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Effects of oxygenates and moisture on adsorptive desulfurization of liquid fuels with Cu(I)Y zeolite

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Abstract

Oxygenates (i.e., ethanol and MTBE as required additives in gasoline) and moisture were found to have strong inhibiting effects on desulfurization by adsorption with zeolite. The effects of each individual molecule were studied quantitatively by using a model fuel (500 ppmw thiophene in 80% *n*-octane + 20% benzene). Cu(I)Y was used as the π-complexation sorbent. Ab initio molecular orbital calculations showed that the adsorption bond energies with Cu(I)Y were: 21.4 kcal/mol for thiophene; 31.0 kcal/mol for MTBE and 41.6 kcal/mol for ethanol. Separation or selectivity factors can be estimated from heats of adsorption, and the inhibiting effects were predicted to follow the order of the relative heats of adsorption: water > ethanol > MTBE > thiophene. The inhibiting effects were measured by the decreases in the desulfurization capacities of Cu(I)Y in the presence of each additive in the model fuel. The results were in agreement with the theoretical prediction. In addition, the desulfurization capacity was strongly dependent on the liquid hourly space velocity because of the diffusion limitation of thiophene in the zeolite crystals.

Keywords: Fuel desulfurization; Oxygen compounds; Zeolites; π-Complexation; Adsorption

1. Introduction

In recent years, selective desulfurization of transportation fuels (gasoline, diesel and jet fuel) by adsorption at ambient temperature and pressure has attracted increasing interest [1]. Our recent results have shown that a class of sorbents that rely on a process called π-complexation are very promising for selective removal of organosulfur (i.e., thiophenic) molecules from commercial fuels [2]. Using the best sorbent, vapor-phase ion exchanged Cu(I)Y [3], 34 cm^3 of clean diesel (at <0.2 ppmw S) per gram of zeolite can be obtained from a commercial diesel (with 430 ppmw S) at room temperature [2].

The Cu(I)Y sorbent could lose its sulfur selectivity and capacity significantly in the present of compounds that adsorb on the zeolite more strongly than the thiophenic compounds, and a number of such compounds exist in the commercial fuels. We have found that Cu(I)Y was capable of selectively removing nitrogen compounds from the commercial diesel because these compounds all adsorb more strongly than the thiophenes [4]. Thus, some additives (such as oxygenates) and high levels of moisture, which are normally present in the commercial fuels, would also be strongly adsorbed and subsequently quickly deactivate the Cu(I)Y sorbent for desulfurization of commercial fuels. So it is important to understand the effects of oxygenates and moisture on desulfurization in order to guide the rational design of adsorptive desulfurization process using π-complexation sorbents.

In this work, we report results on desulfurization of a model fuel that contained 500 ppmw thiophene (i.e., 190 ppmw S) in *n*-octane (80 wt%) and benzene (20 wt%) by Cu(I)Y sorbents. The model fuel was used so the effect of each additive could be assessed individually and quantitatively. The effect of the important operating parameter, flow space velocity, was also included for investigation. The effects of space velocity, two oxygenates (ethanol and methyl *tertiary*-butyl ether, a.k.a., MTBE) as well as H_2O on desulfurization were investigated.

2. Adsorption bond energy and separation factor (or selectivity factor)

In separation science and adsorption, ‘‘separation factor’’ or ‘‘selectivity factor’’ is used as the best indicator for the

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feasibility/quality of separation for a given mixture [5,6]. Using thiophene (representing sulfur in fuel) and benzene (representing aromatics in fuel) as an example, the separation or selectivity factor for the separation of thiophene over benzene is given by:

$$\alpha_{21} = \frac{X_2/X_1}{Y_2/Y_1} \quad (1)$$

where X and Y are mole fractions in the adsorbed and solution phases, respectively; and the subscripts 1 and 2 denote benzene and thiophene, respectively. For a lowest estimate of α_{21}, we assume Henry's law for the isotherms of thiophene and benzene. The Henry constant is approximately proportional to $e^{E/RT}$ (Ref. [6], p. 18), where E is the adsorption bond energy. Thus, the selectivity/separation factor for thiophene/benzene on Cu(I)Y is (based on 22 kcal/mol for thiophene versus 20 kcal/mol for benzene [1,2]):

$$\alpha_{21(\text{thiophene/benzene})} = 30 \quad (2)$$

Combined with the high separation power of chromatography (i.e., elution in packed columns), many binary mixtures are routinely separated commercially by Sorbex (simulated moving-bed processes) with separation factors around 2 [6]. The estimates above are based on Henry's law isotherms. In fact, benzene is at high concentrations in the fuels, so X_1 is much lower than that estimated from Henry's law. Therefore, the separation factor would be much greater than 30.

