

# Density Functional Theory Study of Chemical Composition Influence on the Acidity of H–MCM-22 Zeolite

Yan Wang,<sup>†</sup> Gang Yang,<sup>†</sup> Danhong Zhou,<sup>†,‡</sup> and Xinhe Bao<sup>\*,†</sup>

State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, 116023, Liaoning, P. R. China, and Department of Chemistry, Liaoning Normal University, Dalian 116029, P. R. China

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In this work, the influence of the chemical composition (species and number of trivalent substitution atoms) on the acidity of the isomorphously substituted MCM-22 zeolite was investigated in detail by density functional theory. By calculating the proton affinity and NH<sub>3</sub> adsorption energy, it was found that the acidity of the MCM-22 zeolite decreased with increasing number of trivalent substitution atoms introduced into the zeolite framework. Moreover, the acidity of the substituted MCM-22 increased in the sequence of B–MCM-22 < Fe–MCM-22 < Al–MCM-22, independent of the number of trivalent substitution atoms. The calculation results also showed that when Fe or B elements were incorporated into the framework of the aluminosilicate MCM-22 zeolite, the proton affinity of MCM-22 zeolite decreased in the order of B–MCM-22 > [Al,B]–MCM-22 > Fe–MCM-22 > [Al,Fe]–MCM-22 > Al–MCM-22. All these results were in good agreement with the experimental results.

## 1. Introduction

With a proper understanding of the nature of zeolites, there is great potential for zeolites to replace homogeneous acids in a wide range of catalytic applications. The reaction activity of zeolites as acid catalysts mainly depends on their acidic properties, and their acid strength is known to be influenced by their chemical composition, such as the species and the number of trivalent substitution atoms. In the past, many experimental studies focused on the acidity of isomorphously substituted zeolites. Chu and Chang<sup>1</sup> used IR spectroscopy and TPD–NH<sub>3</sub> to study the acidity of several isomorphously substituted ZSM-5 zeolites and reported that the acid strength increased as B–ZSM-5 < Fe–ZSM-5 < Ga–ZSM-5 < Al–ZSM-5. The dependence of the acidity of zeolites on the number of incorporated framework Al atoms has also been confirmed by experiments.<sup>2–5</sup> Because one Al atom cannot be connected directly to another Al atom through an oxygen atom (Lowenstein's law), the closest Al pairs are the next-nearest-neighbor (NNN) sites in a zeolite. Pine et al.<sup>6</sup> proposed a next-nearest-neighbor theory for explaining the dependence of the acidity of zeolites on the number of incorporated framework Al atoms that is still widely accepted today. According to their theory, the acidic strength decreases as the number of Al atoms occupying the NNN sites increases. Therefore, although the total number of acid sites increases as the Al content becomes higher, the number of strong acid sites decreases.

Because of the difficulties and ambiguities connected with the experimental determination of the acidity of the Brønsted sites in zeolites, quantum chemical calculations have been extensively used to study the effect of the chemical composition on the acidity of the zeolites. Considering the effect of the

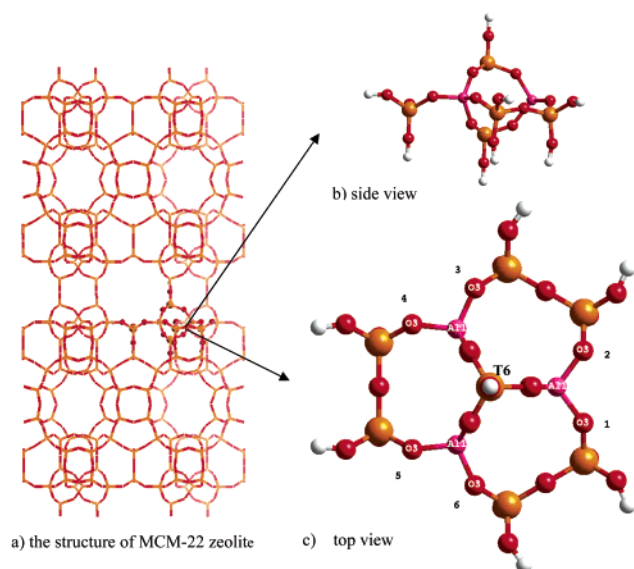
substitution species, density functional theoretical calculations on isomorphously substituted ZSM-5 clusters by B, Al, Ga, and Fe have been reported, and the calculated acidity agreed well with the experimental results.<sup>7–14</sup> Recently, our group also compared the properties of isomorphously substituted MCM-22 zeolites with a small cluster model into which only one substitution atom was introduced and has correctly predicted their acidity.<sup>15</sup> In studying the influence of the number of trivalent substitution atoms by using four-membered-ring models for the substitution from Si to Al at the NNN site, Schroeder and Sauer<sup>16</sup> pointed out that a structure with Al–O–Si–O–Al linkage (the NNN model) was more stable than a structure where two aluminum atoms were separated as far as possible. Based on the NNN model, a series of calculations have been performed.<sup>17–27</sup> In these studies, the strength of the Brønsted acid sites was often characterized by the proton affinity (PA), which is defined as the energy difference between the optimized protonated and deprotonated (anionic) forms of the zeolite. The models with low PA values were found to be better proton donors, and thus had higher Brønsted acidity. From the calculations using four-membered-ring models, Kramer and van Santen<sup>17</sup> found that the substitution from Si to Al at the NNN site increased the PA (decreased the acidity). On the other hand, by analyzing the mordenite and faujasite zeolites, Teraishi et al.<sup>19,22,25</sup> proposed that the effect of the substitution on the acid strength was not unique but site dependent. The NH<sub>3</sub> adsorption energy ( $E_{\text{ads}}$ ) is also a good criterion for estimating the acidity of zeolite, which was reasonably calculated by the reaction  $\text{ZH} + \text{NH}_3 \rightarrow \text{ZH-NH}_3$ . The zeolite with stronger acidity would have larger adsorption energy.

