Siting of B, Al, Ga or Zn and bridging hydroxyl groups in mordenite: an ab initio study

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Abstract

The siting of B, Al, Ga or Zn and bridging OH groups in the framework of mordenite was studied by ab initio Hartree–Fock MO methods. The basis set effect on the calculation results was investigated in details. It was shown that heteroatoms including B, Al, Ga and Zn prefer the same T sites, T_3 and T_4, when replacing Si in mordenite framework. The presence of the charge-balancing protons does not influence the siting sites of heteroatoms, but stabilizes the structure of the substituted clusters. For the two preferred substitution sites T_3 and T_4, the charge-compensating protons prefer to attach to O_9 and O_{10}, respectively, in case of B, Al or Ga substitution. For Zn substitution at T_3 or T_4 site, the two charge-compensating protons favor bonding with O_9 and O_1 or O_{10} and O_2, respectively. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Ab initio; B, Al, Ga or Zn; Bridging OH; Siting; Mordenite

1. Introduction

Zeolites have been extensively used as catalysts in many industrial processes due to their Bronsted acid sites and pore-related shape-selectivity.

Recently, much effort has been devoted to the synthesis, characterization, and application of metallosilicates containing elements in the framework other than Si and Al, such as B, Ga, Fe, Ti or Zn, etc. [1–5]. The incorporation of heteroelements can modify the acidity and pore structure of zeolites. The new materials thus produced show different catalytic behavior with altered activity, selectivity and stability, offering the potential to design zeolites for new applications. For example, Fe-ZSM-5 has been shown to be an active catalyst for the production of methanol by the direction

oxidation of methane [6] and for the oxidation of benzene to phenol [7]. Ga-ZSM-5 shows high selectivity in the aromatization of alkanes [8]. TS-1 is famous for its excellent performance in oxidation reactions [9].

Mordenite is a particular useful catalyst for several applications including cracking and isomerization of hydrocarbons, dewaxing of heavy petroleum fractions and conversion of methanol to hydrocarbons [10,11]. It has been shown that heteroatoms, such as B, Ga or Zn cloud be introduced into mordenite framework [12,13]. Dong et al. [13] synthesized zincosilicate mordenite with high crystallinity and Zn concentration in the framework by using citric acid as a complexing agent. The incorporation of zinc into the framework was verified by various techniques including ICP, XRD, FTIR as well as EXAFS, and a bond length of 0.1938 nm for Zn–O was obtained.

Mordenite has a two-dimensional (2D) channel structure with straight 12-ring 0.70 nm × 0.65 nm channels connected by short alternating 8-ring

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channels (0.3 nm). There are four crystallographically different tetrahedral (T) sites in mordenite framework at which substitution of heteroatoms for Si could take place. As each T atom is surrounded by four oxygen atoms, the total number of formally possible isolated bridging OH groups associated with isomorphous substitution is 16.

Knowledge of the positions of these heteroatoms and the bridging OH groups enables one to locate the acidic site, and then leads to a clear understanding of catalytic reaction mechanisms. X-ray powder crystallography cannot, however, distinguish between Si and Al or other metal cations in the frameworks, and it is therefore necessary to resort other less direct methods to obtain this information.

It has been shown that ab initio molecular orbital calculations can be used to predict the structure and reactivity of zeolites [14–18]. A lot of work have been done to examine the preferred T sites for the replacement of Si by Al in zeolite ZSM-5 [19–23], ferrierite [24], and Theta-1 [25] frameworks by ab initio molecular orbital calculations. Chatterjee and Vetrivel [26] studied the siting of Al in ZSM-5 and concluded that Al favors longer bond length and smaller bond angles than Si.

For siting of Al in mordenite framework, Derouane and Fripiat [27] firstly carried out non-empirical SCF-MO calculations in 1983. The positions of the atoms used to simulate different tetrahedral sites were fixed to their crystallographic positions and the clusters were not allowed to relax. The preferred siting sites of Al were derived from the calculations.

