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# Periodic ab initio study of the oxidizing sites in Ti-containing zeolites

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## Abstract

A periodic Hartree–Fock study of Ti-containing zeolites was performed. The zeolitic framework was modeled by means of the chabazite structure. Two framework compositions were considered ( $Ti/(Si + Ti) = 0$  and 0.5) and the corresponding periodic structures were optimized in order to evaluate the structural and electronic features of the Ti sites. Cluster models were also considered for comparison. Despite the high Ti concentration, the theoretical cell expansion coefficient, 0.394, agrees very well with accurate experimental values. The adsorption of a single water molecule on a Ti site was studied and it was observed that a 5-fold coordination holds for the Ti atom in a deformed trigonal dipyramid.

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## 1. Introduction

The synthesis in 1983 of the first zeolite with titanium atoms in the framework, Ti-silicalite-1 or TS-1 [1] has introduced the use of Ti-zeolites as selective and efficient heterogeneous oxidizing catalysts.

Selective oxidation of unsaturated organic compounds can be performed by using Ti-zeolites with aqueous hydrogen peroxide. This possibility, which is of great interest for industry and fine chemistry [2,3], has stimulated the

synthesis of new Ti-zeolites with different selectivity [3–5].

Zeolite frameworks consist of corner-shared  $TO_4$  tetrahedra, where T is usually a Si or Al atom. In the case of Ti-zeolites, a fraction of the T sites is occupied by Ti atoms [2,6–8]. Titanium is 6-fold coordinated in oxides [9]; in zeolites, however, T sites are 4-fold coordinated. The local structure and site of Ti atoms in the framework are still controversial because at the moment only zeolites with low framework titanium content ( $Ti/(Ti + Si) < 0.03$ ) can be synthesized and the crystallinity of the obtained samples is low. As a consequence, physico-chemical techniques suitable for the accurate investigation of the structure of crystalline solids are not very useful [10]. On the

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other hand, the unique catalytic properties of Ti-zeolites in oxidation reactions involving  $H_2O_2$  makes the knowledge of the Ti site geometry and electronic structure of fundamental importance for understanding its properties.

In the last years only a few ab initio calculations of Ti containing zeolites have been reported [10–12]. In all the cases the cluster model was used to represent the Ti site and its environment. The present work is a theoretical study, performed with the periodic Hartree–Fock method, of the energetic, electronic and structural aspects related to the presence of Ti sites in zeolites. Chabazite has been adopted as a model framework for this investigation. With respect to other more interesting zeolites such as MFI, MEL or \*BEA, chabazite presents the advantages of a relatively small unit cell (12  $SiO_2$  units) and high symmetry (its space group is rhombohedral  $R\bar{3}m$ ) [13–16]. Channels and cavities of molecular size are present that allow

the diffusion and adsorption of small molecules. The main channel is limited by an 8-atom ring and the corresponding pore diameter is 3.8 Å [17]. Its framework density ( $0.015 T/\text{Å}^3$ ) is similar to that of more interesting compounds, such as the Beta and Y zeolites.

## 2. Method

In this preliminary work, we consider a chabazite structure in which one by two silicon atoms of the framework are substituted by titanium atoms. In this way only a mirror plane is lost with respect to the pure Si-chabazite structure and the symmetry becomes  $R\bar{3}$  (6 point symmetry operators). In spite of the high Ti concentration, each Ti atom is surrounded by four Si atoms as second neighbors, and the minimal distance between a pair of Ti atoms is 4.7 Å. Only six non-equivalent atoms occur in

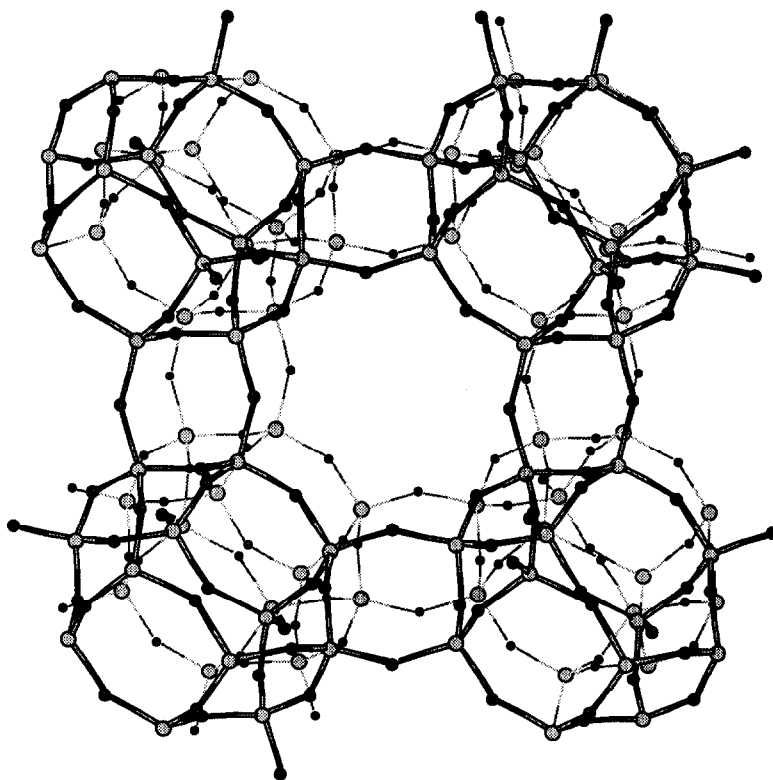


Fig. 1. The structure of silico-chabazite.

