Probing Lewis acidity and reactivity of Sn- and Ti-beta zeolite using industrially important moieties: A periodic density functional study

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Abstract
The Lewis acidic nature and reactivity of two industrially important catalysts, viz., Sn and Ti substituted beta zeolite (T-BEA) are analyzed using a unique combination of structural parameters, energetics and reactivity descriptors. To achieve this purpose, we adsorb the industrially important moieties (L) namely NH₃, H₂O, CH₃OH, CH₃CN on the active sites of T-BEA. The calculations were performed using a periodic density functional method where the valence electrons are described using a plane wave basis set in conjunction with pseudo-potentials for the core electrons. The analysis of the structural properties of these complexes reveals that TO₄ shows typical characteristic splitting 120°/90°, close to bipyramidal geometry as compared to tetrahedral symmetry observed in the bare T-BEA. This is associated with small variations in the framework bond lengths (≥0.08 Å) and a substantially large variation of bond angles (≤10°) in all the ligand-zeolite complexes. Further in both cases of Sn and Ti substituted beta zeolite, ligand interacts at optimum inter-atomic bond distance. Our interaction energies show that adsorption of all ligand moieties is stronger at Sn center than that of Ti. In general, the order of stability of the different T-BEA adducts is NH₃ > H₂O > CH₃OH > CH₃CN. The ligand interaction is associated with the corresponding bond elongation and bond reduction of the adsorbed molecules on catalyst active site, which can be taken as measure of red or blue shifted frequencies. Finally, the global descriptors of reactivity justify the fact that soft acid, Sn-BEA, interacts strongly with soft bases following the Pearson’s HSAB principle. However, hard acid, Ti-BEA interacts with soft bases to form a stable Lewis adduct. Furthermore, the HOMO–LUMO gap of all Sn-BEA–L adducts is lower than that of Ti-BEA–L adducts indicating to its higher Lewis acidic nature compared to Ti-BEA.

1. Introduction

In the development process of new, selective and recyclable eco-friendly catalyst, zeolite beta (BEA) was synthesized in 1967 [1]. Later, on successive resolution of beta structure, such as high Si/Al ratio and its large pore size (12-membered ring channel) [2,3] over CHA and TS-1, attracted a great industrial interest in organic chemical conversions [4–7]. It was successfully used for acid catalyzed reactions [4], catalytic cracking [6], aromatic and aliphatic alkylation [7]. Some of the industrially important reactions catalyzed by BEA are alcohol and alkane oxidation, olefin epoxidation, aromatics hydroxylation, and cyclohexanone aminoximation. The broad catalytic activity of this solid material was attributed to the presence of isolated tetrahedral T(IV) (T-site) atoms in the framework position.

Titanium is one of the important metals which have been incorporated into the zeolite framework of larger pore and into mesoporous molecular sieves [8]. An important development to this class of catalyst was the synthesis of aluminium-free-titanium beta zeolite in fluoride medium [9]. Thus, Ti incorporated BEA zeolite not only resulted in good adsorption and catalytic properties, but also it opened the possibility for introducing other Lewis acid metals into the beta zeolite framework. Consequently, Corma et al. introduced Sn in the BEA framework and it was shown to have better catalytic activity than Ti-BEA [10]. In addition to this Mal and Ramaswamy, for the first time, synthesized and characterized the Al-free–Sn-BEA [11]. The Sn-BEA showed singular activity for Bayer–Villiger (BV) oxidation reaction, Meerwein–Ponndorf–Verley reduction of aldehydes and Oppenauer’s oxidation of alcohols (MPVO) [10a,12–14]. In addition, it was active for all reactions named above, all of them involving carbonyl compound. On the contrary, Ti-BEA showed no activity for BV oxidations. Sn was predicted, to be a stronger Lewis acidic site than the Ti, due to higher electronic negativity of Sn than Ti. The isolated Sn(IV) in BEA was
characterized by Sn MAS NMR and in situ EXAFS spectroscopy [12].

Since the catalytic properties are inherently connected to the structural properties of a site, there have been several studies attempting to understand the structural issues in these two zeolites. The various experiments successfully proved the tetrahedral coordination of tin atoms in the BEA framework [12]. However, the structural features of the local active sites in isomorphically substituted zeolites have not been well understood from the experimental techniques. This necessitates a theoretical investigation [15–17] so as to have a better understanding on the nature and the structure of the active sites and their respective reactivities. The periodic approach is the most correct model [18–20] and the only one able to account for long range effects and for constraints acting on a [TO4] (where T stands for tetrahedral, T-site) unit and thus predicts the structural features more accurately. This was verified from one of our recent studies [21], where we had reported the structural and reactivity differences of the Ti-BEA and Sn-BEA using periodic-DFT.

