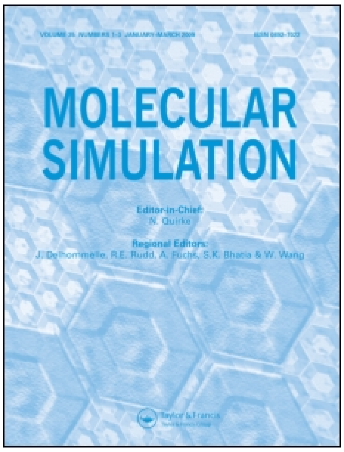

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THEORETICAL CALCULATIONS ON ZEOLITES: THE ALUMINIUM SUBSTITUTION IN MORDENITE, FERRIERITE AND ZSM-5

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The experimental determination of Al siting in zeolites involves the use of multiple techniques. Great effort has been made on both, experimental and theoretical approaches. The present study presents a novel methodology for calculating Al/Si replacement energies. Simple semiempirical calculations were applied on Modenite, Ferrierite and ZSM-5 zeolites, resulting in good agreement with the experimetal evidences. We have found that the favored Al substitution sites are T3 and T4 in Mordenite, while T2 and T4 are in Ferrierite, and only the T9 site is favored in ZSM-5. The method presented is based on an average of partial Al/Si replacement energies, evaluated for all rings belonging to each T site, rather than in the calculation of a total replacement energy evaluated for only one representative aggregate.

KEY WORDS: Al substitution, morderite, ferrierite, ZSM-5.

INTRODUCTION

In order to understand the stability, acidity and some other catalytic properties of zeolites, a knowledge of the exact location of aluminum in the framework is required. The application of multiple experimental techniques is needed for this purpose. The detail determination of the crystal structure by diffraction methods together with the high resolution solid state NMR are the most commonly experimental techniques used. However, most crystallographic studies are often unable to locate precisely and unequivocally the aluminum atoms in zeolites, and therefore, a great deal of effort in quantum chemical caluclations has been made.

Molecular dynamics studies [1] has demonstrated that besides the direct electronic effects caused by the aluminum presence in zeolites, there are some non direct influences which stem from the location of counterions in the neighborhood of these aluminum atoms. Several quantum molecular orbital (MO) studies have been carried out on zeolites, self-consistent field (SCF) MO non-empirical calculations by Hartree-Fock (HF) method using the STO-3G basis set were performed on such systems. Selected clusters reflecting more intimately the structure of the zeolite under study with the atoms involved occupying their actual framework positions derived from X-ray diffraction data are used for calculations. Typical replacement energies for a given T sites were evaluated as:

$$E_r(T_i) = E(T_{\mathrm{Al}}) - E(T_{\mathrm{Si}}) \tag{1}$$

Where E_r stands for the total replacement energy of silicon by aluminum in a specific T_i site and $E(T_i)$ stands for the total energy of the chosen cluster with atom "i" in that T site. From the experimentally derived structure of mordenite, topological open (pentameric) and closed (tetrameric, four membered ring) clusters were considered [2], for all the clusters investigated , no occupied MO had a positive energy and consequently the wave functions were stable and indicated a minimum on the total electronic energy of the system. However, it was soon realized that the usual calculated replacement energies gave positive values even in the case where most exhaustive ab initio calculations had been undertaken. Therefore the use of relative replacement energies with respect to the most favorable T_i^* substitution site became generalized. In this formalism, E_r was redefined as:

$$E_r(T_i) = (E(T_{\mathrm{Al}}) - (E(T_{\mathrm{Si}})) - (E(T^*_{\mathrm{Al}}) - E(T^*_{\mathrm{Si}})) \qquad (2)$$

Using equation 2, Derouane and Friapat [2], and Friapat *et al.* [3] successfully calculated replacement energies for mordenite and ferrierite in very good agreement with the experimental findings, although in all cases the silicon aggregates were found more stable than the correspondent aluminum clusters.

Recently, Alvarado-Swaisgood *et al.* [4], made very accurate ab initio calculations for aluminum substitution in ZSM-5 using STO-3G and VDZ basis. The importance of the T-O-T angle contributions to the Al/Si replacement energies was found to be the major difference between the results of the STO and VDZ calculations, concluding that minimum basis sets are unreliable for predicting relative replacement energies, due to their lack of flexibility. The replacement energies reported in Ref. [5] were not found to change very much with T-O bond lengths.

