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The effects of local structural relaxation on aluminum siting within H-ZSM-5

Stephen R. Lonsinger, Arup K. Chakraborty *, Doros N. Theodorou
and Alexis T. Bell

Department of Chemical Engineering and Center for Advanced Materials,
Lawrence Berkeley Laboratory, University of California, Berkeley, CA 94720, U.S.A.

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Semiempirical molecular orbital calculations have been performed to study aluminum siting in H-ZSM-5 zeolites. Local structural rearrangements upon substituting aluminum (with a charge compensating proton) for silicon are found to be important. The T12 site is found to be the most preferred site for aluminum substitution. However, the calculated energetics for substitution show that several tetrahedral sites are energetically comparable with regard to aluminum siting. Results pertaining to the electronic properties of the acidic site upon aluminum substitution at each of the twelve distinct tetrahedral sites are presented. The acidic center is found to be a rather soft species, with the HOMO-LUMO energy gap being roughly 8 eV.

Keywords: ZSM-5; molecular orbital theory; aluminum siting

1. Introduction

The catalytically active sites in ZSM-5 are protons situated on oxygen atoms bridging between aluminum atom and a neighboring silicon atom [1]. In its high temperature, orthorhombic form ZSM-5 has twelve distinct tetrahedral (T) sites (depicted in fig. 1). An issue of some importance is the extent to which these sites are preferentially occupied by aluminum, and the effects of aluminum siting on the electronic properties of the acidic site. The need for theoretical investigation of these questions stems primarily from the fact that experimental studies cannot clearly discriminate between aluminum and silicon atoms. Theoretical studies may be able to shed light on these and related questions. In

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* Author to whom all correspondence should be addressed.

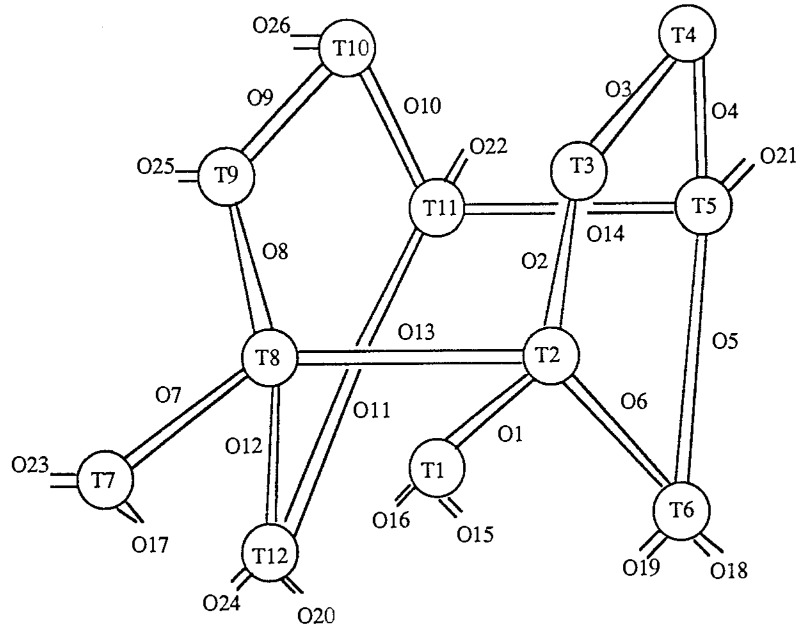

Fig. 1. Secondary building unit of ZSM-5 depicting the twelve distinct T-sites and the numbering scheme for the oxygen atoms.

recent years, much progress has been made in the theoretical investigation of zeolitic systems. A recent review of these efforts has been provided by Sauer [2].