The accuracy of ab initio methods depends strongly on the size of the cluster model, the basis set and the level of electron correlation included in the calculation. In this paper, we report cluster model calculations on the siting of B, Al, Ga or Zn and the bridging OH groups in mordenite frameworks by using ab initio Hartree–Fock MO methods. Topologically open pentamers, which have been proven to be adequate for studying of the substitution process [28], are employed and the basis set effect is examined in details. It is shown that heteroatoms including B, Al, Ga and Zn prefer the same T sites, T_3 and T_4, when replacing Si in mordenite framework. For the two preferred substitution sites T_3 and T_4, the charge-compensating protons prefer to attach to O_9 and O_{10}, respectively, in case of B, Al or Ga substitution. While for Zn substitution

at T_3 or T_4 site, the two charge-compensating protons favor bonding with O_9 and O_1 or O_{10} and O_2, respectively.

2. Models and methods

2.1. Models

The geometry of the cluster models used in this work is taken from the framework structure of Na-mordenite [29]. There are four distinct tetrahedron sites (T sites) in the unit-cell of mordenite (see Fig. 1). Therefore, the cluster models selected here are open pentamers centered on each of the four T sites as shown in Fig. 2. Terminal hydrogen atoms, being used to maintain the neutrality of the clusters and to ensure a higher reliability of the calculations, are located at a O–H distance of 0.1 nm from the corresponding oxygen and oriented along the bond direction to what would otherwise have been the next silicon atom. The cluster charge is 0 when the central T atom is Si and -1 when trivalent M substitutes Si, where M = B, Al or Ga. The cluster charge is 0 when the charge-compensating proton is included in the cluster. When Si is substituted by divalent Zn, the total charges are -2, -1 and 0, respectively, for the clusters without or with one or two charge-balancing protons in them.
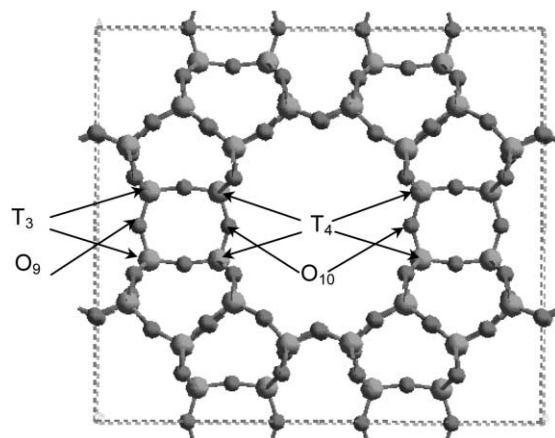

