

# Flow calorimetric and thermal gravimetric study of adsorption of thiophenic sulfur compounds on NaY zeolite

Ming Jiang, Flora T.T. Ng\*, Aatur Rahman, Viral Patel

*Department of Chemical Engineering, University of Waterloo, 200 University Avenue West, Waterloo, Ont., Canada N2L 3G1*

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## Abstract

A study of adsorption of thiophenic sulfur compounds (thiophene, benzothiophene, dibenzothiophene and 4,6-dimethyl benzothiophene) in normal alkane solvents (octane, dodecane and hexadecane) on NaY zeolite has been performed by using flow calorimetry technique and thermogravimetric analysis. The measured heat of adsorption of sulfur compounds includes the heat from the displacement of the adsorbed solvent molecules by sulfur compounds and it is therefore much lower than that obtained by gas phase adsorption of sulfur compounds in the zeolite. The apparent heat of adsorption of sulfur compounds per gram of sorbent decreases when the solvent changes from octane, dodecane to hexadecane, but the heat of adsorption per mole of sulfur compound calculated based on the sorption data does not vary significantly with the solvent used. The measured heat of adsorption per gram of sorbent is also influenced by the molecular size of the sulfur compound and decreases in the order: thiophene > benzothiophene > dibenzothiophene due to the higher sorbent capacity for the smaller sulfur compound. Thermogravimetric analysis of the adsorbed sulfur compounds under combustion condition used for the sulfur elimination from the sorbent indicates that the combustion of the refractory sulfur compounds occurs at higher temperatures. Analysis of the effluent from the calorimeter could be used to estimate the breakthrough characteristics of the sorbent. This indicates that the flow calorimetry is a promising technique for establishing the relationship between sorption capacity and heat of adsorption of sulfur compounds. The information obtained from the flow calorimetry and thermogravimetry could be used for the development of selective sorbents for the production of ultra-clean fuels.

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## 1. Introduction

Deep removal of sulfur-containing compounds in fuels has become an ever more important subject of environmental protection due to the required lower limit of sulfur content in fuel products set by the government legislation. US Environmental Protection Agency mandates a reduction of sulfur content of gasoline from the current 300 to 30 parts per million (ppm) by weight and diesel from 500 to 15 ppm by 2006 [1–3]. Eu-

ropean legislation also calls for a reduction of sulfur content to less than 50 ppm for gasoline and diesel fuels by 2005 [4]. On-board or on-site reforming of the fuels to produce hydrogen for fuel cells also requires ultra-clean fuels since traces of sulfur will poison the reforming and electrode catalysts [2,3,5]. Conventional hydrodesulfurization process has been used in the refineries worldwide to remove sulfur compounds from the liquid fuels. This process is very effective to remove light sulfur compounds such as thiophene and bezothiophene, but it is difficult to remove refractory sulfur compounds such as dibenzothiophene and, especially, 4,6-dimethyl dibenzothiophene. Furthermore, hydrodesulfurization also reduces the octane number of the fuels due to the saturation of olefins

\* Corresponding author. Tel.: +1 519 888 4567x3979; fax: +1 519 746 4979.

*E-mail address:* [ftng@cape.uwaterloo.ca](mailto:ftng@cape.uwaterloo.ca) (F.T.T. Ng).

under high pressure and high temperature operation conditions [6].

Adsorption technology has been proposed for the removal of sulfur compounds in fuels. Compared to the hydrodesulfurization process, the adsorptive removal of sulfur compounds seems very promising since adsorption can be accomplished at ambient temperature and pressure and the sulfur in fuels can be removed to a very low level. Different types of adsorbents such as mixed metal oxides, active carbon, clays, zeolites and mesoporous materials have already been studied for the removal of sulfur compounds in fuels. Among the various kinds of adsorbents, zeolites have been found to be very effective for the removal of sulfur compounds. Yang and coworkers [7–9] reported that cation-exchanged Y zeolites, Cu(I)Y, AgY and NiY, are selective for the removal of sulfur compounds in fuels by  $\pi$ -complexation of sulfur compounds with the transition metal cations in the zeolites. Song and coworker [10] reported that cation-exchanged Y zeolites (Cu, Ni, Zn, Pd and Ce) are effective for the adsorption of sulfur. Zeolites such as ZSM and X have also been reported to be effective for the removal of sulfur compounds in fuels [11,12].

Calorimetric technique has widely been applied to the characterization of adsorption of molecules on solid materials. It determines the strength and numbers of adsorption sites on the solid materials [13]. However, most of calorimetric studies have been carried out in gas phase and only limited information is available from liquid phase calorimetry. In the case of adsorptive removal of sulfur compounds from fuels, the adsorption must be carried out in the liquid phase and therefore liquid phase calorimetry would be unique to the study of the heat of adsorption of sulfur compounds in fuels. The intrinsic heat of adsorption of sulfur compounds is difficult to determine from the liquid phase calorimetry because of the adsorption of other hydrocarbons in fuels. However, the apparent heat of adsorption of sulfur compounds obtained from liquid phase calorimetry would be useful for the practical design of a selective sulfur adsorption process. We have employed flow calorimetric technique to investigate the adsorption of thiophenic sulfur compounds dissolved in normal hexadecane to mimic sulfur in diesel fuel on different types of commercially available zeolite extrudates that contain alumina binder [14]. In that exploratory work, it has been found that the characteristics of the heat flux resulting from the adsorption of sulfur compounds strongly depend on the types of the sulfur compounds and zeolitic sorbents used. To our knowledge, there is so far no other report of heat of adsorption of sulfur compounds in zeolites by means of flow calorimetric technique in the literature. In this work, a more detailed investigation of the experimental parameters affecting the characteristics of the heat flux resulting from the adsorption of sulfur compounds on NaY zeolite (without alumina binder) has been carried out. The desorption/combustion of the adsorbed sulfur species analyzed by thermal gravimetric analysis to assess the regeneration of the sorbent is also provided.

