Rationalizing the dependence of electronic properties on site geometry in ZSM-5

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We report the results of MNDO calculations on large pentameric cluster models with regular geometry as well as on those derived from different crystal structure reports for ZSM-5. We discuss the dependence of the calculated total energy, aluminum substitution energy, and charge density on different atoms on the cluster geometry and the calculation procedure. The charge density on oxygen sites shows linear variations with respect to Si–O distance and Si–O–Si angle in the cluster models.

Keywords: ZSM-5 zeolite; aluminum substitution; site geometry; MNDO calculations; charge density

INTRODUCTION

Although all zeolites are formed by corner sharing of SiO_4 and TO_4 (where T = Al, B, P, Ti, V, Fe, etc.) tetrahedra, the geometry, environment, and symmetry of the lattice sites are not equivalent. The minute variations in these parameters play a crucial role in deciding their catalytic properties. Experimental techniques have not provided the siting of heteroatoms in the lattice in an unambiguous manner. Quantum chemical calculations have provided valuable insights regarding the substitution process.

Derouane et al.[1–3] used nonempirical SCF–MO techniques to study monomer and dimer clusters to propose preferential siting of Al in different zeolites. They performed charge distribution analysis to show that the anionic framework behaves as a weak but soft base. They also explained the high acid strength of zeolites as well as their strong affinity for large and polarizable cations. O'Malley and Dwyer performed *ab initio* calculations on the acidic properties of boralite[4] and on the siting of Al in the Theta-1 framework.[5] The semiempirical quantum chemical MNDO technique has been adopted to calculate the substitution energy for boron at different possible framework sites in the ZSM-5 structure.[6] EHMO calculations on ferrisilicate zeolite models was used to report preferential siting of iron in ZSM-5 lattice.[7] Recently, Alvarado Swasigood et al.[8] used *ab initio* calculations for the monomeric cluster models to model the 12 different T sites of the ZSM-5 lattice. They also proposed a model to explain the dependence of the energy cluster models on the geometry of T sites. Schroder et al.[9] used an energy minimization method to calculate the defect energy and to predict the preferential siting of Al as well as protons over different oxygen sites of the ZSM-5 lattice.

In the present study, we used the MNDO technique to study larger pentameric cluster models pertaining to all crystallographic sites of ZSM-5 as well as clusters with ideal geometry. The dependence of energy values on the size of the cluster and minor variations in geometry are brought out. The formal charges on central "Si" and "O" atoms attached to them, which decide the electrostatic field and acidity of ZSM-5, are correlated with T–O and O–T–O parameters.

COMPUTATIONAL DETAILS AND CLUSTER MODELS

The semiempirical quantum chemical MNDO (modified neglect of diatomic overlap) technique is adopted to perform cluster calculations[10] from AMPAC (QCPE Program 506). A localized cluster model approach to study the crystal lattice properties proposed by Derouane et al.[1,2] also was used. Calculations have been performed on monomeric [$T(OH)_4$], dimeric [$(OH)_3$–T–O–$T(OH)_3$], and pentameric [T–$O_4\{T(OH)_3\}_4$] cluster models. The pentameric cluster model is a representation of a T site that is connected to four adjacent T sites through oxygen sites, whereas in the monomeric cluster models, the adjacent T sites are approximated by a hydrogen atom. The dimeric cluster models, the numbering scheme of T sites, and substitution energy calculations are as reported in our earlier studies.[6,7]

RESULTS AND DISCUSSION

We carried out calculations for the cluster models derived based on the crystal structure reports of Olson et al.[11] and Van Koningsveld et al.[12]. The relative energies calculated for monomeric clusters are reported in *Table 1*. The low-energy and high-

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Table 1 Relative energy of monomeric silicon clusters representing the 12 crystallographic sites of ZSM-5 reported by *ab initio* and MNDO calculations

