Interaction of Ti-Zeolites with Water. A Periodic *ab Initio* Study

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The interaction of water molecules with Ti sites in Ti-containing zeolites has been studied by means of the ab initio periodic Hartree−Fock program CRYSTAL. The zeolitic part of the system has been represented by a perfect crystalline chabazite framework. The Ti content and distribution within the model structure have been designed so as to keep the maximum symmetry. Water physisorption has been accomplished by adding one (two) water molecule to each symmetry equivalent Ti-site; the geometry has been fully optimized; the calculated adsorption energy is −34.4 (−43.6) kJ mol^{-1}. The stability and electronic structure of the hydrated sites are shown to be largely dependent on the framework flexibility. The hydrolysis of the Ti−O−Si bridge to yield Ti−OH and Si−OH has also been studied. This reaction is endothermic within the present model ($\Delta E = 35.3$ kJ mol^{-1}). The activation energy was estimated in about 84 kJ mol^{-1}.

1. Introduction

In the last 10 years a considerable effort has been devoted to the synthesis[1−7] and characterization[8−17] of a variety of Ti-substituted zeolites. This interest is due to the fact that these materials show unique catalytic properties in oxidation processes with strong industrial implications.[18,19]

From a fundamental point of view, in contrast to other catalysts based on transition metal compounds,[20] Ti-zeolites show the remarkable property of being highly active in the presence of water and other polar solvents. Therefore, much attention has been paid to the study of this new class of materials, but little is known about what gives Ti-zeolites their peculiar properties.

The local structure of Ti sites within the zeolite framework is still a matter of discussion. The main reason for this is due to the fact that physicochemical techniques commonly used for structure determination of solids are not able to give unequivocal microscopic information in this particular case.[12,14] Nevertheless, it is generally accepted that, after synthesis, about 2−3% of the framework tetrahedral positions are occupied by Ti atoms, which are 4-fold coordinated in anhydrous conditions.[2,10,21−23] Such intrantraframework Ti atoms are considered to be the active sites for the catalytic oxidations.[2,12] Spectroscopy studies on Ti-zeolites[24,25] indicate that in many cases Ti centers are not completely linked to the framework, but some of the Ti−O−Si bridges around the center are broken into Ti−OH and Si−OH groups. This kind of defects can be formed either during synthesis or by further hydrolysis of the Ti−O−Si group, and it has been proposed that they are the actual catalytic sites in mesoporous Ti-silica catalysts.[26]

However, controlling the synthesis conditions, for instance, with F$^-$ medium instead of the most usual OH$^-$, it is possible to reduce the content of framework defects in Ti-zeolite samples.[27−29] Applying this technique in the synthesis of Ti-β, it has been observed in a recent study[30] that most of the Ti

centers in the dehydrated sample are fully connected to the framework, and this structure is stable even after rehydration and subsequent calcination. In addition, these nondefective materials show a good catalytic activity.

It then appears that the structure, stability, and activity of Ti sites in zeolites are closely related to the way these sites can interact with water molecules, either during the crystallization process when Ti−O−Si bonds are being formed, or in the catalytic reaction, where water molecules can coadsorb with other ligands or react with the Ti sites yielding partial hydrolysis of the Ti−O−Si bridges.

Theoretical methods can be successfully used to interpret the considerable amount of published experimental data on Ti-zeolites, as they permit us to obtain a precise description of microscopic features with an accuracy that only depends on how reasonable the selected model is. In the last years, a few ab initio calculations have been reported, concerning Ti centers in zeolites. The geometry and stability of 4-fold coordinated Ti atoms within a silica environment have been studied using the cluster model approach at density functional theory (DFT)[31] and Hartree−Fock[32−34] levels. Periodic Hartree−Fock (PHF) calculations on Ti-zeolites have been also reported,[35,36] and in this case structural, electronic, and energetic features of Ti sites have been investigated by comparing different frameworks and Ti/Si ratios. The reactivity of Ti sites in oxidative reactions was also explored by using the DFT approach applied to small cluster models.[37]

Previous works[26,26] have been devoted to study the interaction of Ti sites with probe molecules, and more specifically, reactions involving the hydrolysis of Ti−O−Si bridges by water have been considered. Calculations have been carried out on cluster models at DFT level and the relative stability between the different species together with the optimized geometries have been used to discuss experimental EXAFS results on mesoporous Ti-MCM-41.[39]

In the present work, we have investigated the interaction of Ti-zeolites with water, when H$_2$O molecules are both physisorbed and chemisorbed on the Ti sites. To account for the influence of the zeolitic framework on the active sites, which

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is usually neglected in cluster model calculations, this study has been carried out on periodic chabazite (CHA) models in which part of the framework T positions are occupied by Ti atoms. Because relaxation of structures is mandatory to properly account for the framework constraints acting on the active sites, the geometries of stable species have been fully optimized.