For non-empirical calculations still some questions remain, those which may clarify the relative importance of the selection of the adequate cluster and of the basis set, together with the preliminary minimization of the geometry. However, when one is interested in the knowledge of a particular structure, is hard to match the relaxed cluster with the actual framework.

Though questioned as less reliable, some semiempirical methods (EHT, CNDO and MNDO) have been used [6,7]. The MNDO has been proven to be more useful as an aid for the interpretation of chemical behavior, an example was given by Mintova *et al.* [7] who calculated basic characteristic of templates used in zeolite synthesis. In our view, Alvarado-Swaisgood's work has taught us, that the calculations of replacement energies are dramatically dependent on the model cluster chosen rather than in the atomic base selected. Therefore, in this study we have calculated partial replacement energies for all the rings belonging to each T site in mordenite, ferrierite and ZSM-5, and then evaluated statical averages. Here we present very simple MNDO calculations for which, as will be shown, negative replacement energies have been obtained.

CALCULATION PROCEDURE

Model representation of mordenite, ferrierite and ZSM-5 zeolites have been built using the Cluster-Construct module of Biosym's Catalysis software [8], and the crystallographic data reported by Alberti *et al.* [9], Vaugham [10], and Koningsveld *et al.* [11]. All rings corresponding to each *T* site were extracted from the built structure. In order to preserve the (near) neutrality of each atomic aggregate, the remaining dangling bonds were saturated with hydrogen and this cluster was considered for calculations. Since crystallographic data was being used, no further geometry optimization was performed for reflecting the actual position of atoms in the framework. Each ring was calculated with RHF-MNDO, from the MOPAC module of Biosym's Catalysis software [8], placing both silicon or aluminum at the corresponding *T* site. By MNDO approximation, the values of total energy, heat of formation, ionization potentials molecular geometry and dipole moment might be obtained.

The evalution of the replacement energies was based on the heats of formation (H_f) of the *T* site rather than on the total energies. Since only energy differences are computed, either one could be suitably selected. The H_f was evaluated on each of the rings forming a cluster considering first a ring where all metal sites are Si atoms, $H_{f(\mathrm{Si})}$ and another calculation where the *T* site Si atom has been substituted by an Al atom, $H_{f(\mathrm{Al})}$. For each ring, a partial replacement energy, H_i, was evaluated as:

$$H_i = H_{f(\mathrm{Al})} - H_{f(\mathrm{Si})} \tag{3}$$

The partial replacement energies were divided by the number of tetrahedral sites for ring, in order to have a partial replacement energy per site, statistically weighed. In other words, the inverse of the number of tetrahedral sites per ring, P_i, was used to statistically weigh the contribution of each ring to the complete cluster describing the *T* site. Afterwards, total replacement energies of a site were estimated by summing up the statistically weighed values of the partial replacement energy for all the rings conforming a site as:

$$H_r = \sum H_i * P_i \tag{4}$$

RESULTS AND DISCUSSION

The three zeolites considered namely, mordenite, ferrierite and ZSM-5 have received strong interest particularly for their wide application range, specially in catalysis for which composition and structure are the key factors. Regarding structure, they are closely related. Ferrierite most closely resembles mordenite, the same chains of five-membered rings are present parallel to the *c* axis in both structures. The *c* axis in mordenite has a length of 752 pm while in ferrierite is of 749 pm. In the same way, the crystal structure of ZSM-5 is closely related to ferrierite, a skeletal projection of the later along [001] looks the same representing a ZSM-5 layer in projection along [010] for which the channel parallel this direction.

The existence of a wide variety of commercially available zeolites is due to the fact that their synthesis are governed by metastable crystallization, and therefore, determined by kinetic factors rather than thermodynamic ones. This is one of the major problems in the theoretical prediction of zeolite structures, since those metastable phases correspond to local minima of the model structures and not the global energy minimum associated with thermodynamic stability [12]. Thus, as pointed out by Fitzgerald *et al.* [13], the applicability of geometry optimization procedures to the modelling of solid structures is severely limited. In their case, 'the complete geometry optimization was not a reasonable choice, since the optimal geometry of a finite gas phase cluster is expected to be quite different from the geometry of an infinite crystal'. As an example they cited the fact that all T-$(OH)_4$ cluster will end up the same if allowed to relax to the DFT minimum energy structure.

