

Theoretical studies on the properties of acid site in isomorphously substituted ZSM-5

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Abstract

The structure and electronic properties of the Brønsted acid site in B, Al or Ga isomorphously substituted ZSM-5 zeolites were studied by ab initio HF or DFT methods. The dependence of the calculation results on the employed methods, cluster size and basis sets was examined in details. Several measures for determining of the acidity including the proton affinity, the charge on proton, the hydroxyl group vibrational frequencies, γ_{OH} , as well as the adsorption energy of NH_3 showed that the acidity of the substituted ZSM-5 increases in the sequence: B-ZSM-5 < Ga-ZSM-5 < Al-ZSM-5, which is in good agreement with experimental results. Studies on the interaction of NH_3 with the Brønsted acid site indicated that NH_3 becomes protonated in contact with the zeolite cluster and the configurations in which the protonated NH_3 interacts with two lattice oxygen atoms are favored energetically. In addition, the calculated adsorption energy of NH_3 on Al-ZSM-5 is comparable with the experimental data. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Ab initio; DFT; Isomorphous substitution; ZSM-5; Brønsted acidity

1. Introduction

Zeolites are important microporous inorganic materials which play significant roles as catalysts in oil and chemical industries [1,2]. Many of the catalytic properties of zeolites can be directly related to their Brønsted acidity. The source of the Brønsted acidity in zeolites is the bridging hydroxyl group that arises from the presence of Al replacing Si in their structures. In fact, many other elements such as B, Ga, Fe and Zn, etc. known as heteroatoms can be introduced into the framework of ZSM-5 [3–9] by the replacement of Si atoms. Recently, the catalytic interest of

isomorphously substituted zeolites arises because the heteroatoms help in fine-tuning the strength of the acid sites and in introducing bifunctional features to zeolite catalysts.

The importance of zeolites in many industrial processes has prompted an increasing number of studies both experimental [10–14] and theoretical [15–22] to get insight into the nature of their properties. Many of these studies were focused on predicting the acidity of different zeolites and isomorphously substituted ZSM-5 zeolites. Chu and Chang [12] used IR spectroscopy and TPD- NH_3 to study the acidity of several isomorphously substituted ZSM-5 zeolites. According to both techniques the acid strength increases in the order: Si-(OH) < B-(OH)-Si \ll Fe-(OH)-Si < Ga-(OH)-Si < Al-(OH)-Si. Chatterjee et al. [20] reported local density functional (LDF) calculations

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on isomorphously substituted ZSM-5 clusters with substituents including B, Al, Ga and Fe. The relative acidity of these materials derived from the proton affinity showed a good agreement with the experimental results.

Although a significant number of studies have been done on the properties of the isomorphously substituted zeolites, our understanding of how heteroatoms modify the structure and electronic properties of the acid sites, and therefore, to affect their adsorption and catalytic behaviors is far from complete. In this paper, we report a quantum mechanical study on the properties of the acid sites in B, Al or Ga isomorphously substituted ZSM-5 zeolites. The interaction between the acid site and ammonia is investigated. The calculations are carried out by using both ab initio HF and density functional theory (DFT) methods with different basis sets and different sizes of clusters. The Brønsted acidity is examined by using several measures of acidity including the proton affinity, the charge on the proton, and the hydroxyl group stretching vibrational frequencies, ν_{OH} , as well as the adsorption energy of NH_3 , which show that the acidity of the substituted ZSM-5 increases in the sequence: B-ZSM-5 < Ga-ZSM-5 < Al-ZSM-5, being in good agreement with experimental results. Moreover, studies on the interaction of NH_3 with the Brønsted acid site indicated that NH_3 becomes protonated in contact with the zeolite cluster and the configurations in which the protonated NH_3 interacts with two lattice oxygen atoms are favored energetically.

2. Computational details

2.1. Models

The coordination of the atoms in the zeolite model is taken from the crystal structure of ZSM-5 reported by Koningsveld et al. [23] There are 12 distinct tetrahedral sites in the unit cell of ZSM-5. In this paper, the T_{12} site is selected because it is located at the intersection of the straight and sinusoidal channels which is characteristic of ZSM-5 and allows significant interaction between the bridging hydroxyl and adsorbed molecules and thus being considered as catalytically active sites [24].

