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模板效应对 β 分子筛中 Al 原子分布的 DFT 理论计算研究

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摘要: 基于量子化学中的密度泛函理论(DFT),通过 β 分子筛同模板剂四乙胺阳离子(TEA^+)的主客体相互作用来讨论了模板剂分子对骨架 Al 的靶向作用。计算采用了密度泛函理论中的 B3LYP 方法在 6-31G(d,p)基组上研究了 β 分子筛同 TEA^+主客体相互作用的几何结构、分子轨道、电荷分布以及 9 个不同骨架位置的相互作用能。研究结果表明:带正电荷的 TEA^+吸引 β 分子筛上 Al 原子形成的阴离子中心($Zeo\text{-}AlO_4^-$),两者具有很好的匹配关系。通过主客体相互作用影响了 Al 原子在分子筛中的分布。骨架 Al 最有利于落位在 β 分子筛的 T5 和 T6 位,落位的稳定性顺序是 Group Ⅱ(T5,T6)>Group Ⅲ(T7-T9)>Group Ⅰ(T1-T4)。

关键词: β 分子筛; Al 落位; 模板剂(TEA^+); 相互作用; 密度泛函理论
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Guest-Host Interactions of Tetraethylammonium Cations and Zeolite Framework for Distributions of Al in β Zeolite: a Density Functional Theory Calculation

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Abstract: Guest/host interaction between the tetraethylammonium (TEA) cations molecule and the model cluster of zeolite, calculated with DFT method, was used to investigate the Al preferential location in β zeolite. The calculations were performed based on cluster model by using of B3LYP hydride functional and 6-31G (d, p) basis set. For these species the geometries, molecular orbitals, Mulliken atomic, and interaction energies were analyzed. According to the calculated results of orbital picture and charge distribution it was proposed that the template has a good fit with the host framework and the role of the template is shown to be crucial in order to elucidate the Al distributions. Therefore, the energetics during the synthesis process (zeolite+template) that has to be considered, and in this scene the template accommodation within the microporous space acts not only as a structure director but also as a director of the Al distribution. Based on the distances and energies of the guest/host interaction about different T (T=Al) sites, it was predicated that the T5 and T6 sites are the most stable sites for the substitution of Al in the β zeolite framework; and the stability is in the order of Group Ⅱ (T5,T6) > Group Ⅲ (T7-T9) > Group Ⅰ (T1-T4).

Key words: β zeolite; Al location; tetraethylammonium cations; interaction; density functional theory

0 Introduction

β zeolite is one of the aluminosilicate materials with large-pored structure and high silica crystalline. It has three-dimensional system of interconnected 12-membered ring channels. The pore opening of tortuous channel comprising the interaction of two linear channels is approximately 0.56 nm×0.56 nm, and the

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pore opening of linear channels is 0.57 nm×0.75 nm[1]. The protonic form of β is an active catalyst for many reaction requiring acidic sites such as catalytic cracking, olefin isomerization, isobutene alkylation with *n*-butene, and Beckmann rearrangement[2~6]. Indubitably, the acidity plays an important role in the catalysis. This is mainly due to the presence of tetrahedrally coordinated framework Al in the silica frame introduces a negative charge in the structure that can be compensated by a proton, and the resultant Brönsted acid (B-acid) site. Therefore, the distribution of Al atoms in the tetrahedral and octahedral sheets of phyllosilicates plays an important role in determining the distribution and magnitude of the surface charge, which is further responsible for the various properties of phyllosilicates.

The distribution of Al atoms in phyllosilicates can be estimated from the structural formula which is calculated from chemical analyses data. Some studies by Lobo et al.[7~9] have focused on this subject by using different NMR techniques to study the aluminum distribution of Al-ZSM-12 zeolite. They found that the distribution of Al sites is not random but is controlled by the structure directing agent (SDA) used in the synthesis process. The Al sites (a negative defect with respect to a silica framework) tend to locate near the positive charge introduced by the SDA used in the synthesis process. In this way, the SDA has not only the effect of directing the synthesis toward a particular structure(s) but is also responsible for the Al distribution in the as-made zeolite. The case of ZSM-18 has been studied and the template molecule has been shown to play an important role not only in stabilizing the structure formed but also orientating the Al location in the structure[10].