## 2. Experimental

Zeolite NaY powder with a pore volume of 0.6 ml/g and Langmuir surface area of 820 m<sup>2</sup>/g as determined by N<sub>2</sub> adsorption at 77 K was obtained from Strem Chemicals. It was pressed, crushed and sieved into the size range of 250–500  $\mu$ m or otherwise stated. Prior to loading into the calorimeter vessel, it was dehydrated at 450 °C in air for 1 h.

Sulfur compounds, thiophene, benzothiophene and dibenzothiophene, obtained from Aldrich were used as supplied. Normal octane, dodecane and hexadecane obtained from Aldrich were used as solvents for dissolving the sulfur compounds.

Heat of adsorption of sulfur compounds on the NaY zeolite was measured on a Setaram C80 heat-flux calorimeter at 30 °C. Two identical percolation vessels used for the sample and reference were employed for the measurements. The reference vessel was filled with the solvent used for dissolving the sulfur compound and the sample vessel was loaded with 250 mg of the zeolite sorbent. The solvent was introduced into the sample in a constant flow of 6.3 ml/h or otherwise stated by using a high precision HPLC pump obtained from Waters Inc. Because of the wetting of the sample with the solvent, an exothermic heat associated with the adsorption of solvent can be observed. When the heat flow came back to the baseline and became steady, the solvent was switched to a solution containing sulfur compound dissolved in the corresponding solvent at the same flow rate. The heat flux resulting from the adsorption of the sulfur compound on the zeolite was recorded as a function of time. The effluent from the calorimeter was collected at a certain time interval and analyzed on a Perkin-Elmer 8500 gas chromatograph using a DB1701 column and FID detector.

The sorption capacity of the sulfur compounds on the zeolite was measured by placing 100 mg of the zeolite into 5.0 g of the solution containing sulfur compound (1800 ppm S) in a 20 ml vial. A vial containing the same amount of sulfur solution but without the sorbent was used as the control. The vials were shaken at 150 rpm in a thermostated bath maintained at 30 °C for 20 h. The concentrations of the sulfur compounds in the solutions in the sample and control vials were analyzed on the same Perkin-Elmer GC as mentioned above. Based on the previous report [14], the saturation adsorption can be reached at the sulfur concentration less than 1500 ppm for different sulfur compounds. Therefore, the amount of the sulfur compounds adsorbed determined from the adsorption measurements will correspond to the saturation sorption capacity of the sorbent.

Thermal gravimetric analysis (TGA) and differential thermal analysis (DTA) were carried out using a TGA/DTA instrument from TA Instruments. Prior to the thermal analysis, the samples with sulfur compounds adsorbed were pre-heated at certain temperatures to remove the weakly adsorbed solvents. About 8 mg of the sample was loaded into a sample cell and alumina was used as reference. The sample loaded into the cell was heated from 50 to 700 °C at a heating rate of

10 °C/min. Helium containing 5% oxygen was used as carrier gas. Thermal gravimetric profiles and temperature differences between the sample and alumina reference were simultaneously recorded as a function of temperature.

### 3. Results and discussion

#### 3.1. Influence of solvent, flow rate and particle size of the sorbent on heat flux

Heat of adsorption of sulfur compounds on NaY zeolite in the liquid phase is dependent on the solvents used. The heat flow resulting from the adsorption of benzothiophene in different solvents on NaY recorded as a function of time is shown in Fig. 1 (curves a–c). The concentration of the sulfur compounds in the solvents calculated based on the weight of sulfur is 1800 ppm. It can be seen that the total heat arising from benzothiophene adsorption, as indicated by the peak area, decreases with increasing chain length of the alkane solvent molecule. The results demonstrate that

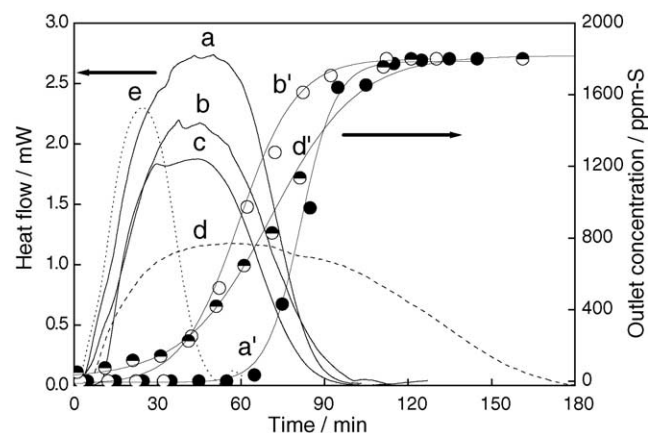


Fig. 1. Heat fluxes obtained from the adsorption of benzothiophene on NaY in different solvents (1800 ppm S): (a) octane; (b) dodecane; (c) hexadecane; (d) octane (large particle size of NaY: 850–1000  $\mu\text{m}$ ); (e) octane (high flow rate, 12.6 ml/h); (a', b' and d') the concentrations of benzothiophene collected at the outlet of the calorimeter at different time intervals corresponding to (a, b and d), respectively.