The structural studies in the above paper revealed that the Sn and Ti atoms preferably occupy the T2 and/or the T1 sites among the nine in-equivalent T-sites of zeolite beta. The cohesive energy results demonstrate that the incorporation of Ti is more favorable than Sn in BEA. With the use of LUMO energies and the local Fukui Functions, we compared the Lewis acidity of these two substitutions and confirm the higher acidic nature of Sn. However, surprisingly, the Sn-BEA exhibited higher hydrophilicity than the Ti-BEA. Apart from the hydrophilic and/or hydrophobic nature comparison, we can take the water adsorption as the measure of the strength of Lewis acid base interaction. The strong interaction of the basic water molecule at the active Sn site than that of Ti assures its higher acidic nature.

The catalytic activity of a Lewis acid for oxidation is related to its ability to form acid–base adducts with either the substrate or the oxidizing agent, enhancing its reactivity. The formation of adduct implies an electron density transfer from the Lewis base to the Lewis acid which is directly proportional to the energy difference and degree of overlap between the occupied orbital of the base and the empty orbital of the acid. Therefore, the strength of a Lewis acid can be related to the energy of its LUMO in such a way that the lower the LUMO energy, the easier its interaction with a base molecule [21–24]. However, other factors influence the acid–base interaction. For example, one such factor is the HSAB (hard–soft acid–base) principle, which states that hard acids coordinate preferentially to hard bases and soft acids with soft bases [25,26]. Another factor to be considered is the possibility of back-donation of electron density from the Lewis acid to the unoccupied orbital of the Lewis base [21]. An interaction may or may not occur, depending on the energy difference and degree of overlap between the orbital involved [22]. Modification of the electronic levels of both the metal and the molecule, after the adsorption of a basic molecule on the metal center, should also be taken into account. Hence, the activity of a catalyst for a given reaction depends not only on the properties of the isolated active site, but also on the changes caused by its interaction with the reactant molecules [25,26]. This latter approach has been adopted by several experimentalists using in situ IR and EXAFS spectroscopies [12,18] and theoricians [20,22,24,27–31] using simple adsorption model of basic moieties at catalytic active centers. The above mentioned parameters are analyzed in the present paper on metal substituted beta zeolite-ligand complexes.

In the past [20,24,27–31] main attention has been devoted to study of the Ti(IV) center reactivity in various zeolites such as TS-1, CHA etc., through the adsorption of NH3 and H2O. Bor-diga et al. [27,32,33] study the adsorption of CO2 and pyridine on Ti centers of the TS-1. They confirm their results with the experimental vibrational spectra. Similarly, Corma and co-workers [28] performed the in situ IR and DFT calculations with deuterated acetonitrile to outline the peculiarities of Sn-BEA. However, most of these studies consider a cluster model approach. The main drawback of the cluster model in the characterization of Ti(IV) Lewis centers using adsorption model is twofold: (1) the high dilution of the Ti(IV), where T/Si is lower than 1/30 (here in BEA also we have only one T/Si ratio) and (2) the presence of the framework defects (Si vacancies) generating internal hydroxyl groups.

Hence, in our present paper, we execute periodic-DFT (p-DFT) for the interaction study of important basic moieties adsorbed at the active sites of Sn-BEA and Ti-BEA. To study the interaction, we consider the basic moieties such as NH3, H2O, CH3OH, CH3CN. The clear interest towards NH3 and H2O molecules is the direct comparison with previous results. In addition, the NH3 molecule is used in ammoximation of cyclohexanone to give cyclohexanone oxime as reagent. Also it is a stronger base than the H2O molecule which helps direct comparison due to the effect induced by the Lewis base of the increasing strength. The choice of other molecules such as CH3OH and CH3CN is justified by the important role played by these moieties in the industrial application of BEA. The Lewis acid–base adducts thus formed is taken as measure of strength of interactions to compare the acidity of Sn and Ti centers in the BEA. The results are in qualitative agreement with previous studies. The bond elongation, bond reduction of adsorbed bases and deformation of TO4 moiety is reported in detail for each adduct. In particular, we also report the discrepancy played by the weak bonds such as hydrogen bond in predicting misleading strength of interaction for that of Sn-BEA. In addition, difference in the interaction energies for Sn-BEA and CH3CN using periodic and cluster model is clearly highlighted.