	Relative energy (kcal/mol)			
Site represented by the monomeric cluster	*Ab initio*[2] for Olson et al. structure	MNDO for Olson et al. structure	*Ab initio*[8] for Van Koningsveld et al. structure	MNDO for Van Koningsveld et al. structure
1	49.20	41.30	2.60	2.47
2	0.0	0.0	10.09	6.57
3	27.51	20.25	16.62	12.27
4	52.02	43.24	12.45	6.66
5	36.25	30.46	2.00	1.80
6	38.10	36.80	0.0	0.0
7	17.53	13.47	3.25	2.37
8	68.62	57.66	12.48	5.30
9	41.92	35.56	0.0	0.78
10	35.12	31.71	4.0	3.60
11	42.03	32.54	11.89	6.69
12	2.69	3.63	3.89	3.02

energy sites predicted by both *ab initio* (STO-3G basis) and MNDO calculations are the same. However, the crystal structures reported by Olson et al. and Van Koningsveld et al. predict a different pattern of relative energy for monomeric clusters representing all the 12 sites. Alvarado Swasigood et al.[8] also showed that the pattern changes when a better set of basis (VDZ) is used in the *ab initio* calculations than when a minimal set of basis (STO-3G) is used. Consequently, the relative substitution energy for Al^{3+} in place of Si^{4+} also shows different patterns with different methods of calculations and for the cluster models of different crystal structure reports.

Relative substitution energy

The geometry of monomeric tetrahedral units in the crystal structure of Olson et al.[11] and Van Koningsveld et al.[12] are different and, hence, their relative energy also follows different patterns (*Table 1*). The Si–O and O–Si–O parameters decide the geometry of monomeric tetrahedral units, whereas both the Si–O–Si and Si–O–Si–O decide the stacking of monomeric tetrahedra in three dimensions, leading to different topography. However, in pentameric cluster units, Si–Si and O–O distances are similar for both crystal structures. The variations in Si–O and O–Si–O parameters in the monomer clusters are compensated by the variations in Si–O–Si and Si–O–Si–O parameters. A systematic study of all the pentameric clusters representing 12 T sites by *ab initio* calculations have not been reported in the literature. Our results presented in *Figure 1* show that the relative energy of all 12 pentameric cluster models according to the Van Koningsveld et al. structure[12] are close to each other, whereas the energy of the pentameric cluster models according to the Olson et al. structure[11] cover a wide range. However, the two crystal structures lead to same pattern of relative substitution energy for all the sites when pentameric cluster models are used as shown in *Figure 2*. The substitution energy was calculated by considering the following process:

$$H_{12}Si_5O_{16} + AlO_4^- \rightarrow H_{12}Si_4AlO_{16}^- + SiO_4 \qquad (1)$$

The above results indicate that pentameric cluster models containing 33 atoms are satisfactory cluster models to study the substitution energy of aluminum in ZSM-5 lattice, since small variations in the geometry of tetrahedral sites due to experimental inaccuracy are taken care of. Schroder et al.[9] reported aluminum siting in the low-temperature monoclinic structure[13] of ZSM-5 studied by an energy-minimization procedure. They concluded that aluminum will have random distribution among the 24 possible lattice sites in the monoclinic structure. However, ideally, a larger cluster model has to be treated with accurate *ab initio* calculations, which are computationally prohibitive at this moment. The results presented in *Table 2* show that there is no consistency in the preferred siting of aluminum as predicted by different studies. Hence, it is still necessary to derive some empirical relations between the site geometry and the electronic properties. This is being attempted in the following section by correlating the formal change density on oxygens with T–O bond length and T–O–T angles.

