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Selective Adsorption of Organosulfur Compounds from Transportation Fuels by π-Complexation

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ABSTRACT

Ab initio molecular orbital (MO) calculations were performed on the adsorption bond energies between the main sulfur compounds and the Cu^+ on CuCl and CuY zeolite, for desulfurization of transportation fuels by π-complexation sorbents. The relative adsorption bond energies of these compounds were measured by the elution order, based on the breakthrough curves of these compounds, from a column of CuY zeolite using commercial diesel and gasoline as the influents. The order from the elution followed: 4,6-dimethyldibenzothiophene $\geq$ dibenzothiophene $>$ benzothiophene $\geq$ 2-methylthiophene $>$ thiophene. The order is in agreement with that predicted from the calculations. The calculated values for benzene and thiophene were also in excellent agreement with the

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measured values that we reported earlier. The methyl and benzo groups have an electron-donating effect on the aromatic rings that undergo π-complexation. For the sulfur compounds, the thiophene ring was bonded to Cu^+. For π-complexation on both CuY and CuCl, the amount of electron forward donation was more than that of electron back donation for thiophenic adsorbates, but the reverse was true for benzene and toluene.

Key Words: Organosulfur compounds; Transportation fuels; π-Complexation; Adsorption bond.

INTRODUCTION

Deep desulfurization of transportation fuels (gasoline, diesel, and jet fuels) is being mandated by US and foreign governments, and is also needed for future fuel cell applications. However, it is extremely difficult and costly to achieve with the current technology, which requires catalytic reactors operated at high pressure and temperature. Recently, it was found that adsorption by π-complexation can be used effectively for deep desulfurization of transportation fuels at ambient temperature and pressure.[1–5] For example, by using 1–2 g of Cu(I)Y zeolite added by a thin layer of guard bed of activated carbon at room temperature, 34 cm^3 of clean diesel (at <0.2 ppmw S) can be obtained from a commercial diesel (with 430 ppmw S). The Cu(I)Y is regenerable.

The starting point of this work was the finding that the π-complexation bond between Cu(I)Y and thiophene is stronger than that between Cu(I)Y and benzene. The transportation fuels each contain over 150 different compounds. They are desulfurized in the refineries by hydrodesulfurization (HDS). HDS is effective in removal of mercaptans, sulfides, and disulfides, but is not effective in removal of the thiophenic compounds. Thus, the sulfur compounds in transportation fuels are thiophenic compounds. The main sulfur compounds are thiophene, 2-methylthiophene, benzothiophene, dibenzothiophene, 4-dimethyldibenzothiophene, and 4,6-dimethyldibenzothiophene. The latter two are particularly problematic for HDS, because the two methyl groups sterically hinder their chemisorption on the Mo sites (on the CoMo catalyst). Hence, these two compounds are referred to as "refractory" sulfur, and are the two most predominant sulfur compounds in diesel and jet fuels. The transportation fuels contain, very approximately, 70–80% alkanes and the balance is aromatics.[6] For adsorption, particularly by π-complexation, aromatics offer the most competition for the thiophenic compounds. Therefore, benzene and thiophene were used as a model pair for testing sorbents for desulfurization.

In the development of the adsorption technology for desulfurization, and also for a basic understanding of the adsorption process, a crucially important question is on the relative bonding strengths, or selectivities, of the different sulfur compounds for adsorption. The bond strengths can be measured as the heats of adsorption. However, due to the high boiling points of these compounds (e.g., 221°C for benzothiophene), such measurement is no trivial matter.[7] In this work, we used molecular orbital (MO) theory to calculate the relative bond energies with Cu(I)Y zeolite for: thiophene, 2-methylthiophene, benzene, toluene, benzothiophene, dibenzothiophene, and 4,6-dimethyldibenzothiophene. The results will shed light on the effects of the methyl and benzo groups on the π-complexation bonds between CuY and the thiophene ring. They will also shed light on the bonding mechanism. The relative bond strengths, or the qualitative trend of the adsorption strengths, are verified by the elution sequence from an elution column.