the solvent has an effect on the characteristics of adsorption of the sulfur compound on the zeolite. The features of the profiles of the heat flow, however, do not vary significantly with the solvents as indicated by the small variation of the initial rate of heat flow from 0.09 to 0.12 mW/min and the total adsorption time which ranged from 90 to 100 min. The effluent from the calorimeter was collected at certain time intervals and analyzed by GC. The plots of the concentration of the sulfur compound in the effluent versus time for the adsorption of benzothiophene in octane and in dodecane are presented in Fig. 1 (curves a' and b'), which are similar to the breakthrough curve although the shallow bed of the sorbent in the calorimeter is not typical for obtaining the breakthrough curves. From the plots, little or no sulfur compounds are detected in the effluents for the initial 30 min because of the complete adsorption by the sulfur compound in the zeolite. After the “breakthrough” point (>30 min), the concentration of the sulfur in the effluents increases rapidly. Compared to the adsorption of benzothiophene in octane, the breakthrough of benzothiophene in dodecane occurs earlier, indicating that the adsorption capacity decreases as the chain length of the alkane solvent molecules increases. Based on the sulfur concentration in the effluents and the flow rate used for the calorimetric measurements, the adsorption amounts for benzothiophene in octane and in dodecane can be estimated as 1.38 and 1.15 mmol S/g NaY, respectively. The adsorption amount of sulfur compounds on NaY was also determined independently by adsorption measurements as described in the experimental section and listed in Table 1. For the adsorption of benzothiophene in octane and in dodecane, the saturated adsorptions are 1.62 and 1.28 mmol S/g NaY, respectively. The difference of the sorption data obtained from the “breakthrough” and sorption capacity measurements may be due to the experimental error in determining the zero time of the “breakthrough” curves when the solution contacts the sorbent. The heat of adsorption of benzothiophene in the different solvents measured by flow calorimetry is plotted as a function of the sulfur sorption capacity obtained from the adsorption experiments (Fig. 2). A good straight line is observed suggesting that the mechanism of adsorption is probably the same for the sulfur compounds in the different solvents. An adsorption mechanism involving  $\pi$ -complexation

Table 1  
Data obtained from the calorimetric and sorption capacity measurements

Sulfur compounds	Sorption capacity <sup>a</sup> (mmol S/g NaY)	Heat of adsorption (J/g NaY)	Heat of adsorption (kJ/mol S)
Thiophene/octane	–	64.3	–
Thiophene/hexadecane	–	51.5	–
Benzothiophene/octane	1.62	36.3	22.4
Benzothiophene/dodecane	1.28	28.5	22.3
Benzothiophene/hexadecane	1.02	22.7	22.3
Dibenzothiophene/octane	1.10	24.0	21.8
Dibenzothiophene/dodecane	1.04	22.5	21.6
Dibenzothiophene/hexadecane	0.94	20.6	21.9
4,6-Dimethyl dibenzothiophene/hexadecane <sup>b</sup>	0.69	12.1	17.6

<sup>a</sup> Measured by adsorption experiments.

<sup>b</sup> The sulfur concentration was 900 ppm and commercial NaY with alumina binder was used (see Ref. [14]).

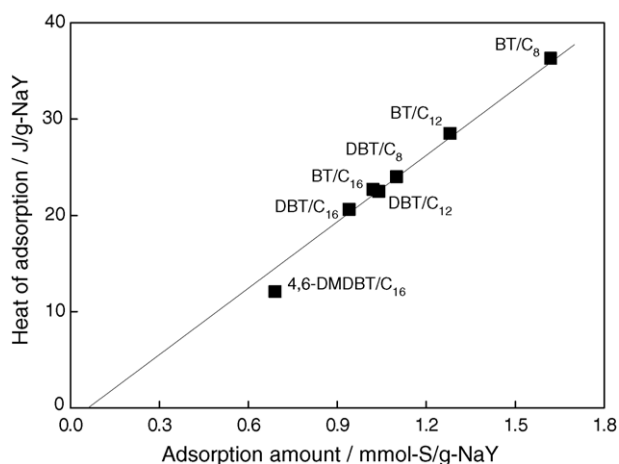


Fig. 2. Heat of adsorption (J/g NaY) measured by calorimeter vs. sulfur adsorbed (mmol S/g NaY) obtained from the adsorption experiments (BT: benzothiophene; DBT: dibenzothiophene; 4,6-DMDBT: 4,6-dimethyl dibenzothiophene).

has been proposed [7–9]. The apparent average heat of adsorption determined from the slope of the straight line is about 22.8 kJ/mol S, which is very similar to that previously reported for the commercial zeolite extrudates containing alumina binder (20.9 kJ/mol S) [14]. The heat of adsorption per mole of sulfur represents the average heat of adsorption and also includes the heat of displacement of the solvent. The data shown in Table 1 (last column) and Fig. 2 indicate that the apparent average heat of adsorption of benzothiophene per mole of sulfur is essentially independent of the solvent used.

In order to understand the effect of the solvent on the adsorption of sulfur compounds, the wetting of the zeolite with the different alkane solvents was investigated calorimetrically. The heat measured during the wetting of the zeolite is contributed by both the endothermic wetting of the cell

wall with the solvents and the exothermic adsorption of the solvents in the zeolites. As an example, the heat flow obtained from the wetting of the cell wall and from that of the zeolite (250 mg) by octane is shown in Fig. 3. The endothermic heat from the cell wetting varies with the solvent used and decreases from 5.6 J for octane to 3.5 J for hexadecane. The exothermic heat measured from the wetting of the zeolite (which includes the heat from the cell wetting) also decreases from 14.0 J for octane to 8.4 J for hexadecane. By considering the endothermic heat from cell wetting, the exothermic heat arising from the wetting of the zeolite only can be estimated and used as a relative comparison of the adsorption of the solvents in the zeolite as shown in Fig. 4. It can be seen that the heat from the wetting of the zeolite per gram of NaY decreases with the increase of the chain length of the alkane. This result seems to suggest that the adsorption of alkane solvents with longer chains in the zeolite is weaker than that with shorter chains and thus the solvents with longer chains adsorbed on the zeolite might easily be displaced by the sulfur compounds. This contradicts the results shown in Fig. 1 where the heat of adsorption of sulfur compound decreases with increasing chain length of the solvent molecules. Considering the structure of the zeolite, the number of the solvent molecules adsorbed into the zeolite is limited by the zeolite pore volume. The larger the size of the solvent molecule, the smaller the number of the molecules that can be adsorbed into the pores. Groszek [15] investigated the adsorption of normal alkanes on different solid materials such as graphite, active carbon, MoS<sub>2</sub>, WS<sub>2</sub>, and BN where there is no steric hindrance arising from the pore structure like in zeolites and found that the heat of adsorption of alkanes on those materials increases with an increase in the chain length of the alkanes because of the increased molecular interaction areas. Adsorption of the alkane solvent molecules in the zeolite may have the feature similar to the cases described by Groszek, that is, alkane molecules with longer chains interact more

