

The influence of the geometric parameters on the electronic properties of faujasite cluster models as derived from density functional theory and Hartree Fock–self consistent field methods

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Abstract

We report here the results of our density functional theory calculations at local density and nonlocal density approximation levels and Hartree Fock–self consistent field calculations on disilicic acid type cluster models representing faujasite zeolite lattice. The geometric parameters such as Si–O and Al–O bond distances and Si–O–Si, Si–O–Al, O–Si–O and O–Al–O bond angles are derived from the geometry optimization calculations. The predicted geometric parameters are reasonably close to the experimentally reported values, wherever available, except for the slightly overestimated Si–O bond distances. The influence of the geometric parameters on the electronic properties such as total energy, dissociation energy of charge compensating cations and the net charge on bridging oxygen are studied in detail. © 1998 Elsevier Science B.V.

Keywords: Faujasite; Quantum chemical calculations; Geometry versus electronic properties; Density functional theory; HF–SCF

1. Introduction

Zeolites are popular industrial ion-exchangers, adsorbents and catalyst materials; they are microporous materials composed of three dimensional networks of SiO₄ and AlO₄ tetrahedra. The corner sharing between these units in different ways leads to different zeolitic lattices with intriguing pore architecture consisting of channels, cavities and cages. There are more than 100 structurally distinct zeolites, which are

either naturally occurring or man made [1]. Interestingly, the structural differences of all these zeolites arise from the variation of the local geometry of the TO₄ tetrahedra (T–O distance and O–T–O angle) and the ways in which these TO₄ units are connected to others (T–O–T angle, O–T–O–T dihedral angle and T–O–T–O dihedral angle). Almost 95% of all known commercial catalytic applications of these materials come from just five known type of zeolites; namely LTA, MFI, FAU, LTL and MOR [2]. Hence, the design of efficient zeolite catalysts involves finer variations in the above geometric

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parameters to obtain suitable structure for final applications. For the same reason, there have been enormous efforts to study the stability and energetics of zeolite cluster models theoretically and rationalize their dependence on the geometric parameters.

Several cluster models are being used to mimic the three dimensional lattice of zeolite structures and to calculate their electronic properties. A disiloxane ($\text{H}_3\text{Si}-\text{O}_b-\text{SiH}_3$) model has been widely used by Nicholas et al. [3–5] and Brand et al. [6] considering the lesser computational efforts needed. However, the influence of next neighbour atoms and the terminal silanol groups on the electronic characteristics of the central bridging oxygen (O_b) could not be studied by this cluster model. Hence, a disilicic acid $[(\text{OH})_3-\text{Si}-\text{O}_b-\text{Si}-(\text{OH})_3]$ model was used by Derouane and coworkers [7,8], Beran and Kubelkova [9], Vetrivel et al. [10]. Later Stave and Nicholas [11] and Brand et al. [12] also switched over to these cluster models. Sauer [13] made a detailed comparison of these and several other studies which brings out the advantages of using disilicic acid type cluster models over disiloxane type cluster models. The above studies have shown that the electronic characteristics of the central O_b as well as the optimized Si–O bond distance and Si–O–Si bond angles could be simulated well by incorporation of terminal silanol groups as in the case of disilicic acid cluster models. It must be noted that larger cluster models have also been used by Shah et al. [14], Zygmunt et al. [15] and Teunissen et al. [16], but with different aims of understanding the long range effects, electrostatic fields generated, influence of Si/Al ratio as well as the adsorption, diffusion, dissociation and reaction mechanisms. In this paper, we report the electronic properties of the disilicic acid type cluster models representing the active sites in faujasite zeolite lattice, as derived from density functional theory (DFT) and Hartree Fock–self consistent field (HF–SCF) calculations and discuss the influence of local geometry on them.

