Titanium Site Preference Problem in the TS-1 Zeolite Catalyst: A Periodic Hartree-Fock Study

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Dedicated to the memory of Professor Ljubo Golič

Abstract

The problem of titanium location within the silicalite framework of the well known TS-1 catalyst has been studied by means of periodic Hartree-Fock all-electron quantum calculations using split valence atomic basis functions. Periodicity of the system, including the fully featured space group symmetry, has been rigorously considered. Two distinct space groups have been employed in the calculations, namely the experimentally determined orthorhombic *Pnma* space group and its monoclinic $P112_1/a$ subgroup. The latter makes it possible to effectively reduce the titanium content to a slightly overestimated but still plausible value of 4.17 atomic %. In the first step, the structure of the MFI zeolite which is the parent structural template of TS-1 has been optimized, exhibiting very good agreement with the experimental structure. The order of site preference in TS-1 has been determined for both space groups and it has been found that the order is notably affected by symmetry restrictions imposed by the space group, particularly for the sites that lie close to the mirror plane of the *Pnma* group. In partial agreement with the experimental evidence and with the earlier periodical study, we found the T4, T5, T3, T12, T11 and T8 sites to be energetically most favorable, the respective energies spanning a narrow range of 1.37 kcal/mol in the $P112_1/a$ space group. In contrast to the previous experience, we found the otherwise preferred T10 site to be among the least favorable ones for Ti substitution. The calculated energy range of the isomers is relatively narrow (about 5 kcal/mol) and the energy differences calculated per one Ti site tend to decrease on the decreasing Ti concentration. Because of small energy differences between the site isomers, consideration of the free energy (entropy terms) seems to be a reasonable upgrade of the present approach and an important focal point of the future studies of the Ti-siting problem in TS-1.

Keywords: Periodic quantum-chemical calculations, titanosilicalite zeolites, TS-1, space groups.

1. Introduction

The importance of TS-1, probably the most well known titanium-doped zeolite-type catalyst, derives from the fact that it is able to efficiently catalyze a variety of technologically relevant oxidative transformations of small organic molecules.[1,2] Despite considerable experimental and computational efforts on the properties of TS-1, aimed to achieve the essential understanding needed for the design of novel and improved catalysts with desired properties, many details of its local structure, the origin of the reactivity and nature of the reaction mechanisms are still poorly known. Among the long standing problems which have not been fully resolved yet is the location of the titanium active sites within the MFI zeolite

framework on which the structure of TS-1 is based (Fig. 1). It is widely accepted that the siting of the active metal species will determine the local coordination environment around the active site and is thought to be important for determining the catalytic properties. The TS-1 structure contains 12 crystallographically inequivalent silicon sites which could be substituted by titanium, but no consensus has been reached on the distribution of Ti among these sites. Some authors have proposed that Ti siting is entirely random,[3,4] but others have obtained results showing non-random occupancies;[5,6,7] even among the latter there is no univocal agreement on which sites are preferentially occupied or avoided by titanium. This is at least in part due to the fact that an unambiguous experimental assignment of the Ti siting is very difficult because of the

low concentration of Ti which is only about 2.5 atomic %. In this sense, computational methods can be regarded as a welcome support to experimental studies since they allow for a detailed, atomic-level insight into the structure of matter.

Computational studies on the Ti-siting problem in TS-1 have been so far severely limited by the size of the system. The MFI unit cell consists of 96 silicon and 192 oxygen atoms and has a volume of about 5 340 Å,[3] which currently puts it near the upper limit of affordable periodic *ab initio* and DFT quantum-mechanical methods. In the past, a variety of quantum-mechanical, empirical force field or mixed QM/MM calculations have been applied to address this and other related TS-1 problems on simplified, isolated cluster models.[5,8–14] However, most of such models bring inevitable complications that severely limit their applicability, comparability and reliability. In general, it is very hard or not at all possible to construct cluster models of different sites within a zeolite framework that would have their local environment sampled in exactly the same way. Many such simplified, yet at the time the only affordable attempts of modelling the Ti-substitution within the MFI structure, showed barely any agreement with experimental findings or produced unreasonable results, for instance high energy differences between the isomers.[13] The lack of agreement between the various computational approaches and between calculations and experiment may even suggest that the Ti substitution is governed by the kinetics during the synthesis.