In this work, the influence of chemical composition on the acidic characteristics of a relatively new MWW type zeolite, MCM-22, is investigated in detail by density functional theory (DFT). The MCM-22 zeolite consists of two different independent porous systems<sup>28,29</sup> and has been regarded as a promising catalyst for many reactions.<sup>30–33</sup> Both calorimetric and IR

\* Corresponding author. Telephone: 086-0411-84686637. Fax: 086-0411-84694447. E-mail: xhbao@dicp.ac.cn.

<sup>†</sup> Chinese Academy of Sciences.

<sup>‡</sup> Liaoning Normal University.



**Figure 1.** Chosen cluster model of MCM-22 zeolite. (The crystallographic labeling of pure silica MCM-22 is accordance with the *Atlas of Zeolite Framework Types*<sup>40</sup>) The pink atoms represent the T1 site, which will be substituted by B, Al, and Fe, respectively, or together. The numbers 1–6 represent six different locations of protonic H atom at bridging oxygen O3 when the cluster model is substituted by B, Al, and Fe, and the corresponding O<sub>3</sub> atoms are named as O<sub>3</sub><sup>n</sup> (*n* = 1–6), respectively.

experiments confirmed that the acid strength of the MCM-22 zeolite increased as the Si/Al ratio increased.<sup>34</sup> By infrared (IR) spectroscopy and pyridine adsorption, Wu et al.<sup>35</sup> also compared the Brønsted acidity of the Fe-MCM-22 and Al-MCM-22 zeolites and reported that the acidity of the Fe-MCM-22 zeolite was much weaker than that of the Al-MCM-22 zeolite. By investigating the acidity of Fe- and [Fe,Al]-MCM-22 zeolites, Testa et al.<sup>36</sup> got similar results. The higher wavenumber observed on the Si(OH)Fe also suggests that the Brønsted acidity of Fe-MCM-22 was much weaker than that of the Al-MCM-22 zeolite. However, compared with experimental investigations, theoretical studies on the acidity of the MCM-22 zeolite are still rather limited, besides those done by us recently.<sup>15,37–39</sup>

## 2. Models and Methods

In the present work, a perfectly symmetrical cluster model (see Figure 1b,c), was chosen for the calculation since only the variation of acid strength upon changing the chemical composition of MCM-22 zeolite was discussed; long-range interactions were thus expected to be canceled out when the differences were taken. The chosen cluster model originated from a part of the crossing of 12-MR supercages of the MCM-22 zeolite<sup>40</sup> (see Figure 1a). There were three T1 sites that were at least terminated by OSi(OH<sub>3</sub>)<sub>3</sub> in the model and a symmetrical structure composed of three five-membered rings (5-MR) was formed. The model contains 54 atoms for the anionic form and 55–57 atoms for different protonic forms, much bigger than those of previous calculations.<sup>17–25,27</sup> The model was chosen because of the following: First, the T1 site is one of the most preferred locations for aluminum substitution in the MCM-22 zeolite based on our previous calculation<sup>37–38</sup> and it may play an important role in some catalytic reactions. Second, the three T1 sites in the chosen model become NNN sites because each of them is connected by a common T6 site. Thus, the model chosen obeys Lowenstein's rule and the NNN model. Third, previous calculations adopted a smaller cutoff surrounding for

the second Al at the next-nearest-neighbor position, as compared to the first one (the center one), and considered the acidity of the whole zeolite by only calculating the proton affinity of the one connected to the first Al atom (the center one),<sup>24</sup> while the acidity of the zeolite should be actually represented by all existing acidic protons. In our model, the surroundings of all the substituted atoms were equally and all terminated by OSi(OH<sub>3</sub>)<sub>3</sub> or more, and the acidity of the zeolite was estimated by considering the whole effect of all protonic H atoms. Obviously, the model we chose was more reasonable, and thus the calculation results will represent more accurately the acidity of the whole zeolite. Last, the three T1 sites in the chosen model are completely equivalent. Thus, the variation in the acidity can be caused only by the chemical composition (the species and the number of trivalent substitution atoms), rather than by the variation in T sites.