2. Computational procedure

2.1. Methodology

Self consistent solutions to the DFT [17] equations were calculated using the DEMON package developed by Salahub et al. [18]. This method relies on the solution of single particle equations and hence is computationally efficient. Yet, the method is quite accurate since it can include all many body contributions like exchange and correlation in the one particle effective potential defined by an energy functional. Approximate schemes of the DFT differ in the choice of the functionals. In the present paper, two levels of approximation have been used, namely local density approximation (LDA) using the Dirac–Slater exchange term and the Vosko–Wilk–Nusair (VWN) [19] parametrization for the correlation energy and nonlocal density approximation (NDA), which uses Becke’s [20] gradient corrections of the density for the exchange and Perdew’s [21] correlation energy values. All electron orbital basis sets were used for all atoms. The atomic orbital basis sets for LDA and NDA, which are used to fit the charge density and exchange correlation potential for different atoms are as follows: Si, Al, Li and Na (6321/521/1); O (5211/411/1) and H (41/1) as described in detail elsewhere [22]. We used the restricted HF–SCF calculations with extended basis sets including polarization functions (6-31G^{*}) to calculate the electronic properties and compared these results with the DFT results. HF–SCF calculations were performed with the standard HONDO package version, 7.0 developed by Dupuis et al. [23].

2.2. Models

The atom positions for the disilicic acid type cluster models were derived from the X-ray crystal structure reported for faujasite zeolite [24] with Si/Al \approx 1.2. This report provides the structure, where Si and Al are almost regularly alternating. As discussed earlier, a disilicic acid

type cluster model has several advantages. We have used such a cluster model and its structural analogues in our study as shown in Fig. 1. The faujasite lattice has 4 crystallographically distinct oxygen atoms, namely O_1 , O_2 , O_3 and O_4 . Among these O_1 and O_4 occur in the 12-member ring, whereas O_2 and O_3 occur in the hexagonal prisms connecting the sodalite cages. Cluster models which are centered on all these oxygen sites were generated. Initially both the tetrahedral (T) sites bridged by oxygen were substituted by Si as shown in Fig. 1A. While the geometry of two corner sharing TO_4 groups are derived from the X-ray crystal structure, the terminal hydrogen atoms are fixed at a distance of 0.97 Å from the oxygen atoms. The orientation of the hydrogen atoms are such that they always lie along the vector of the adjacent ‘T’

sites in the lattice. During all the geometry optimization calculations to obtain the T–O bond distances, T–O–T and O–T–O bond angles, the positions of hydrogen atoms are held fixed. The geometry optimization calculations of the cluster model shown in Fig. 1A for all the four cluster models centered at O_1 , O_2 , O_3 and O_4 converged to produce almost equivalent Si–O bond distances, Si–O–Si and O–Si–O bond angles. Hence, all the further calculations (where the detailed geometric parameter versus electronic property correlations are analyzed) were performed for the cluster model generated with O_1 as the central bridging oxygen.

Cluster model A (Fig. 1A) represents the dealuminated form, where the Si/Al ratio is increased to obtain Ultra Stable Y (USY). Cluster model B (Fig. 1B) indicates a hydrogen