An ultimate solution of the size problem is the construction of fully periodical models which faithfully reproduce the structure of crystalline matter and properly include the entire body of explicit interactions in the solid state. However, until quite recently such periodic studies of zeolites have been limited to smaller and technologically less important systems such as Ti-chabazite.[15–18] A major breakthrough in the computational treatments of TS-1 has been achieved when Gale published the first fully periodic quantum-mechanical study on the Ti-siting problem in this material.[19] His approach was based on the SIESTA methodology[20] and utilized the PBE density functional[21] in conjunction with gridded atomic valence basis sets while the core electrons were approximated by atomic pseudopotentials. In agreement with some experimental findings, Gale proposed the T8 and T10 sites to be energetically preferred while at lower Ti concentrations the T4 and T11 sites are also favored. The energy range of the site isomers of TS-1 was very small with the energy difference between the most and the least favourable site being about 2 kcal/mol.

As the work of Gale pushed the forefront of computational studies of the structure of TS-1 into the fully periodical regime, one can expect additional periodic quantum-mechanical studies on this problem to emerge in the future. The progress in available computational resources makes it now possible to perform periodic calculations on TS-1 and systems of similar size by a variety of quantum mechanical methodologies that support periodic boundary conditions. The main motivation for the present work is to enlighten the TS-1 siting problem by another well established and in a sense, as compared to Gale's work, improved and complementary methodology, namely that of the periodic Hartree-Fock (HF) approach implemented in the Crystal program package.[22] The main key features of this approach distinct to the ones used by Gale are (i) that all the electrons of the system are treated explicitly and (ii) ri-
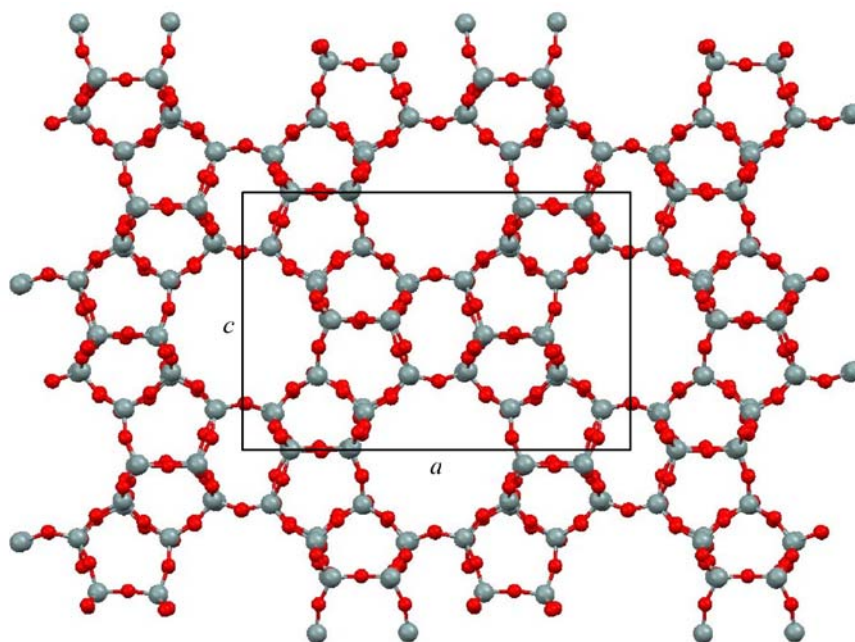

Figure 1. MFI zeolite structure viewed along the *b* axis with the *a* and *c* unit cell sides indicated. Atom colors: Si – grey; O – red. (see online version)

gorous crystallographic symmetry features can be applied. While the former is clearly an advantage, the rigorous implementation of symmetry is somewhat ambivalent. Although it boosts the performance by treating only the asymmetric unit, thus making it possible to simulate structures with high content of titanium (in this sense, the present study is complementary to that of Gale), it on the other hand produces undesired artifacts in that the distribution of titanium atoms over the crystalline framework is forced to strictly follow the space group symmetry restrictions, which is unlikely to be the real case, at least with the highly symmetric space groups. Additionally, with 288 atoms and 2880 electrons in the unsubstituted unit cell, TS-1 is still at the upper limit of applicability (or even beyond) of the all-electron Crystal methodology in the least symmetric *P*1 regime. Nevertheless the wide range of applications offered by Crystal clearly makes it a challenge to use its methodology in the studies of the present problem.

2. Computational Details

All calculations reported in this work were performed by the program package Crystal06[22] and were carried out at the VRANA PC/Linux clusters (4- and 8-core workstations) of the Center of Molecular Modeling at the National institute of Chemistry, Ljubljana, Slovenia. A three-dimensional periodic Hartree-Fock approach was used and the crystallographic space group of the model was fully considered (*see below*). All electrons of the system were treated explicitly. The electron wavefunction was expressed in terms of atomic basis functions of the Pople type, which are well known from gas-phase quantum calculations. Periodicity of the basis set was established through Bloch functions modulated over the infinite crystal lattice. We used modified versions of the 6-21G(d) and 6-31G(d) basis sets on silicon and oxygen atoms, respectively, and the 86-411G(d31) on titanium.[23,24] These basis sets have been designed and optimized by the Crystal development group, among the rest on various forms of SiO_2 (including quartz and zeolites) in the crystalline state, as well as on Ti-substituted zeolites and other crystalline materials containing titanium.[16,23,25] Various *k*-point sampling schemes of the Brillouin zone were tested. In agreement with the work of Gale[19] and consistently with the quite large MFI unit cell, the resulting single point energies were only marginally different from one another (by <0.1 kcal/mol per unit cell), even when the Γ-point approximation was applied. Thus we performed the calculations solely at the Γ-point of the Brillouin zone. The mono- and bielectronic integrals were computed according to the direct SCF scheme in order to avoid massive storage issues.

