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Ti atom in MFI zeolite framework: a large cluster model study by ONIOM method

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Abstract

Ti atom siting in MFI zeolite framework was studied using one large cluster model containing about 200 atoms, which was made by trimming of MFI zeolite crystal, by means of ONIOM quantum mechanics/molecular mechanics (QM/MM and QM/QM hybrid) method. Si atoms at 12 T sites were replaced succeedingly with a Ti atom and resulted $Ti(OSi)_4$ moiety was locally relaxed by ONIOM (B3LYP/Lanl2dz:UFF) method. The other atoms at crystallographic structure of MFI zeolite framework were treated as an inorganic matrix and fixed at its original position. Single-point energies of T sites were calculated for the optimized structure by ONIOM (B3LYP/Lanl2dz:B3LYP/Lanl2mb) and the relative stability between T sites was compared.
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Keywords: MFI zeolite framework; Cluster model; ONIOM

1. Introduction

Ti containing MFI type zeolite (Titaniumsilicalite-1, TS-1) shows a superior catalytic activity for the oxidation reactions of organic substances. For example, ethene epoxidation or phenol hydroxylation are effectively catalyzed by TS-1 [1–3]. Supported Ti oxide also shows catalytic activity for these oxidation reaction. However, the catalytic activity of supported Ti oxide is lower than that of TS-1 [1]. The difference of the catalytic activity of these systems, supported Ti oxide over a catalyst support material and TS-1, has been considered to be due to the environmental difference around Ti atom. Therefore, in order to elucidate the

cause of the specific catalytic activity of TS-1, Ti siting has been extensively studied by using several analytical experimental techniques [4,5] and reviewed in [6].

Many theoretical works have been done for clarify the exact siting and chemical action of Ti atom as a catalytic center in MFI structure [7–9]. However, the environment around Ti atom and a behavior of it in catalysis have yet been subjected. Main reason of the difficulties of theoretical work for zeolite by ab initio or *first principle* calculation is that zeolite unit cell contains too many atoms. Typically, more than 200 atoms in a unit cell. Therefore, in order to examine the behavior of Ti atom in zeolite framework theoretically, very much computational time has to be consumed. On the other hand, molecular mechanics (MM) or moleculer dynamics (MD) using potential parameter can easily treat more than 1000 atoms. However, these methods can not represent the electronic behavior of a catalytic center and reactants, therefore, MM

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and MD methods are not suiting for the investigation of catalytic reactions.

Recently, some calculation methods have been elaborated for a large-scale system [10]. ONIOM [10,11], implemented in Gaussian 98 [12], is one of the widespread quantum mechanics (QM/QM) and QM/MM hybrid method suit for large-scale calculation. This method is expected to apply to the reaction in large-scale system, for example homogeneous metal complex catalyst having bulky ligand [1,2] and heterogeneous supported catalyst on inorganic matrix.

ONIOM method can be applied to a very large system of zeolite framework. If we can assume that the zeolite framework atoms distant from Ti center do not influence a local structure around Ti, these zeolite framework atoms can be fixed and tentatively treated by MM force field calculation. If necessary, calculated MM energy would be replaced by QM energy. Also, if we can assume that the nearest oxygen atoms influence Ti atom electronically, high level QM calculation should be done for the local structure around Ti atom. By these assumptions, we treated the zeolite framework Si–O network as an inorganic matrix such as silica gel of catalyst support, and central TiO_4 moiety as a supported metal oxide. However, these Si–O atoms having zeolite structure constrained local structure around Ti atom.

In this report, by using ONIOM QM/MM and QM/QM hybrid method, we examined relative stability of T sites of one large-scale cluster model containing about 200 atoms.