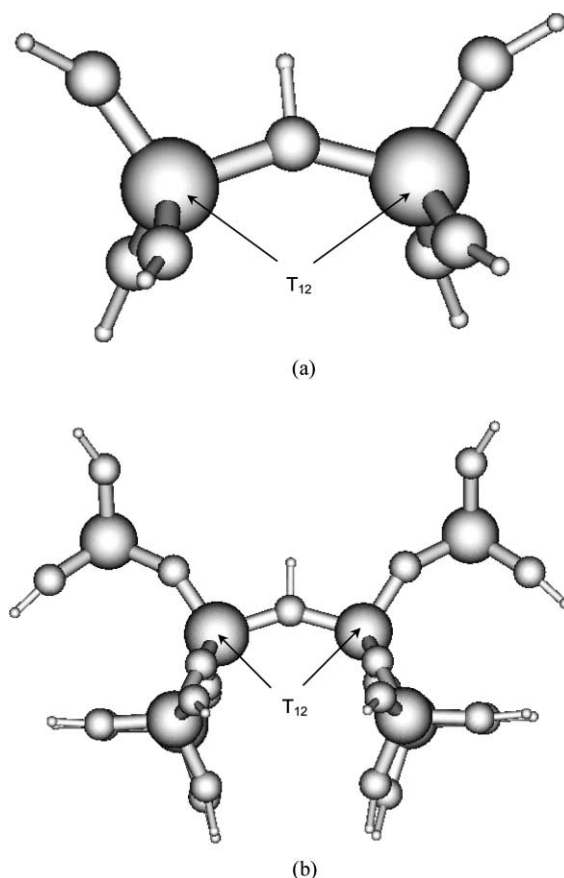


Fig. 1. Cluster models of ZSM-5 centered on O_{24} site with one of the T_{12} site being B, Al or Ga atoms ((a) 2T cluster; (b) 8T cluster).

The models examined here are made up of atoms surrounding the hydroxyl group and later designated as ZOH (or ZO^- when the proton is removed to infinity). To investigate the dependence of calculation results on cluster size, the clusters in form of $(\text{OH})_3\text{Si}-\text{O}(\text{H})-\text{T}(\text{OH})_3$ as shown in Fig. 1a, and later noted as 2T, are firstly considered, where T is B, Al or Ga atoms, respectively. Then the second shell of silicon atoms and the third shell of oxygen atoms are included, leading to clusters with the form $((\text{OH})_3\text{SiO})_3-\text{Si}-\text{O}(\text{H})-\text{T}((\text{OH})_3\text{SiO})_3$ and later noted as 8T (see Fig. 1b). In all the clusters, each peripheral oxygen atom is saturated with a hydrogen atom. The terminal hydrogen atoms are located at a O–H distance of 0.1 nm from the corresponding

oxygen, oriented along the bond direction to what would otherwise have been the next silicon atom.

2.2. Methods

All the calculations in this study are performed by using Gaussian 98 program [25]. Both *ab initio* HF and DFT methods are used to predict the acidity of the substituted ZSM-5 clusters. The B3LYP hybrid method is used to all the DFT calculations.

Geometry optimization is important in quantum chemical cluster calculations to obtain reliable results. However, Sauer [26] pointed out that the full optimization of the clusters might lead to structures that do not resemble experimental zeolite geometry. Thus the structures of all the clusters representing ZSM-5 framework in this study are partially optimized with the inner atoms of $O_3Si-O(H)-TO_3$ relaxed while the other atoms anchored to their ZSM-5 positions. This allows the atoms in the vicinity of the acid site and

