

Thiophenic compounds adsorption on Na(I)Y and rare earth exchanged Y zeolites: a density functional theory study

Xionghou Gao · Wei Geng · Haitao Zhang · Xuefei Zhao · Xiaojun Yao

Received: 7 June 2013 / Accepted: 18 July 2013 / Published online: 8 September 2013
© Springer-Verlag Berlin Heidelberg 2013

Abstract We have theoretically investigated the adsorption of thiophene, benzothiophene, dibenzothiophene on Na(I)Y and rare earth exchanged La(III)Y, Ce(III)Y, Pr(III)Y Nd(III)Y zeolites by density functional theory calculations. The calculated results show that except benzothiophene adsorbed on Na(I)Y with a stand configuration, the stable adsorption structures of other thiophenic compounds on zeolites exhibit lying configurations. Adsorption energies of thiophenic compounds on the Na(I)Y are very low, and decrease with the increase of the number of benzene rings in thiophenic compounds. All rare earth exchanged zeolites exhibit strong interaction with thiophene. La(III)Y and Nd(III)Y zeolites are found to show enhanced adsorption energies to benzothiophene and Pr(III)Y zeolites are favorable for dibenzothiophene adsorption. The analysis of the electronic total charge density and electron orbital overlaps show that the thiophenic compounds interact with zeolites by π -electrons of thiophene ring and exchanged metal atom. Mulliken charge populations analysis reveals that adsorption energies are strongly dependent on the charge transfer of thiophenic molecule and exchanged metal atom.

Keywords Charge transfer · Density functional theory (DFT) · Desulfurization · Rare earth · Zeolites

Introduction

Removal of sulfur-containing compounds in fossil fuels, such as crude petroleum oil, has drawn extensive attention [1]. Sulfur or more precisely sulfuric compounds in fuels remains a major source of air pollution [2]. Sulfur emission has many direct and indirect negative effects on the environment. Direct combustion of organic sulfuric compounds presented in the fuel leads to SO_x emission, which harms human health and results in acid mist and acid rain. Therefore, increasingly quality standards for environment and fuel specifications are being implemented. According to Euro IV specifications for fuel, the maximum allowable sulfur content is less than 50 ppm in gasoline and diesel. In the United States, the Environmental Protection Agency (EPA) requires reduction sulfur less than 30 ppm and 15 ppm in gasoline and diesel under Tier II regulations. Future legislations may require limiting sulfur to levels as low as 10 ppm.

Conventional hydrodesulfurization (HDS) process is effective for removing thiols, sulfides and disulfides. However, this process is less competent in meeting the tightening regulations of sulfur limits. Since HDS is less effective to remove heterocyclic sulfur containing compounds such as thiophene (T), benzothiophene (BT), dibenzothiophene (DBT) and their alkylated derivatives, which are mainly compositions of sulfur that remain in the transportation fuels [3]. In addition, HDS process generally requires extreme conditions of temperature and pressure [4], meets the problems of catalyst poisoning [5] and cost expensive. Thus, refineries are facing urgent challenges to meet the new fuel sulfur requirements expected in the near future. Alternatively, utilizing zeolites as selective adsorbent seems to be a promising approach to highly efficient ultra-deep desulfurization from transportation fuels [6–12]. Zeolites can be successfully used for the selective adsorption of sulfur-containing molecules at low temperature and pressure without consuming pressurized hydrogen or oxygen gas,

X. Gao (✉) · H. Zhang
Petrochemical Research Institute, Lanzhou Petrochemical Research Center, PetroChina Company Limited, Lanzhou 730060, China
e-mail: gaioxionghou@petrochina.com.cn

X. Gao
e-mail: xionghougao@163.com

W. Geng · X. Zhao · X. Yao
Department of Chemistry, Lanzhou University, Lanzhou 730000, China

and the sulfur in fuels can be removed to a very low level. Since zeolites have a well defined crystalline lattice which contains uniform pore sizes, and provides a very high surface area per unit mass. Success in development of zeolites would lead to a major advance in petroleum refining. However, the practical use of the zeolites as sulfur adsorbent would depend on the development of highly selective zeolites with high sulfur capacity. Zeolites have unique properties of selectively adsorption depending on the basis of their size, configuration, polarity, and other physical characteristics [13]. Many reports have shown that the introduction of different cations into the zeolite structure leads to different catalytic and adsorption properties of the zeolites [14, 15]. Yang and Hernandez-Maldonado reported Cu–Y and Ag–Y zeolites can adsorb sulfur compounds from commercial fuels selectively and with high sulfur capacities at ambient temperature and pressure [3]. Velu et al. synthesized transition metal ion-exchanged Y zeolites (with Cu, Ni, Zn, Pd, and Ce ions) and evaluated the adsorptive desulfurization of a model jet fuel (MJF) and a real jet fuel (JP-8). Among the adsorbents tested, Ce-exchanged Y zeolites exhibited better adsorption capacity [16]. Tian et al. found that La(III)Y can improve the adsorption selectivity of organic sulfur compounds in solutions containing aromatics [17].

