

## Hydrogen Bonding versus Coordination of Adsorbate Molecules on Ti-Silicalites: A Density Functional Theory Study

Nurbosyn U. Zhanpeisov\*<sup>†</sup> and Masakazu Anpo

Contribution from the Department of Applied Chemistry, Osaka Prefecture University,  
1-1 Gakuen-cho, Sakai, Osaka 599-8531, Japan

Received September 17, 2003; E-mail: nurbosyn@orgphys.chem.tohoku.ac.jp

**Abstract:** The present study discusses the results of theoretical calculations obtained at the B3LYP/6-31G\* level on the structural, electronic, and energetic properties of Ti-silicalites. Particularly, the relevance of 5T cluster models, either H- or OH-terminated, in large-scale calculations has been critically considered. It was shown that an open surface structure with one OH group and a closed-bulk structure with no bonded OH group at the Ti site are responsible for the observed UV-vis properties of Ti-silicalite materials. Both water and methanol can preferably interact with Ti-silicalites through the H-bonding mechanism, while ammonia can form either H-bonded or coordination complexes. The calculations support the existence of highly dispersed Ti sites in a tetrahedral environment only in Ti-silicalites because an increase in the coordination number of the Ti site by next-neighbor lattice oxygens is the energetically less favorable process.

Since the discovery of Ti-silicalite (TS-1) as an active and selective catalyst in a remarkable number of low-temperature oxidation reactions with aqueous hydrogen peroxide,<sup>1–3</sup> there is growing interest in applications of mesoporous Ti-silicalites also as effective environmental pollution control catalysts, especially for the photocatalytic removal of NO and other nitrogen oxides as well as in the reduction of carbon dioxide with water into valuable chemicals.<sup>4</sup> These Ti-containing molecular sieves due to their unique and large pore structures are found to be very attractive as they catalyze many reactions and processes such as alcohol oxidation, olefin epoxidation, ketone ammoximation, etc.<sup>5</sup> It has been one of the most studied, both experimentally and theoretically, materials in heterogeneous catalysis in past years.<sup>6–13</sup> These catalysts also have some potential in the photooxidation of methane to produce more valuable oxygenated compounds such as methanol, acetaldehyde, formaldehyde, and small amounts of unsaturated hydrocarbons such as ethylene under mild oxidation conditions.<sup>14</sup>

It is generally believed<sup>9–11</sup> that the incorporation of Ti into silicalite structure produces two types of catalysts, in which Ti sites are either in the framework (formed through an isomorphous substitution of Si by Ti) or in the extraframework positions (formed through dehydroxylation of the surface silanol groups by TiOH or TiOR groups where R stands for an alkyl fragment of impregnated Ti-containing compound). Because the latter catalyst with extraframework Ti sites (called also as

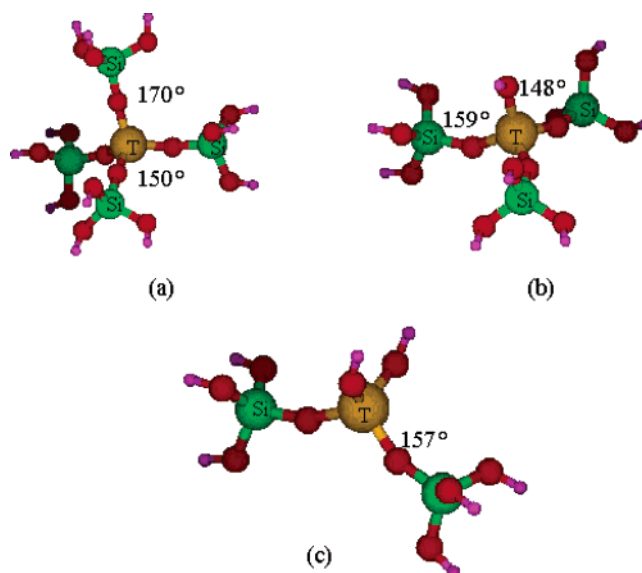
<sup>†</sup> Present address: Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan.

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“grafted” catalyst) has a higher probability to agglomerate or form a new titania phase on silicalite surface, the former Ti-silicalites with highly dispersed framework Ti sites attract much attention over the “grafted” ones.

