

The effect of framework organic moieties on the acidity of zeolites: A DFT study

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Abstract

Acidic properties of H-CHA, H-ZOL-C, and H-ZOL-N have been investigated using periodic density functional calculations to understand the effect of organic moiety incorporation on their acidities. Results from NH₃ adsorption energy, deprotonation energy, and relative nucleophilicity calculations are consistent and show that the relative Brønsted acid site strength decreases in the order H-CHA > H-ZOL-C > H-ZOL-N. The geometrical parameters of the optimized structures indicate the easier incorporation of NH rather than CH₂ in the chabazite framework. Moreover, the basicity of the lattice O, N, and C atoms increases in the order C < O < N.

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1. Introduction

Hybrid microporous and mesoporous materials are attracting much attention due to their various applications as optoelectronic devices, sensors, sieves, and catalysts [1–4]. Recently, Yamamoto et al. [5,6] have prepared successfully a new family of microporous molecular sieves (MMS) called ZOL. ZOL refers to zeolites with organic groups bridged lattices and are defined as a true hybrid organic–inorganic material, where true means that the organic moieties, i.e., methylene groups (CH₂) are incorporated in the framework of the zeolites. Subsequently, a computational study on sodalite structure by Astala and Auerbach indicated the possible incorporation of organic moieties, viz., CH₂ and NH in high concentrations into the framework with minimal strain [7]. Other computational studies on cluster models by Waroquier and co-workers [8,9] showed the possible application of zeolites with nitrogen in the framework as bifunctional acid–base catalysts due to the presence of basic NH and Brønsted acid site in the same structure. However, the effect of introducing an organic moiety as CH₂ or amine species as NH on the zeolitic Brønsted acid site strength has not been investi-

gated yet. Furthermore, the acidic properties of these materials, and other MMS in general, are of primary significance regarding their applications as solid acid catalysts. Hence, density functional theory (DFT) calculations on chabazite (CHA) topology have been carried out in this study to tackle this goal. In addition to the short comes of using cluster models such as neglecting the long range electrostatic interactions, it is well known that small clusters are not reliable in mimicking zeolite crystals especially when the dangling bonds are close to adsorbates or any reacting molecule [10–12]. Therefore, periodic models of CHA are considered in this study. Choosing CHA topology has three folds. First, its UC is relatively small with 36 atoms. Second, CHA has an analogous structure, i.e., SAPO-34. Third, CHA and SAPO-34 have pronounced catalytic activities in the methanol-to-olefin (MTO) industrial process [13,14].

The energy of ammonia adsorption, deprotonation energy (DPE), and the relative electrophilicity (s_x^+/s_x^-) (i.e., the proton reactivity toward a nucleophilic attack) have been used to measure the changes of the Brønsted acid site strength upon the organic moiety incorporation. It should be mentioned here that the adsorption energy of NH₃ and DPE have been used carefully to measure and to predict the acidic properties of doped AlPO-34 [15], H-MOR [16], and doped AlPO-5 [17]. The choice of these molecular sieves was made on the basis of their potential applications to several industrial processes [13,18,19].

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2. Models and computational details

2.1. Models

To understand the effect of replacing oxygen in the framework by CH₂ or NH group, we started by considering the following molecular species, H₃SiOSiH₃, H₃SiCH₂SiH₃, and H₃SiNHSiH₃ as shown in Fig. 1a–c, respectively. The choice of these molecules was made on the basis of the available experimental geometries for H₃SiOSiH₃. This allows making a direct comparison between the calculated and the experimental parameters.

Chabazite (CHA) structure has three-dimensional small pores controlled by 8-membered ring (8-MR) channels [20]. The unit cell (UC) of the acidic structure has the formula (HAlSi₁₁O₂₄) and contains equivalent silicon atoms in the tetrahedral (T) positions. Creation of Brønsted acid site was achieved by replacing Si with Al. To keep charge neutrality, a proton was attached to the bridging oxygen O₂ in the 8-MR. The SiOSi in chabazite framework (Fig. 2a) was modified to SiCH₂Si in H-ZOL-C and to SiNHSi in H-ZOL-N as shown in Fig. 2b and c, respectively.