the structure: one Ti, one Si, and four O that correspond to the four non-equivalent oxygens of Si-chabazite. This structure will be indicated as P-1, whereas P-0 will indicate the Si-chabazite (Fig. 1).

Unit cells with a lower Ti content ( $Ti/(Ti + Si) = 1/3$  or  $1/6$ ) have been disregarded for the moment because of the lower symmetry ( $C_3$  and  $C_2$ , respectively), resulting in higher disk and CPU requirements, and in a larger number of variables to be taken into account in the optimization process.

A finite cluster model, shown in Fig. 2, was also considered as a complementary tool to the periodic model. It represents a central T site ( $T = Si$  or  $Ti$ ) surrounded by 3 shells of neighboring atoms of the chabazite framework where the relative position of the atoms belonging to the third shell are the same as in the perfect crystal. The ‘dangling’ bonds resulting from the broken connection with the rest of the structure were saturated by hydrogen atoms [18]. In this case, no symmetry was imposed to the model. The labels C-0 and C-1 will indicate the clusters with a titanium or silicon atom at the center T, respectively.

As a preliminary probe of the reactivity of the Ti site, an  $H_2O$  molecule has been approached to each Ti site in the periodic and in

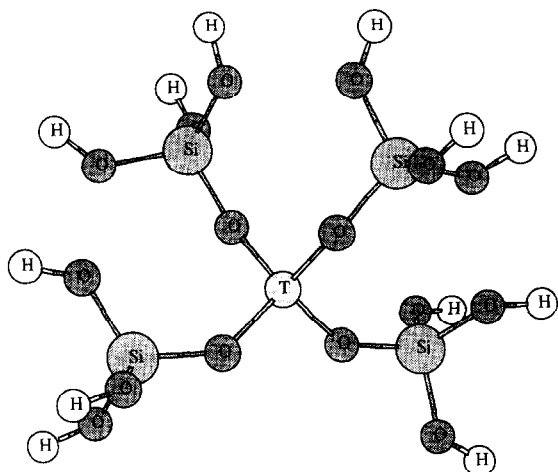


Fig. 2. The T  $[Si(OH)_3]_4$  cluster model adopted for the present study. T can be a Si (C-0 model) or a Ti atom (C-1 model).

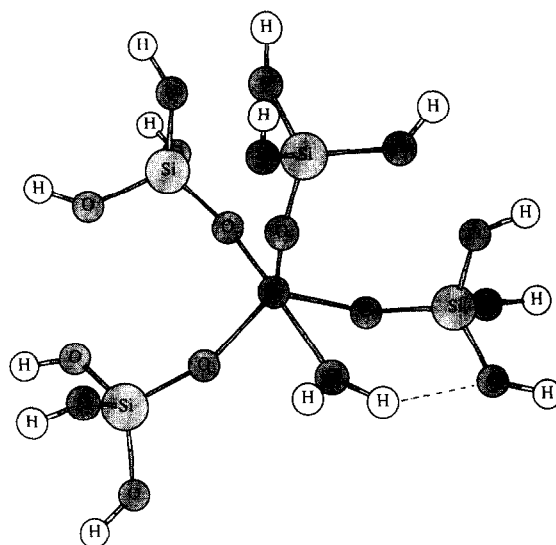


Fig. 3. The T  $[Si(OH)_3]_4 + H_2O$  cluster model (C-2) in its optimized structure.

the cluster models (see Fig. 3). The obtained models will be indicated as P-2 and C-2, respectively.

$SiO_2$   $\alpha$ -quartz and Si-chabazite, and  $TiO_2$  rutile were used as reference systems for testing the adopted computational conditions, basis set and optimization procedure.

Periodic and cluster calculations were carried out within the Hartree–Fock (HF) approximation using the CRYSTAL95 [19] and the GAUSSIAN92 [20] codes, respectively. The basis set consists in a split valence 6-21G\* [21] for Si ( $\alpha_d = 0.5$ ). The exponent of the most diffuse Gaussian was optimized in Si-chabazite. The best value is larger than the one for the isolated atom (0.13 versus  $0.09 \text{ bohr}^{-2}$ ) because of the partial ionic nature of the SiO bond. For Ti, an 86411/411/3 (s/p/d) contraction originally designed for TiC [22] and then reoptimized in  $TiO_2$  [23] was used. A standard 6-21 G [21] basis set was used for oxygen and active hydrogen atoms, while for the hydrogen atoms that saturate the ‘dangling’ bonds of the clusters an STO-3G basis set [24] was adopted.

