Modifying the Catalytic Activity of Ti-Zeolites by Isomorphic Substitution of Si by Ge Atoms. A Periodic Quantum-Chemical Study

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The role of isomorphic substitution of Si atoms by Ge on the properties of Ti sites in Ti-zeolites has been studied in periodic models by means of the ab initio code CRYSTAL98. Several zeolitic models with different Ti, Si, and Ge contents have been considered for calculation, and differences in structural, energetic, and electronic features at the equilibrium geometry have been investigated. The behavior regarding the interaction with a given probe ligand (a water molecule) was also studied. It has been observed that introduction of Ge atoms close to the Ti centers results in the catalyst stabilization mainly due to increased flexibility. From the electronic point of view, the decrease in the framework electronegativity upon substitution of Si by Ge atoms increases the ionicity of the system as well as decreases the Lewis acidity. However, structural effects derived from framework flexibility can mask inductive effects on acidity, to the point that the expected trend can be reverted.

1. Introduction

Since the discovery of the unique catalytic properties of Ti zeolites in oxidations of unsaturated organic compounds with peroxides,[1] several new related materials with improved efficiency have been synthesized. Both zeolitic[2−5] and amorphous mesoporous[6,7] Ti-containing molecular sieves have been proved to be selective catalysts in oxidation reactions. At the same time a considerable effort has been devoted to understand the chemical features that make isolated Ti sites particularly active for these reactions. Advanced characterization techniques[10−19] together with accurate theoretical methods[20−34] have been employed, and it is now generally accepted that active sites in Ti-zeolites are related to fourfold-coordinated Ti(IV) centers occupying framework cationic sites, even though in some cases one and even two of the TiOSi linkages may be hydrolyzed giving TiOH and SiOH groups.[26−28]

As is well−known, Ti^{4+} ions are preferentially sixfold coordinated in natural TiO$_2$, since this is the most stable coordination state of Ti(IV) in oxides. However, during the hydrothermal synthesis of some zeolites a significant number of tetrahedral Ti sites are formed (about 3% of the overall cation content), and at least two factors have been shown to contribute to the formation of such unusual coordination of Ti:

1. Previous theoretical calculations[29] indicate that tetrahedral Ti sites are more stable in mixed TiO$_2$/SiO$_2$ than in pure TiO$_2$ compounds, the stabilization energy being about 2−3 kcal·mol^{-1}, depending on the Ti/Si ratio and the framework type. When the electronic structure of a hypothetical pure TiO$_2$ zeolitic framework is compared with the analogue TiSiO$_4$, it arises that the lower stability of the former is to be mainly attributed to some increased repulsion between Ti3d and O2p electrons when the first neighbors of the Ti site are Ti instead of Si atoms. This effect is a consequence of the additional polarization of O electrons in TiOTi bridges induced by the higher ionic character

of TiO than SiO bonds. It thus results in a larger stability of SiOTi with respect to TiOTi bridges and thereby in a higher ability of tetrahedral Ti centers to exist in silica than in a pure TiO$_2$ environment.

Both theoretical[32] and experimental[14,35] data indicate that monohydrated and dihydrated Ti sites can exist in Ti-zeolites, even for those structures with a low number of defects, and that hydration energy is such that can mostly compensate the energy required to form a framework Ti site. As a result of water adsorption, the coordination state of Ti centers increases from four- to five- or sixfold. Thus, during the hydrothermal synthesis it is likely that hydrated Ti sites can be formed directly without much cost in energy, the process being mainly controlled by the kinetic conditions. However, formation of hydrated sites is only possible if framework flexibility allows local distortion toward the octahedral configuration needed for efficient five- or sixfold coordination. This would explain the fact that only a few frameworks are able to admit a significant content of Ti centers by direct synthesis.

Concerning the mechanism of the catalytic reaction, it is generally accepted that the oxidizing agent is formed after adsorption of the peroxide on the Ti center,[23,28,30,31] the latter acting as a Lewis acid.[36] It can then be expected that an adequate control of the Ti center Lewis acidity would allow an increase of the selectivity and activity toward a given reaction.