Fripiat et al. [3] and Derouane and Fripiat [4] have attempted to address questions pertaining to aluminum siting and the nature of the acidic site in H-ZSM-5 by performing ab initio Hartree-Fock calculations using minimal basis sets (STO-3G). Based on monomeric cluster calculations [3] it was concluded that aluminum substitution occurs preferentially at T12 and T2 sites. Subsequent calculations [4] with pentameric clusters supported this conclusion, and demonstrated that the zeolite framework behaves as a weak but soft base. While the work of Derouane and Fripiat [4] has led to important new insights, their calculations suffer from two obvious weaknesses. The first is neglect of the far-field crystalline charges in the Hamiltonian, and the second is neglect of local geometric relaxation around the T-site wherein substitution occurs. While we note that Derouane and Fripiat [5] have performed some calculations wherein ad hoc structural relaxations were allowed, their results merely indicate that local structural relaxation may be important. In this note, we address the issue of local structural relaxation in the vicinity of the aluminum site systematically, and in detail. The consequences of local structural relaxation on the preference for aluminum siting, and the structure and electronic properties of the acidic site are then discussed.

2. Computational method

Our aim is to determine the T-site that is most favorable for aluminum siting, and to elucidate the key electronic and geometric features of the acidic site that is thus created. It has been recognized heretofore, and will be made even more clear in this note, that rather sophisticated ab initio methods must be used to study these issues in detail. However, as a starting point, we have used semiempirical molecular orbital calculations to address the questions under consideration. Semiempirical calculations are far less computationally intensive than ab initio calculations, and as such, they allow us to focus on the most important issues that must be investigated using more accurate theoretical methods (such as density functional theory [6]). In this note, we report the results of such studies that point out some important features of the energetic, geometric and electronic properties of the acid site in H-ZSM-5 that have not been noted in earlier studies.

Semiempirical molecular orbital computations were carried out using the MNDO Hamiltonian [7]. The most recent set of parameters for silicon were used. In all cases wherein we allowed geometric relaxation to occur, the energy minimization was performed such that the coordinates of the atoms were calculated to within 0.001 Å. Following Derouane and Fripiat [4], we have used isolated cluster models to investigate the relevant issues. By so doing, we neglect the effect of far field charges in the Hamiltonian. For the starting geometry, the silicon and oxygen atoms were placed at locations determined from the X-ray crystal structure for silicalite [8]. The clusters were terminated with protons placed at the crystallographic locations of the nearest silicon atoms. This method of cluster termination produces an artificial boundary effect. However, as will be discussed later, the cluster sizes were chosen so as to minimize this effect. In determining the most favorable site for aluminum, the energy of the corresponding purely siliceous cluster was used as the reference.

3. Results and discussion

Prior to investigating the preferred siting of aluminum, the effects of geometric relaxation on the nature of the acidic site were explored. This was accomplished using a T12 centered $Si_7AlO_{25}H_{19}$ cluster, depicted in fig. 2. The effects of relaxing the geometry were studied by systematically relaxing different portions of the cluster. In particular, we report the results of three cases. In the first case, only the charge compensating proton was allowed to relax, and all other atoms were held at the crystallographic positions for the purely siliceous cluster. In the second case, the hydroxyl group was allowed to relax. In the third case, the atoms containing to $O_3SiOHAlO_3$ group were allowed to relax. A few selected properties for each of these cases are listed in table 1. It is apparent

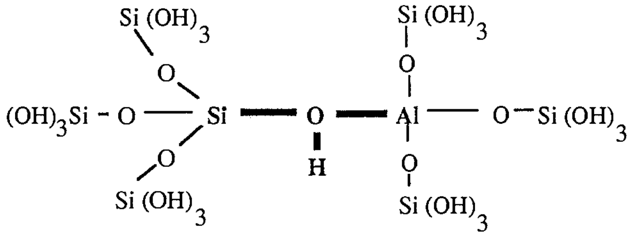

Fig. 2. Cluster on which geometric relaxation studies were performed; the aluminum atom resides at a T12 site.