The work is organized as follows: Section 2 elaborates the periodic model of T-BEA and the respective adducts formed after adsorption of L. Section 3 discourse the computation used to model and calculate the systems. Section 4 imparts the finding of these calculations, mainly, the comparative study of adsorption of the above mentioned basic moieties to study the deformation and hence resulted reactivity. Section 5 finally concludes the results.

2. Simulation model

In this simulation, we use the periodic-DFT (p-DFT) to built the Ti-BEA, Sn-BEA and their adducts with different basic molecules (L=NH3, H2O, CH3OH, CH3CN). The unit cell of BEA is shown in Fig. 1. BEA is highly siliceous material, with 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 dimensions (12.6 Å × 12.6 Å × 26.2 Å). There are nine distinct crystallographically defined T-sites. We adopt the structure of the BEA from our earlier theoretical study [21b]. In our earlier analysis [21b], we found that the Sn and Ti atom occupy T2 and/or T1 crystallographic positions in BEA. Hence, in the rest of the calculations we use single substituted Sn at T2 and Ti at T1 positions. The interaction of basic molecules at the active site is very important, since it gives rise to geometric perturbation and the energetic differences. We tried the various possible approaches of the basic molecule at the active site. Many of these resulted in high energy and high force values. The most favorable ligand approach at the active T-site is along the b axis (see Fig. 2). This insertion gives rise to geometric distortion [27–29]. Schematic representation of T-BEA–L is given in Figs. 2 and 3. We built the same periodic environment i.e. size of unit cell, grid size etc for the T-BEA–L adducts and bare L molecules as that of the bare solid i.e. T-BEA.
3. Computational details

All the calculations are performed using VASP code which utilizes p-DFT [34]. The periodic boundary conditions facilitate one to add long range electrostatic interactions that are included in Ewald summations. Similar to normal DFT programs, the stationary ground state in p-DFT is calculated by solving Kohn-Sham equations. However, the most common practice of p-DFT programs to represent valence electrons is the use of plane waves (PW) in conjunction with pseudo-potentials (PP) for the core electrons. We use Vanderbilt's ultrasoft pseudo-potentials [35]. The optimized T-BEA model [21b] was employed as the starting geometry to study the interaction of T-BEA zeolite with all probes. The adducts so formed have been fully optimized at 500 eV PW basis cut-off without any geometrical constraints. The interactions thus obtained are further evaluated at 1000 eV cut-off considering single point convergence. The impact of high PW cut-off in the calculation of energy dependent properties, such as interaction energy, is recently illustrated in the literature [36]. The exchange-correlation functional is expressed by the generalized gradient approximation (GGA) with the Perdew-Wang 91 functional [37]. The calculations were restricted to the gamma point in the Brillouin zone sampling. The structural optimization of the Sn- and Ti-BEA has been carried out using conjugate gradient method. The optimization was considered to be achieved when the maximum force on the atoms was less than 0.08 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. This is due to the fact that the percentage of Sn and Ti in BEA is only 1/u.c. Similar optimization procedure is repeated for the calculation of Sn-BEA and Ti-BEA with all basic molecules, L, interacting at the Sn and Ti centers, respectively. The optimization of bare L moieties is derived with same computational procedure.

4. Results and discussion: interaction of T-BEA with NH3, CH3CN, CH3OH and H2O

The least energetic approach of the ligand moieties on the active T-site in the BEA are shown in Figs. 2 and 3. The NH3 and CH3CN interact with Sn and Ti centers via N atom as shown in Fig. 2, where as CH3OH and H2O interact via O atom as shown in Fig. 3. This sec-
tion first discusses the common structural features of all adducts and further it investigates the comparative interaction energy differences and predicts the trend of reactivity of all moieties with the respective catalyst. Following this with the help of global descriptors of reactivity, LUMO (of catalyst) and HOMO (of ligands) we will summarize the inter-reactivity trend for Sn and Ti substitutions.

