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Brønsted Acidity of Isomorphously Substituted ZSM-5 by B, Al, Ga, and Fe. Density Functional Investigations

S. P. Yuan,[†] J. G. Wang,*,[†,§] Y. W. Li,[†] and Haijun Jiao*,[†,‡]

State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, P.O. Box 165, Taiyuan 030001, People's Republic of China, and Institut für Organische Katalyseforschung (IfOK) an der Universität Rostock e.V., Buchbinderstrasse 5-6, 18055 Rostock, Germany

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The Brønsted acidity of isomorphously substituted ZSM-5 by B, Al, Ga, and Fe has been studied at the B3LYP level of density functional theory. On the basis of the calculated proton affinity, natural charge on the acidic proton, and the adsorption energy of NH_3, the Brønsted acidity increases in the order: B−(OH)−Si < Fe−(OH)−Si < Ga−(OH)−Si < Al−(OH)−Si, in agreement with the experiment. In both Al and Ga modified clusters, the adsorbed NH_3 becomes ammonium (NH_4^+) stabilized by two N−H···O hydrogen bonds, while the physisorbed NH_3 is stabilized by one N···H−O hydrogen bond in Fe and B substituted clusters. It is also found that NH_3 adsorption changes the B coordination sphere.

Introduction

As being important microporous inorganic materials, zeolites are used as catalysts with a wide range of applications due to their Brønsted acidity and shape-selectivity.[1,2] The acid sources are bridging hydroxyls, which arise from the presence of formal trication replacing Si in their parent structures. Many efforts have been devoted to the synthesis, characterization and application of the isomorphously substituted zeolites with elements in their framework other than Si and Al, such as B, Ga, Fe, Ti, or Zn.[3−7] Incorporation of heteroatoms can change the acidity and pore structure of zeolites and the modified zeolites have altered catalytic activity, selectivity and stability. This offers the potential to design zeolites for novel applications. For example, Fe−ZSM-5 is an active catalyst for the oxidations of methane to methanol[8] and benzene to phenol.[9] Ga−ZSM-5 shows high selectivity in alkane aromatization.[10] TS-1 is well-known for its excellent performance in oxidation reactions.[11]

Many experimental studies[12−16] have investigated the structures and acidity of zeolites and the isomorphously substituted zeolites containing different framework atoms. Chu[15] used infrared (IR) spectroscopy and temperature-programmed desorption (TPD) of adsorpted NH_3 to study the acidity of several isomorphously substituited M−ZSM-5 with the increased acid strength: Si−(OH) < B−(OH)−Si ≪ Fe−(OH)−Si < Ga−(OH)−Si < Al−(OH)−Si. For design and characterization of zeolites, and understanding of their catalytical mechanisms, it is desired to get the insight into the detailed structural information. However, X-ray analysis and even more sensitive neutron scattering techniques cannot distinguish between Si and Al or other metal cations in these materials, and these needed information could not be obtained directly from experiments. Thus it is necessary to resort other methods to aquire the information.

It has been shown that ab initio and DFT quantum mechanical methods can be used to predict the acidity and reactivity of zeolites.[17−30] Chatterjee[22] reported DFT calculations on isomorphously substituited ZSM-5 clusters by B, Al, Ga, and Fe, and the relative acidity derived from proton affinities agrees well with the experimental results. For understanding the adsorption properties of zeolite catalysts, the interactions of substrates with the Brønsted acid site have been studied extensively,[18,21,31−45] since this is an important step in many reactions catalyzed by zeolites. However, studies on the adsorption properties of the isomorphously substituted zeolites are rather limited.[15,46]

The acidic properties of zeolites include type (Brønsted or Lewis), strength and amount of the acid sites. In this paper, we report cluster models and DFT calculations on the strength of the Brønsted acid sites in isomorphously substituted ZSM-5 by B, Al, Ga, and Fe on the basis of (i) the estimated proton affinity (PA), describing the facility of proton migration from some sites located on the proton donor toward a proton acceptor,[47] (ii) the natural charge on the acidic proton (q_H), and (iii) the NH_3 adsorption energy as the measure of the Brønsted acidity.