It was found that rare earth (RE) exchanged zeolites were efficient for sulfur removal. However, because the framework and pore structure of zeolites are complex, the adsorption process is complicated and the key fundamental mechanism of desulfurization is still not clear. In industrial, RE exchanged zeolites are often prepared by using mischmetal salt aqueous solutions for ion exchange with Na(I)Y zeolite. Therefore, the industrial products often contain Na, and several RE species. As we know, little has been reported on the systematic research about possible adsorption configurations and mechanism of the heterocyclic sulfur compounds over rare earth exchanged Y zeolites (REY). The main goal of this study is to get a better understanding about the adsorption mechanisms in deep desulfurization of gasoline and diesel fuels, and to guide the manufacture of industrial product. Therefore, we investigated the possible adsorption configurations and charge transfer of sulfur containing compounds on Na(I)Y and RE exchanged zeolites using DFT method. We found that charge transfer played an important role for adsorption process of thiophenic compounds.

Computational details

In Y zeolite, the catalytically active extra-framework cations are located at several crystallographic sites [18]. Here, we mainly considered site II in our investigations. This site is located in the supercage and coordinates with three oxygen atoms of the six-ring window of the sodalite cage. Since

thiophenic molecules could be adsorbed into supercage, site II cations located in supercage are closer to these molecules and are apt to interact with them. In addition, our Monte Carlo method using the Adsorption Locator module in Materials Studio software package (Accelrys Ltd., USA) demonstrates that most of the cations are located in site II. This is similar to the result from other work [19]. In order to consider the influence of zeolite framework and pore on the adsorption behavior, we employed the widely used finite cluster. A 12 T (T means tetrahedral unit of zeolite) cluster which has a six-membered ring and six other Si atoms of the partial of supercage was cut from the framework of the FAU zeolite. The dangling bonds of oxygen atoms located at the cluster edge were saturated by hydrogen atoms directed along the bond vector of what would have been the next zeolite framework atom in the crystal structure. The terminal OH bonds were set to be 1.0 Å. The positions of the terminal OH groups were fixed during geometry optimizations, whereas all the other atoms were allowed to relax. For cation-exchanged zeolites, to stabilize the exchanged cation, the Na(I)Y ($\text{NaAlSi}_{11}\text{O}_{33}\text{H}_{18}$) cluster model should have one Al atom to maintain the system neutral. In the same way, La(III)Y, Ce(III)Y, Pr(III)Y and Nd(III)Y ($\text{REAl}_3\text{Si}_9\text{O}_{33}\text{H}_{18}$) should also have three Al atoms, respectively, which substituted three Si atoms of the six-member ring in an alternating sequence following Loewenstein's rule [20] that two tetrahedrally coordinated aluminum atoms cannot share an oxygen atom.

All the DFT calculations were performed by applying the Dmol3 program in Materials Studio 5.5 package of Accelrys Ltd. The generalized gradient approximation (GGA) with the Becke [21] gradient exchange functional and Lee–Yang–Parr [22] correlation functional (BLYP) were used to treat all electronic energy of exchange correlation. Double-numeric quality base set with the polarization functions (DNP) [23] was employed, which is comparable with the Gaussian 6-31G** basis set in size and quality. The core electrons were treated with DFT semicore pseudopotentials (DSPPs). A thermal smearing of 0.005 Ha and an orbital cut-off of 5.8 Å was used to improve the computational performance. The convergence criteria for the geometric optimization and energy calculation were set as follows: (a) an energy tolerance of 1.0 E-5Ha, (b) a maximum force tolerance of 0.002 Ha/Å, and (c) a maximum displacement tolerance of 0.005 Å. The adsorption energies were calculated by using the expression:

$$E_{\text{Ads}} = E_{\text{thiophenic/zeolite}} - E_{\text{thiophenic}} - E_{\text{zeolite}}$$

where $E_{\text{thiophenic/zeolite}}$ is the total energy of the optimized complex compounds of the thiophenic compounds on the zeolite clusters, $E_{\text{thiophenic}}$ is the energy of the optimized thiophenic compounds and E_{zeolites} is the energy of the optimized zeolite clusters.