The adsorption bond energy is approximately equal to the heat of adsorption for physical adsorption and weak chemisorption (as in π-complexation). Heats of adsorption are routinely obtained from pure-gas isotherms. The situation for adsorption from liquid solutions is, however, quite different and is more complicated because of the solute–solvent interactions. Here, the solute molecule breaks the bonds with the solvent molecules upon forming an adsorption bond with the solid surface site. Thus, as shown by Ng et al. [7], the heats of adsorption from solution are considerably lower than that measured from pure-gas adsorption. For example, the heat of adsorption of thiophene on NaY from its solution in hexadecane was 20.9 kJ/mol, compared to 80.7 kJ/mol that was measured for pure-vapor thiophene adsorption [7]. More examples for the effects of solvent on heat of adsorption are given elsewhere [6]. Nonetheless, for comparison of different solute molecules from the same solvent where the solute–solvent interactions are similar, the pure-gas heats of adsorption data provide a good basis for assessment of the separation factor for these solutes.

3. Ab initio molecular orbital calculations

Molecular orbital (MO) studies on the π-complexation bonding for thiophene and related aromatic compounds on copper zeolites were investigated recently [8]. In this work, MO studies were extended to other adsorbates known as oxygenates, such as MTBE (methyl tertiary-butyl ether) and ethanol, and compared them to thiophene. The Gaussian 98 package [9] and Cerius2 molecular modeling software [10] were used for all MO calculations. Geometry optimizations were performed at the Hartree–Fock (HF) level first, then binding energy analysis was performed at density functional theory (DFT) level using effective core potentials (ECPs) [11–14].

3.1. 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 [15] at an affordable computational cost. A hybrid method consisting of HF and DFT, known as the self-consistent hybrid (SCH) approach or B3LYP [16,17] approach is used. The B3LYP method can provide reliable geometric, thermodynamic and spectroscopic parameters for metal–ligand interactions, ranging from covalent bonds to weak non-covalent interactions [18–20]. It is the combination of HF and Becke exchange [21] with the Lee–Yang–Parr (LYP) correlation potential [22].

3.2. Effective core potentials

DFT calculations are performed at B3LYP level with LanL2DZ basis set [23]. 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 which replace the inner shell electrons and orbitals which 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, and the reliability of this basis set has been confirmed by the accuracy of calculation results as compared with experimental data. Therefore, the LanL2DZ basis set was employed for all calculations.

3.3. 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:

$$E_{\text{ads}} = E_{\text{adsorbate}} + E_{\text{adsorbent}} - E_{\text{adsorbent-adsorbate}} \quad (3)$$

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

3.4. Models for Cu–zeolite (CuZ)

The Cu–zeolite model selected for this study is similar to the ones used in our previous work [8] 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.

4. Experimental

The EPA standard for oxygenates in all US gasoline is minimum 2% by weight of oxygen. In our work, less than 5% ethanol or MTBE was added in the model fuel, which corresponded to 1.7% and 0.9% oxygen by weight, respectively. The total water concentration in the commercial fuels is variable. For example, the value of water content is between 100 and 500 ppmw in the BP commercial diesels. Here an average concentration of 300 ppmw H_2O was added into our model fuel.

The Cu(I)Y sorbent used in this study was prepared by the standard liquid-phase ion exchange (LPIE) or a vapor-phase ion exchange (VPIE) technique that was developed in our laboratory [3]. Briefly, LPIE was performed by exchange with aqueous $Cu(NO_3)_2$ solution followed by auto-reduction, and VPIE was achieved by direct reaction between HY zeolite with CuCl vapor at a high temperature. Thus the Cu^+ loading was substantially higher for the VPIE sample, as determined by energy dispersive X-ray spectroscopy (EDX). The EDX analysis showed that the VPIE sample was nearly completely ion exchanged, however, the LPIE sample had only 36% exchange [1]. As a result, more Cu^+ should be located at exposed sites because of the high concentration of these cations in the framework. The zeolite was in powder form of crystals.