2.2. Computational details

Geometry optimizations and energy calculations were carried out by periodic density functional theory (PDFT) employing the Dmol³ program in the MS Modelling 4.0 package [21–23], at the generalized gradient approximation (GGA) level with the Hamprecht, Cohen, Tozer, and Handy (HCTH) exchange and correlation functional [24–26]. It has been shown that HCTH functional has a greater universality than the previous GGA functionals and performs well with systems of weak interactions [24–26]. Furthermore, HCTH was selected among many other functionals to describe the weak interaction between metal organic framework and hydrogen [27]. Double numerical basis set with polarization functions (DNP) has been used in all calculations carried out in this study. This basis set is comparable to 6-31G** set: however, the numerical basis set is much better than the Gaussian basis set of the same size [22,23]. The convergence thresh-

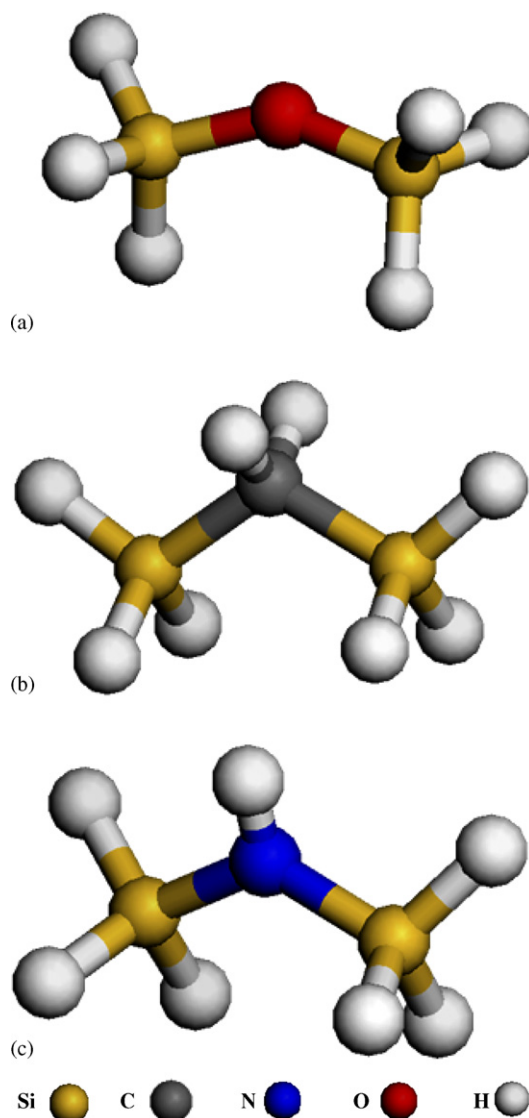


Fig. 1. Three-dimensional optimized structures of the H₃SiOSiH₃ (a), H₃SiCH₂SiH₃ (b), and H₃SiNHSiH₃ (c) molecules.