THEORETICAL SECTION

Ab Initio Molecular Orbital Computational Details

MO studies on the π-complexation bonding for thiophene and benzene on sorbent surfaces and zeolites were investigated recently.[8–10] In this work, similar MO studies were extended to other related adsorbate: toluene, 2-methylthiophene, benzothiophene, dibenzothiophene, and 4,6-dimethyldibenzothiophene. The Gaussian 98 package[11] and Cerius2 molecular modeling software[12] were used for all MO calculations. Geometry optimizations were performed at the Hartree-Fock (HF) level first, then natural bond orbital (NBO) analysis was performed at density functional theory (DFT) level using effective core potentials (ECPs).[13–16]

Density Functional Theory

DFT is an efficient tool for studying molecular properties of transition metal compounds, it can provide an accurate description of the metal–ligand interactions[17]at an affordable computational cost. In this work, a hybrid method consisting of HF and DFT, known as the self-consistent hybrid (SCH) approach or B3LYP[18,19] approach, was used. The B3LYP method can provide reliable geometric, thermodynamic, and spectroscopic parameters for metal–ligand interactions, ranging from covalent bonds to weak noncovalent interactions.[20–22] It is the combination of HF and Becke exchange[23] with the Lee–Yang–Parr (LYP) correlation potential.[24]

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Effective Core Potentials

In this work, DFT calculations were performed at B3LYP level with the LanL2DZ basis set.[25] The LanL2DZ basis set is a double-ζ basis set containing ECP representations of electrons near the nuclei for post-third-row atoms. ECP is simply a group of potential functions that replace the inner shell electrons and orbitals that are normally assumed to have minor effects on the formation of chemical bonds. Calculations of the valence electrons using ECP can be carried out at a fraction of the computational cost that is required for an all-electron calculation, while the overall quality of the computation does not differ significantly from the all-electron calculations.[13,14] The reliability of this basis set was been confirmed by the accuracy of calculation results as compared with experimental data. Therefore, the LanL2DZ basis set was employed for all calculations, i.e., geometry optimization, NBO, and frequency analysis.

Geometry Optimization and Bond Energy Calculations

Frequency analysis was used to verify that all geometry optimized structures were true minima on the potential energy surface. The optimized structures were then used for bond energy calculations according to the following expression:

$$E_{\mathrm{ads}} = E_{\mathrm{adsorbate}} + E_{\mathrm{adsorbent}} - E_{\mathrm{adsorbent-adsorbate}} \tag{1}$$

where $E_{\mathrm{adsorbate}}$ is energy of free adsorbate, $E_{\mathrm{adsorbent}}$ is energy of free adsorbent, and $E_{\mathrm{adsorbent-adsorbate}}$ is energy of the adsorbate/adsorbent system. A higher value of E_{ads} corresponds to a stronger adsorption.

Natural Bond Orbital

The optimized structures were also used for NBO analysis at the B3LYP/LanL2DZ level. The NBO analysis performs population analysis that pertains to localized wave-function properties. It gives a better description of the electron distribution in compounds of high ionic character, such as those containing metal atoms.[26] It is known to be sensitive for calculating localized weak interactions, such as charge transfer, hydrogen, bonding, and weak chemisorption (which is the case of the subject of this study). Therefore, the NBO program[27] was used for studying the electron density distribution of the adsorption system.

Models for Cu Zeolite

The Cu zeolite (CuZ) model selected for this study is similar to the ones used in our previous work[10,28] with the molecular formula of $(HO)_3Si{-}O{-}Al(OH)_3$, and the cation Cu^+ sits 2.14 Å above the bridging oxygen between Si and Al. This is a good cluster model representing the chemistry of a univalent cation bonded on site II (SII) of the faujasite framework (Z). Once the optimized structure of CuZ is obtained at the HF/LanL2DZ level, then an adsorbate molecule is added onto the Cu of zeolite model, and the resulting structure is further optimized at the HF/LanL2DZ level.

EXPERIMENTAL

Cu(I)Y [or reduced Cu(II)Y] was prepared by first ion exchanging Na Y with a $Cu(NO_3)_2$ aqueous solution (0.5 M) for 48 hr followed by reduction of Cu^{2+} to Cu^+. More details about sorbent preparation, including autoreduction of the copper ions, can be found in previous reports.[1–5,8–10]

All adsorption/breakthrough experiments were performed in a vertical, custom-made quartz adsorber equipped with a supporting glass frit. More details can be found elsewhere.[1–5] After activation treatment, the adsorbent under study was allowed to cool down to room temperature under inert gas and then tapped to ensure proper packing. Next, a sulfur-free hydrocarbon was allowed to flow through the sorbent to remove entrapped gases. After wetting the adsorbent for several minutes, the feed was switched to either commercial grade gasoline (379.7 ppmw S) or diesel (297.2 ppmw S) at constant flow rates. Effluent samples were collected at regular intervals and sulfur breakthrough curves were obtained using a gas chromatography/flame photometric detector (GC–FPD).

GC–FPD peaks identification information for sulfur compounds present in gasoline and diesel was gathered after using standards and by retention time comparison with data available in Refs.[1–5]. For standards, thiophene, BT, and DBT solutions were diluted in sulfur-free *n*-octane to a known concentration and then injected for retention time determination.