In traditional catalysis by acid zeolites, acidity is usually controlled adjusting the framework composition, either by changes in the Si/Al ratio or by isomorphic substitution of cations. In the case of Ti-zeolites, wherein hydrophobicity is a desired property, the first possibility is not to be considered since affinity to water molecules increases when increasing the Al content. Taking this into account, it appears that the isomorphic substitution of Si by less electronegative atoms such as Ge can be a useful way to decrease the overall Lewis acidity of the catalyst. The synthesis of TiGeSi zeolites and their catalytic activity toward oxidations with H$_2$O$_2$ have been recently reported.[37,38]

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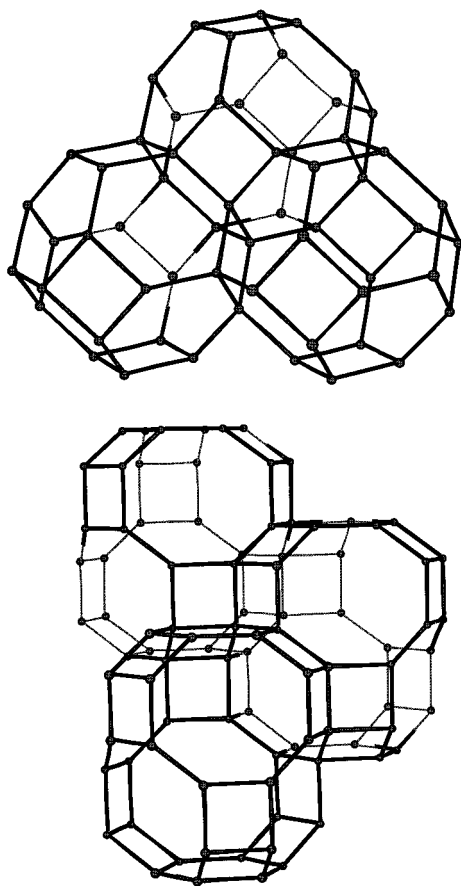*J. Phys. Chem. B, Vol. 104, No. 17, 2000* **4135**

Figure 1. Schematic drawing of SOD (top) and CHA (bottom) frameworks. Circles correspond to cations (Si, Ti, or Ge) bridged by an oxygen atom.

The aim of the present work is to predict the chemical consequences of substitution of Si by Ge framework atoms connected to the catalytic properties of Ti centers in Ti-zeolites. To this scope we have studied several models of zeolitic frameworks with different Si, Ge, and Ti contents, and the related energetic, electronic, and geometrical features were analyzed.

Models are based on two framework types: SOD and CHA[39,40] (see Figure 1), and they are calculated within the periodic approximation. Periodicity allows accurate calculation of bulk and local properties avoiding undesirable border effects existing in the most often employed cluster models. SOD and CHA have been widely used in previous works[29,32,41−45] as models for zeolitic systems. In their pure silica form they are quite symmetric systems with only 36 atoms per unit cell. This makes such systems very attractive from the computational point of view, since it is possible to calculate equilibrium geometries and to consider a set of models large enough to study the most relevant trends with an acceptable cost.

2. Computational Details

Periodic models considered for calculation are listed in Table 1. The most relevant structural data of such systems, i.e., space symmetry group, number of atoms per primitive cell, and number of symmetry-independent geometrical parameters, are also documented. The overall computational cost of each model increases when increasing the number of atoms of the primitive cell and the number of independent geometrical parameters, and decreases when increasing the order of the space group. Other factors such as basis set and composition are also relevant. The

TABLE 1: Main Computational Characteristics of the Periodic Models Considered for Calculations[a]

framework	a:b:c	SG	N_{at}	N_{geo}	HF ener
rutile	1:0:0	$P4_2/mnm$	6	3	−1996.7620
	0:1:0	$P4_2/mnm$	6	3	−4450.4680
SOD	0:0:1	$I\bar{4}3m$	18	3	−2633.5476
	1:1:0	$P\bar{4}3n$	36	4	−19341.5458
	1:0:1	$P\bar{4}3n$	36	4	−8623.6730
	1:1:1	$I222$	18	14	−7325.0268
	1:0:2	$I\bar{4}2m$	18	8	−3752.4075
	1:4:1	$I\bar{4}$	18	14	−10338.2150
	1:1:4	$I\bar{4}$	18	14	−4979.2831
	1:0:5	$I\bar{4}$	18	14	−3192.9667
CHA	1:0:1	$R\bar{3}$	36	20	−8623.6507
	1:1:0	$R\bar{3}$	36	20	−19341.5195
CHA + H$_2$O	1:0:1	$R\bar{3}$	54	27	−9080.0121
	1:1:0	$R\bar{3}$	54	27	−19797.8709

[a] a:b:c is the cation composition of the crystalline part (TiO$_2$)$_a$-(GeO$_2$)$_b$(SiO$_2$)$_c$, SG is the space group label and N_{at} and N_{geo} refer to the number of atoms per unit cell and independent geometrical parameters, respectively. HF ener is the Hartree−Fock energy per cell at the equilibrium geometry (in hartree).

most costly model in terms of computational resources is CHA + H$_2$O(1:1:0), for which a single optimization cycle requires about 10.5 h of elapsed time using three processors in a Silicon Graphics Origin 200.

Calculations have been performed using the periodic Hartree−Fock (PHF) method as implemented in the CRYSTAL-98 code.[46] The parallel version of the code has been used together with the PVM[47] library for message passing.