The periodic MFI model on which all the considered structures are based was built according to the experimental powder neutron diffraction data of Hijar et al.[5] The orthorhombic unit cell of *a* = 20.044 Å, *b* = 19.866 Å and *c* = 13.369 Å belongs to the *Pnma* space group; *Z* = 8. The asymmetric unit of the unsubstituted MFI structure contains 12 silicon atoms (all at general positions) and 26 oxygen atoms, of which 22 are located at general positions (multiplicity 8) and 4 on the mirror plane *m* located at *y* = ±1/4 (multiplicity 4). Each of the inequivalent silicons was replaced, one at a time, by titanium, resulting in twelve different isomers of TS-1. For each isomer geome-
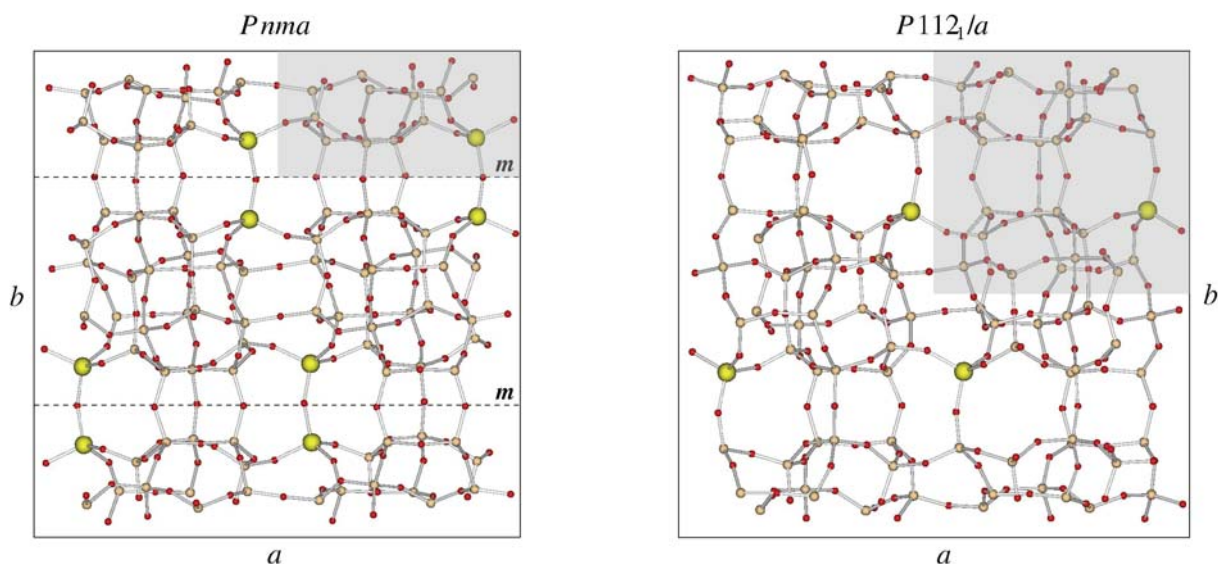

Figure 2. Two distinct models of the TS-1 unit cell (Ti at the position T7) viewed along the c axis. Left: space group Pnma (multiplicity 8, Ti content 8.33%) with the mirror planes m indicated by dashed lines, right: space group P1121/a (multiplicity 4, Ti content 4.17%). The asymmetric unit is denoted by the shaded area. Atom colors: Ti – yellow; Si – orange; O – red. (see online version)

try optimization was performed under the constraint of the fixed unit cell and symmetry restrictions of the space group. An unsubstituted MFI structure was also optimized in the same way. Default optimization criteria for maximum and r.m.s. forces (4.5×10^{-4} a.u. and 3.0×10^{-4} a.u., respectively), as well as for maximum and r.m.s. displacements (1.8×10^{-3} a.u. and 1.2×10^{-3} a.u., respectively) were used.