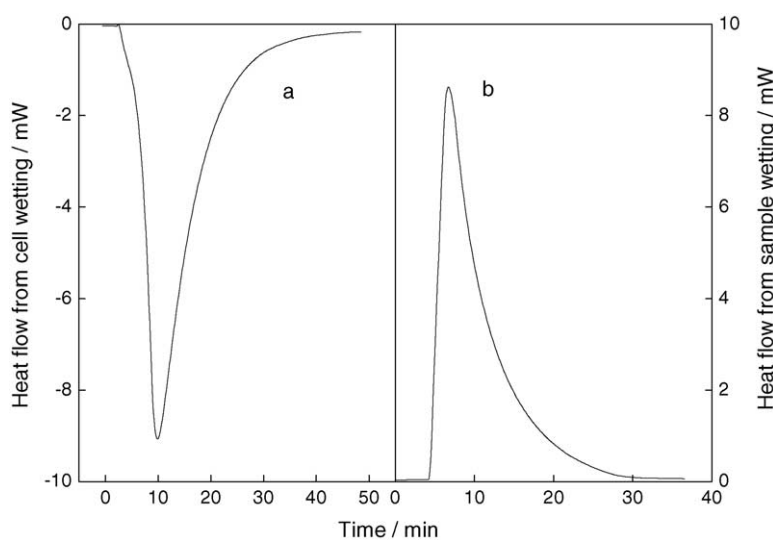


Fig. 3. Heat fluxes measured from the wetting of the cell wall (a) and NaY with octane (b).

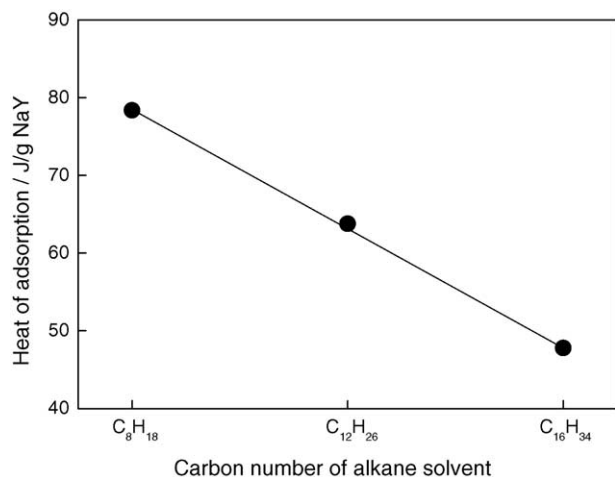


Fig. 4. Heats of adsorption obtained from the wetting of NaY with different normal alkane solvents.

strongly with the cations inside of the zeolite pores to give a higher heat of adsorption for each alkane molecule although the total heat is smaller because of the smaller number of the solvent molecules adsorbed into the pores of the zeolite based on the pore filling mechanism for the adsorption of hydrocarbons. The heat obtained from the subsequent adsorption of sulfur compounds in the solution includes the displacement of the adsorbed solvent molecules by the sulfur compounds and therefore it is smaller when a longer chain hydrocarbon, which is of higher adsorption strength, is used as solvent. Because of the adsorption of the solvents, the heat evolved during adsorption of sulfur compounds in a solution is also significantly lower than the intrinsic value of the heat of adsorption of the sulfur compounds. This can be confirmed by the calorimetric measurements of the adsorption of thiophene in the gas phase and in the liquid phase using octane as solvent on NaY as shown in Fig. 5. The heats of adsorption for both

gas and liquid phase adsorption are 246.7 and 64.3 J/g NaY, respectively. The liquid phase adsorption is completed in a much longer time (about 250 min) compared with the adsorption in gas phase (about 40 min) because of the diffusion resistance in liquid phase. The lower heat of adsorption of the sulfur compounds measured in the liquid phase is due to the heat required to displace the solvent molecules on the adsorption sites of the zeolites. The flow calorimetry measures only the integral heat arising from the endothermic displacement of the solvent molecules in the zeolite and the exothermic adsorption of the sulfur compounds. Although the exothermic heat of adsorption of pure solvents may be estimated calorimetrically, these values cannot be used to evaluate the intrinsic heat of adsorption of sulfur compounds because the solvent molecules adsorbed on different sites of the zeolite will be displaced by the sulfur compounds to different extents depending on the adsorption strength. Furthermore, the adsorbed solvent molecules are not necessarily completely replaced by the sulfur compounds even if the concentration of the sulfur compounds is in excess of the sorbent adsorption capacity. Nevertheless, the adsorption of sulfur compounds in the liquid phase is a true mimic of the practical adsorptive sulfur removal system and therefore the obtained apparent heat of adsorption of sulfur compounds from liquid phase calorimetry would be useful for the design of selective adsorption process for sulfur removal.

