the oxygen in the anionic and neutral pentameric cluster. A T atom is at the center of a trigonal face with a T–O bond length of 1.50 Å defined by the crystal positions of the three second shell oxygens. It is observed that in each case there is very little difference between the free molecule and zeolite models, which suggests that the pentameric cluster model allows significant relaxation of the environment of the substituent atoms. Thus, in case of B, which moves towards a bond length lesser than the crystal structure, it is free to adopt its preferred trigonal geometry without causing significant changes in the position of the neighboring atoms. Assuming the T–O bonds in the crystal are 1.59 Å, the relaxation energy is correlated with the difference between the crystal bond lengths and the bond lengths of the final geometry of the cluster. The relaxation energy increases for Al and Fe, as the substituent atoms distort the neighboring geometry to adopt their preferred bond lengths.

The relative acidity of substituted zeolites can be predicted from the calculated proton affinities of the zeolite model. Models with high proton affinity have a low Brønsted acidity whereas those with low proton affinity will have more Brønsted acidity. Proton affinity can be approximated by deprotonation energy E_{dp} as per the following reaction:



We list the deprotonation energies for the $\text{H}_3\text{T}(\text{OH})\text{TH}_3$ cluster where the T atoms are Al, B and Fe, the partial charges on the proton and

Table 4

T–O bond lengths in the $T(\text{OH})_3$ and pentameric cluster model and relaxation energy

Atom	T–(OH) ₃	Average T–O bond-length		Average relaxation energy (kcal/mol)	
		anion	neutral	anion	neutral
Al	1.70	1.69	1.67	13.2	19.6
B	1.36	1.49	1.39	7.54	16.7
Fe	1.80	1.76	1.74	45.3	42.9

Table 5
Experimental and theoretical comparison of acidity

Property	Al	Fe	B
O–H ^a	3610	3630	3745
E_{dp} ^b	317.2	323.5	335.4
Charge on H ^c	0.25	0.24	0.19

^a O–H stretching frequency in cm^{-1} (experimental).

^b Deprotonation energy in kcal/mol.

^c Partial charge on protonic hydrogen.

the experimental O–H stretching frequency in Table 5. The vibrational frequency of the O–H bond decreases with increasing acidity. The relative acidity of the hydroxyl groups calculated in terms of E_{dp} matches very well with the experimental acidity trend [22] predicted from IR frequencies. The big difference between the E_{dp} values of B–ZSM-5 and other substituents correlates well with the difference in the IR frequencies of bridging hydroxyl in case of B with those of other substituted ZSM-5 types.

4. Conclusion

Our results indicate that significant changes in energy accompany relaxation of the geometry about the substitution site. Thus it seems likely that geometry optimization is needed to accurately predict the relative energetic stability of substitution at different T sites. From the Mulliken population analysis it is observed that there is a high correlation between the partial charges on H and the experimental O–H stretching frequencies. Our calculated acidity trend matches very well with the experimental data. The computational efficiency of DFT allows us to consider larger models to show that the calculated properties display a substantial size dependence. This is the first high accuracy calculation of Fe and B substitution in ZSM-5 zeolite. Our calculations suggest that the preferable siting for Fe is 3 and 11 and for B it is 2 and 12 in the ZSM-5 zeolite framework.

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