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Proton affinity differences in zeolite: A DFT study

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Abstract

In this study we examine the influence of the chemical composition (aluminum content) on structure and proton affinity of zeolite models using first principle density functional procedures. It is shown that changes in the zeolite's aluminum content have a very significant effect on the proton affinity of neighboring protons, making low aluminum zeolites more acidic than high aluminum zeolites. The proton location is also studied.

Keywords: Zeolite; Proton affinity; Density functional theory

1. Introduction

Zeolites are widely used as catalysts in chemical and oil industries. The bridging OH groups of zeolites function as acidic sites in their application in catalysis. As these sites play an important role in most catalytic processes, it is worthwhile to determine the main factors which govern their properties. Because of the difficulties and ambiguities connected with the experimental determination of the acidity of Brønsted sites in zeolites, quantum chemical calculations have been used to study the properties of the bridging OH groups. Although there is no proper definition of acid strength for a solid acid, generally the proton binding energy has been used as a measure of Brønsted acidity. Indeed, there are extensive works on the theoretical determination of acidity from the proton affinity (PA) of small zeolite clusters [1–7]. A detailed account of

such works can be found in the reviews of Beran [8] and Sauer [9,10]. It is now well known that the acidity of the bridging OH group is influenced by both structural characteristics and chemical composition of the zeolites. However, the extent of such influence is yet to determine conclusively. The study of the structurally induced differences in Brønsted acidity is more difficult than that of chemically induced differences, since it requires accurate modelling of entire zeolite lattice. In the present work, we like to address the effect of chemical composition on Brønsted acidity and change in local structure in zeolites from first principle quantum chemical calculations based on density functional theory (DFT).

A 4-ring cluster has been taken for the systematic study of the effect of Al concentration on Brønsted acidity. A finite model always suffers from two uncertainties: the first is due to the uncertainties of the quantum chemical technique and the second arises from the incom-

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pleteness of the model. Hence it is important to know a priori the effect of these approximations on the properties concerned. There are numerous ab initio MO and DFT studies on the theoretical determination of PA of zeolites and thus merits and demerits of these methods are well documented [6–10]. Moreover, it has recently been observed [11,12] that non-local density functional calculation with Perdew's exchange [13] and Proynov's correlation functional [14] (the procedure henceforth referred as PLAP) can be used for the accurate calculation of PA. We use both local and non-local density functional procedures in the present work. In view of the small size of the cluster, we must emphasize that the results obtained from the present calculation may not correspond directly to any particular zeolite. However, it can be taken as the smallest possible model for studying systematically the effect of chemical composition on Brønsted acidity of zeolites. Moreover, combined QM and force field calculations on clusters and extended systems have shown that relaxation is a local property, justifying the geometry optimized zeolite clusters are good model systems for the extended zeolites [15]. Geometry optimized clusters can thus be taken as a reasonable first step toward the modelling of the zeolite lattice.

We have taken a 4-ring cluster from a zeolite of faujasite type structure [16] and consider different possibilities of Al and proton substitution. Recently, Kramer and van Santen [17] made a similar study on a symmetrical hypothetical 4-ring cluster by using ab initio MO techniques. They, along with others [18], observed that two aluminum atoms will avoid neighboring tetrahedra because this is energetically disadvantageous, requiring approximately 1 eV. This observation is in line with the empirical Loewenstein rule. In this context, it is worth to mention the interesting study by Schroeder and Sauer [19]. They pointed out that a structure with Al–O–Si–O–Al linkage is more stable than a structure where two aluminum atoms separated as far as possible. A bridging OH

group represents a large local distortion in a pure silica framework. Hence, effect of such distortion will be the smallest if two such defects are paired and the framework is distorted at only one location. It is also known that while metal ions occupy positions within zeolite structure which are favored by global electrostatic interactions, protons bind directly to a particular oxygen site. Moreover, Kramer and van Santen [17] ruled out the possibility of proton delocalization, recently proposed by Derouane et al. [20], and concluded that there is a one to one coupling between Al-substitution and protons. Most of the theoretical calculations mentioned above are suffering from two shortcomings, first due to the poor quality of the basis set and secondly due to lack of electron correlation effects. It is well-known that DFT is an easy and expedient way to include electron correlation in the electronic structure calculations. Our aim is to ascertain whether a density functional study would lead to similar conclusions and to estimate the extent and magnitude of the effect of chemical composition on Brønsted acidity in a zeolite. Additionally, we obtain some structural information (e.g., deformations upon Al and proton substitution) from the present study.