Fig. 1. The structure of mordenite unit-cell viewed down the [0 0 1] direction (with T_3, T_4 and O_9, O_{10} designated).
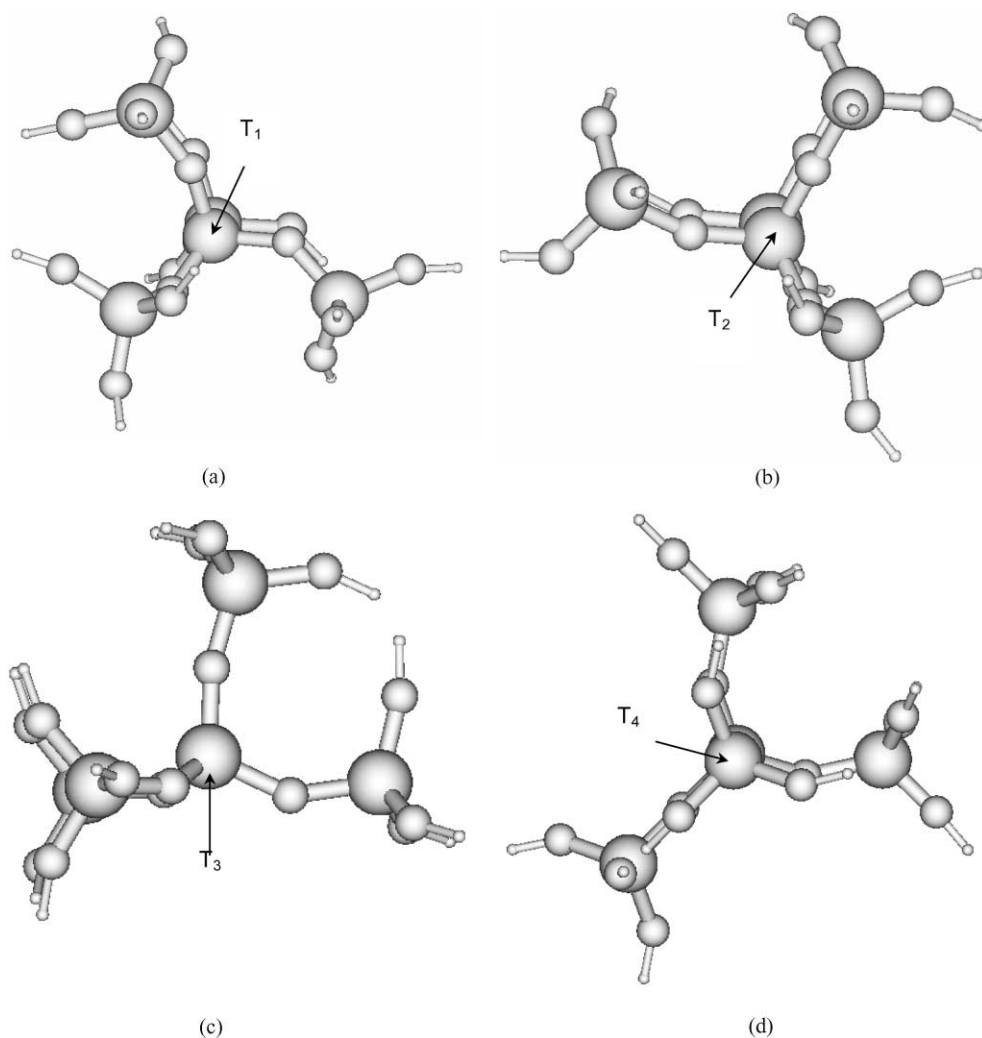
(a)

(b)

(c)

(d)

Fig. 2. Pentameric cluster models of mordenite centered on different T sites.

2.2. Methods

Ab initio Hartree–Fock MO calculations are performed by using Gaussian 98 program [30]. For calculations on Al substitution, two basis sets including the split-valence 3-21G and 6-31G basis sets are adopted and compared.

It has been proven that quantum mechanical calculations can give good agreement with experiment only when the geometry is allowed to relax [31]. However, Sauer [32] pointed out that full relaxation of the clusters might lead to structures that do not resemble experimental zeolite geometries. Thus, considerable care is needed in implementing the relaxation of clusters that mimic the zeolite framework. Taking this view into account, the structure of the clusters containing heteroatoms are partially optimized in this paper, i.e. keeping the inner atoms of $Si–O(H)–TO_3$ (T = B, Al, Ga or Zn) for proton attached clusters and TO_4 atoms for negative charged clusters relaxed while the rest of the clusters fixed to their framework positions. This allows the atoms in the vicinity of the acid site and substituted atoms to relax, while the cluster retains its position in the zeolite lattice.

For cluster with its central T_i site being Si atom, the geometry is not allowed to relax.

3. Results and discussion

3.1. Siting of Al in the absence of charge-compensating protons

The substitution energy ΔE_{sub} of the clusters centered on the four different T sites upon replacement of Si by Al calculated with different basis sets are represented graphically in Fig. 3. It is calculated by

$$\Delta E_{sub} = (E_{T_i-Al} + E_{Si^{4+}}) - (E_{T_i-Si} + E_{Al^{3+}}),$$
$$i = 1, 2, 3, 4$$

which corresponds to the energy change of reaction

$$\text{Si–(OSi(OH)}_3)_4 + Al^{3+}$$
$$\rightarrow [\text{Al–(OSi(OH)}_3)_4]^- + Si^{4+}$$
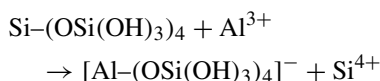
where Si–(OSi(OH)$_3$)$_4$ and [Al–(OSi(OH)$_3$)$_4$]$^-$ are the clusters with Si and Al at their central T_i site, E_{T_i-Si} and E_{T_i-Al} correspond to their total energies, respectively. The substitution energies reported in this paper do not include zero-point energies. It is shown that the two basis sets give the same trends of the substitution energy. By balancing computer cost with the reliability of the calculation results the following