Three basis set levels have been considered for calculations. The best quality set is used to evaluate the energy and electronic properties of models at the equilibrium geometry. Hereafter, it will be called B1. The following contractions of Gaussian primitives are used for cations: for Ti and Si the same basis sets as in ref 32 are used, i.e., a (20s,12p,3d)/[5s,4p,2d] and a reoptimized 6-21G(d), respectively. In the case of Ge, a basis set originally designed for bulk Ge,[48] (26s,17p,7d)/[5s,4p,2d], has been reoptimized on Ge−sodalite. A standard 31G(p) has been employed for H.

As most of the bonds involving O atoms are of ionic character, the choice of the oxygen basis set is more critical than in the case of cations. Therefore, a 6-311G(d)[49] basis set has been chosen for O. Exponents and contraction coefficients are the standard ones except for d and the most external sp exponents (0.60 and 0.260 b^{-2}, respectively) that have been reoptimized on Ti and Ge sodalite.

The remaining basis sets, namely B2 and B3, has been used for geometry optimizations depending on the dimension of the system considered. Both sets are similar to B1 with differences with regard to only polarized functions and to the most external sp shells. In both cases, Ti and Ge, d shells are now contracted to a single one, while for H no p functions are considered. The Si basis set is the same in all the three sets. Concerning O atoms, a 6-31G[50] has been used with and without d functions in B2 and B3, respectively. The d and most external sp shell exponents have been reoptimized for periodic calculations (0.5 and 0.279 84 b^{-2}, respectively). Details on the basis sets employed can be found in ref 52.

In Table 2 we report some selected internal valence coordinates corresponding to the equilibrium geometries of model SOD (1:1:0) calculated at the three basis set levels considered. Basis B2 behaves rather similarly to B1, and differences are negligible resulting in a reasonable basis set for geometry optimizations. In the case of basis B3, the lack of polarized functions on O yields large differences in TOT and torsion

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TABLE 2: Selected Internal Valence Coordinates (Distances in Å, Angles in deg) for Equilibrium Geometry of SOD 1:1:0 Calculated Using Three Different Basis Sets on O Atoms[a]

	B1	B2	B3
r(OGe)	1.72	1.72	1.71
r(OTi)	1.80	1.80	1.80
a(GeOTi)	154	155	165
a(OGeO)	110	109	106
	109	109	111
a(OTiO)	110	110	112
	109	109	105
t(TiOGeO)	38.5	38.3	0.2
t(OTiOGe)	−38.7	−38.1	−0.2

[a] r, a, and t are bond distances, angles, and torsion angles, respectively.

angles. Nevertheless, other relevant parameters such bond distances and OTO angles are well reproduced with respect to B1. Hence, for very large systems, i.e., those builded starting from the CHA framework (see Table 1), B3 has been used to calculate equilibrium geometries. For the rest of the models we have used basis B2.

All the models have been optimized employing a numerical conjugated gradient algorithm.[51] Some relevant details of the method are described elsewhere.[53]

Concerning the conditions for periodic calculations with CRYSTAL98, the standard tolerances in integrals evaluations, and a shrinking factor of 2 for sampling in the Brillouin zone, have been used for zeolitic models. In the case of models with rutile structure, tolerances and shrinking factor are (7, 7, 7, 7, 14) and 4, respectively. Density of state (DOS) calculations of zeolitic models have been performed using a more dense k-mesh in the Brillouin zone than energy calculations (shrinking factor of 4); 10 Legendre polynomials have been used to expand DOS diagrams.[46]

3. Results and Discussion

Let us initially discuss the influence of the framework content in Ge on the electronic and structural properties of the Ti sites. In this scope, SOD framework models of general formula $(TiO_2)_a(GeO_2)_b(SiO_2)_c$ have been considered for calculation. For the sake of simplicity hereafter we shall use the brief notation $a:b:c$ to label models. All the systems considered have been fully optimized keeping the system symmetry, except in the case of model 1:1:1, whose unit cell has been constrained to be tetragonal instead of orthorhombic as corresponds to space group *I222* (see Table 1). This does not result in a critical loss of accuracy of the obtained equilibrium geometries as shown elsewhere.[29]

The most relevant optimized geometric parameters of SOD models are summarized in Table 3. The lengths of OTi and OX (X = Si, Ge) bonds at equilibrium exhibit a slight dependence on the framework composition. OTi bond distance (r(OTi)) roughly decreases with increasing framework Si content, the lowest and highest values being 1.77 and 1.80 Å for models 1:0:5 and 1:4:1, respectively. The trend follows the reverse direction of framework electronegativity, whose order can be estimated from simple chemical considerations as 1:1:0 < 1:4:1 < 1:1:1 < 1:0:1 < 1:0:2 < 1:1:4 < 1:0:5.

