

## Effect of NNN Site Si/Al Substitution on the Acid Strength: Mordeinite

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The acidity variations upon Si/Al substitution at NNN sites were calculated for mordenite by the *ab initio* molecular orbital method. The conclusions obtained from our previous work on faujasite hold with mordenite, e.g., the effects of Si/Al substitution at NNN sites on the acid strength are not uniform. Mordenite was synthesized with various Si/Al ratios and the acidic properties were examined by means of ammonia adsorption calorimetry. The analysis of the experimental results based on the binomial distribution of Al indicates that not only 0NNN sites but some of 1NNN, 2NNN, etc. should also be strong acid sites, which is consistent with the calculation.

### Introduction

The activity of the zeolite as the cracking catalysts depends on its acidic properties.<sup>1</sup> It is well-known that the acidity of the zeolite is influenced by the Si/Al ratio of which it is composed.<sup>2–5</sup> Pine et al.<sup>6</sup> explained this phenomenon using the next-nearest-neighbor (NNN) model. In zeolite, one Al cannot be connected directly to another Al through an oxygen (Lowenstein's law); i.e., the nearest-neighbor tetrahedral sites (T sites: Si or Al) are all Si. Thus, the closest Al's are at NNN sites. According to their theory, the acidic strength decreases as the number of Al occupying the NNN sites increases. Therefore, as the Al content becomes higher, although the total number of acid sites increases, the number of strong acid sites decreases.

Computational simulations have become powerful tools to analyze the target from the atomic level and have been applied to the zeolite studies.<sup>7</sup> In our previous work,<sup>8</sup> we reported the effect of Si/Al substitution at NNN site on the acid strength in the case of faujasite type zeolite. It was studied by means of *ab initio* molecular orbital calculations and led to the following conclusions.

1. The effects of Si/Al substitution at NNN sites on the acid strength are not uniform.
2. The variations of the acid strength are due to the electrostatic effect rather than electronic.
3. The proton affinity and the heat of ammonia adsorption are not equivalent as the evaluation of the acidic strength.

Mordenite is also often used as catalyst. It has one-dimensional 12-ring channel and shows higher acidity and catalytic activity than Y (faujasite) type.<sup>9</sup> It is easily synthesized with broad range of Si/Al ratio, particularly high silica zeolite, contrary to the Y type which is difficult to synthesize with high Si/Al ratio without losing crystallinity.

Parrillo et al.<sup>5</sup> reported that high silica zeolites where the acid sites are isolated have the same Brønsted acidity regardless of their types. Stach et al.,<sup>4</sup> on the other hand, found that the heat of ammonia adsorption on mordenite is substantially different from the one on Y. The effect of the structure on the acid strength is still controversial.

In this study we applied the same computational procedure as was conducted in the previous work<sup>8</sup> to mordenite in order to evaluate its acidity. The results revealed that the conclusions

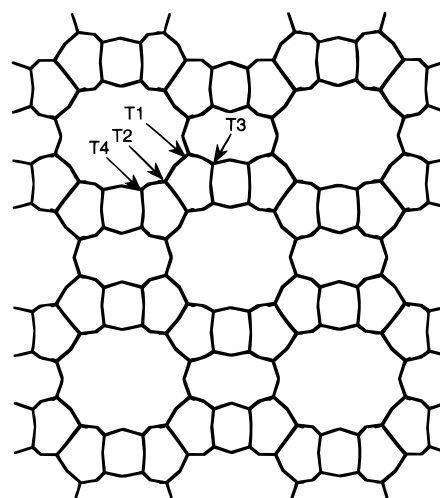


Figure 1. Crystal structure of mordenite and four unequivalent T sites.

drawn from the previous work with faujasite hold with mordenite; i.e., the effects of Si/Al substitution at NNN sites on the acid strength are not uniform and depend on the substitution sites, and the acidity was even strengthened upon Si to Al substitution at some sites.

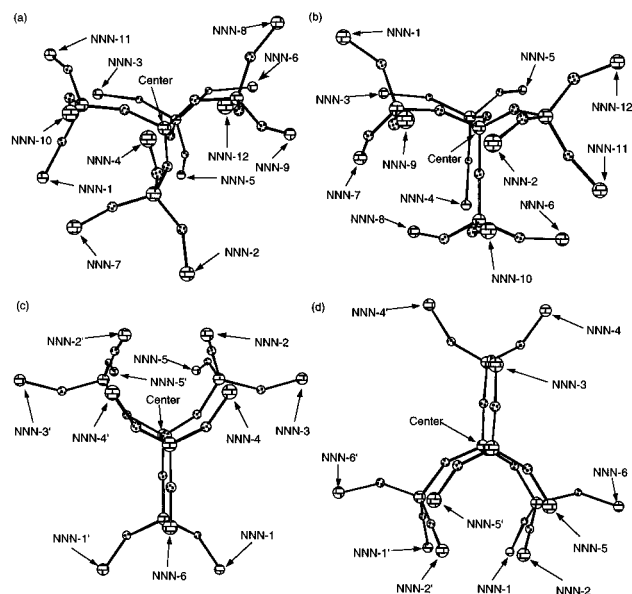
We also synthesized mordenite with various Si/Al ratio and measured the acidity by means of ammonia adsorption calorimetry. The analysis of the experimental results based on the binomial distribution of Al indicates that not only 0NNN sites, where all NNN sites are occupied by Si, but some of 1NNN (only one NNN site is occupied by Al) should also be strong acid sites, which is consistent with the calculated result. Furthermore, from the low Si/Al result, some of 2NNN (two NNN sites are occupied by Al) etc. are also indicated to be strong acids.