RESULTS AND DISCUSSION

Optimized Geometries

The optimized structures of adsorbents, CuCl and CuZ, are shown in Fig. 1, and those of the adsorbates are shown in Figs. 2 and 3. There are several

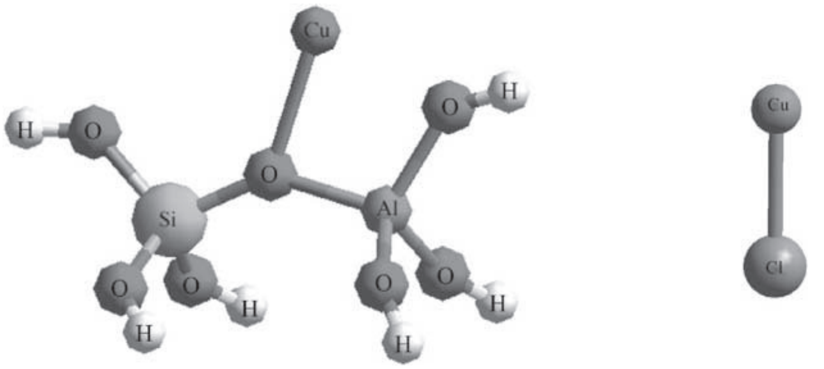

Figure 1. Optimized structures of adsorbents: Cu Zeolite and CuCl.

known coordination geometries of thiophene in organometallic complex,[29] however, to compare π-complexation strengths between thiophenic compounds and benzene type of compounds, only the η^5 geometry was considered in this study, where the aromatic ring is placed horizontally on top of Cu^+. The optimized structures of the adsorption complex are shown in Figs. 4–6. For CuCl, all adsorbates remained horizontal on top of Cu^+ after optimization, but that not the case for CuZ, where all adsorbates were in a tilted position.

A summary of bond distance in Å between Cu and the bridging oxygen in CuZ, and Cu and Cl in CuCl, is listed in Table 1. For free CuZ and CuCl, the bond distances were 2.14 and 2.21 Å. This indicates that the zeolite anion is more electronegative than chloride anion. The bond distance between Cu and Cl in CuCl complex remained unchanged after an thiophenic adsorbate

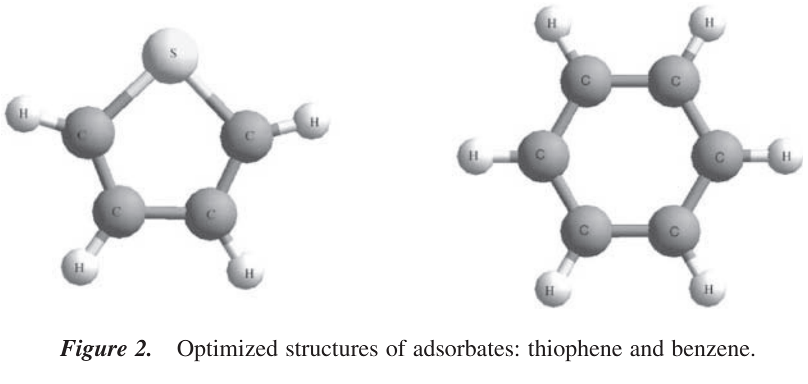

Figure 2. Optimized structures of adsorbates: thiophene and benzene.