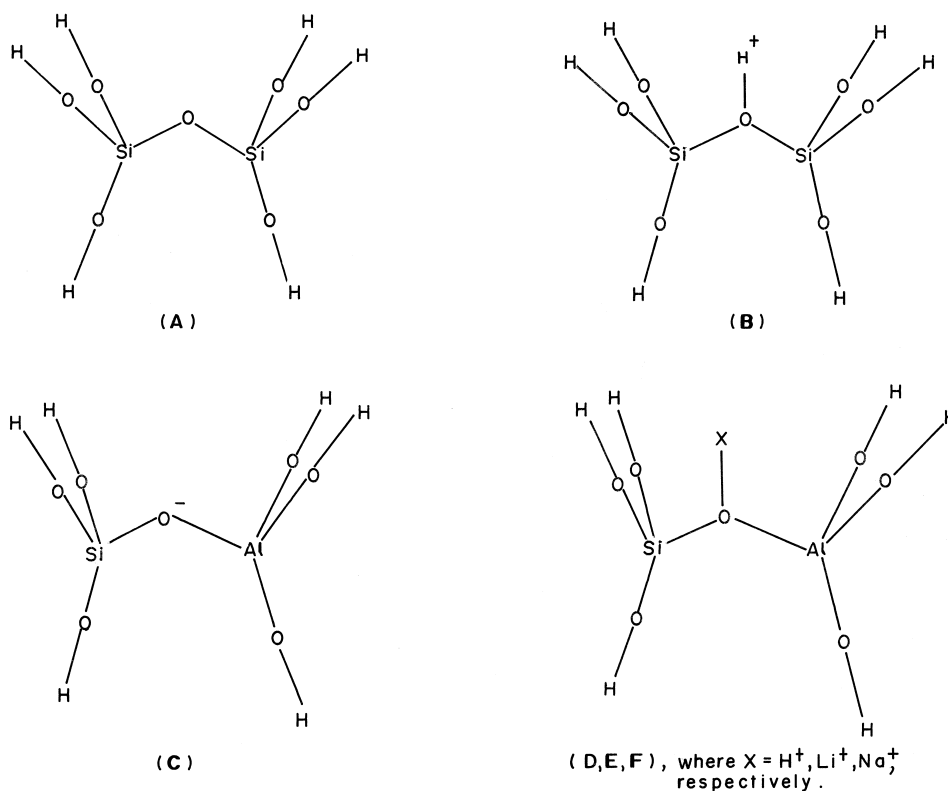


Fig. 1. Schematic representation of the disilic acid type cluster models used in the electronic structure calculations. A neutral siliceous cluster model (A), protonated form of the siliceous cluster model (B), a dimer cluster model with a negative charge where a SiO_4 and AlO_4 tetrahedra are corner shared through the bridging oxygen O_b (C) and the cluster model where the negative charge of the cluster model C is compensated by H^+ , Li^+ and Na^+ (D, E and F, respectively).

attached to O_b imparting a positive charge to the cluster. Cluster model C (Fig. 1C) represents the faujasite zeolite lattice with $Si/Al = 1$, as taken from the crystal structure. This cluster model is anionic and the anionic charge is normally compensated by a cation (X), as shown in the cluster models D, E and F in Fig. 1D–F. The cation could be either a proton or a metal ion and we have studied three cases where the compensating cations are H^+ (cluster model D), Li^+ (cluster model E) and Na^+ (cluster model F).

3. Results and discussion

Faujasite zeolite lattice is highly symmetrical and it has only one crystallographically distinct Si site. Except, in the case of faujasite with high Al content ($Si/Al \approx 1$), where there is a regular ordering of Si and Al, the location, distribution and geometry of $[AlO_4]^-$ groups are not known from experimental studies. In cases where $Si/Al > 1$, the T–O bond distance is the average of Si–O and Al–O bond distances, so also T– O_b –T bond angles are the average of Si– O_b –Si and Si– O_b –Al bond angles and O–T–O bond angles are the average of O–Si–O and O–Al–O bond angles. As well known, commercially useful faujasite (zeolite Y and USY) have $Si/Al > 1$ having siliceous islands, whose local structures are not known from bulk analytical techniques. Hence, we have undertaken this elaborate theoretical study to derive the geometric parameters and analyze their influence on the electronic and catalytic properties at the molecular level.

3.1. Geometric parameters for various cluster models

The cluster models (A–F) shown in Fig. 1 were built from the crystal structure of faujasite [24] and the bridging oxygen is O_1 . Complete geometry optimization calculations were carried out by LDA, NDA and HF–SCF methods. The

T– O_b bond distances, O_t –T– O_b and T– O_b –T bond angles and T–O–T–O dihedral angles (where T = Si or Al; O_t = terminal oxygen; O_b = bridging oxygen) were optimized to obtain minimum energy configurations. The total energy values of these cluster models by different calculation procedures are given in Table 1. The total energy obtained by NDA method is the lowest for all the cluster models, as expected from its level of accuracy. Indeed, the choice of the exchange and correlation functional is not variational in our calculations and hence the lowest total energy predicted by NDA method alone can not be used as a criterion to assess the merits of these methods. Hence, the optimized geometry of the cluster models obtained by each of these methods were analyzed in detail. The calculated geometry parameters such as T– O_b bond distances, T– O_b –T and O_t –T– O_b bond angles are summarized in Table 2. The experimentally reported geometries from XRD studies, wherever available, are included in Table 2 for comparison.