2. Theoretical calculation

The cluster model including all 12 T sites is shown in Fig. 1. This model was made by trimming of MFI structure supplied as structure library in Cerius 2_4.2MS (MSI—Accelrys [13]), which was used as a graphical user interface for Gaussian 98-ONIOM
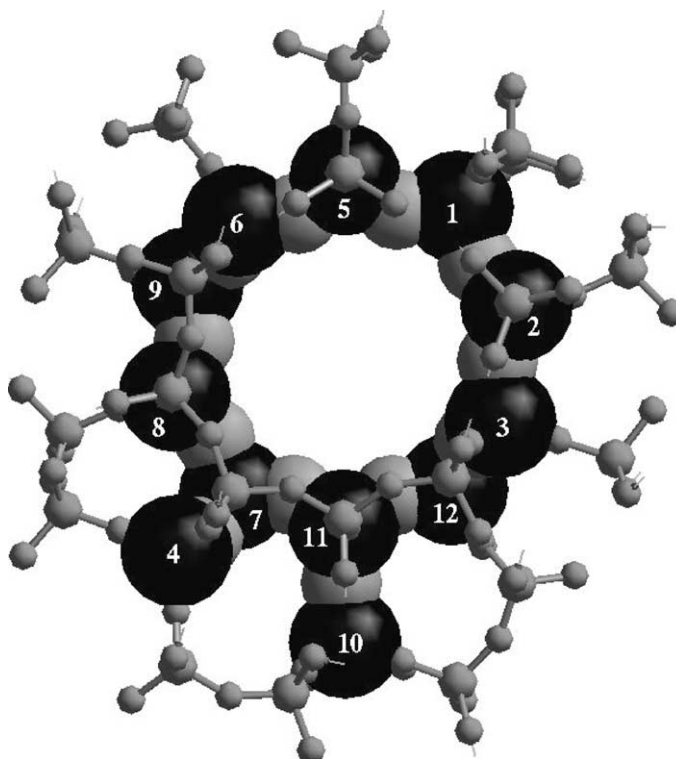

Fig. 1. Model cluster of 12 T sites in MFI structure. Big black ball: Si or Ti at T site; big gray ball: O; medium gray ball: Si at T site; small gray ball: O. Terminating H atoms are omitted.

job. In this cluster model, four $(OSiO_3)$ moieties in MFI crystal structure surrounded all examined T site atoms. Relative stability of each T sites was examined using this cluster model.

The details of ONIOM method are given in [1,2] and manual book of Gaussian 98 [12]. One T site in a cluster model was replaced with a Ti atom, which was written as Tn ($n = 1, 2, \ldots, 12$) in the follow, and resulted $Ti(OSi)_4$ moiety was allowed to relax. Remained atoms at MFI zeolite crystallographic structure were all fixed. TiO_4 moiety was chosen as a high layer, which was subjected for QM (B3LYP/Lanl2dz) calculation, and remained atoms were chosen as a low layer, which were all fixed and tentatively treated with MM (UFF) force field for partial geometry optimization. ONIOM (B3LYP/Lanl2dz:B3LYP/Lanl2mb) single-point energy calculation was done for the whole system of the partially optimized structure.

3. Results and discussion

The partially optimized structures by ONIOM (B3LYP/Lanl2dz:UFF) calculation are shown in Fig. 2a and b. The arrowed atom in each figure is replaced Ti atom. The structure parameters, Ti–O bond length and Ti–O–Si bond angle, of each T sites are listed in Table 1. Those parameters of original T sites, which are cited from Cerius2_4.2MS zeolite structure library [13], are also given in the table. Ti–O bond lengths of about 172–178 pm are very comparable to that experimentally obtained value of 180 pm [6]. It would be said from these results that our modeling for ONIOM study was reasonable, and it is worth developing the application of ONIOM (QM/MM hybrid) method for the study of zeolite local structures.

The pore of each cluster, which can be seen in each figure, is the straight pore of MFI structure. It is easily recognized from Figs. 1, 2a and b that T1–T3, T5–T9, T11, and T12 are faced to the straight pore of MFI structure. These sites are also members of the zigzag pore of MFI. All T sites, including T4 and T10, construct the zigzag pore wall (about the structure of MFI type zeolite [8] and references cited therein is preferentially referenced).

