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Adsorption of benzothiophene on Y zeolites investigated by infrared spectroscopy and flow calorimetry

Ming Jiang, Flora T.T. Ng *

Department of Chemical Engineering, University of Waterloo, 200 University Avenue West,
Waterloo, Ontario, Canada N2L 3G1

Abstract

Diffuse reflectance infrared spectra of benzothiophene adsorbed on different Y zeolites reveal that the cations and protons in the zeolites are the sites responsible for the adsorption of benzothiophene. On NaY, benzothiophene was molecularly adsorbed on the cations through the electrophilic interaction between the cations and the thiophenic rings. On the transition metal ion exchanged NiY and CuY zeolites, because of the presence of the d-electrons in the cations, the thiophenic rings interact with the cations to form the π-complexes through the σ–π electron donations. In the presence of hydroxyl species in the zeolites, the adsorbed sulfur compounds attach to the protons molecularly via the electrophilic interaction and undergo the opening of the thiophenic rings depending on the acidity of the zeolites and the adsorption amount. The apparent heat of adsorption of benzothiophene in normal octane on the Y zeolites determined by flow calorimetry shows that the adsorption strength based on the measured heat for each mole sulfur adsorbed on the Y zeolite is in the order of CuY > NiY > NaY ~ USY. For USY, due to the endothermic breakage of the thiophenic ring of benzothiophene induced by the acid sites of the zeolite, the apparent heat of adsorption is similar to that obtained from the adsorption on NaY. This work demonstrates that the transition metal ion exchanged zeolites exhibit excellent properties for sulfur adsorption because of the formation of the π-complexes and that the acidity of the zeolites is not advantageous for sulfur removal due to the strong adsorption and decomposition of the adsorbed species.

Keywords: DRIFT; Flow calorimerty; Thiophenic sulfur compounds; Adsorption; Zeolites; Sulfur removal

1. Introduction

Deep removal of organosulfur compounds in fuels has been mandated by government legislations. The Environmental Protection Agency (EPA) of USA requests a reduction of sulfur content of gasoline from current 300 to 30 parts per million (ppm) by weight and diesel from 500 to 15 ppm by 2006 [1–3]. European legislation mandated a reduction of sulfur compounds in fuels to less than 50 ppm in 2005 [4]. The production of hydrogen for fuel cells also requires sulfur-free fuels since trace amount of sulfur compounds in the fuels will poison fuel cell catalysts [2,3,5]. Conventional hydrodesulfurization has been used to remove reactive sulfides, disulfides, mercaptans and light thiophenic sulfur compounds, but it is difficult to remove refractory sulfur compounds such as dibenzothiophene and their alkyl derivatives that are abundant in gasoline and especially in diesel. On the other hand, hydrodesulfurization also significantly reduces the octane number of fuels because of the saturation of alkenes and arenes by hydrogenation reactions at high temperatures and high pressures [6]. An alternative to hydrodesulfurization is adsorptive removal of sulfur compounds from fuels. Adsorption can be performed at ambient temperature and pressure and the content of sulfur in fuels can be reduced to a very low level. Compared to the conventional hydrodesulfurization process, the adsorptive removal technique is very promising in the removal of refractory sulfur compounds to produce ultra-clean fuels. So far, various types of adsorbents, which include metal oxides, active carbon, clays, zeolites and mesoporous materials, have been reported for the adsorptive removal of sulfur compounds in fuels [7–20]. Among them, zeolites have been found to be very effective for the adsorption of sulfur compounds [7–15,18–20]. The adsorption of sulfur compounds on metal ion exchanged zeolites such as NaY, ZnY, NiY, CuY and CoZSM and on acidic

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* Corresponding author. Tel.: +1 519 888 4567x3979; fax: +1 519 746 4979.
E-mail address: fttng@cape.uwaterloo.ca (F.T.T. Ng).