NDA predicts longer Si– O_b bond distances than those obtained by other methods, whereas Al– O_b bond distances are more accurately predicted. Stave and Nicholas [25] also observed that NDA predicts longer bond distances than the LDA method. It is observed that the Si– O_b bond distance decreases when one of the T sites is aluminium (cluster model C), while simultaneously the Si– O_t bond distances increase. Although Si– O_b bond distances decrease, the Al– O_b bond distance increases and ultimately the

Table 1

Energy values in a. u. of the disilicic cluster models at the optimum geometries^a obtained by LDA, NDA and HF–SCF

Cluster model	LDA	NDA	HF–SCF
A	–1103.50090	–1109.57665	–1105.72990
B	–1103.80423	–1109.88870	–1105.04846
C	–1056.62732	–1062.60949	–1058.76657
D	–1057.11596	–1063.10433	–1059.28375
E	–1063.99741	–1070.10259	–1066.24654
F	–1218.04417	–1224.86429	–1220.62710

^aThe optimized geometric parameters for these cluster models are given in Table 2.

Table 2
The optimized geometric parameters for different cluster models as predicted by the three methods

Parameters	Method	Cluster model					
		A	B	C	D	E	F
Si–O (Al–O) bond distance (Å)	LDA	1.645	1.787	1.597 (1.788)	1.700 (1.950)	1.647 (1.836)	1.635 (1.824)
	NDA	1.664	1.823	1.607 (1.820)	1.723 (2.007)	1.661 (1.870)	1.647 (1.860)
	HF–SCF	1.633	1.797	1.581 (1.798)	1.696 (1.994)	1.633 (1.839)	1.620 (1.830)
	Experiment	1.619			1.729		
O _b –Si–O _t (O _b –Al–O _t) bond angle (°)	LDA	110.4	110.7	113.0 (109.3)	107.7 (101.3)	110.6 (105.0)	110.9 (106.0)
	NDA	110.4	105.4	113.6 (109.3)	108.8 (101.3)	110.9 (105.9)	111.7 (107.7)
	HF–SCF	109.7	104.2	113.4 (108.6)	107.6 (100.6)	110.5 (105.0)	111.1 (106.3)
	experiment	109.5			109.5		
Si–O–T bond angle (°) (T = Si or Al)	LDA	140.0	126.8	123.0	126.0	119.6	121.4
	NDA	140.0	132.1	142.0	134.7	123.9	133.0
	HF–SCF	140.0	129.9	135.0	128.7	128.6	129.6
	experiment				139.2		
O _b –X bond distance (Å)	LDA				0.980	1.758	2.080
	NDA				0.979	1.795	2.130
	HF–SCF				0.949	1.763	2.110

The experimental values reported from X-ray crystallographic studies are included for comparison.

Si...Al distance is more in cluster model C compared to the original Si...Si distance in cluster model A. The Si–O_b bond distance increases when a proton is added to the O_b (cluster models B and D). The increase in the Si–O_b bond distance with the addition of a proton is more in the cluster model B than in the cluster model D. This bond distance variation is also associated with minor decrease in Si–O_b–Al angle relative to Si–O_b–Si angle, except in the case of cluster model C by NDA method. In fact, these geometry variations are interdependent and are due to the delicate balance of several parameters including the O–Si–O–Al dihedral angle variation. Table 2 also shows that the O_b–X (where X = H, Li or Na) bond distance increases in the order of O–H < O–Li < O–Na. It is seen that the O_b–X bond distance increases with the ionic radii of the cation.

We observe that the Si–O_b–T (where T = Si or Al) bond angle is the largest for cluster model A and smallest for cluster model E as derived from any of the methods. Li⁺ cation possesses the highest charge/radius ratio among the alkali cations and will thus produce a strong

polarizing effect on the local geometry, leading to a decrease of the Si–O_b–Al bond angle in the cluster model E. This trend is predicted by all the three methods. NDA predicts larger Si–O_b–T bond angles than the other methods which has also been observed earlier by Stave and Nicholas [25]. As far as the Si–O_b–Si angles are concerned, all methods are good. However, for the Si–O_b–Al bond, angle NDA predictions are closest to the experimental values and LDA predictions are poor, whereas the HF–SCF is slightly better than LDA. All the methods are equally good in predicting the O–T–O angles. Overall, it may be concluded that these calculations are useful in predicting the equilibrium geometry values, particularly the bond angles. We further analyze the implications of the geometric variations on the adsorption of small acidic and basic molecules [26].