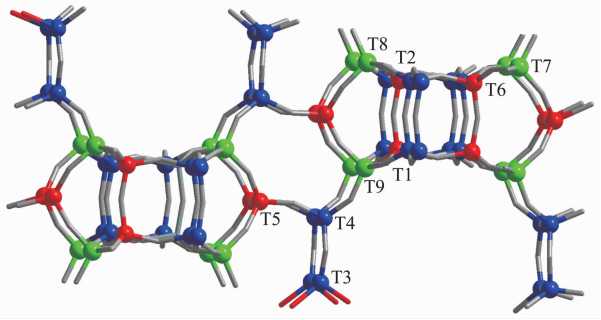
Theoretical calculations[11~13] are very useful for studying the energetics of substitution of aluminum for silicon at different T sites, and also for the prediction of acid strength, stability, and the possible location of B-acid in zeolites. A lot of theoretical calculations have made contributions for sitting framework Al atoms in ZSM-5 and MCM-22 zeolites[14~21]. A few of theoretical calculation studies were carried out for β zeolite. Papai et al.[22] have performed the theoretical calculations on the substitution energy of aluminum at distinct T sites. In our previous work, the DFT method has been also applied to calculate the substitution of aluminum in the β zeolite through comparing the relative substitution energies[23]. There is no study so far to monitor the templating phenomenon for distributions of aluminum in the β zeolite framework.

In this work, we present results of a study of the interaction between templates and zeolite framework structures, to reveal the locations of aluminum in the β zeolite. The geometries, molecular orbitals, Mulliken atomic, and interaction energies of the TEA^+ molecule with the zeolite framework were calculated by B3LYP/6-31G (d, p) method.

1 Models and methodology

Zeolite β is a large-pore synthetic zeolite with a three-dimensional 12-ring channel system. There are two straight channels in the [100] and [010] directions and a third sinusoidal channel located parallel to the [001] direction in the A polymorph. These channels intersect, leading to a three-dimensional open-pore structure. The secondary building units consist of six-, five-, and four-membered-ring cages, each of them facing at least one side to a 12-membered-ring channel. Within this crystal structure (Fig.1) there are nine crystallographically different silicon sites, designated as T1 through T9. Within the zeolite framework, Al could substitute either randomly or into specific sites for any of the Si atoms of this structure. Fig.1 also shows that the radial distribution of Si and O atoms about each of these Si sites for the pure β-zeolite structure falls into three distinct groups. Because all nine T-sites have tetrahedral coordination, each sharing an oxygen atom with the neighboring Si tetrahedral, on the basis of the ring structure, these sites can be readily sorted into three groups by reason of their coordination sequence[24,25]. Group Ⅰ contains sites T1, T2, T3, and T4. These T-sites occupy a vertex of two 4-rings. Group Ⅱ contains sites T5 and T6, which occupy a vertex on a 4- and 5-ring. Group Ⅲ contains sites T7, T8, and T9, which share several 5- and 6-rings. A unique property

of the T5 and T6 sites is an almost linear bond from the Si atoms of the T5 site through a corner oxygen atom of the tetrahedron to the neighboring T6 site. None of the other T-sites have this unique geometry.



Nine crystallographically different Si sites, designated as T1 through T9, in the β lattice looking through the *b*-axis (for clarity the oxygen atoms are not shown)

Fig.1　Schematic representation of the T sites in β-zeolite

The cluster approach is particularly suited to describe local phenomena like the interaction of organic molecules with active sites of catalysts. Concerning the size of the quantum clusters, we should mention that a former work[26] indicated that good convergence of adsorption properties could already be reached by the 5T cluster. We are quite aware of the limitations of this cluster-model but as shown in other publications, at least for small sized substrates, the larger clusters do not introduce any changes in the mechanism but only in the energetics of the reactions [27]. Considering the important effect of zeolite framework structure, using a large cluster to represent the zeolite would, of course, be necessary. However, the TEA $(CH_3CH_2)_4N^+$ model contains 30 atoms were fully opti-mized, accurate quantum calculation with a large zeolite cluster model is very expensive. Therefore, the relative energies can be well established with the 5T model.