### Calculation

Faujasite has only one symmetrically unique T site (all other T sites can be generated by symmetry operations), while mordenite has four unequivalent ones (Figure 1). For faujasite, since all the T sites are equivalent, when one chooses a certain T site as a center, there are always nine NNN sites. For mordenite, however, there are 12 NNN sites when T1 or T2 is center, and all 12 are unequivalent. When T3 or T4 is center, there are 11 NNN sites, of which five pairs are symmetrically

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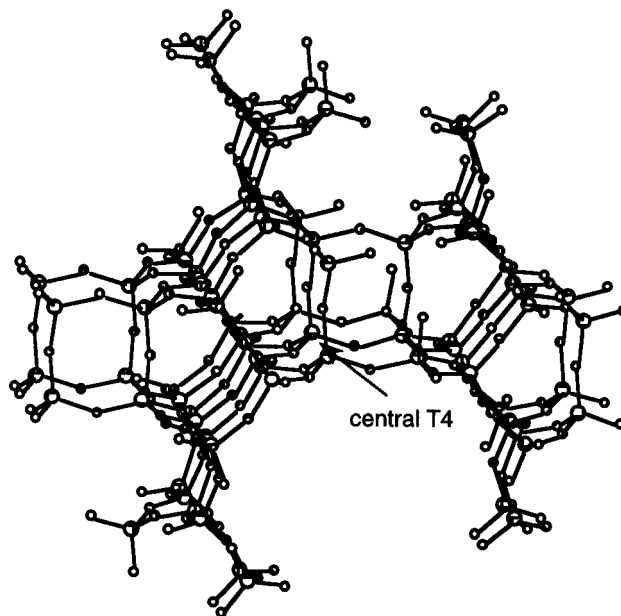
**Figure 2.** Next-nearest-neighbor (NNN) sites when T1 (a), T2 (b), T3 (c), and T4 (d) are taken as a center, respectively.

related, and hence there are six unequivalent NNN sites (Figure 2). Here, each atom present at 36 NNN sites was changed from Si to Al one by one and the variation of the acidic strength was calculated. Following the previous work,<sup>8</sup> we employed two models, a small one and a large one. Here, the framework atoms are all fixed at the crystal structure (rigid model) and only hydroxyl proton and ammonia are relaxed because a full geometry relaxation of these small clusters leads to a structure which is very different from zeolite. Note that the aim of this study is to shed the light on the relative acid strength between 0NNN and 1NNN with regard to a particular center which would not be much influenced by the structural constraints since the effect is expected to be of the same magnitude for both cases and thus will be canceled out when the difference is taken.

**Large Model.** This model includes all NNN sites, which are terminated by  $\text{OSi}(\text{OSiH}_3)_3$ . Taking one T site as a center, up to the ninth atoms from it along the bond were taken. Among the outermost atoms (oxygen), those which were not involved in the bridging of two T sites, i.e., connected to only one T site, were replaced by hydrogen. Placing Si on every T site, the lengths of the terminal Si–H were optimized while all other structural parameters were fixed. Figure 3 shows the large model of T4 center. After this, the bond lengths of the terminal Si–H were also frozen.

For the 0NNN model, where only the center is Al and all NNN sites as well as other T sites are Si, a proton was placed at one of four oxygen bonded to the central Al, and only this proton was optimized while zeolite framework and terminal H were fixed. The most stable conformation was obtained by comparing the energies of four hydroxyl positions. Similarly, for 1NNN model, where the center and only one NNN are Al while other T sites are Si, two protons were placed at one of four oxygens bonded to the center and to the NNN site associated with Al, respectively. Only these two protons were optimized and the most stable conformation was chosen from the 16 combinations.

**Small Model.** For 36 1NNN models with the most favorable proton conformation obtained above, the smallest parts which include two Al's and hydroxyl bridge (Al–OH–Si) were taken. Basically the Al's and Si's were terminated by OH. The terminal H were placed along the O–Si bond, with the OH distance of 0.946 Å. But if the replacement of Si by H causes

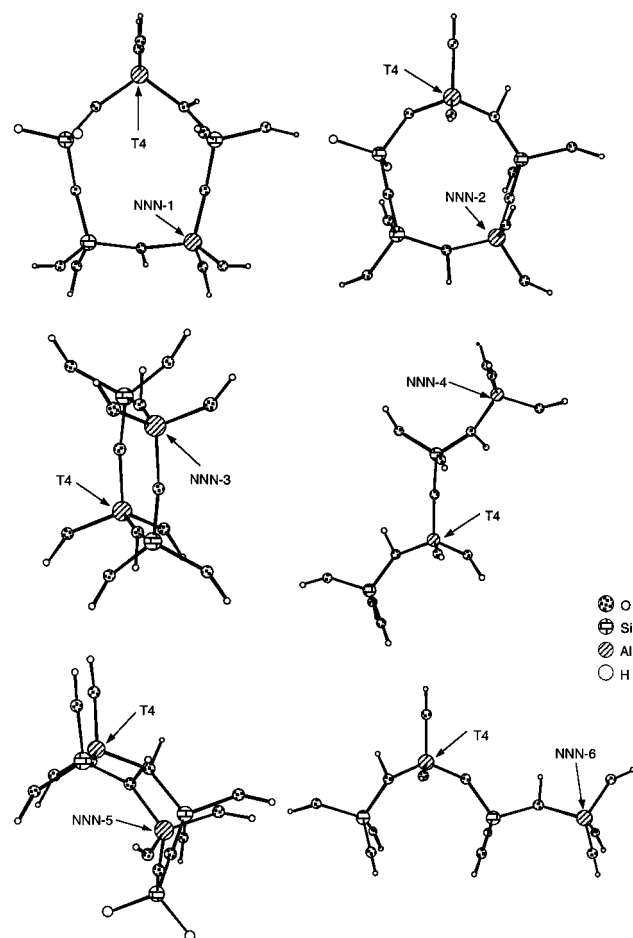


**Figure 3.** A large model when T4 is taken as a center. The same model is used for 0NNN and all 1NNN except for the substitution site.

the collision of atoms within the van der Waals radii, Si was not replaced but was left and terminated by H (Si–H = 1.474 Å). These structures are small 1NNN models and from each of them a small 0NNN model was derived by replacing Al at the NNN site by Si and removing the associated hydroxyl proton. Figure 4 shows the six small 1NNN models with T4 center.

