Effect of Si/Al ratio on tetralin adsorption on Y zeolite: a DFT study

Yajun Wang, Chaohe Yang, Yibin Liu, Xiang Feng, Hui Fu & Honghong Shan

To cite this article: Yajun Wang, Chaohe Yang, Yibin Liu, Xiang Feng, Hui Fu & Honghong Shan (2017) Effect of Si/Al ratio on tetralin adsorption on Y zeolite: a DFT study, Molecular Simulation, 43:12, 945-952, DOI: 10.1080/08927022.2017.1308509

To link to this article: http://dx.doi.org/10.1080/08927022.2017.1308509

Published online: 10 Apr 2017.

Article views: 81

View supplementary material

Submit your article to this journal

View related articles

View Crossmark data
Effect of Si/Al ratio on tetralin adsorption on Y zeolite: a DFT study

Yajun Wang, Chaohe Yang, Yibin Liu, Xiang Feng, Hui Fu and Honghong Shan

ABSTRACT
Probing the adsorption of tetralin on zeolite is of prime scientific and industrial importance with the aim to upgrade the industrial process of tetralin cracking. In this work, the effect of Si/Al ratio ranging from 12 to 39 on tetralin adsorption property on Y zeolite is studied by DFT calculations. Tetralin adsorption on Y zeolite corresponds to a π-stacking adsorption mechanism between double bonds of aromatic ring and Brønsted acid sites. Therefore, the number of Brønsted acid sites influences the adsorption properties. Lower Si/Al ratio with more Brønsted acid sites interacting with the aromatic ring of tetralin leads to a higher adsorption energy. Furthermore, the charge and frontier molecular orbital analysis are also performed to understand the influence of Si/Al ratio on adsorption performance. Y zeolite with lower Si/Al ratio shows larger charge difference values and lower HOMO–LUMO gap, which directly manifests the stronger adsorption ability of tetralin and indicates bigger possibility of reacting.

1. Introduction
Cracking of heavy oil molecules is a fundamental catalytic reaction operated in petroleum refinery process. In China, FCC gasoline and light cycle oil (LCO) are used as blend composition of commercial gasoline and diesel, respectively [1]. However, with the declining quality of crude oil and stricter operating conditions, the quality of FCC procts becomes more deteriorative, especially for LCO. LCO is abundant of aromatic content, which induces its low cetane number (CN) [2]. Therefore, much attention has been focused to upgrade approaches to improve the quality of LCO. Hydrotreating [3] is a method to decrease aromatics and to increase CN simultaneously. However, the simple saturation is not enough to reach the required CN because of the low CN of naphthenic rings [2,4]. Therefore, upgrading LCO into commercial diesel is not an effective way. To the contrary, the abundant aromatic components in LCO are favourable in high octane number (ON) gasoline. Cracking of LCO components into gasoline fraction through breaking long sides chains or naphthenic rings can reduce the aromatic content and incerase gasoline ON. For multiring aromatics, they should be firstly saturated into one-ring aromatic and then cracked into gasoline fractions. Therefore, LCO can produce high ON gasoline through hydrogenation–FCC process.

A review of the experimental analysis reported that tetralin was the main intermediate products of the hydrogenation process [5,6]. Tetralin can be the probing molecule for one-ring aromatics that are used as feedstocks of FCC process. Therefore, mechanism of the tetralin cracking can be very important to upgrade the industrial process. Nowdays, density functional theory (DFT) method has become an effective tool to complement experimental results [7,8], predict the preferred T location for the replacement of Si by Al in zeolite [9,10] and analyse the Brønsted acid strength of the zeolite [11,12]. Although the mechanism has been predicted experimentally for tetralin cracking reactions, few theoretical studies have been reported to understand the reaction mechanism and adsorption performance of tetralin on zeolite through the molecular level [13–15]. The first step of tetralin cracking on zeolite is tetralin adsorption. As a result, the adsorption performance of tetralin on zeolite was investigated by means of DFT in this work. An elaborate understanding of adsorption mechanism of tetralin inside zeolite is prerequisite for clarifying catalytic cracking mechanism.