All adsorption/breakthrough experiments were performed with down-flow in a vertical custom-made quartz adsorber equipped with a supporting glass frit. After in situ activation of the adsorbent, a model fuel was allowed to contact the bed and the effluent sulfur concentration was monitored as a function of time. The liquid hourly space velocity (LHSV) was carefully controlled by adjusting the helium pressure in the empty space above the bed in the reactor in order to overcome the pressure drop through the bed. Effluent samples collected during the breakthrough experiments were analyzed using a Shimadzu GC-17A v3 unit equipped with a flame photometric detector (FPD). Details of the sulfur calibration and analysis are given elsewhere [5]. Adsorption breakthrough curves were generated by plotting the transient total sulfur concentration normalized by the feed total sulfur concentration versus cumulative fuel volume that was normalized by total bed weight. The breakthrough adsorption amounts were obtained at the point where the outlet fuel sulfur content was less than approximately 1 ppmw. More details about adsorbent preparation, in situ activation, and adsorption test can be found in our previous papers [1–5].

5. Results and discussion

5.1. Molecular orbital calculations

The optimized structures of the oxygenates MTBE and ethanol are shown in Fig. 1, and the optimized structures of MTBE and ethanol adsorbed on CuZ (CuY model) are shown in Fig. 2. The oxygen in MTBE and ethanol can bind to the positively charged Cu in CuZ. Oxygen being more electronegative than sulfur, one would expect the oxygenates to bind more strongly to CuZ than thiophene, as indicated in the bond energies calculations, summarized in Table 1. The binding energy of MTBE is less than that of ethanol as can be explained by the steric effect from the *tert*-butyl group. Among these molecules, ethanol has the highest heat of adsorption (of 41.6 kcal/mol). No experimental data have been found for the heat of adsorption of ethanol on zeolites; but this value is close to the heat of adsorption of ethanol on Co/ZnO catalyst (35.9 kcal/mol) measured by calorimetry [24].

A summary of bond distances in Å between Cu and the bridging oxygen in CuZ, for MTBE and ethanol compared to thiophene, is listed in Table 2. A summary of bond distance in Å between Cu and O in MTBE and ethanol, again compared to thiophene, is given in Table 3. From these two tables one can see that as the binding energy increases, the distance between Cu and the bridging oxygen in CuZ increases, and at the same time, the distance between Cu and the adsorbate decreases.

The molecular orbital calculations indicate that the bond energies for ethanol, MTBE and thiophene on Cu(I)Y zeolite are significantly different and follow the order:

ethanol > MTBE > thiophene

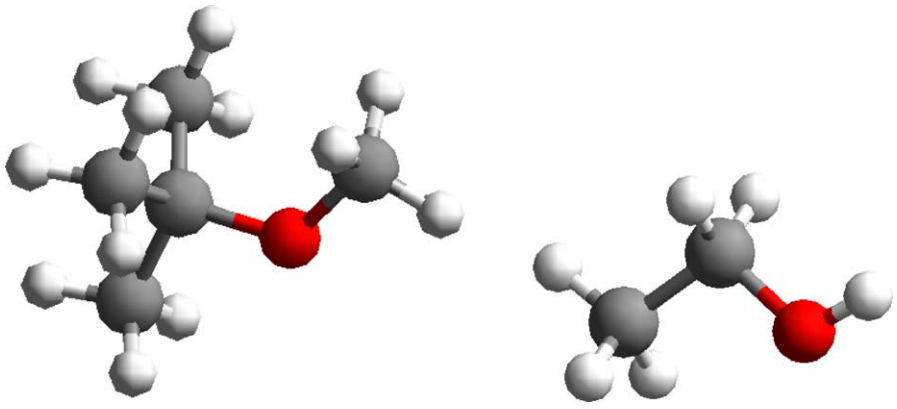

Fig. 1. Optimized structures of oxygenates: MTBE and ethanol. Atoms in decreasing sizes are: carbon, oxygen and hydrogen.