There are two competing viewpoints, however, on active site species' nature when the catalytic activity of Ti-silicalite materials with the framework Ti sites is considered. According to the first, the active sites responsible for the observed catalytic activity are associated with the presence of a framework fourfold coordinated Ti site surrounded by four SiO<sub>4</sub> tetrahedra. This is also called a “perfect” or “nondefective” Ti(IV) center in which Ti atoms are linked to four Si through four oxygen bridges. This follows from the crystal structure of precursor silicalite materials that has an ordered ring structure containing fourfold coordinated T atoms, for example, in microporous TS-1 and Ti- $\beta$  or in mesoporous silicas such as the one-dimensional MCM-41 or three-dimensional MCM-48 catalysts. For these structures, the catalytic activity is thought to be related mainly to the Lewis acidity of the Ti(IV) sites. Recently obtained experimental and theoretical computational results<sup>9</sup> support this idea, showing that ammonia (strong Lewis base) perturbs the local environment of Ti(IV) to a greater extent than does water. This assumption, however, neglects the presence of “defective” sites associated with the TiOH or SiOH groups formed via a partial hydroxylation of “nondefective” sites with water which are the basis for the second viewpoint. According to the latter, the observed catalytic activity of the Ti-containing silicalite materials can be explained by the presence of these “defective” sites associated with the surface TiOH groups.<sup>10,11b</sup> However, we must note that TiOH species are very hard to distinguish from the more abundant SiOH species by FTIR and UV-vis spectroscopic techniques due to their small concentrations.<sup>6a,12b</sup> In fact, the surface hydroxyl groups are hardly fully removed, if any, from the surface of the catalysts and are thus still present even after high temperature calcinations and pretreatments. They can be easily confirmed by experimental techniques such as FTIR, UV-vis, etc.<sup>7cd,12</sup>

The “defective” and “nondefective” Ti(IV) sites in porous titanosilicates are an important topic to address. Sinclair and Catlow<sup>13</sup> have shown that a mixture of the above sites, that is, the Ti site having 0, 1, and 2 hydroxyl groups, is probable in titanosilicates where the metal ions have been isomorphously substituted into the framework of silicas. Bordiga et al.<sup>9</sup> have claimed that only “nondefective” sites can be responsible for the changes that appear in XANES spectra of adsorbed ammonia on Ti silicalite materials; thus, they have neglected the presence of “defective” sites. However, in their previous works,<sup>6a,7c</sup> these authors affirm that all experimental evidence is compatible with both “nondefective” and “defective” Ti(OSi)<sub>3</sub>OH sites. In that specific case,<sup>9</sup> the increase of ammonia dosage leads to the stronger distortion of the original Ti site's environment of titanosilicate from a tetrahedral to pentacoordinated trigonal bipyramid structure. Moreover, they have found that a reliable description of the Ti environment up to the second shell can be obtained only if the zeolitic constraint is included in the model. Thus, they have concluded that the 5T model which does not take into account the presence of third and higher order shell effects cannot be adequate to reliably describe the observed phenomena, in particular, the energetic features of Ti(IV) centers in Ti-containing silicas.



**Figure 1.** Cluster models mimicking closed-bulk (a) and/or open surface structures (b and c) containing either one or two hydroxyl groups attached to the central T atom. T is Si for silica or Ti for Ti-silicalite. The selected bond angles are in degrees.

Below, we would like to show that Ti-containing silicalite materials could be indeed considered as a “mixture” of both “defective” and “nondefective” Ti sites in line with the above papers. However, we have found that only two of the three representatives could be more or less reliable to explain the observed UV-vis properties. Also, the reliability of the use of the 5T model is readdressed. It will be shown that the failure to correctly describe the observed features by the 5T model applied by Bordiga et al.<sup>9</sup> arises from the use of cluster models that introduce highly simplified Si-H boundaries instead of more natural Si-OH ones. In such a sense, the basicity of oxygens in the first shell around the target Ti site is substantially increased in that explicit 5T cluster model. The interaction of water, methanol, ammonia, and some defective Si sites of silica with these 5T cluster models has been discussed on the basis of our density functional theory calculations.

## Method and Cluster Models

Density functional theory calculations were performed using the Gaussian 94 program packages.<sup>15</sup> Precursor silicalite was simulated by the 5T cluster model that consisted of a central SiO<sub>4</sub> tetrahedron sharing its corners with four other SiO<sub>4</sub> tetrahedra as depicted in Figure 1a (denoted as model I). This model I is further used to obtain the terminal and/or vicinal silanol groups of silicalite via a replacement of one or two SiO<sub>4</sub> tetrahedra around the central Si atom (models I-1 and I-2, respectively) by OH group(s) as well as to mimic the respective Ti-silicalite structures (denoted as I-Ti-*n* where *n* stands for the number of hydroxyl groups attached to the Ti site at the central position of the 5T cluster model, Figure 1b and c). Because the case in which Ti is in one of the terminal T positions of the 5T cluster model was found to

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be less favorable by energetics,<sup>11b,16</sup> it was excluded from further considerations.