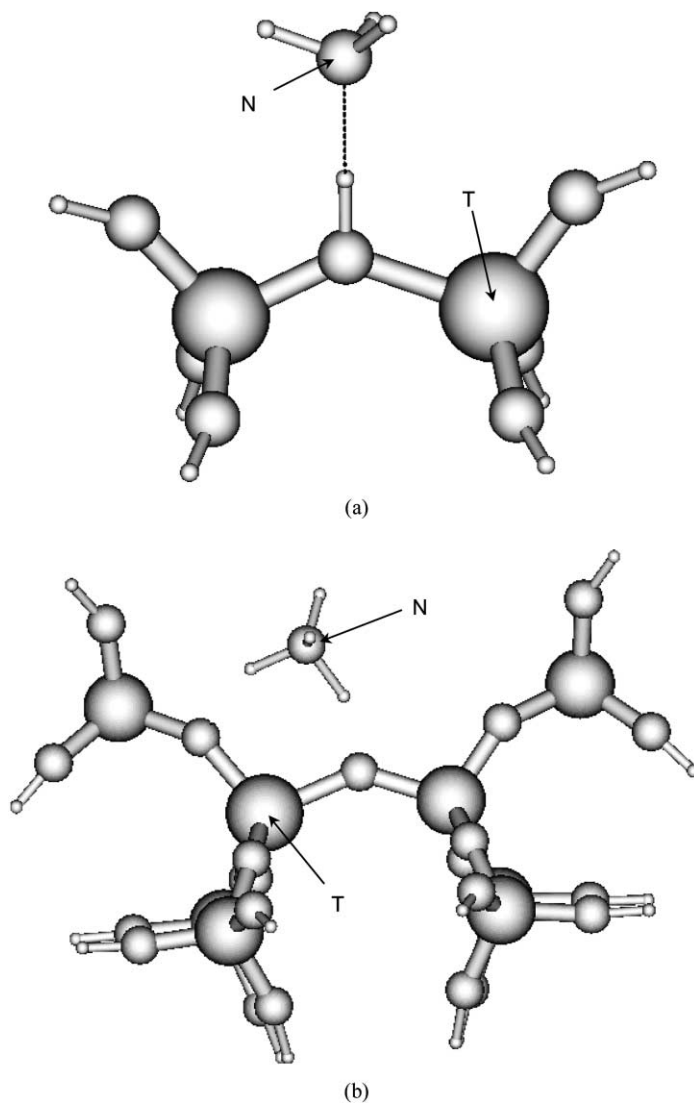


Fig. 2. Initial configurations of NH_3-ZOH clusters (with T, where T = B, Al or Ga, respectively, and N atom in NH_3 molecule designated: (a) 2T cluster; (b) 8T cluster).

the substituted atom to relax, while the cluster retains its position in the zeolite lattice.

Calculations on the interaction between the Brønsted acid site in substituted ZSM-5 and NH_3 molecule are firstly carried out by using 2T clusters. The initial structure of $\text{NH}_3\text{-ZOH}$ based on 2T clusters, as shown in Fig. 2a, is built up by combining the configuration of the partially optimized geometry of ZOH cluster with the fully optimized geometry of NH_3 molecule. The distance between the central bridging oxygen atom of the zeolite model and the nitrogen atom of NH_3 molecule, $r_{\text{N-O}}$, is set to 0.25 nm [27]. The geometry of $\text{NH}_3\text{-ZOH}$ based on

2T clusters are partially optimized at B3LYP/6-31G* level with TO(H)Si and NH_3 allowed to relax. The optimized structure parameters associated with NH_3 and the Brønsted acid proton obtained from 2T clusters are then used to set the initial configurations of NH_3 with 8T (see Fig. 2b). And then the geometry of $\text{NH}_3\text{-ZOH}$ based on 8T clusters are optimized at B3LYP/3-21G level, again with the TO(H)Si and NH_3 part allowed to relax. Fig. 3 shows the optimized geometry of $\text{NH}_3\text{-ZOH}$ based on 2T and 8T clusters. The vibration frequency calculations are carried out on clusters directly obtained from the optimization calculations.