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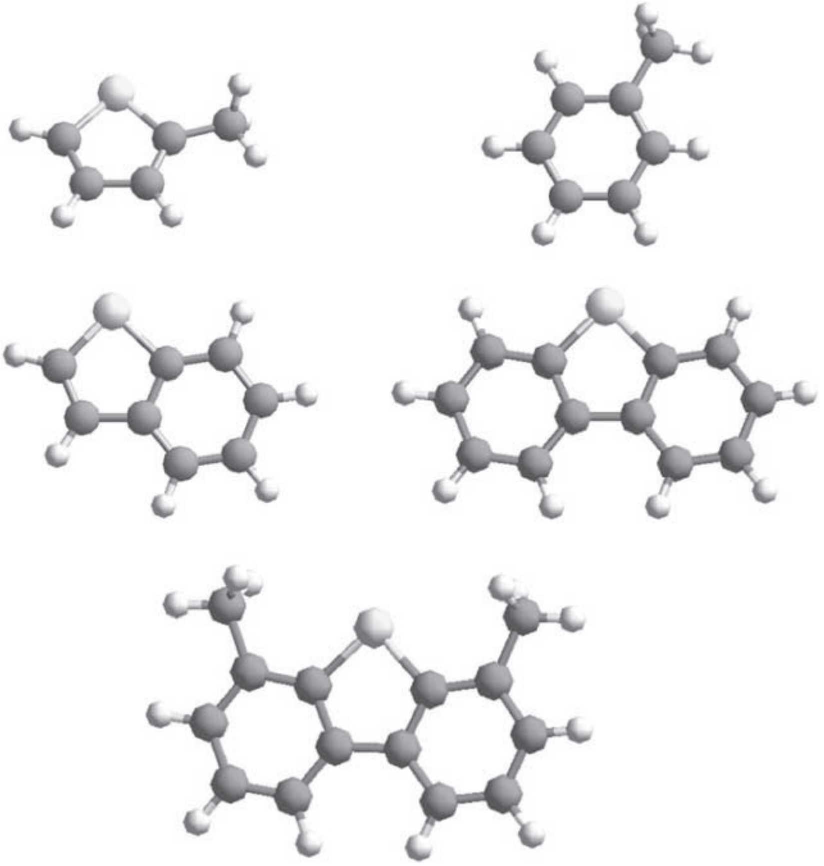
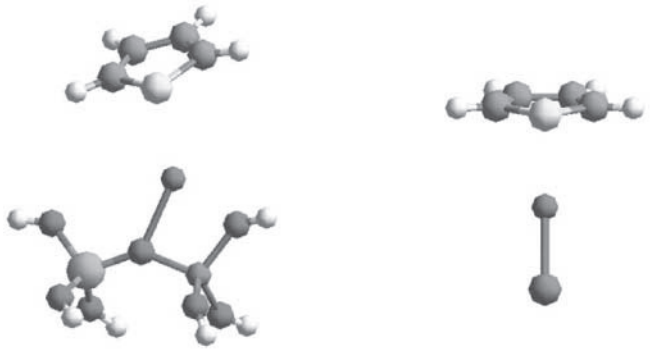


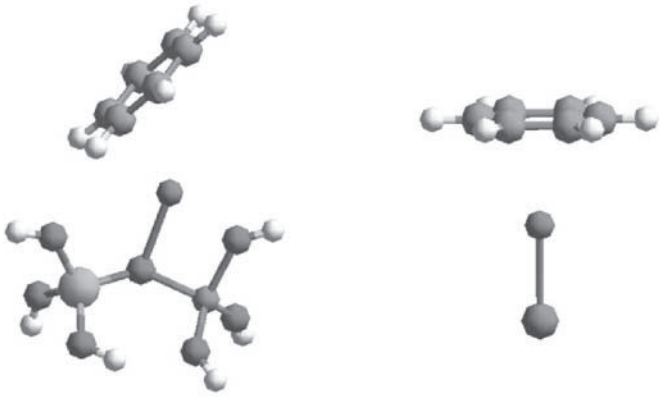
Figure 3. Optimized structures new adsobates: 2-methylthiophene, toluene, benzothiophene, dibenzothiophene, and 4,6-dimethyldibenzothiophene.

was added onto the Cu, and increased slightly when a benzene or a toluene was added. The bond distance between Cu and oxygen in CuZ complex increased for all adsorbates.

A summary of bond distance in Å between Cu and S in thiophenic molecules and C in benzene type of molecules is given in Table 2. For CuCl, the distance between Cu and S for all thiophenic adsorbates was 2.5 Å, and the distance between Cu and C for both benzene and toluene was 2.8 Å. For CuZ, the distance between Cu and S of the adsorbate was 2.5 Å for all thiophenic adsorbates, and increased to 2.7 Å for benzene and 2.8 Å for toluene.



Thiophene-CuZeolite Thiophene-CuCl



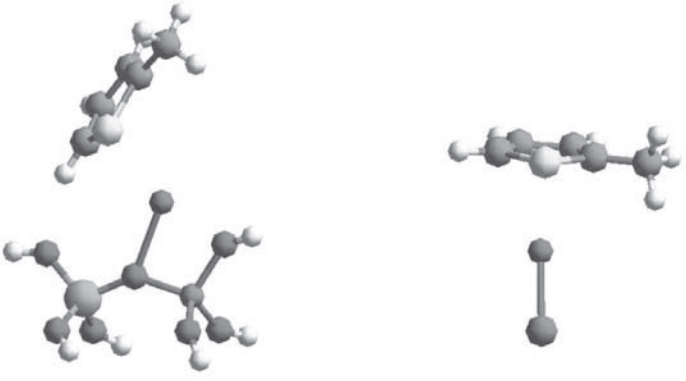
Benzene-CuZeolite Benzene-CuCl

Figure 4. Optimized structures of thiophene and benzene on CuZeolite and CuCl.