Because cutting the substructures from the silicalite and/or Ti-silicalite generates dangling bonds, they have been saturated with hydrogen atoms to avoid boundary effects via the formation of terminal OH groups. Also, because the border H atoms are aimed to mimic the remaining part of the zeolite lattice, the formation of an artificial net of intramolecular H-bonds<sup>6b,8,11b</sup> is excluded from the considerations via fixing their dihedral angles at 180°. In the latter case, the border H atoms lie in the extension directions for the next SiO<sub>4</sub> tetrahedron. For comparison, the H-terminated 5T cluster model that leads to the formation of terminal Si–H bonds was also used. The final cluster models satisfy the stoichiometry, boundary conditions, and electroneutrality.<sup>11b,17</sup>

Geometry optimizations were carried out at the density functional theory (DFT) using the standard 6-31G\* basis sets. DFT calculations were performed with the use of Becke's three-parameter hybrid method with the Lee, Yang, and Parr (B3LYP) gradient-corrected correlation functional.<sup>18</sup> To estimate the vertical excitation energies, calculations on the excited states using a single excitation CI (configuration interactions) method were also performed. The active space in the latter includes all configurations originating from the single excitations from the core (except the deepest ones) and valence orbitals to all empty molecular orbitals. For all adsorption complexes considered in this study, the adsorption energies were calculated as the total energy difference between the adsorption complex and the sum of the isolated initial cluster and adsorbate molecule(s):

$$E_{\text{ads}} = E_{\text{AC}}(\text{AC}) - [E_{\text{A}}(\text{A}) + E_{\text{C}}(\text{C})] \quad (1)$$

where indexes AC, A, and C stand for adsorption complex, adsorbate, and cluster, respectively. Note that all energies of AC, A, and C are those estimated at their respective equilibrium geometries. The adsorption energies thus obtained were then corrected for basis set superposition errors (BSSE) by using the full Boys–Bernardi counterpoise correction scheme.<sup>19</sup> For more clarity, the definition of the latter BSSE corrected adsorption energies is:

$$E_{\text{ads}}^{\text{BSSE}} = E_{\text{AC}}(\text{AC}) + \Delta\text{BSSE} - [E_{\text{A}}(\text{A}) + E_{\text{C}}(\text{C})] \quad (2)$$

where  $\Delta\text{BSSE}$  stands for the basis set superposition error that is defined as follows:

$$\Delta\text{BSSE} = [E_{\text{A}}^{\text{C}}(\text{AC}) - E_{\text{A}}^{\text{C}}(\text{AC})] + [E_{\text{C}}^{\text{A}}(\text{AC}) - E_{\text{C}}^{\text{A}}(\text{AC})] \quad (3)$$

where  $E_{\text{A}}^{\text{C}}(\text{AC})$  stands for the total energy of adsorbate with ghost atoms of cluster, while  $E_{\text{C}}^{\text{A}}(\text{AC})$  corresponds to that of cluster with ghost atoms of adsorbate; both are estimated at the adsorption complex geometry. Note, however, that  $E_{\text{A}}(\text{AC})$  or  $E_{\text{C}}(\text{AC})$  corresponds to the energy of respective fragments estimated at the adsorption complex geometry only.  $\Delta\text{BSSE}$  is always positive and corresponds to an artificial stabilization of adsorbate (or cluster) due to ghost orbitals of cluster (or adsorbate).