Y zeolite has been widely used as the main component of industrial FCC catalyst due to its environmental-friendly, non-corrosive essence in petrochemical processes [16,17]. Its protonic form has been found to be a significant active constitutent for the catalytic cracking of hydrocarbons [18,19]. During the past decades, great progress has been made towards understanding the structural properties of Y zeolites and corresponding performance. Among other parameters, Si/Al ratio is reported to have great influence on zeolite structures and properties [20–22]. Liu et al. [20] synthesized high-silicon Y zeolite with the Si/Al ratios of 4.54–6.46 and got conclusion that the synthesised zeolite showed high N2 adsorption and BET surface area [23,24]. Namuangruk et al. [25] studied the effect of framework structure on the unsaturated hydrocarbons and pointed out that the essence of adsorption performance is the interaction between Brønsted acid site and C=C bonds. Therefore, these Brønsted
to study the influence of Si/Al ratio on adsorption performances can get some adsorption tendency and explain the adsorption mechanism from microscopic level at the same time.

In this work, the effect of Si/Al ratio on adsorption behavior of tetralin on Y zeolite was elaborated through DFT calculations. The substitution energies of Al and Brønsted acid site are used to confirm the structures of zeolite clusters with different Si/Al ratios. Subsequently, the adsorption energy of tetralin on Y zeolite is calculated to investigate the effect of Si/Al ratio on adsorption property. Moreover, the charge and HOMO–LUMO gap from the perspective of electron transfer are calculated to further understand the influence of Si/Al ratio on adsorption performance. The insights reported here not only unravel the relationship between Si/Al ratio and adsorption property theoretically, but also shed new light on the principle of preparing zeolite with suitable Si/Al ratio based on its application properties.

2. Computational details

2.1. Computational models

The FAU zeolite is composed of sodalite building blocks that contain 192T atoms [28]. As reported in literature, there are two main regions for discussing active sites. One region is a 12-membered ring connected two supercages, which has been widely

![Figure 1](image1.png)

**Figure 1.** (Color online) 40T model in Y zeolite from different angles of view. Note: Yellow, silicon; red, oxygen; purple, aluminium; white, hydrogen.

![Figure 2](image2.png)

**Figure 2.** (Color online) Y zeolite clusters with different Si/Al ratios of 39 (a), 19 (NNN, NNNN) and 12 (c).
investigated for reaction mechanisms and adsorption properties [29,30]. The other is SII site (the centre of the six-membered rings connecting the sodalite cage with the supercage) of Y zeolite [31,32]. Experimental studies [33] showed that SII cation rather than the 12-ring window cation are the preferential adsorption sites for benzene. Additionally, according to spectroscopic studies and molecular simulations, aromatics prefer to adsorb on SII sites of Y zeolites with their aromatic ring planes nearly parallel to the six rings of the sodalite cages [34,35]. Therefore, SII sites of Y zeolites are the preferred active sites for studying aromatic adsorption performance and it was mainly chosen to be the active site in this work. Besides, to fully understand the effect of the framework aluminium content on adsorption performances, we also considered other possible active sites in framework. The dangling bonds resulting from cutting the Si–O bonds were terminated by the H atoms, which were fixed at their initially optimised positions and the negative charge from the substitution of Al atom was saturated by H⁺ (proton of hydroxyl). Optimised structure of the 40T cluster model is shown in Figure 1 and the number of the hydrogen atoms, oxygen atoms and the T′ (Si atoms or Al atoms) sites in the following discussion all correspond with the number in Figure 1.

2.2. Computational details
All calculations were performed with Dmol, module of Materials Studio [36]. The meta-generalised gradient approximation (mGGA) in M06-L parameterisation was used in the DFT simulation. M06 functional was employed in order to capture dispersion interactions between the zeolite and tetralin molecules, which have provided results in good agreement with experimental values [37,38]. To test the simulation accuracy, the adsorption of aromatic molecules has been calculated. The tetralin molecule has a benzene ring and a naphthalene ring, which is similar to alkylbenzene. Therefore, we calculated the ethylbenzene adsorption on the above 40T cluster of Y zeolite in mGGA/M06-L level. The calculated adsorption energies is −86.3 kJ/mol, which is in good agreement with experimentally reported values of −85.3 kJ/mol. As a result, although there is no direct experimental data of tetralin adsorption energy, the calculated results of ethylbenzene in such model and level indicates our simulation is reasonable. The double numerical plus polarisation (DNP) basis set was used with the consideration of the electronic polarisation effect. All electron calculation was performed for the complexes, spin unrestricted for the spin state of the system and 1.0e−6 for the SCF tolerance. During the optimisation of the zeolite, only the six-membered ring and the bonded silicon atoms were optimised. The rest of atoms in the cluster model were fixed to the crystallographic coordinates, which could improve the accuracy of calculations. In addition, it takes into account the effect of the entire framework on zeolite and reduces the amount of the calculations at the same time.