Proton affinity (PA) of the conjugate base  $\text{Z-O}^-$  was calculated as a energy difference between the protonated and unprotonated (ionic) states with regard to the central acid (hydroxyl) site:  $\text{PA} = E(\text{Z-O}^-) - E(\text{Z-OH})$ . In this calculation, only the hydroxyl protons were optimized while the zeolite framework and terminal H were fixed. For the sake of the direct comparison with the experimental values, the heat of ammonia adsorption (HOA) was also calculated as the energy difference before and after the adsorption of ammonia:  $\text{HOA} = E(\text{Z-OH}) + E(\text{NH}_3) - E(\text{Z-OH} \cdots \text{NH}_3)$ . The initial structure of the adsorbed ammonia was chosen so that the symmetry axis of ammonia points to the central hydroxyl proton (N–H = 1.7 Å). Again all the framework was fixed and only hydroxyl protons and ammonia were optimized. Here we did not impose any constraints on the proton transfer between zeolite and ammonia and the adsorption structure was obtained as the lowest energy state from the geometry optimization without distinguishing the physisorption and chemisorption. The ammonium ion affinity (AA) was calculated as the energy difference before and after the adsorption of ammonium ion:  $\text{AA} = E(\text{Z-O}^-) + E(\text{NH}_4^+) - E(\text{Z-OH} \cdots \text{NH}_3)$ . The ammonium ion adsorbed state is actually the same as the ammonia adsorbed state, because we are not partial to either the adsorption as ammonia or as ammonium ion.

All the calculations with the large models, i.e., to find the most stable proton conformation and to calculate the proton affinity, were performed by AM1 semiempirical method. For the proton affinity and the ammonia adsorption calculations using the small models, the geometry optimization was performed at ab initio RHF/3-21G and the energy, atomic charge, and bond order were calculated at RHF/6-31G\* level. Our choice of the calculation method is based on the preliminary tests with a small model, which revealed that the trend of the proton affinity can be reproduced by AM1 method with



**Figure 4.** Small models when T4 is taken as a center. Figures shown here are 1NNN, and Al at NNN site of each model was replaced by Si to yield the respective 0NNN models.

acceptable accuracy, being consistent with Ozment's report.<sup>10</sup> But once the hydrogen bond is involved, semiempirical methods are not reliable, and one must go to ab initio methods. The inclusion of the electron correlation changes the absolute values but does not affect the relative values significantly due to the cancellation. MOPAC93<sup>11</sup> was used for semiempirical calculations and Gaussian92<sup>12</sup> for the ab initio methods.

## Experimental Section

Five samples were prepared by the following procedures: a given weight of aluminum sulfate, H<sub>2</sub>SO<sub>4</sub>, and NaCl was dissolved into distilled water and the appropriate amount of sodium silicate was added subsequently. The mixture was aged for 1 h at room temperature and then heated at 180 °C for 20 h in an autoclave. After filtration and water washing, the solid product was dried at 110 °C. At this stage, the product was confirmed to possess the structure of mordenite by XRD. In order to obtain the acidic form, ion exchanges were performed 5 times with 5% NH<sub>4</sub>Cl solution for 1.5 h at 70 °C. After water washing, the product was dried at 110 °C and calcined at 600 °C for 3 h. Chemical analysis revealed that the Si/Al ratio of the samples are 4.6, 7.6, 10.5, 12.3, and 20.7, respectively. The acidic properties, i.e., the acid site population and the acid strength, of these samples were determined by the calorimetric measurements of ammonia adsorption at 300 K and using Multi Micro Calorimeter MMC-5111 (Tokyou Riko).

## Results

The differences of the proton affinity, heat of ammonia adsorption, and ammonium ion affinity between 0NNN and

**TABLE 1: Proton Affinity, Heat of Ammonia Adsorption, and Ammonium Ion Affinity When T1 Is Center<sup>a</sup>**

	1NNN-1	1NNN-2	1NNN-3	1NNN-4	1NNN-5	1NNN-6
PA-L	7.5	-41.3	34.0	-2.3	-39.9	-26.8
PA-S	13.9	-59.6	52.3	1.9	-57.9	-36.4
HOA	11.3	17.6	-22.2	46.0	2.9	-28.5
AA	25.2	-42.0	30.1	47.9	-55.0	-64.9

	1NNN-7	1NNN-8	1NNN-9	1NNN-10	1NNN-11	1NNN-12
PA-L	26.3	27.9	34.8	-4.5	-17.2	3.9
PA-S	42.5	57.6	51.5	-3.0	-19.2	7.9
HOA	-31.4	-33	-21.1	-6.7	0.2	-48.8
AA	11.1	24.6	30.4	-9.7	-19.0	-40.9

<sup>a</sup> PA-L: proton affinity calculated with the large models. PA-S: proton affinity calculated with the small models. HOA: heat of ammonia adsorption calculated with the small models. AA: ammonium ion affinity calculated with the small models. Data are differences between 0NNN and 1NNN in kJ/mol: e.g. PA(1NNN)–PA(0NNN).