Models and Methods

Models. Due to their three-dimensional networks, it is not possible to compute the complete real structures of ZSM-5, therefore model systems are employed. The model coordinates are taken from the ZSM-5 crystal structure by Koningsveld[48] in which there are 12 distinct tetrahedral sites (T_x, $x = 1-12$) in the unit cell. Theoretical study[49] indicated that T_{12} is the favorable site for Al substitution, but the small energy differences among various isomers show a distribution of Al over a number of substitution sites. In this paper, the T_{12} site is selected because it is located at the intersection of the straight and sinusoidal channels of ZSM-5 and allows significant interaction between the bridging OH and adsorbed molecules and thus being consisdered as the catalytically active site.

The chosen models are made up of atoms surrounding the hydroxyl group and designated generally as ZeOH (ZeO^- when the proton is removed). To investigate the cluster size effect, the first generation cluster with two tetrahedral centers in the $(OH)_3Si-O(H)-M(OH)_3$ formula (M = B, Al, Ga, or Fe,

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[*] To whom correspondence should be addressed.

[†] State Key Laboratory of Coal Conversion.

[§] E-mail: iccjgw@sxicc.ac.cn.

[‡] Institut für Organische Katalyseforschung (IfOK) an der Universität Rostock e.V.

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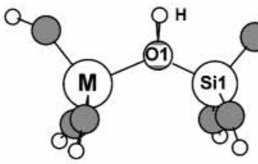
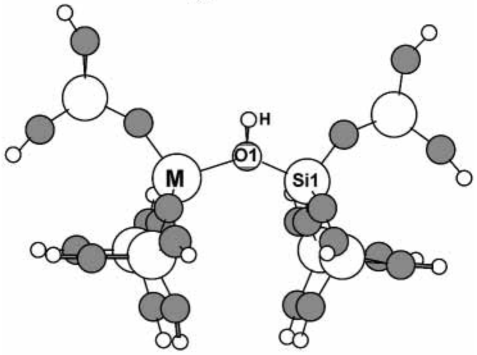
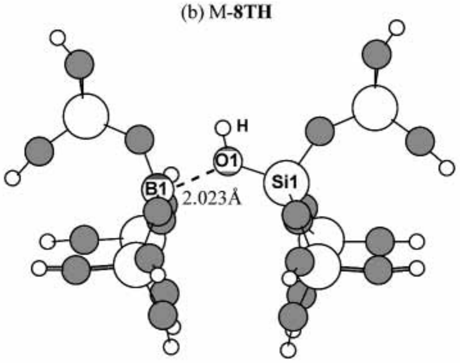


(a) M-**2TH**



(b) M-**8TH**



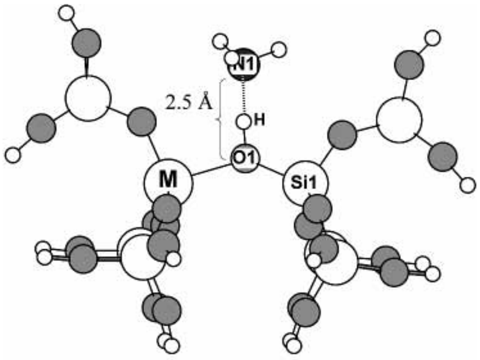
(c) B-**8TH**

Figure 1. Cluster models for ZSM-5 framework with T_{12} site being Al, Ga, Fe, and B: (a) M−**2TH**, (b) M−**8TH**, and (c) partially optimized B−**8TH**.

donated as M−**2TH**) as shown in Figure 1 are considered. The second generation cluster with eight tetrahedral centers in the formula $((HO)_3SiO)_3Si{-}OH{-}M(OSi(OH)_3)_3$, donated as M−**8TH**, are investigated. In all the clusters, the peripheral oxygens are saturated with hydrogens with a fixed O−H distance of 1.0 Å from the corresponding oxygen, oriented along the bond direction to what would otherwise have been the next silicon atoms.

