A Comparative Study of Structural, Acidic and Hydrophobic properties of Sn-BEA with Ti–BEA using Periodic Density Functional Theory

Sharan Shetty,†§ Dilip G. Kanhere,† Annick Goursot,‡ Sourav Pal§∗

Contributions from the Centre for Modeling and Simulation, Department of Physics, University of Pune, Pune 411007, National Chemical Laboratory, Pune 411008 and Ecole de Chimie, Montpellier, Cedex 5 France
s.pal@ncl.res.in

Abstract

Periodic density functional theory has been employed to characterize the differences in the structural, Lewis acidic and hydrophobic properties of Sn–BEA and Ti–BEA. We show that the incorporation of Sn increases the Lewis acidity of BEA compared to the incorporation of Ti. Hence, the present work gives an insight into the role of Sn in increasing the efficiency of the oxidation reactions. The results also justify that the percentage of Sn substituted in BEA is less than Ti. The structural analysis shows that the first coordination shell of Sn is larger than that of Ti. However, the second coordination of both sites remains the same. Moreover, the water resistant properties of these substituted zeolites are quantified.

1 Introduction

Zeolite beta (BEA) has been used as one of the active catalysts for carrying out several organic reactions such as epoxidation of olefins,1 aromatic and aliphatic alkylation,2 acid catalyzed reactions,3 etc. Some of the important reactions which can be catalyzed by BEA include, the Baeyer–Villiger oxidation (BVO) reaction and the Meerwein–Ponndorf–Verley reduction of aldehydes and Oppenauer’s oxidation of alcohols (MPVO) reaction.4 The reasons for using BEA as an efficient catalyst are its relatively large pore size, its flexible framework and high acidity.5 It has been well established that the acidity of BEA can be finely tuned by the incorporation of various atoms such as B, Al, Ti, Zr, Fe etc.5−8 These sites substituted in the
BEA framework act as active Bronsted or Lewis acid sites depending upon their valence states. Among these atoms, Ti–substitution in BEA framework has proven to be an active catalyst for the epoxidation of olefins in the presence of H\textsubscript{2}O\textsubscript{2}. The other Ti–zeolites, which have been successfully used for the oxidation of small organic molecules, are the titanium silicates (TS–1, TS–2). Several studies have been reported to understand the differences of the activity and selectivity between these two zeolites. Corma et al have shown that these differences are due to the hydrophilic/hydrophobic nature of the Ti sites. They showed that the Ti–sites in TS are more hydrophobic than the Al–Ti–BEA. Hence, TS was prefered over Al–Ti–BEA when the solvent used in the reaction is prepared in aqueous medium.

One of the challenges in this field is to increase the efficiency of a zeolite by substitution with other elements. Such an attempt has been made recently by incorporating Sn in BEA. Mal and Ramaswamy successfully synthesized the Al–free Sn–BEA. In an interesting experimental work, Corma et al showed that the incorporation of Sn in the BEA framework results into a more efficient catalyst for the BVO reaction in the presence of H\textsubscript{2}O\textsubscript{2}. In their study, a new mechanism was proposed for the oxidation of ketones. They showed that the Sn site in BEA activates the carbonyl group of the cyclohexanone followed by the attack of H\textsubscript{2}O\textsubscript{2}, unlike the Ti sites which initially activate the H\textsubscript{2}O\textsubscript{2}. This result was attributed to the higher Lewis acidity of the Sn site with respect to the Ti site. Hence, incorporation of Sn in BEA leads to a high selectivity towards the formation of lactones in the BVO reaction. On this background, highly selective MPVO reactions were carried out more efficiently with Sn–BEA than Ti–BEA. In these studies, it was shown that the Sn site is situated within the framework and no extraframework Sn was detected. Although much of the experimental studies have focused on the efficiency of the Sn–BEA, the higher Lewis acidity of the Sn site compared to the Ti site in BEA is still not known. Recently, Sever and Root used the M(OH)\textsubscript{4} (M = Sn, Ti) cluster models to investigate the reaction pathways for the BVO reaction.