4.1. Structural deformation of T-BEA framework upon ligand adsorption

Table 1 presents the optimized structural details and the reactivity descriptors of Sn-BEA and Ti-BEA. It should be noted that only the active site of zeolite and interacting atom of adsorbed ligand, T–L, and metal active center, T–Sieq bond reduces by \(0.14\) Å in both the Sn- and Ti-BEA framework upon interaction with all ligands. The average variations of Ti–O bonds reported above agree well with the EXAFS data [32,33]. Interestingly, earlier cluster calculations [38] also report a similar range of variations. Accordingly, the T–Si bond distances also show variation in the T-BEA–L complexes compared to the bare T-BEA. Unlike T–Oeq bonds, T–Sieq bonds optimize to lower bond lengths compared to T–Si distances present in the bare T-BEA. Once again, irrespective of ligand nature and metal active center, T–Sieq bond reduces by \(0.04\) Å. However, the T–Sieq bond further elongates by \(0.14\) Å in respect to Ti and Sn–BEA adducts. The Sn–BEA–CH\(_3\)OH adduct is exception here, where the Sn–Sieq bond show strong reduction where as the Sn–Sieq bond result in shorter elongation.

As discussed, hydrogen bond (H\(_L\)–O\(_T\)) is observed between the ligand hydrogen (H\(_L\)) and framework oxygen (O\(_T\)). At T1 site (Ti substituted site) these hydrogen bonds formed are shorter in bond length but at T2 site (Sn substituted site) these bonds result in weak bonding. In the case of Ti–BEA–NH\(_3\) adduct, we report strong hydrogen bond of 2.23 Å which later on results in elevated interaction energy of NH\(_3\) with Ti center as will be elaborated in next section. The most important inter–molecular bond length, distance between active site of zeolite and interacting atom of adsorbed ligand, T–L, is reported in Table 2. It is seen from the table that NH\(_3\) molecule is optimized at a distance of 2.35 Å from the Ti center (T1 site) of BEA, being slightly shorter (about 0.017 Å) compared to that obtained on the Ti-CHA model [26b]. The Sn–BEA–NH\(_3\) distance optimizes at 2.38 Å. Similarly, the CH\(_3\)CN interaction optimizes at 2.35 and 2.38 Å from Ti and Sn centers of BEA, respectively. In general, the ligands containing oxygen atom as donor atom converge to longer inter–molecular bond. The CH\(_3\)OH optimizes, respectively, to 2.46 and 2.44 Å at Ti and Sn centers. The Sn–BEA–OH\(_3\) inter–molecular bond optimizes at 2.38 Å. The Ti–BEA–OH\(_2\) bond length optimizes at 2.44 Å.

To conclude, the Ti–O–Si bond angles, which range between 144° and 163°, are larger than the Sn–O–Si angles (142–159°). This can be attributed to the angular flexibility of small sized Ti. This angle reduces exceptionally during the formation of Sn–BEA–CH\(_3\)OH adduct. In addition, ligand approach at active T2 site
is more linear, L–T–O_T angle being close to 180°, where as same angle at T1 site is close to ~170° (see Fig. 4). Consequently, six O–T–O angles in the respective adduct of Sn- and Ti-BEA split to different extent. The order of O–T–O angle splitting vary with respect to strength of ligand as NH₃ > CH₃CN > CH₃OH. Thus, the structural study of adducts conjecture that irrespective of the ligand nature, the bond length variation of the framework atoms is restricted in fixed range, however, bond angles deviates to different magnitudes. Similarly, irrespective of the catalyst active center, Sn or Ti, ligand interacts at optimum bond distance.

4.2. Energetics of interacting T-BEA and ligands (L)

In this subsection, we discuss the strength of interaction of various ligands with Sn-BEA and Ti-BEA so as to highlight the distinct Lewis acidic nature of Sn and/or Ti centers. For this purpose, we calculate the interaction energy defined as the difference between the energy of adduct formed at equilibrium and the energy of the constituent molecules in their ground state. This is calculated as follows,

\[
\text{Interaction energy} (E_{\text{int}}) = (E_{\text{T-BEA + L}}) - E_{\text{T-BEA-L}}
\]

In our earlier investigation on the hydrophilicity of Sn- and Ti-BEA [21b], we showed that the energy of H₂O interaction with Sn-BEA is 0.3323 eV and that of with Ti-BEA is 0.1342 eV. The Sn site in BEA is more hydrophilic compared to Ti site. This also confirms the higher Lewis acidic nature of Sn-BEA. As the water is the most common reaction medium, H₂O gains extreme importance in determining the catalyst activity study. Thus, water not only coordinates with catalyst active center but many times poisons the site and reduces its reactivity. Here, we do not consider the structural details of the T-BEA and H₂O adduct. The geometric features concerning the T-BEA–H₂O adducts are reported by us in the earlier study [21b]. For detailed interest one can refer to this study. We are going to extrapolate the analysis of this exothermic interaction of water to analyze the interaction of all ligands with both the Sn and Ti centers. The interaction energy of all ligands with Sn- and Ti-BEA is reported in Table 3. The interaction energies reported in bracket are calculated at high PW cut-off of 1000 eV.