A similar tendency is observed in the overall ionic character of the systems. Table 4 documents the Mulliken atomic net charges averaged per species, ⟨Y⟩, Y = Si, Ti, Ge, O, in the Ti-SOD models considered. While absolute charges calculated using the Mulliken analysis are not in general reliable because of the somewhat arbitrary density partition involved in the method, it is expected that trends in the atomic population of related compounds such as the series of Ti-SOD models will give relevant information on the electronic structure at the semiquantitative level. The increase in the ionic character when substituting Si by Ge within the framework is apparent within the three series of models along which Ti molar fraction, X_{Ti}, is constant: 1:1:0, 1:0:1 (X_{Ti} = 0.5); 1:1:1, 1:0:2 (X_{Ti} = 0.33); and 1:4:1, 1:1:4, 1:0:5 (X_{Ti} = 0.17). The influence of the overall framework ionicity on the TiO bond has been previously reported[22,29] and is to be connected to the repulsion between electrons in the TiO bond and those of the Ti d shell discussed in the Introduction.

When considering the whole set of models, the overall trend is also to increase the ionicity and r(OTi) with decreasing framework electronegativity. However if one focuses on the Ti site and looks for the mean charges on Ti and O atoms within the first coordination sphere, ⟨Ti⟩ and ⟨O_{Ti}⟩ in Table 4, respectively, the trend is less pronounced as well as, in some cases, reversed. The latter occurs in particular for ⟨Ti⟩ between 1:0:1 and 1:0:2, where the charge is slightly larger in 1:0:2, despite the lower Ti content and thereby the higher framework electronegativity. It is likely that structural conditions can modify the trend induced by the framework electronegativity on the electronic properties of the Ti site, a fact that will be discussed latter.

SiO and GeO bond lengths are less sensitive to the overall composition, and differences observed are within the numerical error of the optimization method in most cases. The large range of SiO bond lengths in model 1:0:5, 1.60−1.63 Å, is a consequence of the structural strains promoted by the insertion of isolated TiO_4 units within a framework of smaller SiO_4 tetrahedra.[32]

On the other hand, no clear trend is observed in TiOX and XOX angles (X = Si, Ge) regarding composition changes, and it appears that they are mainly determined by the way each overall structure moves to reach the most stable tetrahedra packing.

TABLE 3: Selected Geometrical Parameters (Distances in Å, Angles in deg) at the Equilibrium for SOD Models with Different Ti:Ge:Si Framework Contents[d]

	X	r(OTi)	r(OX)	a(TiOX)	a(XOX)	D(OTiO)	D(OXO)
0:0:1	Si		1.61		151		0.811
1:1:0	Ge	1.80	1.72	155		0.583	0.012
1:0:1	Si	1.79	1.62	160		0.637	0.774
1:1:1	Ge	1.79(80)[a]	1.72	161	159[b]	0.385	1.13
	Si		1.62	160			0.669
1:0:2	Si	1.79	1.61(62)[a]	161	160	0.128	0.606
1:4:1	Ge	1.80	1.72(73)[a]	138	141	2.33	1.95
	Si		1.62		149[b]		1.10
1:1:4	Ge	1.78	1.72		158[b]	1.78	1.54
	Si		1.61(62)[a]	158	158		1.21
1:0:5	Si	1.77	1.60−3[c]	155	158−161[c]	1.02	1.06−1.92[c]

[a] Nonequivalent parameter within brackets. [b] a(GeOSi). [c] Range of nonequivalent parameters. [d] See details in text.

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TABLE 4: Selected Mean Mulliken Atomic Net Charges in *e*; Bottom of Conduction Band (BC), Band Gap (BG), in hartree, and Formation Energies (FE, See Eq 1), in kcal/mol, for SOD Models Containing Ti

	1:1:0	1:0:1	1:1:1	1:0:2	1:4:1	1:1:4	1:0:5
⟨Ti⟩	2.655	2.627	2.648	2.631	2.653	2.620	2.608
⟨Ge⟩	2.583		2.567		2.574	2.553	
⟨Si⟩		2.024	2.034	1.995	2.050	2.002	1.990
⟨O⟩	−1.310	−1.163	−1.208	−1.103	−1.250	−1.099	−1.047
⟨O_{Ti}⟩	−1.310	−1.163	−1.163	−1.161	−1.297	−1.152	−1.147
FE	15	17	16	17	17	19	23
BC	0.155	0.157	0.162	0.160	0.162	0.166	0.163
BG	0.587	0.572	0.581	0.574	0.598	0.592	0.599

In order to analyze the dependence of local distortions of TO_4 units on the framework composition, let us consider the global behavior of the six OTO angles associated to each T site. The angle distribution around a given site is described at this level by the average and dispersion of OTO angles. The former does not give in this case meaningful information as it is almost constant and close to 109.5°, which is the typical value for regular tetrahedra. Therefore, we shall pay attention to the second parameter, the OTO angle dispersion around site T, D(OTO), that could be used as a measure of the distortion from regularity of the tetrahedra. Angle dispersions of the Ti-SOD systems considered are listed in Table 3.