The DFT calculations in this work were carried out with Dmol3 module in Cerius2, similar to our previous calculation on the MCM-22 zeolite.<sup>38</sup> The calculations were performed at the nonlocal exchange and correlation functionals, BLYP. A double numerical with polarization (DNP) basis set was adopted, which is comparable in size to the commonly used 6-31\*\* Gaussian orbital basis set. However, the numerical basis set is much more accurate than a Gaussian basis set with the same size. All of the models were optimized using spin-restricted procedures, except for those containing Fe element as open-shell systems. The dangling bonds were saturated by hydrogen atoms with a distance of 0.98 Å from the connected framework oxygen atoms. During the optimization, the 14 terminating hydroxyl groups were fixed in their crystallographic positions, whereas the remaining atoms of the clusters and NH<sub>3</sub> molecules were fully optimized. Considering both the size of the model and the level of calculation method, we are convinced that the conclusions that will be drawn in the following should be quite reliable.

## 3. Results and Discussion

**3.1. The Stable Position of the Acidic Proton.** Although all T1 sites were crystallographically equivalent and symmetrical in the chosen clusters, the compensating proton H atoms would destroy the symmetry when introducing some substitution atoms into the zeolite framework. Around each T1 site there are three unequivalent framework oxygen atoms, namely, O2, O3, and O4, which can be bound with a proton to form a hydroxyl. In principle, different positions of the acidic protons in the framework can lead to different bond distances and angles and, hence, to different properties of the bridging hydroxyl group. As shown in our previous work,<sup>37–38</sup> the energy for Al substitution was minimum in the MCM-22 zeolite when the proton was connected to the O3 atoms. To reduce the calculation time, all the compensating protons in this work were connected to O3 atoms. Since there are two O3 sites for locating the acidic proton for each substitution atom, the possible locations of protons are rather complex for different substitution types. When only one substitution atom is introduced in the model (single substitution), only one structure I(H) is obtained because the bridging hydroxyls situated on the O<sub>3</sub><sup>1</sup> as well as on the O<sub>3</sub><sup>2</sup> are equivalent. With two substitution atoms in the cluster model (double substitution), there are two kinds of substitution types. When two substitution atoms are of the same element, three different structures are obtained and denoted as I(H1)I(H3), I(H1)I(H4), and I(H2)I(H3), respectively. When two substitution atoms are of different elements, four different structures are obtained and denoted as I(H1)J(H3), I(H1)J(H4), I(H2)J(H3),

**TABLE 1: Possible Locations of Protonic H Atoms at Bridging Oxygen O3 for Different Substitution Types When MCM-22 Zeolite Is Substituted by B, Al, and Fe<sup>a</sup>**

single substitution	double substitution		triple substitution elements are the same
	elements are the same	elements are different	
one structure: <i>I(H)</i>	<i>I(H1)I(H3)</i> <i>I(H1)I(H4)</i> <i>I(H2)I(H3)</i>	<i>I(H1)J(H3)</i> <i>I(H1)J(H4)</i> <i>I(H2)J(H3)</i> <i>I(H2)J(H4)</i>	<i>I(H1)I(H3)I(H5)</i> <i>I(H1)I(H4)I(H5)</i>

<sup>a</sup> Single substitution means that there is one substitution atom introduced into the cluster model; double substitution means that there are two substitution atoms introduced into the cluster model; triple substitution means that there are three substitution atoms introduced into the cluster model. Different substitution elements are denoted as I (I = B, Al, Fe) and J (J = B, Al, Fe), respectively. *Ha* (*a* = 1–6) represents the six possible locations of protonic H atoms at bridging oxygen O3 (see Figure 1).