Methods. All calculations in this paper are performed by using the Jaguar program[50] and the B3LYP density functional method. Four basis sets, LAV3P(d), LAV3P(d,p), LACVP(d), and LACV3P(d), were used to test the basis set effect. LAV3P(d) and LAV3P(d,p) represent the combination of the LAV3P[51] effective core potentials (ECP) for Al, Si, Ga, and Fe, and the 6-31G(d) or 6-31G(d,p) basis set for all other elements. For LACVP(d) and LACV3P(d), only Ga and Fe atoms are described by LACVP[52] or LACV3P[53] ECP, respectively, while 6-31G(d) is used for all other atoms. Natural population analysis is performed by the Natural bond orbital (NBO) method.[54] Since Fe (III) usually has a high spin ground state (d^5) in tetrahedral coordination sphere,[55] all Fe-contanining clusters are calculated with spin multiplicity of six, while the other clusters have closed shell configuration as singlet states.

Quantum chemical calculations can reproduce experimental results reasonably only when geometries are allowed to relax. However, Sauer[56] pointed out that full cluster relaxation may lead to structures that do not resemble experimental zeolite structures. Therefore considerable care is needed in explementing relaxation of clusters that mimic zeolite framework.[57] Therefore, clusters representing ZSM-5 framework are partially optimized in this study as keeping the first and second cycles around OH group ($O_3Si{-}O(H){-}MO_3$, M = B, Al, Ga, and Fe) relaxed while other atoms fixed to their ZSM-5 positions. This allows the atoms in the vicinity of the acid site and the substituent to relax, while the cluster retains its position in the zeolite lattice.



M-**8TH** + NH_3

Figure 2. Initial configuration of M−**8TH** + NH_3 cluster with $d_{N1\cdots O1}$ distance of 2.5 Å.

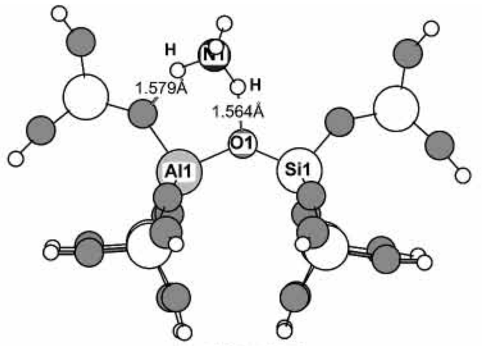
To study the interaction between NH_3 and the acid site, partially optimized ZSM-5 clusters and free optimized NH_3 are used. The initial orientation of ZeOH−NH_3 cluster is show in Figure 2, in which the distance between the central bridging oxygen in ZSM-5 cluster and nitrogen in NH_3, $d_{N1\cdots O1}$, is set to 2.5 Å.[34] The ZeOH−NH_3 clusters are optimized by keeping $O_3MO(H)SiO_3$ and NH_3 relaxed, while the rest of the clusters are anchored to their framework positions. The equilibrium configuration of the ZeOH−NH_3 complexes are shown in Figure 3.

Results and Discussion

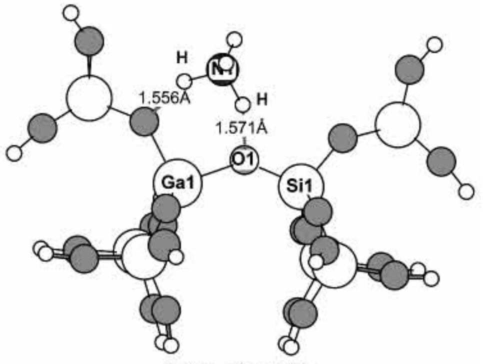
Table 1 summarizes the calculated total energies and proton affinities (PA) of the M-**2T** clusters with four different basis sets. Proton affinity, considered as the energy required to remove the acidic proton from the zeolite structure (ZeOH) and leading to the anionic cluster (ZeO^-), is calculated as the energy difference between ZeO^- and ZeOH.[58] It is obvious that, the smaller the PA, the more acidic the acid sites. On the basis of this, the relative acidic order of the substituted M−ZSM-5 is: B−(OH)−Si < Fe−(OH)−Si < Ga−(OH)−Si < Al−(OH)−Si, consistent with the experimental results.[15]

The relative order of PA is nearly independent of the size of the employed basis sets, although small variations within 5% are observed. Therefore, the basis set effect for qualitative purpose might be negligible. It is also to note that all energies reported do not include corrections for zero-point energy due to their partial optimizations, and basis-set-superposition-error (BSSE). BSSE is expected to be roughly the same for each of the clusters examined[19] and compensated in large extent in the PA calculation, and we are only interested in the relative trends of energy with the nature of substituents. On the bases of these results, further results and discussion are obtained with the LAV3P(d,p) basis set.