The most controversial part of this model is that the minimal titanium content that can be achieved is $1/12 = 8.33\%$ (corresponding to a single Si → Ti substitution within the asymmetric unit), which is more than three times higher than in the actual material (~2.5%). Additionally, the sites T7, T9, T10 and T12 (and to minor extent T8 and T11) lie close to the mirror plane *m* so that some of the distances between equivalent titanium atoms are very small (see Fig. 2 and Table 1). This conflicts the widely accepted belief that the Ti sites are well separated. To avoid these issues, we constructed another model with less symmetry operators and larger asymmetric unit. We removed the mirror plane *m* and expanded the asymmetric unit by the replica atoms which are generated from the original asymmetric unit by that plane. The resulting model belongs to the $P112_1/a$ subgroup of the original space group *Pnma*. It features the same cell constants, although it formally belongs to the monoclinic type of the unit cell (note that β remains at 90°); $Z = 4$. The resulting asymmetric unit contains 24 silicons and 48 oxygens (all at general positions). This model effectively lowers the titanium content to a more reasonable value of $1/24 = 4.17\%$ and increases the separation between Ti atoms (Fig 2. and Table 1). The Ti-substituted models were constructed and their geometries were optimized in the same way as with the *Pnma* space group.

Although further reductions of titanium content are possible by reducing the symmetry and increasing the asymmetric unit, we found that not to be practical because of the significantly increased computational costs. The cost of the periodic Hartree-Fock approach based on local atomic orbitals is predominantly determined by the size of the crystallographic asymmetric unit. It should be noted that even the original *Pnma* asymmetric unit of MFI which contains 12 silicons and 26 oxygens (376 electrons) is quite expensive in terms of requested CPU time and memory; thus the perspectives of extending the calculations to larger asymmetric units or even supercells are quite limited. The same is true of harmonic frequency calculations which are effectively performed in the *P*1 symmetry and require about 30 days even for the *Pnma* MFI model and twice as much for the $P112_1/a$ model. For that sake we did not perform any harmonic frequency calculations, although this is an established verification of geometry optimization. Nevertheless the use of larger asymmetric units and the application of harmonic vibrational analysis remain the challenge for our further work (see section 4).

3. Results and Discussion

Unsubstituted MFI structure. The MFI structure was successfully optimized under the constraint of a fixed unit cell for both the *Pnma* and $P112_1/a$ space group and both optimized structures are very similar to one another. The optimized Si–O distances vary from 1.602 to 1.619 Å in the *Pnma* space group, and from 1.604 to 1.619 Å in the $P112_1/a$ space group, with the median Si–O distance being about 1.61 Å in both cases. This corresponds quite well to the experimentally determined Si–O distances in both the orthorhombic and monoclinic singony, which are, depending on experimental conditions, in the range between 1.59 and 1.61[26,27] Our calculated values are at the higher limit of this interval and are slightly more dispersed than most of the experimentally observed ones. The opposite is true of the Si–O–Si valence angles, which cover the range between 131 and 167 degrees in both optimized structures, the average value being about 151 degrees, compared to the more scattered set of experimental values that are between 135 and 175 degrees, with the average of about 155 degrees. Apparently the calculation, on the average, slightly underestimates the Si–O–Si valence angles. The calculated Si–O distances are also in fine agreement with previous periodic Hartree-Fock calculations performed on related silicon-oxide systems;[23] on the other hand, they are slightly shorter than ones obtained by Gale in a related periodic DFT study,[19] most probably due to the slightly different optimization strategy – the latter also included the optimization of the unit cell parameters which resulted in a slight expansion of the unit cell.

We found the energy of the $P1121/a$ optimized structure to be by 9.99 kcal/mol per unit cell (equivalent to only 0.10 kcal per one mole of SiO_2 stoichiometric unit) lower than that of *Pnma*. This small difference is due to the fact that when lowering the symmetry, certain restrictions to atomic positions are lifted, providing more flexibility to relax the strain. Interestingly, during optimization under the $P112_1/a$ space group the oxygen atoms formerly residing on the mirror plane were only marginally (by no more than 7×10^{-4} Å) displaced from that plane, even though their fractional coordinates were no longer symmetry-restricted to the value of $y = 1/4$. Qualitatively, the $P112_1/a$ structure retained much of the symmetry created by the mirror plane, although the plane was removed from the list of symmetry elements. This suggests that application of the lower symmetry does not provide sufficient evidence against the experimentally determined *Pnma* space group.