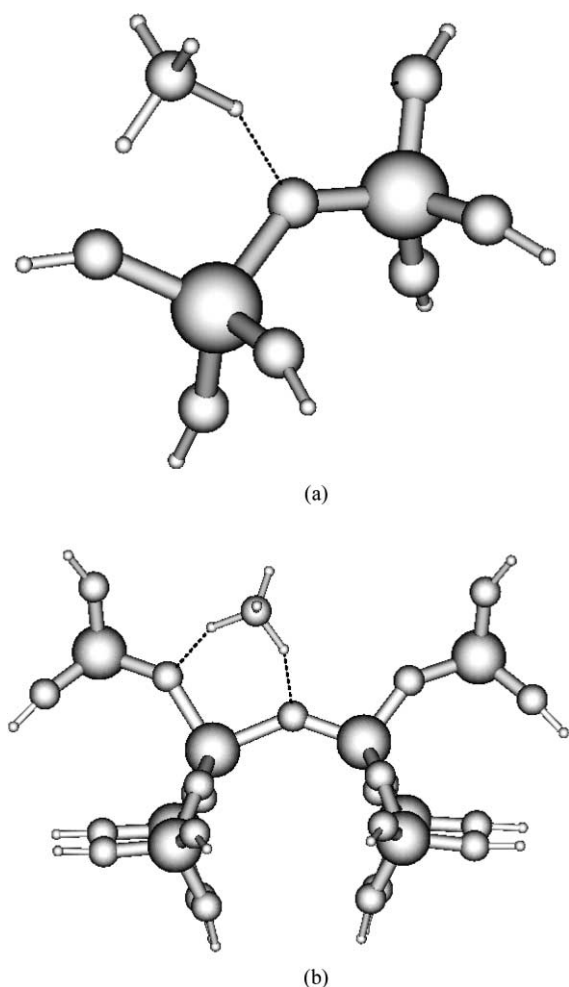


Fig. 3. Equilibrium configurations of $\text{NH}_3\text{-ZOH}$ clusters ((a) 2T cluster; (b) 8T cluster).

3. Results and discussion

3.1. Proton affinity of the substituted ZSM-5 clusters

Proton affinity (PA) can be served as a measure of the acid strength of zeolite Brønsted sites. Indeed, direct experiments of the PA are not feasible. However, the data can be easily obtained from quantum mechanical calculations in which PA is considered as the energy required to remove the acidic proton from the zeolite structure, and is calculated by

$$\text{PA} = E_{\text{ZO}^-} - E_{\text{ZOH}}$$

where E_{ZO^-} and E_{ZOH} are the energies of the deprotonated and the neutral clusters, respectively [28]. It is obvious that the larger the PA, the weaker the acidity of the bridged hydroxyl group.

Table 1 shows the PA data calculated from 2T clusters at B3LYP/6-31G* level, which predict the trend of the acid strength as: B-ZSM-5 \ll Al-ZSM-5 < Ga-ZSM-5, being not in agreement with experimental sequence. For comparison, the energy of the clusters and their PA values calculated at HF/6-31G* level are also presented in Table 1. It is indicated that ab initio HF method can give the same qualitative results as DFT method with the same basis set.

To investigate the dependence of the calculation on the basis sets, calculations with B3LYP/6-31G** and B3LYP/6-31 + G** are carried out. The results are presented in Table 2, which indicate that PA values calculated with the different basis sets predict the same erroneous ordering of acidity.

Table 1

PA calculated on 2T clusters by DFT and HF methods with 6-31G* basis set

| T | B3LYP/6-31G* | | | HF/6-31G* | | |
|----|------------------|-------------------|---------------|------------------|-------------------|---------------|
| | E_{ZOH} (a.u.) | E_{ZO^-} (a.u.) | PA (kcal/mol) | E_{ZOH} (a.u.) | E_{ZO^-} (a.u.) | PA (kcal/mol) |
| Al | -1062.96690 | -1062.44351 | 328.4 | -1059.22323 | -1058.69619 | 330.7 |
| Ga | -2743.36489 | -2742.84398 | 326.9 | -2738.46280 | -2737.93842 | 329.0 |
| B | -845.27302 | -844.72349 | 344.8 | -841.88409 | -841.33118 | 347.0 |

Table 2

PA and γ_{OH} calculated on 2T clusters by DFT method with different basis sets

| T | PA (kcal/mol) | | | γ_{OH} (cm ⁻¹) | | |
|----|---------------|---------|------------|-----------------------------------|---------|------------|
| | 6-31G* | 6-31G** | 6-31 + G** | 6-31G* | 6-31G** | 6-31 + G** |
| Al | 328.4 | 332.0 | 318.4 | 3732 | 3805 | 3778 |
| Ga | 326.9 | 330.8 | 317.8 | 3744 | 3815 | 3792 |
| B | 344.8 | 348.4 | 332.5 | 3742 | 3813 | 3783 |

As experimental results cannot be reproduced with the 2T model, calculations with 8T models have been performed to examine the cluster size effect on PA values. Since 8T clusters are so large that it might be too time consuming to calculate with large basis set, the split-valence 3-21G basis set are firstly considered. The data obtained from ab initio HF and DFT methods with the 3-21G basis set are given in Table 3.

