A Combination of the Monte Carlo Method and Molecular Mechanics Calculations: A Novel Way To Study the Ti(IV) Distribution in Titanium Silicalite-1[†]

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A combination of the Metropolis Monte Carlo method and molecular mechanics calculations is used to study the Ti(IV) distribution in titanium silicalite-1 (TS-1). Calculations are carried out in which the Ti atoms are placed at crystallographically different T-sites rather than at symmetry-related T-positions. In this way, also the effect of already incorporated Ti atoms on the accommodation of new Ti atoms can be studied. It is shown that the Ti atoms are distributed over all crystallographically different lattice positions rather than located at one preferred T-site. The distribution, however, is not random: T2 and T12 are clearly favored. Modeling of the Ti distribution at loadings above the experimentally determined maximum limit of $2^{1}/_{2}$ Ti atoms per unit cell seems questionable. The framework symmetry is related to both the location of the Ti atoms and the Ti loading. There are much less Ti atoms present as neighbors than can be expected from a random substitution, which might indicate that Loewenstein's rule is dependent not only on electrostatic effects but also on framework deformations.

1. Introduction

Titanium silicalite-1 (TS-1), first synthesized in 1983,[1] is well-known for its outstanding ability to catalyze various oxidation and hydroxylation reactions.[2] This catalytic activity is ascribed to the presence of Ti atoms in the zeolite. Knowledge of the effect of the Ti atoms on the framework structure and of the location of the Ti atoms in the zeolite is of great importance to understand the catalytic properties of TS-1. Although TS-1 has been characterized extensively,[3] the location of the Ti atoms in the zeolite is still under discussion. The maximum amount of framework Ti has been reported to be $2^{1}/_{2}$ Ti atoms per unit cell (Ti/(Si + Ti) = 0.026). Higher Ti loadings give rise to nonframework Ti.[4] It is supposed that only framework Ti(IV) is responsible for the catalytic properties of TS-1.[5] The actual location of the Ti atoms in the framework is difficult to determine experimentally. Therefore, information obtained from theoretical methods is of considerable interest.

In the orthorhombic MFI structure substitution can take place at 12 crystallographically different tetrahedral (T-) sites (numbered T1–T12). In the monoclinic MFI framework the mirror symmetry is lost, and 24 crystallographically different T-sites can be distinguished (Figure 1).

Several computational studies[6,11] have been conducted on the location of Ti in TS-1. Jentys et al.[6] have used defect energy minimization techniques and quantum mechanical cluster calculations to study the Ti substitution in monoclinic MFI. Their calculations showed that incorporation of Ti atoms into the zeolite lattice at T-sites is preferred over the formation of bridges that consist of a Ti atom bonded to four oxygen atoms, which are pairwise bonded to Si atoms located in the lattice. With respect to the incorporation of Ti atoms at T-sites, it was found that none of these sites were clearly preferred. A slight preference was found for T6 and T19, while T18 was least favored. Note that T6 and T18 are related by mirror symmetry in the orthorhombic structure. Millini et al.[7] have conducted
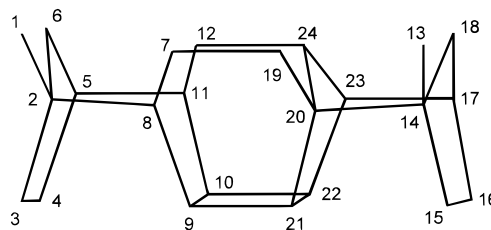
Figure 1. Crystallographically different T-sites in MFI. T1 (T2, ..., T12) and T13 (T14, ..., T24) are related by a mirror plane in orthorhombic MFI.