## Results and Discussion

Before discussing the results, let us first address the question on reliability of the use of H- or OH-terminated 5T cluster models in large-scale calculations. To distinguish these cluster models from each other, they have been denoted as 5T(h) and

**Table 1.** Selected Bond Distances ( $R_{\text{Ti-O}}$ ,  $R_{\text{Si-O}}$ , Both in angstroms) and Mulliken Charges ( $Q_{\text{Ti}}$ ,  $Q_{\text{O}}$ ,  $Q_{\text{Si}}$ , All in  $e^-$ ) on Atoms of the Second and Third Shells of the 5T Cluster Models As Calculated by the B3LYP/6-31G\* Level of Theory

cluster	$R_{\text{Ti-O}}$	$R_{\text{Si-O}}$	$Q_{\text{Ti}}$	$Q_{\text{O}}$	$Q_{\text{Si}}$
5T(h)	1.795	1.660	1.35	−0.709	0.644
5T(oh)	1.794	1.627	1.269	−0.680	1.155
5T(oh) <sup>a</sup>	1.794	1.627	1.253	−0.672	1.201

<sup>a</sup> Constrained model with T–O–H angles for the border H atoms fixed at 141°.

5T(oh), respectively. According to Bordiga et al.,<sup>9</sup> the 5T model is not adequate to reliably describe the energetic features of Ti(IV) centers in Ti-containing silicas. This is partly due to the use of the 5T(h) model that does not reliably reproduce the Lewis acidic properties of the Ti(IV) site. The latter arises because the 5T(h) cluster model does not take into account the third and higher order shell effects when considering an adsorption process involving the Ti(IV) acid sites. To overcome this deficiency, these authors<sup>9</sup> have suggested the use of either larger cluster models or some embedding techniques. Both of the latter techniques could be well applied to reproduce the target phenomenon related to the Lewis acidity of the Ti(IV) site,<sup>9</sup> however, it can be done at the expense of increased computational time and computer resources. A more careful comparison of the structure and electronic properties of the 5T(h) and 5T(oh) models presented in Table 1 shows that (i) the 5T(h) model results in relatively more negative charges on oxygens in the first shell, while the charges on the border Si atoms of the second shell are substantially decreased. This would result in strong repulsion between these oxygens and the adsorbate molecule that approaches the Ti site, while its attraction by Si atoms in the second shell would be effectively compressed. At the same time, the charge at the central Ti site is slightly increased in the 5T(h) model. Overall, the adsorption process via coordination to the Ti site becomes energetically less favorable as was observed by Bordiga et al.<sup>9</sup> On the other hand, these factors are more or less well balanced in the 5T(oh) model. Note also that the charges for the latter 5T(oh) model with a fixed SiOH angle at 141° (that resembles the common SiOH angles in zeolites) do not substantially differ from those with the optimized SiOH angles equal to about 120°. (ii) Both 5T models result in consistent Ti–O bond distances formed by Ti with the first-shell oxygens. The optimized Ti–O bond distances in these 5T models are in good agreement with the experimental estimations<sup>7c,d,9a</sup> (as well as with other theoretical calculation results<sup>8,11b</sup>) and are larger than the Si–O distances, which can be expected due to larger ionic radii for Ti<sup>4+</sup> as compared to those for Si<sup>4+</sup>. The minor difference between the calculated and experimental results of ca.  $\pm 0.02$  Å is well within the experimental uncertainty in determining the interatomic distances. However, Si–O bonds for the second shell atoms are substantially elongated as a result of a substantial decrease in the electrostatic attraction between these atoms in the 5T(h) model as compared to that of the 5T(oh) model. Thus, the former 5T(h) model should be indeed less adequate to describe all peculiarities of the adsorption process involving the Lewis acid Ti sites of Ti-containing silicas, while it might be yet sufficient to describe local interactions involving only surface basic sites of the catalyst. However, the 5T(oh) model does not suffer these deficiencies, so it may produce more or less excellent results for local interactions of adsorbate molecules involving either

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**Table 2.** Characteristics of the Three Different Types of Active Sites of Ti-Silicalites Estimated at the CIS//B3LYP/6-31G\* Levels of Theory<sup>a</sup>

property	I-Ti-1	I-Ti-2	I-Ti
$E_i$ (au)	-2702.579908	-2186.023522	-3219.129817
HOMO (au)	-0.28242	-0.28612	-0.27951
LUMO (au)	-0.04262	-0.04554	-0.03809
(LUMO-HOMO) (au)	0.23980	0.24058	0.24142
$E_{exc}$ (eV)	5.44	5.57	5.71
$\lambda$ (nm)	227.9	222.5	217.2

<sup>a</sup> I-Ti, I-Ti-1, and I-Ti-2 model clusters correspond to the central TiO<sub>4</sub> unit of Ti-silicalites having 0, 1, and 2 hydroxyl groups in the first coordination shell, respectively.

the active Ti site or its next-nearest-neighbor surrounding basic oxygens. Thus, preference should be given to the 5T(oH) cluster model because the boundary effects are taken into account by introducing more physical Si-OH fragments than those of Si-H in the 5T(h) cluster model.