**TABLE 2: Calculated Proton Affinity (kcal/mol) of MCM-22 Zeolite in Which the Chemical Composition Changed<sup>a</sup>**

	neutral (hartrees)	anion <sup>R</sup> (hartrees)	PA <sup>R</sup>	anion <sup>L</sup> (hartrees)	PA <sup>L</sup>	PA <sup>aver</sup>	anion <sup>-2</sup> (hartrees)	PA <sup>-2</sup>
Al(H)	-5330.987 684 2	-5330.493 126 3	310.34					
Al(H1)Al(H3)	-5284.514 885 7	-5284.012 344 3	315.35	-5284.006 623 3	318.94	317.14	-5283.419 965 8	371.72
Al(H1)Al(H3)Al(H5)	-5238.035 000 1	-5237.528 302 8	317.96				-5236.925 308 0	
Fe(H)	-6352.222 426 9	-6351.718 889 7	315.97					
Al(H1)Fe(H4)	-6305.752 549 1	-6305.252 557 8	313.74	-6305.240 525 9	321.30	317.52	-6304.650 519 2	379.49
Fe(H1)Fe(H3)	-7326.998 346 2	-7326.495 202 8	315.73	-7326.488 401 9	320.23	317.98	-7325.889 267 7	380.23
Fe(H1)Fe(H3)Fe(H5)	-8301.761 458 6	-8301.251 458 6	320.03					
B(H)	-5113.327 283 4	-5112.821 591 2	317.33					
B(H1)Al(H4)	-5066.850 872 9	-5066.354 008 8	311.79	-5066.328 612 3	327.72	319.76	-5065.740 380 8	385.06
B(H1)B(H3)	-4849.189 920 0	-4846.678 982 9	320.62	-4848.675 906 4	322.55	321.58	-4848.064 075 3	385.86
B(H1)B(H3)B(H5)	-4585.052 919 2	-4584.535 223 0	324.86				-4583.915 723 9	

<sup>a</sup> For double substitution, there are two kinds of protons. The corresponding anions are named as anion<sup>R</sup> and anion<sup>L</sup>, and the corresponding proton affinities are named as PA<sup>R</sup> and PA<sup>L</sup>. PA<sup>aver</sup> = (PA<sup>R</sup> + PA<sup>L</sup>)/2. When both of two protons are removed from the model, the corresponding anions and proton affinity are denoted as anion<sup>-2</sup> and PA<sup>-2</sup>. For triple substitution by three atoms of the same element, the protons H1, H3, and H5 are equally in the model. Therefore, only one kind of proton affinity was obtained.

and I(H2)J(H4), respectively. I and J (I, J = B, Al, Fe) represent the different substitution elements in the model. *Ha* (*a* = 1–6) represents the six possible locations of protonic H atoms at bridging oxygen O3 (see Figure 1). By further introduction of the third substitution atoms into the model (triple substitution), two different structures are obtained when the three substitution atoms are of the same element, denoted as I(H1)I(H3)I(H5) and I(H1)I(H4)I(H5), respectively. Those different structures with the same substitution type are isomers, and the value of the electronic energy could be used as a measure of stability for those isomers. Table 1 lists the possible locations of the proton H atoms at O3 atoms for different substitution types. The italicized locations represent the most stable locations for each substitution type. It was found that the protonic H atoms were always located in different five-membered rings for all the stable isomers of multiple substitutions. Moreover, for a specific substitution type, variation of the substitution element does not change the stable positions of the acidic protons. For example, for double substitution in which two substitution atoms are of the same element, the stable isomers are always I(H1)I(H3) whether I changes from B to Al or Fe. The variation in the electronic energy of different isomers was about 6–12 kcal/mol for double substitution and 4–8 kcal/mol for triple substitution, which implied that a preferential site was expected for locating the protonic H atom. In the following, all calculations were based on these stable isomers.

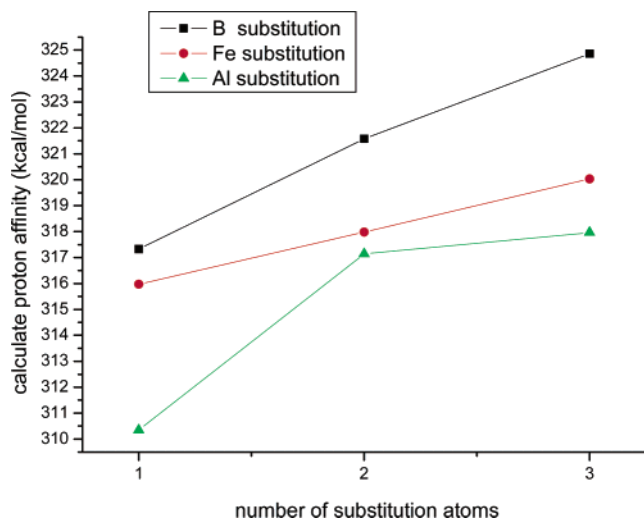
**3.2. Influence of Chemical Composition on the Proton Affinity of the MCM-22 Zeolite.** **3.2.1. Influence of the Species of Substitution Atoms on the Proton Affinity of MCM-22 Zeolite.** First, the effect of the species of substitution atoms on the proton affinity is discussed. Four kinds of substitution types were considered as discussed above, namely, single substitution, double substitution by two atoms of the same element, double substitution by two atoms of different elements, and triple substitution by three atoms of the same element. We discuss

the first, second, and fourth substitution types in this section, and the third substitution type will be discussed in detail in section 3.2.3.