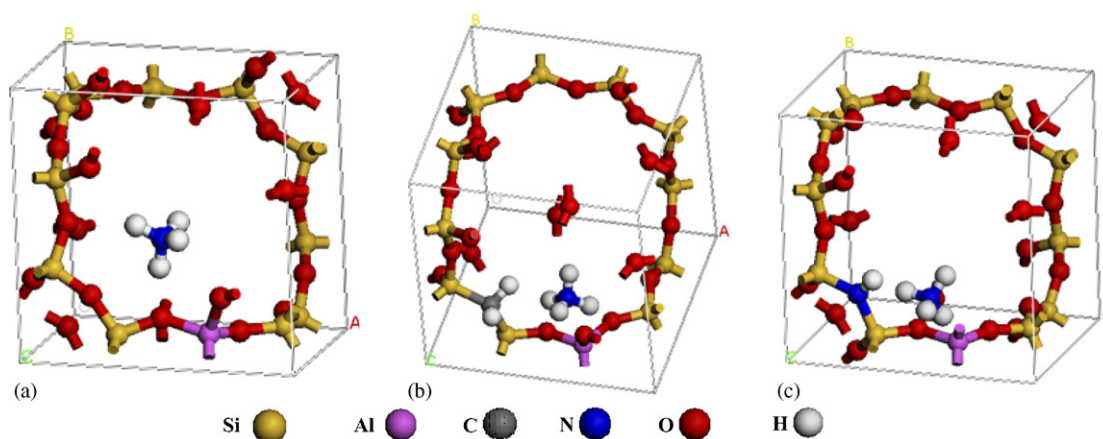


Fig. 2. Three-dimensional optimized periodic models of NH₄-CHA (a), NH₄-ZOL-C (b), and NH₄-ZOL-N (c).

old tolerance was set as follows: total energy = 2×10^{-5} Ha; force = 4×10^{-3} Ha/Å; displacement = 0.01 Å. The adsorption energy E_{ads} was calculated as

$$E_{\text{ads}} = E_{\text{NH}_4\text{-M}} - E_{\text{H-M}} - E_{\text{NH}_3}$$

where E_{ads} , $E_{\text{NH}_4\text{-M}}$, $E_{\text{H-M}}$, and E_{NH_3} refer to the calculated adsorption energy, total energy of the adsorption complex, energy of the acidic molecular sieve, and the energy of free ammonia, respectively. Deprotonation energy (DPE), the energy required to detach a proton from an acidic molecular sieve, was calculated as

$$\text{DPE} = E_{\text{M}} - E_{\text{H-M}}$$

In DFT, the ground state energy $E[\rho]$ of an atom or a molecule is expressed in terms of its electron density $\rho(r)$. The first and second partial derivatives of $E[\rho]$ with respect to the number of electrons N , under the constant external potential $v(r)$ that also includes the nuclear potential, are defined as the chemical potential $\mu = (\delta E/\delta N)_{v(r)}$ and the global hardness $\eta = (\delta^2 E/\delta N^2)_{v(r)}$ of the system, respectively [28,29]. The inverse of the global hardness is the global softness $S = 1/2\eta$. The operational definition of η and μ are obtained by the finite difference approximations for the energies of N , $(N+1)$, and $(N-1)$ electron systems as $\mu \approx -(\text{IP} - \text{EA}/2)$, $\eta \approx (\text{IP} - \text{EA}/2)$, where IP and EA are the first vertical ionization energy and electron affinity of the chemical species, respectively [30].

A particular site selectivity can not, however, be investigated using the global descriptors of reactivity. An appropriate local descriptor, the local softness $s(r)$ is given as $s(r) = (\delta\rho(r)/\delta\mu)_{v(r)}$ keeping that $\int s(r)dr = S$. The local softness can be rewritten as $s(r) = (\delta\rho(r)/\delta N)_{v(r)}(\delta N/\delta\mu)_{v(r)} = f(r)S$ where $f(r)$ is defined as the Fukui function (FF) [31]. Hence, the local softness contains the same information as the FF (i.e., the sensitivity of a system to a local external potential [32]) as well as additional information about the molecular softness. Using left and right derivatives with respect to the number of electrons, electrophilic and nucleophilic FF and local softness can be defined. To describe the site selectivity or reactivity it is then necessary to condense the values of $f(r)$ and $s(r)$ around each atomic site into a single value that characterizes the atomic contribution in a molecule. This can be achieved by electron population analyses. Therefore, for an atom x in a molecule one has $f_x^- = q_x - q_x^{\text{cation}}$, $f_x^+ = q_x^{\text{anion}} - q_x$ where f_x^- corresponds to the reactivity with respect to electrophilic attack. Conversely, f_x^+ corresponds to the reactivity with respect to nucleophilic attack. q_x refers to the atomic-centered charge that can be computed from Mulliken [33] or Hirshfeld [34] population analysis. The local softness for an atom x is then calculated by multiplying the corresponding FF by the global softness S :

$$s_x^+ = f_x^+ S, \quad s_x^- = f_x^- S$$

Recently, Roy et al. proposed that relative electrophilicity (s_x^+/s_x^-) and relative nucleophilicity (s_x^-/s_x^+), i.e., the ratio of electrophilic and nucleophilic local softnesses and its inverse, are more reliable descriptors to locate the preferable sites for nucleophilic and electrophilic attack, respectively, within a molecule