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zeolites such as USY, HY, HZSM and H-Beta have been investigated by Yang and co-workers [7–15], Song and co-workers [18] and Iglesia and co-workers [21]. The adsorption mechanisms have also been explored by different research groups. Yang and co-workers [7–15] proposed that the interaction of thiophenic compounds with transition metal ions exchanged into zeolites is through the π-complexation of the heterocyclic rings of the thiophenic sulfur compounds with metal ions. Interaction of thiophene with acidic protons of zeolites has been investigated by using different techniques such as infrared spectroscopy, UV–vis spectroscopy and quantitative adsorption measurements [20–25]. Recently, we have employed flow calorimetry to the study of adsorption of different thiophenic sulfur compounds in alkane solvents on zeolites and found that the adsorption of sulfur compounds depends on the types of the sulfur compounds, adsorbents, solvent used for dissolving sulfur compounds and the conditions under which the adsorption is performed [26,27].

This paper reports the adsorption and thermal desorption of benzothiophene on acidic and metal ion exchanged Y zeolites, USY, NaY, NiY and CuY, monitored by diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy. The apparent heat of adsorption of benzothiophene dissolved in normal octane on the Y zeolites was determined by using flow calorimetry. The adsorption on the different Y zeolites was compared and interpreted based on the results obtained from the infrared spectroscopic and flow calorimetric study to provide an understanding of the interaction of the thiophenic sulfur compounds with the zeolites.

2. Experimental

Zeolites of NaY and ultra-stable Y (USY) were obtained from Strem Chemicals and Grace Division Chemicals, respectively, and used as supplied. NiY and CuY zeolites were prepared by twice aqueous ion exchange of NaY in 0.2 M $Cu(NO_3)_2$ and $Ni(NO_3)_2$ solution at about 50 °C. The obtained samples were washed and dried in an oven at about 100 °C for 12 h.

DRIFT spectra were obtained on a Bio-Rad FTS 3000 FTIR spectrometer recorded with a resolution of 4 cm^{-1}. The DRIFT cell equipped with a dome ZnS window was attached to a stainless steel line that allows performing in situ treatment of the samples and measurements of adsorption/desorption either in a gas flow or in vacuum at different temperatures. A powder zeolite sample loaded into the cell was pre-treated at 450 °C in helium flow for 1.5 h and cooled down to 40 °C for sulfur adsorption. The adsorption of benzothiophene was performed by exposing the sample, which had been evacuated, to the benzothiophene vapor coming from a reservoir that was warmed up to 50 °C. After adsorption, the sample was purged by helium for 0.5 h and subjected to the thermal desorption of the adsorbed sulfur compound in helium flow at different temperatures monitored by DRIFT spectroscopy.

Heat of adsorption of benzothiophene dissolved in normal octane (n-C_8H_{18}) adsorbed on the zeolite samples was measured at 30 °C on a Setaram C80 heat flux microcalorimeter. The concentration of benzothiophene in n-C_8H_{18} was 1800 ppm by sulfur weight. Two identical percolation vessels were used as sample and reference cell. The reference cell was filled with n-C_8H_{18}. A sample (250 mg, 250–500 μm) pre-treated at 450 °C for 1.5 h in helium flow was loaded into the sample cell and wetted by flowing n-C_8H_{18} continuously in a flow rate of 6 ml h^{-1} using a peristaltic pump. When the heat flow reached steady state without drift of the baseline, the n-C_8H_{18} flow was switched to that of benzothiophene/n-C_8H_{18} solution. The heat flux resulting from the adsorption of sulfur compound on the sample was recorded as a function of time.

Adsorption capacities of benzothiophene on the zeolites were measured by mixing 100 mg zeolite sample with 5 g of benzothiophene/n-C_8H_{18} solution (1800 ppm-S) in a 20 ml vial. The vial together with a control vial with the same amount of the solution but without the zeolite sample were placed in a shaker and shaken for 15 h at 30 °C. A Perkin-Elmer 8500 gas chromatograph was used to analyze the adsorption capacity of the sulfur compound on the zeolite sample by comparing the contents of the sulfur compound in the sample and control vial.

3. Results and discussion

3.1. DRIFT spectra of benzothiophene adsorbed on the zeolites

Zeolites have well-defined pore structure, high surface area and sites for cation exchange. The pore size of the supercage of Y zeolites is the largest among the different types of conventional zeolites such as A, ZSM and mordenite. Thiophenic sulfur compounds with two or more aromatic/heterocyclic rings can penetrate into the supercage, which makes Y zeolites potential adsorbents for the adsorptive removal of thiophenic sulfur compounds from fuels [7–15,18–25].