**TABLE 2: Same as Table 1 but When T2 Is Center**

	1NNN-1	1NNN-2	1NNN-3	1NNN-4	1NNN-5	1NNN-6
PA-L	-40.8	-22.9	28.4	33.0	-45.5	34.2
PA-S	-56.1	-31.1	47.9	51.5	-65.6	47.0
HOA	4.5	-16.7	-18.3	-23.8	-5.8	-8.9
AA	-51.6	-47.8	29.6	27.7	-71.4	38.1

	1NNN-7	1NNN-8	1NNN-9	1NNN-10	1NNN-11	1NNN-12
PA-L	1.2	0.5	-10.3	-5.1	25.5	-35.9
PA-S	1.9	2.6	-9.9	-4.4	41.4	-53.8
HOA	-10.9	-7.9	-7.2	-5.9	-29.3	-5.3
AA	-9.0	-5.3	-17.1	-10.3	12.1	-59.1

**TABLE 3: Same as Table 1 but When T3 Is Center**

	0NNN	0NNN	0NNN	0NNN	1NNN-1	1NNN-2
PA-L	30.4	35.8	-43.9	-27.6	-8.2	19.0
PA-S	58.9	54.4	-62.4	-35.4	-6.0	19.4
HOA	-10.0	-37.0	27.9	13.7	61.5	-7.3
AA	48.9	17.4	-34.5	-21.7	55.5	12.1

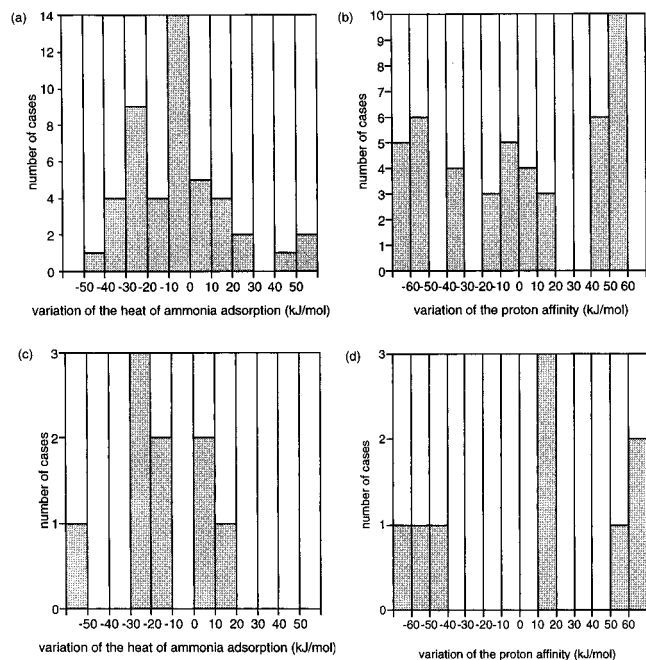
**TABLE 4: Same as Table 1 but When T4 Is Center**

	0NNN	0NNN	0NNN	0NNN	1NNN-1	1NNN-2
PA-L	29.1	33.0	18.5	-43.1	-13.5	-38.6
PA-S	49.4	50.7	18.5	-61.8	-18.0	-55.7
HOA	-21.7	-28.3	-10.5	1.2	-1.8	-9.0
AA	27.7	22.4	8.0	-60.6	-19.8	-64.7

1NNN are given in Tables 1–4. For proton affinity, both the one calculated with the large models and the one calculated with the small models are given. The behaviors (up or down) of the proton affinities upon substitution of both series are identical except for one case, the substitution at NNN4 of T1 center. But in this exceptional case, the proton affinity variation is -2.3 kJ/mol with the large model and +1.9 kJ/mol with the small model; thus the absolute values are both small and consistent that the substitution at this site does not have a significant influence on the acid strength. We may conclude that these small models include all the necessary effects to discuss the variation of the acid strength upon Si/Al substitution at NNN site.

In the case of faujasite,<sup>8</sup> there were six cases where the proton affinities were higher (acidity is lower) when the NNN site is Al (1NNN) than when it is Si (0NNN), while other three behaved opposite, and thus the former cases are dominant. For mordenite, however, the number of the cases where the acidity decreased as the NNN site is substituted from Si to Al is almost the same as the opposite cases.

In the course of the optimization of ammonia and the hydroxyl protons, the proton at the central acid site was transferred from zeolite hydroxyl site to ammonia, i.e., ammonia adsorbed as an



**Figure 5.** Distribution of the variations of the heat of ammonia adsorption (a, c) and proton affinity (b, d) upon substitution from Si to Al at NNN site: (a, b) mordenite; (c, d) faujasite.

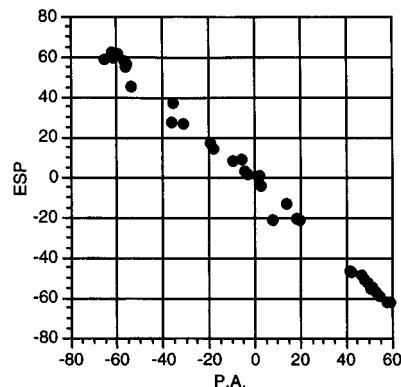
ammonium ion in all cases except for one, 0NNN of the model NNN2 of T3 center (see below). The occurrence of the proton transfer was evidenced by IR and NMR<sup>13</sup> and consistent with the previous calculations.<sup>14,15</sup> Jacobs<sup>16</sup> reported that neutral ammonia was only observed at high loading. In case of faujasite,<sup>8</sup> the heat of ammonia adsorption is higher for 0NNN than for 1NNN in 6 out of 9, or 2/3, cases. For mordenite, by double counting the symmetrically equivalent pairs, there are 32 cases where the heat of ammonia adsorption is higher for 0NNN than for 1NNN, while 14 behaved opposite (Tables 1–4); thus the acidity decreased upon Si/Al substitution at NNN site in approximately 2/3 cases.