Let us now briefly clarify the nature of the active sites of Ti-silicalites. This question is also important in view of further considerations as well as to find the sites that are responsible for the different band positions in the observed photoluminescence spectra of such materials.<sup>12</sup> Evidently, the observed band differences arise from the distinct silicalite framework structures involving Ti-containing fragments. As has been pointed out above, they might be either an open surface structure with one (or two) terminal OH group(s) bonded to (as I-Ti-1 and I-Ti-2, respectively) or a closed-bulk structure with no bonded OH group at (as I-Ti) the target Ti site (Figure 1). Table 2 lists characteristics of those three different types of active sites used to mimic Ti-silicalites and estimated at the CIS//B3LYP/6-31G\* level of the theory. As is evident, Ti-silicalites containing 1 and 0 hydroxyl groups at the Ti site (Figure 1) show the highest and the lowest excitation band positions, respectively. Excitation is shifted into longer wavelengths at lower energy values when going from I-Ti to I-Ti-1, thus manifesting a bathochromic shift, while I-Ti-2 represents an intermediate case. Although the DFT level of theory highly overestimates the HOMO-LUMO band gap,<sup>20</sup> it produces much better agreement with the experiment. However, the tendency of changes in the excitation energies as well as in the frontier orbitals might be also well reproduced by the less expensive HF level of theory.<sup>16</sup> Thus, the order of changes in the excitation for I-Ti and I-Ti-1 correlates well either with the difference in the lowest unoccupied and highest occupied molecular orbitals (LUMO-HOMO) energies or with the LUMO energy for both levels of theories applied. They can be represented as follows:

$$E_{exc}: \text{I-Ti-1} < \text{I-Ti-2} < \text{I-Ti}$$

$$\lambda: \text{I-Ti-1} > \text{I-Ti-2} > \text{I-Ti} \quad (4)$$

Both the conduction (LUMO) and the valence (HOMO) band edges become more stabilized when going from I-Ti to I-Ti-1. Particularly, the higher reactivity of the “defect” I-Ti-1 over the “nondefect” I-Ti is also indirectly supported by both of

**Table 3.** Total Energy ( $E_{AC}(AC)$ , hartree), Relative Energy ( $\Delta$ , kcal/mol), Adsorption Energies of Adsorbates Estimated Either via a Conventional Way ( $E_{ads}$ , kcal/mol) or Corrected to the BSSE ( $E_{ads}^{BSSE}$ , kcal/mol) As Calculated at the B3LYP/6-31G\* Level of Theory Using the 5T(oH) Cluster Model<sup>a</sup>

adsorption complex	$E_{AC}(AC)$	$\Delta$	$E_{ads}$	$E_{ads}^{BSSE}$
H <sub>2</sub> O/Ti-silicalite	-2779.01837	0.0	-18.2	-11.8
	-2779.00265	9.9	-8.3	-2.6
CH <sub>3</sub> OH/Ti-silicalite	-2818.31798	0.0	-14.5	-9.6
	-2818.30862	5.9	-8.6	-3.1
NH <sub>3</sub> /Ti-silicalite	-2759.15717	0.0	-18.1	-13.8
	-2759.15269	2.8	-15.2	-9.6

<sup>a</sup> The first and the second lines for each adsorbate correspond to the formation of an H-bonded or coordination complex, respectively. For each adsorbate, the lower energy adsorption form is a reference for relative stability. The (-) sign for the adsorption energies corresponds to the favorable adsorption process.

these calculations. Note that the latter “nondefect” I-Ti sites are less effective as catalytic centers as are those of higher coordination Ti species due to the lack of coordination sites for relatively weak base molecules as is shown below.