[35]. Deka et al. used the relative electrophilicity (s_x^+/s_x^-) as a local reactivity descriptor in predicting the strength of Lewis acidity for alkali cation-exchanged zeolites [36,37]. Furthermore, Chatterjee used the (s_x^+/s_x^-) values to rationalize the effect of dopants on Brønsted and Lewis acidity of isomorphously substituted aluminophosphate-34 structures [38]. We here also calculated the relative electrophilicity (s_x^+/s_x^-) to measure the reactivity of the acidic proton in the bridging O–H, of the investigated molecular sieves, toward a nucleophilic attack.

3. Results and discussion

Table 1 presents the optimized structural parameters for $\text{H}_3\text{SiOSiH}_3$, $\text{H}_3\text{SiCH}_2\text{SiH}_3$, and $\text{H}_3\text{SiNHSiH}_3$ molecules, which are shown in Fig. 1a–c, respectively. It can be seen that the calculated structural geometries for $\text{H}_3\text{SiOSiH}_3$ (Si–O = 1.651 Å, SiOSi = 144.9°) are in very good agreement with the experimental parameters (Si–O = 1.634 Å, SiOSi = 144.1°) [39]. Furthermore, modifications of $\text{H}_3\text{SiOSiH}_3$ by substituting oxygen by CH_2 or NH lead to structural changes. These changes are described by a decrease of the bond angle in the order SiOSi (144.9°) > SiNHSi (129.1°) > SiCH₂Si (117.5°) and an increase of the bond length in the order Si–O (1.651 Å) < Si–N (1.740 Å) < Si–C (1.886 Å). Therefore, introducing NH instead of oxygen in the $\text{H}_3\text{SiOSiH}_3$ molecule induces smaller structural changes as compared to CH_2 . Reactivity descriptors toward an electrophilic attack like Fukui function (f_x^-) and local softness (s_x^-) are calculated using the Mulliken (MPA) and Hirshfeld (HPA) population analyses as shown in Table 1, for O, C, and N atoms in these molecules as a measure of their basic properties. Results in Table 1 show that f_x^- (MPA) values for O (0.202), C (0.043), and N (0.258) have a similar trend as s_x^- (MPA) values for O (0.814), C (0.150), and N (1.159). This indicates the relative basicity order N > O > C. f_x^- (HPA) values O (0.184), C (0.115), N (0.241) and s_x^- (HPA) values O (0.741), C (0.400), N (1.082) ensure the above basicity trend in $\text{H}_3\text{SiOSiH}_3$, $\text{H}_3\text{SiCH}_2\text{SiH}_3$, and $\text{H}_3\text{SiNHSiH}_3$ molecules.

Table 2 summarizes the optimized structural parameters for the periodic models of the acidic molecular sieves, viz., H-CHA, H-ZOL-C, and H-ZOL-N. Replacing the lattice oxygen

Table 1
Optimized structural parameters for $\text{H}_3\text{SiOSiH}_3$, $\text{H}_3\text{SiCH}_2\text{SiH}_3$, and $\text{H}_3\text{SiNHSiH}_3$ molecules

| | $\text{H}_3\text{SiOSiH}_3$ | $\text{H}_3\text{SiCH}_2\text{SiH}_3$ | $\text{H}_3\text{SiNHSiH}_3$ |
|---------------|-----------------------------|---------------------------------------|------------------------------|
| Si–x | 1.651 (1.634) ^a | 1.886 | 1.740 |
| Si–x–Si | 144.1 (144.1) ^a | 116.4 | 129.1 |
| S (a.u.) | 4.030 | 3.478 | 4.491 |
| f_x^- (MPA) | 0.202 | 0.043 | 0.258 |
| s_x^- (MPA) | 0.814 | 0.150 | 1.159 |
| f_x^- (HPA) | 0.184 | 0.115 | 0.241 |
| s_x^- (HPA) | 0.741 | 0.400 | 1.082 |

Fukui functions (f_x^-) and local softness (s_x^-), x referring to O, C or N computed on the basis of the Mulliken (MPA) and Hirshfeld (HPA) population analyses as well as global softness (S). Bond distances are given in (Å) and angles in (°).