Results and discussion

Configurations and energies of thiophenic compounds adsorption on zeolites

The isolated thiophenic molecules and zeolite clusters were first optimized. The optimized structures and atom labeling of Na(I)Y and La(III)Y clusters are given in Fig. 1. The distances between the metal site and the six O atoms are given in Table 1. As shown in Fig. 1a and Table 1, the distances between the Na site and the six O atoms are quite different, indicating that Na migrates slightly from site II. Compared with Na(I)Y, La(III)Y exhibits a higher symmetry (Fig. 1b), the lengths between the La and the O1, O3 and O5 are 2.411, 2.409 and 2.415 Å, and the distances between the La and O2, O4 and O6 are 2.694, 2.699 and 2.701 Å. The average distance of La-O is shorter than that of Na-O, which means La atom is closer to the center of the 6 T ring for the optimized cluster models. The configurations of Ce(III)Y, Pr(III)Y and Nd(III)Y are similar to La(III)Y. Distances between RE atoms to the six O are shown in Table 1, the average distances of RE-O are in the order of Pr(III)Y < Nd(III)Y < Ce(III)Y < La(III)Y.

To investigate the favorable adsorption configuration, thiophenic compounds were placed above zeolite cluster with different initial states with S atom toward metal atom were considered. After full relaxation, the most energetically stable optimized geometrical structures for the thiophenic compounds adsorption on Na(I)Y are listed in Fig. 2 and on La(III)Y are listed in Fig. 3. Configurations of thiophenic compounds on the other RE(III)Y are similar to La(III)Y. The distances, adsorption energies as well as Mulliken charge populations are listed in Table 2.

The optimized geometrical configuration for the thiophene adsorption on the Na(I)Y shows the thiophene molecule lies on Na (Fig. 2a, b), which indicates thiophene interacts with Na by π -electrons. The adsorption energy is $-33.05 \text{ kJ mol}^{-1}$, indicating that the interaction between Na(I)Y zeolite and thiophene is very weak. To describe the distance between molecule and metal atom more accurately, we gave the

distances between the S atom of thiophene and exchanged metal atom (S-M) as well as the centroid of thiophene and exchanged metal atom (C-M). For thiophene adsorption on Na(I)Y, the distance of S-M is 3.397 and C-M is 2.908 Å.

The adsorption conformation of BT on the Na(I)Y is shown in Fig. 2c, d. Its adsorption configuration is different from thiophene on the Na(I)Y. BT is upright over the Na with a little tilted and S atom is toward Na, S-M (3.004 Å) is shorter than C-M (4.067 Å). These results suggest thiophene coordinates with the metal atom through both direct sulfur–metal interaction and π -electrons interaction. However, this does not enhance the adsorption energy with a value of $-29.09 \text{ kJ mol}^{-1}$. Figure 2e, 2f exhibits that DBT adsorbs on the Na(I)Y with a lying configuration. Adsorption energy of DBT on the Na(I)Y is $13.49 \text{ kJ mol}^{-1}$. The adsorption energies of the Na(I)Y to T, BT, and DBT molecules are in the order of T > BT > DBT, the adsorption capability decreases with the increasing number of benzene rings.

When RE atom substitutes Na, similar adsorption configuration is found at thiophene on the La(III)Y (Fig. 3a, b). However, adsorption energies of thiophene on the four types of RE exchanged zeolites: La(III)Y, Ce(III)Y, Pr(III)Y and Nd(III)Y dramatically increase to -95.31 , -93.19 , -96.15 and $-93.21 \text{ kJ mol}^{-1}$ respectively. The differences in adsorption energies of four types of RE exchanged zeolites are no more than 3 kJ mol^{-1} , and all of them are over 3 times larger than that of thiophene on the Na(I)Y zeolite. The increase indicates RE exchanged zeolites are energetically favorable for thiophene adsorption. The S-M distances of the four REYs are 3.314, 3.274, 3.209 and 3.186 Å, and the C-Ms are 2.949, 2.924, 2.845 and 2.815 Å respectively. The distances are in the order of La(III)Y > Ce(III)Y > Pr(III)Y > Nd(III)Y. Compared with Na(I)Y zeolite, RE exchanged zeolites show shorter S-M bonds, however, C-M bonds of La(III)Y and Ce(III)Y are longer than that of Na(I)Y.

Both BT and DBT on La(III)Y (Fig. 3c–f) exhibit lying configurations. All adsorption configurations of thiophenic compounds on Na(I)Y or La(III)Y with the thiophene ring toward the exchanged metal atom indicate thiophene ring is