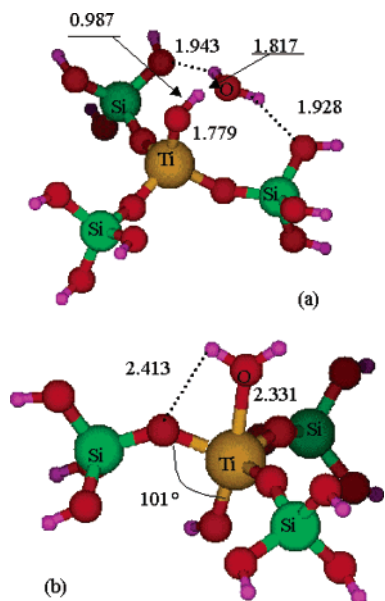
Next, the interaction of potential adsorbate molecules (like H<sub>2</sub>O, CH<sub>3</sub>OH, NH<sub>3</sub>) on the Ti-silicalite catalyst is considered. Because the I-Ti-1 cluster model is found to be more active than that of I-Ti, as well as it is more reliable to discriminate between the two possible mechanisms of interactions of the adsorbate molecules considered, below we would like to present the results obtained by the explicit use of this I-Ti-1 cluster model. The latter two mechanisms arise from the possibility of interaction of these molecules with Ti-silicalites either via formation of an H-bond or via coordination directly to the Ti site by increasing its environment from a tetrahedral to a fivefold coordinated one. Table 3 lists the adsorption energies estimated in a conventional way and those corrected for the BSSE, while some structural data of these adsorption complexes are given in Figures 2–4. An analysis of these data shows the following peculiarities:

(i) In the case of water, the difference in energy amounts to about 9.9 kcal/mol when comparing the H-bonded and coordination adsorption complexes, the former H-bonded complex being more preferable. Inclusion of the BSSE decreases the adsorption energy value for 6.4 kcal/mol for the H-bonded complex, and it amounts to -11.8 kcal/mol. This obtained BSSE corrected adsorption energy value is more than 4 times stronger than that of the coordination complex. The less profitability for the coordination complex formation arises here due to the larger energy necessary for the deformation of the initial tetrahedral geometry of the Ti site into that of the fivefold coordinated adsorption complex geometry (see Figure 2). Thus, water would prefer to be adsorbed as an H-bonded complex rather than the formation of a coordination complex on the Ti-silicalite.

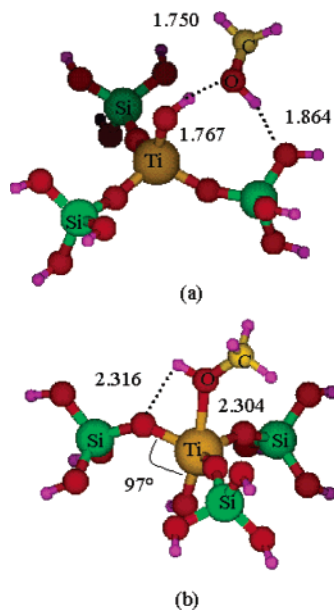
(ii) In the case of methanol, the adsorption leads also to the formation of the relatively strongly bound H-complex as in the case of zeolites,<sup>21</sup> in which methanol acts simultaneously as a proton donor to and proton acceptor from Ti-silicalite. However, its adsorption energy estimated either in a conventional way or with a correction to the BSSE is slightly lower (for 3.7–2.2 kcal/mol) than those of water, respectively, and can be ascribed only to a physisorption complex rather than to a chemisorption complex (Figure 3). This H-bonded adsorption complex of

(20) Kasahara, A.; Nukumizu, K.; Takata, T.; Kondo, J.; Hara, M.; Kobayashi, H.; Domen, K. *J. Phys. Chem. B* **2003**, *107*, 791. Here, from an experimental point of view, DFT “overestimates” the band gap because of the too narrow locations of the conduction and valence bands. In such a sense, there is an overestimation of band gap via bringing too much closer both HOMO and LUMO. However, if one looks into the origin of errors obtained by DFT methods, this is due to underestimation of HOMO-LUMO band gap, see, for details: Sham, L. J.; Schluter, M. *Phys. Rev. B* **1985**, *32*, 3883.

(21) Sauer, J.; Ugliengo, P.; Garrone, E.; Saunders, V. R. *Chem. Rev.* **1994**, *94*, 2095.

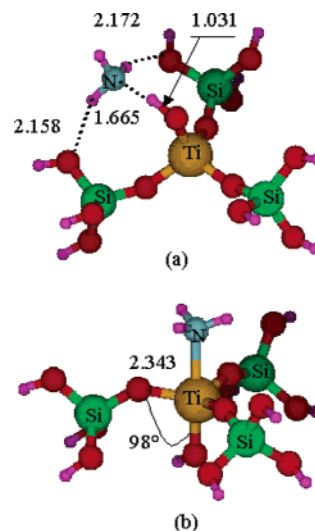


**Figure 2.** Adsorption complexes of water with Ti-silicalite formed either via H-bonding (a) or via coordination (b) mechanisms. The selected bond distances and bond angle are in angstroms and degrees, respectively.