2. Model and method

The 3D structure of the cluster model chosen for this study is displayed on Fig. 1 with the same labelling of oxygen atoms as in faujasite. The various possibilities of Al and proton substitution are illustrated on Fig. 2. The dangling bonds have been saturated by hydrogen atoms with O–H distance of 0.96 Å and the OH bonds are aligned with the corresponding O–Si bonds in the faujasite structure. During the geometry optimization the terminal O and H atoms are held fixed and all the other atoms of the ring were allowed to vary. The density functional calculations were performed within the LCGTO-DF formalism [21–23] using the DeMon program package [24–26]. Geometry opti-

mizations were performed at the local level of theory using the Dirac–Slater exchange term [27] and the Vosko–Wilk–Nusair (VWN) [28] parametrization for the correlation energy. For Si (or Al) and O, (6321/521/1) and (5211/411/1) orbital basis sets with corresponding (5, 4; 5, 4) and (5, 2; 5, 2) auxiliary bases were employed respectively. (41/1) orbital and (5, 1; 5, 1) auxiliary basis sets were used for H-atom. PLAP calculations were performed only for some key configurations and with the optimized geometry obtained at the local level of theory and using the same bases as mentioned above.

3. Results and discussion

Table 1 presents the total energies at the stationary points of the various 4-ring clusters shown in Fig. 2. As our prime interest is in the trends of the proton affinity, we focus on PA differences rather than on absolute values. However, as we already mentioned that quantitative PA can be obtained from PLAP calculations. But as the geometries are not optimized with PLAP, it's better to look on the PA differences between different configurations. Table 2 shows the PA values of different 4-ring clusters. One can easily notice various points from Tables 1 and 2. As expected, in the case of low aluminum zeolites, i.e. only one Si is replaced by Al, the highest PA is observed for the Si–O–Al bridge. There are two possibilities of placing the charge balancing proton (either O₁ or O₂ in configuration 2d, which corresponds to O₁ and O₂ in the normal nomenclature of faujasite) leading to different proton affinities. However, the O₁–H bond is stronger than O₂–H since the corresponding PA is larger by 8 kJ mol⁻¹. When there are many ways of placing the proton, the reported configuration corresponds to the minimum in energy. On the other hand, the protonated form on O₁ (Fig. 2d) is about 84 kJ mol⁻¹ (81 kJ in PLAP) more stable than the 4-ring where protonation site is the oxygen

atom of a Si–O–Si bridge (Fig. 2e). The difference in PA is smaller than what Kramer and van Santen found from their calculations on 4-ring clusters [17]. Although the two oxygen sites are not same and small PA differences may result from that difference but the large PA difference between these two configurations are certainly due to the basic nature of the bridge. This clearly shows that the proton is necessarily localized on a Si–O–Al bond. This is not always the case for another cation, since experimental structures of Na–X zeolites show that Na⁺ may be located on a Si–O–Si unit [29]. It also implies that acidity differences in different zeolites arise due to the differences in acidic properties of Si–OH–Al units.

Considering now the models with a ratio Si/Al = 1 (configurations shown in Fig. 2f–j), we note that the configuration bearing a negative charge (Fig. 2g) has, as expected, a very high proton affinity compared to the low aluminum model. Charge compensation requires two protons to be present in the 4-ring of high aluminum clusters. Here again, there are many possibilities of placing two protons in the 4-ring. However, they reduce, in fact, into three categories (i) the protons are farthest apart (Fig. 2i), (ii) the protons are next to an aluminum atom (Fig. 2h) and (iii) the protons are next to a silicon atom (Fig. 2j). The energies and proton affinities of the most stable configuration of

Table 1
The total energies at the stationary points of various 4-ring clusters obtained from density functional calculations at local level of theory

| Figure Ref. No. | Configuration | Energy (a.u.) |
|-----------------|--------------------------------------|---------------|
| Fig. 2a | SiSiSiSi | -2055.26073 |
| Fig. 2b | Si ^H SiSiSi | -2055.57364 |
| Fig. 2c | SiAlSiSi | -2008.40664 |
| Fig. 2d | Si ^H AlSiSi | -2008.88211 |
| Fig. 2e | SiAlSiSi ^H | -2008.84990 |
| Fig. 2f | SiAlSiAl | -1961.41438 |
| Fig. 2g | Si ^H AlSiAl | -1962.03444 |
| Fig. 2h | Si ^H Al ^H SiAl | -1962.50924 |
| Fig. 2i | Si ^H AlSi ^H Al | -1962.52204 |
| Fig. 2j | Si ^H AlSiSi ^H | -1962.49264 |

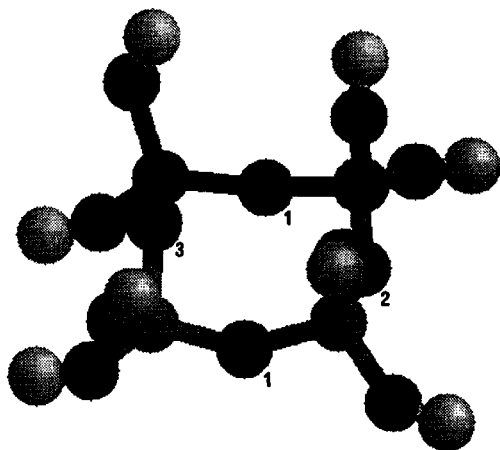


Fig. 1. 4-membered ring used in the present calculations. The bridging oxygen atoms are numbered following the same way as in faujasite.