The largest distortions are observed in TiO_4 units, in particular when symmetry is low, i.e., 1:4:1, 1:1:4, and 1:0:5. SiO_4 and GeO_4 range within similar values. However, it is to be noted that the largest value of D(OSiO) occurs in model 1:0:5, and this is probably due to the structural strains mentioned above. Excluding model 1:0:5 from comparison, it turns out that GeO_4 are in general less regular than SiO_4 tetrahedra at equilibrium, which is to be attributed to the larger ionic character of GeO than SiO bonds as can be deduced from the atomic charges listed in Table 4.

The different framework flexibility promoted by cation substitution is to be reflected in the relative stabilities of the models considered. Formation energies (FEs) are calculated from total PHF energies listed in Table 1 as the balance of the hypothetic reaction

$$aTiO_2[1:0:0] + bGeO_2[0:1:0] + cSiO_2[0:0:1] \rightarrow$$
$$(TiO_2)_a(GeO_2)_b(SiO_2)_c[a:b:c], \quad (1)$$
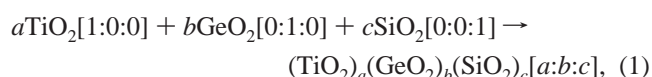
and are useful to compare the stabilities of systems with different composition. Calculated FE values are documented in Table 4. In general, FE follows the trend expected from the local geometrical features of TO_4 units, and it is found that distortion of SiO_4 tetrahedra is the most costly in terms of energy, as it arises from comparison between D(OSiO) and FE data.

A more detailed interpretation is to be performed when analyzing the substitution of Si by Ge atoms following the above-mentioned series of models with constant Ti content: X_{Ti} = 0.5, 0.33, and 0.17. In the three series, isomorphic substitution results in the stabilization of the zeolitic compound. The stabilization effect is more dramatic when Ti sites are isolated as it occurs in models with X_{Ti} = 0.17. In such a case, single substitution of silicon by germanium, i.e., in going from model 1:0:5 to 1:1:4, involves an energy gain of about 4 kcal·mol⁻¹, even if the framework position where substitution is done is at the second neighbors of the Ti center. This is likely because of the larger flexibility given by Ge atoms in framework tetrahedral positions that allows an efficient packing of the TO_4 units.

From the electronic point of view, the role of Ge atoms at the first neighbors of the Ti centers is to be similar to the case of Ti atoms discussed in the Introduction owing to electronegativity considerations. However, it should be noted that the ionic character of the MO bonds is smaller for M = Ge than for M = Ti, as can be deduced from Mulliken analysis in Table 4. This fact results in a weaker electronic repulsion within the GeOTi bridge. Consequently, the energy cost due to such a repulsion is largely compensated by the stabilizing structural relaxation allowed by framework Ge atoms, and, hence, substitution of Si by Ge atoms in a Ti-zeolite does yield in general an overall stabilization of the system.

On the other hand, it has been previously observed that grafting of Ti centers in TiGe−MCM-41 catalysts[54] mainly occurs at the vicinity of framework Ge atoms. In spite of the structural differences between our zeolitic models and the semidisordered MCM-41 framework, the present results seem to indicate that the preferred vicinity of Ti and Ge atoms in both cases is due to a similar stabilization effect, which results from the increased flexibility promoted by GeO_4 units.

Let us now consider the possible changes in the Lewis acidity of the Ti site upon substitution of Si by Ge atoms. In a previous work[33] the LUMO energy within the cluster approximation has been used to investigate the Lewis acidity of Ti sites in different structural conditions, exploiting the correspondence between that quantity and electron affinities. Indeed the connection of LUMO energy to Lewis acidity is better described in terms of the second-order perturbational theory as shown in the earliest statements of frontier orbital theory.[55] At variance to electron affinity considerations, this approach is valid, even within the Hartree−Fock approximation, if the acid−base interaction fulfills at least two conditions: (1) the LUMO is to be mainly localized in the reactive part of the acid site; (2) interaction does not involve large electronic and structural change of the acid moiety.

In the case of Ti-zeolites,[29,32] it has been shown that the bottom of the conduction band (BC), which is the equivalent to the LUMO in solid-state systems, is mainly localized on Ti atoms, thus fulfilling the first condition. On the contrary, the second statement is not generally valid as a large structural distortion of the TiO_4 unit is required to interact with a base like H_2O[25,32] or H_2O_2. Nevertheless, it is reasonable to suppose that inductive effects of the environment atoms are to be similar in both the distorted and undistorted sites. Thus, in the present case wherein the interest is on qualitative trends upon changes of framework composition, BC energies of undistorted models will give useful information on the actual chemical behavior of Ti centers in Ge zeolites.