For single substitution, there is only one acidic site per model. The calculated PA for isomorphously MCM-22 zeolites by B, Al, and Fe showed the same sequence as in H-ZSM-5:<sup>7–14</sup> Al-MCM-22 < Fe-MCM-22 < B-MCM-22. The result was consistent with our previous calculation of isomorphously substituted MCM-22 zeolites by B, Al, Ga, and Fe, although the model was smaller than the present one and the center was another most probable substitution site T4.<sup>15</sup> Data of several index properties for characterizing the relative acidity, including proton affinity, bond length and bond angle, OH stretching frequency, and charge on the acidic proton, were all compared in that paper. The sequence of singly substituted MCM-22 zeolites in the present paper was also consistent with the Pauling electronegativities of substitution elements:  $X_{\text{Al}}^{\text{a}}$  (1.61) <  $X_{\text{Fe}}^{\text{a}}$  (1.83) <  $X_{\text{B}}^{\text{a}}$  (2.04).<sup>41</sup>

For double substitution by two atoms of the same element, there are two acidic sites in one cluster model. We calculated the proton affinity per acidic site, and the results are listed in Table 2. The two anions in the stable isomer I(H1)I(H3) (I = B, Al, Fe) were named anion<sup>R</sup> (the proton denoted as H1 was removed from the stable isomer) and anion<sup>L</sup> (the proton denoted as H3 was removed from the stable isomer) with corresponding proton affinities of PA<sup>R</sup> and PA<sup>L</sup>, respectively. From the calculation results, it was found that, for this substitution type, the values of PA<sup>R</sup> were always smaller than those of PA<sup>L</sup>, which reflected the effect of the structure situation of protonic H atoms on the proton affinity of MCM-22 zeolite, and the deprotonation of doubly substituted cluster models should take a two-step process. Each value of PA<sup>R</sup> and PA<sup>L</sup> decreased as Al < Fe < B, respectively. However, such a trend was not necessarily correct when comparing all the data of the proton affinity. The PA<sup>L</sup> of Al-MCM-22 (Al(H1)Al(H3)) was 318.94 kcal/mol,





**Figure 2.** Dependency of proton affinity on the chemical composition of MCM-22 zeolite. When the number of the substitution atoms is 2, the data in the figure show the average proton affinity ( $PA^{\text{aver}} = (PA^{\text{L}} + PA^{\text{R}})/2$ ).

larger than the  $PA^{\text{R}}$  of Fe-MCM-22 (Fe(H1)Fe(H3)), which was 315.72 kcal/mol. It was obvious that the acidity of the zeolite could be more accurately measured by the average proton affinity caused by all substituted atoms. The average proton affinity for both acidic sites was represented as  $PA^{\text{aver}}$  ( $PA^{\text{aver}} = (PA^{\text{L}} + PA^{\text{R}})/2$ ). The calculated  $PA^{\text{aver}}$  order was consistent with not only that of  $PA^{\text{R}}$  and  $PA^{\text{L}}$  but also that of the single substitution.

For the case of triple substitution by three atoms of the same element, there was only one kind of anion in the stable isomers I(H1)I(H3)I(H5) (I = B, Al, Fe) since all three H atoms were equivalent in the isomer. The calculated proton affinities are also presented in Table 2 and show the same order as those of the single substitution and double substitution.

On the basis of the above calculations, it was easy to deduce a conclusion that the proton affinity of substituted MCM-22 decreased in the sequence of B-MCM-22 > Fe-MCM-22 > Al-MCM-22, independent of the number of trivalent substitution atoms (see Figure 2). The models with low PA values were better proton donors, and thus had higher Brønsted acidity. Consequently, the acidity of substituted MCM-22 was predicted to be B-MCM-22 < Fe-MCM-22 < Al-MCM-22, regardless of the number of trivalent substitution atoms. Wu et al.<sup>35</sup> have investigated the Brønsted acidity of the Fe-MCM-22 zeolite by using infrared (IR) spectroscopy and pyridine adsorption, and reported qualitative results indicating a much weaker acidity than that of Al-MCM-22 zeolite. By studying the acidity of Fe- and [Fe,Al]-MCM-22 zeolites, Testa et al.<sup>36</sup> got similar results. Our calculation results were in good agreement with those experimental results.