The charge density correlations

The formal charge density values on oxygen atoms

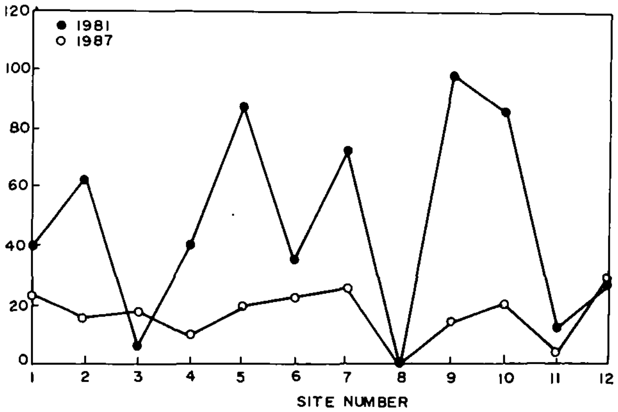

Figure 1 The relative energy calculated for pentameric silicon clusters representing the 12 crystallographic sites in the ZSM-5 structure. 1981 and 1987 represent calculations for the structure reported in Refs. 11 and 12, respectively.

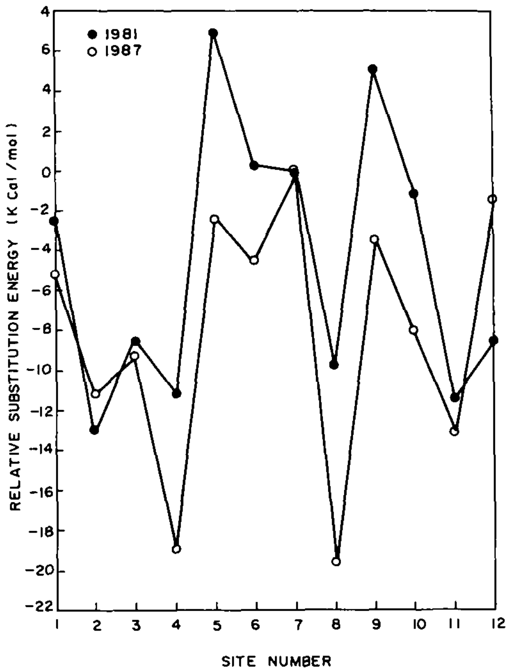

Figure 2 The relative substitution energy for aluminum in the place of silicon in the ZSM-5 lattice calculated according to Equation (1). 1981 and 1987 represent calculations for the structure reported in Refs. 11 and 12, respectively.

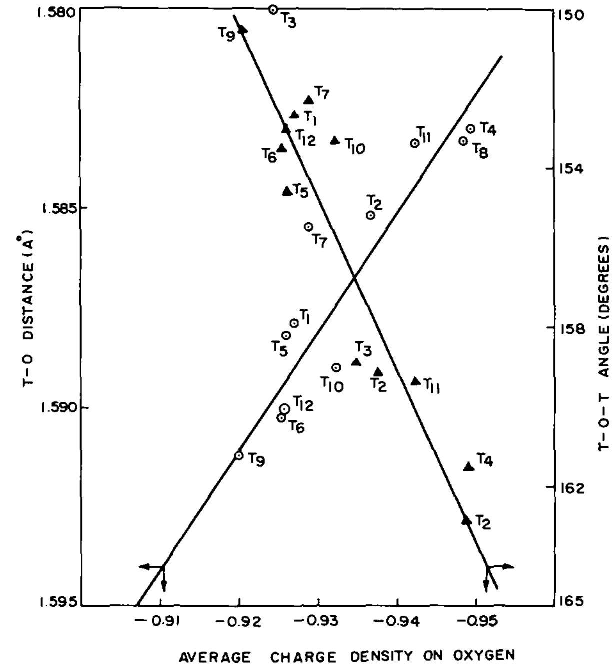

Figure 3 The variations of average charge density on oxygens attached to each T site with respect to T–O and T–O–T values of the Si sites reported in Ref. 12.

linking two tetrahedra are calculated from the dimeric cluster models. The charge on four oxygens attached to a Si site is averaged and correlated with Si–O and Si–O–Si. The Si–O distance and Si–O–Si angle values are again the average of the four Si–O distances and four Si–O–Si angles, respectively, around each Si site for pentameric clusters and as average value of four corresponding clusters for dimeric cluster models. The charge density on oxygen calculated for dimeric cluster models is directly proportional to Si–O–Si and inversely proportional to the Si–O with few exceptions, as shown in *Figure 3*. The deviations observed for a few sites could be attributed to distortions from the regular tetrahedral geometry of the SiO_4 units. For Al-substituted cluster models also, the same correlations are valid with all the oxygen atoms attached to aluminum having a uniformly lesser negative charge. The pentameric clusters also show a similar correlation. The energy values calculated for the cluster models representing each of the Si sites themselves do not show any correlation such as this. The reasons that one could assign for this are as follows:

(i) The relaxations in the cluster due to the cluster termination procedure by attaching hydrogen are not included in the energy calculations, and

(ii) The energy variations may be due to combined factors of T–O, T–O–T, O–T–O, and T–O–T–O parameters and their contributions are not equal.

Table 2 Preferred aluminum siting in ZSM-5 lattice reported by different calculation procedures

	Derouane et al.[2]	Schroder et al.[9]	Alvarado Swasigood et al.[8]		This work			
Structure	D.H.O.[a]	H.V.K.[a]	D.H.O.	H.V.K.	D.H.O.	D.H.O.	H.V.K.	H.V.K.
Cluster model	Dimer	Lattice	Monomer	Monomer	Monomer	Pentamer	Monomer	Pentamer
Calculation procedure	*Ab initio* STO-3G	Energy minimization	*Ab initio* STO-3G	*Ab initio* VDZ	MNDO	MNDO	MNDO	MNDO
Most preferred sites for Al substitution in ZSM-5 lattice	2,12	Random	4,8	6,12	2,12	2,11	6,9	4,8
Least preferred sites for Al substitution in ZSM-5 lattice	4,8	Random	7,9	3,7	4,8	5,9	3,11	7,12

[a] D.H.O. = Ref. 11. H.V.K. = Ref. 12

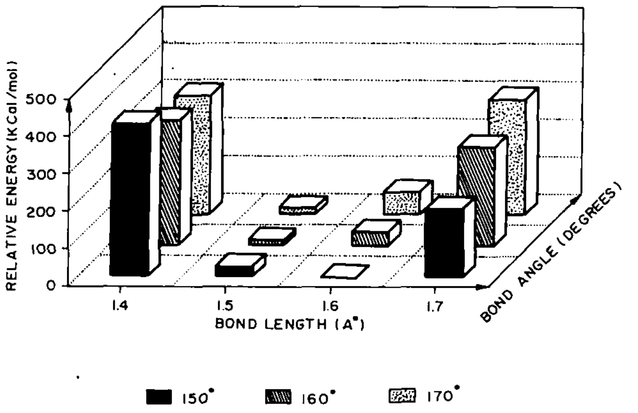

Figure 4 The variation of relative energy of pentameric silicon clusters [Si–O$_4$–{Si(OH)$_3$}] with respect to Si–O bond length and Si–O–Si bond angle. O–Si–O angles are uniformly 109.5° and Si–O–Si–O dihedral angles are uniformly 120.0° in all the clusters. When all Si–O distances are 1.60 Å and Si–O–Si angles are 150.0°, the total energy of the cluster model is minimum with the value of −5729.234 eV. This was treated as a cluster with zero energy and the energy values of other clusters are calculated relative to this cluster.

However, the formal charge density is a more localized property and, hence, it shows better correlations with site geometry than with energy. Furthermore, charge density on oxygen has been shown[14] to be indicative of the strength of Brönsted acidity of these sites. The Brönsted acidity could be correlated to catalytic activity of ZSM-5 for many hydrocarbon conversion reactions.[15] Thus, the charge density correlations are useful to derive information regarding the acidic and catalytic properties of zeolites.