As regards the computational conditions for the CRYSTAL95 calculations of the chabazite structure, the following values have been used

for the parameters controlling the truncation of the Coulomb and exchange series [19]: 6, 6, 6, 10. A shrinking factor equal to 2 was used, corresponding to only 4  $k$  points in the irreducible part of the Brillouin zone. The energy difference with respect to calculations with shrinking factor 4 is  $3 \times 10^{-6}$  hartree for Si-chabazite. For the calculations, a modified version of the CRYSTAL code was used that implements symmetry adapted crystalline orbitals for obtaining a block-diagonal Fock matrix representation at each calculated  $k$  point with a considerable reduction in computational time [25].

The geometry optimizations in the periodic systems have been carried out by using a modified Polak–Ribiere algorithm [26] in which the gradients are calculated numerically. For simple potential energy surfaces this method yields quite accurate results with a minimum number of evaluations. For clusters, the standard analytic gradient techniques implemented in the GAUSSIAN92 code [20] have been used.

Each model was optimized using a different criterion according to its nature. The periodic models were constrained to keep their spatial symmetry during the optimizations. In such a way, the number of geometrical parameters is reduced as much as possible, making the numerical optimization computationally feasible. The periodic model does not present discontinuities

at the border of the active site and accounts for the cell expansion which is characteristic of the titanium insertion in zeolites [2,6]. Within such a model, all the Si atoms of the framework are symmetry equivalent; this implies that the second shell of neighbors around the T site is relaxed in a dependent way in the periodic optimization.

On the other hand, the cluster models were optimized by only constraining the border oxygen atoms (3rd shell of neighbors of the central atom) to keep their relative position as in the perfect crystal and the saturating hydrogen atoms to keep a OH distance of 0.98 Å and a SiOH angle of 130°. Such a constraining scheme avoids spurious distortions of the model and simultaneously allows the asymmetric relaxations of first and second neighbors.

### 3. Results and discussion

#### 3.1. Reference systems

The quality of the adopted basis set and computational conditions, as well as the numerical optimization procedure were tested by performing the geometry optimization of well known crystalline systems, namely SiO<sub>2</sub>  $\alpha$ -quartz and Si-chabazite, and the TiO<sub>2</sub> rutile. The results are reported in Table 1. The agree-

Table 1  
Optimized crystallographic parameters (experimental values in brackets;  $a$  and  $c$  in Å,  $\gamma$  in degrees;  $x$ ,  $y$  and  $z$  in fractionary units)

Atoms	$x$	$y$	$z$	Cell parameters
Si-chabazite ( $R\bar{3}m$ ) [27]				
Si	0.107 (0.104)	0.334 (0.334)	0.879 (0.875)	$a = 9.36$ (9.42)
O <sub>1</sub>	0.254 (0.264)	-0.254 (-0.264)	0.	$\gamma = 94.7$ (94.2)
O <sub>2</sub>	0.146 (0.155)	-0.146 (-0.155)	0.5	
O <sub>3</sub>	0.249 (0.252)	0.249 (0.252)	0.894 (0.895)	
O <sub>4</sub>	0.022 (0.025)	0.022 (0.025)	0.327 (0.328)	
$\alpha$ -quartz ( $P3_121$ ) [28]				
Si	0.470 (0.467)	0.	0.	$a = 4.94$ (4.91)
O	0.414 (0.415)	0.268 (0.268)	0.214 (0.214)	$c = 5.42$ (5.41)
rutile ( $P4_2/mnm$ ) [29]				
Ti	0.0	0.0	0.0	$a = 4.48$ (4.59)
O	0.305 (0.305)	0.305 (0.305)	0.0	$c = 2.95$ (2.96)

ment with experiment for Si-chabazite is reasonable. Small differences can, at least partially, be attributed to the fact that calculations refer to the pure Si structure, while experiments refer to samples with a small amount of Al in the framework [27]. A more accurate comparison may be carried out by using a purely silicic structure as experimental reference, namely  $\alpha$ -quartz [28]. In this case (see Table 1) the agreement is excellent. In Table 2 the energies at equilibrium of  $\alpha$ -quartz and Si-chabazite are reported. It is shown that the former is more stable than the latter by about 2 kcal/mol [15]. As regards the P-0 and C-0 comparison, bond lengths and bond angles are listed in Table 3. The results for the two systems are very similar, the largest differences being 0.02 Å ( $O_4$ -Si) and 2° ( $TO_2$ Si).