The activity and selectivity of the zeolite mainly depend on the nature of the active sites, such as local coordination, interaction with the incoming molecules, percentage of substitution of T atoms in the framework, etc. One of the important issues concerning the activity and selectivity of the zeolite is its hydrophobic/hydrophilic nature. It is known that if the zeolite is hydrophilic in nature, the water present in the solvent poisons the active sites. This hinders the kinetics of the reaction and decreases the activity of the zeolite. Corma et al have bypassed this problem by modifying the catalyst design, which allows the use of Sn–BEA in the presence of aqueous media. Very recently, Boronat et al have done theoretical calculations using a Sn(OSiH\textsubscript{3})\textsubscript{3}OH cluster model to understand the effect of H\textsubscript{2}O during the BVO reaction. Their results show that one water molecule is permanently attached to the Sn active site. Interestingly, Fois et al have studied the interaction of water
molecules with the Ti sites in Ti–Offretite using Car–Parrinello molecular dynamics.\textsuperscript{21} They found that at higher loading of water molecules, the Ti atom expands its coordination number.

In the last decade, several experimental and theoretical studies have been employed to characterize the role of Ti sites at a microscopic level in various Ti-zeolite systems.\textsuperscript{1,7,22} It has been revealed that due to high crystallinity, low Ti content and large quadrupolar moment of Ti, accurate information on the Ti sites in BEA is not possible through experimental techniques.\textsuperscript{23} Hence, it is necessary to use theoretical methods to explore the local behavior for eg. structure, electronic and bonding properties of these sites. Sastre and Corma have used \textit{ab initio} calculations to discuss the role of the Ti sites in Ti–BEA and TS–1.\textsuperscript{24} The energies of the lowest unoccupied molecular orbital (LUMO) of Ti–BEA and TS–1 with one Ti substituted in turn at every T site, were shown to be different. Furthermore, the Ti–sites in Ti–BEA were found to be more acidic than in TS–1 and this acidity varies among all the Ti–sites in both zeolites.\textsuperscript{24} This proves that not only different Ti–containing zeolites have different acidity, but also different T–sites within a particular zeolite would have varying acidity. Very recently, Bare et al have used EXAFS technique to investigate the Sn–site in Sn–BEA.\textsuperscript{25} They showed that Sn was not randomly distributed in BEA, and takes specific crystallographic sites, i.e. T5/T6 sites in their nomenclature, which corresponds to T1 and T2 in our nomenclature, following Newsam \textit{et al.}\textsuperscript{26} Surprisingly, they found that this substitution takes place through pairing of these sites, within the six membered ring i.e. two T1 or two T2. However, no explanation was given for this distribution. At the same time, in a theoretical work using a periodic approach based on density functional theory (DFT) we characterized the Sn–sites in BEA.\textsuperscript{27} We showed that the T2–site would be the most probable site for the Sn substitution based on thermodynamics consideration of the largest cohesive energy in a dehydrated BEA zeolite. Moreover, we found that the substitution of 2 Sn atoms per unit cell was thermodynamically unfavorable. This was consistent with the earlier experimental results. Parallel to this, Boronat \textit{et al} carried out a cluster calculation of the Sn–BEA interaction with cyclohexanone and H\textsubscript{2}O\textsubscript{2}.\textsuperscript{28} They showed that the BVO reaction in Sn–BEA is due to the activation of cyclohexanone at the Sn site.

As it can be seen from the above description, the incorporation of Sn in BEA proves it to be a better catalytic site than Ti. Hence, a detailed information on the differences in the properties of Sn and Ti sites in BEA, such as the quantification of the Lewis acidity, number of Ti atoms to be substituted in the unit cell and hydrophobicity, are of fundamental importance and are still to be resolved. The aim of the present theoretical study is to bring out the differences in these substituted BEA zeolites by analyzing their structural, electronic and hydrophobic properties. Moreover, it is also important to understand why the framework Sn site activates...
the carbonyl group of cyclohexanone and not \( \text{H}_2\text{O}_2 \) in the BVO reaction, while Ti behaves the other way. We investigate this issue on the basis of hard–soft acid–base (HSAB) principle.