Table 1
Relative substitution energy of Si by Al at different T sites to T_3 site calculated with different basis sets

	T_1	T_2	T_3	T_4
ΔE_{rel} (kcal/mol) (3-21G[a])	45.4	34.1	0.0[b]	8.5
ΔE_{rel} (kcal/mol) (6-31G[b])	45.0	33.7	0.0	7.4

[a] E_{T_i-Al}, E_{T_3-Si}, E_{Al}^{3+} and E_{Si}^{4+} are −2589.50378, −2636.20123, −238.68286, −283.68376 AU, respectively.
[b] E_{T_i-Al}, E_{T_3-Si}, E_{Al}^{3+} and E_{Si}^{4+} are −2602.64757, −2649.47157, −239.97826, −285.15559 AU, respectively, 1 AU = 627.51 kcal/mol.

calculations on the substitution of B, Ga and Zn are performed with the split-valence 3-21G basis set. It can be also seen from Fig. 3 that the lowest value of the substitution energy corresponds to T_3 and the largest value to T_1, indicating that T_3 and T_1 are respectively the most and the least favored T sites for Al substitution.

The relative substitution energy ΔE_{rel} given in Table 1 is noted as the energy difference between the substitution of Al at T_i ($i = 1, 2, 4$) and the favorite site T_3

$$\Delta E_{rel} = (E_{T_i-Al} - E_{T_i-Si}) - (E_{T_3-Al} - E_{T_3-Si})$$

ΔE_{rel} data show that the difference of the substitution energies between T_3 and T_4 sites is as low as 7–9 kcal/mol only, suggesting that the replacement of Si by Al in mordenite framework takes place most probably at T_3 and T_4 sites while the substitution at
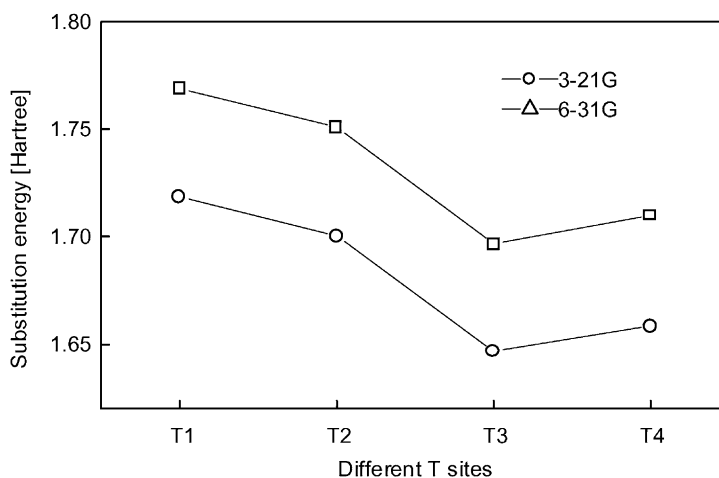

Fig. 3. Substitution energies for the replacement of Si by Al at different T sites calculated with different basis sets.

other T sites which requires 34–45 kcal/mol more energy is less favored energetically. From the structure of mordenite framework, it is known that T_3 is located at the 8-ring channel with pore dimensions 0.26 by 0.57 nm while T_4 is at 12-ring channel with pore dimensions 0.65 by 0.70 nm [33]. It is obvious that only very small molecules like O_2, N_2 or H_2O, etc. can access the 8-ring channel while the 12-ring channel is large enough for a lot of molecules, such as organic hydrocarbons. Therefore, T_4 is more accessible and important in catalytic reactions.

3.2. Influence of charge-compensating protons on Al substitution

Each Si atom connects with four oxygen atoms in zeolite frameworks, and when Si^{4+} is replaced by T^{3+} or T^{2+} atoms, the charge-compensating protons could thus be attached to any one or two of these four oxygen atoms. Therefore, to investigate the influence of the protons on the substitution of Al for Si, it is necessary to calculate the energy of the four clusters with protons attached on each of the four oxygens bonding with each T site.