The rutile structure [29,30] was optimized with the basis set described above. In this case there is a larger discrepancy (about 2%) with respect to experiment for one of the geometrical parameters ( $a$ , see Table 1); for the rest the agreement is very good. The use of a 6-21G basis set for oxygen is probably responsible for part of the discrepancy. Such a basis set is perfectly adequate for the description of covalent situations, as in the case of  $SiO_2$  based systems, but not so much for very ionic situations as in  $TiO_2$ , where usually slightly more diffuse valence functions are used [23]. In the case of Ti-chabazite this basis set effect is expected to be negligible, both because of the

Table 2

Hartree-Fock energies for the optimized structures (in Hartree per unit cell or molecule)

P-0 <sup>a</sup>	-5264.6732
C-0 <sup>a</sup>	-2648.7643
P-1 <sup>a</sup>	-8620.9913
C-1 <sup>a</sup>	-3208.1630
P-2 <sup>a</sup>	-9076.5564
C-2 <sup>a</sup>	-3284.0878
$\alpha$ -quartz (3 $SiO_2$ units)	-1316.1790
Rutile (2 $TiO_2$ units)	-1996.3310
$H_2O$	-75.8884
$H_2O$ (periodic)	-75.8873

<sup>a</sup> See label definition in text.

Table 3

Optimized parameters and energy for periodic and cluster models (distances in Å, angles in degrees)

	P-0 <sup>a</sup>	C-0 <sup>a</sup>	P-1 <sup>a</sup>	C-1 <sup>a</sup>	P-2 <sup>a</sup>	C-2 <sup>a</sup>
$r(TO_1)$	1.61	1.62	1.79	1.79	1.89	1.84
$r(TO_2)$	1.61	1.62	1.79	1.81	1.80	1.82
$r(TO_3)$	1.61	1.62	1.79	1.80	1.78	1.80
$r(TO_4)$	1.62	1.62	1.78	1.78	1.80	1.79
$a(O_1Si)$	1.61	1.60	1.62	1.60	1.65	1.61
$a(O_2Si)$	1.61	1.61	1.61	1.60	1.62	1.59
$a(O_3Si)$	1.61	1.61	1.62	1.60	1.58	1.58
$a(O_4Si)$	1.62	1.60	1.63	1.60	1.63	1.59
$a(TO_1Si)$	154	153	157	155	144	158
$a(TO_2Si)$	148	150	150	152	144	146
$a(TO_3Si)$	153	153	155	156	167	160
$a(TO_4Si)$	152	152	155	155	158	157
$a(O_1TO_2)$	111	111	114	113	102	107
$a(O_1TO_3)$	109	108	106	106	95	101
$a(O_1TO_4)$	107	108	105	105	102	100
$a(O_2TO_3)$	111	111	115	115	124	121
$a(O_2TO_4)$	108	108	106	105	116	111
$a(O_3TO_4)$	110	110	112	111	112	114
$r(TO_w)$	—	—	—	—	2.24	2.26
$r(HO_w)$	—	—	—	—	2.04	2.23
$a(O_1TO_w)$	—	—	—	—	175	179
$a(O_2TO_w)$	—	—	—	—	76	74
$a(O_3TO_w)$	—	—	—	—	82	78
$a(O_4TO_w)$	—	—	—	—	83	80
$a$	9.36	—	9.94	—	9.95	—
$\gamma$	94.7	—	94.7	—	94.7	—
Cell volume ( $\text{\AA}^3$ )	811.8	—	971.5	—	974.1	—

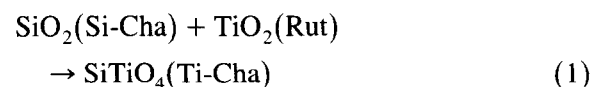
T stands for Ti (P-1, C-1, P-2, C-2) or Si (P-0, C-0);  $O_i$  indicates non equivalent O atoms of Table 1.

<sup>a</sup> See label definition in text.

4-fold Ti coordination (leading to less ionic bonds) and because here oxygen is just 2-fold coordinated (3-fold in rutile) and one of its nearest neighbors is a silicon atom.

### 3.2. The substitution of Si by Ti atoms in the zeolite framework

The Si-by-Ti substitution can be modeled by the following reaction:



The energy balance of Eq. (1) can be calculated using P-0 and P-1 as models for Si- and Ti-chabazite, respectively. The energies are listed

in Table 2. The resulting energy difference,  $\Delta E$ , is 35 kcal/mol per Ti atom. As expected, the inclusion of the Ti atom into the framework in 4-fold coordination is endothermic with respect to the most stable 6-fold coordination in the rutile structure.