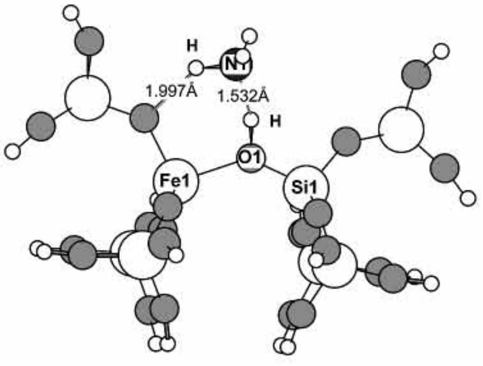
In addition to the basis set effects, we have also calculated the effects of cluster size. As shown in Table 1, the relative PA order for M-**8T** clusters is the same as for M-**2T**, in agreement with the experimental results. With the increased cluster size from M-**2T** to M-**8T**, the PA values have a change of 6−8 kcal/



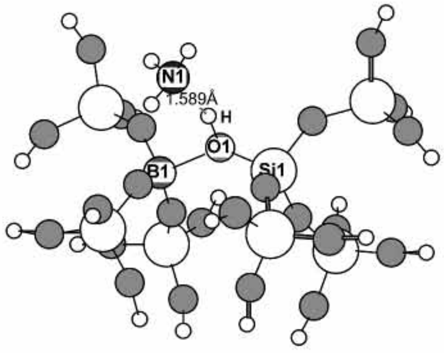
(a) Al-**8TH**-NH_3



(b) Ga-**8TH**-NH_3



(c) Fe-**8TH**-NH_3



(d) B-**8TH**-NH_3

Figure 3. Equilibrium configurations of ZeOH−NH_3 complexes: (a) Al−**8TH**−NH_3, (b) Ga−**8TH**−NH_3, (c) Fe−**8TH**−NH_3, and (d) B−**8TH**−NH_3.

mol for M = Al, Ga, Fe, and this is only 2% of the total value. However, significant change of 32.8 kcal/mol or 8.4% for B−ZSM-5 is observed, this means that the additional shell of atoms in M−**8TH** clusters effect the B-containing model much significantly, and this is reflected by the structural parameters of the equilibrium geometries discussed below.

The key parameters for the equilibrium geometries of M−**2TH** and M−**8TH** clusters are given in Table 2. It shows that the distance between the bridging oxygen and Si atom (d_{Si1-O1}) of the M−**8TH** clusters is slightly longer than those of the M−**2TH** models, and both are longer than that in the parent ZSM-5 cluster (1.60 Å), and the bridging O−H bonds (d_{O1-H}) in M−**8TH** and M−**2TH** are nearly the same. It is found that the distances between bridging oxygen and metal (d_{M-O1}) and silicon (d_{O1-Si1}) are longer than the other corresponding bonds. The angle of M−O−Si (α_{MO1Si1}) in M−**8TH** are smaller than that in the parent ZSM-5 (146.2°) by around 7−13°. The distance between the bridging oxygen and the substituents (d_{M-O1}) increases only slightly with the increased electronegativity and ion radius (Table 3) for M = Al, Ga, or Fe. For M = B, however, the d_{B-O} distance in B−**2TH** cluster of 3.736 Å is much longer than that in B−**8TH** (2.023 Å) and the other average B−O distances (1.355−1.382 Å), indicating that there is no bonding between B and the bridging oxygen, and therefore terminal rather than bridging OH in B−**2TH** is observed. This might be ascribed to the small size of B^{3+} cation which prefers tri- rather than tetra-coordination,[59−61] and the larger B−**8TH** cluster with shorter d_{B-O} distance is due to the additional shell of atoms. This agrees with the LDF calculations on B−ZSM-5 clusters by Miyamoto.[22] That the boron center has tri- rather than tetracoordination is indicated by the sum (357.4°) of the OBO angles of the three short B−O bonds in B−**8TH** cluster. Therefore we can conclude that the first generation M−**2TH** cluster is too small to model the isomorphously substituted ZSM-5, while the second generation M−**8TH** clusters are adequate to represent the bonding properties of heteroatoms and the acid sites in zeolite framework. Thus the following discussion is based on M−**8TH** clusters.