Fig. 1 displays the DRIFT spectra recorded from thermal desorption of benzothiophene adsorbed on NaY in the regions of O–H and C–H stretching vibrations. All the spectra are referenced to the spectrum recorded for the sample prior to

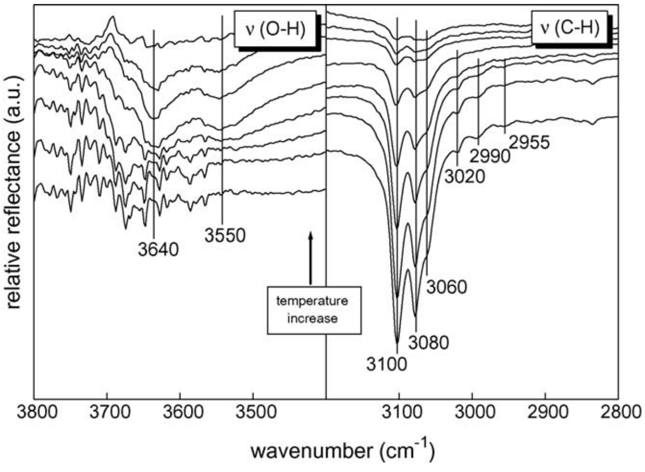

Fig. 1. DRIFT spectra recorded from the thermal desorption of benzothiophene adsorbed on NaY (40–360 °C, ΔT = 40 °C).

benzothiophene adsorption. Therefore, the bands appearing with the *downward* direction represent the production of the species on the sample and those with the *upward* direction indicate the disappearance of the species from the sample.

NaY is a kind of non-acidic zeolite without acidic hydroxyl species. The sodium cation in the zeolite is responsible for the adsorption of sulfur compounds. As shown in Fig. 1 (right), in the region of C–H stretching vibrations, the C–H bands are observed at about 3100, 3080 and 3060 cm^{-1}. Minor bands are also detected at 3020, 2990 and 2955 cm^{-1}. The bands with the frequencies higher than 3000 cm^{-1} can be assigned to aromatic/heterocyclic C–H vibrations. The bands with their frequencies lower than 3000 cm^{-1} could arise from aliphatic C–H vibrations and/or combination and overtones of the thiophenic compound, however, the intensities of the latter are very low [28]. For adsorption of benzothiophene, the occurrence of the aliphatic C–H species will involve the opening of the heterocyclic rings of the sulfur compounds, which will give relatively strong C–H bands [21,24,25,29]. Due to the low intensities of the bands below 3000 cm^{-1}, it can be inferred that no aliphatic C–H species is produced on NaY. The interaction of thiophenic sulfur compounds with sodium cations of zeolites has been proposed to be through the electrophilic attachment of the cations to the conjugated π-electrons of the heterocyclic rings of the sulfur compounds [7]. This type of interaction is not expected to be strong. The spectra recorded from the thermal desorption from 50 to 400 °C show that the adsorbed species can be significantly removed at a temperature lower than 300 °C. The proportional decrease in intensity of the C–H stretching bands indicates that no new species appear with increasing temperature and only molecularly adsorbed benzothiophene is eliminated from NaY.

In the region of O–H stretching vibrations (Fig. 1, left), upon adsorption of benzothiophene at low temperatures (<120 °C), hardly any band can be detected due to the lack of the hydroxyl species in NaY. With increasing desorption temperature up to 200 °C, however, two weak bands develop at about 3640 and 3550 cm^{-1}, which are typical of the acidic hydroxyl species located in the supercage and sodalite cages of the zeolite. The origin of the acidic hydroxyl species is not clear and will require further investigation.

Fig. 2 displays the DRIFT spectra recorded from the thermal desorption of benzothiophene adsorbed on the USY zeolite in the regions of O–H and C–H stretching vibrations.