The CHA structure has been widely used in previous works[36,40−44] as a model framework for zeolites. Despite the fact that Ti-chabazite has not been still synthesized, CHA frameworks are good models for investigating interactions between zeolites and small molecules, since pores are not so small to limit the diffusion; moreover the relatively small unit cell size (12 TO$_2$ units per cell) permits ab initio calculations to be performed at a reasonable computational cost.

2. Models and Methods

In our calculations the host catalyst is represented by a CHA structure with an equal number of framework Ti and Si atoms per cell; the space symmetry is R$\bar{3}$ in all cases. Si and Ti atoms alternate, and each TiO$_4$ group is only surrounded by SiO$_4$ tetrahedra. The unit cell then contains six symmetry equivalent sites with composition TiSiO$_4$. There are 18 independent atomic coordinates and 2 cell parameters to be considered in the optimization process. The first neighbors of the Ti atom in the present model are totally unconstrained, while second neighbors are at a general position but forced to be symmetry equivalent. For comparison, we can consider a hypothetical unconstrained cluster model containing the atoms of the site up to the second coordination sphere, Ti(OSi)$_4$. In this case we would have $3 \times 9 - 6 = 21$ degrees of freedom, only one more than in the periodic model. This means that, for the actual catalyst and within the present model, the structural constraint resulting from the connection of the Ti(OSi)$_4$ group to the rest of the solid is somehow represented by the loss of a single degree of freedom with respect to the unconstrained Ti site. As regarding the interaction between Ti sites resulting from the high Ti/Si ratio, it has been shown in a previous paper[36] that both the electrostatic and electronic reciprocal perturbation is negligible when Ti sites are separated by at least one SiO$_4$ tetrahedron. For this reason, and because of the much higher computational costs that prevent a full geometry optimization, periodic models with lower Ti concentration (and therefore lower symmetry) have not been considered in the present study.

The local structures of the most relevant species considered are depicted in Figure 1. The reference model, 0a, corresponds to the pure host structure optimized within the above-mentioned symmetry constraints. Models 1a and 2a (see Figure 1a and b, respectively), are obtained from 0a by adding one and two physisorbed water molecules per Ti site, respectively. The geometry of the water molecule is unconstrained; molecules at different sites are however symmetry related. In model 1x$_0$, one water molecule reacts with the Ti site, hydrolizing a Ti−O bond to form a Ti−OH and a silanol group (see Figure 1 c). Models 1x$_1$ and 1x$_2$ represent different points along the reaction path connecting 1x$_0$ and 1a.

Models 0a, 1a, 2a, and 1x$_0$ have been fully optimized; thus, they are stable systems under the considered symmetry constraints. As regarding 1x$_1$ and 1x$_2$, they are supposed to be close to the transition state and have been obtained as follows. First, a series of calculations were performed by fixing the H$_x$ −O$_4'$ distance to several values between 1.85 and 1.05 Å starting from model 1a. O$_4'$ indicates one atom that is symmetry equivalent to O$_4$ (see Figure 1). The only allowed relaxations were (i) the Ti atom along the O$_x$ − O$_4$ axis (see Figure 1), (ii) the remaining
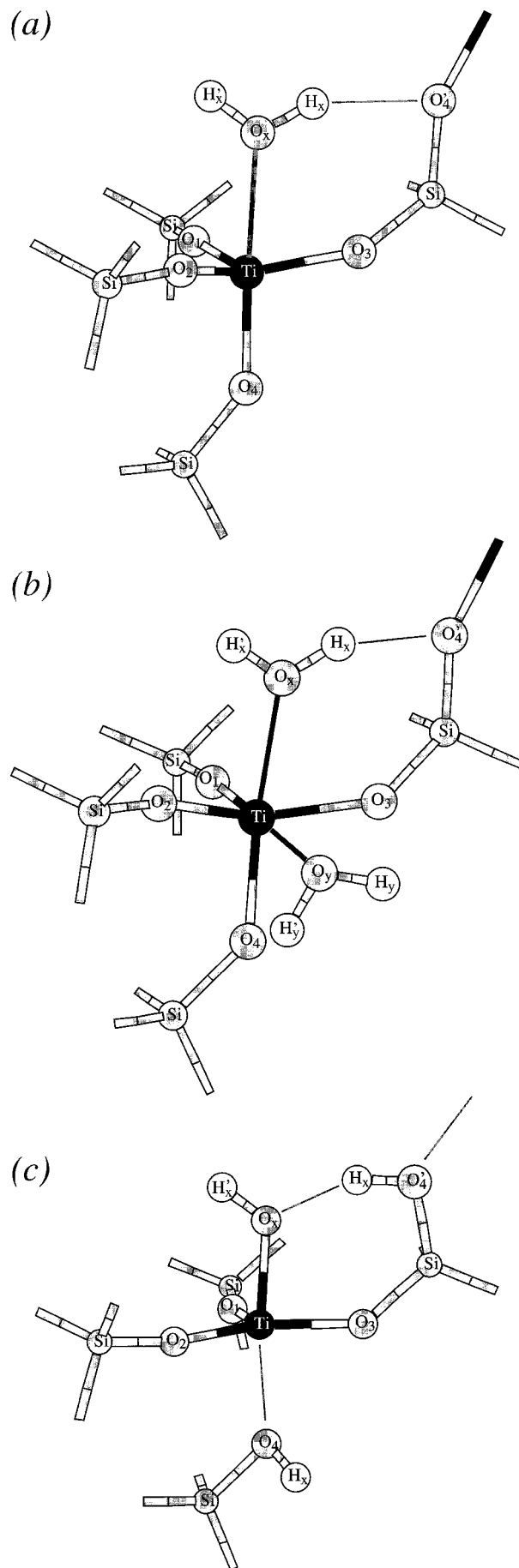

