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Structural properties of titanium sites in Ti-ZSM5

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The geometry of Ti sites in ZSM5 has been studied using defect energy minimisation techniques and quantum mechanical cluster calculations. We found an energetic preference for the substitution of Si by Ti at lattice T sites. The results also indicated that titanium oxide species would form in the channels at higher Ti concentrations.

Keywords: Ti-ZSM5; computer simulations

1. Introduction

Titanium silicalite, first synthesized in 1983 [1], promotes important oxidation and hydroxylation reactions in various catalytic processes [2–4]. The incorporation of Ti into the zeolite can be achieved directly during the hydrothermal synthesis of the zeolite or via a post synthesis treatment of the zeolite with $TiCl_4$ [5]. The concentration of Ti atoms that can be incorporated into the lattice corresponds to $Ti/Si \leqslant 0.025$.

Although Ti-silicalite has been extensively characterized with respect to its structure and catalytic activity [6–8], the location of the Ti atoms is still under discussion. There are two contrasting structural models: (i) replacement of Si atoms from the zeolite lattice resulting in tetrahedral coordination or (ii) formation of extraframework species with the Ti atoms octahedrally coordinated.

Recently, X-ray absorption spectroscopy studies [9,10] were carried out to determine the environment of Ti in Ti-silicalite: XANES probed the coordination of Ti and EXAFS the local geometry of the Ti atoms in the zeolite. While the XANES of both studies showed clearly the presence of tetrahedrally coordinated Ti atoms in the samples, the EXAFS data were noisy, making the analysis of the data in terms of local structural models difficult [9] or impossible [10]. The more recent study [9] suggests, that a part of the Ti is incorporated in an edge sharing type structure, forming bridges across the zeolite channels; these comprise a Ti atom bond to four oxygen atoms, which are pairwise bond to Si atoms located in the lattice. A picture of this structure is shown in fig. 1. The sample analysed in this work was

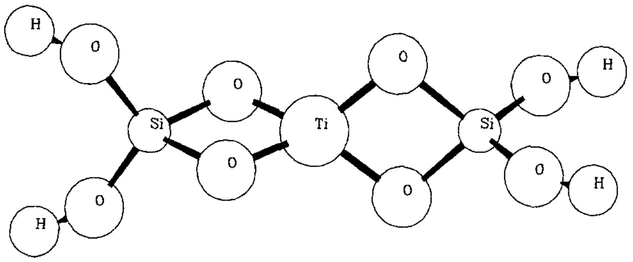

Fig. 1. Extraframework Ti-containing cluster as proposed in ref. [9]. The diagram shows the quantum mechanical cluster investigated in the present study. In the model of ref. [9] terminal oxygen atoms are bonded to framework silicon atoms.

Ti-ZSM11, which has MEL structure [11]. In agreement with the authors of this study we assume that both materials are so similar, that the results can be applied to the ZSM5 structure.

In this work we address the problem of the location of Ti using theoretical methods, which have been successfully applied to a wide range of structural problems in zeolite science [12]. We used atomistic simulation and quantum mechanical calculations to obtain the geometry of Ti in ZSM5. The first approach has been used to study the substitution of Al [13] and Fe [14] into the zeolite lattice. The latter method has also been employed for calculating the geometry of Al in zeolites [15]. The basis of the simulations is the calculation of the lattice energy of the system using interatomic potentials comprising short range interaction and long range Coulombic forces. The quantum mechanical studies calculate the electronic structure of representative clusters which contain the sites of interest. Cluster calculations of this type have been extensively employed in solid state studies [12].

2. Methodology

The techniques used in this study have been described extensively [12,16], therefore only a brief overview is given here. The lattice energy was calculated by standard summation procedures including the Ewald method [17] for the long range terms. The polarizability of the atoms was represented with a shell model [18]. The directional properties of the covalent bonding are modelled using bond harmonic three body terms around the tetrahedral angle of the silicon atoms in the lattice. For the zeolite framework, potentials described by Jackson and Catlow [19] and for Ti, potentials derived from rutile [20] were used. The potential parameters are compiled in table 1.