Firstly, T_4 is used to investigate the basis set effect with considering the charge-compensating proton. Only three of the four oxygens around T_4 site, O_2, O_4 and O_{10}, are inequivalent. As a result, the calculations are performed for three cases corresponding to those

with proton attached to O_2, O_4 and O_{10}, respectively. Fig. 4 gives the comparison of the substitution energies calculated with two different basis sets. The substitution energies here are calculated by the equation

$$\Delta E_{sub}(H^+) = (E_{O_i-H} + E_{Si^{4+}})$$
$$-(E_{T_4-Si} - E_{Al^{3+}} - E_{H^+}),$$
$$i = 2, 4, 10$$

This corresponds to the energy change of reaction

$$Si-(OSi(OH)_3)_4 + Al^{3+} + H^+$$
$$\rightarrow Al-OH-O_3(Si(OH)_3)_4 + Si^{4+}$$
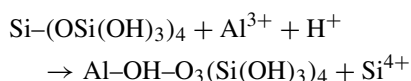
where E_{O_i-H} is the total energy of the cluster with proton on O_i oxygen surrounding T_4 site while E_{T_4-Si} is the total energy of the cluster with Si centered on T_4 and E_{H^+} is 0. The analysis of Fig. 4 shows that 3-21G and 6-31G give the same trends of the substitution energy. This suggests that the split-valence 3-21G basis set is the minimal for the calculations involving protons. As a consequence, the following discussion is based on the results obtained by using 6-31G basis set.

The average substitution energies for proton attached to each of the distinct oxygens surrounding T_i ($i = 1, 2, 3, 4$) site are given in Table 2. The relative substitution energies $\Delta E_{rel}(H^+)$ also listed in Table 2 are calculated by

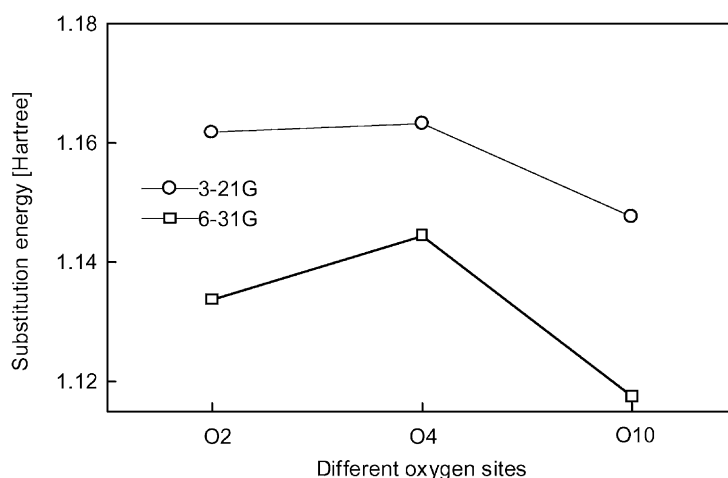$$\Delta E_{rel}(H^+) = \Delta E_{T_i-avr} - \Delta E_{T_3-avr}$$

Fig. 4. Energies required for the replacement of Si by Al at T_4 site with charge-compensating proton at each of the three distinct oxygens calculated with different basis sets.

Table 2
Average and relative substitution energies for the replacement of Si by Al at different T sites with charge-compensating protons[a]

	T_1	T_2	T_3	T_4
ΔE_{avr} (AU)	1.1826	1.1603	1.1190	1.1320
ΔE_{rel} (H^+) (kcal/mol)	39.9	25.9	0.0	8.2

[a] E_{Si}^{4+} and E_{Al}^{3+} are −285.15559, −239.97826 AU, respectively.

where ΔE_{T_i-avr} and ΔE_{T_3-avr} are respectively the average substitution energies of the clusters centered on T_i ($i = 1, 2, 4$) and T_3. It can be seen that the favorite sites for Al substitution are T_3 and T_4, while the substitution at other T sites which requires 26–40 kcal/mol more energies are less favored energetically. This is consistent well with the results obtained in the absence of the charge-compensating protons in Section 3.1.