By the simple chemist intuition, we expect the higher acidic Sn center to result in stable interaction with the strong base NH₃ to form a better Lewis adduct than the less acidic Ti center. However, interaction energies of NH₃ ligand with the Sn and Ti substituted beta zeolite contradict these findings. Table 3 highlights the increase of interaction energy by 0.02 eV (0.06 eV at 1000 PW cut-off), while going from Sn to Ti center. Although this increase in the interaction energy is not considerable, we attribute this discrepancy to the distortion in the local environment after the adsorption of NH₃ as discussed below. The interaction of NH₃ is considered at T1 site of Ti-BEA where as for Sn-BEA it is at T2. Although the Sn–O–Si bond angles are smaller than Ti–O–Si, the Ti center shows better angular flexibility due to its small atomic radius [21b]. As a result, hydrogen bond formed between the framework oxygen and the ligand hydrogen atoms (NH₃) is retained during the optimization. However, due to lack of Sn–O–Si angular flexibility there is no such hydrogen bonding observed for the adsorbed NH₃ in the case of Sn-BEA (ref. Table 2). The H₂–O₂ bond lengths are reported in Table 2. The shortest bond distance between hydrogen atom of ammonia and framework oxygen in Ti-BEA–NH₃ adduct is 2.24 Å where as same for Sn-BEA–NH₃ adduct is 2.72 Å. This strong hydrogen bonding interaction of Ti-BEA–NH₃ adduct reflects in step up interaction energy compared to Sn-BEA–NH₃ adduct. We also carry a test calculations of NH₃ interacting with Sn-BEA, where, Sn is now substituted at T1 site. Surprisingly, interaction energy is 0.78 eV (an increase of 0.49 eV from its T2 site). At T1 site, Sn-BEA–NH₃ does not fail to count the strong hydrogen bond. The shortest hydrogen bond thus formed is 2.33 Å and NH₃ optimizes at shorter bond length of 2.33 Å. Therefore, though the structural arrangement of atoms look equivalent in the unit cell model of BEA, the electronic difference in local environment of the active site plays an extensively important role in deciding materials catalytic behavior. The corresponding adsorbed N–H bonds are very weakly elongated in Ti-BEA–NH₃ adduct (about 0.001 Å). On the other hand, elongation is about 0.016 Å for Sn-BEA–NH₃ adduct. This elongation of interacting ligand–N–H bond can be taken as evidence of red shift in IR frequency and hence measure of strength of interaction at catalyst active site.

An earlier experimental study of the vibrational properties of CH₃CN adsorbed on different zeolite, TS-1, as an evidence for the presence of Lewis acidic centers [27] associated with Ti(IV) was given by Bonino et al. They found that acetonitrile forms a labile adduct with the Ti of TS-1 with a Δυ(CN) stretching frequency of +37 cm⁻¹. Analogous experiment on Sn-BEA has been recently carried out by Corma and co-workers [28,29]. Their study also predicted a blue shifted Δυ(CN) stretching frequency of +42 cm⁻¹. In addition, to study the structure–activity relation of catalyst they had carried out a computational study based on a cluster model approach. Interestingly, their model comprised of various reaction sites and various neighboring groups. For the comparison purpose, we restrict ourself to pure siliceous environment of Sn center and do not consider their hydrolyzed model. In line with their frequency analysis, the CN distance in our calculation passes from 1.16 Å (bare one) to 1.156 Å (engaged one) predicting blue shift of the υ(CN) stretching frequency. This result is in qualitative agreement with the results reported in previous literature [27–29]. In particular, the interaction of probe molecule such as acetonitrile with Lewis acid center involves electron density transfer from lone pair

### Table 1

Optimized structural parameters of Sn-BEA and Ti-BEA.