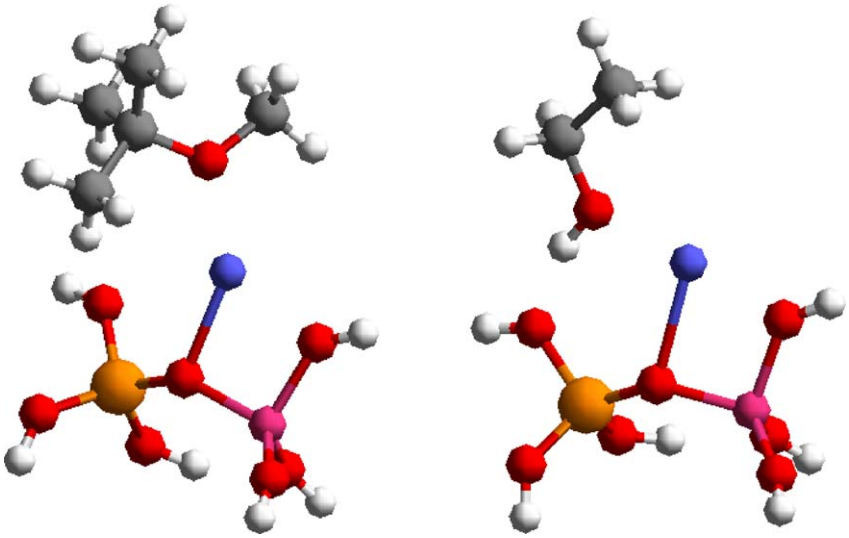

Fig. 2. Optimized structures of MTBE and ethanol adsorbed on site II of Cu(I)Y zeolite. The zeolite cluster model consists of a SiO_4 and an AlO_4 tetrahedra linked by an O atom which is also bonded to a Cu atom.

Thus, strong inhibiting effects on desulfurization by ethanol and MTBE are expected, and that the inhibiting effect of ethanol should be stronger than that of MTBE.

The effects of water molecule are more difficult to assess because it is known that water can easily disproportionate Cu^+ into Cu^0 and Cu^{2+}, which would lose its π-complexation ability. The heat of adsorption of water on NaA is ∼20 kcal/mol at low loading and declines rapidly at higher loadings [25]. Similarly, the heats of adsorption of water on NaX and KNaX zeolites are also ∼20 kcal/mol at low loadings [26]. Unlike thiophene and the two oxygenates, water is nearly insoluble in the liquid fuels (in this case, benzene/*n*-octane). In fact, it was difficult to dissolve water in the model fuel, and empirically, 500 ppmw appeared to be the limit. As discussed by Ng et al. [7], the heats of adsorption of thiophene from the organic liquid solution are much lower than that from pure-gas phase because of the solvent–solute interactions. This would not be the case for water because of its very low solubility. Thus, water molecule is expected to have a stronger inhibiting effect on desulfurization, and the inhibiting effects should follow the order:

water > ethanol > MTBE > thiophene

Table 1
Energy of adsorption (in kcal/mol) for different adsorbates

Adsorbate	Δ*E* on CuZ	Experimentel Δ*E*
Thiophene	21.4 [8]	20.8–22.4 [8]
MTBE	31.0	
Ethanol	41.6	

Table 2
Bond distance in Å between Cu and the bridging oxygen in CuZ

Adsorbate	CuZ
Free	2.14 [8]
Thiophene	2.17 [8]
MTBE	2.20
Ethanol	2.33

Table 3
Bond distance in Å between Cu and S in thiophene, and O in MTBE and ethanol

Adsorbate	CuZ
Thiophene	2.50 [8]
MTBE	2.09
Ethanol	2.02

5.2. *Effect of liquid hourly space velocity*

The breakthrough adsorption amounts were obtained at the point where the outlet fuel sulfur content was less than approximately 1 ppmw, which are summarized in Table 4.

Fig. 3 shows the breakthrough curves for thiophene in 80% octane and 20% benzene mixture with Cu(I)Y (LPIE) sorbent at

Table 4
Breakthrough sulfur loadings for thiophene on Cu(I)Y sorbent

Sorbent	Additive	Liquid hourly space velocity (h^{-1})	Breakthrough loading (mmol/g)[a]
Cu(I)Y (LPIE)	–[b]	1.6	0.176
Cu(I)Y (LPIE)	–	4.1	0.106
Cu(I)Y (LPIE)	–	10.4	0.044
Cu(I)Y (VPIE)	–	2.1	0.247
Cu(I)Y (VPIE)	–	4.9	0.168
Cu(I)Y (VPIE)	–	9.8	0.084
Cu(I)Y (VPIE)	1 wt% ethanol	4.9	0.066
Cu(I)Y (VPIE)	5 wt% ethanol	4.9	0.022
Cu(I)Y (VPIE)	5 wt% MTBE	4.9	0.040
Cu(I)Y (VPIE)	300 ppmw H_2O	4.9	0.026

[a] Loading amounts normalized by total bed weight. Breakthrough was based on effluent showing 1 ppmw total sulfur.
[b] 500 ppmw thiophene, 20 wt% benzene, and 80 wt% *n*-octane.