3.2. Influence of the geometric parameters on the energy values

In the process of optimization, all the geometric parameters vary to give the lowest en-

ergy configuration. To study the influence of the individual geometric parameters on the total energy, we varied one of the geometric parameters, while all the other geometric parameters were non-variant as in the lowest energy configuration. Although the absolute values were different, the pattern of curves showing the variation of energy with respect to geometric parameters are the same, as predicted by all three methods. Hence, only the typical results obtained by NDA method are discussed here. The variation in energy with respect to the changes in Si–O_b bond distance, Al–O_b bond distance and Si–O_b–T (T = Si or Al) bond angles are shown in Figs. 2–4 respectively.

Figs. 2 and 3 show that the variation of energy with respect to the bond distances for various cluster models is almost harmonic in behavior. The results obtained reiterate the observations made in Section 3.1. Thus, it can be inferred that the low energy configurations made by geometry optimization procedures are the global minimum and not ‘local minima’. On the other hand, Fig. 4 shows that variation of energy with respect to bond angles is not so harmonic in behavior. The more sensitive de-

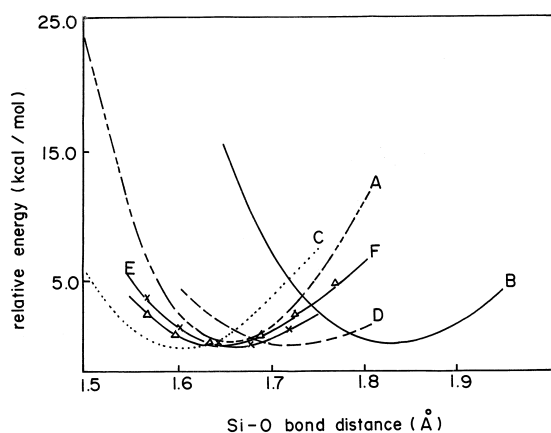


Fig. 2. The dependence of relative energy of the cluster models shown in Fig. 1 on the variation of Si–O bond distance. The lowest energy values obtained for all the cluster models are set to 0.0.

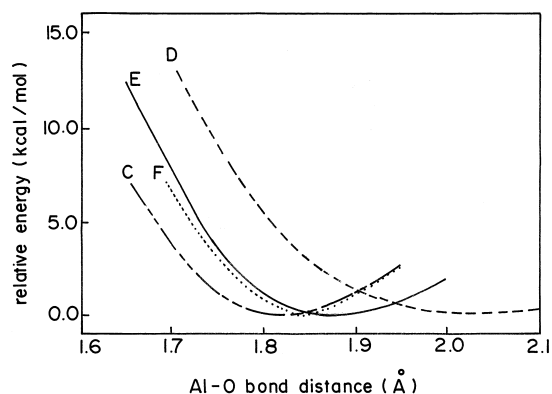


Fig. 3. The dependence of relative energy of the cluster models shown in Fig. 1 on the variation of Al–O bond distance. The lowest energy values obtained for all the cluster models are set to 0.0.

pendence of the energy values on the T–O_b bond distances compared to the T–O_b–T bond angles can be brought out by comparing the results shown in Figs. 2–4, for the cluster models A to D. Using these results, we have derived a simplistic force field expression and the parameters for the T–O stretching and T–O–T bending, assuming harmonicity which will be reported elsewhere [26].