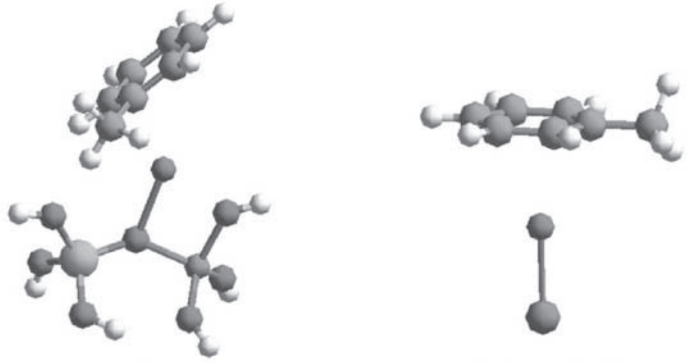
Bond Energies

The energies of adsorption calculated using Eq. (1) for thiophene, benzene, and their derivatives are summarized in Table 3.

The increase in energy of adsorption from thiophene to 2-methylthiophene in both CuZ and CuCl can be explained by the electron-donating effect of the methyl group to the aromatic ring. Such an increase is also expected in going from benzene to toluene, which is seen for both CuCl and CuZ. In going from thiophene to benzothiophene to dibenzothiophene



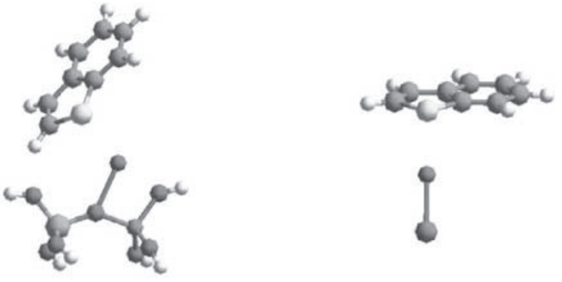
2-MethylThiophene-CuZeolite 2-MethylThiophene-CuCl



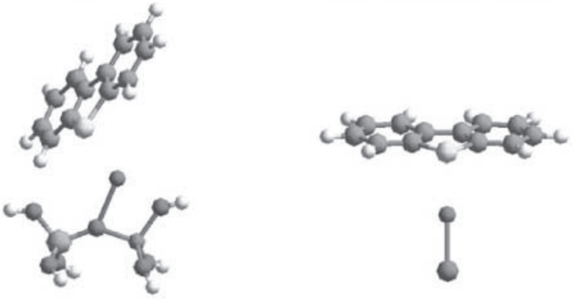
Toluene-CuZeolite Toluene-CuCl

Figure 5. Optimized structures of 2-methylthiophene and toluene on CuZeolite and CuCl.

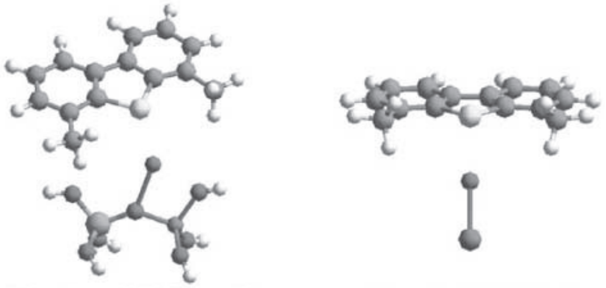
to 4,6-dibenzothiophene, one would also expect to find an increasing trend for energies of adsorption, since additional benzene ring(s) and methyl groups would increase aromaticity, thus enhance the π-complexation. Such an increasing trend was indeed seen in case of CuCl; but in case of CuZ, the increasing trend stoped at dibenzothiophene. The energy of adsorption for 4,6-dibenzothiophene was essentially the same as that of dibenzothiophene. It is possible that the two methyl groups can form steric hindrance between adsorbates and CuZ, and this steric effect plays a larger role than the electron-donating effect.



Benzothiophene-CuZeolite Benzothiophene-CuCl



Dibenzothiophene-CuZeolite Dibenzothiophene-CuCl



DimethylDBT-CuZeolite DimethylDBT-CuCl

Figure 6. Optimized structures of benzothiophene, dibenzothiophene, and 4,6-dimethyldibenzothiophene on CuZeolite and CuCl.

Column Elution Results

Figures 7 and 8 show adsorption breakthrough curves for individual organosulfur compounds in Cu(I) Y zeolites for gasoline and diesel feeds, respectively. For the former, the breakthrough order was thiophene $>$ 2-methylthiophene $>$ benzothiophene. This order agrees excellently with the data shown in Table 3,

Table 1. Bond distance in Å between Cu and the bridging oxygen in CuZ and Cu and Cl in CuCl.