It is interesting to note that when the molecular size of the sulfur compound increases, the difference in the heat of adsorption of sulfur compound arising from the effect of the solvent becomes less significant. This is indicated by the plot of heat flow arising from the adsorption of dibenzothiophene in different alkane solvents on NaY recorded as a function of time as shown in Fig. 6. The features of the heat flow versus the adsorption time for solvents used are very similar and the total heat of adsorption differs by about 3 J/g NaY when solvent is changed from octane, dodecane to hexadecane.

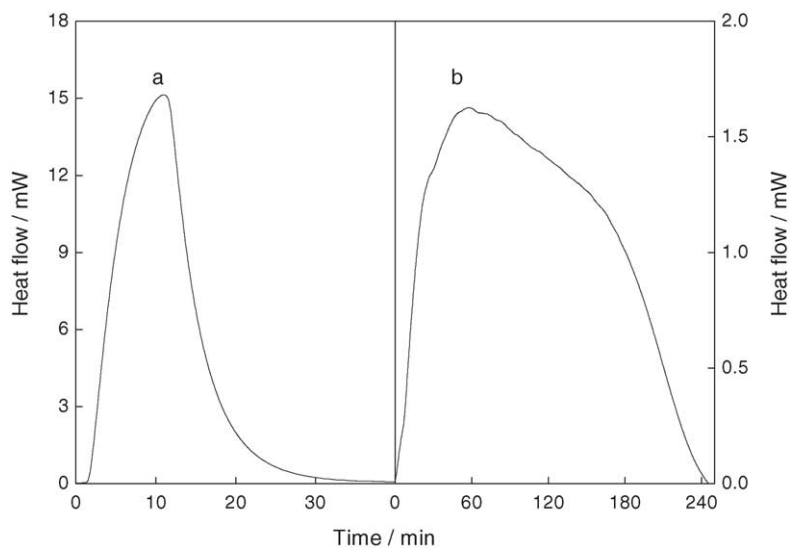


Fig. 5. Heat fluxes obtained from the adsorption of thiophene in gas phase (a) and in the liquid phase using octane as solvent (1800 ppm S) (b).



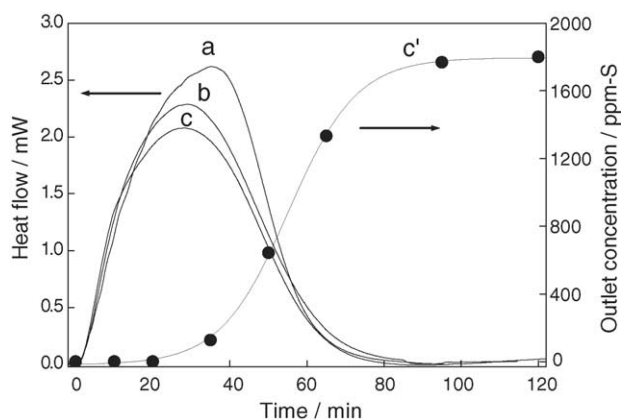


Fig. 6. Heat fluxes obtained from the adsorption of dibenzothiophene on NaY in different solvents (1800 ppm S): (a) octane; (b) dodecane; (c) hexadecane; (c') the concentrations of dibenzothiophene collected at the outlet of the calorimeter at different time intervals corresponding to (c).

The adsorption capacity of dibenzothiophene in hexadecane calculated from the “breakthrough” curve (Fig. 6, curve c') is about 0.84 mmol S/g NaY, which agrees fairly well with the sorption data shown in Table 1 (0.94 mmol S/g NaY).

The effect of the zeolite particle size on the heat of adsorption was also investigated. As an example, the heat of adsorption of benzothiophene in octane on NaY with larger particle size (850–1000  $\mu\text{m}$ ) and a plot of the concentration of sulfur in the effluent from the calorimeter versus time are shown in Fig. 1 (curves d and d'). The profile of the heat flux is significantly changed with the increase of the particle size of the sorbent and the adsorption time is prolonged compared with the adsorption on the small zeolite particles probably due to the intraparticle diffusion of the sulfur compounds. The total heat calculated from the heat flux (30.4 J/g) is smaller compared to the results obtained with the small zeolite particles (250–500  $\mu\text{m}$ , 36.3 J/g). The liquid phase adsorption of the sulfur compounds on the zeolite with smaller particle sizes (<250  $\mu\text{m}$ ) was also carried out on the C80 calorimeter, but the resistance of the flow increases significantly because the support structure in the percolation vessel provided for placing the sorbent in the calorimeter is easily blocked by the very small zeolite particles.

The flow rate of the liquid solution passing through the sample affects significantly the measurements of the heat of adsorption of the sulfur compounds. The heat flow of benzothiophene in octane adsorbed on NaY recorded as a function of time at a high flow rate (12.6 ml/h) is displayed in Fig. 1 (curve e). The obtained heat is much smaller (14.4 J/g) and the adsorption is completed at a very short time (<1 h). Clearly, the flow rate is an important factor affecting the determination of the heat of adsorption in the liquid phase. This issue has also been addressed by Groszek [15] who suggested a value below 6 ml/h without further explanation. It is possible that at the high flow rate the system cannot attain thermal equilibrium and bypass of the solution on the sorbent also occurs.