Fig. 1 Optimized structures of the Na(I)Y (a) and La(III)Y clusters

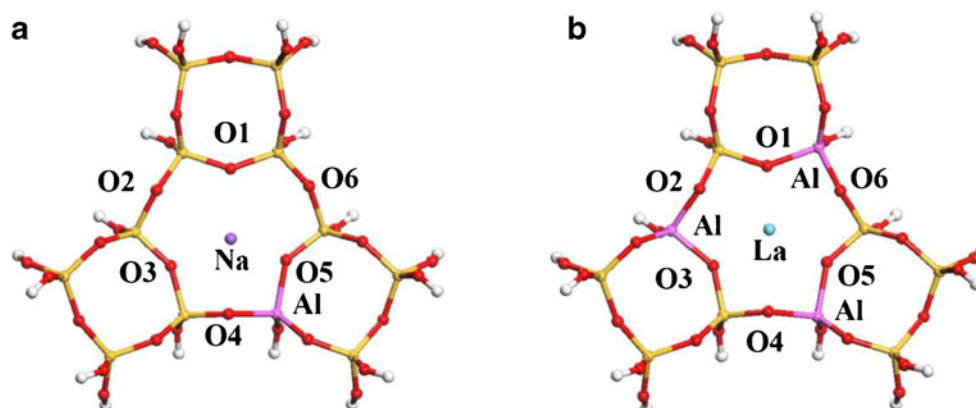


Table 1 Distances between metal site and O atoms of the optimized zeolite clusters

| | Distances(Å) | | | | |
|----|--------------|-------|-------|-------|-------|
| | Na | La | Ce | Pr | Nd |
| O1 | 2.568 | 2.411 | 2.362 | 2.344 | 2.353 |
| O2 | 2.964 | 2.694 | 2.678 | 2.662 | 2.688 |
| O3 | 2.375 | 2.409 | 2.363 | 2.346 | 2.350 |
| O4 | 2.508 | 2.699 | 2.667 | 2.663 | 2.663 |
| O5 | 2.232 | 2.415 | 2.365 | 2.345 | 2.348 |
| O6 | 3.213 | 2.701 | 2.676 | 2.661 | 2.673 |

stronger than benzene ring for interaction with exchanged metal atom. The adsorption energies of BT on the La(III)Y, Ce(III)Y, Pr(III)Y and Nd(III)Y zeolites are -94.23 , -78.17 , -64.85 and -96.57 kJ mol^{-1} respectively, and DBT on REYs are -72.21 , -75.25 , -81.18 and -66.28 respectively. La(III)Y

and Nd(III)Y show enhanced interactions to BT and Pr(III)Y show enhanced interaction to DBT. The steric effect of thiophenic compounds increases as the number of benzene rings grow. However, distances between thiophenic compounds and metal atoms do not comply with this order and the adsorption energies are not consistent with distance order. This is because thiophenic compounds are planar molecules, steric hindrance affects strongly on the side but weakly on interaction with metal atom. Steric hindrance is not the major factor influencing adsorption energy. We suspect that both steric and electronic properties of adsorption systems play a crucial role on interaction process.

Charge density and charge population analysis of thiophenic compounds adsorption on zeolites

To better understand the electronic properties of thiophenic compounds adsorption on zeolites, electronic total charge density plots of thiophenic compounds on Na(I)Y and La(III)Y are

