

# PERIODIC QUANTUM MECHANICAL METHODS AS A SUPPORTING TOOL TO CRYSTALLOGRAPHY: THE TITANIUM SITE PREFERENCE PROBLEM IN THE TS-1 ZEOLITE CATALYST

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## ABSTRACT

The structure of TS-1, probably the most well known titanium-doped zeolite-type catalyst with a number of industrial applications, poses a long standing problem that has been addressed by a number of experimental techniques, in first place by diffraction methods. However, due to very low concentration of titanium, experimental assessment of the local structure of titanium active sites is difficult and so far no consensus has been reached on which of the twelve crystallographically inequivalent sites is preferentially occupied or avoided by titanium. In this sense, accurate computational methods can provide valuable support, because they offer an atomic-level representation of matter. However, until recently computational treatment of TS-1 has been severely limited by the size of the system and was restricted to (over)simplified cluster models which lack size consistency. We will present a first principle theoretical study of the titanium site preference in TS-1 based on the fully periodic all-electron Density Functional Theory (DFT) quantum-mechanical methods. We constructed the twelve substitution isomers of TS-1 by four distinct models based on the experimental *Pnma* space group and its *P112<sub>1</sub>/a*, *Pc* and *PI* subgroups. For each substitution isomer we performed geometry optimization and determined the Ti site preference order from their energies.

Keywords: periodic quantum-mechanical calculations, DFT, zeolites, TS-1 catalyst, space groups

## INTRODUCTION

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 DFT approach. Our preliminary study included similar calculations at the rather more simplified Hartree-Fock approach [1]. 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. [1] 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 also feature higher concentrations of titanium.

## COMPUTATIONAL DETAILS

The problem of titanium location within the silicalite framework of the well known TS-1 catalyst has been studied by means of periodic DFT (B3LYP) all-electron quantum calculations using split valence atomic basis functions. All calculations reported in this work were performed by the program package *Crystal06*. [2] The periodic MFI model on which all the considered structures are based was built according to the experimental powder neutron diffraction data of Hajar et al. [3] Various *k*-point sampling schemes of the Brillouin zone were tested. We performed the calculations at the  $\Gamma$ -point of the Brillouin zone. Periodicity of

the system, including the fully featured space group symmetry, has been rigorously considered. Four distinct space groups have been employed in the calculations, namely the experimentally determined orthorhombic *Pnma* space group and its *P112<sub>1</sub>/a*, *Pc* and *P1* subgroups. The subgroups make it possible to effectively reduce the titanium content. The vibrational zero point and entropy terms were used in the calculation of free energies for the *Pnma* isomer.

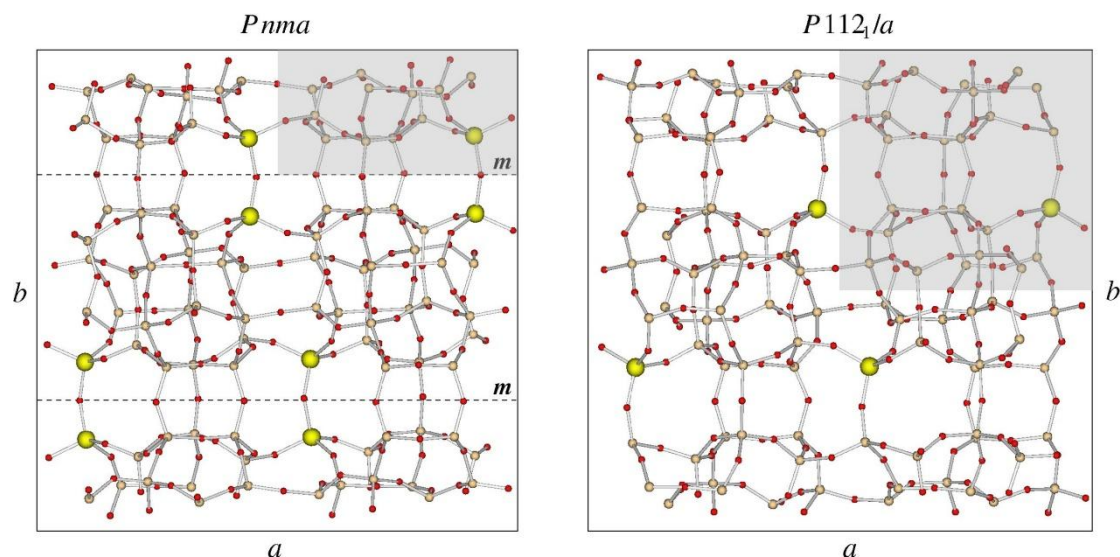


Figure 1. Two distinct models of the TS-1 unit cell, the shaded area denoting the asymmetric unit. Atom colors: Ti – yellow; Si – orange; O – red.

## RESULTS AND DISCUSSION

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 all space groups and it has been found that the order is notably affected by symmetry restrictions imposed by the space groups (Table 1, Figure 2).