Charge Distribution. The second criterion for characterizing the relative acidity of M−ZSM-5 is the partial charge of the bridging OH group, and these are listed in Table 3. Natural population analysis for M, O and H atoms show that the partial charges on M (q_M) and on the bridging group (q_H, q_O) decrease with their increased electronegativities,[62] although q_O for M = Fe is an exception. The charge on the proton of the OH group can serve as a measurement for the Brønsted acidity.[63] On this basis, the relative acidity of M−ZSM-5 shows the order of M = Al > Ga > Fe > B, being in good agreement with the result from proton affinity.

Adsorption of NH_3. The third criterion for estimating the relative acidity of M−ZSM-5 is the NH_3 adsorption energy (ΔE_{ads}), which is defined as the energy difference between $E(ZeOH + NH_3)$ and $E(ZeOH-NH_3)$.[34] It is obvious that the acid site with stronger acidity would have larger adsorption energy, i.e., the smaller the PA, the larger the energy of adsorption.[58] As given in Table 4, the relative acidic order deduced from the calculated ΔE_{ads} of M−ZSM-5 agrees well with the order from PA and partial atomic charges of the OH group. In addition, it is shown that the calculated ΔE_{ads} of Al−ZSM-5−NH_3 (25.6 kcal/mol) is close to the microcalometric results (34 kcal/mol).[64,65]

The partial optimized structures of the adsorbed M−**8TH**−NH_3 complexes are shown in Figure 3 with the selected N−H and O−H bond distances in Table 5. On the basis of the N−H(O) separations, it can be seen directly that NH_3 becomes protonated (NH_4^+) for M = Al and Ga with proton transfer, while only physisorbed NH_3 for M = Fe and B without proton transfer is found. The former two clusters with hydrogen bonding interaction of N−H···O, while the latter two show the reversed pattern (N···H−O). It is also to note that there are

TABLE 1: B3LYP Total Energies (*E*, au) and Proton Affinities (PA, kcal/mol) for Model Clusters

basis set		Al	Ga	Fe	B
LAV3P(d)	*E*(**2TH**)	−536.862 48	−536.871 21	−557.206 69	−559.714 62
	E(**2T**)	−536.318 66	−536.325 97	−556.651 24	−559.060 18
	PA	341.2	342.1	348.6	410.7
LACVP(d)	*E*(**2TH**)	−1062.977 24	−822.530 40	−943.854 31	−845.369 76
	E(**2T**)	−1062.433 81	−821.984 54	−943.305 41	−844.718 69
	PA	341.0	342.5	344.4	408.6
LACV3P(d)	*E*(**2TH**)	−1063.218 62	−822.747 33	−944.101 00	−845.583 19
	E(**2T**)	−1062.679 08	−822.204 32	−943.555 72	−844.939 54
	PA	338.6	340.7	342.2	403.9
LAV3P(d,p)	*E*(**2TH**)	−536.908 65	−536.917 31	−557.251 75	−559.723 40
	E(**2T**)	−536.359 54	−536.366 73	−556.690 24	−559.101 68
	PA	344.6	345.5	352.4	390.1
LAV3P(d,p)	*E*(**8TH**)	−1922.115 66	−1922.131 53	−1942.443 96	−1944.914 70
	E(**8T**)	−1921.577 20	−1921.590 45	−1941.894 95	−1944.345 26
	PA	337.9	339.5	344.5	357.3

TABLE 2: Selected Bond Lengths (Ångstroms) and Angles (Degrees) in M−2TH and M−8TH Clusters