The β zeolite was modeled by substituting an Al atom using a 5T in $Al(OSiH_3)_4$ cluster. The models of nine inequivalent T sites were cut from the crystallographic structure of β. This model represents the β zeolite′s pore structure which is the straight channel in the [100] direction. The dangling Si atoms were terminated by H atoms along the bond direction of next lattice oxygen atoms with a distance of 0.149 nm. Terminating of Si with OH was found not possible because some framework oxygen atoms are shared with two Si atoms. During geometric optimizations the Cartesian positions of terminal silyl groups were held fixed in their crystallographic positions to retain the zeolite structure, while other lattice atoms relaxed. As shown in Fig.2, the figures are modeled by substituting an Al atom into the β zeolite structure at site T1, T5, or T9. These sites are taken as representatives from each of the three distinct groups, since these sites span all the possible loop configuration of T-atoms in β.

All calculations in this work were carried out with Gaussian 03 program package[28]. We used density functional theory (DFT)[29,30] with the hydride B3LYP exchange correlation functional for all calculations. DFT is used throughout using the B3LYP functional[31,32] providing an optimal quality/cost radio, an approach which nowadays gained the status of a standard procedure, applicable to a wide range of systems and properties. Although it is known that van der Waals interaction is not properly computed by DFT method, it was also shown that the hydride DFT methods such as B3LYP give accurate results for some calculations about zeolite complexes, including weak interactions[33, 34]. The basis set used for all elements was 6-31G (d, p). Vibrational frequencies were calculated at the same

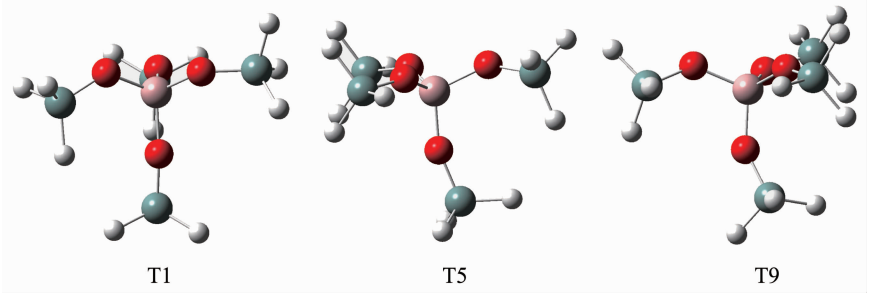


Fig.2　$Al(OSiH_3)_4$ model clusters of β zeolite on T1, T5, and T9

level to identify the nature of the stationary points and obtain the zero-point-energy (ZPE) corrections. Basis set superposition errors (BSSE) were estimated by the counterpoise method[35].

2 Results and discussion

Microporous materials provide a host-type environment for stabilizing charged molecular species occluded in their cavities. The stabilization of the "zeolite-guest" system with respect to the separate components, "zeolite+guest", is due to the interactions between the guest and the zeolite. The energy change in the synthesis process starts from the initial reactants (a silica-alumina gel plus the organic SDAs) and goes toward the final zeolite-SDA system.

2.1 Structural properties of the template-host interaction

2.1.1 Structure of clusters in Al-β

The nine clusters from the force-field optimizations were taken as the starting point for B3LYP calculations, with the aim of comparing how the initial geometry may influence the quality of the results. The optimized structural parameters of Al-β for all the nine T-sites (T1-T9) are given in Table 1. The average Al-O, Al-Si distances and Al-O-Si bond angles are present. The optimized average Al-O bond lengths and the Al-O-Si bond angles of β are 0.017 22~0.017 35 nm and 139.6°~147.3°, respectively; these values are in good agree-ment with the earlier studies [22]. We observe from Table 1, that the T5 and the T6 positions have the shortest Al-O bond lengths of 0.017 22 and 0.017 26 nm, respectively. However, the bond angle of the Al-O-Si at the T5 position is the largest with 147.3°. The Al-Si distance is the largest for T5 position, which can be attributed to the larger Al-O-Si bond angle. The T4 position has the largest Al-O bond length of about 0.01735 nm and the smallest Al-O-Si bond angle of 139.6°. The change in the structural parameters of each T-site can drastically affect the energetics of the zeolite. Hence, the stability of each site would be different.