### 3.2. Influence of the molecular size and concentration of the sulfur compound on heat flux

Fig. 7 displays the heat flux obtained from the adsorption of thiophene, benzothiophene and dibenzothiophene in normal hexadecane on NaY recorded as a function of adsorption time. The kinetic diameter of thiophene is comparable to that of benzene (ca. 0.55 nm). Benzothiophene and dibenzothiophene will have the similar molecular width to that of benzene or thiophene although their lengths are much larger due to the presence of the aromatic and heterocyclic rings. The aperture of the Y zeolite is about 0.74 nm, which is larger than the molecular width of the sulfur compounds. Therefore, the sulfur compounds can be adsorbed into the pores of the zeolite. However, the profiles of the heat flux for the adsorption of the sulfur compounds are affected by the molecular size of the sulfur compounds. This is reflected by the change in the initial rate of the heat flow as shown in Fig. 7d. With the increase of the molecular size of the sulfur compounds, the initial rate of the heat flow increases, while the total heat for each gram of NaY evolved during adsorption and the total adsorption time decrease (also see Table 1). It is generally accepted that the cations and acidic sites in the zeolite function as the adsorption sites. Their accessibility is affected by the size of the sulfur compound molecules although they do not vary in number during adsorption. The small molecule like thiophene is easier to penetrate into the zeolite pores compared to the refractory sulfur compounds. For those sulfur compounds with two or more aromatic rings, the diffusion of the molecules of the sulfur compounds from the solvents to the adsorption sites will become slower and the number of the accessible adsorption sites become relatively less because of the steric restriction of the zeolite pore structure to these large sulfur compounds and thus the rate of the heat of adsorption may be expected to be smaller. This is contrary to the results shown in Fig. 7, suggesting that the profiles of the heat flux may be determined not only by the diffusion of the

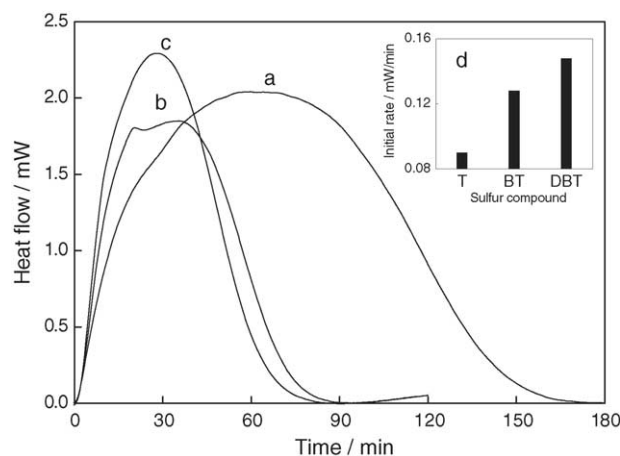


Fig. 7. Heat fluxes obtained from the adsorption of sulfur compounds on NaY in *n*-hexadecane (1800 ppm S): (a) thiophene; (b) benzothiophene; (c) dibenzothiophene.

sulfur compound in the solvent and/or in the structure of the zeolite, but also by the interaction of the sulfur compounds with the adsorption sites, which could be different depending on the sulfur compound used and the positions of the adsorption sites in the zeolites. At the initial time of the adsorption, the sulfur compound molecules may interact preferentially and strongly with certain adsorption sites of the zeolite that are accessible. The higher initial heat flux for the larger sulfur compounds may reflect that initially the interaction of these sulfur compounds with the zeolite is stronger. More importantly, for different sulfur compounds, their Lewis base nature is different, which may have the effect on the adsorption of sulfur compounds. For bulkier sulfur compounds, the sulfur is more basic because of the electronic donation from the aromatic conjugation system and therefore the interaction with the cations or protons can be stronger to give a higher heat flux. However, the average heat of adsorption for each mole of sulfur adsorbed does not change significantly with the molecular size of the sulfur compounds as indicated by the data shown in Table 1 and Fig. 2. Further studies are required to elucidate the characteristics of the adsorption of the sulfur compounds in the liquid phase.

Our previous liquid phase calorimetric investigation has also demonstrated that the concentration of the sulfur compound in liquid solution strongly affects the characteristics of the heat flux. The profiles of the heat flux obtained from the adsorption of 300–3000 ppm dibenzothiophene in hexadecane on NaY extrudates have been presented in Ref. [14]. It was found that the total heat of adsorption levels off when the sulfur concentration increases to about 1500 ppm and the entire adsorption process is completed in a shorter time for the solution with higher concentration of the sulfur compound (3 h for a solution with 300 ppm S and 1 h for a solution with 3000 ppm S). Fig. 8 displays the initial rate of heat flow from the adsorption of dibenzothiophene in hexadecane on NaY versus the concentration of dibenzothiophene. It can be seen that the initial rate of heat flow increases with increasing the sulfur concentration in the solution. Since there is no change

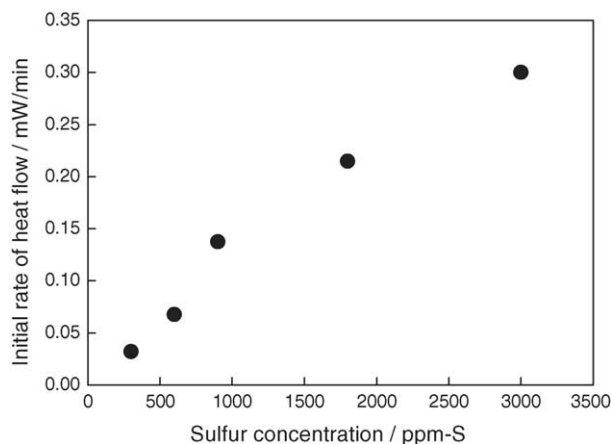


Fig. 8. Initial rate of heat flow vs. the sulfur concentration in solution for dibenzothiophene in hexadecane adsorbed on NaY.

in number and accessibility of the adsorption sites for the adsorption of dibenzothiophene at different sulfur concentrations, the variation in the rate of adsorption follows the generally known kinetics of adsorption. However, the adsorption process in the liquid phase involves the diffusion of the sulfur compound in a solution into the pores of the zeolite and the displacement of the solvent molecules already adsorbed by the sulfur compound. A number of different adsorption steps occur in the liquid phase and hence the evaluation of the intrinsic heat of adsorption of sulfur compound in liquid phase is quite complex.