It is also recognized from the structures given in the figures and tables that TiO_4 moiety is slightly larger than SiO_4 at a T site. Ti–O–Si angle decreased

in order to fit the moiety in constrained zeolite framework compensating the enlargement of Ti–O bond length and consequent TiO_4 size. No bond broken occured by the replacing Si at T site with Ti. The pore size was slightly changed because the Ti atom at T site pushed up some O atoms, which bonded to the Ti, to the pore. These oxygen atoms are expected to be more interactive to an electron acceptable molecule such as H_2O and CH_3OH. The interaction of these molecules to the oxygen bonded to Ti is very important in order to understand the action of Ti as a catalytic center [3,6,7]. We already reported that H_2O and CH_3OH molecules stabilize the coordination of hydrogen peroxide to $Ti(OSiH_3)_4$ cluster [7]. However, the calculation was done using a cluster model without structural constraint, and the behavior of atoms around Ti and chemical reaction with a substrate have been remained to debate.

Energies of T sites calculated by ONIOM (B3LYP/Lanl2dz:B3LYP/Lanl2mb) for the structures by ONIOM (B3LYP/Lanl2dz:UFF) were shown in Fig. 3 and Table 2. The ONIOM total energy and corresponding core cluster, TiO_4 moiety held in a T sites, energy are given. The energy sequence by the ONIOM total energy difference from which by the corresponding core cluster energy. This difference would be due to local deformation energy at a T sites, because the atoms in zeolite framework, except for the atoms around a substituted Ti, were all fixed at the original crystallographic position. The effect of local deformation could not be included in the core cluster energy, so that we judge the relative stability of T sites by the ONIOM total energy.

The most stable Ti substituted T sites by ONIOM (B3LYP/Lanl2dz:B3LYP/Lanl2mb) were T9 and T10. The difference of ONIOM energies of T9 and T10 was very small, 4.7259 kJ/mol, and that of T9 and T12 or T1 was about 80 kJ/mol. Therefore, T9 and T10 were dominant site among T sites if thermodynamics controls the structure of Ti containing MFI zeolite. The stability sequence of T sites was T9 > T10 > T12 > T1 > T6 > T5 > T3. The other T sites were energetically very unstable, and the energy difference of these sites and T9 were larger than 160 kJ/mol.

Hijar et al. [4] and Jentys and Catlow [8] investigated T siting in MFI zeolitic framework by powder neutron diffraction technique, and the former group observed Ti at T3, T7, T8, T10, and T12 sites, and

the later group found Ti at T3, T8, and T10 sites. Both groups claimed that the most probable siting is T8 and T10. Also by the same diffraction technique, Lamberti et al. [14] proposed the preferential T siting is at T6, T7, and T11. Judging from their reports, it is hard to say the debate about Ti siting in MFI zeolitic structure based on experimental method has been completed.