Table 1 Average Al-O, Al-Si distances and Al-O-Si bond angles of the optimized structures for the nine different T-sites in β zeolite

T sites	Al-O / nm	Al-O-Si / (°)	Al-Si / nm	$d_{N\text{-}Al}$ / nm
T1	0.173 1	140.0	0.314 6	0.464 0
T2	0.172 7	140.8	0.312 2	0.453 9
T3	0.172 9	144.7	0.315 1	0.465 0
T4	0.173 5	139.6	0.311 9	0.457 7
T5	0.172 2	147.3	0.317 5	0.447 4
T6	0.172 6	145.1	0.316 4	0.447 7
T7	0.173 0	143.8	0.315 8	0.451 2
T8	0.172 7	143.3	0.315 2	0.449 0
T9	0.173 3	140.3	0.313 5	0.450 6

2.1.2 Matching of TEA^+ molecules with the internal space of β zeolite

The distance between the molecule and the framework has important influence on the interaction, and requires a suitable value. Sabater et al.[10] reported that the initial Al distribution was obtained by minimizing the Al-N distance. In this way, each of the nine Al atoms present in the zeolite framework was located in the position closest to the corresponding N atom of the template. This was done because the negative charge brought by Al is expected to locate close to the concentration of positive charge in the methyl groups of the template. Instead of defining a more complicated set of distances between the Al atom and the center of mass of the methyl groups, the close by N atom (bonded to two methyl groups) was selected instead for the sake of simplicity. In order to investigate the matching situations of TEA^+ molecule with the internal space of zeolite, $d_{N\text{-}Al}$, the shortest distance between the nitrogen atoms of TEA^+ molecule and the aluminium atoms of the zeolite framework is calculated after energy minimization (see Fig.3). Table 1 lists the

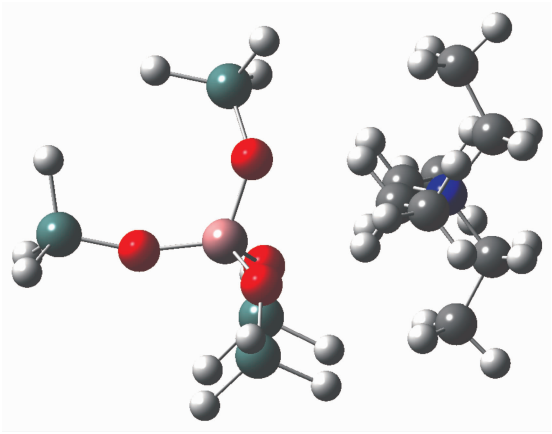


Fig.3　Calculated structure of adsorbing complex of the TEA^+ on the T5 site in β zeolite

values of $d_{N\text{-}Al}$ for all nine T sites.

The value of $d_{N\text{-}Al}$ can be used to compare the structure-matching situation of TEA^+ molecules with the internal space of the investigated zeolite. The T5 and the T6 positions have the shortest $d_{N\text{-}Al}$ lengths of 0.044 74 and 0.044 77 nm, respectively. The values of $d_{N\text{-}Al}$ at T7-T9 are around 0.044 9 ~0.045 12 nm. The values of $d_{N\text{-}Al}$ at T1-T4 are longer than 0.045 39 nm. That implies that the interactions of TEA^+ with T5 and T6 are stronger than that with other T sites. On this view, T5 and T6 sites are favorable for Al location in β zeolite.

2.2　Orbital picture for charge transfer interaction

The analysis of the molecular orbitals can provide much useful information about a molecular, such as the site of electron attachment and detachment, as well as chemical reactivity[36,37]. Charge transfer interactions are short-range and site specific forces, that arise from orbital overlap between the reacting species. Since, it has been found that charge transfer is relevant in the stabilization of anionic inclusion complexes with TEA^+, it is very useful to visualize these interactions in terms of the orbitals involved in the host-guest charge transfer.