Again the two methods give the same trends of acid strength, which shows an agreement with that from 2T clusters but is not consistent with the experimental results. As a consequence, calculations by B3LYP method with polarized basis set 6-31G* are then carried out. The results (also see Table 3) show that 6-31G* basis set can give reasonable results of the relative acidity derived from PA, which reproduce the

experimental trend [12]: B-ZSM-5 \ll Ga-ZSM-5 < Al-ZSM-5.

It is also shown by the PA data presented in Tables 1 and 2 that PA are almost uniformly shifted when different methods (see Table 1) or different basis sets (see Table 2) are employed. In addition, although the PA calculated on 2T clusters by the two methods predict the same erroneous ordering of acidity, Al-ZSM-5 < Ga-ZSM-5, the difference of PA between Al-ZSM-5 and Ga-ZSM-5 is reduced when DFT/B3LYP method is used as compared to HF method, indicating that DFT/B3LYP method can give better results. Also, for the three basis sets employed, the PA difference between Al-ZSM-5 and Ga-ZSM-5 obtained from 6-31 + G** is smaller than that from 6-31G** which is in turn smaller than

Table 3

PA calculated on 8T clusters by different methods

| Methods | Energies | Al | Ga | B |
|--------------|-------------------|-------------|-------------|-------------|
| HF/3-21G | E_{ZOH} (a.u.) | -4126.40476 | -5799.62558 | -3910.24715 |
| | E_{ZO^-} (a.u.) | -4125.85829 | -5799.08026 | -3909.67053 |
| | PA (kcal/mol) | 342.9 | 342.2 | 361.8 |
| B3LYP/3-21G | E_{ZOH} (a.u.) | -4139.78806 | -5814.10995 | -3923.29674 |
| | E_{ZO^-} (a.u.) | -4139.24571 | -5813.56834 | -3922.72871 |
| | PA (kcal/mol) | 340.3 | 339.9 | 356.4 |
| B3LYP/6-31G* | E_{ZOH} (a.u.) | -4162.09552 | -5842.50937 | -3944.42495 |
| | E_{ZO^-} (a.u.) | -4161.57690 | -5841.98868 | -3943.88301 |
| | PA (kcal/mol) | 325.4 | 326.7 | 340.1 |

that from 6-31G*, indicating that the basis set which adds polarization and diffuse functions to the hydrogen can give better results for the studies in relation to the binding energy of proton.

From the previous discussion, it can be indicated that: (i) the acid site in the substituted ZSM-5 framework can be well simulated by 8T clusters; (ii) the polarized 6-31G* basis set is adequate in predicting the relative acidity based on the proton affinity of the clusters; and (iii) ab initio HF and DFT methods based on the first principle of quantum chemistry with the same basis sets can give the same qualitatively results, but DFT is better than HF methods.

3.2. Structure and electronic properties of the acid site

The selected bond lengths and angles for the equilibrium structures of 8T clusters are presented in Table 4. It can be seen that for B, Al or Ga-ZSM-5 framework, d_{T-O} and d_{T-H} , the bond length between the substituted atom and the bridged oxygen and the charge compensating proton, increase with the increase of the radius of T ions. The distance between Si and the bridged oxygen atom, d_{Si-O} , is lengthened as compared to the Si-O bond distance in ZSM-5 framework while the angle between the T-O and the O-Si bonds (O is the bridged oxygen atom shared by these two bonds), α_{T-O-Si} , decreases as compared to the original $\alpha_{Si-O-Si}$ (146.2°) in ZSM-5 framework. It can be also found that d_{Al-H} , the distance between Al and the proton in Al-ZSM-5 cluster (0.2387 nm) is in good agreement with the NMR measurement of 0.238 ± 0.004 nm [29].