that the energy of the most relaxed structure is significantly different from that obtained when only the charge compensating proton is allowed to relax. It may be argued that the decrease in energy upon relaxation is purely due to the fact that the artificial termination of the cluster with protons leads to the geometry relaxing from that found in the extended zeolite framework. If this were so, however, allowing the purely siliceous structure to relax should lead to a comparable decrease in the energy. We have performed such control calculations, and find that only about 10% of the change in energy can be attributed to artificial termination effects. Thus, it is clear that substituting aluminum for silicon leads to rather significant changes in the local geometry around the T site where substitution has occurred. In particular, as shown in table 1, we find that the aluminum-bridging oxygen distance increases to 1.8 Å (compared to 1.65 Å for the purely siliceous structure). This is consistent with experimental Al–O distances in aluminosilicates that have been reported to be 1.73 Å [9], and that calculated [9] using ionic radii (1.76 Å). The distance between the aluminum atom and the charge compensating proton is found to be 2.36 Å. This compares very well with recent NMR experiments [10], wherein this distance is reported to be 2.48 Å, providing further evidence for the fact that the geometric relaxation effects that we predict are indeed important, and at least qualitatively correct. Table 1 shows that the net charge on the aluminum site (as obtained from a Mulliken population analysis [11]) is, as expected, quite different from that for the silicon atom in the purely siliceous structure (table 2). The impact of structural relaxation on the distribution of charge is discussed in detail later. However, we turn first to the central issue addressed in this paper; viz., the

Table 1
Heats of formation, bond distances, and net atomic charges for selected atoms.

Case (atoms relaxed)	Heat of formation (kcal/mol)	Bond distances (Å)			Net atomic charge (e)			
		Al–O	O–H	O–Si	Al	O	H	Si
1 (H)	199	1.59	0.96	1.59	0.99	−0.42	0.27	1.91
2 (OH)	165	1.77	0.94	1.67	1.01	−0.49	0.28	1.92
3 ($O_3SiOHAlO_3$)	124	1.80	0.94	1.69	1.02	−0.49	0.26	1.93

Table 2
Net atomic charges for selected atoms for the purely siliceous cluster, and that for the cluster with aluminum substituted at the T12 site. The last column reports the charge differences upon aluminum substitution.

T or O atom	Charge on atoms in siliceous cluster	Charge on atoms in aluminum containing cluster	Charge difference upon aluminum substitution
Al 12 or Si 12	1.914	1.013	0.901
Si 12	1.842	1.829	0.013
Si 3	1.915	1.875	0.040
Si 11	1.895	1.848	0.047
Si 8	1.908	1.886	0.022
O 24	−0.889	−0.473	−0.416
O 20	−0.931	−0.836	−0.095
O 11	−0.947	−0.824	−0.123
O 12	−0.934	−0.864	−0.070
H	–	0.256	–

preferred aluminum T-site as determined from calculations wherein the geometry around the T-site is allowed to relax upon substituting aluminum for silicon.

A series of calculations were performed to determine how far the effects of the terminating protons propagate into the cluster. The purpose of this effort was to determine the smallest cluster that could be used without affecting the local geometry and charge distributions near the central part of the cluster due to the artificial termination of the cluster. We do not report the details of these scouting calculations here. Rather, we state our finding that the effects of artificial termination do not propagate farther than two bonds from the terminating proton. One is cautioned, however, that this does not mean that the effect of termination is inconsequential; the effect of neglecting the far field charge in the Hamiltonian may still be important, and will be explored in the future. In the present study, we have chosen the size of the cluster to be such that the direct effect of having a proton, rather than a silicon atom, terminating the cluster is minimized at the cluster center. Based on our screening studies, we have chosen to perform all our calculations with pentameric clusters ($Si_4AlO_{16}H_{13}$). One such cluster, centered at the T12 site, is depicted in fig. 3 with the terminating protons omitted for clarity. This cluster is similar to that chosen by Derouane and Fripiat [4].

Four calculations were performed for each of the twelve T-sites in order to determine the preferred location of the charge compensating proton. In other words, the proton was placed near each of the four bridging oxygens, and the energy of the structure was minimized. In each case, the central $SiOHAlO_3$ atoms were allowed to relax. Of these four calculations, the structure with the minimum energy was taken to be representative of the aluminum containing