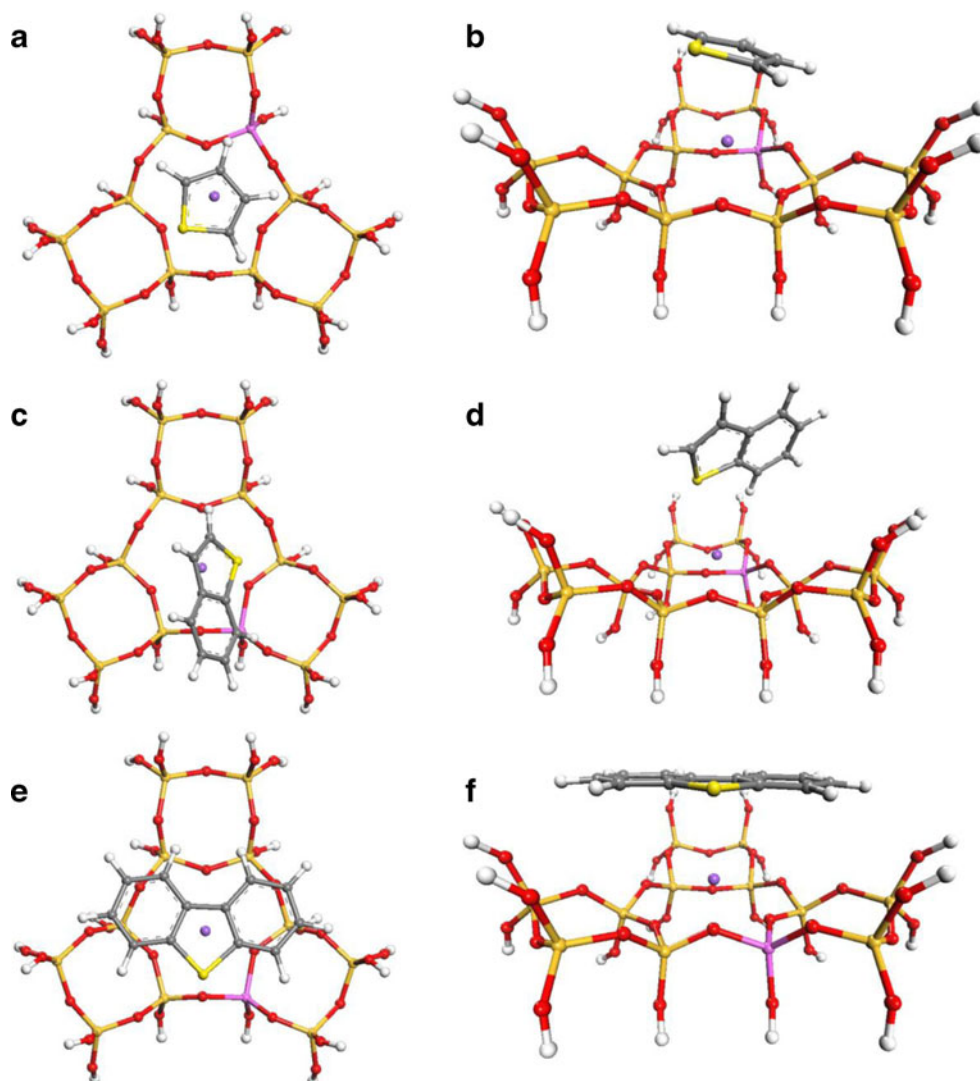
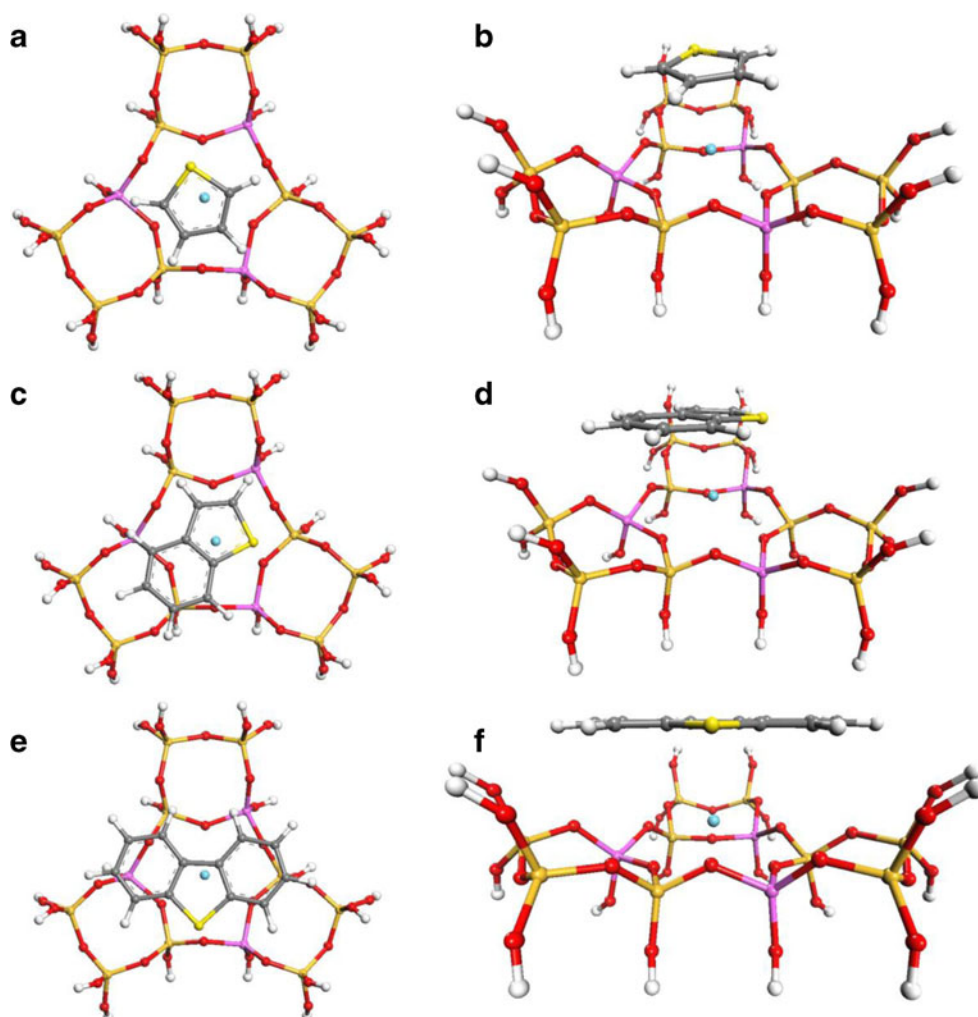
Fig. 2 Adsorption configurations of (a,b) thiophene, (c,d) benzothiophene and (e,f) dibenzothiophene adsorbed on Na(I)Y zeolite. (a,c,e) are top views, (b,d,f) are side views