The Mulliken charges associated with T, O and H atoms, where T = B, Al or Ga, obtained from 8T

clusters are listed in Table 4. It is shown that q_T , the charge on T atom, increases with the decrease of its electronegativity. The charge on the bridged oxygen atom, q_O , increases with the increase of q_T , leading to the increase of the charge on the proton (q_H) attached to it. Brønsted acidity, which is principally a measure of the ease at which an O-H bond dissociates heterolytically, can be well characterized by the charge on the proton [30]. The increase of the charge on the proton corresponds to the increase of the ionicity, and thus, to the increase of the acidity. Therefore, it can be stated from the q_H data that the acid strength of the substituted ZSM-5 clusters increases in the order: B-ZSM-5 \ll Ga-ZSM-5 < Al-ZSM-5, which is consistent with the order indicated by the proton affinity. It can be also seen from $|q_H q_O|$ that ionicity, another reliable measurement of acidity [31], increases with the same order: B-ZSM-5 \ll Ga-ZSM-5 < Al-ZSM-5.

The selected structure and electronic parameters listed in Table 4 are in good agreement with those obtained by Gonzales et al [19].

3.3. OH stretching frequency

It has been generally accepted that the stretching frequency of the OH bond, γ_{OH} , can be taken as an indicator of Brønsted acidity [30], i.e. lower wavenumber of γ_{OH} is related to weaker O-H bond strength and hence corresponds to stronger acid strength. Considering vibration frequencies are determined by short-range covalent effect [32], frequency analysis calculations on partially optimized 2T clusters are carried out. The calculations are performed directly after the geometry optimization by B3LYP method with three basis sets: 6-31G*, 6-31G** and 6-31 + G**. The positions of γ_{OH} are given in

Table 4

The selected structure parameters and Mulliken atomic charges on substituted 8T clusters^a

| T | d_{O-H} | d_{T-H} | d_{T-O} | d_{Si-O} | α_{T-O-Si} | Mulliken atomic charges | | | |
|-----------------|-----------|-----------|-----------|------------|-------------------|-------------------------|---------|--------|-------------|
| | | | | | | q_T | q_O | q_H | $ q_H q_O $ |
| Al | 0.0977 | 0.2387 | 0.1922 | 0.1704 | 141.5 | 1.6211 | -0.9883 | 0.5077 | 0.5018 |
| Al ^b | 0.0975 | 0.236 | 0.1807 | 0.1692 | 134.6 | 1.710 | -0.990 | 0.490 | 0.485 |
| Ga | 0.0976 | 0.2463 | 0.1995 | 0.1700 | 139.5 | 1.5055 | -0.9725 | 0.5052 | 0.4913 |
| B | 0.0976 | 0.2104 | 0.1664 | 0.1695 | 142.8 | 1.4545 | -0.9435 | 0.4900 | 0.4623 |

^a Bond lengths are in nanometer and bond angles in degree.

^b Data in this line are taken from [19].

Table 5
 γ_{OH} calculated on 8T clusters at HF/3-21G level

| | T | | |
|---|------|------|------|
| | Al | Ga | B |
| γ_{OH} (cm ⁻¹) | 3816 | 3825 | 3830 |
| γ_{OH} from IR [12] (cm ⁻¹) | 3610 | 3620 | 3725 |

Table 2. The data calculated with 6-31G* basis set should be scaled by 0.9614 as recommended by Scott et al. [33]. To be consistent with the scaled B₃LYP/6-31G* frequency, the 6-31G** and 6-31 + G** frequencies must be scaled by 0.950 and 0.956, respectively [34]. It is shown that the three basis sets give the same qualitative results. That is, the acid strength increases in the order: Ga-ZSM-5 < B-ZSM-5 < Al-ZSM-5, which is not in agreement with the experimental trend and is also inconsistent with the order derived from PA. Thus it can be stated that 2T clusters cannot meet the current requirement of calculations, and 8T clusters are then used. Calculations on 8T clusters are performed by ab initio HF method with 3-21G basis set. The study by Brand et al. [34] showed that calculations at this level could give reliable frequencies compared to those of IR spectroscopy. The calculated positions of γ_{OH} from 8T clusters are listed in Table 5. To compare the HF/3-21G frequencies with experimental values, the data listed in Table 5 should be scaled by 0.947 [34]. Table 5 also presents the γ_{OH} data obtained from IR spectroscopy [12]. It is shown that the increase in the acid strength as noted by a decrease in γ_{OH} is in the order: B-ZSM-5 < Ga-ZSM-5 < Al-ZSM-5, being in qualitatively agreement with the experiment.