In the P-1 model, however, all the Si atoms are equivalent by symmetry and then strongly constrained in the optimization. This would not be the case in a system with a lower Ti content, but, as mentioned in the introduction, at the moment we are unable to run the periodic system at lower symmetry. For this reason and in order to verify the degree of transferability of the information from periodic to finite cluster calculations, we considered the C-1 cluster, whose geometry has been optimized without symmetry constraints between the Si atoms and their neighbors. In order to estimate the substitution energy, in this case C-0 and C-1 were adopted as models of Si- and Ti-chabazites. The following equation was used for obtaining the substitution energy:

$$\Delta E = E(\text{C-1}) + E(\text{P-0}) / 6 - E(\text{C-0}) - E(\text{Rut}) \quad (2)$$

Using the data of Table 2, the calculated substitution energy is 27 kcal/mol per Ti atom, that is about 8 kcal/mol less than for the periodic model. This difference is to be attributed both to the larger relaxation freedom and to the lack of long range electrostatic effects in the cluster. At the moment, however, we cannot neither separate the two effects, nor formulate hypotheses on their relative importance and sign.

As regards the optimized geometry, the calculated parameters for models P-1 and C-1 are listed in Table 3. It turns out that the TiO bond lengths is between 1.78–1.81 Å in agreement with previous theoretical and experimental values [10,12,31–33]. Cluster and periodic optimized geometries are similar, the largest difference being 0.02 Å for TiO and 2° for the TiOSi angles.

By comparing the geometry of the SiO<sub>4</sub> tetrahedra in P-0 and P-1, it turns out that they are

very similar. This seems to confirm the conclusions of de Man and Saner [12], who, on the basis of cluster calculations, state that structural effects of Ti substitution are mainly local. The present energetic and geometric results are therefore expected to be representative also of structures with a lower Ti content.

The TiO<sub>4</sub> tetrahedron of P-1 is less regular than the SiO<sub>4</sub> tetrahedron of P-0 (see Table 3). This might be a consequence of the larger ionicity and d orbital contribution to the bond in the former (see Figs. 4 and 5, where the valence density of states of P-0 and P-1 is shown).

One of the outcomes of the periodic calculation is the variation of the lattice parameter due to the cation substitution (Table 3). The cell expansion coefficient ( $\alpha$ ) is defined as

$$\alpha = \frac{V/V_0 - 1}{x} \quad (3)$$

where  $V$  and  $V_0$  are the cell volumes of Ti- and Si-chabazite, respectively, and  $x$  is the molar fraction of Ti atoms. The calculated cell expansion coefficient is 0.394, in very good agreement with accurate measurements (0.395) performed by using XRD techniques on TS-1 samples [6]. Thangaraj et al. [34] reported a smaller value for the cell expansion coefficient of TS-1 (0.308). However, as proposed in Ref. [6], the discrepancy might come from the existence of extra-framework Ti atoms in the used samples that are expected to cause minor or null cell expansion.

Table 3 shows that TOSi angles slightly increase from Si-chabazite to Ti-chabazite and such an increment is expected to contribute to the cell expansion. Nevertheless it is currently assumed [35] that the cell expansion coefficient only depends on the increment of the TiO distance according to the relation

$$\alpha = \frac{r_{\text{TiO}}^3}{r_{\text{SiO}}^3} - 1 \quad (4)$$

Using in Eq. (4) the calculated mean TiO and SiO bond lengths of P-1 and P-0 the resulting cell expansion coefficient is 0.362. About 10%

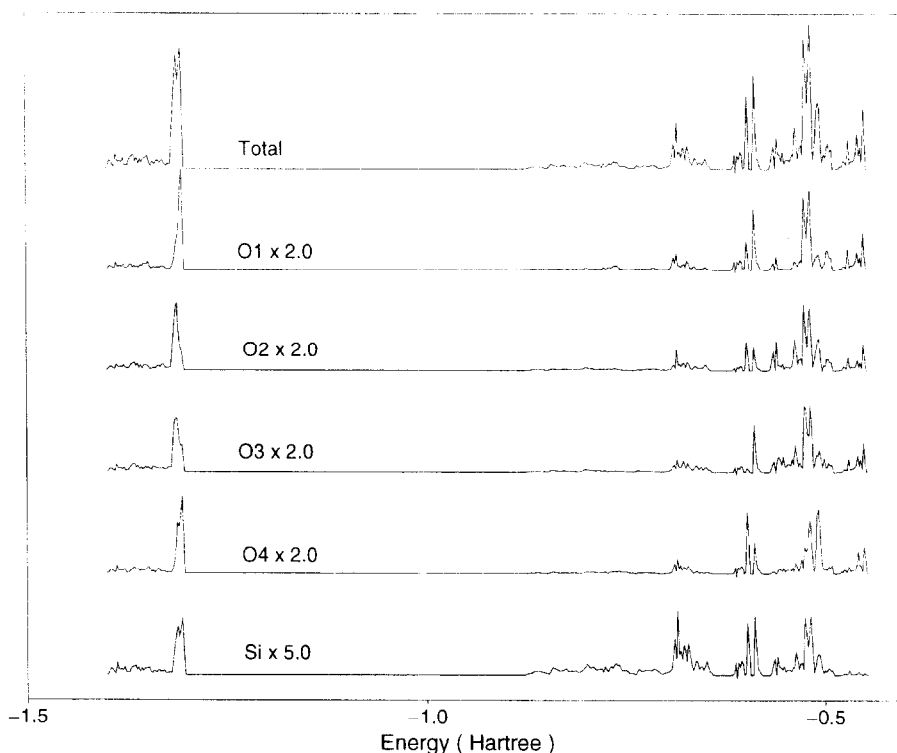


Fig. 4. Total and projected density of states (DOS) of Si-chabazite. Arbitrary units have been used. The intensity of some projected DOS has been magnified with respect to the total DOS by a factor indicated in the figure. Only valence electrons were calculated.