## 2 Methodology and Computational Details

Several theoretical studies based on a classical as well as quantum potential have been proposed to study the properties of zeolites. It has been a practise to adopt cluster models cut from the zeolite crystals to study these properties. One of the obvious reasons to use cluster model is that it is computationally cheap. Sauer et al have done an extensive study of zeolites using cluster models. However, the active site represented in the cluster model is in a different electronic environment than in which it would be in a crystal. A periodic approach provides a more realistic description to study the properties of a crystal. Although zeolite catalysts are neither crystals nor periodic solids, it is more convenient to use periodic boundary conditions, when there are very few substituted sites per unit cell.

Earlier experimental studies have indeed proved that Sn and Ti sites in BEA are very few, that they are situated within the framework and during the BVO or MPVO reaction these sites do not dissociate from the framework. In the present work we have employed the periodic DFT to investigate the properties of Sn–BEA and Ti–BEA. Advantage of using periodic boundary conditions is that the long range electrostatic interactions are included within Ewald summations. The instantaneous stationary electronic ground state is calculated by solving the Kohn-Sham equation based on DFT. The valence electrons have been represented by the plane waves in conjunction with the Vanderbilt’s ultra–soft pseudopotential for the. It is worth mentioning that during the interaction between two systems the complete plane wave avoids the basis set superposition error. The exchange correlation functional is expressed by the the generalized gradient approximation (GGA) with the Perdew–Wang 91 functional. The calculations were restricted to the gamma point in the Brillouin zone sampling. All the calculations have been performed by the VASP code.

BEA is a high silica zeolite and consists of two different ordered polytypic series viz. polymorph A and polymorph B. It has two mutually perpendicular straight channels with a cross section of 0.76*0.64 nm which run along a and b directions. Intersecting to these, at right angles, a helical channel of 0.55 x 0.55 nm also exists along the c-axis. This gives rise to a three dimensional pore system of 12–membered ring aperture. The unit cell of an ideal fully siliceous BEA consists of 192 atoms with 64 Si and 128 O atoms distributed within the tetragonal lattice of dimension 12.6 x 12.6 x 26.2 Å. There are 9 distinct crystallographically defined T sites as shown.
Figure 1: Crystallographically defined 9 T sites of BEA. The grey spheres represent the Si sites.
in Fig. 1. We adopt the experimental structure as defined by Newsam et al and accordingly define the 9 T sites in the unit cell of BEA.

The structural optimization of the Si, Sn and Ti–BEA have been carried out in two steps. In the first step, conjugate gradient method was used to optimize the unit cell of BEA. The optimization was considered to achieve when the forces on the atoms were less than 0.1 eV/Å. In the second step, these optimized geometries were re–optimized with quasi–Newton method unless the forces on the atoms were less than 0.06 eV/Å. One should note that during the optimization the cell shape of the unit cell has been fully relaxed, while keeping its volume constant. In the case of Sn and Ti–BEA each of the 9 distinct T sites were substituted by Sn and Ti atoms (i.e. Si/(Sn or Ti) = 63/1, respectively, and were optimized. Once the active site in Sn and Ti–BEA was confirmed, one water molecule was introduced near to these active sites and the same optimization procedure was followed as discussed above. The structural data for the Sn–BEA has been taken from a recent publication by us.

In addition to this, we have also carried out DFT calculations of cyclohexanone and H₂O₂ molecules using a supercell. These systems were optimized by the conjugate gradient methods only, until the forces on the atoms were less than 0.005 eV/Å.

3 Results and Discussion

3.1 Structure of Sn–BEA and Ti–BEA

We have already discussed the structure and energetics of Sn–BEA in a recent publication. In the present work we briefly recall this discussion which is necessary for comparing it with the structure and energetics of Ti–BEA and also to study its hydrophobic characteristic.