^a The available experimental values [39] are given between parentheses.

Table 2
Optimized structural parameters for periodic models of the acidic molecular sieves of CHA topology

| | H-CHA | H-ZOL-C | H-ZOL-N |
|-----------------------------------|--------|---------|---------|
| O ₂ –H _p | 0.966 | 0.966 | 0.965 |
| Al–O _b | 1.892 | 1.891 | 1.880 |
| Si–O _b | 1.702 | 1.726 | 1.711 |
| Si–x | 1.617 | 1.845 | 1.703 |
| ∠Si–x–Si | 147.6 | 121.5 | 130.4 |
| ∠Al–O ₂ –Si | 133.2 | 138.2 | 134.2 |
| qH _p | 0.349 | 0.345 | 0.311 |
| f _x [−] (MPA) | 0.012 | 0.004 | 0.122 |
| s _x [−] (MPA) | 0.055 | 0.018 | 0.693 |
| f _x [−] (HPA) | 0.012 | 0.009 | 0.115 |
| s _x [−] (HPA) | 0.055 | 0.040 | 0.653 |
| DPE (kJ/mol) | 1349.1 | 1355.4 | 1374.5 |

Fukui functions (f_x[−]) and local softness (s_x[−]) x referring to O, C or N are computed on the basis of the Mulliken (MPA) and Hirshfeld (HPA) population analyses. Bond distances are given in (Å), angles in (°), Mulliken charges q in (e[−]), and deprotonation energy (DPE) in (kJ/mol).

by CH₂ or NH in the acidic structures decreases the Si–x–Si (x = O, C or N) bond angles as follows: SiOSi (147.6°) > SiNHSi (130.4°) > SiCH₂Si (121.5°). Furthermore, the Si–x bond length increases in the order Si–O (1.617 Å) < Si–N (1.703 Å) < Si–C (1.845 Å). These trends are similar to the ones observed above for the molecules shown in Fig. 1. The longer Si–C as compared to Si–O and Si–N is accompanied by a smaller SiCSi (121.5°), which tends to contract the UC. This explains the small changes in the UC of the new ZOL sieves observed experimentally [5] despite the replacement of Si–O by Si–C. It should be pointed here that for CH₂ and NH doped sodalite, a similar trend of bond angles was observed SiNHSi (133.2°) > SiCH₂Si (119.1°) [7].

Fukui function (f_x[−]) and local softness (s_x[−]) values based on the MPA scheme for the lattice O, C, and N are (0.012, 0.004, and 0.122) and (0.055, 0.018, and 0.693), respectively. Therefore, the most basic site is the N atom in the lattice, i.e., N is the most reactive site toward the interaction with an electrophile. Results from (f_x[−]) and (s_x[−]) based on the HPA scheme are consistent with those obtained on the basis of MPA. These results also confirm the basicity order of the lattice atoms: N > O > C. Indeed cluster models of zeolites including NH group showed a significant activity as a bifunctional catalyst [8]. It should be mentioned here that the basicity order of these lattice atoms is similar to the one obtained above for the smaller molecules, viz., H₃SiOSiH₃, H₃SiCH₂SiH₃ and H₃SiNHSiH₃.