## Discussion

First, the conclusions drawn from the previous work<sup>8</sup> on faujasite are tested for mordenite.

1. The effects of Si/Al substitution at NNN sites on the acid strength are not uniform: The distributions of the variation of the heat of ammonia adsorption and proton affinity upon NNN site substitution from Si to Al are shown in Figure 5. The variation is not uniform. Particularly for the proton affinity, the data scatters and no general tendency upon the substitution can be observed (Figure 5b,d). The heat of ammonia adsorption shows a statistical trend, with a curve whose peak is on the left of the origin; i.e., the acidity is weakened upon the substitution from Si to Al (Figure 5a,c). This is consistent with the experimental result that the ratio of strong acid sites measured by the heat of ammonia adsorption decreases as the Si/Al ratio decreases. But the calculation predicts that there are some cases where the adsorption energy increases upon Si/Al substitution.

Further analysis on the proton affinity revealed that there is a following relationship. Because two hydroxyl groups cannot be attached to one Si, there are three possibilities for the relative positions of the hydroxyl groups, (1)  $\text{—O—Al—OH—Si—O—Al—OH—}$ , (2)  $\text{—OH—Al—O—Si—O—Al—OH—}$ , and (3)  $\text{—OH—Al—O—Si—OH—Al—O—}$ , where the left Al is the center and right Al is the substitution (NNN) site. For faujasite, only case 1 and 3 appeared, and it was found that the proton affinity increases upon Si/Al substitution for case 1 and decreases for

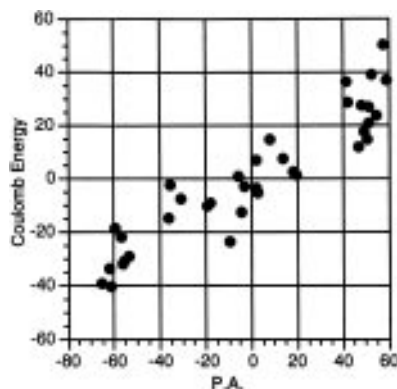


**Figure 6.** Correlation between the proton affinity (horizontal) and the electrostatic potential at the hydroxyl proton (vertical). Values represent the difference between 0NNN and 1NNN in kJ/mol.

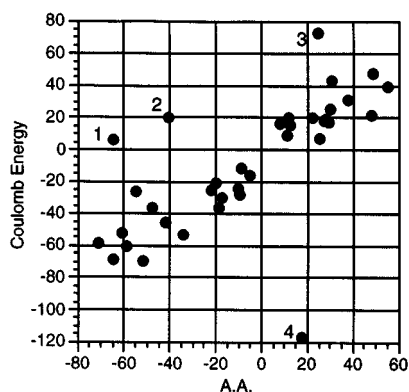
case 3. Four-membered rings satisfy both relationships 1 and 3, but the proton affinity always increased and we regarded them as case 1. For mordenite this rule still holds. Furthermore, for mordenite case 2 also appeared and the proton affinity always increased.

2. The variations of the acid strength are not caused by electronic effect but mainly by the electrostatic effect: In order to investigate this point, we performed the same analysis as was conducted on faujasite. The electronic effect on the proton affinity was tested first. From the atomic (ESP derived) charge calculation (not shown here), the charge on the proton, the sum of the atomic charges around the central Al ( $\text{AlO}_4^-$ ), and the sum of the atomic charges around the substitution site ( $\text{SiO}_4$ ,  $\text{AlO}_4\text{H}$ ) were found insensitive to the substitution (maximum change was 0.13 au, which is not considered significant since ESP charges were merely fitted to reproduce the electrostatic field around the molecule and fluctuation of the order of 0.1 au can be caused by changing the fitting procedure), and therefore no electronic flow occurred between the substitution site and other parts. Also, Mulliken bonding population analyses were performed and the bonding populations between the hydroxyl O and H were monitored (not shown here). Although the values derived from the Mulliken population analyses depend strongly on the basis set and their meaning is rather obscure, the comparison was made here under the same condition and thus one can expect that the change of this value indicates the change of the character of the bond. No significant changes (less than 0.01 electrons) were observed before and after the Si/Al substitution at any of NNN sites; thus the variations of the proton affinities are not caused by the change of the covalency between hydroxyl OH. From this we can conclude that the variations of the proton affinities are not caused by the electronic effect. In other words, the effect of substitution on the electronic structure is local and does not change the electronic state of the acid site. Likewise, for the ammonia adsorbed states, the sum of the atomic charges of ammonium ion ( $\text{NH}_4^+$ ), the sum around the central Al, and the sum around the substitution site were calculated (not shown here). No significant changes (maximum deviation of 0.19 au) were observed upon the substitution again; thus the difference of the heat of ammonia adsorption is not generated by the electronic effect.

Next, the electrostatic potential analyses were studied. The difference of the electrostatic potential (ESP) at the position of the hydroxyl proton between 0NNN and 1NNN was plotted against the difference of the proton affinity (Figure 6). A perfect correlation can be seen between the ESP and the PA, which was pointed out previously.<sup>17</sup> Also the electrostatic interaction energies between the proton and the zeolite framework were calculated by the Coulomb formula making use of the ESP



**Figure 7.** Correlation between the proton affinity (horizontal) and the electrostatic interaction energy (vertical). Values represent the difference between 0NNN and 1NNN in kJ/mol.