BC energies for the Ti-SOD models considered have been obtained from DOS calculations. In order to be compared, calculated DOS diagrams have been aligned using the Ti1s level as reference. The Ti localized character of the conduction band has been verified in all the cases by comparing the total DOS with that projected onto the Ti subspace given by the basis set chosen. The band gap (BG) has been also calculated as the difference between BC and the top of the valence band. BG values provide another view of changes in the conduction band, the reference level being in this case the top of the valence band. Calculated values for BC and BG for the Ti-SOD models considered are documented in Table 4.

At variance with other indexes studied, as, for instance, atomic charges or geometric parameters, both BC and BG show no clear trend with respect to changes in the framework composition. This indicates that inductive effects are not dominant in determining BC energies, but other effects are to be also relevant. In particular, it has been shown[32] that BC (LUMO)

energies of Ti centers are quite sensitive to geometrical distortions of the TiO$_4$ unit. Therefore, it is likely that in the Ti-SOD systems considered geometrical differences around the site are actually masking the inductive trend owing to framework electronegativity.

A more accurate but costly way to investigate changes in the reactivity of Ti centers upon substitution of Si atoms by Ge is to study the electronic properties of the catalysts during interaction with a given probe ligand. In the present work a water molecule has been chosen as probe ligand to interact with the Ti site.

The interaction with a single water molecule per site is studied by using two models for the catalytic site, namely, TiGeCHA and TiSiCHA (see Table 1). These are the two limiting cases of Si/Ge ratio, 0 and ∞, respectively. The CHA framework has been chosen instead of SOD because of its larger pore size and flexibility. The latter is very important as it allows the Ti site to be deformed as needed for the efficient coordination of the water molecule. Concerning the high Ti concentration of the zeolitic model, $X_{Ti} = 0.5$, more than 10 times the one obtained by synthesis, it has been chosen because of computational considerations. It is to be noted that this high loading allows one to perform calculations keeping six symmetry operators, which results in a significant savings in computational cost in both electronic calculations and geometry optimizations. Moreover, the relatively high symmetry reduces the differences in structural constraints between Ge and Si models, a fact that permits one to disregard structural differences and mainly focus on electronic effects. On the other hand, as shown previously,[29] mutual interaction of Ti sites is negligible when they are further than in a second-neighbor position.

The most relevant equilibrium geometrical parameters of the four systems studied, i.e., anhydrous and hydrated TiGeCHA and TiSiCHA, are listed in Table 5. In both the Si and Ge compounds, the adsorption of the water molecule on the Ti center involves large structural changes. Details of this reaction in TiSiCHA have been extensively described in a previous work;[32] therefore, we shall only state here the most relevant features. Local structure of monohydrated Ti sites are depicted in Figure 2. Upon interaction, the Ti site loses the nearly regular tetrahedral coordination and takes a trigonal dipyramid conformation in which the principal axis roughly matches TiO(w) and TiO(1) bonds. Water is attached to the zeolitic framework through two different interactions: the stronger acid−base coordination with the Ti center and a weak hydrogen bond between H(1) and O′(1) (a symmetry replicate to O(1)).

On the other hand, when looking for differences between Si and Ge models, it arises that they are in general small and within the numerical error of the method. Besides the expected increase in OX bond length when X changes from Si to Ge, the most relevant differences are found in the position and orientation of the water molecule with respect to the Ti site. Although differences are small, they show a clear trend regarding changes in framework composition. In particular, this turns out when comparing TiO(w), O′(1)H(1), and TiO(1) distances between both systems. With regard to the TiO(w) and O′(1)H(1) distances, the lower values observed in the Si model reveal a slightly stronger interaction between the water molecule and the Ti site, and simultaneously in the hydrogen bonding between H(1) and O′(1). In addition, the increase in the TiO(1) bond length goes in the same direction as slight changes in the OTiO angles that correspond to an increased dipyramid conformation of the Ti site in the Si compound.