The acidity trend is not clear when considering the O–H_p distances. However, the proton charge (qH_p) results

Table 3
Optimized structural parameters for periodic models of the molecular sieves of CHA topology after NH₃ adsorption, x referring to O, C or N

| | NH ₄ -CHA | NH ₄ -ZOL-C | NH ₄ -ZOL-N |
|--------------------------------|----------------------|------------------------|------------------------|
| O ₂ –H _p | 1.795 | 1.732 | 1.581 |
| N–H _p | 1.051 | 1.056 | 1.079 |
| Al–O ₂ | 1.779 | 1.774 | 1.778 |
| Si–O ₂ | 1.602 | 1.616 | 1.618 |
| Si–x | 1.639 | 1.850 | 1.705 |
| ∠Si–x–Si | 154.8 | 123.2 | 132.4 |
| ∠Al–O ₂ –Si | 138.9 | 139.6 | 132.0 |
| E _{ads} (kJ/mol) | −128.8 | −117.9 | −108.5 |

Bond distances are given in (Å), angles in (°), and adsorption energy of ammonia in (kJ/mol).

indicate the following acidity order: H-CHA (0.349e[−]) > H-ZOL-C (0.345e[−]) > H-ZOL-N (0.311e[−]). DPE for the acidic structures increases as: H-CHA (1349.1 kJ/mol) < H-ZOL-C (1355.4 kJ/mol) < H-ZOL-N (1374.5 kJ/mol). This clearly shows that the Brønsted acid site strength decreases in the order: H-CHA > H-ZOL-C > H-ZOL-N.

Table 3 presents the optimized structural parameters for the periodic models of the molecular sieves of CHA topology after NH₃ adsorption, i.e., NH₄-CHA, NH₄-ZOL-C, and NH₄-ZOL-N, as well as the adsorption energy values. It can be seen that there is NH₄⁺ formation after NH₃ adsorption on all protonic structures. This is confirmed by the following changes. First, the increase of O–H distances (1.795, 1.732, and 1.581 Å) as compared to those of the acidic structures H-CHA, H-ZOL-C, and H-ZOL-N (0.966, 0.966, and 0.965 Å), respectively. Second, the decrease of the N–H_p distances (1.051, 1.056, 1.079 Å) to form N–H_p bonds. Third, the decrease of the negative charge of N after the adsorption (−0.385, −0.386, and −0.329e[−]) as compared to that in free NH₃ molecule (−0.528e[−]). Si–x bond length in H-CHA, H-ZOL-C, and H-ZOL-N structures are Si–O (1.639 Å), Si–C (1.850 Å), and Si–N (1.705 Å), respectively. Therefore, there are not any significant changes in Si–x bond length in these structures after NH₃ adsorption as compared to those in the acidic ones. The same can be noticed for Si–x–Si bond angles. The calculated adsorption energies of ammonia on the acidic structures H-CHA, H-ZOL-C, and H-ZOL-N are −128.8, −117.9, and −108.5 kJ/mol, respectively. This indicates a similar acidity trend obtained earlier from the DPE results: H-CHA > H-ZOL-C > H-ZOL-N. The calculated values are in reasonable agreement with the experimental adsorption energies for low ammonia loading in various zeolites, which fall in the range −106 to −164 kJ/mol [40]. Taking into account the

Table 4
Global softness, Fukui functions, local softness, and (s_x⁺/s_x[−]) values for the protons of the bridging O–H groups in periodic models of the acidic molecular sieves of CHA topology using the Mulliken (MPA) and Hirshfeld (HPA) population analyses

| Acidic structure | Global softness, S (a.u.) | MPA derived parameters | | | | | HPA derived parameters | | | | |
|------------------|---------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|--|-----------------------------|-----------------------------|-----------------------------|-----------------------------|--|
| | | f _x ⁺ | s _x ⁺ | f _x [−] | s _x [−] | s _x ⁺ /s _x [−] | f _x ⁺ | s _x ⁺ | f _x [−] | s _x [−] | s _x ⁺ /s _x [−] |
| H-CHA | 4.619 | 0.317 | 1.464 | 0.011 | 0.051 | 28.706 | 0.117 | 0.540 | 0.007 | 0.032 | 16.875 |
| H-ZOL-C | 4.419 | 0.267 | 1.179 | 0.011 | 0.049 | 24.061 | 0.098 | 0.433 | 0.008 | 0.035 | 12.371 |
| H-ZOL-N | 5.682 | 0.327 | 1.858 | 0.015 | 0.085 | 21.859 | 0.123 | 0.699 | 0.011 | 0.062 | 11.274 |

long range electrostatic potential of the CHA crystal, Teunissen et al. calculated the adsorption energy of NH_4^+ as -117 kJ/mol [10,12]. An earlier computational study also reported an adsorption heat of -114 kJ/mol for NH_3 in CHA [41].