local density functional quantum mechanical calculations on monomeric, Ti(OH)$_4$, and pentameric, Ti(OSiO$_3$H$_3$)$_4$, clusters to study the Ti substitution in orthorhombic MFI. They kept the geometry of the cluster, abstracted from the orthorhombic MFI framework, fixed while replacing a Si atom by a Ti atom. No clear preference for a substitution site was found, though sites T12 and T3 were energetically slightly favored, while T4 and T5 were least preferred. Oumi et al.[8] have investigated the Ti substitution in orthorhombic MFI using molecular dynamics (MD) calculations. They studied the influence of substitution of one Ti atom per unit cell on the lattice parameters and compared their results with X-ray diffraction analyses.[9] This comparison does not invoke thermodynamic equilibrium to predict the Ti distribution as opposed to all other studies. T8 was found as the most probable site for Ti substitution. In contrast, Smirnov et al.[10] did not find any correlation between the unit cell expansion and the Ti location. Their MD calculations, in which the Ti atoms are randomly placed in the framework, perfectly reproduced the experimental unit cell expansion as a function of the Ti loading. De Man et al.[11] have performed ab initio calculations on molecules containing Ti, Si, O, and H which represent substructures of titanozeolites. Their study showed that Ti atoms prefer a 4-fold coordination in zeolites: their calculated relative energies and vibrational spectra make other forms of incorporation very unlikely.

The computational studies in the literature all support the experimentalist's opinion that Ti atoms are incorporated in the framework at regular T-sites. There is still controversy about

TABLE 1: Potentials and Parameters of the Force Field

bonds	$E_B(r_{T-O}) = k_{T-O}(r_{T-O} - r_0)^2$
	Si-O: $r_0 = 1.59$ Å, $k_{Si-O} = 415$ N/m
	Ti-O: $r_0 = 1.80$ Å, $k_{Ti-O} = 211$ N/m
angles	$E_\theta(\theta) = k_\theta(\theta - \theta_0)^2$
	O-T-O: $\theta_0 = 109.47°$, $k_\theta = 95 \times 10^{-20}$ J/rad^2
	$E_\alpha(\alpha) = k_\alpha(\cos\alpha - \cos\alpha_0)^2$
	Si-O-Si: $\alpha_0 = 156°$, $k_\alpha = 12.6 \times 10^{-20}$ J/sin$^2 \alpha_0$
	Si-O-Ti: $\alpha_0 = 150°$, $k_\alpha = 12.6 \times 10^{-20}$ J/sin$^2 \alpha_0$
	Ti-O-Ti: $\alpha_0 = 150°$, $k_\alpha = 12.6 \times 10^{-20}$ J/sin$^2 \alpha_0$

the exact siting of the Ti atoms in the zeolite structure. The small substitution energy differences found in the ab initio studies indicate that the Ti atoms are distributed over all lattice positions rather than located at one preferred T-site. In this study, therefore, we use the Metropolis Monte Carlo[12] (MC) method in combination with molecular mechanics (MM) calculations to investigate the Ti atom distribution over the T-sites. The basic assumption is that the Ti atoms are incorporated at random T-sites, which is in contrast to the studies presented in the literature so far where Ti atoms are incorporated at symmetry-related positions. In our approach, information regarding the influence on the substitution of both the T-sites themselves and the distances between the T-sites can be obtained. The present paper reports on the Ti distribution in TS-1 calculated using a novel computational method.

2. Method

There are $n!/(k!(n - k)!)$ possibilities to distribute k Ti atoms over n T-sites. At maximum Ti loading of $2\frac{1}{2}$ Ti atoms per unit cell there are approximately 2×10^9 possible distributions. From all these structures the energy minimum should be determined to get insight into the most favorable distribution. MC is applied to sample only those configurations that are energetically favorable, which saves computational time considerably. The following scheme is employed. After energy minimization a Ti distribution is immediately accepted if its energy is lower than that for the previous Ti distribution. If its energy is higher, its Boltzmann probability, $w = \exp[-(E_{new} - E_{old})/k_B T]$, is evaluated and compared with a randomly generated number between 0 and 1. If w is higher than the random number, the distribution is accepted; otherwise, it is rejected and the system is returned to its previous distribution. A new distribution is generated from the previous one by exchanging a randomly chosen Si atom with a randomly chosen Ti atom. In this way the Ti/Si ratio is kept constant. This new distribution is energy minimized, and the procedure is repeated. The sequence of distributions generated in this way satifies the conditions of a Markov chain: (i) all distributions are part of a finite set, and (ii) the result of each step only depends on the result of the preceding step.