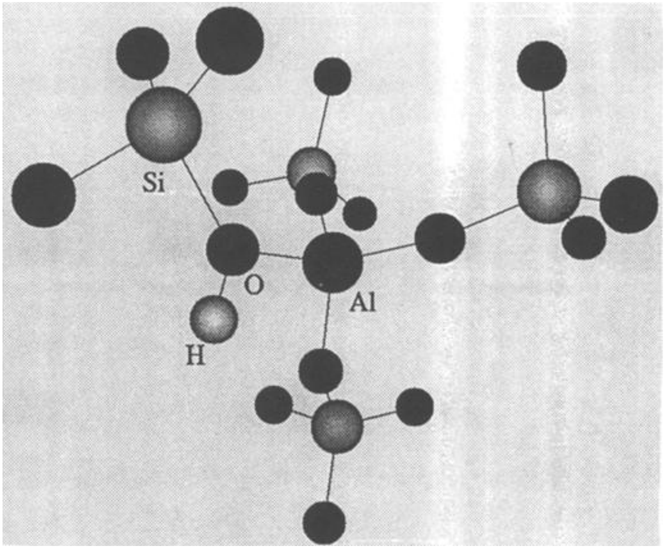

Fig. 3. Minimum energy configuration of the T12 centered pentameric cluster; terminating protons are omitted for clarity.

cluster. The energy difference between this cluster and the corresponding purely siliceous cluster was computed for each of the twelve different T-sites. These energy differences are plotted in fig. 4; the preferred locations of the charge compensating proton for each case are also shown. Several points are immedi-

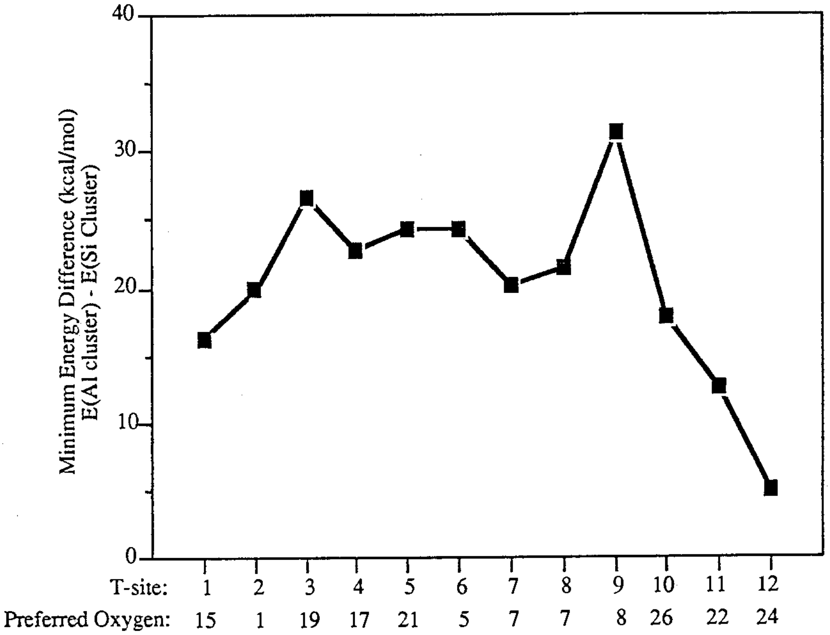

Fig. 4. Energetics for aluminum substitution as a function of T-site. The preferred bridging oxygen site for proton placement is also indicated for each T-site.

ately obvious. Firstly, we find that the most favored site for aluminum substitution and the least favored site are separated in energy by 26 kcal/mol. However, most of the energy differences are much smaller than this value. The T12 site is found to be the most preferred site. However, the energy differences between this site and the next most favored sites, T11 and T1, are only 7 kcal/mol and 11 kcal/mol, respectively. The results shown in fig. 4 are to be contrasted with the calculations performed by Fripiat and Derouane [4], wherein geometric relaxation was not allowed. In their pioneering study, these authors found that substitutions at the T12 and T2 sites were favored over that at the T1 site. Furthermore, they reported that the T12 site was favored over the T1 site by 17.9 kcal/mol. As can be seen from fig. 4, the results are quite different when structural relaxation is allowed. The T1 site is now found to be more favorable than the T2 site, and furthermore, it is only 11 kcal/mol less favorable than the T12 site. Comparison between our calculations and those of Fripiat and Derouane [4] cannot be made for other T-sites, since these authors carried out calculations only for substitution at the T1, T2, and T12 sites. However, several other sites appear to be energetically comparable to the T2 and T1 sites, and furthermore, substitution at these sites is not significantly more favorable than that at the T12 site. In fact, the energetic differences (for aluminum substitution) between some of these sites are small enough that it is fair to say that, within the resolution of the semiempirical calculations we have performed, they are essentially equivalent. Further calculations using more accurate Hamiltonians that also include the effect of the far field charge distribution must be performed in order to resolve these small energy differences. Thus, in contrast with unrelaxed calculations, we conclude that several sites are comparable in terms of the energetics of substitution, and that the T2 site is not favored over the T1 site. The existence of several T-sites with similar energetics for aluminum substitution suggests that aluminum siting in H-ZSM-5 may be controlled by kinetics rather than thermodynamics.