Table 4 shows the global softness, Fukui functions, local softness, and the relative electrophilicity (s_x^+/s_x^-) for the protons of the bridging O–H groups in periodic models of the acidic structures of CHA topology, viz., H-CHA, H-ZOL-C, and H-ZOL-N, using the Mulliken (MPA) and Hirshfeld (HPA) population analyses. (s_x^+/s_x^-) indicates the nucleophilicity of the bridging hydroxyl proton and therefore represents its Brønsted acidity. One can see that the (s_x^+/s_x^-) values based on MPA for the acidic structures H-CHA (28.706) > H-ZOL-C (24.061) > H-ZOL-N (21.859) reflect the same trend as the (s_x^+/s_x^-) values based on HPA: H-CHA (16.875) > H-ZOL-C (12.371) > H-ZOL-N (11.274). These indicate the following order of Brønsted acidity: H-CHA > H-ZOL-C > H-ZOL-N. Chatterjee found that (s_x^+/s_x^-) values give clear acidity trend as compared to local softness values for transition metal ions doped AlPO-34 models [38].

4. Conclusions

Highly accurate and computationally time consuming periodic density functional calculations have been carried out on models of novel zeolites with organic lattices, viz., ZOL-C and ZOL-N to predict their acidic properties and compare them to the acidity of the normal zeolite structure of chabazite (CHA) topology. The adsorption energy of ammonia, deprotonation energy, and relative electrophilicity (s_x^+/s_x^-) showed that the Brønsted acid site strength of the acidic structures decreases in the order: H-CHA > H-ZOL-C > H-ZOL-N. Furthermore, the small structural changes upon the replacement of oxygen suggest the easier incorporation of NH as compared to CH_2 in the framework.

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References

- [1] A.P. Wight, M.E. Davis, Chem. Rev. 102 (2002) 3589.
- [2] S. Inagaki, S. Guan, T. Ohsuna, O. Terasaki, Nature 416 (2002) 304.