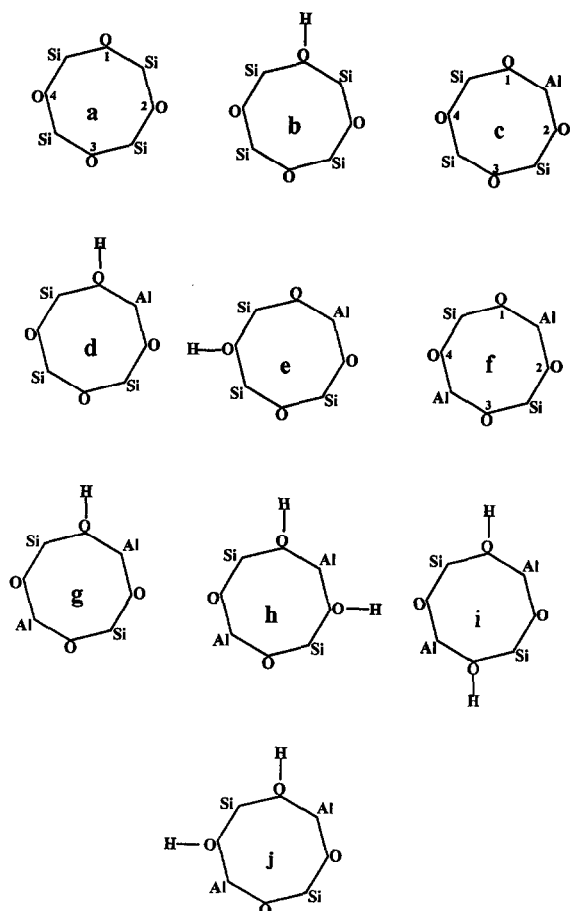


Fig. 2. Schematic diagrams of various 4-rings with different possibilities of Al and proton substitution.

Table 2

The proton affinities (in kJ/mol) of various 4-ring clusters

| Figure Ref. No. | Configuration | PA (VWN) | PA (PLAP) |
|-----------------|--------------------------------------|-------------------|-------------------|
| Fig. 2b | Si ^H SiSiSi | 822 | |
| Fig. 2d | Si ^H AlSiSi | 1248 | 1296 |
| Fig. 2e | SiAlSiSi ^H | 1164 | 1215 |
| Fig. 2g | Si ^H AlSiAl | 1628 | 1705 |
| Fig. 2h | Si ^H Al ^H SiAl | 1246 ^a | 1305 ^a |
| Fig. 2i | Si ^H AlSi ^H Al | 1280 ^a | 1351 ^a |
| Fig. 2j | Si ^H AlSiSi ^H | 1203 ^a | 1274 ^a |

^a Values correspond to single proton abstraction.

each type are mentioned in Tables 1 and 2 respectively. The minimum energy configuration of the first type are nearly 34 and 77 kJ mol⁻¹ more stable than the configurations of second and third type respectively. When going from low to high aluminum clusters (i.e., from one Al to two Al), substituting Si–O–Si by Si–OH–Al, the PA increases by 32 and 55 kJ mol⁻¹ for VWN and PLAP respectively. Thus intrinsic Brønsted acidity decreases with increasing Al concentration. Decreasing heterolytic proton bond dissociation energy with increasing Si/Al ratio was also observed from experiment [30]. Here again, smaller PA differences has been obtained from the present DFT calculation between any two configurations than the reported values in Ref. [17]. The effect of Al concentration will certainly be more pronounced for extended systems because out of six possible T-atom substitution only two are substituted in the present study. Hence acidity of the Si–OH–Al unit is influenced by the 2nd shell of T-atoms, making low Al zeolites more acidic than high Al zeolites. With the increase in Al content, the deprotonation energy increases for a cluster with two protons (Fig. 2i) as well as negatively charged clusters (Fig. 2g).