TABLE 5: Selected geometric parameters (Distances in Å, Angles in deg) at Equilibrium of Anhydrous and Hydrated TiXCHA (X = Ge, Si)[a]

	Ge		Si	
X	anh	hyd	anh	hyd
r(O(1)X)	1.73	1.74	1.62	1.63
r(O(2)X)	1.72	1.72	1.61	1.62
r(O(3)X)	1.72	1.71	1.61	1.60
r(O(4)X)	1.74	1.73	1.62	1.62
r(O(1)Ti)	1.79	1.85	1.80	1.86
r(O(2)Ti)	1.79	1.82	1.80	1.82
r(O(3)Ti)	1.79	1.82	1.79	1.81
r(O(4)Ti)	1.79	1.78	1.79	1.79
a(O(1)XO(2))	113	109	112	109
a(O(1)XO(3))	106	112	107	111
a(O(1)XO(4))	104	106	106	107
a(O(2)XO(3))	115	111	113	111
a(O(2)XO(4))	106	107	107	107
a(O(3)XO(4))	112	112	111	112
a(O(1)TiO(2))	114	97	113	96
a(O(1)TiO(3))	106	96	106	96
a(O(1)TiO(4))	104	101	104	102
a(O(2)TiO(3))	115	131	115	130
a(O(2)TiO(4))	106	111	106	112
a(O(3)TiO(4))	111	112	111	113
a(TiO(1)X)	157	145	155	142
a(TiO(2)X)	153	144	153	143
a(TiO(3)X)	158	169	157	171
a(TiO(4)X)	158	165	156	164
a(O(w)Ti)		2.25		2.23
r(O(1)H(1))		2.10		1.98
r(O(w)H(1))		0.96		0.96
r(O(w)H(2))		0.95		0.95
a(TiO(w)H(1))		122		120
a(TiO(w)H(2))		120		121
a(O(1)TiO(w))		168		167
a(O(2)TiO(w))		78		78
a(O(3)TiO(w))		80		80
a(O(4)TiO(w))		91		91
a(H(1)O(w)H(2))		115		115

[a] See Figure 2 for atom labels.

Water adsorption energies have been calculated from total energies listed in Tables 1 and 6. The obtained values are 9.9 and 11.0 kcal·mol^{-1} for the Ge and the Si compounds, respectively. Values are corrected subtracting additional water−water interaction energy in the periodic system as explained in ref 32. The trend indicates that interaction is stronger in the latter, a fact that is in agreement with geometrical data, and it also goes in the direction expected from framework electronegativity estimations. The small energy difference does not necessarily mean that Lewis acidity is almost similar in both compounds, as properties other than the acid strength such as acid softness[56] do control the acid−base interaction energy.

Another picture of the acid−base interaction is obtained by considering the differences in the electronic structure of both the Si and the Ge models. In Table 7, atomic charges obtained using the Mulliken density partition are listed for the four considered models and free water at equilibrium geometry.

Once water is adsorbed, relevant changes are observed in the charge distribution of both the Ti site and the water molecule. While the total charge in the host and in the guest remains roughly constant, indicating that practically no charge transfer occurs, the charge distribution within each moiety is largely affected by the mutual interaction. In the water molecule, ionicity is increased as a result of the inductive effect promoted by the Ti site. The subsequent enhancement of the Bronsted acidity of the adsorbed water molecule can be described in terms of Gutmann's rules[57] and is to be compared with the effect

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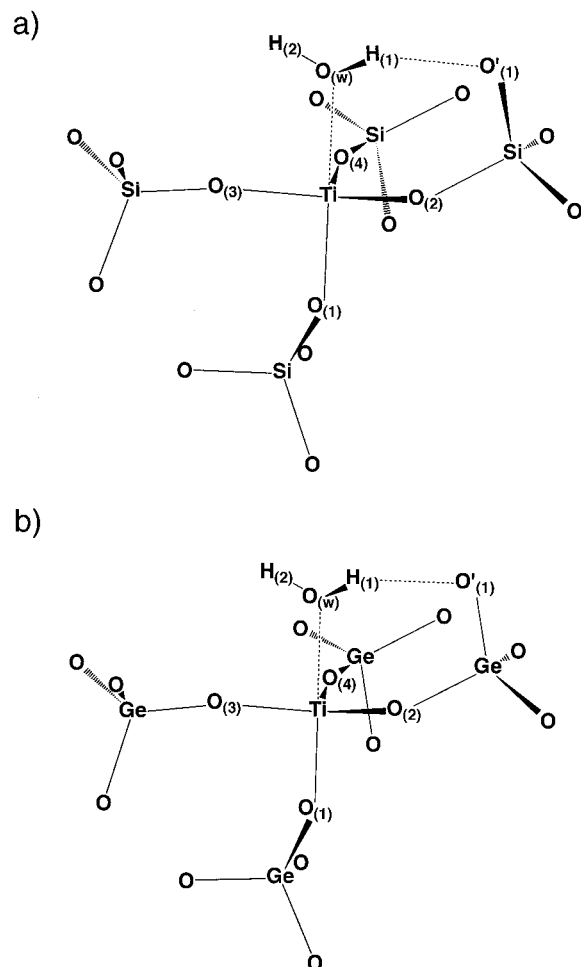
a)

b)

Figure 2. Schematic representation of the Ti center interacting with a water molecule in (a) TiSiCHA and (b) TiGeCHA.