Table 1 and Table 2 present the optimized structural details of all the 9 T sites of Sn–BEA and Ti–BEA, respectively. It should be noted that only the average bond distances and bond angles are presented. It can be seen from Table 1 that the Sn–O bond distance range between 1.908 to 1.917 Å, the Sn–O–Si bond angle range from 136 to 144.2 deg and the Sn–Si distance is around 3.241 ± 0.100 Å. Very recently, Bare et al, with the help of EXAFS technique showed that the Sn–O bond distances and the Sn–Si distances in Sn–BEA were around 1.906 Å and 3.5 Å, respectively. This clearly shows that the theoretical results presented by us are in good agreement with the experimental results. However, the theoretical results of Bare et al were not consistent with their experimental data. This may be due to keeping the shape of the unit cell fixed during the optimization and using the local density approximation exchange–correlation potential in their study. On the other hand, we have relaxed the lattice vectors of the unit cell during the optimization and also used the GGA exchange–correlation potential, as explained in the earlier section. The change in
Table 1: Optimized structural parameters of Sn–BEA. Average Sn–O bond lengths, Sn–O–Si bond angles and Sn–Si distances of all the 9 T sites of Sn–BEA.

| T-sites | Sn–O (Å) | Sn–O–Si (deg) | Sn–Si (Å) |
|---------|----------|---------------|-----------|
| T1      | 1.911    | 143.5         | 3.336     |
| T2      | 1.909    | 144.2         | 3.341     |
| T3      | 1.910    | 140.6         | 3.241     |
| T4      | 1.917    | 136.0         | 3.281     |
| T5      | 1.913    | 142.2         | 3.297     |
| T6      | 1.910    | 141.2         | 3.297     |
| T7      | 1.911    | 140.6         | 3.282     |
| T8      | 1.908    | 140.0         | 3.282     |
| T9      | 1.912    | 137.8         | 3.270     |

the local coordination of the T site in Sn–BEA compared to the Si–BEA has been illustrated in the earlier study. As already mentioned above, sites T5 and T6 of ref. 25 correspond to sites T1 and T2 in our work, in which we use the nomenclature of Newsam et al.26

Table 2 shows that the average Ti–O bond distances of the 9 T sites in BEA vary from 1.794 to 1.799 Å. These values are in good agreement with the earlier works on Ti–BEA.7 Compared to Sn–O bond distances, the Ti–O distances are smaller. This is due to the larger atomic size of Sn with respect to Ti. From the data of Tables 1 and 2, it can be noticed that the average Sn-O and Ti-O bond lengths are very similar for all T sites, whereas the corresponding bond angles have a large range of variation. Moreover, in both Sn and Ti-BEA models, the largest average angles belong to the T1 and T2 sites. The average experimental values of T1–O–T and T2–O–T angles in the unsubstituted Si-BEA are 155.3 and 155.9 deg respectively, and they also correspond to the largest T–O–T angles in the framework. If we compare Sn and Ti substituted in the framework with Si, we get the expected order for average T-O bond lengths Sn-O>Ti-O>Si-O, with around 0.12 to 0.15 Å difference at each replacement. The average T1–O–T or T2–O–T bond angles vary as Sn–O–Si<Ti–O–Si<Si–O–Si.

This Ti–O–Si bond angles which range between 144 to 152 deg, are larger than the Sn–O–Si bond angles with a range between 136–143.5 deg. Due to the angular flexibility, the Ti–Si distance differ only by ~0.04 Å from the Sn–Si distance. Although the first coordination shell radius of Ti is smaller than that of Sn, the second coordination shells are at similar distances. The adaptation of the BEA framework to Sn and Ti substitution results thus into a quite localized deformation of the siliceous
Table 2: Optimized structural parameters of Ti–BEA. Average Ti–O bond lengths, Ti–O–Si bond angles, Ti–Si distances of all the 9 T sites of Ti–BEA.