Figure 1. Local structure of Ti sites in models (a) 1a, (b) 2a, and (c) 1x$_0$.

degrees of freedom of the transferring H_x atom. The rest of the coordinates were kept fixed to their value in 1a. The energy profile along the H_x-O_4' path is continuous, which indicates that the reaction is mainly controlled by the H_x-O_4' distance. A maximum was obtained at $r_{H_x-O_4'} = 1.44$ Å; the *overall* structure was then relaxed by keeping this value fixed, and the resulting geometry is indicated as $1x_2$. The process was then repeated by using $1x_2$ as the starting geometry; the final geometry is $1x_1$, and the total energy increased by 15.8 kJ mol^{-1} per asymmetric unit with respect to $1x_2$. Iterating up to convergence in energy, such a scheme is expected to yield an accurate geometry for the transition state. Nevertheless, because of the large computational cost of each step, we performed it only twice, assuming $1x_1$ is a reasonably good approximation to the transition state.

Geometry optimizations have been carried out by using the Polak–Ribiere[45] method with numerical derivatives; the accuracy of the calculated optimum parameters is mainly conditioned by numerical errors in the evaluation of derivatives.

All the calculations have been performed at the PHF level by using the CRYSTAL95 code.[46] Point symmetry is exploited in the diagonalization of the reciprocal space Fock matrix by using a basis of symmetry adapted Bloch functions.[47,48] Two different kinds of atomic basis sets have been considered. For geometry optimizations, a relatively cheap basis set is mandatory as the number of single energy point calculations required by the numerical procedure is usually very large. For this reason a 6-21G(d), a 6-21G, and a 21G basis[49] have been used for Si, O, and H, respectively, whereas for Ti a 86411/6411/3 (s/p/d) contraction has been adopted.[36] For the single-point energy calculations (at the equilibrium geometry or along the reaction path) a more flexible basis set has been used on O (6-311G(d)),[50] H (31G(p)) and Ti (the 3G d contraction has been substituted by a 21G one). This scheme has been shown in previous studies to provide accurate equilibrium geometries and formation energies of both pure[51] and Ti-substituted zeolites.[34,35] As regarding the parameters controlling the accuracy of the calculations, they are the same as indicated in the CRYSTAL95 users manual[46] and used in previous calculations on similar systems.[36]

3. Results and Discussion

3.1. Geometries and Electronic Structure. The most important geometrical parameters for the six models here considered are reported in Table 1. Comparison between the 0a and 1a data shows that physisorption of a single water molecule involves important modifications in the structure of the Ti site. Upon optimization, the water molecule locates opposite to one of the oxygens of the TiO$_4$ tetrahedron (O$_4$ in Figure 1). The oxygen atom of the water molecule (O$_x$ in Figure 1), the framework Ti and O$_4$ are nearly collinear, whereas Ti and the other three oxygen atoms are nearly coplanar. The Ti–O$_4$ bond distance increases (1.87 vs 1.79 Å in the anhydrous compound, see Table 1), whereas the other Ti–O bonds remain essentially unaltered.

This is in good agreement with previous cluster calculations,[26] and the experimental results obtained with Ti-β in calcined dehydrated samples where Ti–O bond distance is 1.79 Å for a sample prepared in the presence of F- and 1.81 Å when prepared in OH$^-$ media.[30] In these cases the coordination is clearly tetrahedral, the Debye–Waller factors are smaller than that of anatase, indicating that the Ti–O distances of the four bonds are quite similar. When the Ti-β sample was prepared in F– (Ti-β(F)), it was seen experimentally that, after rehydration, one