Calculations were carried out at constant strain on a double unit cell containing 5 Ti, 187 Si, and 384 O atoms (Ti/(Si + Ti) = 0.026). The structure refinement of van Koningsveld[13] was taken as a start (orthorhombic, *Pnma*, $a = 20.078$ Å, $b = 19.874$ Å, $c = 26.744$ Å). Out of computational time considerations, a very simple force field (Table 1), yet reproducing both structure and dynamics of zeolites well,[10] was chosen to describe the interactions between the atoms in the framework. The SHANNO[14] minimization technique was employed in each calculation step. All calculations were carried out on an SG Indigo workstation.

3. Results and Discussion

The MC + MM run comprised 72 350 steps, from which 20 627 steps were accepted. The number of times a T-site is
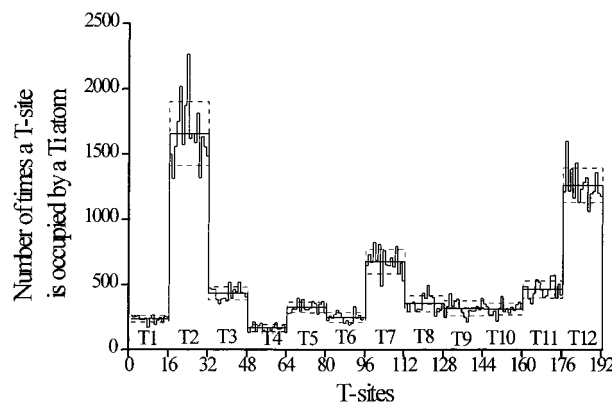

Figure 2. MC + MM run: distribution of 20 627 (number of accepted sets) times 5 Ti atoms over the 192 T-sites and the average occupation (—) and standard deviation (- - -) per crystallographically different T-site.
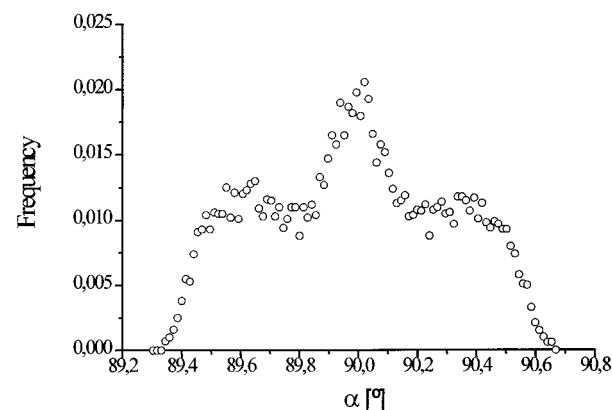

Figure 3. MC + MM run: unit cell parameter α distribution.

occupied by a Ti atom in the accepted sets is given in Figure 2. The 192 T-sites are grouped into 12 crystallographically different T-sites, T1 to T12, with a multiplicity of 16 (= number of equivalent positions (8) × number of unit cells considered (2)). Furthermore, the average number of visits and the standard deviation per crystallographically different T-site are shown. It can be concluded that the Ti atoms are distributed over all lattice positions rather than located at one preferred T-site. The distribution, however, is not random: T2 and T12 are clearly favored.

The rather large standard deviations found in Figure 2 prompted us to look at the accepted sets in more detail. A check on the unit cell parameters revealed that the symmetry of about one-third of the accepted structures is orthorhombic and of about two-thirds of the accepted structures is monoclinic. In the accepted sets with monoclinic symmetry there are 24 instead of 12 crystallographically different T-sites. T13 (T14, ..., T24) and T1 (T2, ..., T12) are related by the lost mirror plane and are both sampled at T1 in Figure 2. This explains the rather large standard deviations found in Figure 2. In Figure 3 the distribution for unit cell parameter α is given. The structures are considered to be orthorhombic when $\alpha = 90.0 \pm 0.1°$ and monoclinic for other values of α. In Figure 4 the Ti occupancies per unit cell for the separated orthorhombic and monoclinic structures are shown. In the orthorhombic structures T12 is preferred, whereas T2 is preferred in the monoclinic structures. Apparently, the incorporation of Ti at specific T-sites is strongly correlated with the symmetry.