3. Results and discussions
3.1. Structures of Y zeolites with different Si/Al ratios
Zeolite clusters with different Si/Al ratios (i.e. 39, 19 and 12) were determined, and these ratios correspond to the number of substituted Al atoms of one, two, three, respectively. Although the specific locations of Brønsted protons and framework Al atoms can’t be easily characterised, several experimental studies together with theoretical work [8,39] have provided that Al and H distributions are nonrandom and depend on the Si/Al ratio. Therefore, the substitution energies of (Al/Si) and (Al, H)/Si of the clusters with different Si/Al ratio were calculated to define the positions. The optimised structures of the three cluster models are shown in Figure 2. The formulas of the substitution energy are shown as follows:

$$E_{\text{Al/Si}} = E_{\text{Al-O-Si}} - E_{\text{Si-O-Si}}$$  
(1)

$$E_{\text{Al,H/Si}} = E_{\text{Al-OH-Si}} - E_{\text{Si-O-Si}}$$  
(2)

Figure 3. (Colur online) The adsorption complexes of tetralin on Y zeolite with different Si/Al ratios.
Table 1. Calculated Al/Si substitution energies $E_{\text{ads}}^\text{al}$(a.u.), Al/H/Si substitution energies $E_{\text{ads}}^\text{al,H/Si}$(a.u.) and relative Al/H/Si substitution energies $E_{\text{ads}}^\text{al,H/Si}$(kJ/mol) of zeolites with different Si/Al ratios.

<table>
<thead>
<tr>
<th>Si/Al ratio</th>
<th>$E_{\text{ads}}^\text{al}$</th>
<th>$E_{\text{ads}}^\text{al,H/Si}$</th>
<th>$E_{\text{ads}}^\text{al,H/Si}$(kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>39</td>
<td>19</td>
<td>NNN</td>
<td>93.888</td>
</tr>
<tr>
<td></td>
<td></td>
<td>NNN4</td>
<td>93.882</td>
</tr>
<tr>
<td></td>
<td></td>
<td>NNNN</td>
<td>93.882</td>
</tr>
</tbody>
</table>

Table 2. Calculated adsorption energies $E_{\text{ads}}$(kJ/mol), relative adsorption energies $E_{\text{ads}}^\text{rel}$(kJ/mol) and O–H bond length O–H (Å) of adsorption complexes on Y zeolite clusters with different Si/Al ratio.

<table>
<thead>
<tr>
<th>Si/Al ratio</th>
<th>$E_{\text{ads}}$</th>
<th>$E_{\text{ads}}^\text{rel}$</th>
<th>$d_{O-H}$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>39</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>19</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note: ad* stands for the complex that tetralin adsorbs on *zeolite and the values in parentheses are O–H bond length changes before and after tetralin adsorption.

In Equation (1), $E_{\text{Si–O–Si}}$ and $E_{\text{Al–O–Si}}$ stand for the total potential energies of the cluster before and after the replacement of the aluminium atoms. The lower $E_{\text{ads}}$ represents the easier replacement of silicon atoms by aluminium atoms. In Equation (2), $E_{\text{Si–O–Si}}$ and $E_{\text{Al–O–Si}}$ are the total potential energies of the clusters without and with the substitution of Bronsted acid site, respectively. Lower $E_{\text{ads}}$ means easier (Al, H)/Si substitution.