M	Al	Ga	Fe	B
		M−**2TH**		
d_{M-O1}	1.975	2.033	2.221	3.736
d_{Si1-O1}	1.695	1.691	1.662	1.631
d_{O1-H}	0.980	0.982	0.981	0.979
α_{MO1Si1}	131.3	132.1	152.8	109.8
d_{M-O} (av)[a]	1.711	1.738	1.872	1.355
d_{Si1-O} (av)[a]	1.606	1.607	1.614	1.632
		M−**8TH**		
d_{M-O1}	1.983	2.105	2.131	2.023
d_{Si1-O1}	1.717	1.721	1.687	1.656
d_{O1-H}	0.970	0.970	0.968	0.966
α_{MO1Si1}	133.8	139.1	133.3	136.9
d_{M-O} (ave)[a]	1.717	1.754	1.841	1.382
d_{Si1-O} (ave)[a]	1.619	1.624	1.620	1.627

[a] The average length of the other three M−O or Si1−O bonds.

TABLE 3: Pauling Electronegativity of M Atoms (X_M), Radius of M^{3+} Ions ($R_M{}^{3+}$, Ångstroms), and the Natural Charges in M−8TH Clusters

M	Al	Ga	Fe	B
X_M[a]	1.61	1.81	1.83	2.04
$R_M{}^{3+}$ [a]	0.53	0.61	0.63	0.25
q_M	2.088	2.032	1.614	1.372
q_{O1}	−1.158	−1.142	−1.155	−1.084
q_H	0.566	0.558	0.554	0.550

[a] Reference 62.

TABLE 4: NH_3 Adsorption Energy (ΔE_{Ads}, kcal/mol) of M−8TH Clusters

M	*E*(M−**8TH**−NH$_3$)	*E*(M−**8TH** + NH$_3$)	ΔE_{ads}
Al	−1978.712 95	−1978.672 12	25.6
Ga	−1978.726 20	−1978.687 99	24.0
Fe	−1999.034 74	−1999.000 42	21.5
B	−2001.502 67	−2001.471 16	19.8

two N−H···O interactions in the former two clusters, one with the original bridging oxygen, and the other with the next oxygen in the same orientation. Associated with these interactions, lengthening of the O−H (d_{O1-H}) bond and the shortening of the M−O (d_{M-O1}) and Si−O (d_{Si1-O1}) bonds as compared to the bare M−8**TH** clusters (Table 2 vs Table 5), as expected, are observed. The geometric difference of M−ZSM-5−NH$_3$ clusters is reflected by the calculated NH$_3$ adsorption energies, i.e., double hydrogen bonds for Al or Ga substitution have larger adsorption energy than single hydrogen bond in B substitution. The different acidity of the B, Al, Ga, and Fe substituted ZSM-5 is responsible for the different structures of the adsorbed complexes of NH$_3$ which in turn reflects the nature of substituents.

TABLE 5: Selected Bond Lengths (Ångstroms) in M−8TH−NH$_3$ Clusters

M	Al	Ga	Fe	B
d_{O1-H}	1.564	1.571	1.061	1.043
d_{N1-H}	1.081	1.081	1.574	1.589
d_{M-O1}	1.839	1.906	2.080	1.801
d_{Si1-O1}	1.639	1.647	1.659	1.669
d_{M-O} (av)[a]	1.754	1.802	1.851	1.406
d_{Si1-O} (av)[a]	1.644	1.649	1.630	1.634

[a] The average length of the other three M−O or Si1−O bonds.

Indeed, such proton transfer between the acidic site of zeolites and NH$_3$ has been investigated theoretically,[44,45] and experimentally with the help of ^{15}N NMR[66] and IR[67,68] techniques. On the basis of the calculated adsorption energies, van Santen found that proton transfer from the aluminum zeolite clusters to NH$_3$ was favorable in case the formed NH$_4{}^+$ is stabilized at the same extent with two or three hydrogen bonds to the zeolite clusters, while the coordination of one additional NH$_3$ (coadsorption) is less favored energetically.[45] He also pointed out that clusters without proton transfer are stabilized through only single hydrogen bond.[44] In full agreement with these theoretical considerations, and on the bases of the IR spectra of NH$_4{}^+$ ions in zeolites, Zecchina found that the resulting NH$_4{}^+$ is stabilized mainly by two or three hydrogen bonds inside the channels and cages of aluminum ZSM-5, MOR, β, SAPO-34 and Y zeolites, and also by four hydrogen bonds in aluminum MOR.[67,68] The features of the IR spectra of the adsorbed NH$_4{}^+$ are influenced by the types of zeolites, and different acidic sites in turn give different contribution to the spectra.