Both the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are the main orbitals taking part in chemical reaction. The HOMO energy characterizes the ability of electron giving, the LUMO characterizes the ability of electron accepting. From DFT molecular descriptor analysis it has been already stated that anions act as electron donor species in the inclusion interaction with TEA^+. Therefore, according to the Frontier Molecular Orbitals reactivity theory[38,39], one can expect that charge transfer is governed by the maximum overlap between the HOMO of the zeolite anionic guest (donor species) and the LUMO of the TEA^+ molecule (acceptor species). Three dimensional plots of the corresponding HOMO of anions and LUMO of TEA^+ were constructed from DFT calculations at B3LYP/6-31G (d, p) level and were employed to build a pictorial representation of the orbital interaction that lead to host-guest charge transfer. The shape and location of the frontier orbitals, that is, HOMO and LUMO, of all molecules are illustrated in Fig.4. The HOMO of anions is located near the Al of the molecule, and the LUMO of TEA^+ is on the core of the molecule, the overlapping of the electron clouds have been done between HOMO and LUMO. It can be proved that the template has a good fit with the host framework. In this scene, the template influences the Al location due to electrostatic effects: the Al acts as a negative charge in a silica network and tends to locate nearby the TEA^+. Therefore, the role of the TEA^+ template is shown to be crucial in order to

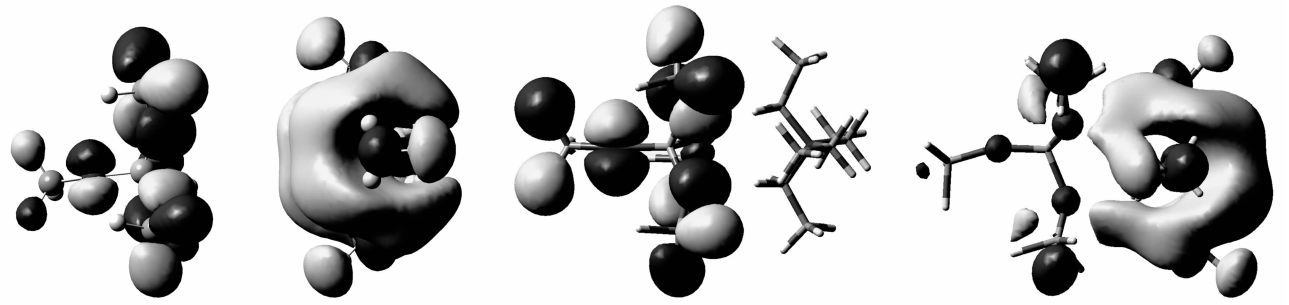


Fig.4　Orbital picture for charge transfer interactions involved in the inclusion complexation of β zeolite with TEA^+

elucidate the Al and acid site distributions, and the TEA^+ template accommodation within the microporous space acts not only as a structure director but also as a director of the Al distribution in β zeolite. Our obtained result is similar to the studies by Lobo et al.[7] for the aluminum distribution of Al-ZAM-12 zeolite. These interactions should also be helpful to understand why highly hydrophobic species such as cations can penetrate the hydrophilic cavity of zeolite framework.

2.3 Mulliken atomic populations

Mulliken atomic populations (MAP) give a chemical intuitive representation of the degree of charge on one atom in a molecule and should be regarded as a qualitative tool for interpreting tendencies about intramolecular charge transfer in a molecular system. The MAP of the atoms involved in the interaction between TEA^+ and β zeolite cluster in Table 2. The most important changes in these atomic charges are observed in atoms of the zeolite and the atoms of the TEA^+. These MAPs suggest that the formation of the TEA^+-zeolite complex induces electronic charge reorganization where the atoms of zeolite act as electron donor with a polarization charge of +0.12*e*. On the other hand, the TEA^+ operates as an electron acceptor, where the corresponding polarization charge values are −0.12*e*. Fig.5 displays the model of charge polarization of the TEA^+-zeolite adsorption complex with the corresponding charge variations. Additionally, the charges located at the each atom of the complex are slightly affected by the interactions between guest/host. Such as the MAP of Table 2 show for the Al atom a charge transfer at +0.07*e* of theory occur in the complex. The charge distribution also indicated that the template has matched with the host zeolite framework. The obtained explanation result of charge distribution is in good agreement with that of the molecular orbitals.