As for the single Al atom substitution of zeolite with Si/Al 39 (denoted by a), the Al atom lies in T6 site that is the junction of supercage and sodalite cage because of the symmetry of Y zeolite [40,41]. The corresponding substitution energy of T6 is 46.903 a.u. (Table 1). Based on the single Al atom replacement, the double acid site cluster models (Si/Al 19) have been considered. Due to Lowenstein's rule that the structure of Al–O–Al is unstable, the positions of the two substituted Al atoms have two possibilities: Al6–Si–Al2 (NNN: next-nearest-neighbours) and Al6–Si–Si–Al3 (NNNN: next-next-nearest-neighbours) with the substitution energies of 93.888 and 93.882 a.u., respectively. The same, there is only one possibility of the triple acid sites: Al2–Si–Al4–Si–Al6 (c) according to the Lowenstein's rule with the substituted energy of 140.956 a.u. Due to the substitution of Al atoms, H atoms should be added to keep the electric neutrality of zeolite cluster. The formation of the hydroxyl group as Bronsted acid site can remarkably influence the catalytic properties of zeolite. For the cluster with single acid site, H atom was located in O5 inside of the six-membered ring belonging to the sodalite cage because this site has been studied as the most stable position and the distribution of this OH exits most in nature [42] (denoted by a1).

As for the cluster with two acid sites, there are four possible positions of the hydrogen atoms, corresponding to HAI–HAI, HAI–AlH, AlH–HAI and AlH–AlH. By comparing the relative substitution energies of Bronsted acid sites in NNN models, structures NNN1 and NNN4 are more stable with the relative substitution energies 18.643 and 0 kJ/mol, while the relative substitution energies of the other two clusters are 31.768 and 36.767 kJ/mol, respectively. The NNNN model follows the same rule that can be explained the proton prefers to ipsilateral distribution of Al atoms pair, which is consistent with the research on the acidity of the relative acid sites in zeolite studied by Zhou [41,43] and also conforms to the Tielens' view that the structure of Al–O(H)–O(H)–Al was too unstable to exist [44]. About the zeolite with three aluminium atoms located in T2, T4, T6, respectively, two possibilities are considered corresponding to H atoms located in the same sides of Al atoms, where in O1, O3, O5, (denoted by c1) and O2, O4, O6, (denoted by c2), respectively. The corresponding relative substituted energies of the triple Bronsted acid sites are 63.012 and 0 kJ/mol. Combined with the above calculated results, the more stable structures of different Si/Al ratios are chosen to be candidates to discuss adsorption property of Y zeolite.

3.2. The adsorption property of Y zeolite with different Si/Al ratios

It is reported that the tetralin adsorption is the first step of tetralin cracking reactions [45]. Hence, the cracking reactions are affected by adsorption properties of tetralin, which can be evaluated by the adsorption energy ($E_{\text{ads}}^\text{rel}$). It is the difference between the total potential of the adsorption complex ($E_{\text{ads}}$) and the sum of the isolated tetralin molecule ($E_{\text{tetralin}}$) and the isolated zeolite ($E_{\text{Zeo}}$):

$$E_{\text{ads}} = E_{\text{ads}} - (E_{\text{tetralin}} + E_{\text{Zeo}})$$  \hspace{1cm} (3)

The configurations of adsorption complexes are shown in Figure 3 and the adsorption energies and corresponding structure parameters (i.e. $E_{\text{ads}}$, $d_{O-H}$) are presented in Table 2. It is
found that the $E_{\text{ads}}$ increases in the following trend: $\text{ada1}<\text{adNNNN1}<\text{adc1}$, in other words, the adsorption is getting strong with low Si/Al ratios.

This phenomenon is mainly because the number of hydroxyl groups can affect the intensity of adsorption. Aromatic hydrocarbon adsorption on Y zeolite is along with a π-stacking adsorption mechanism between tetratin molecule and hydroxyl group of zeolite [46]. Therefore, the decrease of Si/Al ratio, means the increase of hydroxyl groups in zeolite, leading to the increase of acid density and subsequent stronger adsorption. It is noted that although double acid sites and triple acid sites models have multiple hydroxyl groups, like adNNNN4, adNNNN1, adNNNN4 and adc2, their adsorption energy differences were all less than 5 kcal/mol when compared with ad1a. Different configurations of them accounted for such above differences. Focusing on these four configurations in Figure 3, the distances between the hydroxyl groups of these structures are far from each other, leading to only one hydroxyl group directly pointing to tetratin molecule in these complexes, which means only one proton interacts with the tetratin molecule like ada1. Thus, their adsorption energies are similar. We regard the adsorption complexes with the largest adsorption energies of each Si/Al ratio as the most stable existing in nature. As a result, we can get the conclusion that with the increase of Si/Al ratio, the adsorption energies decreases.