Fig. 3 Adsorption configurations of (a,b) thiophene, (c,d) benzothiophene and (e,f) dibenzothiophene adsorbed on La(III)Y zeolite. (a,c,e) are top views, (b,d,f) are side views



given in Fig. 4. It can be seen from Fig. 4 that the minimum of iso-surfaces are $0.05 \text{ e}/\text{\AA}^3$ on Na(I)Y and $0.1 \text{ e}/\text{\AA}^3$ on La(III)Y respectively. Electron orbital overlaps between thiophenic compounds and Na(I)Y are very weak with values about $0.05 \text{ e}/\text{\AA}^3$. In particular, no electron orbital overlap is observed in DBT on Na(I)Y. However, thiophenic compounds on La(III)Y exhibit strong overlaps with values about $0.1 \text{ e}/\text{\AA}^3$. The electron orbital overlaps are located below the thiophene ring. The electron cloud of the thiophenic compounds hardly overlaps with zeolites on the edge of thiophenic molecules. The electronic total charge density plots prove that the thiophenic compounds mainly interact with zeolites by thiophene ring π -electrons and exchanged metal atom.

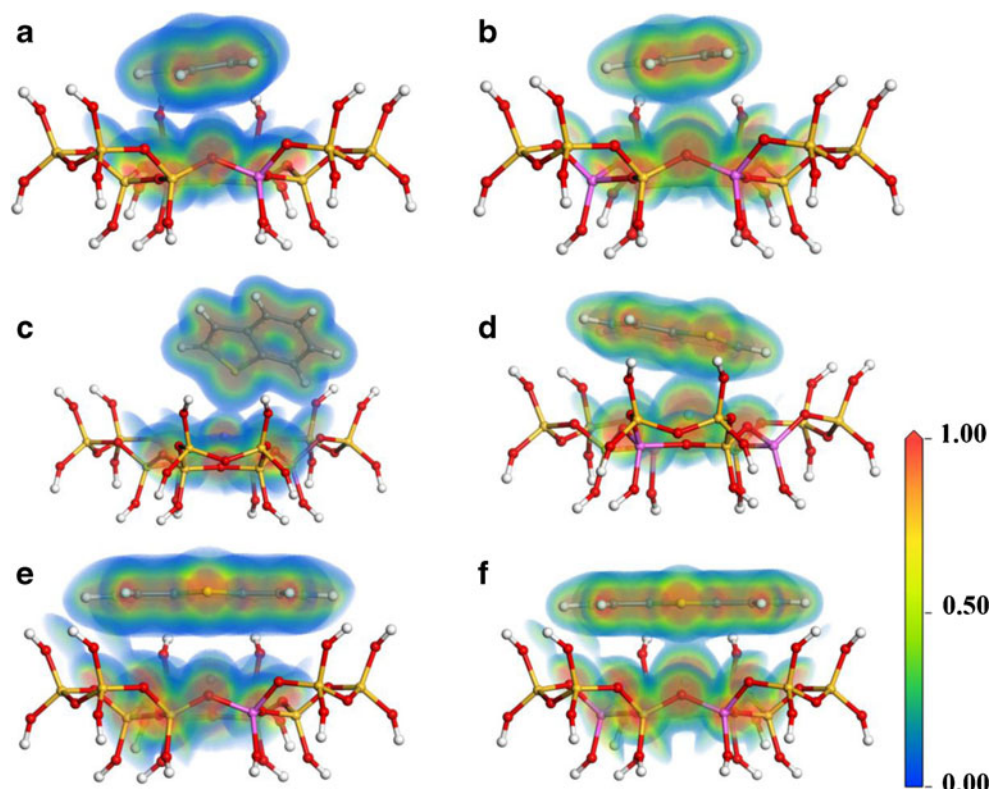
To further understand the influence of the electronic property of Na(I)Y and RE(III)Y on the adsorption, Mulliken charge populations for the thiophenic compounds and zeolites [24] are calculated. For the Na(I), La(III), Ce(III), Pr(III) and Nd(III) on the zeolites before thiophenic compounds adsorption, Mulliken charge populations are 0.73, 1.45, 1.54, 1.17 and 1.16 respectively. All of the metal atoms show positive

charges. However, these values are lower than their valences, indicating a part of the positive charges of metal atoms are dispersed to framework atoms. Ce often shows a +4 valence in nature, which is higher than +3 valences of the other RE. Similarly, it also shows a higher positive charge than the other in RE(III)Y, because Ce prefers to donate an additional 4f electron to form a more stable empty f orbit.

The charge transfers of the adsorption systems were also calculated, Δe_{ad} is charge transfer from thiophenic compound to zeolite after adsorption, Δe_{M} is the difference between charge population of exchanged metal atom after and before thiophenic compound adsorption. As shown in Table 2, $0.028e$ charge transfer (Δe_{ad}) from thiophene to Na(I)Y, and Δe_{M} of Na is -0.012 , indicating that charge transfers of both thiophene molecule and Na are very weak, the small amount of Δe agrees with the low adsorption energy.