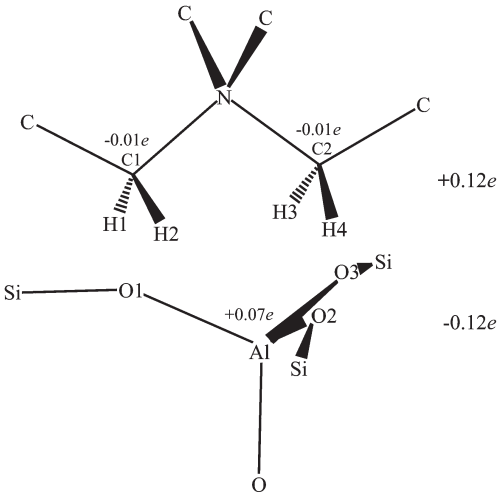


Fig.5 Model for charge polarization for the β zeolite model on T5 site and the TEA^+

Table 2 Mulliken atomic population MAP of the atoms involved in the β zeolite model on T5 site

Mulliken atomic populations	Zeolite	TEA^+	Zeolite-TEA^+ complex
Q(Al)	0.877		0.943
Q(O1)	−0.635		−0.687
Q(O2)	−0.644		−0.697
Q(O3)	−0.649		−0.703
Q(N)		−0.412	−0.415
Q(C1)		−0.067	−0.076
Q(C2)		−0.067	−0.078
Q(H1)		0.161	0.167
Q(H2)		0.161	0.185
Q(H3)		0.161	0.206
Q(H4)		0.161	0.201
Q(5T)	−1		−0.877
Q(TEA^+)		1	0.877

2.4 Interaction energy of guest/host system and stability

The interaction of TEA^+ with β zeolite leads to the formation of a molecular adsorption complex. An important property of the adsorption complexes is their interaction energy $E_{interact}$, which is defined as the

difference between the total energy $E_{\text{zeo-TEA}^+}$ of the complex and the corresponding to the isolated species:

$$E_{\text{interact}}=E_{\text{zeo-TEA}^+}-E_{\text{zeo}}-E_{\text{mol}}$$

Where E_{zeo}, E_{mol} is the potential energy of the zeolite framework and the template molecule, respectively. E_{interact} is a property that gives an energetic measure of the degree of the interacting in the formation of the adsorption complex.

The interaction energy was calculated with CP corrections for BSSE, and then obtained E_{interact}'.

$$E_{\text{interact}}'=E_{\text{interact}}+E_{\text{BSSE}}$$

Where E_{BSSE} are the energy of Zeo-TEA$^+$ with the CP correction.

In this subsection we discuss the interaction energies and hence the stabilities of all the nine Al sites. We can estimate the preferable sites in these zeolites for the molecule according to the data of E_{interact}'. The lower the interaction energy of the TEA$^+$ and zeolite framework, the more stable it is and the more energy is required to decompose the complex. Fig.3 shows the molecule of TEA$^+$ interacts with framework of a Al-β zeolite. The primary plane of investigated template molecule is parallel to (100) in the 12-MR channel. The orientations of TEA$^+$ molecules in the conformers are almost the same as those reported in Jon et al.′s paper[40]. The data of the calculated interaction energy for TEA$^+$ molecule with the aluminous zeolites are listed in Table 3. The values in bold font type suggest the favorable positions for TEA$^+$ molecule. The calculated relative interaction energies for 9 unequivalent sites in β are also listed in the Table 3, ranging −19.12~0 kJ·mol^{-1}. Comparing the relative substitution energies of the different sites, it can be seen that T5 and T6 sites show lower interaction energies are −19.12 and −18.27 kJ·mol^{-1}, respectively, and hence show the most stable sites for the Al atom in β zeolite. One should note that, the difference in the interaction energy of T5 and the T6 site is very little, this is can be attributed to the similar structure property of two sites in Group Ⅱ. The most unstable site is the T3 site which has 19.12 kJ·mol^{-1} higher energy than the T5 site. The calculation results indicate that the order of the preferable location of Al atom in β zeolite is Group Ⅱ (T5, T6) > Group Ⅲ (T7-T9) > Group Ⅰ (T1-T4). This result is in the same as we found in our previous study[23], and Papai et al.[22] are also reported that the least favorable site for the Al substitution is the one associated with two four-membered rings in the framework of β zeolite. Our data show that the Al does not randomly insert into the β zeolite structure but rather occupies identical, specific crystallographic sites. These sites are T5/T6 sites in the six-membered rings. Moreover, the Al is substituted in pairs on opposite sides of the six-membered ring. This uniform site distribution of the Al suggests that there is likely a symbiotic relationship between the template in the zeolite synthesis and the Al heteroatoms during the framework formation.