When, on the other hand, the geometrical characteristics of model clusters are taken from X-ray data, a statistical average bond length for both Al-O and Si-O bonds is used, in a clear contrast to the fact that Si-O distance is shorter than Al-O one. Whether or not to use geometry optimization is still a matter of controversy. However, Sauer [14] has also stressed that: 'a way to check whether a given local structure is optimal for accommodating Al, is to perform quantum chemical calculations of an $Al(OH)_4$ model adopting the observed atomic coordinates. The difference of the obtained energy and the energy of the corresponding $Si(OH)_4$ model at the same geometry yields the substitution energy.'

Despite the usual inaccuracies found in X-ray data and the knowledge that cations may significantly affect the relative order of substitution energies, this approach to the calculation of replacement energy has been previously used with success by Beran [15] in the quantum chemical description of the physical characteristics of ZSM-5; Fripiat *et al.* for the Al/Si substitution energies in ferrierite [3] and in the molecular calculation of ZSM-5 and ZSM-11 [16], Derouane and Fripiat in the quantum chemical approach to the aluminum siting in MFI zeolites [17] and for the aluminum sitting and pairing in mordenite [2]. Needless to say, the substitution energy represent a hypothetical process in which a Si atom is replaced by Al-, though it is difficult to corroborate the values with experimental data, indirectly the stability trends might be used as a measure of the Al site occupation level.

Mordenite

The crystal structure of mordenite determined by Alberti *et al.* [9] from a natural specimen corresponds to an orthorhombic symmetry (Cmcm), They also suggest from their own results that the Si/Al distribution is partially ordered, with an enrichment of Al in the tetrahedral of the four-membered ring. the Al/Si replacement energy values for mordenite are shown in Table 1. The energetic data reported in this table suggest that considering a cluster formed only by the atoms of a given ring might mislead the derived interpretation of stability. For instance, considering the T1 site, based on H_i values the stability ranking suggest that the aluminum substitution would be favored on the ring following the order 6-membered > 5-membered 12-membered and the 8-membered results slightly unstable. However, this order is significantly different when considering the T2 site. According to these results the most favorable Al substitution site is T3 followed by T4 and T1. The data also indicates that T2 site would be rarely substituted. Comparing with the experimental data of Alberti *et al.* [9], according to which natural mordenite shows 30%, 19%, 14% and 7%

Table 1 Al/Si Replacement Energy for Mordenite.

T Site	$1/P_i$	H_i *(kcal/mol)*	$H_i{*}P_i$ *(kcal/mol)*	H_r *(kcal/mol)*
T_1	5	−7.00	−1.40	
	6	−13.00	−2.17	
	8	5.76	0.72	
	12	−7.84	−0.65	
				−3.50
T_2	5	−7.00	−1.40	
	5	−4.00	−0.80	
	6	7.00	1.17	
	8	3.00	0.38^e	
	12	−7.72	−0.64	
				0.30
T_3	4	−9.00	−2.25	
	5	−19.00	−3.8	
	8	−9.79	−1.22	
				−7.27
T_4	4	−5.00	−1.25	
	5	−5.00	−1.00	
	8	−9.00	−1.13	
	12	−10.56	−0.88	
				−4.26

of aluminum content at the T3, T4, T1 and T2 sites, respectively, the trend obtained from our theoretical results, thereby, is in good agreement with experimental observations. The prediction of Derouane and Fripiat [2] non-empirical calculations indicated that stability observed on T3 and T4 was due to the diagonally paired Al-sites across the four-membered rings. As can be seen in Table 1, all four-membered rings showed stable replacement energies, while the most negative partial replacement energy was exhibited by the five-membered ring of the T3 site. Though in the case of T4, the replacement energy of the four-membered ring was slightly lower than that of the five-membered ring, for the T3 there was a clear difference favoring the five-membered ring stabilization.

Based on the occuptional experimental data, there should exist a higher energy differential barrier between T3 and T4 (Al occupation level of 30% and 19%, respectively), than that observed between T4 and T1 (Al occupation level of 19% and 14% respectively). Derouane and Fripiat found differences of at least 10 kcal/mol between the T3 and T4 energies and those of T1 and T2. We found a difference of 7.57 kcal/mol between T3 and T2 but a difference of only 0.76 kcal/mol between T4 and T1, values which are much more compatible with the occupational percentages exhibited by these sites (19% and 14% respectively)

All silicon rings showed ionization potentials which ranged from 11.06 eV to 11.95 eV. The Homo-Lumo differences varied between 11.94 and 15.51 eV, while the diatomic Si-O energies went from 21.00 to 31.31 eV. In contrast, the aluminum substituted rings showed ionization potentials between 5.34 and 6.21 eV, Homo-Lumo differences between 8.32 and 10.25 eV, and Al-O diatomic energies which ranged from 14.73 and 15.37 eV.

