

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

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Received 9 October 2004; received in revised form 26 November 2004; accepted 5 January 2005

Available online 30 January 2005

## 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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*Keywords:* Flow calorimetry; Thermogravimetry; Sulfur adsorption; NaY zeolite

## 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

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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

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