| T–sites | Ti–O (Å) | Ti–O–Si (deg) | Ti–Si (Å) |
|---------|---------|--------------|---------|
| T1      | 1.799   | 151.7        | 3.302   |
| T2      | 1.797   | 152.4        | 3.304   |
| T3      | 1.794   | 145.0        | 3.220   |
| T4      | 1.797   | 145.4        | 3.233   |
| T5      | 1.799   | 148.1        | 3.257   |
| T6      | 1.799   | 148.5        | 3.263   |
| T7      | 1.794   | 149.0        | 3.269   |
| T8      | 1.795   | 147.4        | 3.249   |
| T9      | 1.798   | 144.0        | 3.225   |

framework. Hence, we can infer that the difference in adsorption properties between Sn and Ti-BEA should be mainly due to the electronic differences of these sites.

3.2 Energetics of Sn–BEA and Ti–BEA

In this subsection, we discuss the thermodynamic stability of Sn–BEA and Ti–BEA. This is done by calculating the cohesive energies for each of the 9 T–sites in Sn–BEA and Ti–BEA. Cohesive energy of a solid is defined as the difference between the energy of the bulk (solid) at equilibrium and the energy of the constituent atoms in their ground state.\(^\text{27}\) Cohesive energy does not account for the kinetic formation of the system, neither for the different nature of the synthesis intermediates generated in aqueous solution, which can generate different routes for the solid growth.

The cohesive energies of all the 9 substituted T–sites of Sn–BEA and Ti–BEA are given in Table 3. In our earlier investigation on the energetics of Sn–BEA, we showed that the substitution of Sn in the BEA framework decreases the cohesive energy.\(^\text{27}\) Hence, the incorporation of Sn in BEA was shown to be thermodynamically less stable than the Si–BEA. On this basis, we explained the fact that the incorporation of Sn in the BEA framework is restricted. Interestingly, Bare \textit{et al} predicted the formation of Sn pairs as the active sites, where the two Sn atoms were shown to be on the opposite sides of a six membered ring.\(^\text{25}\) They showed that one of these pairs is present per 8 u.c of BEA. Unfortunately, at present, it is out of scope to consider 8 u.c of BEA. Nevertheless, we have carried out the calculations placing 2 Sn atoms per u.c. at T1 and T2 (T5 and T6 according to Bare \textit{et al}) positions which are situated in the six membered ring and are on the opposite side of each other (Fig. 1). We found that this does not increase the cohesive energy.
Table 3: Cohesive energies of all the 9 T–sites of Sn–BEA and Ti–BEA

| T–Sites | Cohesive Energies (eV) Sn–BEA | Ti–BEA |
|---------|-----------------------------|--------|
| T1      | -1521.387                   | -1530.797 |
| T2      | -1521.681                   | -1530.767 |
| T3      | -1521.468                   | -1530.210 |
| T4      | -1521.523                   | -1530.045 |
| T5      | -1521.405                   | -1530.014 |
| T6      | -1521.431                   | -1530.570 |
| T7      | -1521.457                   | -1530.359 |
| T8      | -1521.621                   | -1530.415 |
| T9      | -1521.323                   | -1530.282 |

The cohesive energy of Si–BEA is -1527.902 eV. From Table 3 we see that the cohesive energy of Ti–BEA is about 3 eV higher than that of Si–BEA. This indicates that the incorporation of Ti in BEA is thermodynamically more favorable than that of Sn. Among the 9 T–sites of Ti–BEA we found that the T1 and T2 sites have the highest stability, and that T5 is the least stable. We have also calculated the cohesive energy with two Ti/u.c (i.e. Ti/Si = 2/62 per u.c). The two Ti atoms were incorporated at two different T2 positions at a distance of 9 Å. This showed an increase in the cohesive energy of about 3 eV compared to one Ti/u.c. This reveals that more Ti could be incorporated in BEA than Sn. We want to stress that these calculations are carried out on a dehydrated solid resulting from a thermodynamically driven synthesis, ignoring the effects of the various ingredients and formation conditions, i.e. the nature and energies of the synthesis intermediates. Nevertheless, these results are consistent with the earlier experimental works, where it has been shown that the amount of incorporated Ti is larger than that of Sn in BEA.7,15