TABLE 1: Geometrical Parameters in Anhydrous and Hydrated Ti−Chabazite[a]

	models					
	0a	1a	2a	$1x_0$	$1x_1$	$1x_2$
$r(TiO_1)$	1.78	1.79	1.78	1.78	1.78	1.78
$r(SiO_1)$	1.63	1.62	1.61	1.61	1.61	1.63
$\theta(SiO_1Ti)$	155	161	173	165	169	164
$r(TiO_2)$	1.79	1.79	1.83	1.81	1.78	1.80
$r(SiO_2)$	1.62	1.60	1.60	1.59	1.57	1.60
$\theta(SiO_2Ti)$	155	169	158	169	172	173
$r(TiO_3)$	1.79	1.81	1.86	1.83	1.82	1.83
$r(SiO_3)$	1.61	1.62	1.63	1.61	1.62	1.63
$\theta(SiO_3Ti)$	150	144	139	134	129	136
$r(TiO_4)$	1.79	1.87	1.89	2.14	2.07	1.92
$\theta(SiO_4)$	1.62	1.64	1.66	1.67	1.67	1.68
$\theta(SiO_4Ti)$	157	142	140	129	138	142
$\theta(O_1TiO_2)$	111	113	101	109	106	107
$\theta(O_1TiO_3)$	106	116	102	116	122	120
$\theta(O_1TiO_4)$	105	101	98	94	96	99
$\theta(O_2TiO_3)$	115	124	147	135	132	129
$\theta(O_2TiO_4)$	106	96	100	87	89	92
$\theta(O_3TiO_4)$	114	101	100	88	93	98
$r(TiO_x)$		2.25	2.21	1.89	2.02	2.26
$r(TiO_y)$		2.23				
$\theta(O_xTiO_4)$		174	170	168	169	170
$\theta(O_yTiO_1)$		177				
$r(H_xO_x)$		0.97	0.97	1.81	1.30	1.09
$r(H_xO_4')$		2.04	1.83	1.00	1.17	1.44
a	9.94	9.95	9.95	9.94	9.84	9.95
γ	94.7	94.7	94.7	94.7	94.7	94.7

[a] Distances r and a in angstroms, angles θ and γ in degrees. a and γ are lattice parameters. Labels for atoms refer to Figure 1. For the definition of models, see text.

water molecule is inserted in the coordination sphere of Ti, which becomes pentacoordinated, and Ti−O−Si bond hydrolysis does not occur extensively. In this case, using a two-shell coordination model for fitting, four Ti−O bond lengths are 1.82 Å, and the fifth one is 2.12 Å. In the case of Ti−silicalite, the Ti−O distance was 1.81 Å for the calcined dehydrated sample and after hydration 3.3 oxygen atoms were at 1.93 Å, while 1.7 are at 2.0 Å.[52]

The geometry of the monohydrated Ti site is roughly that of a trigonal dipyramid whose equatorial plane is defined by the O$_1$−O$_2$−O$_3$ triangle and the axial direction, normal to the plane, by the O$_x$−O$_4$ segment. The equatorial triangle is not completely regular because the O$_2$−Ti−O$_3$ angle is larger than the other two by 5°−10° (see Table 1). The distance between one of the hydrogen atoms of the water molecule H$_x$ and O$_4'$ (see Figure 1) is relatively short ($r_{H_x-O_4'} = 2.04$ Å, see Table 1), suggesting the existence of a hydrogen bond between them. When a second molecule is adsorbed, the most favorable position is along the equatorial plane and between O$_2$ and O$_3$ (model 2a), and the O$_2$−Ti−O$_3$ angle and the corresponding distances increase. It is to be underlined that the framework is flexible enough to account for the distortion of the sites at every second cationic site.

Water molecules remain essentially undistorted upon adsorption. The interaction is mainly electrostatic, and involves the lone pairs of the oxygen atoms and the positively charged Ti ion; Ti−O (O$_x$ and O$_y$, see Figure 1) distances range from 2.21 to 2.25 Å, and the O$_i$−Ti−O$_j$ angles (i stands for x or y; j for one of the framework oxygens) is close to 180° (170−4° for O$_x$−Ti−O$_4$, 177° for O$_y$ −Ti−O$_1$, as shown in Table 1).

As in 1a, in 2a the water molecule on the vertical octahedral axis interacts with a framework O$_4$ through a hydrogen bond. The presence of a second water molecule results in a shortening of the H$_x$−O$_4'$ bond, indicating that the change in coordination

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TABLE 2: Net Atomic Charges as Resulting from the Mulliken Analysis

Q	0a	1a	2a	$1x_0$	$1x_1$	$1x_2$
			models			
Ti	+2.60	+2.66	+2.72	+2.69	+2.69	+2.68
Si	+1.92	+1.92	+1.94	+1.95	+1.94	+1.96
O_1	−1.13	−1.13	−1.10	−1.11	−1.12	−1.12
O_2	−1.13	−1.11	−1.13	−1.11	−1.08	−1.11
O_3	−1.13	−1.15	−1.19	−1.15	−1.14	−1.15
O_4	−1.13	−1.18	−1.23	−1.03	−1.16	−1.21
O_x		−0.76	−0.78	−1.02	−1.00	−0.90
H_x		+0.40	+0.39	+0.44	+0.53	+0.49
H_x'		+0.36	+0.37	+0.33	+0.34	+0.35
O_y			−0.76			
H_y			+0.39			
H_y'			+0.38			

of the Ti atom also affects the electronic structure of the neighboring O. In particular, as a consequence of the O−O repulsion, the increase in the number of ligands implies the increase of the average TiO distances. Also the ionic character of the Ti−O bond is expected to increase as a result of the lower back-donation from O to Ti.[36]