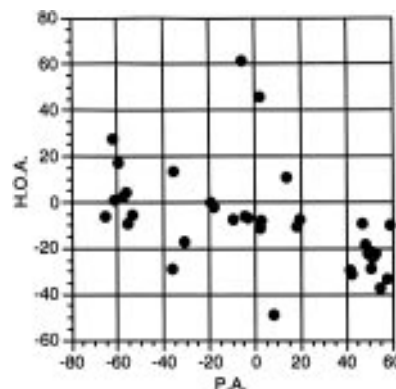


1: NNN6 of T1 center, 2: NNN12 of T1 center  
3: NNN8 of T1 center, 4: NNN2 of T3 center

**Figure 8.** Correlation between the ammonium ion affinity (horizontal) and the electrostatic interaction energy (vertical). Values represent the difference between 0NNN and 1NNN in kJ/mol.

derived charges on respective atoms and compared with the proton affinity. In this calculation, the atomic charges were scaled so that the total charge of each interacting part (zeolite and proton) becomes equal before and after the Si/Al substitution because the electrostatic interaction is very sensitive to the charge transfer between the interacting parts. For example, only 0.01 au transfer of charge from hydroxyl proton to zeolite oxygen may result in the change the electrostatic interaction energy by 20 kJ/mol. This small charge transfer is, however, not significant in the ESP derived charges because of its nature of the fitted parameters and we should think that no charge transfer occurred. Rather, attention should be paid to the variation of the acidity upon the change of the electrostatic potential created by substitution site, which was, from the classical point of view, caused by the replacement of Si to Al, whose formal charge is 3 instead of 4, and the addition of the charge compensating proton. A good correlation between the difference of the proton affinity and that of the electrostatic interaction before and after the substitution was found (Figure 7). This implies that the proton affinity is controlled by the electrostatic interaction.

For the ammonia adsorbed states, also the electrostatic interactions between the ammonium ion and the zeolite framework were calculated similarly and compared with the ammonium ion affinity. Also a good correlation between the two was observed (Figure 8), except for four cases indicated in the figure. For NNN6 and NNN12 of T1 center, one of the hydrogen bonds between ammonia H and framework O is broken upon the substitution from Si to Al, which may be the reason that makes the 1NNN more unfavorable than expected

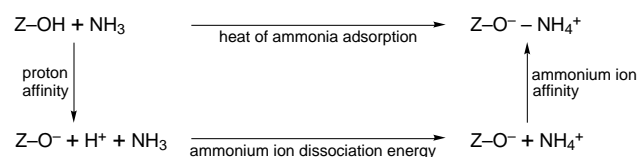


**Figure 9.** Correlation between the proton affinity (horizontal) and the heat of ammonia adsorption (vertical). Values represent the difference between 0NNN and 1NNN in kJ/mol.

from the simple electrostatic interaction. For NNN2 of T3 center, on the other hand, proton transfer from the zeolite hydroxyl site to the ammonia does not occur for 0NNN, which makes the electrostatic interaction between the proton and the oxygen extremely strong and resulted in the overestimation of the 0NNN stability. There were no other cases where proton transfer did not occur, and the reason for this exception is not clear. For NNN8 of T1 center, although the sign is the same, the absolute value differs significantly. The adsorption structures of 0NNN and 1NNN are similar, unlike the former three cases, and the reason for the discrepancy is not clear. From the above discussion we can conclude that the ammonium ion affinities are also mainly controlled by the electrostatic effect, confirming the result of the previous work, although the electrostatic interaction cannot predict properly when the mode of adsorption is changed upon Si/Al substitution.

3. The proton affinity and the heat of ammonia adsorption are not equivalent as the evaluation of the acidic strength: When the proton affinity of the conjugate base ( $Z-O^-$ ) becomes large, it becomes more difficult to release a proton, which means the weakening of the acidity. Heat of ammonia adsorption, on the other hand, gives a smaller value on the weak acid site. Thus, a negative slope is expected when they are plotted. However, a poor correlation between them is seen from Figure 9. One may notice that among 19 cases where 0NNN was calculated to be stronger acid than 1NNN from the proton affinity, 17 were also calculated likewise from the heat of ammonia adsorption. Thus there is a certain relationship between the two evaluation methods, as is discussed below. But the numbers of the cases where 0NNN was calculated to be stronger acid from both methods are apparently different and the absolute values of the energy differences between 0NNN and 1NNN also do not agree. Therefore, the conclusion obtained from the study on the faujasite that the proton affinity does not correlate with the heat of ammonia adsorption as the evaluation method of the acid strength was confirmed for mordenite.

The heats of ammonia adsorption are related with the proton and ammonium ion affinity as follows.



In this scheme, ammonium ion dissociation energy is always constant, and therefore the heat of ammonia adsorption is determined by proton and ammonium ion affinities. From this

diagram, the heat of ammonia adsorption is seen inevitably different from the proton affinity, since the ammonium ion affinity is not constant (Tables 1–4). Parrillo et al.<sup>5</sup> pointed out the importance of the interaction between the ammonia and the lattice oxygen on the heat of adsorption as well as the intrinsic strength of the Brønsted acid site. Furthermore, since both affinities can be estimated from the electrostatic interactions, the heat of ammonia adsorption should be estimated from them, and this study is to be carried out in our laboratory.