Having established the potential model, the lattice energy is calculated and minimized with respect to the positions of the atoms in the unit cell. The Mott–Littleton method [21] was used to treat the incorporation of Ti into the siliceous lattice. In this method an inner core of atoms (~ 300 in the present study) are explicitly

Table 1
Potential parameters

Species	Charges
Si^{4+}	4.0
Ti^{4+}	4.0
O^{2-} core	0.89602
O^{2-} shell	−2.86902
$O^{1.4-}$	−1.426[a]
H	0.426[a]

Buckingham potentials[b]

Species	A (eV)	ρ (Å^{-1})	C (eV Å^{-6})
Si–O	1283.90	0.3205	10.66
Ti–O	760.47	0.3879	0.0
O^{2-}–O^{2-}	22764.47	0.1490	27.88
O^{2-}–$O^{1.4-}$	22764.47	0.1490	27.88
O^{2-}–H	311.97	0.2500	0.0

Morse potential[c]

Species	D_e (eV)	α (Å^{-1})	r_0 (Å)
H–$O^{1.4-}$	7.0525	2.1986	0.9485

Three body terms[d]

Species	K (eV rad^{-2})	θ_0 (deg)
O–Si–O	2.09724	109.47

Shell model parameters

Species	Shell charge ($\|e\|$)	k (eV Å^{-2})
O^{2-}	−2.86902	74.92

[a] Oxygen and hydrogen components of OH.
[b] $E(r) = A\,e^{-r/\rho} - Cr^{-6}$.
[c] $E(r) = D_e\{1 - \exp[-\alpha(r - r_0)]\}^2$.
[d] $E(\theta) = \frac{1}{2}K(\theta_0 - \theta)^2$ (for both O species).

treated and their positions relaxed with respect to the calculated substitution energy, while more distant atoms are treated as dielectric continuum – a procedure that has been extensively and successfully used in modelling defects in solids. The CASCADE code [22] was used for these calculations.

For the quantum mechanical calculations, which were performed at the Hartree–Fock level, the standard 6-31G basis set [23] was employed for all atoms excluding Ti. An sd-model potential of the form developed by Sakai et al. was used for Ti [24], where no 6-31G basis set is defined, with a 41G contraction of the valence orbitals. All calculations were carried out using the program CADPAC version 5.0 [25].

3. Results

3.1. LATTICE AND DEFECT ENERGY CALCULATIONS

The differences in the defect energies resulting from substitution of Ti into tetrahedral lattice positions for silicalite are shown in fig. 2. The site notation of van Koningsveld for the monoclinic P2/N.1.1 structure of ZSM5 with 24 different T sites was used [26]. The geometries for the energetically most (site T6) and least (site T18) favoured substitution sites are given in table 2.

3.2. QUANTUM MECHANICAL STUDIES

In order to obtain a reliable starting geometry for modelling Ti present in structures forming bridges across the zeolite channels, quantum mechanical calculations on $(HO)_2$–Si–O_2–Ti–O_2–Si–$(OH)_2$ clusters were carried out. The size and the symmetry of the clusters results in modest computation requirements, while still enabling us to obtain accurate results. S_4 or C_{2v} symmetry, with the symmetry planes oriented along the Si–Ti–Si axis and perpendicular to it were imposed. In both cases the cluster gave the same minimum energy geometry. The results of the optimization calculations are presented in table 3.

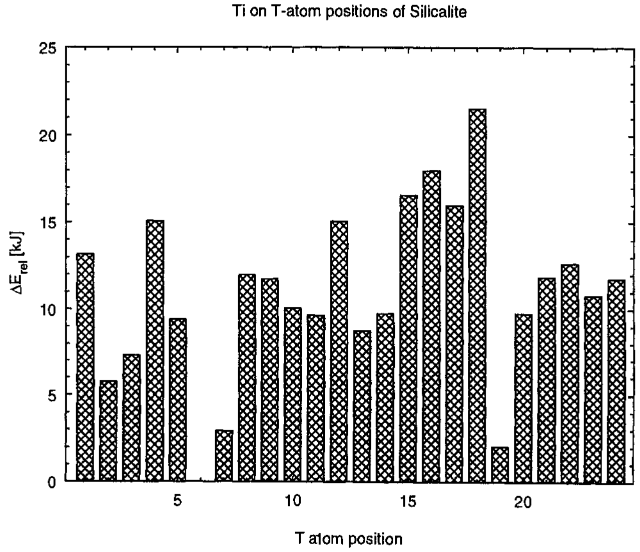

Fig. 2. Energies of Ti substitution at T sites of silicalite relative to the T6 site.