USY is a kind of acidic zeolite. The characteristics of adsorption of sulfur compounds on the zeolite protons are quite different from that observed on the soldium ions of NaY. DRIFT spectrum of the zeolite show the typical stretching vibrations of the acidic hydroxyl groups at about 3650 and 3540 cm^{-1} and silanol group at about 3743 cm^{-1} (not shown as figure for brevity). Zecchina and co-workers [22,23] proposed that the first step of the interaction of sulfur compounds with the protons would be the same as occurred on sodium cations, i.e., the conjugated π-electrons of the heterocyclic rings of the sulfur compounds are attached to the zeolite protons. Because of the acidity of the zeolite, the sulfur compounds adsorbed on the protons can subsequently undergo the opening of the heterocyclic rings, which results in the appearance of the bands with their frequencies lower than 3000 cm^{-1} corresponding to the aliphatic C–H stretching bands [21,24,25,29]. In Fig. 2 (right), the strong bands at about 2950, 2900, 2870 and 2840 cm^{-1} are typical of the aliphatic methyl and methylene groups. Clearly, the adsorbed benzothiophene undergoes the opening of its thiophenic ring although our data do not provide the mechanism for the ring opening. The bands of aromatic/heterocyclic C–H stretching vibrations are also observed at about 3085 and 3065 cm^{-1}. During thermal desorption, both the aromatic/heterocyclic and aliphatic C–H stretching bands decrease in intensity with increasing temperature, but complete elimination of the adsorption species occurs at very high temperature (>400 °C). This result shows that the strong interaction of the sulfur compound with the protons makes the regeneration of the acidic zeolites after sulfur adsorption much more difficult than that of the non-acidic NaY. The strong interaction of the sulfur compound with the zeolite protons is also revealed by the spectra recorded in the region of O–H stretching vibrations (Fig. 2, left). Three bands with the *upward* direction are observed at about 3743, 3650 and 3540 cm^{-1},

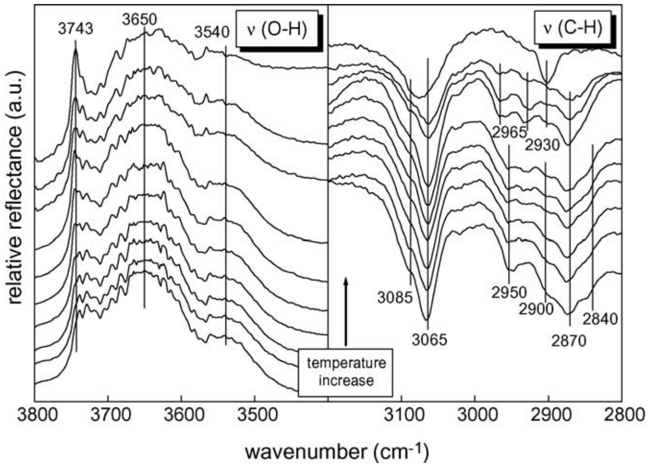

Fig. 2. DRIFT spectra recorded from the thermal desorption of benzothiophene adsorbed on USY (40–400 °C, ΔT = 40 °C).

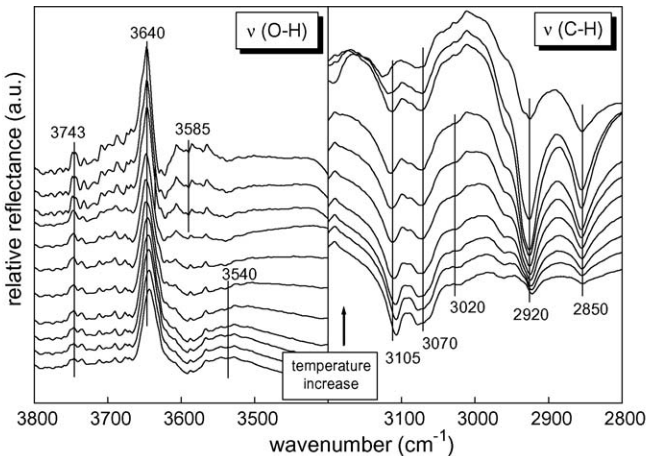

Fig. 3. DRIFT spectra recorded from the thermal desorption of benzothiophene adsorbed on NiY (40–400 °C, ΔT = 40 °C).

which correspond to the interaction of the adsorbed benzothiophene with the hydroxyl groups of the zeolite. The hydroxyl species are not completely recovered after the desorption of the sulfur compound on the zeolite as indicated by the minor decrease in intensity of the bands during thermal desorption.