3.4. Interaction with NH₃

Table 6 shows the energy of the adsorption of NH₃ on the acid site of the substituted ZSM-5 zeolites calculated from the two series of clusters. The energy of adsorption (ΔE_{ads}) is defined as the energy change of the desorption reaction [27]

$$\Delta E_{\text{ads}} = E_{\text{ZOH}} + E_{\text{NH}_3} - E_{\text{NH}_3\text{-ZOH}}$$

where the species NH₃-ZOH corresponds to the partially optimized NH₃-ZOH cluster, ZOH and NH₃ respectively correspond to the isolated partially optimized ZOH clusters and the fully optimized NH₃ molecule. It is obvious that the sites with stronger acidity would have larger adsorption energy.

It is shown that the relative acidity predicted by adsorption energy of NH₃ is consistent with that derived from PA in the previous part of this paper. That is, for 2T clusters the acid strength increases in the serial: B-ZSM-5 \ll Al-ZSM-5 < Ga-ZSM-5, while for 8T clusters, it increases in the order: B-ZSM-5 \ll Ga-ZSM-5 < Al-ZSM-5. Obviously, calculations on 8T clusters give reliable results. Moreover, the adsorption energies calculated with 3-21G are larger than those with 6-31G* basis set, which is in line with the well-known overestimation of hydrogen bonding predicted at the smaller basis set. In addition, the calculated adsorption energies of NH₃ on Al-ZSM-5 (30.3 kcal/mol for 2T cluster at B₃LYP/6-31G* level and 50.7 kcal/mol for 8T cluster at B₃LYP/3-21G level) are comparable with the experimental results. Parillo and coworkers [35,36] reported 33.5–35.6 kcal/mol for the heat of NH₃ adsorption on H-ZSM-5 zeolites measured by microcalorimetry experiments. Moreover, NH₃-TPD experiments performed by Topsoe

Table 6
 Adsorption energy of NH₃ on the acid sites in the substituted ZSM-5 based on two series of clusters^a

| T | 2T (B ₃ LYP/6-31G*) | | | 8T (B ₃ LYP/3-21G) | | |
|----|-------------------------------------|-------------------------|------------------------------------|-------------------------------------|-------------------------|------------------------------------|
| | $E_{\text{NH}_3\text{-ZOH}}$ (a.u.) | E_{ZOH} (a.u.) | ΔE_{ads} (kcal/mol) | $E_{\text{NH}_3\text{-ZOH}}$ (a.u.) | E_{ZOH} (a.u.) | ΔE_{ads} (kcal/mol) |
| Al | -1119.56320 | -1062.96690 | 30.3 | -4196.09796 | -4139.78806 | 50.7 |
| Ga | -2799.96455 | -2743.36489 | 32.4 | -5870.41874 | -5814.10995 | 50.0 |
| B | -901.85599 | -845.27302 | 22.0 | -3979.59118 | -3923.29674 | 41.0 |

^a E_{NH_3} (B₃LYP/6-31G*) = -56.54795 a.u., E_{NH_3} (B₃LYP/3-21G) = -56.22913 a.u.

et al. [11] gave the heat of adsorption of NH_3 as 38.8 kcal/mol.

It can be indicated by the equilibrium geometry of the $\text{NH}_3\text{-ZOH}$ clusters (see Fig. 3) that NH_3 become protonated in contact with the zeolite cluster models, and the configurations in which the protonated NH_3 molecule interacts with two lattice oxygen atoms are favored energetically, which has been predicted by Teunissen et al. [37] by using ab initio studies on the NH_3 adsorption.

4. Conclusion

The present calculations of several measures of acidity including the proton affinity, the charge on the proton, the hydroxyl group vibration frequencies, γ_{OH} , and the adsorption energy of NH_3 predict the increase of the Brønsted acidity in the order: $\text{B-ZSM-5} \ll \text{Ga-ZSM-5} < \text{Al-ZSM-5}$, which shows a good agreement with experiment. The study of the interaction of the Brønsted acid site with NH_3 indicated that NH_3 becomes protonated when contact with the zeolite cluster, and the configurations in which the adsorbed NH_3 molecule interacts with two lattice oxygen atoms are favored energetically. Moreover, the calculated adsorption energies of NH_3 on Al-ZSM-5 are comparable with the experimental results.

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