of the cell expansion comes then from changes in the TOSi angles.

### 3.3. Water adsorption

The adsorption of a single water molecule per Ti site was then considered. The optimized periodic and cluster geometries are given in Table 3 (P-2 and C-2 columns), whereas energy data are listed in Table 2.

The cluster model was optimized following the same scheme as for C-0 and C-1, namely border oxygens (third shell of neighbors of the central atom) and saturating hydrogens were constrained to keep their original position in the unperturbed host lattice (P-1 model). For the periodic system all the active sites were constrained to be symmetry equivalent during the optimization process; the adsorbed water molecule was additionally constrained to keep the same internal geometry as in the optimized

C-2 model. The resulting adsorption energies are  $-25$  and  $-23$  kcal/mol for P-2 and C-2, respectively.

In order to evaluate how important the interaction is between the water molecules contained inside the chabazite cavities, a periodic calculation was performed on a periodic system consisting of 6 water molecules per unit cell located at the same relative positions as in the optimized P-2 model. From the data reported in Table 2 it turns out that the periodic arrangement of water molecules is less stable than the isolated molecule by only 0.7 kcal/mol.

As regards the equilibrium geometry parameters of the periodic and cluster models, they are in general quite similar, with a few exceptions. The  $\text{TiO}_4$  tetrahedra opens in order to permit the water molecule to approach Ti, and the site assumes a trigonal dipyramid-like structure. The resulting  $\text{TiO}_w$  ( $\text{O}_w$  is the oxygen of the water molecule) distance is 2.24 Å in P-2 and 2.26 Å

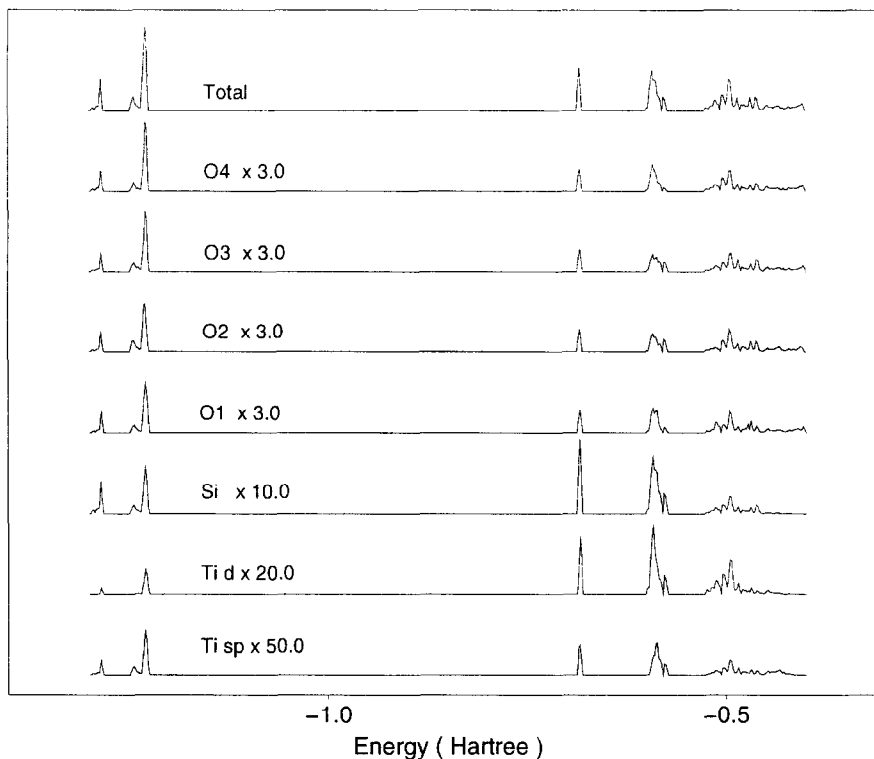


Fig. 5. Total and projected density of states (DOS) of Ti-chabazite. See previous figure for details.

in C-2, indicating that a relatively strong Ti–O bond is formed. In parallel, one of the framework TiO bond distances ( $\text{TiO}_1$ ) increases by 0.1 Å (only 0.05 in C-2), whereas the other ones ( $\text{O}_2$ ,  $\text{O}_3$  and  $\text{O}_4$ ) increase by only 0.01 Å, and lie approximately in a plane containing the Ti atom. The angle  $\text{O}_w\text{TiO}_1$  is very close to  $180^\circ$  ( $175^\circ$  and  $179^\circ$  for P-2 and C-2, respectively) and the  $\text{O}_w\text{—O}_1$  line is approximately orthogonal to the  $\text{O}_2\text{O}_3\text{O}_4$  plane.