Fig. 3 presents the DRIFT spectra recorded from the thermal desorption of benzothiophene adsorbed on the ion exchanged NiY zeolite in the regions of O–H and C–H stretching vibrations. The bands of the aromatic/heterocyclic C–H vibrations can be observed at 3105, 3070 and 3020 cm^{-1} (Fig. 3, right). During thermal desorption, their intensities decrease only slightly, indicating that the interaction of benzothiophene with the nickel cations is stronger than with the sodium cations (cf. Figs. 3 and 1). This is consistent with the suggestion of Yang and co-workers [7–15] that the heterocyclic ring of a thiophenic sulfur compound interacts with the transition metal cation to form π-complexes through σ–π electron donations resulting in a stronger adsorption than that on sodium cation that has no back donation of d-electrons to the heterocyclic ring of the sulfur compounds. The non-proportional decrease of the intensities of the bands at different wavenumbers also indicates that different adsorption species are formed or developed in the zeolite. Compared to the adsorption on NaY, the intensities of the bands with the frequencies lower than 3000 cm^{-1} are relatively high. This indicates that they arise not only from the combinations and overtones of the adsorbed benzothiophene but also from the aliphatic C–H stretching vibrations. Note that during desorption the intensities of the bands first increase with increasing temperature up to 320 °C and then decrease with further increase of the temperature, suggesting that the heterocyclic ring interacting with the nickel cations of the zeolites is further opened up during heating. Similar to the case with USY, it is likely that the acidic protons produced during pre-treatment of NiY zeolite at high temperature are responsible for the opening of the thiophenic ring. It is known that for divalent metal ion-exchanged zeolites, the water molecules associated with the transition metal ions will dissociate at high temperatures and give rise to acidic protons [30]. The presence of the protons in NiY is confirmed by the interaction of the hydroxyl groups with the adsorbed sulfur species as shown by the bands at 3743, 3640 and 3540 cm^{-1} (Fig. 3, left). From the large difference in intensity of the bands at 3640 and 3540 cm^{-1}, it can be derived that the sulfur compound has the preference to interact with the hydroxyl species in the supercage that corresponds to the band at 3640 cm^{-1} because of the accessibility. Since benzothiophene molecule is too large to penetrate into the sodalite cage, only a weak band can be observed at about 3540 cm^{-1}, which can be attributed to the interaction of benzothiophene adsorbed into the supercage with the protons in the sodalite cage through the window that connects the supercage and sodalite cage. At high temperatures (ca. 240 °C), the hydroxyl species in the sodalite cage interacting with the sulfur compound is easy to recover as shown by the disappearance of the band at 3540 cm^{-1}. With the further increase in temperature, a new band at 3585 cm^{-1} is observed which corresponds to the interaction of the benzothiophene with the hydroxyl groups of higher acidity. This type of hydroxyl species may arise from the modification of the pore structure by the desorption of benzothiophene at high temperatures.

Fig. 4 presents the DRIFT spectra recorded from the thermal desorption of benzothiophene adsorbed on the pre-treated CuY in the regions of O–H and C–H stretching vibrations. Compared to NiY, the Cu(II) species in CuY is much easier to auto-reduce to Cu(I) during pre-treatment in helium flow at 450 °C [31,32]. Depending on the pre-treatment conditions, the auto-reduction of the Cu(II) species will lead to the production of the hydroxyl groups and degradation of the zeolite pore structure. The change in property and structure of the zeolite will affect the adsorption of sulfur compounds. From Fig. 4 (right), only very weak bands are observed at about 2900 and 2840 cm^{-1}, indicating that the adsorbed benzothiophene hardly undergoes the thiophenic ring opening although more hydroxyl species may be produced in CuY than in NiY by the auto-reduction. In the region of O–H stretching vibrations (Fig. 4, left), the interaction of benzothiophene with the hydroxyl species is indicated by the upward bands at about 3743, 3670, 3640 and 3580 cm^{-1}. The band at about 3670 cm^{-1} arises from the hydroxyl species attached to the extra framework aluminium species [33,34]. As mentioned above, the pore structure of the CuY degrades to some extent during auto-reduction in the pre-treatment, which enhances the probability of the adsorbate molecules interacting with the protons in the sodalite cage. This is confirmed by the enhanced intensity of the band at about 3580 cm^{-1} compared to the adsorption on NiY (cf. Figs. 4 and 3, left). The spectra in region of the C–H stretching vibrations suggest that benzothiophene interacting with the protons does not undergo the opening of the thiophenic ring because of the absence of the aliphatic C–H species. During thermal desorption, the C–H bands do not decrease proportionally. The band at 3065 cm^{-1} becomes the strongest at high temperatures (>240 °C), indicating the presence of more than one type of adsorption species in CuY due to, most probably, different Cu(I) and/or Cu(II) cationic sites in CuY available for adsorption.