Hijar et al. [4] also examined the stability order of T sites by semi-empirical MO method, PM3(d). Their study was done by using the cluster models containing 95–117 atoms depending on T sites. However, their calculated results did not support their observations. They explained this discrepancy that T siting is not determined by a thermodynamical but kinetical factor during formation of zeolite framework. The kinetical
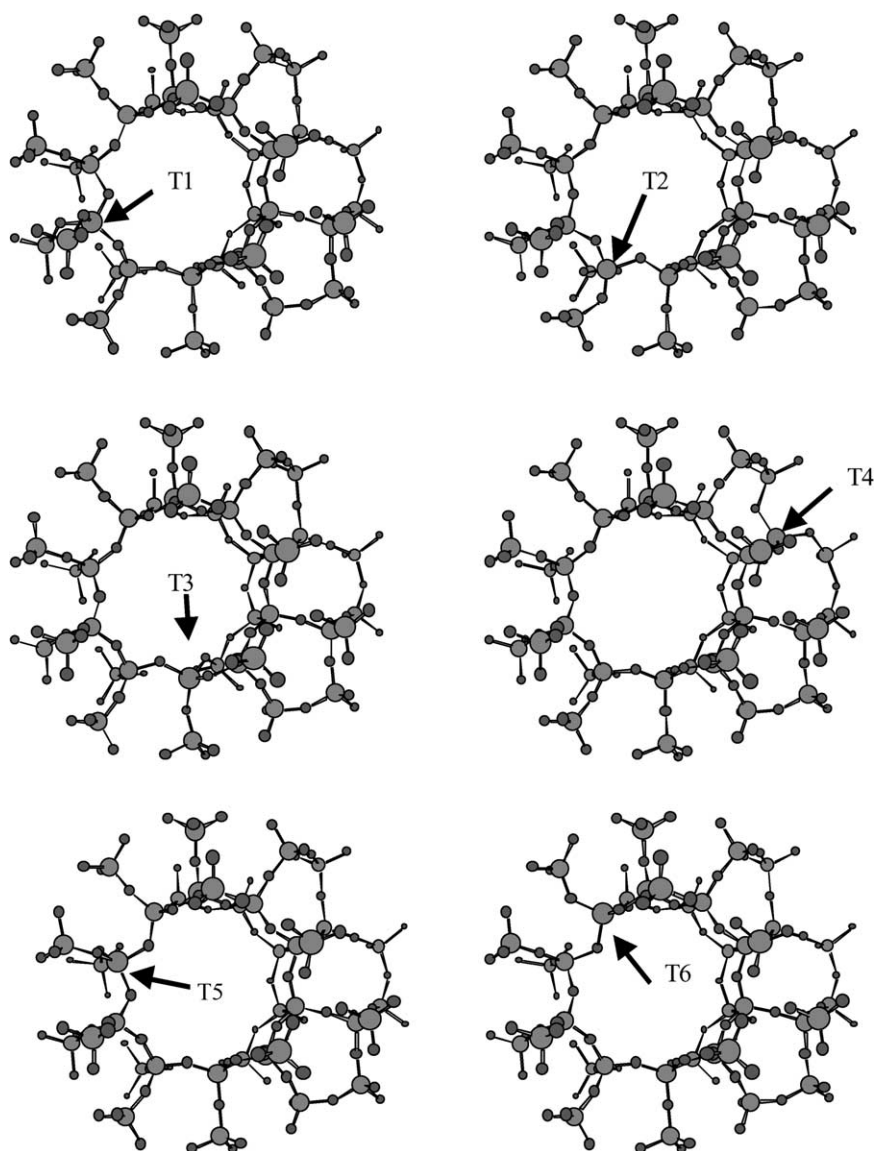