The water molecule is oriented in such a way that the distance between one of the hydrogens and one of the bridging oxygen atoms of the framework ( $\text{O}_x$  in Fig. 3 referring to the cluster) is 2.03 Å (2.23 Å in the cluster) as a consequence of a relatively strong hydrogen bond interaction. It must be noticed that the cell volume remains essentially unchanged upon water adsorption (see Table 3).

Using these results, the energy balance of a Si-by-Ti substitution in a zeolite framework can

be discussed. The energy difference between the two more probable situations of Ti ions in zeolites, i.e. as extra-framework 6-fold coordinated  $\text{TiO}_2$  or as 4-fold coordinated framework Ti, is clearly unfavorable for the latter, because an additional energy that could be as large 35 kcal/mol is required. However, it must be stressed that the synthesis of Ti-zeolites is performed in aqueous conditions [2] and it is expected that before calcination the Ti-sites are fully hydrated. The present results show that the relative stability of the substitution sites can dramatically change when considering the hydrated centers instead of the pure tetrahedral Ti sites. This is due to the large interaction energy with adsorbed water. The interaction with two  $\text{H}_2\text{O}$  molecules per Ti site, which will be the object of future investigation, is expected to further stabilize the framework Ti site with respect to the extraframework situation. It is to be noticed that this aspect of the problem was



not considered in previous theoretical works where Ti substitution in the silicalite framework was investigated [11,10].

#### 4. Conclusions

Preliminary conclusions can be drawn concerning the adopted methodology and the chemistry of the Ti sites in zeolites.

As regards the first aspect, it has been shown that it is now possible to use a periodic *ab initio* approach for the investigation of such a 'complicated' problem as the Ti substitution in chabazite and water adsorption thereon. The periodic scheme presents many appealing features: it takes correctly into account long range effects; the expansion of the zeolite structure is correctly described; the geometry is correctly constrained in the optimization process. On the other hand the cost of the calculation is high, and rapidly increasing as the point symmetry decreases; consequently, a high concentration of Ti atoms in the unit cell had to be adopted in order to keep the computation requirements (disk space and cpu time) within our possibilities. The cluster model has been used as a complementary tool, in order to explore the low Ti concentration limit, and the effect of a larger freedom in the optimization process. It turns out that, when correctly constrained at the border by using the results of the geometry optimization of the periodic structure, the cluster model provides energy and geometry data not too far from these obtained with the periodic model. The differences in the results are a measure of the importance of the many computational and chemical differences in the two adopted models.

As regards the chemical aspects, it turns out that the incorporation of Ti atoms in the zeolite framework is energetically unfavored when Ti is 4-fold coordinated. The flexibility of the framework, however, allows to increase the coordination of the Ti sites through the adsorption of ligands such as water molecules. The resulting additional stability is probably one of the

determinant factors in the formation of titanium containing zeolites.

Future work will include the investigation with the periodic model of Ti-chabazite structures with lower Ti content, and the adsorption of two water molecules per Ti site.

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#### References

- [1] M. Taramasso, G. Perego and B. Notari, U.S. Patent 4,410,501 (1983).
- [2] G. Perego, G. Bellusi, C. Corno, M. Taramasso, F. Buonomo and A. Esposito, in: Y. Murakami, A. Iijima and J. Ward (Eds.), *Studies in Surface Science and Catalysis*, Vol. 28 (Elsevier, Amsterdam, 1986) p. 129.
- [3] M.A. Cambor, A. Corma and A. Martínez, *J. Chem. Soc. Chem. Commun.* (1992) 589; M.A. Cambor, A. Corma and J. Perez-Pariente, *Zeolites* 13 (1993) 82.
- [4] G. Bellusi, A. Carati, M.G. Clerichi, A. Esposito, R. Millini and F. Buonomo, Belg. Patent 1,001.038 (1989).
- [5] T. Blasco, A. Corma, M.T. Navarro and J. Perez-Parierite, *J. Catal.* 156 (1995) 65.
- [6] R. Millini, E. Previde Massara, G. Perego and G. Bellusi, *J. Catal.* 137 (1992) 497.
- [7] M.R. Boccuti, K.M. Rao, A. Zecchina, G. Leofanti and G. Petrini, in: C. Mortera, A. Zecchina and G. Costa (Eds.), *Studies in Surface Science and Catalysis*, Vol. 48 (Elsevier, Amsterdam, 1988) p. 133.
- [8] A. Tuel, J. Diab, P. Gelin, M. Dufoux, J.F. Dutel and Y. Ben Taarit, *J. Mol. Catal.* 63 (1990) 95.
- [9] R.C. Weast (Ed.), *Handbook of Chemistry and Physics* (CRC, Cleveland, 1986).
- [10] R. Millini, G. Perego and K. Seiti, in: J. Weikamp, H.G. Karge, H. Pfeifer and W. Hölderich (Eds.), *Studies in Surface Science and Catalysis*, Vol. 84 (Elsevier, Amsterdam, 1994) p. 2123.
- [11] A. Jentys and C. Catlow, *Catal. Lett.* 22 (1993) 251.
- [12] A.J.M. de Man and J. Sauer, *J. Phys. Chem.* 100 (1996) 5025.
- [13] E.H. Teunissen, C. Roetti, C. Pisani, A.J. de Man, A.P.J. Jansen, R. Orlando, R.A. van Santen and R. Dovesi, *Model. Simul. Mater. Sci. Eng.* 2 (1994) 921.
- [14] E.H. Teunissen, A.P.J. Jansen, R.A. van Santen, R. Orlando and R. Dovesi, *J. Chem. Phys.* 101 (1994) 5865.