<table>
<thead>
<tr>
<th>Adducts</th>
<th>T–O (Å)</th>
<th>T–Si (Å)</th>
<th>T–O–Si (°)</th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
<th>Δ(H–L) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₃/Ti</td>
<td>1.80–1.88</td>
<td>3.24–3.45</td>
<td>2.35</td>
<td>2.23 (1)</td>
<td>110.9–131.2</td>
<td>95.0–104.9</td>
</tr>
<tr>
<td>NH₃/Sn</td>
<td>1.89–1.99</td>
<td>3.29–3.53</td>
<td>2.38</td>
<td>2.71 (0)</td>
<td>105.8–137.3</td>
<td>95.5–103.4</td>
</tr>
<tr>
<td>CH₃CN/Ti</td>
<td>1.79–1.88</td>
<td>3.29–3.45</td>
<td>2.35</td>
<td>2.45 (0)</td>
<td>110.1–125.5</td>
<td>93.9–102.5</td>
</tr>
<tr>
<td>CH₃CN/Sn</td>
<td>1.89–1.99</td>
<td>3.31–3.52</td>
<td>2.38</td>
<td>2.90 (0)</td>
<td>107.0–129.1</td>
<td>94.0–107.0</td>
</tr>
<tr>
<td>CH₃OH/Ti</td>
<td>1.80–1.86</td>
<td>3.26–3.43</td>
<td>2.46</td>
<td>2.54 (1)</td>
<td>111.3–121.7</td>
<td>102.4–105.9</td>
</tr>
<tr>
<td>CH₃OH/Sn</td>
<td>1.89–1.98</td>
<td>3.22–3.45</td>
<td>2.44</td>
<td>2.57 (1)</td>
<td>106.6–129.8</td>
<td>100.6–103.5</td>
</tr>
</tbody>
</table>

### Table 2

Optimized structural parameters of T-BEA–L adducts.

<table>
<thead>
<tr>
<th>Adducts</th>
<th>T–O (Å)</th>
<th>T–Si (Å)</th>
<th>T–L (Å)</th>
<th>H₂–O₁ (Å)</th>
<th>α (°)</th>
<th>β (°)</th>
<th>T–O–Si (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₃/Ti</td>
<td>1.80–1.88</td>
<td>3.24–3.45</td>
<td>2.35</td>
<td>2.23 (1)</td>
<td>110.9–131.2</td>
<td>95.0–104.9</td>
<td>144.1–161.9</td>
</tr>
<tr>
<td>NH₃/Sn</td>
<td>1.89–1.99</td>
<td>3.29–3.53</td>
<td>2.38</td>
<td>2.71 (0)</td>
<td>105.8–137.3</td>
<td>95.5–103.4</td>
<td>142.3–159.4</td>
</tr>
<tr>
<td>CH₃CN/Ti</td>
<td>1.79–1.88</td>
<td>3.29–3.45</td>
<td>2.35</td>
<td>2.45 (0)</td>
<td>110.1–125.5</td>
<td>93.9–102.5</td>
<td>146.6–163.2</td>
</tr>
<tr>
<td>CH₃CN/Sn</td>
<td>1.89–1.99</td>
<td>3.31–3.52</td>
<td>2.38</td>
<td>2.90 (0)</td>
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<td>141.4–150.1</td>
</tr>
</tbody>
</table>
of nitrogen to the catalyst LUMO, as a result CN bond reduces and τ(CN) frequency shifts to higher value. The computed blue shift, accompanied by a reduction of −0.005 Å of the C–N distance (compared to bare CN distance), proves the strong adsorption of the CH$_3$CN on the T-BEA active centers. This fact is well reproduced in the interaction energy calculation with the both T substituted BEA. Although, the cluster model predicted T–L bond lengths match well with our periodic model the interaction energy values differ from ours [28]. The interaction energy of Sn–BEA with CH$_3$CN predicted by the cluster model approach was 0.3 kcal/mol [28]. However, the additive long range interactions covered in periodic model results in an interaction energy increase of 3.45 kcal/mol. This difference can be attributed to the additive interaction. The interaction energy of CH$_3$CN with Ti–BEA adduct is 0.032 eV (0.008 eV at 1000 eV PW cut-off). Thus, the interaction of Sn–BEA is stronger with CH$_3$CN than that of Ti–BEA.