In contrast to the adsorption of benzothiophene on NiY, the hydroxyl species interacting with benzothiophene in CuY can

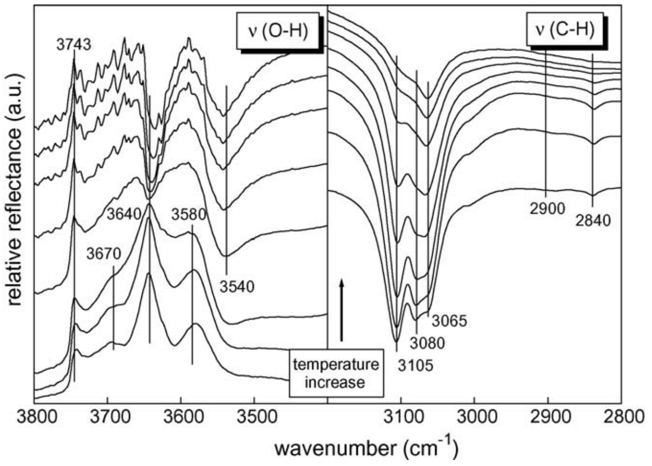

Fig. 4. DRIFT spectra recorded from the thermal desorption of benzothiophene adsorbed on CuY (40–320 °C, $\Delta T = 40$ °C).

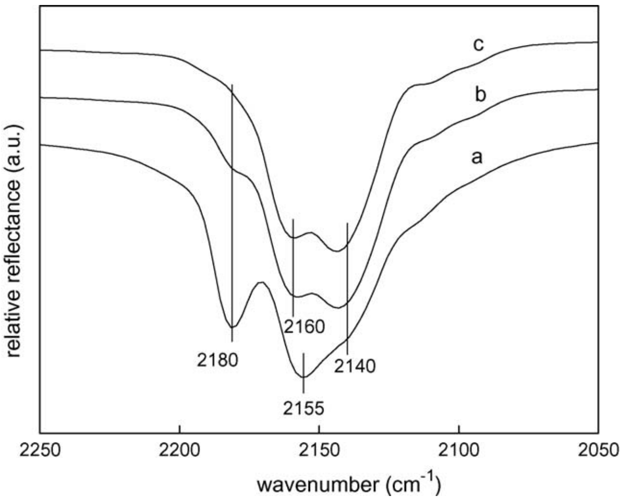

Fig. 5. DRIFT spectra of CO adsorbed on CuY zeolite: (a) in CO flow, (b) purged by helium for 5 min and (c) for 20 min.

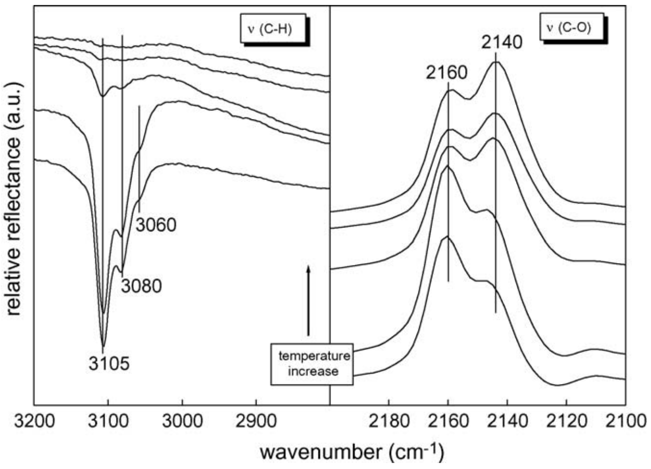

Fig. 6. DRIFT spectra of thiophene adsorbed on CuY at different temperatures after CO adsorption at 30 °C (40–160 °C, $\Delta T = 40$ °C).

be recovered to a certain extent during thermal desorption as shown by the disappearance of the upward bands at 3640 and 3580 cm^{-1} between 120 and 160 °C. At higher temperatures, the bands at 3640 and 3540 cm^{-1} appear in the downward direction, indicating that the thermal desorption of the adsorbed species from CuY modifies the acid properties of the zeolite and produces additional acidic protons due to the sulfur compound interacting, most probably, with copper cations to form sulfur complexes/compounds.