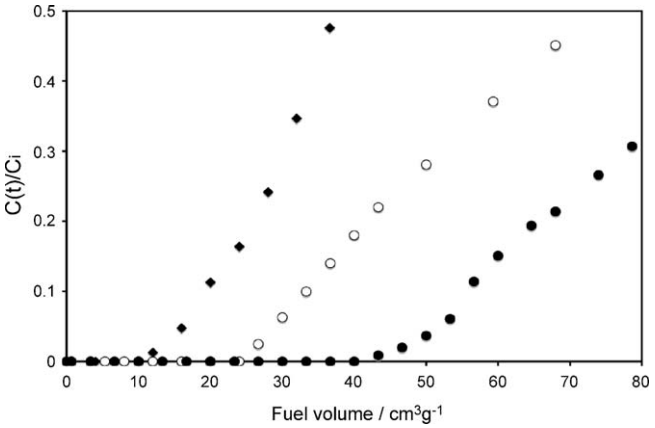

Fig. 3. Effect of space velocity on the desulfurization of model fuel containing 500 ppmw (C_i) thiophene, 20 wt% benzene, and 80 wt% *n*-octane, on Cu(I)Y (LPIE) sorbent. (●) 1.6 h^{-1}; (○) 4.1 h^{-1}; (◆) 10.4 h^{-1}.

various space velocities. At a low space velocity of 1.6 h^{-1}, it can be seen that about 40 ml fuel was desulfurized to below 1 ppmw sulfur per 1 g sorbent, corresponding to a breakthrough capacity of 0.176 mmol (5.65 mg) sulfur per gram sorbent (see Table 4). An increase in space velocity resulted in a decrease of the breakthrough capacity for sulfur. As shown in Table 4, only 0.044 mmol sulfur (corresponding to about 10 ml fuel) was adsorbed on the same fresh sorbent when the space velocity was increased to 10.4 h^{-1}. On the other hand, the sulfur concentration in the effluent after the breakthrough point increased more rapidly with time (i.e., a sharper concentration wavefront) at a higher space velocity. This could be due to the diffusion of thiophene molecules to the cavities of zeolite where the Cu(I) sites are located becoming more difficult at a higher space velocity (e.g., at 10.4 h^{-1} space velocity). These results show that diffusion limitation is important in this adsorption system and a low space velocity is necessary.

The adsorption experiments were repeated using the Cu(I)Y (VPIE) sorbent at similar space velocities, and the breakthrough curves are shown in Fig. 4. Similar effects of space velocity were observed for this sorbent as that for Cu(I)Y (LPIE), while the sulfur breakthrough capacities of this sorbent were all

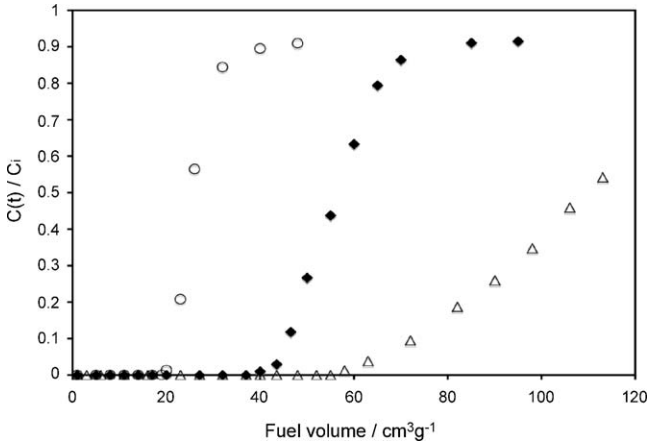

Fig. 4. Effect of space velocity on the desulfurization of model fuel containing 500 ppmw (C_i) thiophene, 20 wt% benzene, and 80 wt% *n*-octane, on Cu(I)Y (VPIE) sorbent. (▲) 2.1 h^{-1}; (◆) 4.9 h^{-1}; (○) 9.8 h^{-1}.