It is also interesting to compare the minimum energy structures obtained from the present study to those obtained from other kinds of theoretical studies. First, we compare the structural parameters of low aluminum models. There are recent force field and ab initio MO calcula-

tions [19,31] on high silica faujasite models. Bond lengths and bond angles of the bridging Si–OH–Al unit obtained from different methods are presented in Table 3. The geometry of the Si–OH–Al unit is reproduced without large variations by all methods, although our calculation yield a slightly longer Al–O bond. This may be due to the fact that initial structure used in our calculation and other calculations mentioned here are not same. Moreover, the restrictions on the movement of the border atoms may introduce some strain in the optimized structure. Anyway, it is clear from the table that structure of the Si–OH–Al unit is well reproduced by the present DFT calculation. The structural information for bridging OH group is sparse in H-faujasite. Al–H distances of 2.39 and 2.48 ± 0.04 Å were predicted from theoretical calculations and experimental NMR study respectively ([30] and references therein) when O_1 bridging oxygen atom is protonated. The calculated distance of 2.46 Å from the present work compares very well with the experimental value. A large structural distortion occurs when one Si atom is substituted by Al and a proton is attached to the oxygen atom, bridging Si with Al. The Si–O(H) bond increases by a significant amount from its value in the corresponding pure silica framework. The Al–O(H) bond length is much longer than the Si–O(H) bond length. Fig. 3 presents the detailed structures of models Fig. 2g and Fig. 2i with two aluminum atoms. Here again, there is a good agreement with the minimum energy 4-ring structure obtained from ab initio MO calculations. Comparison of the geometries (Fig. 3) shows that protonation on O_3 (in standard nomenclature it is O_1 type of bridging

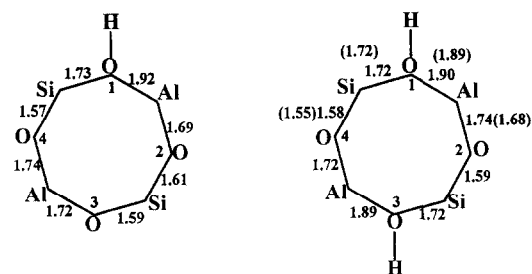


Fig. 3. Structural parameters of the model 4-ring clusters shown in Fig. 2g and Fig. 2i.

oxygen) modifies the structure around O_1 H, in addition to changes around O_3 . In the same time Al– O_3 and Si– O_3 bond lengths increase and Si– O_1 and Al– O_1 bonds decrease upon O_3 protonation. The intermediate Al– O_2 and Si– O_4 bonds increase whereas Si– O_2 and Al– O_4 decrease. This is in consequence of covalent bonding and bond order conservation principle. When one of the bonds to an atom weakens the other bonds become stronger due to availability of more electrons for binding. It is also interesting to notice that Al–O(H) and Si–O(H) bond lengths differ less with increase in Al concentration (Fig. 3). Schroeder and Sauer [19] also observed that the Al–O(H) and Si–O(H) bond lengths differ less in the Al–O–Si–O–Al linkage than in the separated bridging hydroxyls. Compared with separated hydroxyls the Al–O(H) bond length in Al–O–Si–O–Al becomes shorter (1.97 to 1.90 Å) whereas the Si–O(H) bond length becomes longer (1.71 to 1.72 Å).

4. Conclusion

It has been shown that a proton forms the strongest bond with the oxygen atom which bridges Al and Si T-atoms. Protonation on other bridging oxygen atoms is weaker by about 85 kJ mol⁻¹. Hence protons are invariably attached to the Si–O–Al unit. The acidity of the Si–O–Al unit is influenced by the 2nd sphere of T-atoms, making low aluminum zeolites more acidic than high aluminum zeolites. Present calculations

Table 3

Structural parameters obtained for the low aluminum zeolite. Bond lengths and angles are in Angstrom and degree respectively

| Parameter | Present work | Ref. [19] | Ref. [31] | Ref. [32] |
|------------------------------|--------------|-----------|-----------|-----------|
| Si–O(H) | 1.71 | 1.70 | 1.694 | 1.70 |
| Al–O(H) | 1.97 | 1.91 | 1.91 | 1.945 |
| \angle Si–O–Al | 135 | 131.1 | 131.5 | |
| \angle Si–O–H ⁺ | 117.3 | | 123 | 117.5 |

consider only one T-site in the 2nd sphere but in a real zeolite there are many more T-sites. The effect of other T-sites is not negligible as demonstrated by Nicholas and coworkers in their recent studies [7,33]. In presence of full T-site coordination the effect will certainly be more complicated. One needs much bigger zeolite cluster to obtain precise value of PA differences with the variation of protonation site. However, we believe that the present calculations would be useful for the preliminary estimation of PA differences arising out of difference in protonation site. Protons prefer to bind to two bridging oxygen atoms which are farthest apart instead of binding to two near neighbor bridging oxygens. This is expected if one considers the electrostatic interactions of two positive charges, which will be minimum when they are farthest apart. Large structural deformations occur in the isomorphous substitution of Si by Al. The modification of PA due to Al substitution is a covalent process, which can be rationalized from the bond order conservation principle.

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