**Figure 3.** Adsorption complexes of methanol with Ti-silicalite formed either via H-bonding (a) or via coordination (b) mechanisms. The selected bond distances and bond angle are in angstroms and degrees, respectively.

methanol is still more preferable than that formed via a coordination mechanism. However, the energy difference between the two is found to be slightly lower than those of water and amounts to 5.9 kcal/mol. Also, the adsorption energies estimated with corrections to the BSSE show that an H-bonding mechanism is still favorable for methanol over the coordination mechanism (about 3 times more stronger for the H-bonded complex, see Table 3). Further inclusion of zero-point energy (ZPE) corrections estimated by performing frequency calculations did not change this stability order because the difference in ZPE is less than 1.0 kcal/mol. Thus, methanol cannot be considered as a base molecule that would be able to increase the coordination number of 4 for the Ti site to 5 or 6 in the Ti-silicalite.



**Figure 4.** Adsorption complexes of ammonia with Ti-silicalite formed either via H-bonding (a) or via coordination (b) mechanisms. The selected bond distances and bond angle are in angstroms and degrees, respectively.

(iii) In the case of ammonia, the difference in energy between the two structures formed either via H-bonding or via coordination mechanisms amounts only to 2.8 kcal/mol, the H-bonded complex being still favorable. The formation of the latter adsorption complex proceeds via establishing three H-bonds in which ammonia acts as double proton donor to and a proton acceptor from the Ti-silicalite. This form with the three-center stabilization is about 2.0 and 3.6 kcal/mol more stable than those stabilized via the formation of two- and one-center H-bonds, respectively. However, all of these structures can be only considered as H-bonded complexes,<sup>22,23</sup> and, evidently, there is no indication (or evidence) of the formation of ammonium ions (see Figure 4). Although the relative stability of an H-complex is slightly higher than that of the coordination complex, the BSSE corrected adsorption energy is only 4.2 kcal/mol less favorable for the latter coordination complex as compared to that of the H-bonded complex. This adsorption energy is large enough to “drag-out” the Ti site from its initial tetrahedral position into the fivefold coordinated one within the Ti-silicalite structure. Thus, probably, the interaction of ammonia with Ti-silicalite might proceed either via H-bonding or via coordination mechanisms. Thus, the realization of the latter coordination mechanism becomes possible because of the higher basicity of ammonia over those of water or methanol.<sup>22</sup>

It should be also noted that the experimental heat of adsorption of water on zeolite Ti- $\beta$  is about 10.3 kcal/mol,<sup>24</sup> in line with our above estimated result. However, according to other adsorption microcalorimetry results, this value is in the range of 12.4–15.0 kcal/mol and strongly depends on the water pressure.<sup>9</sup> Taking into account the liquefaction enthalpy of water of about 10.5 kcal/mol under standard conditions, this may suggest that the main effect measured by both groups is associated with the condensation of water inside the zeolite pores. As for the ammonia, the experimental heats of adsorption are estimated to be within 14.6–16.3 kcal/mol depending also

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 (23) Teunissen, E. H.; van Duijneveldt, F. B.; van Santen, R. A. *J. Phys. Chem.* **1992**, *96*, 366.  
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**Table 4.** Total Energy ( $E_{AC}(AC)$ , hartree), Relative Energy ( $\Delta$ , kcal/mol), Adsorption Energies of Adsorbates Estimated Either via a Conventional Way ( $E_{ads}$ , kcal/mol) or Corrected to the BSSE ( $E_{ads}^{BSSE}$ , kcal/mol) As Calculated at the B3LYP/6-31G\* Level of Theory Using the 5T(h) Cluster Model<sup>a</sup>

adsorption complex	$E_{AC}(AC)$	$\Delta$	$E_{ads}$	$E_{ads}^{BSSE}$
H <sub>2</sub> O/5T(h)	-2101.57426	0.0	-10.6	-7.0
	-2101.56645	4.9	-5.7	-0.3
CH <sub>3</sub> OH/5T(h)	-2140.87951	0.0	-10.5	-6.8
	-2140.87361	3.7	-6.8	-1.7
NH <sub>3</sub> /5T(h)	-2081.71843	0.0	-13.9	-11.2
	-2081.71494	2.2	-11.7	-6.7

<sup>a</sup> See footnote of Table 3.

on the ammonia pressure.<sup>9</sup> This stresses that an incorporation of Ti into MFI frameworks significantly increases the ability of the silicalite to adsorb ammonia in good agreement with our above calculation results.

