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

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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 $\sim$ 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

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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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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

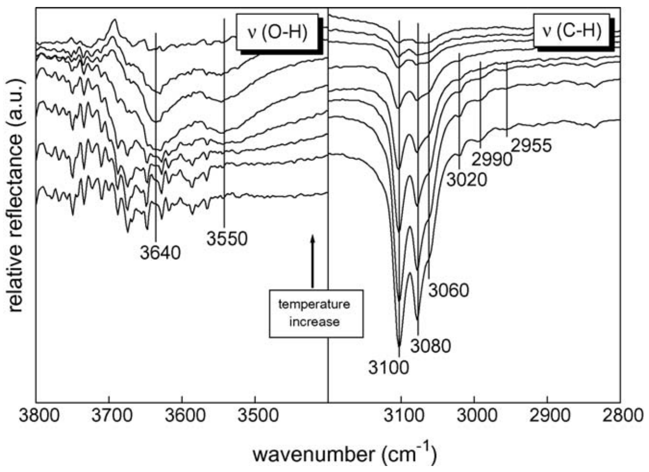

Fig. 1. DRIFT spectra recorded from the thermal desorption of benzothiophene adsorbed on NaY (40–360 °C, $\Delta T = 40$ °C).