3.3 Lewis acidity of Sn–BEA and Ti–BEA

Earlier experimental studies have conjectured that Sn acts as a better Lewis acidic site than Ti in BEA.14−16 Hence, Sn–BEA acts as a more active catalyst for the oxidation reactions. This motivated us to compare the Lewis acidity of Sn and Ti–BEA. First, one must recall that the Lewis acidity, being related with an electron acceptor character, can be correlated with the global electron affinity of the solid. Qualitatively, LUMO energies can be used for a comparison between the electron affinities of Sn and Ti-BEA.24 The HOMO and the LUMO energies, and their corresponding HOMO–LUMO gaps of Sn–BEA and Ti–BEA have been reported in Table
Table 4: Energies of the HOMO, LUMO and the HOMO–LUMO gaps of the 9 T–sites of Sn–BEA and Ti–BEA

| T-Sites | Sn–BEA | | Ti–BEA | |
|--------|--------|--------|--------|--------|
|        | HOMO (eV) | LUMO (eV) | Gap (eV) | HOMO (eV) | LUMO (eV) | Gap (eV) |
| T1     | -3.124  | 1.333  | 4.457  | -3.135  | 1.417  | 4.552  |
| T2     | -3.125  | 1.366  | 4.491  | -3.133  | 1.469  | 4.602  |
| T3     | -3.131  | 1.557  | 4.688  | -3.121  | 1.548  | 4.669  |
| T4     | -3.117  | 1.421  | 4.538  | -3.120  | 1.492  | 4.612  |
| T5     | -3.131  | 1.450  | 4.581  | -3.152  | 1.500  | 4.652  |
| T6     | -3.120  | 1.426  | 4.546  | -3.145  | 1.453  | 4.598  |
| T7     | -3.121  | 1.419  | 4.540  | -3.156  | 1.486  | 4.642  |
| T8     | -3.117  | 1.497  | 4.614  | -3.144  | 1.470  | 4.620  |
| T9     | -3.114  | 1.506  | 4.620  | -3.121  | 1.454  | 4.575  |

4. Globally, the average LUMO energy among the Sn substituted models is lower than that for the Ti ones. In our earlier results on Sn–BEA, we have shown that out of the 9 T–sites the T1 and the T2 sites have low LUMO energies compared to the other T–sites, and would be the probable sites for the reaction.\(^{27}\) Interestingly, T1 and T2 have been proposed as the most probable sites for Sn substitution from EXAFS experiments.\(^{25}\) The two corresponding LUMO’s have similar low energies, making these two models good candidates as Lewis acids. Both sites have also the smallest HOMO-LUMO gap. A smaller gap, in a solid, correlates with a larger global softness. The most probable Sn-BEA solids would thus correspond to the most Lewis acidic and the more “soft” models.

In the case of Ti–BEA, we can see from Table 4 that the T1 site has the lowest LUMO energy, whereas T3 has the highest. We can also notice that T1 and T2, which have the largest cohesive energies, have also low HOMO-LUMO gaps, T1 having the smallest. Considering these two factors together, we propose that these sites would be also the most favorable sites for the substitution by Ti and also for the reaction to take place. We propose thus that, in both cases, Sn and Ti would be more probably substituted at the T1 and T2 sites. Considering their LUMO energies, about 0.1 eV lower for Sn-BEA, we can infer that Sn–BEA is more Lewis acidic than Ti–BEA. Moreover, the corresponding HOMO-LUMO gaps being lower for Sn- BEA than for Ti-BEA, this also suggests that Sn-BEA is a softer acid. This conclusion is also supported by the following trend: whereas the cohesive energies of the T1-T9 substituted Sn-BEA solids spreads on 0.36 eV, those of the Ti-BEA solids...
spread over 0.66 eV. Despite its smaller radius, Ti has thus less ability to adapt to the various geometric environments, showing the behaviour of a "harder" species.