The atomic Mulliken net charges for the nonequivalent atoms are reported in Table 2. It turns out that the addition of ligands to the Ti site increases the ionicity of the framework. In particular Q[O_4] decreases from −1.13 to −1.23 $|e|$ when the Ti coordination increases from 4 (0a) to 6 (2a). As a consequence, the hydrogen bond between H_x and O_4' is expected to be weaker in 1a than that in 2a, as proved by the shortening of the corresponding distance (2.04 and 1.83 Å, respectively; see Table 1).

The increase in the coordination of the Ti atom involves some changes in its electronic structure which are relevant as they are commonly used in the characterization of the coordination state and local geometry of framework Ti sites starting from X-ray adsorption spectra in the Ti K-edge region.[12] In particular, it has been shown that regular tetrahedral Ti sites in silica environment present a single intense preedge peak corresponding to the 1s → 3d electronic transition at 3.5 eV (the zero of the energy scale is taken at 4964.2 eV), while in regular octahedral arrangement, the peak splits into three low intense ones, and the position of the central transition is shifted to about 4.8 eV in silicates.[30] From the present calculations the energy shift of the Ti 1s → 3d transition in going from anhydrous to dihydrated Ti sites can be estimated from the band energy of the lower unoccupied electronic states. In Figure 2, the density of electronic states around the band gap is presented for models 0a, 1a, and 2a. As stated in a previous work,[36] the bands in the region around 4.35 eV (with the present basis set) correspond to Ti 3d unoccupied orbitals. The first peak of this band is located at 4.35 (0a), 4.46 (1a), and 4.54 (2a) eV; an energy shift of about 0.11 (0.19) eV for the adsorption of one (two) water molecules per Ti site is then observed. This lower than expected shift in the latter case might be due to the fact that the TiO_6 octahedron in 2a is quite irregular.

The basic behavior of O_4 has been investigated by considering the proton transfer from O_x (model 1a) to O_4' (model $1x_0$). The reaction path involves the simultaneous displacement of the transferring H and of the Ti atom (the latter along the O_x−O_4 axis). As a result of these geometry modifications, the Ti atom forms a strong bond with the charged OH^- group resulting from water dissociation, and a weaker bond with the neutral silanol group at O_4 (see Figure 1). This modification of the bonds involving O_x and O_4 in going from 1a to $1x_0$ is documented by the Mulliken data of Table 2: the O_x charge population
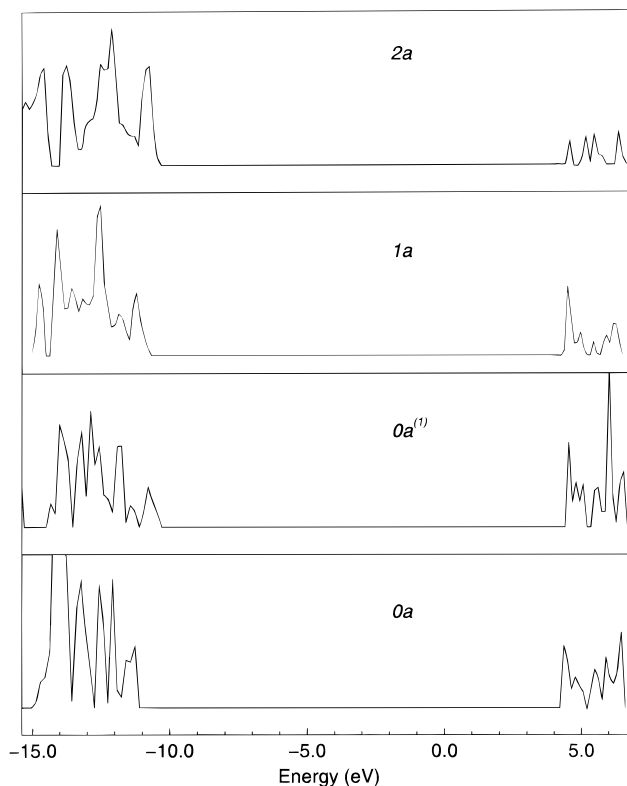
Figure 2. Top valence and bottom conduction density of states for the various models. Densities are in arbitrary units and energies in eV.

decreases by 0.26$|e|$, whereas Q[O_4] increases by 0.16$|e|$ while forming the covalent O_4'−H_x bond.

When considering models $1x_1$ and $1x_2$ that lie along the reaction path connecting $1x_0$ and 1a, an inversion of the $TiO_1O_2O_3$ tetrahedron is observed. Indeed, the best approximation to the transition state $1x_1$ presents a nearly planar configuration of the $TiO_1O_2O_3$ group, and $r_{Ti-O_x} \approx r_{Ti-O_4}$. It is to be noticed that neither the water physisorption nor the chemisorption with hydrolysis−condensation of the Ti−O_4 bond results in an important change of the cell parameter, which indicates that the geometrical changes involved in the reactions are mainly of local character.[34,36] The exception is the transition state, model $1x_1$, that shows a slight reduction of the cell dimensions, as shown in Table 1.