Adsorbate	CuZ	CuCl
Free	2.14	2.21
Thiophene	2.17	2.21
Benzene	2.17	2.23
2-Methylthiophene	2.22	2.21
Toluene	2.16	2.22
Benzothiophene	2.23	2.21
Dibenzothiophene	2.22	2.21
4,6-Dimethyldibenzothiophene	2.15	2.21

since molecules having higher adsorption energies are expected to remain inside the zeolite cages for longer periods of time. In addition, notice that the selectivity between 2-methylthiophene, dibenzothiophenes, and the adsorbent was not significantly demarcated, which also agrees with the MO calculations data.

Since commercial gasoline fuels do not contain dibenzothiophenes and their derivatives (because these are found in higher boiling point fuels), we also analyzed sulfur removal from diesel fuels. Desulfurization of a commercial diesel fuel with Cu(I)Y zeolites resulted in the breakthrough curves shown in Fig. 8. Breakthrough followed the order: benzothiophene > dibenzothiophene > 4,6-dimethyldibenzothiophene. When comparing the adsorption behavior between dibenzothiophene, and 4,6-dimethyldibenzothiophene it is apparent the latter adsorbs stronger than the former. Refractory compounds, such as 4,6-dimethyldibenzothiophene, are the most abundant in diesel fuels since they remain largely unaffected by current commercial HDS treatments. Thus, these are expected to displace the other thiophenic compounds and adsorb in largest quantities.

Table 2. Bond distance in Å between Cu and S in thiophenic molecules and C in benzene type of molecules.

Adsorbate	CuZ	CuCl
Thiophene	2.50	2.48
Benzene	2.69	2.84
2-Methylthiophene	2.49	2.48
Toluene	2.83	2.84
Benzothiophene	2.49	2.48
Dibenzothiophene	2.49	2.48
4,6-Dimethyldibenzothiophene	2.49	2.48

Table 3. Energy of adsorption in (kcal/mol) for different adsorbates.

Adsorbate	Δ*E* on CuZ	Δ*E* on CuCl	Exptl. Δ*E*
Thiophene	21.4 (10)	13.5	20.8–22.4 (10)
2-Methylthiophene	22.4	15.9	
Benzene	20.5 (10)	12.4	19.3–21.8 (10)
Toluene	21.5	15.3	
Benzothiophene	22.9	16.2	
Dibenzothiophene	23.6	17.1	
4,6-Dimethyldibenzothiophene	23.5	18.4	

More information about desulfurization of both gasoline and diesel fuels via π-complexation can be found elsewhere.[1–5]

NBO Results

The nature of the adsorbent–adsorbate bonding can be further understood by analyzing the NBO results shown in Tables 4 and 5. When an adsorbate molecule approaches the Cu cation, some electronic charge is transferred

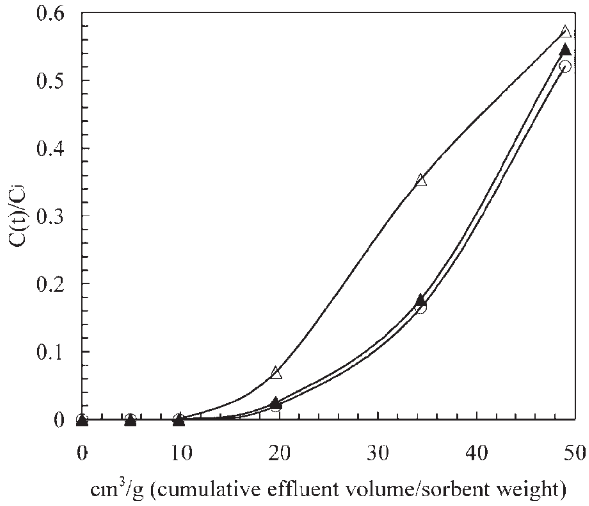


Figure 7. Breakthrough of thiophene (△) or 2-methylthiophene (▲) or benzothiophene (○) in a fixed-bed adsorber of Cu(I)Y adsorbent, for gasoline feed at room temperature. C_j is the sulfur concentration in the feed for each species.

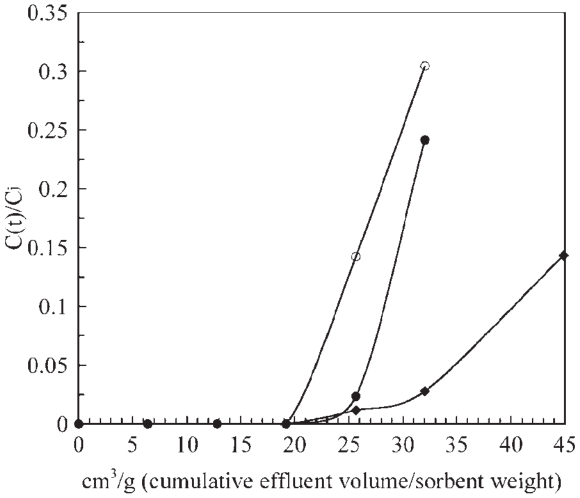


Figure 8. Breakthrough of benzothiophene (○) or dibenzothiophene (●) or 4,6-dimethyl-dibenzothiophene (◆) in a fixed-bed adsorber with Cu(I) Y adsorbent, with diesel feed at room temperature. C_j is the sulfur concentration in the feed for each species.

from the aromatic ring π-orbital to the valence 4s orbital of Cu cation, at the same time, electrons in the filled 3d orbitals of Cu cation are transferred to the symmetry-matched π^* orbital of the aromatic ring.