The significance of site geometry

The importance of the geometry of sites in controlling the electronic properties is studied by performing calculations for symmetrical clusters. The results of these calculations indicating the variation of energy simultaneously with respect to the Si–O bond length and the Si–O–Si bond angle are shown in *Figure 4*. It was observed that the preferred ranges are 1.5–1.6 Å and 150° to 170° for Si–O and Si–O–Si parameters, respectively, in a regular tetrahedral arrangement. The energy values are sensitive to minor deviations in the Si–O bond length, whereas relatively more flexibility is allowed in the Si–O–Si angle. In other words, the contributions of the Si–O variation from equilibrium causes a lot more strain in the lattice than when Si–O–Si varies from the equilibrium value. This is in contrast to the observation made in case of larger cations such as Fe or Al,[7] where there is more flexibility in bond lengths.

Of course, in the ZSM-5 system, the geometry of regular tetrahedron (O–Si–O and Si–O–Si–O parameters) undergoes distortion to compensate the strain created in the lattice. From our model, it is observed that all these parameters contribute to a different extent in minimizing the strain in the lattice. Indeed, a larger number of combinations are possible that generate minimum-energy site geometries, thus leading to different zeolite structures with a varying number of crystallographically distinct sites. In the future, we shall be deriving parameters for performing molecular mechanics energy calculations for lattice consisting of silicon and oxygen to arrive at all possible minimum-energy conformations.

CONCLUSIONS

In recent years, there have been concerted efforts to calculate the siting of aluminum in the ZSM-5 lattice by different quantum chemical methods. The models adopted also vary from monomeric (with 9 atoms) to pentameric (with 33 atoms) clusters. There are also crystal structure reports for the low-temperature monoclinic phase of ZSM-5 as well as for the high-temperature orthorhombic phase of ZSM-5 with and without templates. Due to the above variations, there is no consistency among the reports in the literature regarding the preferred siting of aluminum in ZSM-5. The present study indicates that larger pentameric cluster models give consistent results for different crystal structures. From the calculations performed for clusters with regular geometry, it is predicted that the contributions of different geometric parameters for the relative energy and substitution energy are not uniform. Further, it is shown that the charge density on oxygen, which is an indication of acidity in zeolites, shows a better correlation to geometric parameters such as Si–O and Si–O–Si rather than to the total energy and the substitution energy.

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REFERENCES

1 Fripiat, J.G., Berger-André, F., André, J.M. and Derouane, E.G. *Zeolites*, 1983, **3**, 306
2 Derouane, E.G. and Fripiat, J.G. *Zeolites* 1985, **5**, 165
3 Derouane, E.G. and Fripiat, J.G., in *Proceedings of the 6th International Zeolite Conference, Reno* (Eds. D. Olson and A. Bislo) Butterworths, London, 1984, p 717
4 O'Malley, P.J. and Dwyer, J. *J. Chem. Soc., Chem. Commun.* 1987, 72
5 O'Malley, P.J. and Dwyer, J. *Zeolites* 1988, **8**, 317
6 Vetrivel, R. *Zeolites*, 1992, **12**, 424
7 Vetrivel, R., Pal, S. and Krishnan, S. *J. Mol. Catal.* 1991, **66**, 385
8 Alvarado Swasigood, A.E., Barr, M.K., Hay, P.J. and Redondo, A. *J. Phys. Chem*, 1991, **95**, 10033
9 Schroder, K.P., Sauer, J., Leslie, M. and Catlow, C.R.A. *Zeolites* 1992, **12**, 20
10 Dewar, M.J.S. and Thiel, W.J. *J. Am. Chem. Soc.* 1977, **99**, 4899
11 Olson, D.H., Kokotailo, G.T., Lawson, S.L. and Meier, W.M. *J. Phys. Chem.* 1981, **85**, 2238
12 Van Koningsveld, H., Van Bekkum, H. and Jansen, J.C. *Acta Crystallogr.* 1987, **B43**, 127
13 Van Koningsveld, H., Jansen, J.C. and Van Bekkum, H. *Zeolites* 1990, **10**, 235
14 Vetrivel, R., Catlow, C.R.A., Colbourn, E.A. and Leslie, M. *Stud. Surf. Sci. Catal.* 1989, **46**, 409
15 Dwyer, J. *Stud. Surf. Sci. Catal.* 1988, **37**, 333