TABLE 6: Hartree–Fock Energy (hartree) of Pure Water in Three Different Arrangements, Derived from Adsorption on TiXCHA (X = Ge, Si) Models: Equilibrium Geometry/Gas Phase (EQ/G), Same Geometry as Adsorbed/Gas Phase (AD/G), Same Geometry as Adsorbed/Periodic Arrangement (AD/P)

	Ge	Si
EQ/G	−76.04369	
AD/G	−76.0420	−76.0417
AD/P	−456.2575[a]	−456.2566[a]

[a] Energies per unit cell (six H_2O).

induced by the Al Lewis acid site on silanol groups to form the zeolitic Bronsted acid site. At the same time the ionicity of the Ti site is also increased since charge is transferred from the neighboring oxygens to the Ti atom as the coordination of the cation changes from tetrahedral to dipyramidal conformation.

While at the qualitative level the behavior of Si and Ge models is the same, it is worth noting that quantitative changes are more significant in the former. It arises from data in Table 7 that adsorbed water is more polarized as well as slightly more positively charged in the Si model. Concerning the host catalyst, in both cases the Ti atom gains about $0.057e$ upon interaction. The picture is, however, rather different when considering the ions in the vicinity of the active site. While in the Ge compound the increase of the Ti charge involves a significant decrease of the charge on Ge and O atoms, in the case of TiSiCHA there is no practical charge transfer from Si atoms and consequently the decrease in the O atomic charges is more pronounced, in

TABLE 7: Mulliken Atomic Charges and Shell Populations of Anhydrous and Hydrated TiXCHA (X = Ge, Si)

	Ge		Si		
X	anh	hyd	anh	hyd	H_2O
Ti	2.657	2.712	2.630	2.687	
X	2.590	2.573	2.036	2.032	
O(1)	−1.312	−1.330	−1.169	−1.213	
O(2)	−1.313	−1.325	−1.166	−1.188	
O(3)	−1.311	−1.323	−1.161	−1.161	
O(4)	−1.312	−1.303	−1.170	−1.159	
O(w)		−0.776		−0.783	−0.697
H(1)		0.400		0.409	0.349
H(2)		0.372		0.376	0.349
Ti3d	0.312	0.296	0.308	0.290	
Ti3d′	0.857	0.814	0.857	0.812	
Ti4s	0.281	0.292	0.291	0.300	

particular in the case of O(1), whose distance to Ti is the most enlarged upon interaction with water (see Figure 2). The enhanced capacity of the O atoms in the Si compound to accept electrons transferred from the Ti center is a consequence of the higher framework electronegativity given by the Si atoms.

4. Conclusions

The changes in chemical properties of Ti-zeolites when introducing Ge atoms in framework positions have been studied using theoretical models based on periodic zeolitic structures. Two different series of models have been explored: clean catalysts and catalysts with a base adsorbed on the Ti center. In the latter, a water molecule has been chosen as ligand.

Concerning the clean models, it has been observed that substitution of Si atoms by Ge close to the Ti sites results in a stabilization of the system owing to the additional framework flexibility provided by the less rigid GeO_4 units. The effect is shown to be more relevant in the case of isolated Ti sites, where framework strains derived from the existence of the Ti defect are larger. As a result of the difference in size and rigidity between SiO_4 and GeO_4 units, local geometry around Ti centers can be substantially modified if cation substitution occurs at its nearest neighbors.

From the electronic point of view, it has been observed that the overall trend when decreasing the framework electronegativity upon substitution of Si atoms by Ge is to increase the ionicity of the systems. However, in most cases the electronic structure of the active Ti site can be more influenced by local geometrical conditions than by the framework inductive effect. This is apparent in the case of the energy of the conduction band, used as an index of Lewis acidity, which largely depends on the Ti hybridization promoted by the conformation of the TiO_4 unit.

When considering the interaction with a water molecule, slight differences in adsorption energies are observed between the germanium and silicon Ti-zeolites, even if the trend is in agreement with the one expected from electronegativity considerations. On the other hand, analysis of the atomic charges shows that the water molecule is slightly more polarized when adsorbed on TiSi than on TiGe zeolites, which indicates a lower acidity in the latter. Nevertheless, differences between systems are rather small.

To summarize: at the calculation level considered in this work, no large inductive effects on Ti sites are observed upon substitution of Si by Ge atoms in Ti-zeolites, those effects resulting from the additional structural flexibility promoted by framework GeO_4 units being more relevant.

A consequence of such a flexibility in the case of TiGe zeolites can be an increased ability of the Ti site to distort from

regular tetrahedral toward near octahedral configuration needed for efficient coordination with bases. This would results in the "opposite" effect than expected from electronegativity as the effective Lewis acidity of the site will be increased.

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