As mentioned before, in this work the SII site (the six-membered ring between sodalite cage and supercage) is active area and T6 site is the referenced active site. Here, for comparison, with extended relaxation area, the conjunct T sites in 12-membered ring are also considered to be the candidates of active sites. Referring to detailed study of possible acid sites on Y [41], based on T6 Acid site, we chose T6–T8, T6–T9 of 12-membered ring for double acid sites (Si/Al 19) and T6–T9, T6–T8, T6–T9, and T6–T4–T8 for describing triple acid sites (Si/Al 12) to explain the contribution of other Brønsted acid sites. The calculated tetratin adsorption energies are listed in Table S1. A similar trend is got that adsorption energies increases with increasing aluminium content. To be noted, the adsorption energies of supplementary active sites are lower than the results we got in six-membered ring active site, indicating that SII active sites are suitable for describing tetratin adsorption performance.

Referring to previous studies of Si/Al ratio on zeolite [23, 47–49], our results present a consistent conclusion. Denayer Group [23, 47] have applied themselves to study the influence of Si/Al ratio on the adsorption properties on zeolites. On Y zeolite [23], they investigated adsorption of alkene and aromatics in gas and liquid phase. In gas phase, the pulse chromatographic method was used to describe the interaction of pure benzene on NaX (Si/Al 1.23) and NaY (Si/Al 2.79). In their experiment, higher Henry constants and adsorption energies were measured on NaX compared to NaY. On ZSM5 zeolite [47], the adsorption properties of n-alkanes with different Si/Al ratio between 12 and 400 have been considered. Their experiment results showed the adsorption enthalpies of C5–C9 in ZSM-5 with Si/Al 12 were all higher than that of Si/Al 400. Obviously, adsorption enthalpies decrease with decreasing AI content experimentally, which is in good agreement with our theoretical conclusion. However, talking about the relative theoretical research, some different conclusions have appeared. Zhang et al. [48] investigated the effect of nonframework cations on alkane adsorption by Monte Carlo simulation. The interaction energies as a function of the nonframework cations (Na+, Ca2+) for X (Si/Al 1.18) and Y (Si/Al 2.56) zeolites were focused. According to their calculations, curve of interaction between alkane and cations of X zeolite was above that of Y, meaning X had less negative interactive potential than Y zeolite, which seemed incompatible with our conclusion. Explaining this phenomenon, the size effect of different zeolites should be noted. The density of nonframework cations (Si/Al ratio) in the zeolite provokes two different effects [49]. As for zeolite with big pores (Y zeolite), nonframework cations provide extra adsorption sites for alkane adsorption, leading to favourable van der Waals interactions between the alkane molecules and cations. As for zeolite with medium size channels (ZSM-5), adding cations can decrease the effective pore volume, therefore, the cations and alkane molecules can't fit next to each other, thus eliminating van der Waals interactions. Recently, Song group [41] investigated the distribution of NNN Al atoms in Y zeolites and the effect of the number of NNN Al atoms on the acid strength of Brønsted acid sites using DFT. The first substitution Al atom was in the intersection of the supercage and the six-membered ring and 0-NNNAl, 1-NNNAl, 2-NNNAI and 3-NNNAl structures were defined based on the first Al atom, which is the same way we chose active sites in this work. The deprotonation energy and ammonia adsorption energy were used to describe the acid strength. According to their calculation, the deprotonation energy got larger and the ammonia adsorption energy became less negative with increasing number of NNN Al atoms. As well known, ammonia is the alkaline probe molecular, whose adsorption energy stands for the acid strength of zeolite. They pay attention to the acid strength of zeolite, while our work focuses on the adsorption properties of zeolite, corresponding to the neutral molecular as object of research. Thus, it is not surprising to obtain different conclusion.

Table 2 shows the changes in specific parameters of optimised complexes. By comparing the change of bond length before and after tetratin adsorption, it can be found that O–H bond is elongated after tetratin adsorption, which is in consistent with the Gutman’s rule [50]. Although all the O–H bond lengths are elongated, the rangeability is different. For example, as to double acid sites adsorption complexes (Si/Al 19), only in adNNN1 both O–H bonds are elongated above 0.010 Å, while the others are not, even several ones nearly don't change anymore. The same phenomenon has been observed in adc1 and adc2. As mentioned above, the hydroxyl group orientation has great influence on the adsorption strength. In short, acid sites change differently after tetratin adsorption.