As observed in both tables, upon adsorption, for all adsorbates, there was an increase in the electron occupancies of the 4s orbital, and there was decrease in the total electron occupancies of the 3d orbitals. This is caused by the donation and back donation of electrons between Cu and the aromatic

Table 4. Summary of the NBO analysis of the π-complexation between different adsorbates and CuCl.

Adsorbate	Δ4s (σ donation)	Δ3d (d−π^* back donation)	Net change
Thiophene	0.092	−0.046	0.046
2-Methylthiophene	0.097	−0.048	0.050
Benzene	0.011	−0.051	−0.040
Toluene	0.012	−0.050	−0.038
Benzothiophene	0.101	−0.049	0.052
Dibenzothiophene	0.106	−0.049	0.057
4,6-Dimethyldibenzothiophene	0.111	−0.050	0.060

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Table 5. Summary of the NBO analysis of the π-complexation between different adsorbates and CuZ.

Adsorbate	Δ4s (σ donation)	Δ3d (d$-\pi^*$ back donation)	Net change
Thiophene	0.101	-0.036	0.066
2-Methylthiophene	0.124	-0.041	0.083
Benzene	0.045	-0.050	-0.005
Toluene	0.041	-0.047	-0.007
Benzothiophene	0.131	-0.042	0.088
Dibenzothiophene	0.129	-0.040	0.089
4,6-Dimethyldibenzothiophene	0.120	-0.037	0.083

ring(s). It is interesting to note that for both CuZ and CuCl, the amount of electron forward donation was more than that of electron back-donation for thiophenic adsorbates, but the reverse was true for benzene and toluene. Since CuZ is a better adsorbent for thiophene than for benzene, this means in π-complexation, the transfer of electronic charge from thiophenic ring is more significant than that of benzene ring. Also in case of CuZ, with zeolite being a stronger anion, the increase in the electron occupancies of the 4s orbital was higher when compared to the increase for CuCl. A more electronegative anion can attract more electrons from the Cu cation bonded to it, thus increasing the positive charge on Cu cation, and this Cu cation in turn will be a better acceptor to form π-complexation with the adsorbates, this explains why CuZ is a better adsorbent.

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REFERENCES

1. Yang, R.T.; Hernández-Maldonado, A.J.; Yang, F.H. Desulfurization of transportation fuels with zeolites under ambient conditions. Science **2003**, *301*, 79–81.
2. Hernández-Maldonado, A.J.; Yang, R.T. Desulfurization of liquid fuels by adsorption via π-complexation with Cu(I)-Y and Ag-Y zeolites. Ind. Eng. Chem. Res. **2003**, *42*, 123–129.
3. Hernández-Maldonado, A.J.; Yang, R.T. Desulfurization of commercial liquid fuels by selective adsorption via π-complexation with Cu(I)-Y zeolite. Ind. Eng. Chem. Res. **2003**, *42*, 3103–3110.