### 3.3. Desorption/combustion of adsorbed sulfur compounds

In order to study the regeneration of the sorbents, the desorption/combustion of the sulfur compounds adsorbed on the zeolite was carried out in a flow of helium containing 5% oxygen analyzed by using TGA technique. Figs. 9 and 10 display the TGA and DTA results for hexadecane and different sulfur compounds in hexadecane adsorbed on the NaY zeolite. Prior to loading into the TGA cell, the sample was pre-treated at 200 °C to remove weakly adsorbed species. The TGA results are shown as the derivatives of the weight losses. The peaks on the derivative curves corresponding to the desorption of different adsorption species were deconvoluted by means of curve fitting. The amounts of the species desorbed and/or combusted at different temperatures are calculated from the peak areas and listed in Table 2. From Figs. 9 and 10 (on the left), a peak at about 90 °C can be observed for all the samples. According to the temperature difference shown as DTA curves (Figs. 9 and 10, right), this peak corresponds to the endothermic desorption and can be ascribed to the removal of physisorbed water in the zeolite arising from the contact of the samples with the moisture in the atmosphere prior to TGA measurements. The physisorbed water amounts to as high as 25% of the total weight loss (Table 2). Although the samples were pre-treated at 200 °C, the adsorbed hexadecane cannot be eliminated completely because of the strong adsorption of the solvent in the zeolite. This is indicated by the endothermic peak observed in the temperature range of 200–250 °C corresponding to the desorption of the adsorbed hexadecane. However, the variation of the weight loss corresponding to this endothermic peak may indicate that the desorption of the sulfur compounds at this temperature range cannot be completely excluded (Table 2). From the DTA curve of hexadecane adsorbed in the zeolite, two exothermic peaks are observed at about 320 and 455 °C and can be attributed to the combustion of the adsorbed hexadecane (Fig. 9, top). The appearance of the two peaks indicates the presence of two types of adsorbed hexadecane species in the zeolites. The two species amount to more than 70% of the total weight loss (Table 2). In the case of adsorption of thiophene in hexadecane, the peak at the higher temperature (~450 °C) becomes more intense, indicating that this peak represents not only the combustion of the adsorbed hexadecane but also

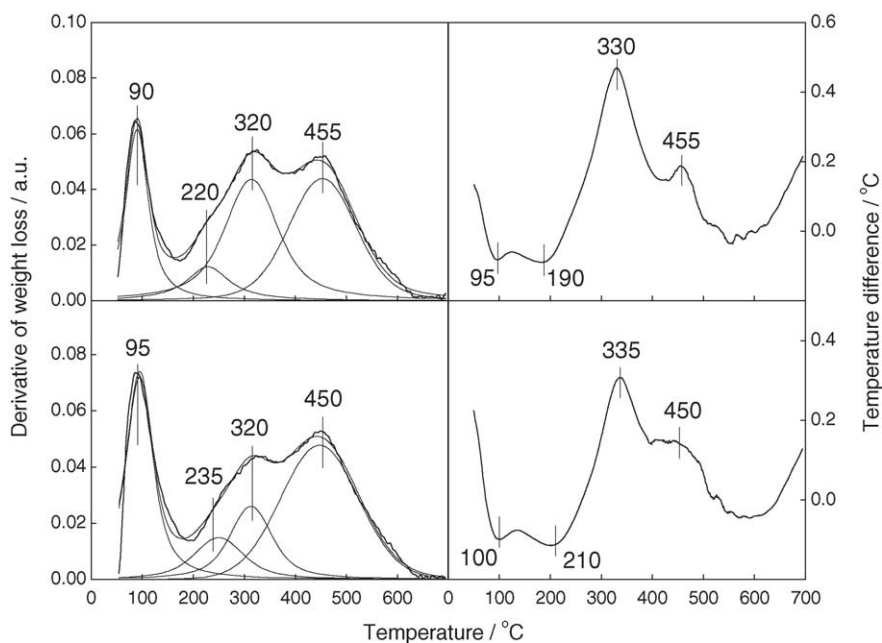


Fig. 9. TGA (left) and DTA (right) profiles of hexadecane (top) and thiophene in hexadecane (1800 ppm S) (bottom) adsorbed on NaY.

the combustion of the adsorbed thiophene. The combustion peak appearing at the lower temperature ( $\sim 315^\circ\text{C}$ ) may also be an overlapping of the combustion of adsorbed thiophene and hexadecane. When the size of the sulfur compounds becomes larger, one more exothermic combustion peak is observed at even higher temperature ( $505^\circ\text{C}$  for benzothiophene and  $550^\circ\text{C}$  for dibenzothiophene). The corresponding weight loss of this peak amounts to about 35% of the total weight loss for both benzothiophene and dibenzothiophene (Table 2).

NaY adsorbed with the more refractory sulfur compound, 4,6-dimethyl dibenzothiophene, in hexadecane was also measured by TGA as shown in Fig. 11. Similar to dibenzothiophene adsorbed on NaY, a larger peak is observed between  $500$  and  $550^\circ\text{C}$ , indicating that this bulky sulfur compound adsorbed in the zeolite could be desorbed via combustion. The TGA results clearly indicate that high temperature is required to desorb the refractory sulfur compounds. Therefore, the regeneration of the sorbents is an important issue to be considered for the commercial application of these sorbents.