Table 3　Calculated interaction energies between the TEA$^+$ and β zeolite of the nine different T-sites

Models	E_{zeo} / a.u.	$E_{\text{zeo-mol}}$ / a.u.	E_{interact} / a.u.	E_{interact}' / a.u.	E_{interact}'' / (kJ·mol^{-1})
T1	−1 708.850 23	−2 080.137 11	−0.111 16	−0.106 059	−0.6
T2	−1 708.846 02	−2 080.135 49	−0.113 75	−0.107 486	−4.34
T3	−1 708.847 95	−2 080.134 54	−0.110 87	−0.105 832	0
T4	−1 708.849 09	−2 080.137 67	−0.112 87	−0.107 678	−4.84
T5	−1 708.848 03	−2 080.141 31	−0.117 57	−0.113 116	−19.12
T6	−1 708.849 21	−2 080.142 04	−0.117 12	−0.112 789	−18.27
T7	−1708.850 68	−2 080.141 23	−0.114 83	−0.110 102	−11.21
T8	−1 708.849 18	−2 080.1403 8	−0.115 48	−0.110 654	−12.66
T9	−1 708.851 67	−2 080.141 85	−0.114 46	−0.109 518	−9.68

Energy of the template molecule (TEA$^+$) is −371.175 72 a.u.

3　Conclusions

In the present work, DFT method was used to study the interaction of TEA$^+$ with β zeolite leading to the formation of the adsorption TEA$^+$-zeolite complex, and thus the preferable Al sites were predicted. B3LYP

methods were employed for the calculations with standard 6-31G (d, p) basis set, and using the cluster models in form $T(OSiH_3)_4$ defined as 5T models. For these species the geometries, molecular orbitals, Mulliken atomic and interaction energies were analyzed.

The structural parameters show shorter Al-N bond lengths of T5 site relative to the other sites. The inclusion complexation of β zeolite with TEA^+ was described by simple two-parameter correlation models containing easily interpretable molecular orbitals descriptors. The analysis of the charge distribution of the isolated molecules and cluster models and the corresponding complexes through the MAP shows that there is an important charge polarization in the zeolite and TEA^+. The zeolite acts as an electron donor and TEA^+ as an electron acceptor. It was proved that the template TEA^+ has a good fit with the host framework and the role of the template is shown to be crucial in order to elucidate the Al site distributions.

Among the nine T-sites, the T5 and T6 sites prove to be the most stable sites for the substitution of Al in the β framework; this stability is due to the lower interaction energy relative to the other T site. Based on the interaction energies with different T sites, we can confirm that the stability is in the order of Group Ⅱ (T5, T6) > Group Ⅲ (T7-T9) > Group Ⅰ (T1-T4). The energy difference between the least and the most favorable site is 19.12 $kJ \cdot mol^{-1}$. It was shown that the Al does not randomly insert into the β zeolite structure but rather occupies identical, specific crystallographic sites. These sites are T5/T6 sites in the six-membered rings.

The present theoretical study gives an insight into the structural and the electronic properties of the T sites in Al-β which is otherwise difficult by using the experimental techniques. Although at present we have limited our work to calculations on frameworks of zeolite, these results indicate that calculations hypothetical structures will prove useful of the design and synthesis mechanism of β zeolite. We will continue our studies to go on this issue, and further work on effect of model using ONIOM method is still in progress.

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