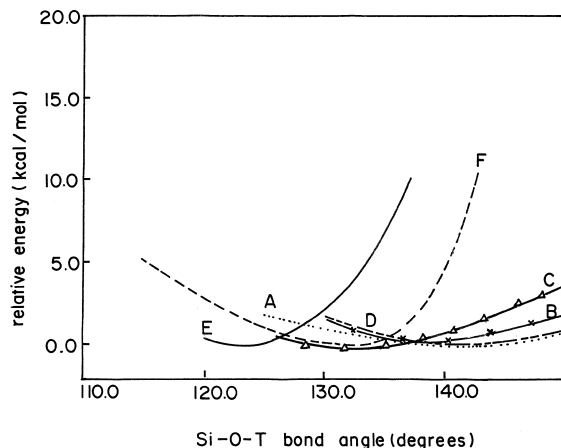


Fig. 4. The dependence of relative energy of the cluster models shown in Fig. 1 on the variation of Si–O–T (where T = Si for cluster models A and B and Al for C, D, E and F, respectively) angles. The lowest energy values obtained for all the cluster models are set to 0.0.

Table 3

Dissociation energy (kcal/mol) of O_b-X bond in $(HO)_3Si-O_bX-Al(OH)_3$ cluster models D, E and F

X (cation)	LDA	NDA	HF-SCF
H^+	306.45	310.42	324.53
Li^+	142.78	135.78	153.38
Na^+	124.13	115.39	126.28

3.3. Influence of the geometric parameters on the dissociation energy values of O_b-X bond

Table 3 presents dissociation energy values of O_b-X (where $X = H, Li$ or Na) bond in the cluster models D, E and F, respectively. It is seen that the dissociation energy of the O_b-Na bond is the lowest while that of O_b-H bond is the largest. In spite of the differences in the absolute values, the same order is predicted by all three methods. Since the proton is a good acceptor of electrons compared to the other cations, the dissociation energy of the O_b-H bond is higher, indicating a stronger O_b-H bond. These results are in line with the results predicted by Derouane and coworkers [27,28] at HF-SCF level with a slightly lower basis set. It is well known [29] that LDA overestimates binding energy values due to a combination of errors (overestimation of correlation and underestimation of exchange energy) which are different for molecules and atoms. NDA corrects this wrong behavior due to its inherent functional nature, leading to more reliable binding energy values.

The variation of the dissociation energy of O_b-X as a function of $T-O_b$ bond distance and $Si-O_b-Al$ bond angle is also analyzed. The dissociation energy for the cluster model D is more sensitive to the changes in the bond distance (typically 0.15 kcal/mol for 1 Å) compared to the changes in the bond angle (typically 0.05 kcal/mol for 5°). However, when the compensating cations are metals (cluster models E and F), the dissociation energy is more sensitive to the $Si-O_b-Al$ bond angle variation than to the $T-O_b$ distance variation.

3.4. Influence of the geometric parameters on the net charge values on the bridging oxygen

The net charge values on the bridging oxygen O_b , derived from the electron density matrix at the NDA level of calculation are shown in Fig. 5A–C. The net charge values are calculated when each of the geometric parameters namely the $Si-O_b$ bond distance, $Al-O_b$ bond distance and $Si-O_b-T$ bond angle were varied, while the other geometric parameters are non-variant as in the lowest configuration. It has been reported that the charge on the bridging oxygen is a property that can be correlated to the acidity and consequently to the catalytic activity in the acid catalysed reactions over various zeolites [30,31]. The net negative charge on O_b can not be directly correlated to the proton affinity of O_b or the O_b-H bond energy. In fact, when the $O-H$ bond dissociates heterolytically to release the proton, the bond energy will depend on the degree of stabilization of the negative charge left on O_b . Hence, it is important to establish the relationship between the charge on O_b and the geometric parameters, in order to predict the acidity of different sites in a given zeolitic structure as well as to compare different zeolite structures. The net negative charge on O_b increases for various cluster models in the order $D < E < F$. This shows that the proton acts as an electron acceptor, while metal ions are electron donors. The charge on the oxygen is more negative when Al replaces one of the Si in the cluster model A. The charge on the bridging oxygen is more sensitive to the variations in $Si-O$ bond distance and $Si-O-Si$ bond angle in the cluster model A than to the variations in $Al-O$ bond distance and $Si-O-Al$ bond angles in cluster models C–F.