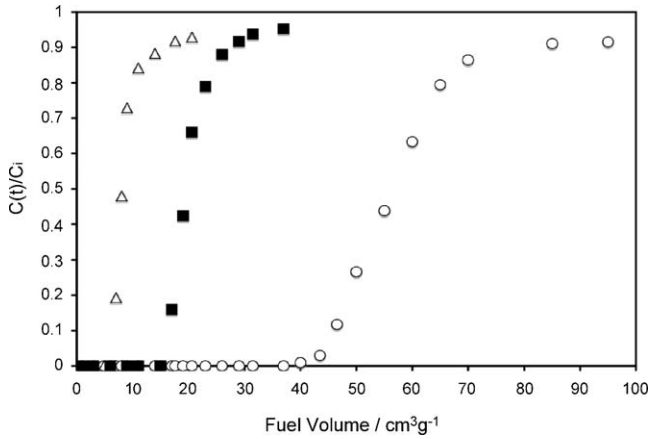

Fig. 5. Effect of addition of ethanol on the desulfurization of model fuel containing 500 ppmw (C_i) thiophene in benzene and *n*-octane on Cu(I)Y (VPIE) sorbent at 4.9 h^{-1} space velocity. (○) 20 wt% benzene and 80 wt% *n*-octane; (■) 1 wt% ethanol, 19.8 wt% benzene and 79.2 wt% *n*-octane; (▲) 5% ethanol, 19 wt% benzene and 76 wt% *n*-octane.

higher than that of Cu(I)Y (LPIE) at the same space velocities (see Table 4). At 2.1 h^{-1} space velocity, it can be seen that about 56 ml of the model fuel was desulfurized to below 1 ppmw sulfur, corresponding to a breakthrough capacity of 0.247 mmol sulfur per gram (Table 4). This value is about 1.4 times that obtained over the Cu(I)Y (LPIE) sorbent under nearly the same experimental conditions. This increase in sulfur capacity can be attributed to the higher content of Cu^+ exchanged into the zeolite framework by using the VPIE method (nearly total exchange) than that by the LPIE technique (36% exchange) [3].

5.3. *Effects of oxygenates and moisture*

The commercial oxygenates are MTBE and ethanol which are added in a blending process in the refinery. Moisture is present in all commercial fuels. The effects of each of these compounds on the breakthrough curves were tested. The space velocity was set at 4.9 h^{-1} and the total sulfur content in the fuel was 190 ppmw (i.e., 500 ppm thiophene). Cu(I)Y (VPIE) was used as the sorbent because which has a higher sulfur capacity as mentioned above.

Fig. 5 shows the results of desulfurization of model fuel containing 1–5% ethanol additive over the Cu(I)Y sorbent. It can be seen that in the presence of ethanol, the sulfur breakthrough capacity sharply decreased in comparison to that without ethanol. For the fuel containing 5% ethanol, the breakthrough capacity dropped to about 0.0221 mmol sulfur per gram, which was less than 10% of the value obtained by the fuel without ethanol. In addition, it is seen that the sulfur concentration in the effluent quickly increased to the inlet sulfur content (Fig. 5). That is, the total sulfur capacity was also sharply decreased. These results indicate that thiophene was not selectively adsorbed on the sorbent in the presence of ethanol in the fuel. This result is attributed to the stronger adsorption energy of ethanol with the sorbent than that of thiophene.

Fig. 6 shows the sulfur breakthrough curves for thiophene obtained on Cu(I)Y (VPIE) treated by a model fuel containing