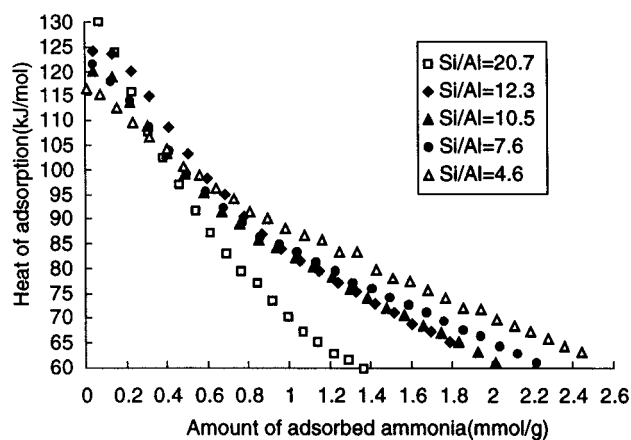
The quantitative investigation of the effect of the structure on the acid strength requires to account for all the interactions between the ammonia and the zeolite framework. The present study using the small cluster models therefore does not answer this question. One of the alternatives to cope with this question is a periodic Hartree–Fock method,<sup>18</sup> which takes account of all the atoms explicitly. The bad points of this method are a high demand for the computational power and a difficulty of the geometry optimization with the existing code. Another option is the embedded cluster techniques. The treatment of the boundary region is, however, still controversial.<sup>19–21</sup> Here only the effect of the Si/Al ratio variation upon the acidity for different types of zeolite is discussed.

The proton affinity variations upon Si/Al substitution at NNN sites are gun shot and have no statistical tendency (Figure 5b,d). Therefore, the difference of the trends according to the type of zeolite cannot be discussed. For the variation of the heat of ammonia adsorption, on the other hand, a statistical trend with a curve whose peak is on the left of the origin is observed for both of the types (Figure 5a,c), and the acidity decreases in about 2/3 cases. Thus the effects of the Si/Al ratio variation upon the heat of ammonia adsorption are expected to be similar for both types of zeolites.

Furthermore, the variations of the acidity upon the substitution are different depending on the substitution site even in the same type of zeolite, and therefore the variations are by no means the same when the different types of zeolites are compared site by site, while the overall tendencies are similar. These tendencies derive to the three-dimensional structures of faujasite and mordenite, since the proton affinity and the heat of ammonia adsorption are influenced by the electrostatic field created by the surrounding framework. But this tendency, i.e., the acidity decreases in about 2/3 cases, does not always have to hold for all types of zeolites.

As mentioned above, the calculated results predict that the substitution from Si to Al at NNN site increases the heat of ammonia adsorption in about 1/3 cases, which means that not only 0NNN sites but also 1/3 of 1NNN sites have strong acidity, postulating that 0NNN sites are strongly acidic. To examine this point with real mordenite, the acidic properties, i.e., the acid site population and the acid strength, of five synthesized samples with various Si/Al ratio were determined by the calorimetric measurements of ammonia adsorption.

Figure 10 illustrates the differential heat of ammonia adsorption measured at 300 K. Masuda et al.<sup>22</sup> related the activities in cumene decomposition and toluene disproportionation reactions to the acidity measured at this temperature. They found that cumene decomposition activity correlates with the number of acid sites with adsorption energy of higher than 80 kJ/mol, while toluene disproportionation activity correlates with the number of acid sites with adsorption energy of higher than 100 kJ/mol. From this result and the fact that toluene disproportionation requires strong acidity, the sites with the adsorption energy of higher than 80 kJ/mol were counted as total acid sites, of which higher than 100 kJ/mol were regarded as “strong” acid sites, and their population ratio was calculated (Table 5).



**Figure 10.** Calorimetric differential heats of ammonia adsorption at 300 K.

**TABLE 5: Population Ratio of the Strong Acid Sites to the Total Acid Sites Determined from Experiment (exp) and Calculated When 0NNN and 1/3 1NNN Are Considered Strong, Which Are Derived from the Probability of 0NNN and 1NNN Calculated Based on the Binomial Distribution of Al (%)**

Si/Al	4.6 <sup>a</sup>	7.6 <sup>a</sup>	10.5 <sup>a</sup>	12.3 <sup>a</sup>	20.7 <sup>a</sup>	7 <sup>b</sup>	9.5 <sup>b</sup>	18 <sup>b</sup>	47.9 <sup>b</sup>
exp	35.0	40.7	41.4	50.8	54.5	29.9	49.7	67.1	82.8
0NNN + 1/3 1NNN	18.6	35.8	47.4	52.9	68.5	32.8	43.8	64.7	85.0
0NNN	10.1	23.7	34.6	40.2	57.7	21.1	31.1	53.2	78.6
1NNN	25.6	36.3	38.4	38.1	32.5	35.1	38.2	34.5	19.1

<sup>a</sup> Our experiment. <sup>b</sup> Reference 4.

Stach et al.<sup>4</sup> also conducted similar measurements on mordenite with several Si/Al ratio but at the temperature of 423 K. Their measurements show somewhat higher adsorption heat than our results (Figure 3 in ref 4), probably due to the difference of the measurement temperature. They reported that the number of adsorbed ammonia with adsorption energy of higher than 80 kJ/mol agreed well with the number of acid sites determined from the ammonia TPD. Also, they found a good correlation between the number of acid sites with adsorption energy of higher than 120 kJ/mol and the activities in the isomerization and disproportionation of *o*-xylene. Therefore, for their data, the sites with the adsorption energy of higher than 80 and 120 kJ/mol were counted as total and strong acid sites, respectively, and their population ratio was also computed (Table 5).