In order to confirm that zeolite cations are responsible for the adsorption of sulfur compounds, alternative adsorption of carbon monoxide and volatile thiophene monitored by the DRIFT spectroscopy was used to probe the adsorption sites in CuY.

The spectra of CO adsorbed on the pre-treated CuY are shown in Fig. 5. At high CO coverage (in CO flow), dicarbonyl Cu(I)(CO)_2 is formed in the supercage and represented by the bands at 2180 and 2155 cm^{-1}. The CO adsorbed into the supercage can also interact with the Cu(I) in the sodalite cage to form monocarbonyl Cu(I)(CO) represented by a band at 2140 cm^{-1} [35,36]. At low CO coverage (after purge with helium), Cu(I)(CO)_2 decomposes into Cu(I)(CO) in the supercage giving a band at 2160 cm^{-1}, in addition to the band at 2140 cm^{-1} due to interaction of CO with Cu(1)in the sodalite cage. Interaction of CO with the Cu(II) cations of CuY is very weak and difficult to detect by infrared spectroscopy [36].

After CO adsorption, CuY was exposed to thiophene at different temperatures. The DRIFT spectra referenced to the spectrum of CuY with CO adsorbed are shown in Fig. 5. The adsorbed CO can be displaced by thiophene as indicated by the bands at 2160 and 2140 cm^{-1} with *upward* direction (Fig. 6, right). From the relative intensities of the two bands, it can be determined that at low temperatures (<100 °C) the CO adsorbed into the supercage is easier to displace by thiophene as shown by the more intense band at 2160 cm^{-1}. In the meantime, the bands of aromatic/heterocyclic C–H species also appear at about 3105, 3080 and 3060 cm^{-1} (Fig. 6, left). With increasing adsorption temperature (>100 °C), the occurrence of the reduction of Cu(I) into Cu(0) was demonstrated by the change of the color of the sample from light grey to black, which results in the decrease of the number of Cu(I) in the zeolite and thus the amount of thiophene adsorbed as indicated by the decrease in intensity of the C–H bands. From this alternative adsorption measurements, it can be concluded that the Cu(I) ions of the zeolite are the sites for sulfur adsorption.

3.2. Calorimetric study of benzothiophene adsorbed on the zeolites

The above DRIFT study shows that the adsorption characteristics of the sulfur compounds on the Y zeolites are dependent on the acidity and properties of the cations in the zeolites. This will also be reflected in the adsorptive removal of sulfur compounds. Fig. 7 displays the heat flux curves obtained from the adsorption of benzothiophene dissolved in $n\text{-C}_8\text{H}_{18}$ on the pre-treated NaY, USY, NiY and CuY zeolites recorded as function of adsorption time.

From Fig. 7, the profiles of the heat flux for benzothiophene adsorbed on NaY and NiY are very similar. At the beginning of

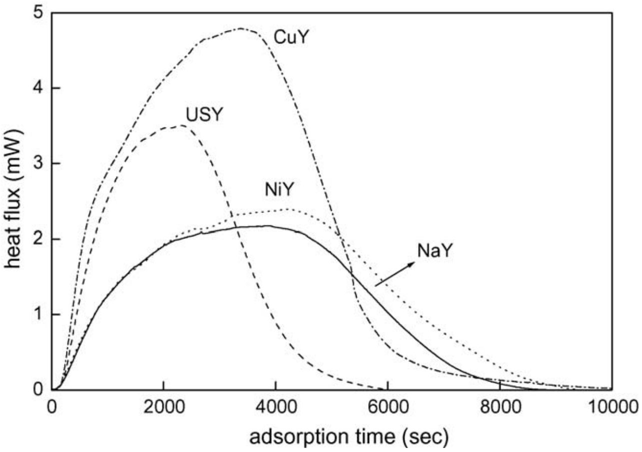

Fig. 7. Heat flux recorded for the adsorption of benzothiophene in $n\text{-C}_8\text{H}_{18}$ adsorbed on Y zeolites.