Fig. 2. (a) ONIOM (B3LYP/Lanl2dz:UFF) optimized structure of T1–T6 sites; (b) ONIOM (B3LYP/Lanl2dz:UFF) optimized structure of T7–T12 sites.
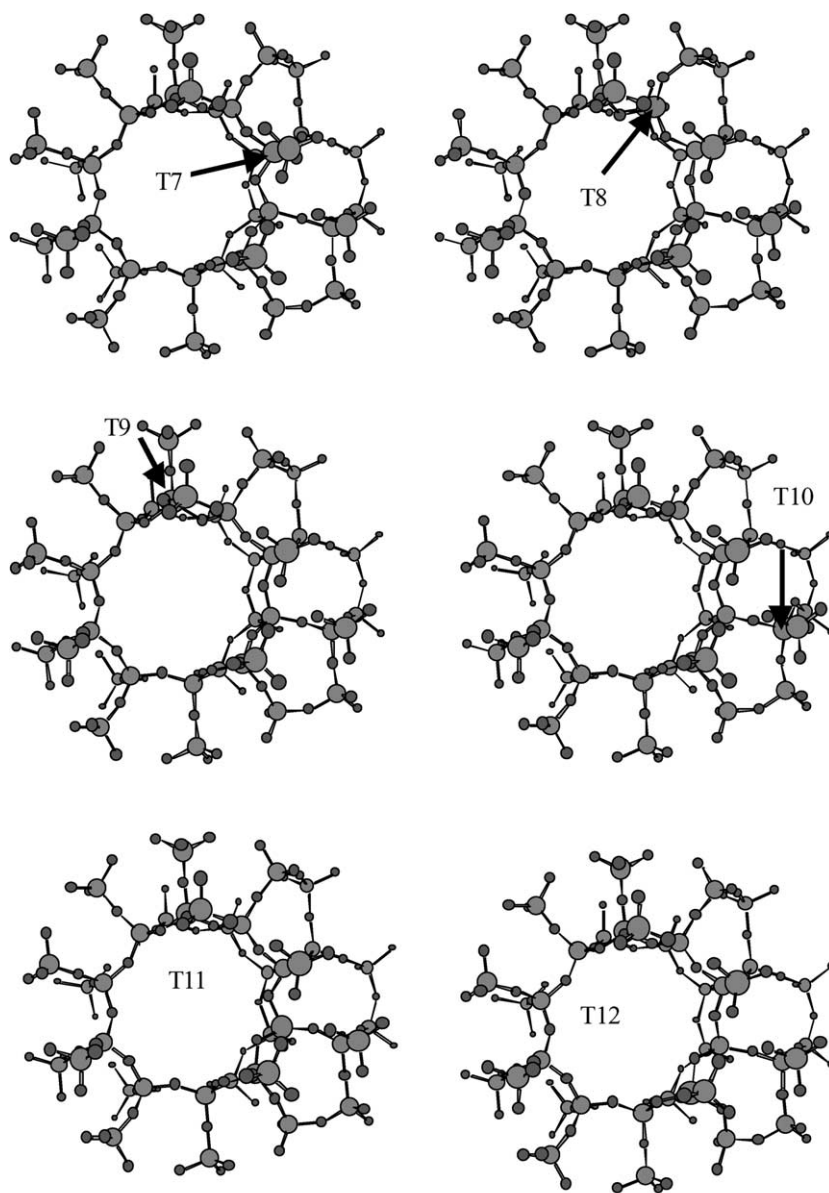
Fig. 2. (*Continued*).

factor can not be denied as a controlling factor of T siting. However, concerning both to their [7] and the other group's [8,14] observation of powder neutron diffraction, the preferential T siting reported by these researchers includes the energetically preferential sites by ONIOM (QM/MM and QM/QM) calculation in this work. Therefore, it is suggested that both kinetical and thermodynamical factors during a formation of precursor blocks of zeolite determine Ti atom siting in MFI zeolite framework. This fact indicates that the zeolite framework structure would be a meta-stable one. In order to establish the mechanism of forming Ti