By comparing the substitution energies for the replacement of Si by Al at different T sites with and without charge-balancing protons (see Fig. 3 and Table 2), it can be found that the former is larger than the latter, indicating that protons enhance the stability of the substituted structures.

The previous work of this paper indicated that 3-21G basis set without taking the charge-compensating proton into account is sufficient to study the substitution energy of heteroatoms in mordenite framework. It should be mentioned that energetically the preferred T sites for the replacement of Si by Al obtained in the present work is consistent well with that reported by Itabashi et al. [34,35]. From ^{29}Si MAS NMR measurements, they suggested that the occupancies of Al on T_1 and T_2 sites decrease in accordance with the reduction of the Al content and

Table 3
The average bond lengths and bond angles for different T sites in mordenite framework

	T_1	T_2	T_3	T_4
d_{T-O} (avr) (nm)	0.1619	0.1587	0.1639	0.1624
α_{T-O-T} (°)	148.2	164.1	150.6	150.4

Al atoms are mainly concentrated at T_3 and T_4 sites in mordenite framework.

The average bond lengths and bond angles for the different T sites in mordenite framework are given in Table 3. It shows that the present work supports the conclusions drawn by Chatterjee et al.: Al favors longer bond length and smaller bond angel than Si [26].

3.3. Siting of B, Ga and Zn atoms in mordenite

According to the previous work of this paper, the split valence 3-21G basis set in the absence of the charge-ompensating protons is selected to study the preferred substitution T sites for heteroatoms including B, Ga or Zn atoms in mordenite framework. The results are listed in Table 4. The difference of the substitution energies between T_i ($i = 1, 2, 4$) and T_3, the favorite T site for substitutions, is calculated as follows:

$$\Delta E_{rel} = (E_{T_i-M} - E_{T_i-Si}) - (E_{T_3-M} - E_{T_3-Si}),$$
$$M = B, Ga, Zn$$

where E_{T_i-M} is the total energy of the clusters with the central atom being B, Ga or Zn, respectively, and E_{T_i-Si} is the total energy of the cluster with Si at the

Table 4
Total energies of clusters with their central T_i site being Si, B, Ga or Zn, respectively, and the relative substitution energies of different T sites for the replacement of Si by B, Ga or Zn, respectively[a]

T_i	Si E_{T_i-Si} (AU)	B		Ga		Zn	
		E_{T_i-B} (AU)	ΔE_{rel} (kcal/mol)	E_{T_i-Ga} (AU)	ΔE_{rel} (kcal/mol)	E_{T_i-Zn} (AU)	ΔE_{rel} (kcal/mol)
T_1	−2636.23330	−2373.28512	37.7	−4262.68570	45.3	−4117.70521	63.2
T_2	−2636.19731	−2373.25793	32.2	−4262.66681	34.6	−4117.68198	55.2
T_3	−2636.20123	−2373.31312	0	−4262.72580	0	−4117.77382	0
T_4	−2636.18527	−2373.25636	25.6	−4262.66994	25.0	−4117.71719	25.5

[a] E_B^{3+}, E_{Ga}^{3+}, E_{Zn}^{2+} and E_{Si}^{4+} are −21.86266, −1911.92144, −1768.27504 and −283.68376 AU, respectively, and all the relative substitution energies are referenced to the T_3 site.

central T_i site. The data show that the substitution energies required by different T sites decrease in the order: $T_3 < T_4 < T_2 < T_1$, which agree well with the order for the substitution of Al for Si obtained above.

We hence conclude that heteroatoms, such as divalent Zn or trivalent B, Al and Ga will preferentially replace Si in mordenite framework at positions T_3 and T_4, and the presence of the charge-balancing protons stabilizes the structure of the substituted clusters.

What should be noted here is that the calculated average bond distance (0.1992 nm) between Zn and the oxygen atoms bonding with it in the present work can match well with that measured by EXAFS (0.1938 nm) [13].