Our results are in line with these theoretical and experimental findings. For example, the forming NH$_4{}^+$ in Al−ZSM-5 is mainly stabilized by two hydrogen bonds, and the same is also for Ga−ZSM-5. In Al-MOR,[55] we also found proton transfer between the acidic side and NH$_3$ and the resulting NH$_4{}^+$ is mainly stabilized by three hydrogen bonds. Therefore, the framework of the specific zeolites determines the number of hydrogen bonds stabilizing the NH$_4{}^+$ ions inside the channels and cages.

In addition, further stabilization of the hydrogen bonded NH$_4{}^+$ by excess NH$_3$ is also found experimentally on the basis of IR spectra.[68] For comparison, we calculated the interaction between NH$_4{}^+$ and NH$_3$ for the formation of [H$_3$N−H···NH$_3$]$^+$.[69,70] The computed stabilization of 33.7 kcal/mol at the same level is stronger than that (25.6 kcal/mol) of Al−ZSM-5 (Table 4). This indicates that the stabilizing interaction in [H$_3$N−H···NH$_3$]$^+$ is stronger than that in Al−ZSM-5−NH$_3$, and this allows the coadsorption of excess NH$_3$ to be favored energetically. The formed $[H_3N-H\cdots NH_3]^+$ is stabilized by hydrogen bonds to the negative charged zeolite frameworks, as found by van Santen.[45]

In contrast to the stronger acidic Al− or Ga−ZSM-5 cluster, no proton transfer between NH_3 and the less acidic Fe− and B−ZSM-5 clusters is found. The interaction has only single hydrogen bond, although an additional much longer $H\cdots O$ interaction (1.997 Å) is found for M = Fe (Figure 3). Therefore, no further stabilization by excess NH_3 can be expected, since the stabilization energy of $[H_2N-H\cdots NH_3]$ of less than 5 kcal/mol[71] is much smaller than the adsorption energies for M = B (19.8 kcal/mol) or Fe (21.5 kcal/mol).

From the optimized geometry of the cluster representing NH_3 adsorbed on B−**8TH**, it can be observed that B^{3+} center becomes less planar than in B−**8TH**, as indicated by the change of the sum of the three OBO angles, which is 350.0° in B−**8TH**−NH_3, while 357.4° in B−**8TH**. This might point to the effect of a reversible change of coordination from tri to tetra coordination of the B^{3+} center when NH_3 is adsorbed. This is in agreement with that observed experimentally.[61,72]

Conclusion

The Brønsted acidity of isomorphously substituted ZSM-5 by B, Al, Ga, and Fe has been studied at the B3LYP level of density functional theory. It is found that the relative order of the acid strength is less dependent on the size of the basis sets employed. The effect of the cluster size was investigated by using the cluster models with two and eight tetrahedral centers, and only the large model is sufficient for representing the isomorphously substituted ZSM-5 approximately. On the basis of the calculated proton affinity, the natural charge on the proton, and the energy of NH_3 adsorption, the sequence of the acid strength is $B-(OH)-Si < Fe-(OH)-Si < Ga-(OH)-Si < Al-(OH)-Si$, which is consistent with the experiment.

The equilibrium structure of the clusters representing the adsorption of NH_3 indicated that NH_3 becomes protonated (NH_4^+) in contact with Al− and Ga−ZSM-5, while is only physisorbed for Fe− and B−ZSM-5. It was found that there are two $N-H\cdots O$ hydrogen bonds in Al− and Ga−ZSM-5, while only single hydrogen bond in reversed pattern ($N\cdots H-O$) for Fe− and B−ZSM-5. In addition, it is found that B^{3+} undergoes a reversible change of coordination sphere when NH_3 is adsorbed, in agreement with experiment.

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