To obtain additional insight into the difference between the considered MFI structures, we overlayed in the Cartesian space the 38 atoms that comprise the *Pnma* asymmetric unit in such a way that for each of the structures the Cartesian origin of these 38 atoms was set to their center of mass. The so obtained overlays allowed for the calculation of the mean differential atomic displacement

between any pair of experimentally determined or geometry optimized structures. While the mean differential displacement between the experimental MFI structures reported in refs.[26,27] and is equal to 0.12 Å per atom, the difference between the *Pnma* and *P*112$_1$/*a* optimized structures is much smaller. The mean atomic displacement between the computed structures is only 0.023 Å, thus validating the observed similarity of the respective models. Comparison between any of the computed structures on one side and any of the experimental ones on the other shows that the mean differential atomic displacement lies in the range between 0.15 and 0.17 Å per atom. This suggests that geometry optimizations reported in this work yield a satisfactory match to the crystallographic structure determination of the MFI zeolite; as seen form differential displacements, the match between the calculated and experimental structures is of about the same magnitude as the match between independent crystallographic measurements. Thus we conclude that the present computational methodology is able to reasonably reproduce the actual MFI structure.

Titanium-substituted isomers. Two sets of twelve independent geometry optimizations on the Ti-substituted MFI structure were performed, corresponding to the *Pnma* and *P*112$_1$/*a* space groups and to the twelve substitution sites, respectively. Basic geometry features of these TS-1 isomers are reported in Table 1. The optimized Ti–O distances, which are probably the most significant metric parameters of TS-1 isomers, are in the range between 1.774 and 1.815 Å with the *Pnma* space group and between 1.783 and 1.815 Å with the *P*112$_1$/*a* space group. Apparently, the change of the space group has a non-uniform effect on the local structure of the Ti-site; in most cases and regardless of the site considered, some of the Ti–O distances slightly elongate while the others slightly shrink when passing from the *Pnma* space group to *P*112$_1$/*a*. The median optimized Ti–O distance is about 1.80 Å, in line

with but slightly shorter than the EXAFS experimentally determined value of 1.81 Å;[28] most likely this small discrepancy is due to the fact that the unit cell parameters were not allowed to relax during optimization. Indeed, the periodic DFT calculations of Gale based on a slightly larger fixed unit cell or relaxed unit cell yield a slightly better agreement with the observed Ti–O distance.[19] Nevertheless, our calculated Ti–O distances are notably shorter (and thus in better agreement with the experimental results) than ones obtained with the more approximate models,[5] demonstrating the improved accuracy of the applied fully periodical all-electron *ab initio* method.

Relative energies of the TS-1 substitution isomers calculated for both space groups are listed in Table 2. The relative energies have been scaled by the number of Ti atoms in the unit cell so that they correspond to one mole of Ti sites and ensure comparability between the *Pnma* and *P*112$_1$/*a* space groups for which the Ti concentration is 8.33 and 4.17 atomic %, respectively. For the *Pnma* space group the order of preference is

T11 > T4 > T3 > T5 > T12 > T8 > T6 > T2 > T1 > T7 > T9 > T10.
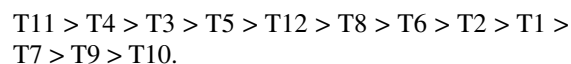
Relative energy increases quite uniformly in the above series, with the largest gap of 1.56 kcal/mol between T6 and T2. The overall energy span between T11 and T10 is 6.27 kcal/mol. Upon passing to the more dilute *P*112$_1$/*a* model, this order changes to

T4 > T5 > T3 > T12 > T11 > T8 > T7 > T6 > T10 > T9 > T1 > T2.
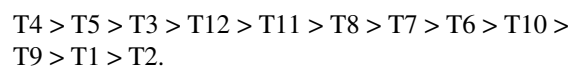
The energy span of the isomers is decreased to 4.96 kcal/mol and they are distributed less uniformly than with the *Pnma* model. In particular, the six lowest sites

Table 1. Range of optimized Ti–O distances, minimal Ti…Ti separation and minimal number of Si atoms on the chemical bond pathway between two Ti atoms, for the twelve distinct substitution sites and two space groups considered. Note that the atomic concentration of Ti within the *P*112$_1$/*a* group is half the one within *Pnma*.

Site	R_{TI-O} [Å]		Min. $R_{TI…TI}$ [Å]		Min. # of Si atoms between Ti	
	Pnma	*P*112$_1$/*a*	*Pnma*	*P*112$_1$/*a*	*Pnma*	*P*112$_1$/*a*
T1	1.774–1.802	1.785–1.799	5.320	5.493	2	2
T2	1.778–1.809	1.788–1.807	7.172	7.159	2	2
T3	1.787–1.800	1.783–1.801	7.105	7.135	2	2
T4	1.793–1.801	1.791–1.803	5.336	5.532	2	2
T5	1.791–1.807	1.798–1.807	6.453	6.303	2	2
T6	1.790–1.810	1.793–1.806	7.185	7.684	2	2
T7	1.789–1.815	1.796–1.815	3.546	9.117	0	3
T8	1.789–1.806	1.794–1.800	4.675	9.117	2	3
T9	1.784–1.809	1.785–1.801	3.346	9.533	0	3
T10	1.785–1.806	1.793–1.806	3.273	8.211	0	3
T11	1.797–1.803	1.794–1.809	4.958	8.014	2	3
T12	1.777–1.811	1.789–1.805	3.334	10.059	0	3