Ferrierite

As already mentioned, structurally speaking, ferrierite resembles most closely mordenite, with an orthorhombic symmetry, not yet unambigously defined between Immm or Imm2. Its main channel is formed by a ten-membered ring parallel to the *c* axis.

The early work of Vaugham [10] has regarded the T2 site of Ferrierite as richer in aluminum content than the other three, although he suggested a random Al distribution on the metal sites. According to Fripiat *et al.* [3] theoretical calculations on open monomers, dimers, pentamer, and cyclic hexamers, show the four different T-sites fall into two classes. The first one constituted by T2 and T4 sites has the most favorable substitutions sites (T4 being slightly less stable than T2). The T3 and T1 sites are about 80 to 150 kcal/mol less stable than the former. These calculations showed the six-membered ring as preferential Al siting locations. They also state that results obtained by using the minimal STO-3G basis set can be utilized for the classification of the various clusters and the identification of preferential Al substitution sites in the ferrierite framework.

As can be observed in Table 2. Our results favor T2 and T4 as the most favorable substitution sites in ferrierite as in Fripiat's work. However, in our case the five-membered rings of the T2 site resulted the most favorable replacement site. The six-membered ring present one positive partial replacement energy values, and other slightly negative value. The difference between the T2 and T4 substitution energies is

Table 2 Al/Si Replacement Energies for Ferrierite

TSite	$1/P_i$	H_i *(kcal/mol)*	$H_i{}^*P_i$ *(Kcal/mol)*	H_r *(kcal/mol)*
T_1	5	−0.24	−0.05	
	5	7.11	1.42	
	6	14.43	2.41	
	8	1.02	0.13	
	10	−6.68	−0.67	
				3.24
T_2	5	−31.00	−6.20	
	5	−7.74	−1.55	
	5	−15.19	−3.04	
	5	1.00	0.20	
	6	5.46	0.91	
	8	3.79	0.47	
	10	−14.15	−1.42	
				−10.62
T_3	5	1.33	0.27	
	5	1.82	0.36	
	5	29.40	5.88	
	6	−0.80	−0.13	
	8	−1.80	−0.18	
				6.20
T_4	5	−5.67	−1.13	
	5	−16.19	−3.24	
	5	−6.00	−1.20	
	5	−15.86	−3.17	
	6	−0.80	−0.13	
				−8.87

of only 1.75 kcal/mol, while difference between T4 and unfavored T1 and T3 sites, amounts to 12.11 and 15.07 kcal/mol, respectively.

ZSM-5

ZSM-5 is a unique zeolite which structure and composition determine its remarkable catalytic properties. A single crystal X-ray study reveals an orthorhombic symmetry (Pnma) with 12 crystallographic Si sites. The X-ray diffraction technique would difficulty provide insights on the Al distribution throughout the framework. In fact distinction between Al and Si, in a highly siliceous material is almost impossible. In most of the synthesized materials the T atoms are practically all Si. Even if the Al atoms present were all concentrated in just one of the T positions, this would represent only 1/8 of that position which would still be hardly detectable by ordinary X-ray crystal refinement. Furthermore, crystallographically ZSM-5 is a much more complex zeolite. Besides the 12 Si metal sites it has 26 different O-sites. From these 26 O-sites, 22 atoms bridge *t*-sites which are crystallographically different, the other 4 atoms bridge symmetrically related T atoms.

Table 3 lists the Al/Si replacement energies calculated for ZSM-5. According to our calculations, only the T9 site exhibited a negative substitution energy of −1.92 kcal/mol. This result is not surprising when one considers the very high Si/Al ratio of this zeolite and the high density structure which disfavors the aluminum substitution. As a matter of fact, the T9 site is situated between the two main channels of the zeolite, where there exist an appreciable amount of void space. The T4, T11, T6 and T8 are slightly disfavored, since their replacement energy values have been found to be 0.02, 0.59, 0.43, and 0.52 kcal/mol respectively. The Al/Si substitution energies for all other T sites range within much more larger positive values.