### 3.4 Hydrophobicity of Sn–BEA and Ti–BEA

One of the important issues concerning the selectivity towards the organic molecules in zeolites, is the hydrophobic character of these catalysts.\(^{18}\) Indeed, for reactions such as BVO and MPVO in the presence of aqueous solvents, zeolites containing both, Lewis acidity and hydrophobicity would be the most appropriate.\(^{20,28}\) In fact, being a product of reaction, water is always present in the catalyst pores. However, this presence is not desirable, because its adsorption is competitive with that of reactants and also due to the product hydrolysis. On a perfect silicate surface, water is physisorbed, i.e., its interaction energy is weak, mainly due to van der Waals forces.

As soon as defects are present, water may bind to the silanols or dissociate and react with the surface.\(^{29}\) In order to be hydrophobic, zeolites must thus present less or no defects. If this is achieved, i.e. for highly hydrophobic samples, experimental results show that substituted Ti- BEA is much more hydrophobic than Sn-BEA.\(^{20}\) Although it is hardly possible to compare Ti-BEA and Sn-BEA with a high loading of water, it is of particular interest to investigate, at the microscopic level, the coordination of Sn and Ti sites in presence and absence of one water molecule. For this comparison, Sn and Ti have been located at sites T2 and T1, respectively. The full systems have then been optimized.

Table 5 gives the averaged optimized T–O(BEA), T–OH\(_2\) bond lengths, T–O–Si bond angles and the T–Si distances, where T = Sn and Ti. We can see that after hydration, the Sn–O distance has been increased by 0.014 Å and the Sn–O–Si angle is also increased by about 2.3 degs with respect to the dehydrated Sn–BEA. The bond distance between the Sn site and the H\(_2\)O is 2.41 Å. The hydrated Ti–BEA shows a similar trend with a Ti–O bond length and the Ti–O–Si bond angle which have been increased by 0.019 Å and 2.9 degs, respectively. The Ti–OH\(_2\) bond distance is 2.35 Å. We see that the Sn–OH\(_2\) distance is longer than Ti–OH\(_2\). In order to understand the adsorption of the H\(_2\)O molecule to the T sites, we have calculated the binding energy (B.E.) (Table 5). This is done as follows

\[
B.E. = E_{\text{complex}}(BEA + H_2O) - \{E(BEA) + E(H_2O)\}
\]

As can be seen from Table 5, the B.E. is positive for both systems. This shows that the formation of the complex is less stable than the separate entities (endothermic), and that water molecules do not like to form a stable complex with either of the sites viz. Sn and Ti in BEA. Furthermore, the Ti–BEA and H\(_2\)O complex is \(\sim 3\) kJ/mol less stable than the Sn–BEA and H\(_2\)O complex.
Table 5: Structural parameters and the binding energies (B.E.) of Sn–BEA and Ti–BEA in the presence of H₂O

|                  | Sn–BEA + H₂O | Ti–BEA + H₂O |
|------------------|--------------|--------------|
| T–O(BEA) (Å)     | 1.923        | 1.818        |
| T–O–Si (deg)     | 146.50       | 154.66       |
| T–Si (Å)         | 3.369        | 3.330        |
| T–OH₂ (Å)        | 2.412        | 2.350        |
| B. E. (kJ/mol)   | 4.87         | 7.82         |

These results are in qualitative agreement with the experimental findings that Sn- and Ti-BEA are hydrophobic Lewis acid catalysts. However, they may also appear surprising since adsorption of one water molecule has been reported on Ti-zeolites with low but exothermic interaction energies. This difference may be due to the nature of the zeolite framework (beta versus offretite) or to the type of calculations (cluster versus periodic). It must be recalled that interaction energies calculated with DFT based methods do not include van der Waals attractive contributions. In recent work, these dispersion terms have been added empirically or using adequate correlation functionals. It is easy to give an a posteriori estimate of the van der Waals stabilization of water bound to the Sn or Ti sites in BEA, using an empirical correction. Using our optimized Sn and Ti structures, the van der Waals stabilization energy of the bound water molecule has been calculated using the universal force field. The following energies have been found: -3.3 kcal/mol for Sn-BEA and -2.4 kcal/mol for Ti-BEA. Since these empirical van der Waals terms are additive, one can infer that a water dimer would form a very low exothermic complex with the Sn-BEA model, but would still be non bonding with the Ti model. Hence, these results show that Ti–BEA is more hydrophobic than Sn–BEA. This confirms the earlier experimental findings.