From the analysis above, it can be deduced that lower Si/Al ratio with higher acid site density improves tetratin adsorption properties of zeolite. Previous studies have shown that the more substitution Al atoms leads to lower Brønsted acid site strength of zeolite [40, 41]. Thus, it can be concluded that lower Si/Al ratio represents stronger adsorption but weaker acid strength. In experiments, a good method to increase the strength of Brønsted acidity of Y zeolite is to increase its framework Si/Al ratio. Therefore, the adjustment of Si/Al ratio during preparation process should make a balance between catalyst acidity and adsorption of reactants.
Table 3. Mulliken charges on selected atoms in adsorption complexes.

<table>
<thead>
<tr>
<th>Structure</th>
<th>ada1</th>
<th>adNNN1</th>
<th>adNNN4</th>
<th>adc1</th>
<th>adc2</th>
</tr>
</thead>
<tbody>
<tr>
<td>O(a)</td>
<td>−0.936 (−0.013)</td>
<td>−0.939 (−0.017)</td>
<td>−0.938 (−0.016)</td>
<td>−0.934 (−0.036)</td>
<td>−0.953 (−0.055)</td>
</tr>
<tr>
<td>O(b)</td>
<td>−0.949 (−0.046)</td>
<td>−0.932 (−0.036)</td>
<td>−0.939 (−0.043)</td>
<td>−0.936 (−0.043)</td>
<td>−0.936 (−0.043)</td>
</tr>
<tr>
<td>O(c)</td>
<td>−0.931 (−0.035)</td>
<td>−0.936 (−0.043)</td>
<td>−0.935 (−0.036)</td>
<td>−0.949 (−0.046)</td>
<td>−0.949 (−0.046)</td>
</tr>
<tr>
<td>H(a)</td>
<td>0.407 (0.009)</td>
<td>0.386 (0.003)</td>
<td>0.385 (0.002)</td>
<td>0.365 (0.02)</td>
<td>0.384 (0.044)</td>
</tr>
<tr>
<td>H(b)</td>
<td>0.397 (0.043)</td>
<td>0.403 (0.049)</td>
<td>0.365 (0.025)</td>
<td>0.370 (0.036)</td>
<td>0.370 (0.036)</td>
</tr>
<tr>
<td>H(c)</td>
<td>0.385 (0.002)</td>
<td>0.365 (0.02)</td>
<td>0.365 (0.025)</td>
<td>0.370 (0.036)</td>
<td>0.370 (0.036)</td>
</tr>
<tr>
<td>g(tetralin)</td>
<td>0.033 (0.033)</td>
<td>0.084 (0.084)</td>
<td>0.028 (0.028)</td>
<td>0.009 (0.099)</td>
<td>0.037 (0.037)</td>
</tr>
</tbody>
</table>

Note: ‘a’, ‘b’ and ‘c’ stand for the O atom or H atom bonded to the Al6, Al2 and Al4, respectively. The values in parentheses are charge changes before and after tetralin adsorption.

Table 4. Frontier orbital energies of some adsorption complexes and HOMO–LUMO energy gap ($\varepsilon_f$).

<table>
<thead>
<tr>
<th>Structure</th>
<th>$E_{\text{HOMO}}$(a.u.)</th>
<th>$E_{\text{LUMO}}$(a.u.)</th>
<th>$E_f$(a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ada1</td>
<td>−0.2097</td>
<td>−0.0270</td>
<td>0.1827</td>
</tr>
<tr>
<td>adNNN1</td>
<td>−0.2287</td>
<td>−0.0488</td>
<td>0.1798</td>
</tr>
<tr>
<td>adc1</td>
<td>−0.2491</td>
<td>−0.0743</td>
<td>0.1749</td>
</tr>
</tbody>
</table>