Table 2
Calculated geometries for the substitution of Ti into lattice positions T6 and T18

	Site T6	Site T18	Si in ZSM5
relative defect energy (eV)	0.0	21.5	
T–O distance (Å)	1.78	1.77	1.59
T–Si distance (Å)	3.22	3.22	3.10
T–O–Si angle	150	150	150

3.3. DEFECT ENERGY CALCULATIONS OF EXTRALATTICE CLUSTERS

In an ensuing set of simulations this cluster was anchored into the zeolite lattice, being placed in a position which allowed it to keep the Si–Ti–Si distance (2.60 Å) as calculated with the quantum mechanical calculations. In order to bond the cluster to the lattice Si it is necessary to break some of the Si–O bonds in the latter. The resulting partially bond oxygen atoms were compensated by adding hydrogen atoms. Stable bridged Ti structures could not be obtained in the following lattice energy minimization calculations. During the computations the bonds between the Si atoms, located in the zeolite lattice and the oxygen atoms, bond to the Ti atoms, tended to break as the energy of the structure was lowered. Moreover, the Ti atom started to move into the channel of the zeolite, remaining close to two of the four oxygens to which it was initially bonded. As we could not find any stable configurations for Ti using the calculated Si–Ti–Si distance, we tried using a distance of 2.2 Å as determined from the EXAFS analysis by ref. [9]. A stable configuration of Ti could also not be obtained in this calculation.

4. Discussion

The difference in energy for the substitution of Ti into the energetically most and least stable positions shows a very small range of about 21 kJ mol^{-1}, compared with the calculations carried out for the substitution of Si with Al $\approx$ 50 kJ mol^{-1} or Fe $\approx$ 26 kJ mol^{-1}. Sites T6 and T19 are determined to be energetically the most favoured; site T18 is the least stable. However, most of the different T atom positions do not differ by more than 10 kJ mol^{-1}, an energy barrier easily to be surpassed at the synthesis temperatures of Ti-ZSM5. This variation between the

Table 3
Results of the quantum mechanical calculation for the $(HO)_2$–Si–O_2–Ti–O_2–Si–$(OH)_2$ cluster

Ti–O distance (Å)	1.79
Ti–Si distance (Å)	2.60
Ti–O–Si angle	86.85

different substitution sites is too small to result in any preferred substitution site for Ti during the synthesis or the postsynthesis treatment of Ti-ZSM5.

Only a small distortion of the zeolite lattice is observed after the incorporation of Ti. The calculated distance between Ti–O for this substitution site of 1.78 Å is in perfect agreement with the distance calculated quantum mechanically, but disagrees with those determined by the analysis of the EXAFS of Ti-ZSM5 [10,9]. Both groups suggested a Ti–O distance of 1.85 Å or even 1.88 Å and a Ti–Si distance of 2.17 Å. Our results clearly differ in this respect, especially as a stable position of Ti in edge sharing or bridging configurations could not be obtained. Recently, further EXAFS experiments on Ti-ZSM5 zeolites have been undertaken [27]. The main difference from the previously discussed studies is that the Ti concentration was significantly lower, around 1 wt%, compared to 1.6 and 4.2 wt% Ti [9] or 3 wt% Ti [10]. Here the authors found for the activated sample a Ti–O distance of 1.8 Å and an average coordinated number for oxygen surrounding the Ti of 4.3. Note that both numbers are in very good agreement with our calculations and suggest the substitution of Si with Ti in lattice positions.

As mentioned before we could not find any stable configurations for tetrahedral coordinated Ti outside the lattice positions. These structures which were proposed in ref. [9], are formed by Ti atoms surrounded by four oxygen atoms in an edge sharing geometry. However, they broke apart when the calculations minimizing the geometry with respect to the lattice energy were carried out. Instead we observed the formation of titanium oxide species in the zeolite channels. This result was obtained even after starting in an optimized geometry for this structure with the proposed geometry of ref. [9].

5. Conclusions

The calculations presented here show clearly that the substitution of Ti into the ZSM5 lattice is preferred over the formation of species with tetrahedral coordinated Ti atoms in edge sharing or bridging positions. For the substitution site no clear preference was obtained, although sites T6 and T19 are energetically slightly favoured. This will result in a broad distribution of Ti over the different lattice positions in Ti-ZSM5.

As no stable configurations for Ti in other than lattice positions was observed, we conclude that instead of the formation of this group, titanium oxide species are formed in the channels. This is nicely underlined by the most recent EXAFS study [27] which suggests that at low Ti concentrations Ti atoms are almost exclusively located in lattice positions.

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