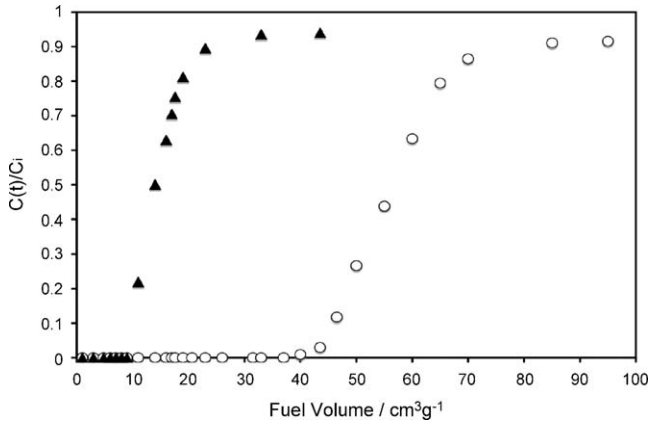

Fig. 6. Effect of addition of MTBE on the desulfurization of model fuel containing 500 ppmw (C_i) thiophene in benzene and *n*-octane on Cu(I)Y (VPIE) sorbent at 4.9 h^{-1} space velocity. (○) 20 wt% benzene and 80 wt% *n*-octane; (▲) 5 wt% MTBE, 19 wt% benzene and 76 wt% *n*-octane.

5% MTBE. A sharp decline of breakthrough fuel volume per gram sorbent was also observed with the addition of MTBE as ethanol. But the inhibiting effect on the sulfur breakthrough capacity by ethanol was stronger that that by MTBE. Additionally, a fast saturation of the effluent sulfur concentration with time to the initial sulfur content was also observed (see Fig. 6), while it was slightly slower than that with ethanol additive in the fuel.

The effect of H_2O on desulfurization of model fuel with Cu(I)Y sorbent is shown in Fig. 7. It can be seen that even 300 ppmw H_2O added into the fuel significantly decreased the sulfur breakthrough capacity to about 0.0265 mmol sulfur per gram sorbent, which were comparable to that with 5% ethanol added (Table 4). As discussed, water is strongly adsorbed on zeolites. In addition, as reported previously [5], Cu^+ ions are not stable in the presence of moisture and can be easily disproportionated into Cu^{2+} and Cu^0 that do not form π-complexation. Therefore, the loss of sulfur selectivity and capacity of the model fuel with the addition of water could be due to the adsorbed water on zeolite strongly interact with Cu^+ ions.

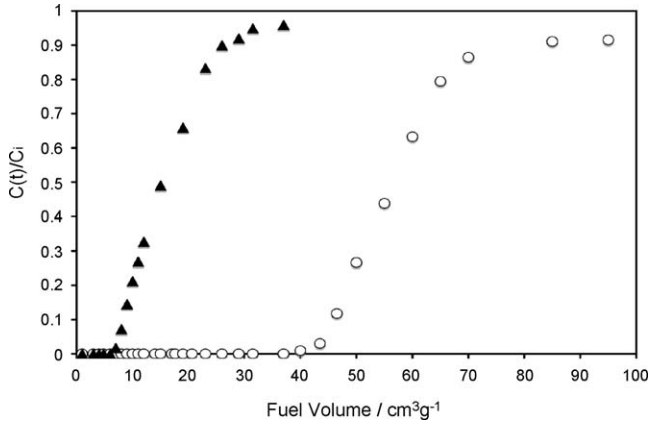

Fig. 7. Effect of addition of H_2O on the desulfurization of model fuel containing 500 ppmw (C_i) thiophene in benzene and *n*-octane on Cu(I)Y (VPIE) sorbent at 4.9 h^{-1} space velocity. (○) 20 wt% benzene and 80 wt% *n*-octane; (▲) 300 ppmw H_2O in ~20 wt% benzene and ~80 wt% *n*-octane.

The inhibiting effect on desulfurization is caused by preferential bonding of the Cu^+ cation with the fuel additive, over the bonding with thiophene. By comparing results in Figs. 5–7, and the inhibiting effects follow the order:

water > ethanol > MTBE

As predicted from molecular orbital calculations, the relative strengths of bonding follow the order:

water > ethanol > MTBE > thiophene

The agreement between theory and experiment indicates that the inhibiting effect on desulfurization by additive molecules can be predicted with molecular orbital calculations.

6. Conclusions

Oxygenates (i.e., ethanol and MTBE) and H_2O are all detrimental to the π-complexation Cu(I)Y sorbent because they all bond with Cu(I) ions more strongly than thiophene. Therefore, in order to achieve high sulfur capacities for potential industrial desulfurization application by the π-complexation sorbents, it is important to operate with minimum amounts of such additives present (i.e., before any oxygenated additives being added). In addition, the process should be operated at low liquid hourly space velocities because of the strong diffusion limitation of thiophene in the zeolite crystals. The inhibiting effects on desulfurization by various additive/impurity molecules can be predicted with molecular orbital calculations.

Acknowledgments

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