- [15] E. Aprà, R. Dovesi, C. Freyria-Fava, C. Pisani, C. Roetti and V.R. Saunders, *Model. Simul. Mater. Sci. Eng.* 1 (1993) 297.
- [16] C. Pisani and U. Birkenheuer, *Int. J. Quantum Chem. Quantum Chem. Symp.* 29 (1995) 221.
- [17] W.M. Meier and D.H. Olson, *Atlas of Zeolites Structure Types* (Butterworth, London, 1992).
- [18] J. Sauer, *Chem. Rev.* 89 (1989) 199.
- [19] C. Pisani, R. Dovesi and C. Roetti, in: *Lecture Notes in Chemistry Series* (Springer, Berlin, 1988) p. 48; R. Dovesi, V.R. Saunders, C. Roetti, M. Causà, N.M. Harrison, R. Orlando and E. Aprà, *CRYSTAL95 user documentation*, Università di Torino, Torino (1995).
- [20] M.J. Frisch, G.W. Trucks, H.B. Schlegel, P.M.W. Gill, B.G. Johnson, M.W. Wong, J.B. Foresman, M.A. Robb, M. Head-Gordon, E.S. Replogle, R. Gomperts, J.L. Andres, K. Raghavachari, J.S. Binkley, C. Gonzalez, R.L. Martin, D.J. Fox, D.J. Defrees, J. Baker, J.J.P. Stewart and J.A. Pople, *GAUSSIAN92/DFT*, Revision G.3, Gaussian Inc., Pittsburgh, PA (1993).
- [21] J.S. Binkley, J.A. Pople and W.J. Hehre, *J. Am. Chem. Soc.* 102 (1980) 939; M.S. Gordon, J.S. Binkley, J.A. Pople, W.J. Pietro and W.J. Hehre, *J. Am. Chem. Soc.* 104 (1982) 2797.
- [22] V.R. Saunders, private communication.
- [23] P. Reinhardt, B.A. Heß and M. Causà, *Int. J. Quantum Chem.*, in press.
- [24] W.J. Hehre, R.F. Stewart and J.A. Pople, *J. Chem. Phys.* 51 (1969) 2657.
- [25] C.M. Zicovich-Wilson and R. Dovesi, unpublished results.
- [26] W.H. Press, B.P. Flannery, S.A. Teukolsky and W.T. Vetterling, *Numerical Recipes* (University Press, 1989).
- [27] M. Calligaris, G. Nardin, L. Randaccio and P. Comin Chiaramonti, *Acta Cryst. B* 38 (1982) 602.
- [28] J.D. Jorgensen, *J. Appl. Phys.* 49 (1978) 5473.
- [29] E.P. Meagher and G.A. Lager, *Can. Miner.* 17 (1979) 77.
- [30] A. Fahmi, C. Minot, B. Silvi and M. Causà, *Phys. Rev. B* 47 (1993) 11717.
- [31] M. Hursthouse and M. Hossain, *Polyhedron* 3 (1984) 95.
- [32] D. Trong On, A. Bittar, A. Sayari, S. Kliaguine and L. Bonneviot, *Catal. Lett.* 16 (1992) 85.
- [33] S. Pei, G. Zajac, J. Kaduk, J. Faber, B. Boyanov, D. Duck, D. Fazzini, T. Morrison and D. Yang, *Catal. Lett.* 21 (1993) 333.
- [34] A. Thangaraj, M. Eapen, S. Sivasankar and P. Ratnasamy, *Zeolites* 12 (1991) 943.
- [35] G. Bellusi and F. Fattore, *Zeolite Chemistry and Catalysis* (Elsevier, Amsterdam, 1991) p. 79.