The calculated Mulliken charge populations show charge transfers (Δe_{ad}) from thiophene to REYs are 0.283, 0.198, 0.357 and 0.371 respectively, and the Δe_{M} of REYs are -0.148 , -0.036 , -0.148 and -0.152 respectively. The large

Fig. 4 Electronic total charge densities for thiophene, benzothiophene, dibenzothiophene adsorbed on Na(I)Y (**a,c,e**) and La(III)Y (**b,d,f**)



charge transfers confirm that the thiophene acts as an electron donor, and the RE atom acts as Lewis acid site, there is strong Lewis acid–base interaction between them. It can be noticed that the charge transfer of Ce system is weaker than the other REYs systems, the Ce prefers to show more positive charge, this agrees well with the low adsorption energy.

Table 2 Adsorption energies, distances and Mulliken charge populations of thiophenic compounds adsorption on zeolites

| | | $\Delta E(\text{kJ mol}^{-1})$ | S-M(Å) | C-M(Å) | $\Delta e_{\text{ad}}(\text{e})$ | $\Delta e_{\text{M}}(\text{e})$ |
|----|-----|--------------------------------|--------|--------|----------------------------------|---------------------------------|
| Na | T | -33.05 | 3.397 | 2.908 | 0.028 | -0.012 |
| | BT | -29.09 | 3.004 | 4.067 | 0.030 | -0.020 |
| | DBT | -13.49 | 3.793 | 3.150 | -0.030 | 0.021 |
| La | T | -95.31 | 3.314 | 2.949 | 0.283 | -0.148 |
| | BT | -94.23 | 3.289 | 3.059 | 0.267 | -0.119 |
| | DBT | -72.21 | 3.751 | 2.998 | 0.194 | -0.075 |
| Ce | T | -93.19 | 3.274 | 2.924 | 0.198 | -0.036 |
| | BT | -78.17 | 3.230 | 3.348 | 0.170 | -0.009 |
| | DBT | -75.25 | 3.176 | 3.100 | 0.150 | 0.018 |
| Pr | T | -96.15 | 3.209 | 2.845 | 0.357 | -0.148 |
| | BT | -64.85 | 3.160 | 4.236 | 0.251 | -0.088 |
| | DBT | -81.18 | 3.142 | 3.032 | 0.340 | -0.089 |
| Nd | T | -93.21 | 3.186 | 2.815 | 0.355 | -0.152 |
| | BT | -96.57 | 3.173 | 3.015 | 0.350 | -0.129 |
| | DBT | -66.28 | 3.893 | 3.117 | 0.299 | -0.055 |

Charge transfers of BT and DBT on REYs are shown in Table 2, except Ce(III)Y, the adsorption energies of thiophenic on zeolites are closely related to the charge transfers. The general trend of adsorption energies decreases as charge transfer decreases. As the number of benzene rings increases, electron donating ability of thiophenic compounds decreases, in particular, Δe_{ad} of DBT on Na(I)Y becomes negative, Δe_{M} of DBT on Na(I)Y and Ce(III)Y become positive. It is noticed that the charge transfers of Ce systems are weaker than the other RE systems, however, charge transfer and adsorption energies are still far higher than adsorption energies of Na(I)Y. No matter isolated or adsorbed on zeolite, S atom shows the highest negative charge on thiophenic molecule. It suggests that electrons accumulate on S atom for thiophenic compounds, however, a direct sulfur–metal bond is not found for all systems.

Conclusions

In summary, adsorptions of thiophenic compounds on Na(I)Y and RE(III)Y are studied by DFT method. Adsorption calculation results show BT on Na(I)Y exhibit stand-up configuration with a little tilt, while other configurations of thiophenic compounds adsorption on zeolites show thiophenic molecules exhibit lying configurations. Direct sulfur–metal interaction does not enhance adsorption energy in the case of BT on

Na(I)Y. BT molecule is strongly adsorbed on the La(III)Y and Nd(III)Y with high binding energy value and large charge transfer. Pr(III)Y shows enhance interaction to DBT. Adsorption configurations and electronic total charge density plots indicate thiophenic compounds interact with exchanged metal atoms mainly by π -electrons. The adsorption energies are closely related to the charge transfers of thiophenic molecules and exchanged metal atoms. It is found that La, Pr and Nd exchanged zeolites served as a good candidate for deep desulfurization of gasoline and diesel fuels.

Acknowledgments This work was supported by PetroChina Company Limited (Grant No.2010E-1901).