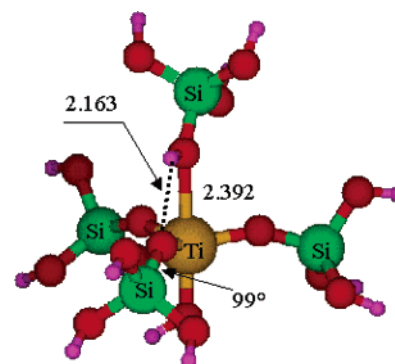
The reliability of the use of the 5T(oh) cluster model instead of 5T(h) is further demonstrated below by explicit consideration of the adsorption properties of these adsorbates on the 5T(h) cluster model. Table 4 lists the results of those calculations. An analysis of the data of Table 4 shows that the adsorption energies estimated as well as the relative stability of the two adsorption forms considered for these adsorbates are smaller in the case of the 5T(h) cluster model than those in the case of 5T(oh). Note also that the H-bonded complexes formed on the 5T(h) cluster model (with an effective involvement of the basic oxygen atom from the first shell) are quite different from those formed on 5T(oh) models (those first-shell basic oxygens are effectively excluded because of the presence of the third-shell oxygens). Inclusion of BSSE corrections lowers the adsorption energies estimated via a conventional way, the coordination complexes being highly unfavorable. This is because the energy quantity associated with the deformation of the cluster is substantially higher in coordination complexes than that in H-bonded complexes.

Finally, let us consider the case in which the Ti site can be seen as the fivefold coordinated one within Ti-silicalite structures based on the above results. The increase in the coordination of the Ti site might proceed via its coordination to the next-neighbor basic oxygens. This case was modeled via coordination of ideal HOSi(OH)<sub>3</sub> to the Ti site, the former mimicking the part that contains a structural basic oxygen site (Figure 5). The B3LYP/6-31G\* results obtained show that such an interaction proceeds with a consumption of energy of about 1.3 kcal/mol (estimated with the BSSE corrections), being much more unfavorable than those of water or methanol. This is a strong indication that the Ti site can be seen only as fourfold coordinated within the highly dispersed Ti-silicalite structures.<sup>12</sup>

## Conclusions

The results obtained can be summarized as follows:

(1) The preference in large-scale calculations should be given to the 5T(oh) cluster model over the 5T(h) model because the



**Figure 5.** The structure mimicking an increase of the coordination number of the Ti site by establishing an additional coordination to the next-neighbor lattice oxygen. The selected bond distances and bond angle are in angstroms and degrees, respectively.

boundary effects in the former are taken into account by introducing more physical Si–OH fragments. The H-terminated 5T(h) cluster model results in imbalanced charge distributions on the first and second shell atoms and thus decreases the coordination ability of an adsorbate molecule to the Ti site due to a strong repulsion.

(2) Only two of the three possible active sites of Ti-silicalites could be more or less reliable to explain the observed UV–vis properties. Excitation is shifted into longer wavelengths at lower energy values when going from a closed-bulk I–Ti structure to the open surface I–Ti-1 structure, thus manifesting a bathochromic shift. The higher reactivity of I–Ti-1 over I–Ti is also indirectly explained when one analyzes the changes in the LUMO–HOMO energy differences and in LUMO energy levels.

(3) For water and methanol, the H-bonding mechanism is more energetically preferable over the coordination mechanism. Due to the large difference in energy, both water and methanol cannot be considered as base molecules that would be able to increase the coordination number of 4 for the Ti site to 5 or 6, at least at low or moderate coverages.

(4) Interaction of ammonia with Ti-silicalite might proceed either via H-bonding or via coordination mechanisms. Adsorption energies estimated with the BSSE corrections show that the NH<sub>3</sub> binds slightly stronger with Ti-silicalite in the coordination complex over the H-bonded complex. Thus, the realization of the latter coordination mechanism becomes possible because of the higher basicity of ammonia over water or methanol.

(5) The increase in the coordination number of 4 for the Ti via interaction with next-neighbor lattice oxygens is energetically unfavorable, being much smaller than those found for water or methanol. This is a strong indication that the Ti site can be seen only as fourfold coordinated within the highly dispersed Ti-silicalite structures.

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