**3.2.2. Influence of the Number of Substitution Atoms on the Proton Affinity of MCM-22 Zeolite.** In this section, the effect of the number of trivalent substitution atoms (B, Al, Fe) on the proton affinity is considered, and the calculated results are given in Table 2. It was found that the value of  $PA^{\text{L}}$  of double substitution in which two substitution atoms were both Al was larger than that of triple substitution. This was also applicable to the situation when the substitution atoms were both Fe. However, considering the average proton affinities ( $PA^{\text{aver}} = (PA^{\text{L}} + PA^{\text{R}})/2$ ) for double substitution, the behaviors of proton affinities upon changing the number of trivalent substitution atoms were identical for Al, Fe, and B substitution; that is, the

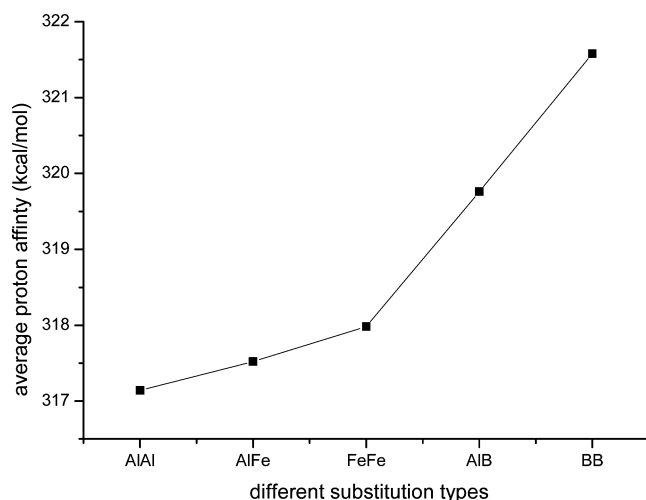
proton affinity of MCM-22 zeolite increased with increasing number of trivalent substitution atoms introduced into the zeolite framework (see Figure 2). When the substitution type was changed from single substitution to triple substitution, the variations in relative proton affinity for Al, Fe, and B were almost the same (about 7.5 kcal/mol). This means that the substitution number had an important effect on the proton affinity of the MCM-22 zeolite. Our calculation results agreed well with the experimental results. Both calorimetric and IR experiments have confirmed that the acid strength of MCM-22 zeolite increased as the Si/Al ratio increased.<sup>34</sup> The results were also in agreement with the theory of Pine and co-workers.<sup>6</sup> According to their theory, the acidic strength decreased as the number of Al atoms occupying the NNN sites increased. However, Teraishi et al.<sup>19,22,25</sup> obtained inconsistent results by calculating the acidity variation on faujasite and mordenite zeolite and reported that the acidity variations upon Si/Al substitution at next-nearest-neighbor (NNN) sites were not unique but were site-dependent. The chosen three sites were of the same T site, namely, the T1 site, and completely equivalent in our model. Thus, the variation in the proton affinity caused by site dependence was canceled and the proton affinity was related only to the number of trivalent substitution atoms in our calculation. Thus, it can be concluded that the acidic strength actually decreased as the number of substitution atoms occupying the NNN sites increased, when all substitution sites were crystallographically identical in the zeolite.

**3.2.3. Influence on the Proton Affinity by the Incorporation of Fe and B Atoms into the Framework of Aluminosilicate MCM-22 Zeolite.** Throughout the above discussion, the substitution atoms were of the same element in each model, despite double or triple substitution. In this section, the variation of proton affinity when Fe and B atoms were incorporated into the framework of aluminosilicate MCM-22 is discussed in detail. According to Table 1, the most stable proton configurations were Al(H1)Fe(H4) and Al(H1)B(H4), respectively. For the configuration of Al(H1)Fe(H4), there are two kinds of acidic sites, namely, Al-O(H)- and Fe-O(H)-. The corresponding anion energies and proton affinities were calculated respectively and are listed in Table 2. From the calculation results, it was found that the difference in proton affinity caused respectively by Al-O(H)- and Fe-O(H)- was rather large. When the proton connecting to the aluminum and oxygen tetrahedron was removed from the stable isomer Al(H1)Fe(H4), the calculated proton affinity ( $PA^{\text{R}}$ ) was 313.74 kcal/mol, smaller than that of double substitution Al-MCM-22 (the  $PA^{\text{R}}$  of Al(H1)Al(H3) was 315.35 kcal/mol). On the other hand, when the proton connecting to the iron and oxygen tetrahedron was removed from the stable isomer Al(H1)Fe(H4), the calculated proton affinity ( $PA^{\text{L}}$ ) was 321.30 kcal/mol, larger than that of double substitution Fe-MCM-22 (the  $PA^{\text{L}}$  of Fe(H1)Fe(H3) was 320.23 kcal/mol). Similar conclusions can be reached if a B atom was introduced into the framework of aluminosilicate MCM-22 zeolite. The calculated proton affinity ( $PA^{\text{R}}$ ) was 311.79 kcal/mol when the proton connecting to the Al and oxygen tetrahedron was removed from the stable isomer Al(H1)B(H4), which was not only smaller than that of double substitution Al-MCM-22, namely, Al(H1)Al(H3), but also smaller than that of Al(H1)Fe(H4). When the proton connecting to the boron and oxygen tetrahedron was removed from the stable isomer Al(H1)B(H4), the calculated proton affinity ( $PA^{\text{L}}$ ) was 327.72 kcal/mol, which was not only larger than that of double substitution B-MCM-22 (the  $PA^{\text{L}}$  of B(H1)B(H3) was 322.55 kcal/mol) but also larger than that of triple substitution