3.4. Location of the bridged hydroxyl groups in substituted clusters

The previous part of this paper revealed that T_3 and T_4 sites in mordenite framework are the favorite sites for the isomorphous substitution by heteroatoms. Therefore, we investigate the location of proton only for the substitution at T_3 or T_4, respectively. Firstly calculations on Al containing clusters are performed. Due to the fact that proton could bond with any of the four oxygens which surround the Al atom, but will bond preferentially with the one which is the lowest in energy [36]. The total energy of each cluster, with a proton attached to one of the three inequivalent oxygens bonding to T_3 and T_4 sites, respectively, is therefore calculated with 6-31G basis set and listed in Table 5. It can be found that the most stable configurations correspond to the clusters with protons on O_9 and O_{10}, respectively, in case of T_3 and T_4 as substitution sites. The energies required for the substitution of Al for Si with a proton to compensate the negative charge (see Table 5) also indicate that the smallest energies are required for the replacement

Table 5

Total and substitution energies with charge-compensating proton attached to one of the oxygens bonding with T_3 or T_4 sites[a]

	T_3			T_4	
	Energy (AU)	ΔE_{sub} (AU)		Energy (AU)	ΔE_{sub} (AU)
E_{T_3-Si}	−2649.47157	–	E_{T_4-Si}	−2649.42760	–
E_{O_1-H}	−2603.17372	1.1205	E_{O_2-H}	−2603.11658	1.1337
E_{O_4-H}	−2603.16302	1.1312	E_{O_4-H}	−2603.10585	1.1444
E_{O_9-H}	−2603.18880	1.1054	$E_{O_{10}-H}$	−2603.13274	1.1175

[a] E_{Si}^{4+} and E_{Al}^{3+} are −285.15559, −239.97826 AU, respectively.

with proton attached to O_9 and O_{10}, respectively, for the substitution at T_3 and T_4.

From the crystallographic structure of mordenite, it is known that O_9 and O_{10} are located at the 12-ring channel and therefore the protons attached to them can be accessed by normal organic reactants in catalytic reactions. As for the other trivalent substituents like B and Ga, it can be inferred that the same oxygen sites are preferred to attach by protons. For the case of Zn as a substituent, the siting positions of protons are investigated specially because two protons are needed to compensate the negative charges caused by the substitution of divalent Zn atom. Firstly, it is presumed that only one proton is attached to one of the four oxygens surrounding Zn atom in the clusters when substitution occurred at T_4 site, and thus the charge of the whole cluster is −1. By comparing the calculated total energies of the clusters in Table 6, it can be found that the configuration in which proton combined to O_{10} is the most energetically stable one, which coincides with the case of Al substitution. Similarly, it can be inferred that for the substitution of Zn at T_3 site the proton favors O_9 site as the same as Al substitution. To find out the oxygen site to which the second proton prefers to attach, calculations are performed on the other two

Table 6

Total energies of clusters with Zn centered on T_3 or T_4 sites having one or two protons attached to one or two of the oxygen sites

	T_3		T_4	
Energies with one proton (AU)	O_1–H	–	O_2–H	−4138.63734
	O_4–H	–	O_4–H	−4138.61855
	O_9–H	–	O_{10}–H	−4138.64100
Energies with two protons (AU)	O_9–O_1–H	−4139.24294	O_{10}–O_2–H	−4139.18317
	O_9–O_4–H	−4139.23423	O_{10}–O_4–H	−4139.17735

distinct oxygen atoms with the first proton at O_9 and O_{10} site, respectively, for T_3 and T_4 are substituted. The calculations reveal that the second proton prefers O_1 and O_2 with the substitution site being T_3 and T_4, respectively (see Table 6).

4. Conclusions

The siting of B, Al, Ga or Zn and the bridging OH groups in the framework of mordenite was studied by ab initio Hartree–Fock MO methods. It was shown that heteroatoms including B, Al, Ga and Zn prefer the same T sites, T_3 and T_4, when replacing Si in mordenite framework. The presence of the charge-balancing protons does not influence the siting sites of heteroatoms, but stabilizes the structure of the substituted clusters. For the two preferred substitution sites T_3 and T_4, the charge-compensating protons prefer to attach to O_9 and O_{10}, respectively, in case of B, Al or Ga substitution. While for Zn substitution at T_3 or T_4 site the two charge-compensating protons favor bonding with O_9 and O_1 or O_{10} and O_2, respectively.

Acknowledgements

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