(T4-T8) are within 1.37 kcal/mol (with the *Pnma* space group only the sites T11, T4 and T3 have been found witin this interval), and the four highest ones (T10-T12) within 0.62 kcal/mol. The widest three gaps of 0.96, 0.83 and 1.18 kcal/mol are observed within the T8 > T7 > T6 > T10 subset. The energy range of the isomers has narrowed to 4.96 kcal/mol, which is in agreement with the reduction of the Ti…Ti strain caused by the dilution of Ti sites and removal of certain symmetry restrictions (*see below*). It is likely that the energy differences between the considered isomers are further decreased on reducing the Ti content in the model.

Table 2. Energies of the TS-1 site isomers for the *Pnma* and $P112_1/a$ space group models, relative to the isomer with lowest energy in the corresponding space group (T11 in *Pnma* and T4 in $P112_1/a$).

Site	Relative energy [kcal per mole of Ti sites]	
	Pnma	$P112_1/a$
T1	4.81	4.54
T2	4.68	4.96
T3	1.36	0.67
T4	0.48	0.00
T5	1.83	0.38
T6	3.12	3.16
T7	5.02	2.33
T8	2.77	1.37
T9	5.60	4.36
T10	6.27	4.34
T11	0.00	1.14
T12	2.64	1.04

From the comparison of the site preference orders it is evident that the titanium concentration in conjunction with symmetry has a considerable effect on the relative stability of the site isomers of TS-1. This effect is additionally displayed in Fig. 3. The most notable changes in the relative stability are observed for the sites T7-T12. Not surprisingly, this is due to the fact that these sites lie in the vicinity of the mirror plane of the *Pnma* space group. As a result, the minimal distance between two titanium atoms is quite small, from 3.3 to 5.0 Å, as opposed to sites T1-T6 where the minimal Ti…Ti distance varies from 5.3 to 7.2 Å (Table 1). In terms of the covalent bond framework which provides a pathway between any pair of sites, each of the T7, T9, T10 and T12 sites has an equivalent site as its closest neighbor (a zero number of O–Si–O links between them). When titanium resides at T1-T6, T8 or T11, there are at least two such links between any pair of titanium atoms (Table 1). Thus the *Pnma* space group with titanium content of 8.33% probably produces undesired artifacts at the mentioned sites in that the Ti atoms are not sufficiently separated and the structure is subjected to higher sterical strains than in the isomers in which the distan-

ce between Ti atoms is larger. This inequivalence between the sites in terms of the undesired close Ti…Ti contacts encountered with some but not all of the sites undermines, at least to some extent, the comparability of their energies. From Fig. 2 and Table 1 it can be seen that this inconsistency is effectively reduced when passing to the $P112_1/a$ space group. The mirror plane is removed, the concentration of Ti is halved to 4.17% and the Ti…Ti distances are enlarged. As a result, the relative energies of T7-T12 site isomers change considerably; with the exception of T11, the change is negative, suggesting that the removal of strain between formerly adjacent Ti sites stabilizes the structure. Without a clear significance, the effect on the T11 site is just the opposite, however it is true that the feature of close separation of titanium atoms within the *Pnma* space group is less pronounced at T11 than at some other sites. Not surprisingly, the structures and relative energies of the T1-T6 isomers are less sensitive to the change of the space group, because Ti atoms are distributed along the lattice much more uniformly in these isomers. An exception is the T5 isomer whose relative energy is notably decreased upon passing from *Pnma* to $P112_1/a$. On the whole, the $P112_1/a$ calculated structures and relative energies can be considered as more reliable than those of the *Pnma* space group, mainly because of the concentration and Ti separation issues.
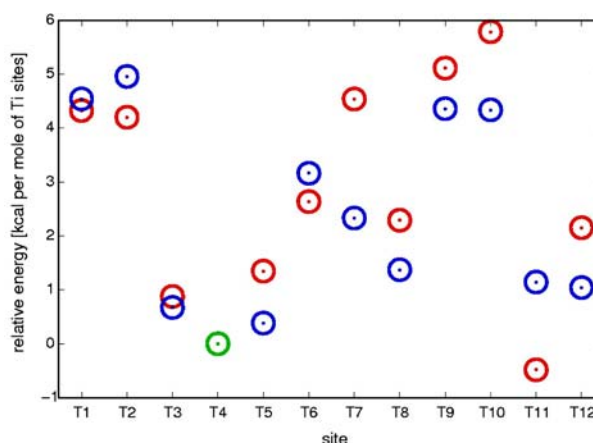

Fig. 3. Energies of site isomers of TS-1 (relative to the T4 isomer). Red circles – *Pnma* space group; blue circles – $P112_1/a$ space group. For both space groups energy of the T4 isomer is set to zero by definition and is displayed in green (see online version).