TABLE 3: Calculated Adsorption Energy (kcal/mol) between MCM-22 Zeolite and NH<sub>3</sub> Molecule

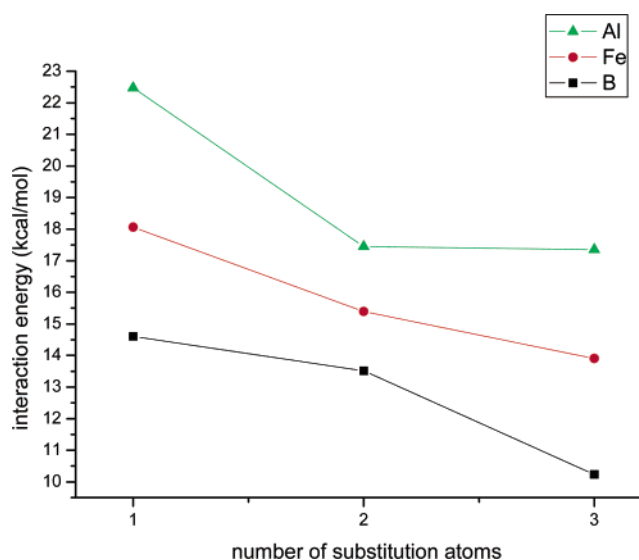
	neutral (hartrees)	neutral-NH <sub>3</sub> (hartrees)	$E_{\text{ads}}$ (kcal/mol)	adsorption structure
Al(H)	-5330.987 684 2	-5387.586 620 9	22.47	ionic
Al(H1)Al(H3)	-5284.514 885 7	-5341.105 804 1	17.44	ionic
Al(H1)Al(H3)Al(H5)	-5238.035 000 1	-5294.625 780 7	17.36	covalent
Fe(H)	-6352.222 426 9	-6408.814 330 3	18.06	ionic
Al(H1)Fe(H4)	-6305.752 549 1	-6362.347 781 5	20.15	ionic
Fe(H1)Fe(H3)	-7326.998 346 2	-7383.585 992 8	15.39	covalent
Fe(H1)Fe(H3)Fe(H5)	-8301.761 458 6	-8358.346 739 2	13.90	covalent
B(H)	-5113.327 283 4	-5169.913 675 0	14.60	covalent
B(H1)Al(H4)	-5066.850 872 9	-5123.445 815 4	19.97	ionic
B(H1)B(H3)	-4849.189 920 0	-4905.774 576 6	13.51	covalent
B(H1)B(H3)B(H5)	-4585.052 919 2	-4641.632 355 2	10.24	covalent

$$^a E_{\text{ads}} = E_{\text{neutral-NH}_3} - E_{\text{neutral}} - E_{\text{NH}_3}$$



**Figure 3.** Variation in average proton affinity ( $PA^{\text{aver}}$ ) for incorporation of Fe and B atoms into the framework of aluminosilicate MCM-22 zeolite. AlAl represents Al(H1)Al(H3); AlFe represents Al(H1)Fe(H4); FeFe represents Fe(H1)Fe(H3); AlB represents Al(H1)B(H4); BB represents B(H1)B(H3).

B-MCM-22 (the proton affinity of B(H1)B(H3)B(H5) was 324.86 kcal/mol). Those results mean that the effect of the inequivalency of the substitution atoms on the electronegativity will cause an unbalanced distribution of the acidity in the corresponding acid sites; i.e., the strong will be further strengthened and the weak will be further weakened. It is well-known that the charge on the proton  $q_H$  has a good relationship with the proton affinity of the acid proton; that is, the increase in the charge of the proton ( $q_H$ ) corresponds to the increase of the ionicity and, thus, to the lower proton affinity and a higher acidity. Comparing the Mulliken charge on the proton ( $q_H$ ), the calculation results reflected the good relation with the proton affinity. Comparing the average proton affinity ( $PA^{\text{aver}}$ ) of the cluster model, the proton affinity decreased in the order B(H1)B(H3) > Al(H1)B(H4) > Fe(H1)Fe(H3) > Al(H1)Fe(H4) > Al(H1)Al(H3); see Figure 3. According to above calculation results, the deprotonation of doubly substituted cluster models actually takes a two-step process; i.e., the proton with stronger acidity will be lost from the models first and then the one with weaker acidity (the corresponding proton affinity was named  $PA^{-2}$ ) will be removed. In doubly substituted cluster models, the value of the second process ( $PA^{-2}$ ) was over 380 kcal/mol in each case, which exceeded the  $PA^{\text{aver}}$  value by almost 17%. However, the data of  $PA^{-2}$  have the same sequence as the  $PA^{\text{aver}}$ . Thus, it was predicted that the acidity of substituted MCM-22 zeolite increased in the order Al-MCM-22 > [Al,Fe]-MCM-22 > Fe-MCM-22 > [Al,B]-MCM-22 > B-MCM-22. These results were in good agreement with the