The theoretical calculations on the replacement energies for the determination of the *Al* distribution on ZSM-5 are rather controversial. Alvarado-Swaisgood *et al.* [4] have pointed out that minimum basis set are unreliable for predicting relative replacement energies for the substitution of Si by Al atoms at the T sites. Small difference in bond lengths and angles might significantly alter the order of the sites respect to the replacement energies. Their results using VDZ concluded by favoring the T6 site rather than the T9 site as the most favorable replacement site. In those calculations, the T12 and T9 site appear also favorable for Al substitution with only 0.4 kcal/mol energy value higher than that of the T6 site. However, the energy difference between the most and least favorable sites was only 3.3 kcal/mol introducing a lack of confidence on their final interpretation. In fact, Derouane [17] has stresed a lower limit of 6 kcal/mol as a realistic value for considering as significant the differences in the computed energies. Fripiat *et al.* theoretical results [11] do not agree at all with the presented findings. In their work the T12 site showed the most favored replacement energy by at least 7 kcal/mol. Consistently, their data agrees with previous findings pointing towards an *Al* substitution in decreasing order of probability T12 > T2 > T1. In our calculations, T12 has been found to be the most disfavored substitution site showing a positive value of 7.82 kcal/mol.

The work of Schroder *et al.* [18] discusses the effects of calculating energies on fixed cluster geometries. They claimed that the difference in bond length for Si-O and Al-O

Table 3 Al/Si Replacement Energies for ZSM-5.

T Site	$1/P_i$	H_i *(kcal/mol)*	$H_i * P_i$ *(kcal/mol)*	H_r *(kcal/mol)*
T_1	5	-0.66	-0.13	
	5	-1.01	-0.20	
	5	4.74	0.95	
	5	-5.42	-1.08	
	5	2.30	0.46	
	5	-1.85	-0.37	
	6	6.50	1.01	
	6	4.99	0.83	
	6	2.94	0.49	
	6	-5.01	-0.84	
	10	10.78	1.08	
	10	14.49	1.45	
	10	9.72	0.97	
	10	11.17	1.12	
	12	15.86	1.32	
				7.06
T_2	5	10.93	2.19	
	5	14.69	2.94	
	5	-4.82	-0.96	
	5	-0.62	-0.12	
	5	5.29	1.06	
	5	-1.00	-0.20	
	6	-2.30	-0.38	
	10	13.00	0.13	
	10	10.28	0.10	
				4.74
T_3	5	7.88	1.58	
	5	-2.23	-0.45	
	5	10.63	2.13	
	5	15.07	3.01	
	5	7.45	1.49	
	5	3.40	0.68	
	8	-9.42	-1.18	
	10	0.20	0.02	
				7.28
T_4	5	1.15	0.23	
	5	-7.24	-1.45	
	5	0.75	0.15	
	5	-5.95	-1.19	
	5	9.63	1.93	
	5	3.14	0.63	
	6	-0.44	-0.07	
	6	-12.92	-2.15	
	7	-1.68	-0.24	
	8	3.69	0.46	
	10	17.23	1.72	
				0.02
T_5	5	0.06	0.01	
	5	-1.41	-0.28	
	5	-2.31	-0.46	
	5	7.34	1.47	
	6	8.44	1.41	
	6	-2.07	-0.35	
	8	16.49	2.06	
	10	12.29	1.23	
	10	19.22	1.92	
				7.01

Table 3 *(Continued)*

T Site	*1/P$_i$*	*H_i (kcal/mol)*	*$H_i * P_i$ (kcal/mol)*	*H_r (kcal/mol)*
T_6	5	4.82	0.96	
	5	−5.29	−1.06	
	5	6.35	1.27	
	5	−9.38	−1.88	
	10	9.57	0.96	
	10	17.43	0.18	
				0.43
T_7	5	0.52	0.10	
	5	−7.19	−1.44	
	5	−4.27	−0.85	
	6	12.23	2.04	
	6	12.39	2.07	
	6	10.60	1.77	
	6	−5.01	−0.84	
	6	0.04	0.01	
	10	3.88	0.39	
	10	12.58	1.26	
				4.51
T_8	5	−5.39	−1.08	
	5	−0.40	−0.08	
	5	5.73	1.15	
	5	−2.88	−0.58	
	5	−7.50	−1.50	
	5	−5.35	−1.07	
	6	10.19	1.70	
	6	−4.06	−0.68	
	6	15.51	2.59	
	6	−2.05	−0.34	
	10	4.12	0.41	
				0.52
T_9	4	−6.45	−1.61	
	5	−0.01	−0.00	
	5	−5.87	−1.17	
	5	−6.08	−1.22	
	6	8.64	1.44	
	6	9.31	1.55	
	6	−10.49	−1.75	
	10	8.44	0.84	
				−1.92
T_{10}	4	5.27	1.32	
	5	−2.77	−0.56	
	5	3.07	0.64	
	5	−3.18	−0.64	
	6	6.07	1.01	
	6	5.69	0.95	
	6	−0.76	−0.13	
	6	−7.29	−1.22	
	10	8.11	0.81	
	10	6.52	0.65	
				2.80
T_{11}	5	−2.16	−0.43	
	6	16.69	2.78	
	6	−13.37	−2.22	
	10	4.58	0.46	
				0.59
T_{12}	5	−1.67	−0.33	
	5	−4.03	−0.81	