4. Conclusions

The results of the quantum chemical calculations on cluster models representing the fau- site lattice are presented. The geometry optimization calculations lend support to the fact

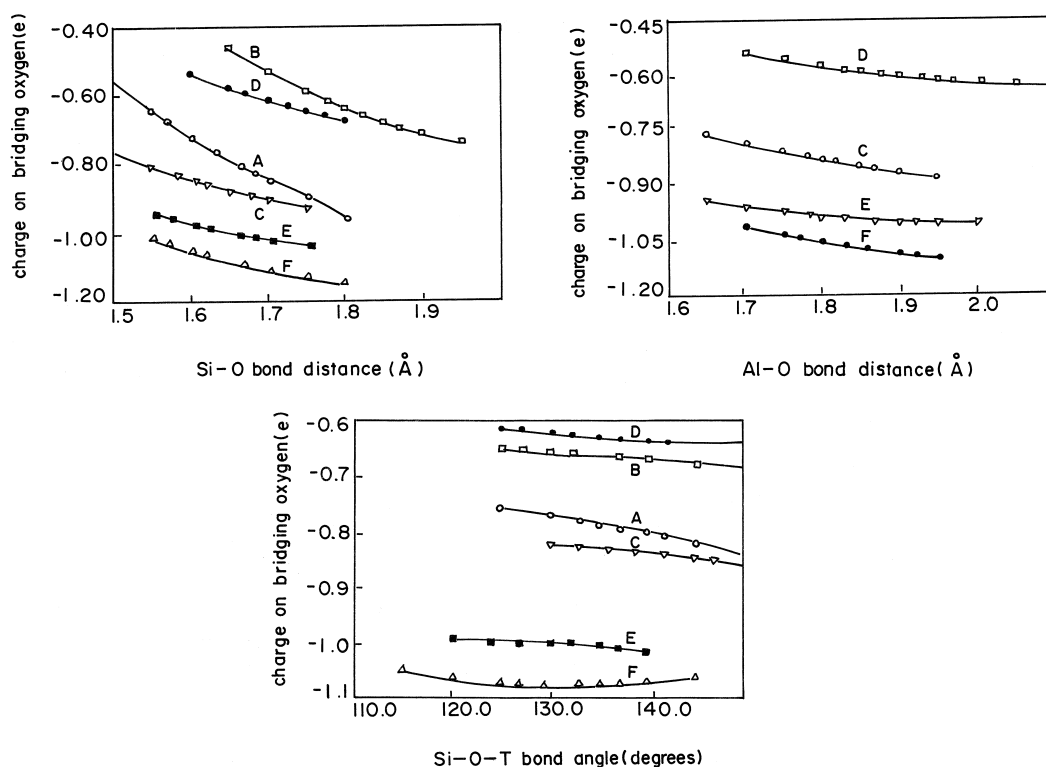


Fig. 5. The dependence of charge on the bridging oxygen (O_b) for the cluster models shown in Fig. 1 on the Si-O bond distance (A), Al-O bond distance (B) and Si-O-Al bond angle (C).

that local cluster models are capable of predicting the geometric parameters correctly. The calculated geometric parameters, such as Si-O and Al-O bond distances as well as Si-O-Si and Si-O-Al bond angles are correlated with the electronic properties such as total energy, O_b -X (where X = charge compensating cation) bond energy and the net charge on bridging oxygen. Salient features arising from these studies could be generalized as:

(i) The variation of total energy values of the cluster models and the dissociation energy values of O_b -X bond are more sensitive to Si- O_b and Al- O_b bond distances than to Si- O_b -Si and Si- O_b -Al bond angles.

(ii) The dissociation energy values of O_b -X bonds increase in the order: O_b -Na < O_b -Li < O_b -H in the equilibrium configuration.

(iii) The net charge on the bridging oxygen increases in the reverse order: H-exchanged cluster model \ll Na-exchanged cluster model < Li exchanged cluster model.

The catalytic implications of the presence of various cations in the cation exchanged zeolite can be predicted from the above generalizations. The derivation of accurate force field parameters suitable for use in atomistic simulations for the Si-O and Al-O bond stretching and for Si-O-Si and Si-O-Al bond bending for the faujasite zeolite lattice are being attempted on these NDA calculations. Preliminary studies indicate that fairly simplistic force field expressions for performing realistic atomistic simulations could be used, if we derive force field parameters individually for each and every zeolite structure.

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