References

- Song C (2003) An overview of new approaches to deep desulfurization for ultra-clean gasoline, diesel fuel and jet fuel. *Catal Today* 86: 211–263
- Song C, Ma X (2003) New design approaches to ultra-clean diesel fuels by deep desulfurization and deep dearomatization. *Appl Catal B: Environ* 41:207–238
- Yang RT, Hernández-Maldonado AJ, Yang FH (2003) Desulfurization of transportation fuels with zeolites under ambient conditions. *Science* 301:79–81
- Hernández-Maldonado AJ, Yang RT (2004) Desulfurization of diesel fuels via π -complexation with nickel(II)-exchanged X- and Y-zeolites. *Ind Eng Chem Res* 43:1081–1089
- Kogan VM, Gaziev RG, Lee SW, Rozhdestvenskaya NN (2003) Radioisotopic study of (Co)Mo/Al₂O₃ sulfide catalysts for HDS: Part III. Poisoning by N-containing compounds. *Appl Catal A Gen* 251:187–198
- Ma X, Sun L, Song C (2002) A new approach to deep desulfurization of gasoline, diesel fuel and jet fuel by selective adsorption for ultra-clean fuels and for fuel cell applications. *Catal Today* 77:107–116
- Montazerolghaem M, Rahimi A, Seyedejn-Azad F (2010) Equilibrium and kinetic modeling of adsorptive sulfur removal from gasoline by synthesized Ce–Y zeolite. *Appl Surf Sci* 257:603–609
- Xue M, Chitrakar R, Sakane K, Hirotsu T, Ooi K, Yoshimura Y, Feng Q, Sumida N (2005) Selective adsorption of thiophene and 1-benzothiophene on metal-ion-exchanged zeolites in organic medium. *J Colloid Interf Sci* 285:487–492
- Hernández-Maldonado AJ, Yang RT (2003) Desulfurization of commercial liquid fuels by selective adsorption via π -complexation with Cu(I)-Y zeolite. *Ind Eng Chem Res* 42:123–129
- Hernández-Maldonado AJ, Yang RT (2003) Desulfurization of diesel fuels by adsorption via π -complexation with vapor-phase exchanged Cu (I)-Y zeolites. *Ind Eng Chem Res* 42:3103–3110
- Hernández-Maldonado AJ, Yang FH, Qi G, Yang RT (2005) Desulfurization of transportation fuels by p-complexation sorbents: Cu(I)-, Ni(II)-, and Zn(II)-zeolites. *Appl Catal B: Environ* 56:111–126
- Bhandari VM, Ko CH, Park JG, Han SS, Cho SH, Kim JN (2006) Desulfurization of diesel using ion-exchanged zeolites. *Chem. Eng Sci* 61:2599–2608
- Bakr A, Salem SH, Hamid HS (1997) Removal of sulfur compounds from naphtha solutions using solid adsorbents. *Chem Eng Technol* 20: 342–347
- Tang K, Song LJ, Duan L, Li X, Gui J, Sun Z (2008) Deep desulfurization by selective adsorption on a heteroatoms zeolite prepared by secondary synthesis. *Fuel Process Technol* 8:91–96
- Wang L, Sun Z, Ding Y, Chen Y, Li Q, Xu M, Li H, Song L (2011) A theoretical study of thiophenic compounds adsorption on cation-exchanged Y zeolites. *Appl Surf Sci* 257:7539–7544
- Velu S, Ma X, Song C (2003) Selective adsorption for removing sulfur from jet fuel over zeolite-based adsorbents. *Ind Eng Chem Res* 42:5293–5304
- Tian F, Wu W, Jiang Z, Liang C, Yang Y, Ying P, Sun X, Cai T, Li C (2006) The study of thiophene adsorption onto La(III)-exchanged zeolite NaY by FT-IR spectroscopy. *J Colloid Interf Sci* 301:395–401
- Frising T, Leflaive P (2008) Extraframework cation distributions in X and Y faujasite zeolites: a review. *Microporous Mesoporous Mater* 114:27–63
- Sung CY, Hashimi SA, McCormick A, Tsapatsis M, Cococcioni M (2012) Density functional theory study on the adsorption of H₂S and other Claus process tail gas components on copper- and silver-exchanged Y zeolites. *J Phys Chem C* 116:3561–3575
- Jentys A, Lercher JA (2001) in: H. van Bekkum, E.M Flanigen, P.A. Jacobs, J.C. Jansen (Eds.), *Introduction to zeolite science and practice, studies in surface science and catalysis, vol. 137*. Elsevier, Amsterdam, p 345
- Becke AD (1993) Density-functional thermochemistry. III. The role of exact exchange. *J Chem Phys* 98:5648–5652
- Lee C, Yang W, Parr RG (1988) Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys Rev B* 37:785–789
- Delley B (2000) From molecules to solids with the DMol3 approach. *J Chem Phys* 113:7756–64
- Mulliken RS (1955) Electronic population analysis on LCAO MO molecular wave functions. *J Chem Phys* 23:1833–1841