We now discuss the electronic properties of the acidic site in the T12-centered cluster. Table 2 reports the charges on selected sites in the purely siliceous and in the aluminum containing cluster. The last column in table 2 also reports the differences in charges upon substitution. These results are to be compared with the case wherein no geometric relaxations were allowed [4]. We find that the charge on the T12 site upon substitution of aluminum for silicon is more negative (as expected). However, the difference in charges is found to be much larger than that observed by Derouane and Fripiat [4], who find the difference to be only 0.138 (compared to 0.90). Furthermore, we find that the increase in negative charge on the TO_4 and the TO_4T_4 clusters surrounding the aluminum substituted site to be 0.20 and 0.32, respectively. This is to be contrasted with previous unrelaxed calculations [4], wherein these differences were reported to be 0.161 and 0.243, respectively. The charge compensating proton in our calculations is found to have a net charge of 0.26, in contrast to the 0.294

Table 3
Hardness parameter and proton charge for aluminum substitution at various T-sites.

T site	Hardness * (eV)	Proton charge
1	3.947	0.256
2	4.029	0.265
3	4.076	0.256
4	4.184	0.260
5	3.789	0.257
6	4.054	0.258
7	3.873	0.256
8	4.199	0.257
9	3.817	0.257
10	3.914	0.257
11	4.036	0.254
12	4.050	0.256

* Hardness $= -\frac{1}{2}$(HOMO energy − LUMO energy).

reported by Derouane and Fripiat. These results imply that upon allowing for geometric relaxation of the region around the aluminum site, the charge at the T12 site is more localized than previously determined, and the proton is less positively charged.

In addition to the partial charges at the various atomic centers, the acidity of a species may also be characterized by its relative hardness, as originally defined by Pearson [12]. The hardness or softness of a species is related to the charges at the atomic centers and the energies of the frontier orbitals [13,14]. The relationship between frontier orbital energies and relative hardness has been placed on a fundamental and quantitative footing by Parr and coworkers [15,16], who defined the relative hardness to be half the difference between the ionization potential and the electron affinity. In other words, the relative hardness is one half the energy gap between the highest occupied and lowest unoccupied levels. The smaller this gap, the softer the species. In table 3 the hardness parameter for the aluminated clusters are reported for the twelve cases that we have studied. As can be seen, the variation in hardness upon aluminum substitution at various T-sites is quite small (ranging from 3.8 to 4.2 eV). The corresponding proton charges are also found to vary over a very narrow range (0.25 to 0.26). Thus, our results indicate that the acidity (as defined by the proton charge and hardness) is not very different for the cases that we have studied. Furthermore, based on the magnitudes of the proton charge and the energy gap between the highest occupied and lowest unoccupied levels, we conclude that the acidic center that we are concerned with is a rather soft species, characterized by low lying unoccupied levels.

4. Concluding remarks

The structure and electronic properties of the acidic site of zeolite H-ZSM-5 were studied using semiempirical molecular orbital theory and cluster models. The effects of geometric relaxation in the region around the aluminum site are found to be important. We find that aluminum prefers to reside at the T12 site. However, in contrast with previous studies which neglected structural relaxation, the T2 site is not favored over the T1 site, and furthermore, several T-sites have comparable energetics of substitution. In order to clearly rank the energetics associated with aluminum substitution at these sites, calculations using more accurate Hamiltonians must be performed. Such efforts are currently in progress in our laboratories using Hohenberg-Kohn-Sham density functional theory [6].

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