Table 1. Titanium site preference order (according to the DFT energies of optimized isomers) in TS-1 for various space groups

	1	2	3	4	5	6	7	8	9	10	11	12
<i>Pnma</i>	T4	T6	T2	T8	T3	T12	T7	T5	T11	T1	T9	T10
<i>Pnma</i> *	T4	T2	T6	T3	T8	T11	T5	T7	T1	T12	T9	T10
<i>P2<sub>1</sub>/c</i>	T4	T3	T5	T11	T8	T12	T7	T9	T6	T10	T12	T1
<i>Pc</i>	T2	T7	T5	T4	T11	T12	T3	T9	T10	T8	T6	T1
<i>P1</i>	T9	T11	T2	T3	T5	T4	T12	T7	T8	T1	T6	T10

\* Free energy calculations via vibrational analysis and statistical mechanics (*Pnma* space group only).

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 *P112<sub>1</sub>/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. Further reductions of titanium concentration, which can be done by removing symmetry elements from the  $P112_1/a$  space group, yielding in the first step to  $Pc$  space group with the titanium content of 2.08 atomic %. Such models are likely to reproduce more faithfully the actual titanium 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. Upon passing to the more dilute  $P1$  model with the Ti content of 1.04 atomic % preferences order changes as listed in Table 1.

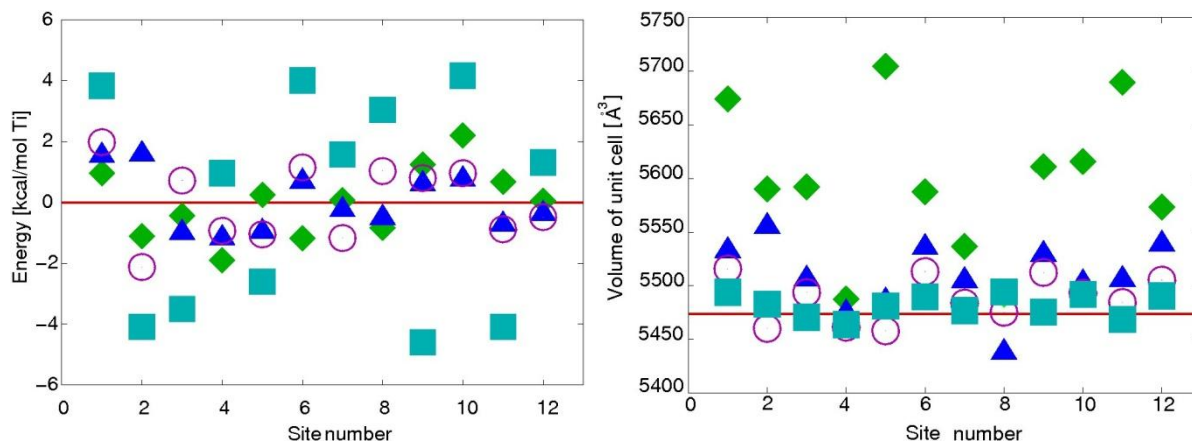


Figure 2. Energies of the TS-1 site isomers (left) and volume of unit cell of the TS-1 site isomers (right) for the space group models. Object colors: green -  $Pnma$ , blue -  $P21/c$ , purple -  $Pc$  and turquoise -  $P1$ . Red line (right): volume of the unit cell of the unsubstituted MFI zeolite.

To obtain additional insight into site preference order (Figure 3), we evaluated vibrational zero point energy and entropy terms by calculations of harmonic vibrational analysis for the  $Pnma$  space group. The calculated free energy preferences agree reasonably well with those experimental studies that predict non-random distribution titanium over the MFI lattice. However, as the energies of isomers are in a quite narrow range, we cannot exclude the possibility that the site preference is governed by other factors such as kinetics in the course of synthesis of the material, or that the Ti-siting is entirely random.

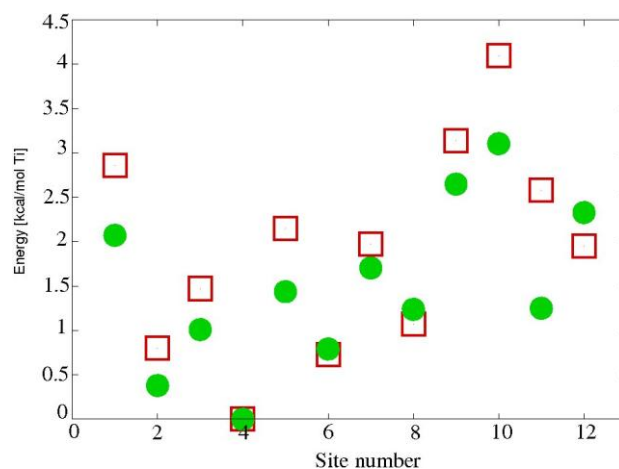


Figure 3. Free energies (green) and energies of the TS-1 site isomers (red) for the  $Pnma$  space group model.

## CONCLUSION

We found the energy differences between the isomers to be relatively small, not exceeding 8 kcal/mol per Ti site. Additionally, space group restrictions were found to have a notable effect on the site preference order. The agreement between our results and previous experimental and computational studies is good, although there is room for improvements. Due to small energy differences between the isomers, we cannot exclude a random distribution of titanium atoms over the structure and the possibility that the site preference is governed by kinetic factors.

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