The CH$_3$OH is reagent of prime interest in several industrial reactions. The lone pair present on the O atom of CH$_3$OH should be more attractive towards the positive centers present in substituted BEA. Similar to CH$_3$CN interaction, the interaction energies computed for Sn–BEA, Ti–BEA and CH$_3$OH show large differences. The Sn–BEA and CH$_3$OH interaction is stronger and turns out to be 0.295 eV (0.301 eV at 1000 eV PW cut-off). On the other hand, the Ti–BEA and CH$_3$OH interaction energy is 0.0716 eV (0.098 eV at 1000 eV PW cut-off). In the optimized structure of Ti–BEA–CH$_3$OH, C–O bond is 1.46 Å and O–H bond is 0.97 Å (i.e. elongates to +0.02 and +0.006 Å with respect to bare molecule). For Sn–BEA adduct, the C–O bond shows elongation by 0.013 Å and OH bond by 0.003 Å. The computed elongations can be accounted as measure of adsorption of CH$_3$OH on the active centers, resulting in the red shifted frequencies. This is a consequence of structural differences around T1 and T2 sites of the beta zeolite.

The present energetics of ligand interaction reveals that all the basic moieties result in exothermic interaction with Sn and Ti sites. Furthermore, the higher interaction energies of Sn–BEA–L adducts confirm their stability compared to Ti–BEA–L adducts. The ligand interaction is associated with the respective bond elongation and bond reduction of the adsorbed molecules on catalyst active site, which can be taken as measure of red or blue shifted frequencies. In general, the order of stability of the different T–BEA adducts is NH$_3$ > H$_2$O > CH$_3$OH > CH$_3$CN. For Sn–BEA, this order is slightly reversed, viz., the H$_2$O interacts strongly with Sn–BEA compared to NH$_3$. However, in next section of reactivity descriptors, frontier orbital energies, justify the permanence of these respective interactions. The interactions of CH$_3$CN and CH$_3$OH are almost negligible with Ti–BEA. In conclusion, the higher acidic Sn site interacts strongly with all basic moieties compared to lesser acidic Ti site.

4.3. Reactivity of T-BEA towards ligands (L)

We have applied the HSAB principle to understand the reactivity of Sn- and Ti-BEA towards ligand moieties. Pearson formulated the concept of HSAB principle for understanding reactivity of chemical systems and their interactions [25,26]. This gave a new insight in interpreting the reactivity of chemical systems on the basis of their HOMO and LUMO energies [25,26]. Thus a system can be categorized as soft acid (SA) with low-lying LUMO, soft base (SB) with high lying HOMO and hard acid (HA) with high lying LUMO where as hard base (HB) with low-lying HOMO. It has 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. Here, we must recall that the Lewis acidity, being related with an electron acceptor character, can be related with the global affinity of the solid [21b,22,23]. Qualitatively, LUMO energies can be used for a comparison between electron affinities of Sn– and Ti-BEA. The HOMO and the LUMO energies and their respective HOMO–LUMO gaps of all the ligand molecules. We summarize the HOMO–LUMO gaps of all T-BEA–L adducts in Table 3. The global descriptors of reactivity thus explain the fact that soft acid, Sn–BEA, interacts strongly with soft bases H$_2$O, NH$_3$ and CH$_3$OH to give a covalent complex whereas as hard acid, Ti–BEA interacts with same bases to form a stable Lewis adduct. In addition, according to the above definition, interaction between CH$_3$CN with Ti–BEA is weakly ionic (see Table 3: interaction energy is negligible) whereas as interaction of CH$_3$CN with Sn–BEA strongly electrostatic (Lewis acid–base adduct) in nature. In general, interaction of Sn–BEA is strong with all ligands compared to Ti–BEA (compare interaction energies of respective adducts). Table 3 also summarizes the HOMO–LUMO gaps of all T–BEA–L adducts. The HOMO–LUMO gaps of all Sn–BEA–L adducts is lower than that of Ti–BEA–L adducts. Thus this explains the greater stability of all Sn–BEA–L complexes. Hence, we can once again state that globally Sn–BEA zeolite results in higher Lewis acidic catalyst forming stable interaction with all basic molecules than the Ti–BEA zeolite.

Other reactivity descriptors such as chemical potential, hardness and philicity of a molecule are also added in Table 4 for the sake of completeness. However, it may be noted that none of these descriptors follow the trend reported by the interactions energies. The reason for this may be attributed to the sensitivity of these descriptors which applies to periodic density functional methods.