3.2. Relative stability of the Species. The total energy of the various species considered in the present study are given in Table 3 and they refer to a formula unit. Thus, for example, in the 0a and 1a cases the energy of the $SiTiO_4$ and $SiTiO_4 \cdot H_2O$ units are given. With reference to these data, let us consider the energy balance of the reactions depicted in Scheme 1.

Figure 3 shows the energy profile for the reactions considered. Reaction R1 is the first hydration of the Ti site; its reaction energy ΔE_1 reads
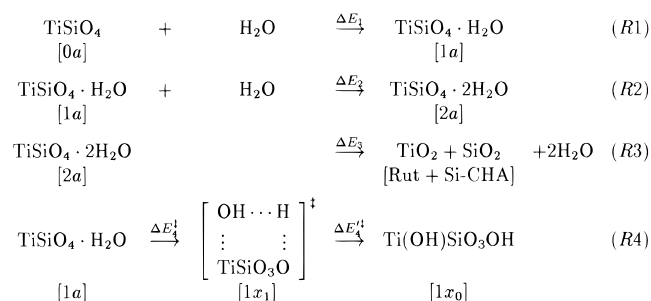
$$\Delta E_1 = E_{1a} - E_{0a} - E_{H_2O} - \Delta E_{w-w}^{(1)} \quad (1)$$

where the first three terms in the right-hand side, are from Table 3, and the last one $\Delta E_{w-w}^{(1)}$ is the water−water interaction energy which is used to correct the effect of the high water concentration in the model. $\Delta E_{w-w}^{(1)}$ is calculated as the difference between the energy (per molecule) in a periodic system composed by six water molecules per cell at the same positions as in model 1a ($6H_2O$ entry in Table 3), and the energy of the isolated molecule (H_2O entry in Table 3). $\Delta E_{w-w}^{(1)}$ is +3.8 kJ mol^{-1}, which yields $\Delta E_1 = -34.4$ kJ mol^{-1}.

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TABLE 3: Total Energy (TE, in kJ mol^{-1}) per Asymmetric Unit for the Various Models^a

model	TE
0a	−377 356 9.7
0a$^{(1)}$	−377 352 6.1
0a$^{(2)}$	−377 346 1.3
1a	−397 324 9.0
2a	−417 292 6.6
1x$_0$	−397 321 4.0
1x$_1$	−397 316 4.2
1x$_2$	−397 318 1.2
Rutile	−262 125 0.6
Si−CHA	−115 239 6.8
H$_2$O	−19 964 8.8
2H$_2$O	−19 964 0.7
6H$_2$O	−19 964 5.1
12H$_2$O	−19 964 8.5

^{a} The symbol nH$_2$O indicates the different models used to evaluate the water−water interaction (see text): $n = 2$ is a molecular system composed by two water molecules; $n = 6, 12$ are periodic systems with n molecules per cell. Energies refer to a single water molecule.

SCHEME 1

$$TiSiO_4 \quad + \quad H_2O \quad \xrightarrow{\Delta E_1} \quad TiSiO_4 \cdot H_2O \qquad (R1)$$
$$[0a] \qquad\qquad\qquad\qquad\qquad\quad [1a]$$

$$TiSiO_4 \cdot H_2O \quad + \quad H_2O \quad \xrightarrow{\Delta E_2} \quad TiSiO_4 \cdot 2H_2O \qquad (R2)$$
$$[1a] \qquad\qquad\qquad\qquad\qquad\quad [2a]$$

$$TiSiO_4 \cdot 2H_2O \quad \xrightarrow{\Delta E_3} \quad TiO_2 + SiO_2 \quad +2H_2O \quad (R3)$$
$$[2a] \qquad\qquad\qquad\quad [Rut + Si\text{-}CHA]$$

$$TiSiO_4 \cdot H_2O \quad \xrightarrow{\Delta E^{\ddagger}} \left[\begin{array}{c} OH \cdots H \\ \vdots \quad\quad \vdots \\ TiSiO_3O \end{array} \right]^{\ddagger} \xrightarrow{\Delta E'^{\ddagger}} \quad Ti(OH)SiO_3OH \qquad (R4)$$
$$[1a] \qquad\qquad\quad [1x_1] \qquad\qquad\qquad\qquad [1x_0]$$

R1 is then exothermic; this means that the first water adsorption in Ti zeolites is thermodynamically favorable, despite the drastic structural modifications involved. This is in very good agreement with recent measurements of the water adsorption heat in Ti-β(F) samples, which give an overall value of 43.3 kJ mol^{-1}.[30] Indeed, reaction R1 can ideally be split into two steps: the first one being the structural deformation required for the coordination of the water molecule with the Ti atom, and the second one being the adsorption itself, that is, the interaction between the water molecule and the previously distorted Ti site. The energy of the first step has been calculated as the energy difference between 0a and 0a$^{(1)}$, the latter being the 0a model distorted as in 1a, which yields 43.6 kJ mol^{-1}. The adsorption step is thus exothermic enough to compensate the energy cost of the lattice distortion.