Provided that the possibility of every T site to accommodate an Al is equal, the probabilities of 0NNN and 1NNN are calculated as follows<sup>23</sup>

$$P(y\text{NNN}) = {}_nC_y (1/1 + R)^y (R/1 + R)^{n-y}$$

where  $R = \text{Si/Al}$  atomic ratio,  $n$  is the number of NNN sites, and  $y$  is the number of Al occupying the NNN sites. In case of mordenite, there are 48 T sites in a unit cell, of which 16 each are T1 and T2, while 8 each are T3 and T4, respectively. And T1 and T2 have 12 NNN sites, while T3 and T4 have 11. The probabilities of 0NNN and 1NNN are then given by

$$P(0\text{NNN}) = (32/48) {}_{12}C_0 (1/1 + R)^0 (R/1 + R)^{12} + (16/48) {}_{11}C_0 (1/1 + R)^0 (R/1 + R)^{11}$$

$$P(1\text{NNN}) = (32/48) {}_{12}C_1 (1/1 + R)^1 (R/1 + R)^{11} + (16/48) {}_{11}C_1 (1/1 + R)^1 (R/1 + R)^{10}$$

The probabilities of 0NNN and 1NNN thus calculated are given in Table 5. Also, the ratio of the strong acid sites to the

total acid sites calculated when 1/3 of 1NNN as well as 0NNN are considered strong is given in Table 5. A better correlation with the experimental results is found when 0NNN and 1/3 of 1NNN are regarded strong than when only 0NNN is regarded strong. At low Si/Al ratio (Si/Al = 4.6), the calculated value underestimates the number of strong acid sites, probably due to a large contribution from 2NNN, 3NNN, and so on in the real zeolite which are neglected in the calculation. This indicates that some of the 2NNN etc. are also strong acids.

## Conclusion

The variations of the acidity upon the substitution from Si to Al at NNN sites were calculated by means of ab initio molecular orbital method for mordenite. The conclusions drawn from our previous work on the faujasite were found to hold for the mordenite; i.e., the effect of Si/Al substitution on the acid strength depends on the substitution sites, the variations of the acid strength are caused mainly by the electrostatic effect, and the proton affinity and the heat of ammonia adsorption are not equivalent measures of the acidity.

Mordenites with various Si/Al ratios were synthesized and the acidic properties were studied by the calorimetric measurements of ammonia adsorption. From the analyses based on the binomial distribution of Al, a good correlation was found when 1/3 of 1NNN as well as 0NNN were considered as strong acid, as is predicted from the calculation. Furthermore, from the low Si/Al result, some of the 2NNN etc. are indicated to be strong acid.

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## References and Notes

- (1) Klyachko, A. L.; Kapustin, G. I.; Brueva, T. R.; Rubinstein, A. M. *Zeolite* **1987**, 7, 119.
- (2) Tsutsumi, K.; Koh, H. Q.; Hagiwara, S.; Takahashi, H. *Bull. Chem. Soc. Jpn.* **1975**, 48, 3576.
- (3) Lohse, U.; Parlits, B.; Patzelova, V. *J. Phys. Chem.* **1989**, 93, 3677.
- (4) Stach, H.; Janchen, J.; Jerschke, H. G.; Lohse, U.; Parlitz, B.; Hunger, M. *J. Phys. Chem.* **1992**, 96, 8480.
- (5) Parrillo, D. J.; Gorte, R. J. *J. Phys. Chem.* **1993**, 97, 8786.
- (6) Pine, L. A.; Maher, P. J.; Wachter, W. A. *J. Catal.* **1984**, 85, 466.
- (7) Sauer, J.; Ugliengo, P.; Garrone, E.; Saunders, V. R. *Chem. Rev.* **1994**, 94, 2095 and the references therein.
- (8) Teraishi, K. *Micropor. Mater.* **1995**, 5, 233.
- (9) Lombardo, E. A.; Pierantozzi, R.; Hall, W. K. *J. Catal.* **1988**, 110, 171.
- (10) Ozment, J. L.; Schmiedekamp, A. M. *Int. J. Quantum Chem.* **1992**, 43, 783.
- (11) Stewart, J. J. P.; Fujitsu, Ltd. *Quantum Chemistry Program Exchange* **1993**, 13, 40.
- (12) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Wong, M. W.; Foresman, J. B.; Robb, M. A.; Head-Gordon, M.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. *Gaussian92*; Gaussian, Inc.: Pittsburgh, PA, 1993.
- (13) Earl, W. L.; Fritz, P. O.; Gibson, A. A. V.; Lunsford, J. H. *J. Phys. Chem.* **1987**, 91, 2091.
- (14) Teunissen, E. H.; Duijneveldt, F. B.; Santen, R. A. *J. Phys. Chem.* **1992**, 96, 366; Teunissen, E. H.; Santen, R. A.; Jansen, A. P. J.; Duijneveldt, F. B. *J. Phys. Chem.* **1993**, 97, 203.
- (15) Kassab, E.; Fouquet, J.; Alavena, M.; Evleth, E. M. *J. Phys. Chem.* **1993**, 97, 9034.
- (16) Jacobs, W. P. J. H.; Santen, R. A. *J. Chem. Soc., Faraday Trans.* **1994**, 90, 1191.
- (17) Sauer, J.; Rhlrichs, R. *J. Chem. Phys.* **1990**, 93, 2575.
- (18) White, J. C.; Hess, A. C. *J. Phys. Chem.* **1993**, 97, 6398. Nicholas, J. B.; Hess, A. C. *J. Am. Chem. Soc.* **1994**, 116, 5428.
- (19) Kyrlidis, A.; Cook, S. J.; Chakraborty, A. K.; Bell, A. T.; Theodorou, D. N. *J. Phys. Chem.* **1995**, 99, 1505.
- (20) Teunissen, E. H.; Jansen, A. P. J.; Santen, R. A.; Orlando, R.; Dovesi, R. *J. Chem. Phys.* **1994**, 101, 5865.
- (21) Greatbanks, S. P.; Sherwood, P.; Hillier, I. H. *J. Phys. Chem.* **1994**, 98, 8134.
- (22) Masuda, T.; Shoji, K.; Taniguchi, H.; Tsusumi, K.; Takahashi, H. *Seisan Kenkyu* **1979**, 31, 589.
- (23) Wachter, W. A. Statistical and Topological Approach to Modeling Zeolite Acidity, Activity, and Stability. Presented at the Sixth International Zeolite Conference, Reno, July 1983.