Table 3 *(Continued)*

T Site	$1/P_i$	H_i (kcal/mol)	$H_i * P_i$ (kcal/mol)	H_r (kcal/mol)
	5	4.64	0.93	
	5	0	0	
	6	11.34	1.89	
	6	12.08	2.01	
	6	9.07	1.51	
	6	8.78	1.46	
	6	−3.26	−0.54	
	8	9.86	1.23	
	10	12.71	0.13	
	10	11.46	0.11	
	10	2.31	0.23	
				7.82

would show up as a lower cluster energy but by fixing the cluster geometry two possible problems will arise. The first, the minor, is the refined structure may not render meaningful bond length differences. The second, the more severe, is that quantum chemical energy differences are only more reliable if they correspond to a fully relaxed structure. They calculations showed very small differences in replacement energy values, from which they concluded that the Al distribute over a broad range of framework sites even at low temperature provided that this was controlled by normal statistical mechanical factors. Clearly that sets a contradiction with Derouane and Fripiat [17] results which was explained based on the lack of nuclear relaxation of the cluster geometry in this later work, and in the use of the monoclinic structure in the former. In fact, the average T–O bond distances in the monoclinic form is between 158–160 pm while the orthorhombic form is between 158–159 pm. However, since we have used Koningsvield data for ZSM-5 [11], our results are not influenced by the lower accuracy found in the former data from Olson [19], as claimed by Schroder *et al.* [18] with respect to the previous works of Beran [15] and Derouane and Fripiat [17]. In our case, the T2 and T12 sites which Schroeder *et al.* predicted to be favored as a consequence of the larger Al-O distance compared to Si-O, are highly disfavored. Besides, it appears interesting the fact that Derouane and Fripiat could have reproduced the experimental aluminum placement in mordenite and ferrierite without using any kind of geometry optimization over the refined X-ray data.

In a recent publication, Kramer *et al.* [20] have put forward again the necesscity or relaxed structures prior to quantum chemical calculations. The flexibility of the zeolite framework is quite large and consequently lattice relaxation upon chemical substitution gets more important. In their work, the large extent of relaxation within the aluminosilicate lattice was justified by the use of geometry-optimized (free) clusters, as a first step toward the modeling of the infinite zeolite lattice. From their results the T4 site was shown to be the most stable (but in our calculations present a slight positive value of 0.02 kcal/mol). With the exception of T4, T8 and T10, the other sites showed positive values for the relative aluminum substitution energies when calculating the orthorhombic structure and using a charge difference of 0.96 between the Si and Al atoms. The differences among the relative aluminum substitution energies of the sites were almost negligible when the charge difference was of 0.48.

There is a lack of experimental data refering to the aluminum siting in ZSM-5. It has been deduced however, from the experimental work of Lin *et al.* [21] regarding the locations of Cs cations on ZSM-5, that the four-membered rings are the most favorable substitution sites. Of the two four-membered rings proven, only the one belonging to the T9 site presented a negative substitution energy (−1.61 kcal/mol). In spite of this, the six-membered rings belonging to the T11 and T4 sites, presented lower values of partial replacement energies of −2.22 and −2.15 kcal/mol.

Regarding geometry optimization, the final optimal structure may represent a stable aggregate but will differ significantly from the real structure subjected to modelling. In this work, for the three studied cases, geometry optimization of the cluster lead to distortions in the structure which can be considered unreal, and thus the positive values of the substitution energy obtained always when doing so, might lack of any validity.

CONCLUDING REMARKS

This work has presented a very simple methodology for calculating replacement energies, based in MNDO calculations of heat of formation of a cluster involving all rings associated to a T site. This methodology has been proven to provide results in agreement with experimental data for the three zeolite structures tested. It is believed that the use of the rings belonging to each T site, as model clusters is not only appropriate to eliminate the problem of selection of a representative aggregate, but is also quite appealing, since it may allow to readily calculate replacement energies for new theoretical zeolites.

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