the adsorption, the heat fluxes gradually increase and approach their maximums at about 3600 s (1 h). On USY and CuY, the heat fluxes approach the maximums relatively faster. The adsorption of the sulfur compound on the zeolites in liquid phase may be influenced significantly by the diffusion of the adsorbate molecules from the solvent into the zeolites. As mentioned above, USY is a kind of acidic zeolite with a highly defect structure. The openings of the pores of the zeolite could be enlarged during dealumination of the zeolite leading to the facilitated diffusion for the adsorption of the sulfur compound into the pores of the zeolite. In the case with NaY and NiY, no noticeable defects are present in the framework structures of the zeolites as indicated by the absence of silanol groups. Therefore, the diffusion of the sulfur compound molecules into the zeolites would be slower than into USY because of the size effect of the windows of the micropores, which leads to the relatively slow increase of the heat flux at the beginning of adsorption. The DRIFT spectra indicate that hydroxyl species, defect silicon and/or aluminium tetrahedrons are produced due to the auto-reduction of CuY during the pre-treatment. Similar heat flux profiles for the adsorption of benzothiophene on CuY and USY also suggest that the defect framework structure is present in the zeolites, which facilitates the diffusion of the molecules into the zeolite.

Table 1 summarizes the results obtained from the calorimetric and adsorption measurements. It can be seen that the sulfur adsorption capacities for each gram of CuY and NiY are very similar. However, their adsorption strengths reflected by the heat of adsorption are quite different. As reported recently [26,27], the heat of adsorption measured using the flow calorimetry technique includes the heat of desorption of the solvent, however, it gives a relative measure of the strength of the interaction between the benzothiophene and the different ion exchanged zeolites. The relatively higher heat of adsorption for NiY and CuY compared with NaY can be attributed to electron donation or back bonding of the d-electrons of Ni or Cu to the π^* orbital (antibonding orbital) of the benzothiophene (π bond). Our measured relative heat of adsorption for NaY, NiY and CuY are in agreement with the π-complexation mechanism proposed by Yang and co-workers [7–15] for the adsorption of thiophenic compounds on transition metal ion exchanged zeolites.

It is interesting to note that the adsorption capacities of NaY and USY are almost the same. Their heats of adsorption for each mole of sulfur adsorbed are also very similar. This suggests that the acidic sites do not enhance sulfur adsorption [26]. The strength of the interaction of the sulfur compound with the zeolites based on the heat of adsorption is in the order of CuY > NiY > NaY ~ USY. This order is consistent with the strength of interaction as determined from the DRIFT studies except for USY. Adsorption of sulfur compounds on the cations of CuY and NiY exhibits higher heat of adsorption than on sodium ions due to the effective π-complexation as proposed by Yang and co-workers [7–15]. For the adsorption on USY, the DRIFT spectra shown in Fig. 2 suggest that sulfur compounds are strongly adsorbed on the acidic hydroxyl species. However, the adsorption mechanism is very different from that of π-complexation. DRIFT studies indicates that the thiophenic rings is opened on adsorption on HY, that is, the endothermic bond breaking of the adsorbate molecules is involved in the adsorption, which will result in a lower apparent heat of adsorption than expected.

Table 1
Calorimetric results and adsorption capacities of benzothiophene in n-C_8H_{18} (1800 ppm-S) adsorbed on Y zeolites

Sample	Adsorption capacity (mmol S/g zeolite)	Heat of adsorption	
		(J/g zeolite)	(kJ/mol S)
NaY	1.69	43.03	24.46
USY	1.68	40.60	24.17
NiY	1.80	54.66	30.37
CuY	1.97	80.28	40.75

4. Conclusion

From the DRIFT study, benzothiophene can be adsorbed molecularly on NaY, NiY and CuY. The conjugated π-electrons of the sulfur compounds interact with the sodium cations of NaY to form an adsorption adduct. In NiY and CuY, due to the presence of d-electrons, the sulfur compounds interact with the cations through π-complexation. The σ–π donations increase the interaction of the sulfur compounds with NiY and CuY, which gives a higher apparent heat of adsorption than on NaY.

For the acidic zeolite USY, benzothiophene first adsorb on the hydroxyl species by the electrophilic interaction and then undergo the opening of the heterocyclic rings depending on the acidity of the zeolites. The decomposed species can be strongly held in the zeolite and desorbed at rather high temperatures. The apparent heat of adsorption will include the endothermic heat for bond breaking in the benzothiophenic ring and therefore is lower than expected.

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