However, adsorption and distortion steps are not really independent as the change in the hybridization imposed by the distorted geometry in model 0a$^{(1)}$ reduces the band gap in 0.35 eV with respect to model 0a (see Figure 2). In the framework of the frontier orbital theory, this means that the distortion toward a planar configuration of the TiO$_1$ O$_2$ O$_3$ group (see Figure 1a) results in an enhancement of the Lewis acidity of the site.

Indeed, the degree of distortion of the Ti site in a given zeolite upon adsorption of any ligand (H$_2$O, H$_2$O$_2$, HO$_2$$^-$, O$_2$$^{2-}$) will depend not only on the nature of the ligand, but also on the structural flexibility of the material. Hence it is expected that the more flexible a given Ti-zeolite is, the higher will be the overall Lewis acidity of the site.

This might have also consequences on the catalytic properties of these materials, as it would explain observed differences between samples with similar chemical composition and crystal-
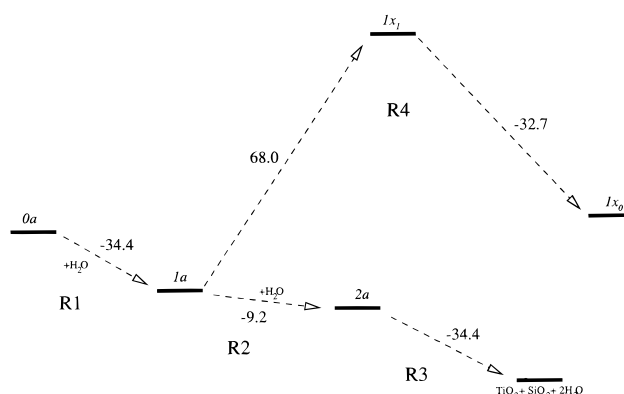
Figure 3. Energy profile of the $R1$−$R4$ reactions discussed in the text. Energy differences are given in kJ mol^{-1}.

linity but different framework structure, as, for instance, Ti-β(F) and TS-1[30].

The structural strain thus plays a rather relevant role in the stability of the hydrated Ti site and presumably in its catalytic properties; its importance is expected to vary in going from the present model to other possible Ti-zeolites. Indeed, reliable Ti containing zeolite samples have been prepared, so far, by synthesis only with silicalite, β, SSZ-33, and UTD-1, all of them being quite flexible structures. In less flexible structures, as for instance ITQ-1, very little Ti content can be introduced in the framework.

Reaction R2 is the second hydration of the Ti site. ΔE_2 is calculated as,

$$\Delta E2 = E_{2a} - E_{1a} - E_{H_2O} - E^{(2)}_{w-w} + E^{(1)}_{w-w}$$

where $E^{(2)}_{w-w}$ is the interaction energy between couples of water molecules adsorbed on different sites in model 2a; it is evaluated in the same way as $E^{(1)}_{w-w}$. $E^{(2)}_{w-w}$ is equal to −15.9 kJ mol^{-1}, and it is obtained by multiplying by two the difference between the 12H$_2$O and the 2H$_2$O entries in Table 3.

The interaction in this case is attractive and is larger in absolute value than in the first adsorption case, as a consequence of the high concentration and favorable disposition of water molecules in model 2a. Using this value, eq 2 yields $\Delta E_2 = -9.2$ kJ mol^{-1}. The lower adsorption energy in R2 with respect to reaction R1 is mainly a consequence of the large (and "costly") structural distortion required to achieve an octahedral coordination for the Ti site. The distortion energy was calculated as the energy difference between 0a$^{(2)}$ and 0a$^{(1)}$, the former being the 0a model with the geometry of the host lattice in 2a. The distortion energy obtained for reaction R2 is 65.5 kJ mol^{-1}, 50% larger than that of reaction R1, which means that octahedral Ti coordination in zeolites involves a large structural strain, and water adsorption is possible only thanks to the high Lewis acidity of Ti(IV) centers. However, the high concentration of Ti sites in model 2a may be in part responsible for the large distortion energy, as the framework has not enough degrees of freedom for relaxation. Despite the limitations of the present model, it is to be stressed that the small second adsorption energy calculated in the present work is in good agreement with measurements reported in ref 30, as it has been observed that, in Ti-β(F) samples, in which Ti sites are fully connected to the framework and therefore strongly constrained, most of the Ti sites adsorb a single water molecule. It is interesting to compare the present results with previous cluster calculations,[26] where framework constraints are not fully included in the model; as a consequence, the calculated second water adsorption energy is

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significantly larger than the first one and then that obtained with the present periodic model.