4. Yang, R.T.; Takahashi, A.; Yang, F.H.; Hernandez-Maldonado, A. Selective Sorbents for Desulfurization of Liquid Fuels. U.S. and foreign Patent applications filed, 2002.
5. Hernández-Maldonado, A.J.; Yang, R.T. New sorbents for desulfurization of diesel fuels via π-complexation. AIChE J. **2003**, *submitted.*
6. Yang, R.T. *Adsorbents: Fundamentals and Applications*; Wiley: New York, 2003.
7. Yang, R.T.; Long, R.Q.; Padin, J.; Takahashi, A.; Takahashi, T. Adsorbents for dioxins: a new technique for sorbeny screening for low-volatile organics. Ind. Eng. Chem. Res. **1999**, *38*, 2726–2731.
8. Yang, R.T.; Takahashi, A.; Yang, F.H. New sorbents for desulfurization of liquid fuels by π-complexations. Ind. Eng. Chem. Res. **2001**, *40*, 6236–6239.
9. Takahashi, A.; Yang, F.H.; Yang, R.T. Aromatics/aliphatics separation by adsorption; new sorbents for selective aromatics adsorption by π-complexations. Ind. Eng. Chem. Res. **2000**, *39*, 3856–3867.
10. Takahashi, A.; Yang, F.H.; Yang, R.T. New sorbents for desulfuration by π-complexations: thiophene/benzene adsorption. Ind. Eng. Chem. Res. **2002**, *41*, 2487–2496.
11. Frisch, M.J.; Trucks, G.W.; Schlegel, H.B.; Scuseria, G.E.; Robb, M.A.; Cheeseman, J.R.; Zakrzewski, V.G.; Montgomery, J.A., Jr.; Stratmann, R.E.; Burant, J.C.; Dapprich, S.; Millam, J.M.; Daniels, D.; Kudin, K.N.; Strain, M.C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G.A.; Ayala, P.Y.; Cui, Q.; Morokuma, K.; Malick, D.K.; Rabuck, A.D.; Raghavachari, K.; Foresman, J.B.; Cioslowski, J.; Ortiz, J.V.; Baboul, A.G.; Stefanov, B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R.L.; Fox, D.J.; Keith, T.; Al-Laham, M.A.; Peng, C.Y.; Nanayakkara, A.; Gonzalez, C.; Chullacombe, M.; Gill, P.M.W.; Johnson, B.; Chen, W.; Wong, M.W.; Andres, J.L.; Head-Gordon, M.; Replogle, E.S.; Pople, J.A. Gaussian, Inc.: Pittsburgh, PA, 1998 Gaussian 98, revision A.7.
12. San Diego, CA Cerius2, version 4.6, Accelrys.
13. Hay, P.J.; Wadt, W.R. Ab initio effective core potential for molecular calculations. Potentials for the transition metals atoms sc to Hg. J. Chem. Phys. **1985**, *82*, 270–283.
14. Wadt, W.R.; Hay, P.J. Ab initio effective core potential for molecular calculations: potentials for main group elements Na to Bi. J. Chem. Phys. **1985**, *92*, 284–298.

15. Hay, P.J.; Wadt, W.R. Ab initio effective core potential for molecular calculations: potentials for K to Au including the outermost core orbitals. J. Chem. Phys. **1985**, *82*, 299–310.
16. Gordon, M.S.; Cundari, T.R. Effective core potential studies of transition metal bonding, structure and reactivity. Coord. Chem. Rev. **1996**, *147*, 87–115.
17. Ziegler, T. Approximate density functional theory as a practical tool in molecular energetics and dynamics. Chem. Rev. **1991**, *91*, 651–667.
18. Becke, A.D. A new mixing of Hartree-Fock and local density functional theories. J. Chem. Phys. **1993**, *98*, 1372–1377.
19. Becke, A.D. Density functional thermochemistry, III, the role of exact exchange. J. Chem. Phys. **1993**, *98*, 5648–5652.
20. Barone, V.; Adamo, C. Validation of hybrid density functional Hartree-Fock approaches for the study of homogeneous catalysis. J. Phys. Chem. **1996**, *100*, 2094–2099.
21. Halthausen, M.C.; Heinemann, C.; Cornhl, H.H.; Koch, W.; Schwarz, H. The performance of density-functional/Hartree-Fock hybrid methods: catalytic transition-metal methyl complexes MCH_3^+ (M = Sc–Cu, La, Hf–Au). J. Chem. Phys. **1995**, *102*, 4931–4941.
22. Ricca, A.; Bauschlicher, C.W. Successive binding energies of $Fe(CO)_5^+$. J. Phys. Chem. **1994**, *98*, 12899–12903.
23. Becke, A.D. Density-functional exchange-energy approximation with correct asymptotic behavior. Phys. Rev. **1988**, *A 38*, 3098–3100.
24. Lee, C.; Yang, W.; Parr, R.G. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. Phys. Rev. **1988**, *B37*, 785–789.
25. Russo, T.V.; Martin, R.L.; Hay, P.J. Effective core potentials for DFT calculations. J. Phys. Chem. **1995**, *99*, 17085–17087.
26. Reed, A.E.; Weinstock, R.B.; Weinhold, F. Natural population analysis. J. Chem. Phys. **1985**, *83* (2), 735–746.
27. Glendening, E.D.; Reed, A.E.; Carpenter, J.E.; Weinhold, F. *NBO Version 3.1*; 1995.
28. Chen, N.; Yang, R.T. Ab initio molecular orbital study of adsorption of oxygen, nitrogen, and ethylene on silver-Zeolite and silver halides. Ind. Eng. Chem. Res. **1996**, *35*, 4020–4027.
29. Song, Chunshan; Xiaoliang, Ma. New design approaches to ultra-clean diesel fuels by deep desulfurization and deep dearomatization. Appl. Cat. B: Env. **2003**, *41*, 207–238.

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