3.3. Charge and frontier orbital theory analysis

The adsorption properties of zeolite are closely related with the charge transfer between the zeolite and the adsorbate. Mulliken charge is analysed in order to study the tetralin adsorption on zeolite from the viewpoint of electron transfer. Mulliken charges on selected atoms are listed in Table 3. Take ada1 for example, the charge of tetralin increases from 0 to 0.033, which means some electrons transfer from tetralin to zeolite. It can be explained that electron transfer occurs between the σ bond (H–O) of zeolite and the π bond (C=C) of tetralin, leading to tetralin adsorption stabilised by σ–π interaction. The adsorption site O–H groups accepted the electron from tetralin as a whole. Then, the electron transferred from H atom to O atom, corresponding to negative charge change (−0.013) on O atom. Other adsorption configurations have the same conclusion. As for the same Si/Al ratio structures, like adNNN1 and adNNN4, the different charge changes were observed on O and H atoms. It was found that adNNN4 has bigger charge change than adNNN1. Since the charge change is caused by tetralin adsorption, here the adsorption energy relevance should be considered. Table 2 have shown that the adsorption energy of adNNN1 was greater than that of adNNN4, meaning tetralin adsorption action is stronger in adNNN1. It seems opposite to the charge change on O and H atoms. However, as mentioned above, O–H group as a whole accepted the electron from tetralin. So analysing the sum of charge on O and H atoms, the total charge of hydroxyl groups (O–H) in adNNN4 didn’t change obviously and the charge of tetralin in it is almost equal to that in ada1. While the charge of O–H group in adNNN1 changed more, corresponding to greater adsorption property. Compared different Si/Al ratio structures, it is obviously to find charge changes is in an ascending order, corresponding to ada1<adNNN1<adc1, which is as same as the adsorption energy sequence.

HOMO–LUMO gap in adsorption complex is helpful to analyse electron transfer process during adsorption molecule electronic purpose and predict the possibility of reaction. DFT studies on the HOMO–LUMO gap has important influence on the cracking properties of zeolite [51]. HOMO stands for the highest occupied molecular orbit, while LUMO stands for the lowest unoccupied molecular orbit. Therefore, the gap between HOMO and LUMO can reflect reactant activity. Low gap means easy reaction. The Frontier orbital energies of the three adsorption complexes on different Si/Al ratio zeolite are shown in Table 4. It can be seen that the gap of the Frontier orbital energies of ada1, adNNN1 and adc1 are 0.1827, 0.1798, 0.1749 a.u., respectively, indicating tetralin is most easily to have reaction on adc1. That is to say adsorbed tetralin will be more active with decreasing Si/Al ratio of zeolite, which is in great agreement with Mulliken charge analysis.

4. Conclusion

The variations of tetralin adsorption property on Y zeolite with change of Si/Al ratio have been studied by means of DFT calculation. It is found that Si/Al ratio has opposite relationship with adsorption energies. Lower Si/Al ratio, namely more acid sites, corresponds to stronger acidity density and adsorption properties. The number of hydroxyl groups interacting with tetralin will affect adsorption intensity. More hydroxyl groups interacting with benzene ring of tetralin result in bigger adsorption energy. Charge and HOMO–LUMO gap analysis proved the above conclusion. That is with decreasing Si/Al ratio of zeolite, the adsorption property gets stronger and the adsorption complexes are more likely to have reaction. From such research about Si/Al ratio effect on tetralin adsorption on Y zeolite, experiments should pay attention to getting proper Si/Al ratio in different reaction environment, in order to achieve a better adsorption performance and reaction activity.

Acknowledgement

We also acknowledge the support from the State Key Laboratory of Heavy Oil Processing (China University of Petroleum).

Disclosure statement

No potential conflict of interest was reported by the authors.

Funding

This work was supported by the Key Subject of Petrochemical Unite Funds [grant number U1462205]; the National Nature Science Foundation of China [grant number 21203250] and the Fundamental Research Funds for the Central Universities [grant number 15CX05066A].
References


学霸图书馆

www.xuebalib.com

本文献由“学霸图书馆-文献云下载”收集自网络，仅供学习交流使用。

学霸图书馆（www.xuebalib.com）是一个“整合众多图书馆数据库资源，
提供一站式文献检索和下载服务”的24小时在线不限IP图书馆。

图书馆致力于便利、促进学习与科研，提供最强文献下载服务。

图书馆导航：

图书馆首页 文献云下载 图书馆入口 外文数据库大全 疑难文献辅助工具