In addition to highlight the charge transfer in the interactions of T-BEA and L, we include a short discussion with the help of difference charge density ($\Delta\rho$) plots. The $\Delta\rho$ plots for each type of interaction, viz., covalent, Lewis adduct and ionic are reported in
Fig. 5. Here, the blue signifies charge gain whereas red represents charge depletion. Fig. 5a shows SA–SB, Sn-BEA–H2O interaction. The charge transfer between H2O and Sn is indicated by small blue sphere. The blue sphere along inter-molecular bond, here, represents the bond critical point which can be taken as measure of a strong bonding such as covalent interaction. Fig. 5b and c shows, SA–HB and HA–SB, Lewis acid–base interactions forming Lewis adducts. As discussed in the beginning of this section these interactions are weakly electrostatic in nature and this is well reflected in their $\Delta \rho$ plots. The presence of small red sphere along the intermolecular bonding space here denotes loss of charge whereas blue sphere on ligand donor atom indicates concentration of charge density on it. Similarly, HA–HB, Ti-BEA–CH3CN, ionic interaction is shown in Fig. 5d (for clear visualization not color coded). Fig. 5d clearly shows a polarized charge density between Ti-BEA–CH3CN bonding region which is an indication of ionic bond. Both the atoms, Ti – blue sphere and N – red sphere, show polarization of electronic densities on them.

Table 4

<table>
<thead>
<tr>
<th>Systems</th>
<th>$\mu$</th>
<th>$\eta$</th>
<th>$\omega$</th>
</tr>
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<tr>
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<td>−2.62</td>
<td>−2.23</td>
</tr>
<tr>
<td>CH3OH</td>
<td>−3.54</td>
<td>−2.79</td>
<td>−2.29</td>
</tr>
<tr>
<td>CH3CN</td>
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<td>−3.63</td>
<td>−2.76</td>
</tr>
<tr>
<td>NH3/Sn</td>
<td>−0.44</td>
<td>−2.35</td>
<td>−0.04</td>
</tr>
<tr>
<td>CH3OH/Sn</td>
<td>−0.61</td>
<td>−2.04</td>
<td>−0.09</td>
</tr>
<tr>
<td>CH3CN/Sn</td>
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<td>−2.48</td>
<td>−0.03</td>
</tr>
<tr>
<td>NH3/Ti</td>
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</tr>
<tr>
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<td>−0.06</td>
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<tr>
<td>CH3CN/Ti</td>
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<td>−0.12</td>
</tr>
</tbody>
</table>

5. Conclusion

The reported geometries of the substituted beta and their respective interactions with NH3, H2O, CH3OH and CH3CN are obtained with the plane wave basis code VASP. Catalyst active site T2 and T1 are substituted by Sn and Ti, respectively. All the interactions are fully optimized without any geometrical constraints. The geometric and energetic deformations are discussed successfully using p-DFT.

In the bare T-BEA, TO4 moiety is quite near to tetrahedral symmetry [21b,27,39]. However, the results discussed here predict the deformation of TO4 moiety due to adsorption of basic molecules. In the optimized ligand adsorbed adducts, TO4 shows typical characteristic splitting $120^\circ$/$90^\circ$ thereby resulting into a nearly bipyramidal geometry. Irrespective of the adsorbed ligand nature, the bond length variation of the framework atoms is restricted in fixed range while the bond angles exhibit a larger variation. Similarly, irrespective of the catalyst active center, Sn or Ti, ligand interacts at an optimum bond distance. The interaction energy results demonstrate that all the basic moieties results in exothermic interaction with Sn and Ti sites. Furthermore, the higher interaction energies of Sn-BEA–L adducts confirm their stability compared to Ti-BEA–L adducts. The strength of interaction is also associated with a corresponding bond elongation and/or bond reduction of the adsorbed molecules on the catalyst active site, which can be taken as measure of red or blue shifted frequencies [27,32,33]. In general, the order of stability of the different T-BEA adducts is NH3 > H2O > CH3OH > CH3CN. For Sn-BEA, this order is slightly reversed. The H2O interacts strongly with Sn-BEA compared to NH3. Overall, the interaction of ligands with Sn and Ti substituted beta zeolite depend on a delicate balance of several
factors such as substitution site of metal, angular flexibility around those sites and weak interactions like hydrogen bonds. All these factors reflect in global reactivity descriptors. The global descriptors of reactivity justify the fact that soft acid, Sn-BEA, interacts strongly with soft bases H2O, NH3 and CH3OH to give a covalent complex whereas interaction of CH3CN with Sn-BEA is weakly ionic whereas interaction of Sn-BEA than Ti-BEA.

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