Table 1
Ti–O bond length (pm) and corresponding Ti–O–Si angle (°) of T site

T site	Before optimization[a]	After optimization
T1		
Ti–O length	158.3, 161.0, 158.0, 159.1	175.0, 175.7, 176.1, 176.6
Ti–O–Si angle	153.1, 131.2, 164.7, 148.2	128.9, 118.3, 131.4, 118.0
T2		
Ti–O length	160.1, 158.7, 156.8, 158.2	175.7, 174.9, 176.6, 175.5
Ti–O–Si angle	149.7, 153.1, 175.9, 158.2	128.1, 127.1, 123.3, 132.2
T3		
Ti–O length	159.1, 157.1, 158.7, 157.1	175.4, 175.1, 175.5, 175.5
Ti–O–Si angle	147.6, 162.8, 149.7, 175.8	122.4, 126.0, 125.2, 125.9
T4		
Ti–O length	158.6, 157.5, 158.9, 158.3	172.7, 175.1, 175.9, 175.9
Ti–O–Si angle	156.0, 175.8, 149.4, 164.7	117.2, 123.7, 116.1, 120.6
T5		
Ti–O length	156.6, 158.9, 158.3, 158.3	176.2, 175.9, 177.1, 175.9
Ti–O–Si angle	147.7, 147.9, 156.0, 169.1	126.3, 125.0, 122.9, 127.4
T6		
Ti–O length	159.4, 158.6, 159.3, 158.8	176.2, 175.6, 175.7, 176.7
Ti–O–Si angle	147.9, 162.8, 145.0, 158.2	122.1, 129.2, 122.8, 128.5
T7		
Ti–O length	158.0, 159.0, 158.5, 158.6	175.1, 177.5, 174.8, 176.8
Ti–O–Si angle	156.2, 150.3, 153.3, 149.4	124.3, 120.6, 121.3, 123.8
T8		
Ti–O length	158.8, 157.7, 156.2, 158.3	173.2, 174.6, 175.4, 175.8
Ti–O–Si angle	154.4, 175.9, 156.2, 164.6	117.7, 123.1, 118.7, 121.8
T9		
Ti–O length	159.7, 157.8 159.8, 159.1	175.5, 177.0, 176.1, 177.2
Ti–O–Si angle	145.0, 154.4, 148.0, 154.6	123.2, 125.5, 125.2, 121.5
T10		
Ti–O length	159.0, 158.8, 160.5, 157.3	178.2, 176.4, 175.7, 176.2
Ti–O–Si angle	154.6, 148.2, 144.9, 164.4	119.1, 115.9, 118.1, 120.9
T11		
Ti–O length	159.4, 156.8, 159.1, 158.1	175.0, 176.1, 175.2, 175.7
Ti–O–Si angle	150.3, 169.1, 153.4, 164.4	118.8, 117.3, 118.0, 123.0
T12		
Ti–O length	158.6, 160.0, 159.5, 157.4	176.2,, 175.4, 175.1, 177.1
Ti–O–Si angle	153.4, 147.6, 146.3, 164.6	122.9, 126.9, 122.0, 124.2

[a] The parameters are cited from crystal structure libraries of Cerius2_4.2MS (MSI—Accelrys).

containing zeolite framework, the light should be shed to the reactivity of a precurcer of zeolite framework by both experimental and calculational work.

The adsorption structure and energy of reactants on a T sites [15,16] would be different from each other owing to those local environments [17]. These factors strongly influence catalytic activity of Ti in MFI zeolite framework. The further theoretical study about the feature of adsorption of reactants on these T sites fixed in MFI zeolite framework is needed.