- [3] M.P. Kapoor, A. Bhaumik, S. Inagaki, K. Kuraoka, T. Yazawa, J. Mater. Chem. 12 (2002) 3078.
- [4] M.P. Kapoor, A.K. Sinha, S. Seelan, S. Inagaki, S. Tsubota, H. Yoshida, M. Haruta, Chem. Commun. (2002) 2902, and references cited therein.
- [5] K. Yamamoto, Y. Sakata, Y. Nohara, Y. Takahashi, T. Tatsumi, Science 300 (2003) 470.
- [6] K. Yamamoto, Y. Nohara, Y. Domon, Y. Takahashi, Y. Sakata, J. Plévert, T. Tatsumi, Chem. Mater. 17 (2005) 3913.
- [7] R. Astala, S.M. Auerbach, J. Am. Chem. Soc. 126 (2004) 1843.
- [8] D. Lesthaeghe, V. Van Speybroeck, M. Waroquier, J. Am. Chem. Soc. 126 (2004) 9162.
- [9] D. Lesthaeghe, V. Van Speybroeck, G.B. Marin, M. Waroquier, J. Phys. Chem. B 109 (2005) 7952.
- [10] E.H. Teunissen, C. Roetti, C. Pisani, A.J.M. de Man, A.P.J. Jansen, R. Orlando, R.A. van Santen, R. Dovesi, Modelling Simul. Mater. Sci. Eng. 2 (1994) 921.
- [11] E.H. Teunissen, A.P.J. Jansen, R.A. van Santen, R. Orlando, R. Dovesi, J. Chem. Phys. 101 (1994) 5865.
- [12] S.P. Yuan, J.G. Wang, Y.W. Li, S.Y. Peng, J. Mol. Catal. A 178 (2002) 267.
- [13] M. Stöker, Micropor. Mesopor. Mater. 29 (1999) 3.
- [14] J.F. Haw, W. Song, D.M. Marcus, J.B. Nicholas, Acc. Chem. Res. 36 (2003) 317.
- [15] M. Elanany, M. Koyama, M. Kubo, P. Selvam, A. Miyamoto, Micropor. Mesopor. Mater. 71 (2004) 51.
- [16] M. Elanany, D.P. Vercauteren, M. Koyama, M. Kubo, P. Selvam, E. Broclawik, A. Miyamoto, J. Mol. Catal. A 243 (2006) 1.
- [17] M. Elanany, D.P. Vercauteren, M. Kubo, A. Miyamoto, J. Mol. Catal. A 248 (2006) 181.
- [18] D.B. Akolekar, J. Catal. 149 (1994) 1.
- [19] Y. Wei, D. Zhang, Z. Liu, B.-L. Su, J. Catal. 238 (2006) 46.
- [20] W.M. Meier, D.H. Olson, Ch. Baerlocher, Atlas of Zeolite Framework Types, 5th rev. ed., Elsevier, London, 2001.
- [21] <http://www.accelrys.com/>
- [22] B. Delley, J. Chem. Phys. 92 (1990) 508.
- [23] B. Delley, J. Chem. Phys. 113 (2000) 7756.
- [24] F.A. Hamprecht, A.J. Cohen, D.J. Tozer, N.C. Handy, J. Chem. Phys. 109 (1998) 6264.
- [25] A.D. Boese, N.L. Doltsinis, N.C. Handy, M. Sprik, J. Chem. Phys. 112 (2000) 1670.
- [26] A.D. Boese, N.C. Handy, J. Chem. Phys. 114 (2001) 5497.
- [27] D. Kim, T.B. Lee, S.B. Choi, J.H. Yoon, J. Kim, S.-H. Choi, Chem. Phys. Lett. 420 (2006) 256.
- [28] R.G. Pearson, J. Am. Chem. Soc. 85 (1963) 3533.
- [29] R.G. Parr, R.G. Pearson, J. Am. Chem. Soc. 105 (1983) 7512.
- [30] R.G. Parr, W. Yang, Density-Functional Theory of Atoms and Molecules, Oxford University Press, New York, 1989.
- [31] R.G. Parr, W. Yang, J. Am. Chem. Soc. 106 (1984) 4049.
- [32] R.F. Nalewajski, R.G. Parr, J. Chem. Phys. 77 (1982) 399.
- [33] R.S. Mulliken, J. Chem. Phys. 23 (1955) 1833.
- [34] F.L. Hirshfeld, Theor. Chem. Acta 44 (1977) 129.
- [35] R.K. Roy, S. Krishnamurti, P. Geerlings, S. Pal, J. Phys. Chem. A 102 (1998) 3746.
- [36] R.Ch. Deka, K. Hirao, J. Mol. Catal. 181 (2002) 275.
- [37] R.Ch. Deka, R.K. Roy, K. Hirao, Chem. Phys. Lett. 389 (2004) 186.
- [38] A. Chatterjee, J. Mol. Graph. Model. 24 (2006) 262.
- [39] D.R. Lide, Handbook of Chemistry and Physics, 84th ed., CRC Press, Washington, DC, 2004, pp. 9–21.
- [40] G.I. Kapstin, T.R. Brueva, I.V. Mishin, in: M.M.J. Treacey, B.K. Marcus, M.E. Bisher, J.B. Higgins (Eds.), Proceedings of the 12th International Zeolite Conference, Materials Research Society, Warrendale, PA, 1999, p. 2637.
- [41] M. Brändle, J. Sauer, J. Am. Chem. Soc. 120 (1998) 1556.