**Figure 4.** Dependency of NH<sub>3</sub> adsorption energy on the chemical composition of MCM-22 zeolite.

experimental results.<sup>36</sup> Testra et al.<sup>36</sup> has studied the acidity of MCM-22 with different Fe contents introduced into an Al-MCM-22 zeolite. They found that the position of the hydroxyl band shifted to higher wavenumbers with increasing Fe content in the samples.

**3.3. Influence of Chemical Composition on the NH<sub>3</sub> Adsorption Energies of MCM-22 Zeolite.** The calculated NH<sub>3</sub> adsorption energies are listed in Table 3 and shown in Figure 4. For the case with different acidic sites in one cluster model, we calculated only the adsorption on the site with the stronger acidity. It was found that the adsorption energies of the substituted MCM-22 increased in the sequence B-MCM-22 < Fe-MCM-22 < Al-MCM-22, regardless of the number of trivalent substitution atoms. The change in the number of trivalent substitution atoms has also an important effect on the NH<sub>3</sub> adsorption energies, which decreased with increasing number of trivalent substitution atoms (see Figure 4). For the case with two different substitution species in one cluster model (such as Al(H1)Fe(H4) and Al(H1)B(H4)), the calculated NH<sub>3</sub> adsorption energies also reflect the unbalanced distribution of the acidity just as the calculation results of proton affinity in section 3.2.3. The NH<sub>3</sub> adsorption interaction with the Al-OH-acidic site of Al(H1)Fe(H4) was stronger than that of the doubly substituted Al-MCM-22. The NH<sub>3</sub> adsorption interaction with the Al-OH-acidic site of Al(H1)B(H4) got similar results, and it was weaker than that of Al(H1)Fe(H4). Since the cluster models with stronger acidity would have larger NH<sub>3</sub> adsorption energies and smaller proton affinities, the predicted acidity

strength by  $\text{NH}_3$  adsorption was consistent with that by proton affinity.

As shown in Table 3, there are two kinds of equilibrium configuration after  $\text{NH}_3$  adsorption. One is an "ionic" structure ( $\text{Z}^-\cdots\text{NH}_4^+$ ), with a proton transfer from the acidic site of zeolites to  $\text{NH}_3$  molecules. The forming  $\text{NH}_4^+$  is stabilized by two  $\text{N}-\text{H}\cdots\text{O}$  hydrogen bonds. Another is a "covalent" structure ( $\text{ZH}\cdots\text{NH}_3$ ), with the proton still attached to the acidic site of zeolites but having a strong hydrogen bond with an  $\text{NH}_3$  molecule. It was obvious that the cluster models with higher adsorption energies are "ionic" structures ( $\text{Z}^-\cdots\text{NH}_4^+$ ), while the cluster models with lower adsorption energies are "covalent" structures ( $\text{ZH}\cdots\text{NH}_3$ ). Such interactions have been investigated theoretically<sup>14,42–44</sup> and experimentally<sup>45–47</sup> on other zeolites, and our present calculation results on H-MCM-22 zeolite are in line with them.

#### 4. Conclusion

In this work, density functional theory was used to study in detail the influence of chemical composition on the acidity of the isomorphously substituted MCM-22 zeolite by B, Al, and Fe. The effects of the species and the number of trivalent substitution atoms were discussed respectively in detail. It was found that the acidity of MCM-22 zeolite decreased with the increasing number of trivalent substitution atoms introduced into the zeolite framework. Moreover, the acidity of the substituted MCM-22 increased in the sequence  $\text{B-MCM-22} < \text{Fe-MCM-22} < \text{Al-MCM-22}$ , regardless of the number of trivalent substitution atoms. Besides them, it was also found that, if there are two different substitution species in one cluster model (such as  $\text{Al(H1)Fe(H4)}$  and  $\text{Al(H1)B(H4)}$ ), the effect of the inequivalency of the substitution atoms on the electronegativity will cause an unbalanced distribution of the acidity in the corresponding acid sites. All these results were consistent with those from the experiments.

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