The differences of energy between the most stable and unstable T sites, max δ in Table 2, were 0.089424 hartree (234.78271 kJ/mol) in ONIOM total energy and 0.034693 hartree (91.086472 kJ/mol) in
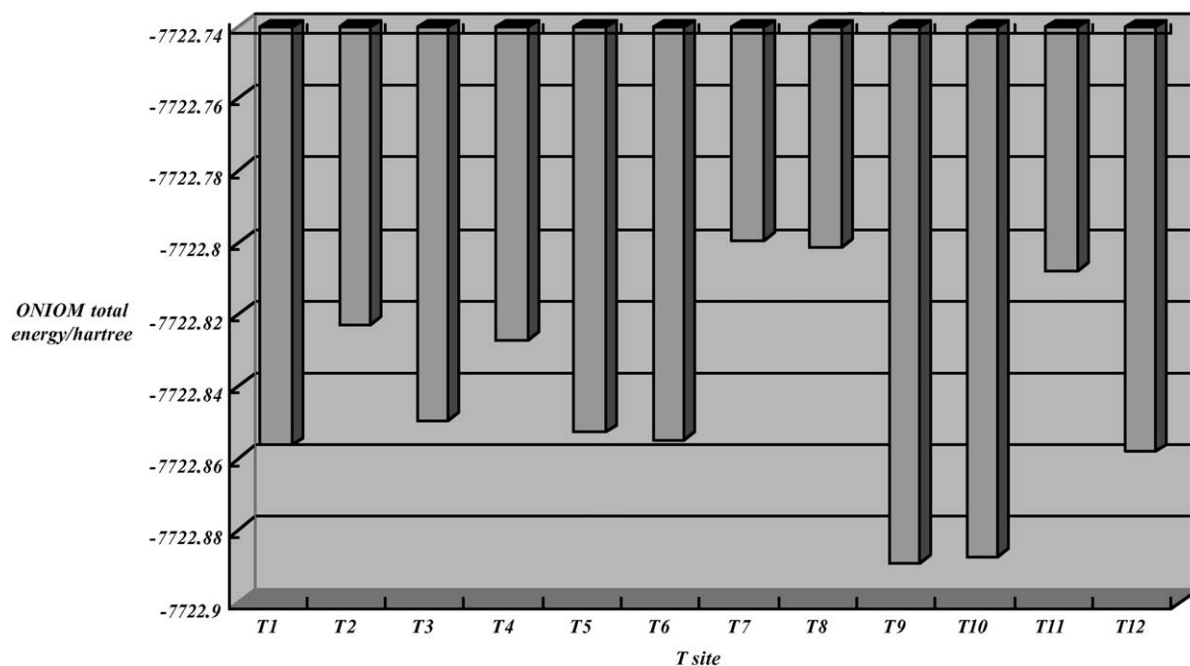
Fig. 3. ONIOM (B3LYP/Lanl2dz:B3LYP/Lanl2mb) total energy of T sites. Energy is given in hartree (1 hartree = 2625.500 kJ/mol).

the energy of corresponding core cluster, respectively. These values are much larger than that was reported in [4,6,8,9], in which the difference was about 20 kJ/mol. The cause of the discrepancy between the value reported in [4,6,8,9] and in this report is not clear. However, the method or the model clusters for the estimation of the relative stability of T sites would influence the results. For example, the authors of [4] chose the substitution energy of Si at a T sites with Ti, for example E(Si-cluster) + E(Ti^{4+} ion) – E(Ti-cluster) – E(Si^{4+} ion) [4], for the discussion of the probable Ti siting. We used integrated ONIOM total energy of the cluster containing all 12 T sites in one cluster for the estimation. This would be the way to compare all T sites without any ambiguity. Also, in spite of the author of [4] used different cluster model for T sites, we used the same cluster model for all T sites. We did not choose the way the same to [4], because the lattice electronical effect would depend on the lattice size.

The optimization of whole system would reduce the energy difference of the most stable and unstable T sites. It should be pointed out, although not confirmed, that the structure of reluxed whole cluster

model trimmed from zeolite crystal data would largely deviate from its original structure, because the zeolite structure is, in general, meta-stable one and, as discussed above, not that at thermal equilibrium.

Table 2
ONIOM energy and corresponding core cluster energy

T site	Core cluster energy (hartree)	ONIOM total energy (hartree)
T1	−361.5648645	−7722.856204
T2	−361.5769271	−7722.822681
T3	−361.5807339	−7722.849315
T4	−361.5658992	−7722.826863
T5	−361.5731492	−7722.852516
T6	−361.5707451	−7722.854844
T7	−361.5567425	−7722.799365
T8	−361.5669412	−7722.801192
T9	−361.5741723	−7722.888789
T10	−361.5748398	−7722.886942
T11	−361.5714854	−7722.807903
T12	−361.5460593	−7722.85797
Max δ[a]	91.0864 kJ/mol	234.7827 kJ/mol

[a] 1 hartree = 2625.5 kJ/mol.

4. Conclusion

We have presented ONIOM (QM/MM and QM/QM hybrid) investigation about Ti atom siting in MFI zeolite framework. T9 and T10 were suggested to be thermodynamically stable sites in MFI zeolite framework. ONIOM method is also applicable to study of adsorption and reaction of molecules over Ti atom in zeolite pore structure. Therefore, further ONIOM study will be concerned to the chemical behavior of Ti atom in zeolite pore structure.

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