Reaction R3 is the overall decomposition reaction of the dihydrated Ti site to form extraframework TiO_2 (Rutile), Si-chabazite, and H_2O. The corresponding reaction energy, ΔE_3 reads,

$$\Delta E3 = E\,Rut + E\,Si{-}CHA + E\,H2O - E2a + E_{w-w}^{(2)}$$

where E_{Rut} and E_{Si-CHA} are the PHF energies of Rutile and Si-chabazite already used in ref 36 and reported for ease of comparison in Table 3; the other terms are the same as those for eq 2. From these data, $\Delta E_3 = -34.4$ kJ mol^{-1}, indicating that extraframework TiO_2 is more stable than the dihydrated Ti-chabazite at high Ti concentration.

In the case of anhydrous Ti-zeolites, the decomposition energy was previously estimated[36] in about 71−84 kJ mol^{-1} for a variety of framework structures and compositions, as resulting from calculations performed with the same code and basis set as adopted in the present study. Water adsorption contributes then to the stability of the Ti site; in the present case, however, it is not sufficient to yield an energy balance favorable to the insertion of Ti in the framework with respect to the formation of extraframework oxide. Such a delicate energy balance between the resistance to deformation of the zeolitic framework and the tendency of Ti(IV) to lower its energy by acquiring the octahedral coordination is probably the most important factor controlling the formation of framework Ti sites. Whether this balance should favor or not the formation of framework Ti in various zeolitic frameworks is a delicate question that cannot be definitively answered at this stage.

It was observed in the previous subsection that physiosorbed water not only interacts with Ti, but also one of its H atoms interacts with basic oxygens of the framework, when possible. In the case of model 1a, the most accessible framework basic oxygen is O_4', which is located in a "neighboring asymmetric unit". Reaction R4 is the proton transfer from the water molecule (model 1a) to O_4' to yield an OH$^-$ group strongly coordinated to the Ti atom and a silanol group attached to the framework and slightly interacting with Ti ($1x_0$). The overall energetic balance for reaction R4 is $+35.3$ kJ mol^{-1}. This means that the hydrolysis of the TiO bond is not thermodynamically favored. Previously cited cluster model calculations[26] yield the same qualitative result, and it has been proposed that Ti sites with partially broken Ti−O−Si bonds can exist thanks to the additional stability given by hydrogen bonds with free silanol groups. In the present case the Si−OH group formed upon hydrolysis is only slightly hydrogen bonded to the adsorbed OH$^-$ group. Similar situations are expected to occur in structures with low content of framework defects. This is in agreement with previous experimental results[30] on Ti-β(F) samples that have a very little number of defects. In fact, the hydrolysis of the Si−O−Ti bonds could not be detected by neither NMR nor IR experiments.

As regarding the kinetics of reaction R4, the activation energy, evaluated from the data listed in Table 3, can be estimated in about 84 kJ mol^{-1}.

4. Concluding Remarks

Water physisorption and chemisorption in Ti-chabazite has been investigated at the periodic ab initio Hartree−Fock level. It turns out that the first and second water physisorption involve large structural modifications in the framework, as Ti atoms change their coordination from 4 to 6. Nevertheless, even in the most unfavorable case, i.e., when two water molecules are present at each site in a high Ti concentration framework, physisorption remains energetically favored, due to the high Lewis acidity of the tetrahedral Ti(IV) sites. The high affinity of framework Ti sites with respect to water suggests that, during the synthesis of Ti-zeolites, the first framework Ti species to form should be hydrated sites in 5- or 6-fold coordination. Therefore the ability of a given structure to incorporate in certain framework positions a hydrated Ti(IV) ion is conditioned by the flexibility of the framework to relax appropriately upon the formation of such sites. The complex equilibrium between the Ti water affinity and the structural strain does not favor in most cases the formation of framework Ti, as it occurs in the present study, and it is expected that only in rare cases the structural conditions are adequate for this. This could explain the difficulties in obtaining more than 3% of Ti in the synthesized samples.

Water chemisorption, involving the hydrolysis of a Ti−O bond to form an adsorbed OH- and a silanol group, was investigated in the present study through a mechanism that requires the presence of a basic oxygen atom (O_4') not belonging to the first coordination sphere of Ti. Such a basic oxygen can exist only if related to a lattice defect like another neighboring Ti site (as in the present case) or, for instance, a framework Al. The "clustering" of Ti impurities is not, however, contradictory with the low mean Ti concentration. In fact, it has been shown in a previous study[36] that isolated Ti sites are less stable than Ti sites surrounded by other Ti sites. The mechanism of hydrolysis proposed in this work has an activation barrier of about 84 kJ mol^{-1} indicating that the reaction is kinetically possible at usual working temperatures, as for instance, during the calcination of the samples. However, the energetic balance of the reaction in perfect framework sites indicates that it is thermodynamically unfavored.

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