Comparison of the calculated site preferences in TS-1 with the published experimental studies on this problem shows that it is hard to devise unambiguous conclusions on the agreement between the present results and experimental observations. Evidently, a considerable part of the quite ambivalent match between the calculations and experimental findings on the Ti siting problem in TS-1 originates from the fact that there are notable disputes even within the available experimental data. In that sense, our

results correspond reasonably well to the findings of Lamberti et al.[6] that the T11 site is among the preferred ones for titanium substitution and that the sites T1, T2 and T9 are at the other end of the preference line. At the same time, the agreement with these authors' work is much worse in the sense that our calculations do not show the T6 and T7 sites to be preferable for titanium, and in even worse clash with their exclusion of the T4 and T5 sites for titanium. Similarly and in agreement with the work of Hijar *et al.*[5] and Henry *et al.*,[7] we predict the T3, T12 and T8 sites to be among the more favorable ones for Ti substitution, while failing at the same time to include in this set the T7 and, particularly, the T10 site.

Parts of the site preference order found in this study are in a relatively fine agreement with the findings of Gale,[19] particularly in the sense that the T4 and T11 (and to a smaller extent the T8) sites are among the more favorable for titanium substitution. Also, sites T1 and T9 are predicted to be less favorable by both studies. On the other hand, the likely high preference of the T10 site, also validated by experimental observations, is fairly reproduced by Gale, but not by our approach. In turn, the above average preference of the T3 and T5 sites found in the present study does not agree well with Gale's calculations. Our calculated overall energy span of the isomers of 6.27 (*Pnma*) and 4.96 kcal/mol (*P*112₁/*a*) is relatively small, for instance about half the one calculated by Hijar *et al.* using semiempirical cluster models[5] and notably less than ones obtained by some of the QM/MM calculations,[13] but still at least twice as large as that calculated by Gale using a periodic DFT approach.[19] In large part this is likely due to the much larger Ti concentration in our model (8 or 4 Ti atoms per unit cell, as opposed to Gale's 1 or 0.5 Ti per unit cell). Additionally, the calculated energy differences between isomers are also likely to be affected by the optimization strategy (fixed or optimized unit cell). Given that the energy differences between the site isomers of TS-1 are fairly small, the diversity of the results obtained by different computational models is likely to be a consequence of a variety of other computational details such as the choice of the model Hamiltonian (*e.g.,* HF or a variety of DFT approaches), type and size of the basis set, treatment of the core electrons, etc.

An important aspect of the relative stability of TS-1 isomers lies in the fact that the present calculations as well as most of the previous quantum-mechanical ones are limited to the internal energy contribution, as reflected in the formulation of the Hamiltonian. However, at ambiental conditions it is the free energy rather than internal energy that governs the relative stabilities of isomers and polymorphs. In that sense, the reliability of the calculated Ti site preference order, is limited by the fact that the vibrational zero-point energies and entropy terms have not been included in the calculation due to the CPU economy. Together with the likely impact of the various possible computational strategies outlined above, this calls for an extensive study of the various aspects that may be crucial for the understanding of the Ti-siting problem within TS-1.

4. Conclusions and Perspectives

In the present work the structure of the MFI zeolite has been studied and the titanium site preference problem of TS-1 has been revisited with a fully periodical, all-electron Hartree-Fock approach. To the best of our knowledge this is the first time that an all-electron periodic quantum mechanical methodology has been applied to the TS-1 catalyst. As such, it is challenging to compare the present results not only to various experimental findings, but also to ones obtained in a related yet partially complementary periodic DFT study of Gale.[19] One of the main distinctions between the present and Gale's approach is, apart from the quantum method, basis set and optimization strategy, in that our symmetry-determined models feature higher concentrations of titanium.

We demonstrate in the present work that the approach used in our calculations is capable of quite an accurate prediction of the unsubstituted MFI structure; at the present level, no sufficient evidence has been found against the experimentally assumed *Pnma* space group, albeit we demonstrate that the *P*112₁/*a* subgroup provides some additional stabilization. The site preference order has been found to vary with titanium concentration in the sense that the highly symmetric *Pnma* model, which only allows for a considerably overestimated titanium concentration of 8.33%, introduces strains at the sites that lie close to the mirror plane (T7, T9, T10 and T12). With removal of the mirror plane, the structure belongs to the *P*112₁/*a* subgroup, and titanium content is halved to 4.17 atomic %. Much of the strain originating from too closely resident Ti-sites is relaxed, and the relative stability order is slightly changed. The present study agrees with Gale's work in that the energy range of the Ti site isomers is quite narrow; we expect this energy range to be even more narrowed on further reductions of Ti concentration.