Incorporation of Ti atoms into the framework not only influences the symmetry but also affects the incorporation of other Ti atoms. This can be concluded from the following
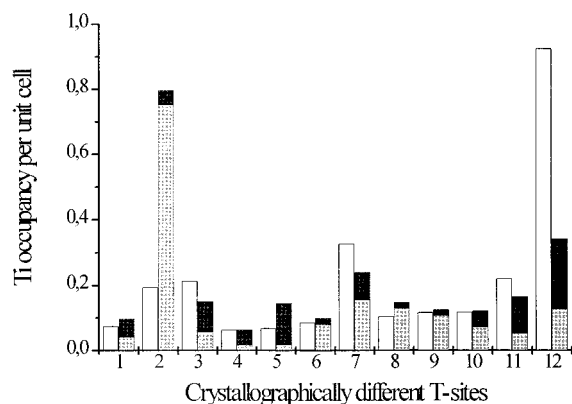
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Figure 4. MC + MM run: Ti distribution per unit cell over the crystallographically different T-sites for the orthorhombic (T1−T12, white) and monoclinic (T1−T12, light gray; T13−T24, dark gray) structures.
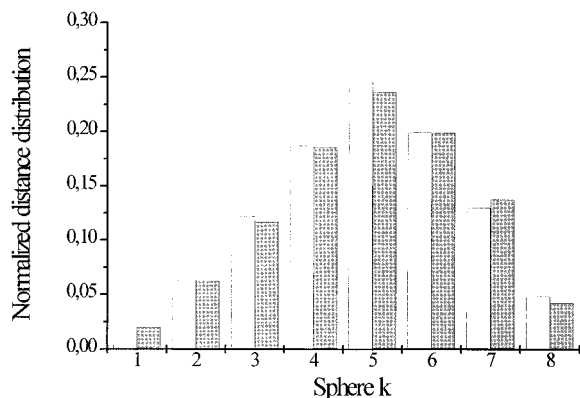
TABLE 2: Framework Symmetries[a] at Different Ti Loadings

T-site	1 Ti/double unit cell	1 Ti/unit cell	8 Ti/unit cell
T1	orthorhombic	orthorhombic	orthorhombic
T2	monoclinic	monoclinic	orthorhombic
T3	orthorhombic	monoclinic	monoclinic
T4	monoclinic	monoclinic	orthorhombic
T5	monoclinic	monoclinic	orthorhombic
T6	monoclinic	triclinic	orthorhombic
T7	orthorhombic	monoclinic	orthorhombic
T8	monoclinic	triclinic	orthorhombic
T9	monoclinic	monoclinic	orthorhombic
T10	orthorhombic	triclinic	orthorhombic
T11	orthorhombic	orthorhombic	orthorhombic
T12	monoclinic	monoclinic	orthorhombic

[a] Structures are considered to be orthorhombic for $\alpha = \beta = \gamma = 90.0 \pm 0.1°$ and monoclinic for other values of α. Structures with other values for α and β and/or γ are considered to be triclinic.

Figure 5. Normalized simulated (white) and random (light gray) distance distribution expressed in *k* spheres.
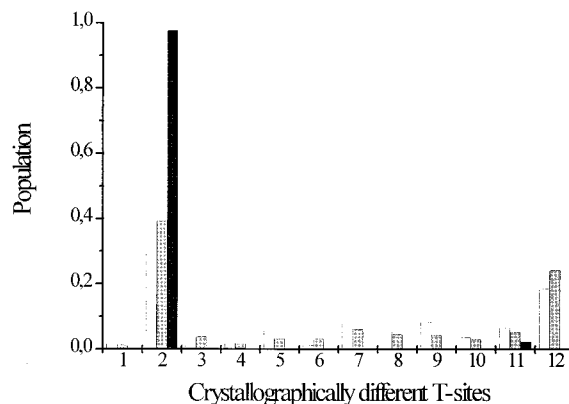

Figure 6. Population for different Ti loadings: (i) 1 Ti atom per unit cell (white), (ii) 1 Ti atom per double unit cell (light gray), and (iii) 8 Ti atoms per unit cell (dark gray).