3.5 Reactivity of Sn–BEA and Ti–BEA towards cyclohexanone and H₂O₂

We have applied the HSAB principle to understand the reactivity of Sn– and Ti–BEA towards cyclohexanone and H₂O₂. Pearson formulated the concept of HSAB principle for understanding the reactivity of chemical systems, and their interactions. This gave a new insight in interpreting the reactivity of chemical systems on the basis of their HOMO and LUMO energies. The systems can be categorized as soft acid (SA) with low lying LUMO, soft base (SB) with high lying HOMO, hard acid (HA) with high lying LUMO and hard base (HB) with low lying HOMO. It has
Table 6: HOMO and LUMO energies of cyclohexanone and H$_2$O$_2$

|        | HOMO  | LUMO  |
|--------|-------|-------|
| Cyclohexanone | -5.066 | -1.333 |
| H$_2$O$_2$    | -5.730 | -1.546 |

been well established that the interactions between SA–SB are covalent, HA–HB are ionic and SA–HB or HA–SB are mostly weak electrostatic and form Lewis adducts.

In earlier experimental studies it has been proposed that the Sn site in BEA polarizes the carbonyl oxygen atom of cyclohexanone and forms a Lewis adduct.\textsuperscript{14,15} From above, we have shown that Sn-BEA behaves as a SA, compared with Ti-BEA. Table 6 presents the HOMO and LUMO energies of cyclohexanone and H$_2$O$_2$. We observe that the HOMO energy of cyclohexanone is $\sim$60 kJ/mol lower in energy than the HOMO of H$_2$O$_2$. Hence, cyclohexanone and H$_2$O$_2$ are HB and SB, respectively. From the HSAB principle we infer that the Sn–BEA interacts with the cyclohexanone molecule to form a SA–HB complex or a Lewis adduct.

4 Conclusions

The present theoretical investigation reveals the differences between the Sn–BEA and Ti–BEA based on their structural, Lewis acidic and hydrophobic properties. Our analysis shows that the Sn and Ti atoms may occupy T2 and/or T1 crystallographic positions in BEA. Although the first coordination shell of Sn is larger than Ti, the second coordination shell in both model zeolites is similar. This explains the relaxation of the local environment of the substituted site. The structural data on Sn–BEA and Ti–BEA presented in this work are in good agreement with the earlier experimental studies. The cohesive energy results demonstrate that the incorporation of Ti is more favorable than Sn in BEA. Nevertheless, we show that Sn–BEA is more Lewis acidic than Ti, and hence proves to be a more efficient catalyst for the oxidation reactions than Ti–BEA. One of the important aspects concerning the activity and selectivity of the zeolite which we have addressed in the present work, is the water resistant property of the Sn–BEA and Ti–BEA. A stable interaction of H$_2$O with the active sites of Sn–BEA and Ti–BEA is more favorable with Sn–BEA. Hence, the hydrophobic property of the Sn–BEA and Ti–BEA zeolites is predicted, as well as their comparison. This clearly justifies the water resistant Lewis acidic sites in Sn–BEA. We also extend our analysis to explain that the interaction of the water molecule with the Ti and the Sn sites in BEA is a mere physisorption rather than chemisorption. Furthermore, we use the HSAB principle to interpret the formation
of Lewis adduct between the Sn site and the cyclohexanone.

The present work gives thus an insight into the microscopic properties of the active sites in Sn–BEA and Ti–BEA and the differences between them, which would have been otherwise difficult to understand through experimental methods.

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†University of Pune.
‡Ecole de Chimie.
§National Chemical Laboratory.
*Corresponding Author

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