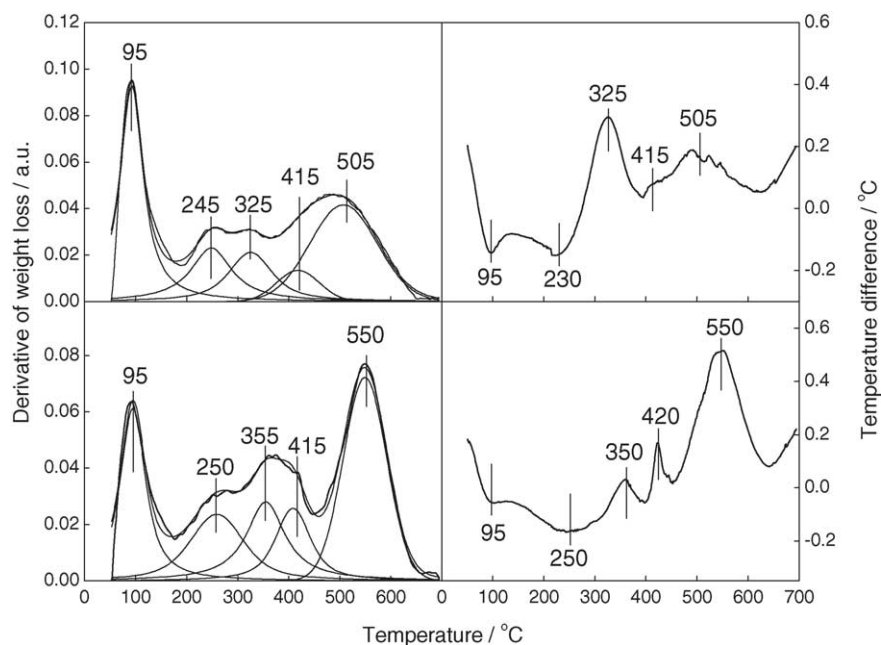


Fig. 10. TGA (left) and DTA (right) profiles of benzothiophene (top) and dibenzothiophene in hexadecane (1800 ppm S) (bottom) adsorbed on NaY.



Table 2  
TGA and DTA results of sulfur compounds adsorbed on NaY

Sulfur adsorbed on NaY	Total weight loss (%)	Percentage of weight loss at different temperatures				
		Species desorbed		Species combusted		
		~90 °C	200–250 °C	320–350 °C	410–450 °C	500–550 °C
Hexadecane	20.16	3.87	1.69	6.92	7.68	–
Thiophene <sup>a</sup>	19.74	5.24	2.12	3.26	9.19	–
Benzothiophene <sup>a</sup>	20.07	6.23	3.11	2.82	1.38	6.78
Dibenzothiophene <sup>a</sup>	21.98	5.32	3.90	4.00	2.89	7.67
4,6-Methyl dibenzothiophene <sup>a</sup>	21.08	4.44	1.86	1.60	0.80	12.34

<sup>a</sup> The concentration of thiophene, benzothiophene and dibenzothiophene in hexadecane is 1800 ppm, and 4,6-dimethyl dibenzothiophene in hexadecane is 900 ppm S.

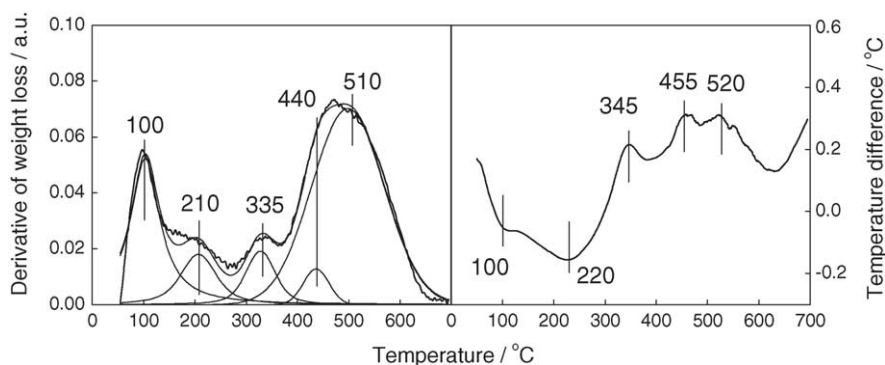


Fig. 11. TGA (left) and DTA (right) profiles of 4,6-dimethyl dibenzothiophene (900 ppm S) adsorbed on NaY.

#### 4. Conclusion

Our results indicate that flow calorimetry is effective for the study of adsorption of sulfur compounds in a liquid solution on solid sorbents. The flow calorimetry measures the integral heat arising from the endothermic displacement of the adsorbed solvent molecules and the simultaneous exothermic adsorption of the sulfur compounds. It appears that it is difficult to evaluate the intrinsic heat of adsorption of sulfur compounds from the flow calorimetric measurements. More studies are required to understand the effect of solvent, flow rate and sorbent particle size on the measured heat of adsorption. However, the liquid phase adsorption measurement is a true representation of the practical adsorptive sulfur removal system and therefore the information would be useful for the design of a selective sulfur adsorption process. The apparent heat of adsorption of sulfur compounds per gram of NaY zeolite is influenced by the solvents used and decreases with an increase of the chain length of the alkanes used as solvents. The measured heat of adsorption for each gram of the sorbent is also dependent on the size of the sulfur compound molecules. The characteristics of the heat flux for the adsorption of the sulfur compounds is influenced by the concentration of the sulfur compound in the solution. Interestingly, the calculated apparent heat of adsorption per mole of sulfur adsorbed is essentially independent of the molecular size of the sulfur compound and the different alkane solvents used suggesting that a similar mechanism for the interaction of sulfur compound with the zeolite. Based on

the TG analysis, it can be seen that a high temperature is required to desorb the refractory sulfur compounds by combustion. The measured heat flux together with the “break-through” characteristics obtained from the analysis of the effluents from the calorimeter could be used to aid the design of a new process for the production of ultra-clean fuels via selective adsorption of sulfur compounds on solid sorbents.

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