analysis of the distance between Ti atoms in the framework. The "coordination sequence" method[15] was applied to define the distance between the T-sites. The sphere number *k*, the minimum number of oxygen bridges that connect two T-atoms, is used as distance. For example, the distance between neighboring T-sites has $k = 1$, whereas for the distance between next-nearest-neighbors $k = 2$. Between all Ti pairs in the accepted sets *k* was determined (5 Ti atoms produce 10 Ti pairs per set), resulting in a normalized distance distribution presented in Figure 5. For comparison, a distance distribution was also determined for a set of 20 627 configurations *randomly* generated from the MC + MM calculation and presented in Figure 5. There are much less Ti atoms present as neighbors ($k = 1$, Figure 5) than can be expected from a random substitution. The disturbance in the lattice geometry caused by an already incorporated Ti atom probably makes the neighboring T-sites in the deformed area unsuitable for substitution. This might indicate that Loewenstein's rule[16] is dependent not only on electrostatic effects but also on framework deformations.

The MC + MM calculation shows that at a loading of five Ti atoms per double unit cell: (i) the Ti atoms are distributed over all crystallographically different T-sites with preference for T2 and T12, (ii) the incorporation of Ti at specific T-sites influences the framework symmetry, and (iii) an already incorporated Ti atom affects the accommodation of new Ti atoms. In order to explore whether these results depend on the Ti loading, some additional MM calculations were carried out on systems comprising (i) 0 Ti atoms per unit cell, (ii) 1 Ti atom per unit cell, and (iii) 1 Ti atom per double unit cell by placing successively 1 Ti atom at each of the 12 inequivalent

T-sites, and (iv) 8 Ti atoms per unit cell by placing successively 8 symmetry equivalent Ti atoms at each of the 12 inequivalent T-sites.

The structure of the all-silica zeolite is orthorhombic, whereas the structure of the Ti-containing zeolites is orthorhombic, monoclinic, or even triclinic as can be seen in Table 2. The framework symmetry seems to be related not only to the substitution site but also to the Ti loading. For example, replacement of one Si at T6 by Ti per unit or double unit cell affords a triclinic or monoclinic framework symmetry, respectively, whereas a framework structure containing eight Ti atoms per unit cell on T6 has orthorhombic symmetry.

Assuming Boltzmann statistics, the populations were determined using the calculated minimized energies of the structures summarized in Table 2. The populations are given in Figure 6. At loadings of 1 Ti atom per unit cell or double unit cell, T2 and T12 are clearly preferred, which is in accordance with the distribution obtained for $2^1/_2$ Ti atoms per unit cell (Figure 2). Therefore, T2 and T12 seem intrinsically suitable substitution sites. Apparently, the "nearest-neighbor" effect ($k = 1$) that occurs at a maximum Ti loading of $2^1/_2$ Ti atoms per unit cell is not large enough to change the overall Ti distribution. However, in unit cells containing eight Ti atoms (at eight equivalent sites), all atoms are predicted to be incorporated at T2. Therefore, modeling of the Ti distribution at loadings above the experimentally determined maximum limit of $2^1/_2$ Ti atoms per unit cell seems questionable.

The calculations yield stable structures that contain more Ti atoms per unit cell than experimentally have been found. This might indicate that kinetics also play a role in the Ti incorporation.

4. Conclusion

This study shows that the Ti atoms in TS-1 are distributed over all lattice positions rather than located at one preferred T-site. The distribution, however, is not random: T2 and T12 are clearly preferred. Modeling of the Ti distribution at loadings above the experimentally determined maximum limit of $2^{1}/_{2}$ Ti atoms per unit cell seems questionable. The framework symmetry is related to both the location of the Ti atoms and the Ti loading. There are much less Ti atoms present as neighbors than can be expected from a random substitution, which might indicate that Loewenstein's rule is dependent not only on electrostatic effects but also on framework deformations.

The combination of the Monte Carlo method with molecular mechanics calculations is a novel way to study the substitution in zeolites. The basic assumption that Ti atoms are incorporated at random T-sites has not been employed in any study in the literature so far. Information regarding the influence on the substitution of both the T-sites themselves and the distances between the T-sites is obtained.

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