The calculated site preference order, obtained from the *P*112₁/*a* model, which we consider to be the more reliable of the two, shows that six of the sites, namely T4, T5, T3, T12, T11 and T8, lie in the low energy range of 1.37 kcal per mole of Ti; other sites are separated from these ones by notable energy gaps. Part of this preference order is well matched with the previous periodic DFT study of Gale and with the experimental results, while other part is in a conflict with the previously published computational and experimental experience on the site preference problem. However, as the energy range spanned by the site isomers is quite narrow, we expect that other factors not included in the present approach may be important for the actual site preference order. Namely, it is the free energy rather than the internal energy that governs the

stability of such isomers under ambiental conditions. In this sense, a challenging upgrade of the approach would be the calculation of the entropy terms and zero-point vibrational energies of the isomers. Nevertheless, it is at this point not possible to rule out an entirely random Ti distribution nor the possibility that the Ti siting is predominantly governed by kinetic factors.

Although evaluation of the vibrational zero point and entropy terms is straightforward, it requires harmonic vibrational analysis be done for each of the considered isomers. Given that the vibrational analysis of such a large system is quite a formidable task (about two months for one structure on a 8-core workstation under the $P112_1/a$ symmetry), it remains a challenge for the near future. The same is true of the further reductions of titanium concentration which can be done by further removing symmetry elements from the $P112_1/a$ space group, yielding in the first step for instance the $P\bar{1}$ space group with the Ti content of 2.08% and ultimately the $P1$ group containing 1.04% Ti. Such models are likely to reproduce more faithfully the actual Ti concentration in the material and would make it possible to more critically address to the problem of which space group other than the *Pnma* can reliably depict the actual TS-1 structure. On the other hand, the reduced symmetry models are very difficult to handle with the present methodology due to the increased asymmetric unit and largely increased computational costs. Another challenging upgrade of the present approach would be the application of the plane-wave periodic DFT methodology whose performance is mainly governed by the volume of the unit cell rather than by the size of the asymmetric unit. At last, a comparative study between HF and DFT methods would also represent an opportunity to critically assess the various available methodologies and contribute to the comparability of their results.

5. Acknowledgements

6. References

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Povzetek

V članku s periodično kvantno-kemijsko Hartree-Fockovo metodo obravnavamo problem lokacije titanovega atoma v zeolitni strukturi katalizatorja TS-1. Vse elektrone smo obravnavali eksplicitno, uporabili smo atomske bazne funkcije z razcepljenim valenčnim nivojem. Pri računanju smo upoštevali periodičnost sistema in vse simetrijske operacije v prostorski skupini. Uporabili smo eksperimentalno določeno ortorombsko prostorsko skupino *Pnma* ter njeno monoklinsko podskupino $P112_1/a$. Slednja omogoča, da se z računskim modelom zadovoljivo približamo koncentraciji titana v dejanskem materialu, četudi je koncentracija 4.17 atomskih % nekoliko previsoka. Na začetku smo geometrijsko optimizirali strukturo MFI zeolita, ki je strukturni prekurzor TS-1; ujemanje optimizirane strukture z eksperimentalno je bilo zelo dobro. Za obe prostorski skupini smo določili preferenčni vrstni red za vgrajevanje titana v MFI strukturo na razpoložljivih 12 kristalografsko neenakih substitucijskih mest. Simetrijske lastnosti in omejitve prostorske skupine znatno vplivajo na preferenčni vrstni red, zlasti pri substitucijskih mestih, ki ležijo v bližini zrcalne ravnine v prostorski skupini *Pnma*. Za vgrajevanje titana so v prostorski skupini $P112_1/a$ energijsko najbolj ugodna mesta T4, T5, T3, T12, T11 in T8, katerih energije ležijo v ozkem območju 1,37 kcal/mol, kar se razmeroma dobro sklada z eksperimentalnimi ugotovitvami. V nasprotju z eksperimentom pa račun kaže, da je mesto T10 med najmanj ugodnimi za vgrajevanje titana. Energijsko območje TS-1 izomerov je razmeroma ozko (okrog 5 kcal/mol); energijske razlike med izomeri, preračunane na en zamenjan titanov atom, pa se z nižanjem koncentracije titana še zmanjšujejo. Zaradi majhnih energijskih razlik bi bilo v prihodnjih študijah smiselno proučiti tudi entropijski prispevek in primerjati proste entalpije izomerov.