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Effect of cyclohexene on thiophene adsorption over NaY and LaNaY zeolites

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ABSTRACT

NaY and LaNaY were used as adsorbents to remove thiophene from model gasoline (MG) with and without cyclohexene (CHE) by static adsorption experiments at room temperature (RT). The adsorbents were characterized by X-ray diffraction (XRD), X-ray fluorescence (XRF), N_2 physisorption and pyridine infrared spectrum (IR). The adsorption experiments show that the desulfurization performance of NaY decreases with the rise of CHE concentration in MG, whereas that of LaNaY first increases then declines. FT-IR spectra of thiophene adsorption indicate that thiophene is mainly adsorbed on NaY via π electron interaction, but adsorbed on LaNaY via π electron interaction, La–S direct interaction and protonation of thiophene. The Brönsted acid sites of LaNaY are found to play a crucial role and be responsible for the protonation of either thiophene or CHE molecules, which results in the alkylation reactions between thiophene and CHE in MG. The gas chromatograph–sulfur chemiluminescence detector (GC–SCD) and ultraviolet–visible (Uv–vis) spectra results also confirm the formation of alkylated thiophenes. The improved desulfurization over LaNaY may be attributed to the formation of alkylated thiophenes, owing to the larger molecular sizes and the higher electron densities on sulfur atoms of the alkylated thiophenes.

1. Introduction

The Environmental Protection Agency of the United States and the European Commission have recently issued regulations that require the refineries to reduce the sulfur content in gasoline less than 10 ppm by weight in 2011 [1–3] (Table 1). Deep desulfurization for ultra-clean gasoline, therefore, has become a more important subject worldwide. Conventional hydrodesulfurization (HDS) is effective in removing reactive sulfides, disulfides, mercaptans and light thiophenic sulfur compounds. However, to remove the sulfur compounds such as thiophene, benzothiophene and their derivatives in gasoline distillate at a deeper level, the HDS process may require substantial hydrogen consumption and has to be accompanied by a significant loss in octane number due to olefin saturation [4–6]. To avoid the above problems, several new technologies for deep desulfurization have been explored to meet the urgent needs for clean fuels in recent years [7–10]. Among these, adsorption desulfurization is regarded as a promising method in the removal of thiophenic sulfur compounds to produce ultra-clean fuels under moderate conditions.

So far, various types of adsorbents, including metal oxides [11], active carbon [12], clays [13], mesoporous materials [14,15] and zeolites [16–26] have been reported for the desulfurization of fuels, and among them, zeolites have been found to be very effective for adsorption desulfurization. The adsorption performance for thiophenic sulfur compounds of faujasite (FAU) zeolites, especially NaY and metal ion-exchanged Y zeolites, in both model and real fuels, has been widely investigated. FAU zeolites possess higher adsorption capacity due to the well-defined three-dimensional channels with a large pore opening of 7.4 × 7.4 Å, supercage cavity of 11.0 × 13.0 Å and large amounts of exchangeable cation sites. Yang and co-workers [19–22] reported the adsorption desulfurization of transportation fuels over Cu(I)Y and AgY zeolites under ambient conditions, and their desulfurization performance was ascribed to the π-complexation of the heterocyclic rings of thiophenic compounds with the transition metal cations in the zeolites. But on the other hand, Song and co-workers [23–26] thought that though π-complexation for removing sulfur compounds from transportation fuels was a novel approach, it was inevitable that the presence of large amounts of aromatics and olefin in the fuels can strongly compete with sulfur compounds. They reported that CeY [24] or prereduced NiY [26] zeolites exhibited higher sulfur adsorption performance, which was mainly attributed to the direct sulfur–metal (S–M) interaction.

From the above literature, we find that more emphasis has been put on the interaction mode of sulfur compounds and the metal ions in the ion-exchanged zeolites, whereas it is worth noting that the introduction of different metal ions into zeolite always leads to the change in the acid property of the zeolite. For example, it has been proposed that the rare earth ions La^{3+} exchanged in X or Y zeolites are hydrolyzed upon calcination, and the resulting protons generate Brønsted acid sites [27–29]: $[La(H_2O)_n]^{3+} = [La(OH)(H_2O)_{n-1}]^{2+} + H^+$. Therefore, when investigating the effect of the adsorption mode of sulfur compounds on

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Table 1
The gasoline standard of Worldwide fuel Charter (WWFC) (gasoline part).

Standard		WWFC		
		II	III	IV
w(sulfur)/(μg/g)	<	200	30	5–10
Benzene/(v/v %)	<	2.5	1.0	1.0
Aromatics/(v/v %)	<	40	35	35
Olefins/(v/v %)	<	20	10	10
w(oxygen)/%	<	2.7	2.7	2.7
Octane(RON/MON)			91.0/82.5	91.0/82.5

desulfurization, we should also consider the influence of acid property on adsorption desulfurization. In fact, several studies have manifested that there existed interactions between thiophene and acidic protons of zeolites by FT-IR, Uv–vis spectroscopy and MS measurements [30–38]. According to these investigations, thiophene conversion took place in the following ways: (a) thiophenic ring opening and reaction with or without hydrogen transfer at lower pressure or at higher temperature [30–34], (b) alkylation with olefin [32,35] and (c) thiophenic oligomerization [35–38]. However, some of the above studies [31–34] were carried out at higher temperatures (from 350 °C to 490 °C), what kind of conversion will occur under adsorption desulfurization condition (mostly at room temperature) still need to be clarified.

In addition, among the large amount of published work that concerning the effect of competitive adsorption on desulfurization, study on the effect of olefin is comparatively limited [17,35]. H.G. Wang et al. [17] studied the adsorption of thiophene over Ce(IV)Y by using model fuels containing thiophene and 1-octene, and the significant drop of the adsorption capacity of thiophene was attributed to the stronger adsorption interaction of 1-octene with Ce(IV)Y zeolite. Guisnet and coworkers [35] investigated thiophene adsorption from a diluted thiophene (0.3 wt.%) solution over HFAU zeolites, and found that the addition of 20 wt.% toluene or hexene or both caused a large decrease in thiophene removal. The decrease caused by hexene was ascribed to the acid catalyzed alkylation by hexene of thiophene. These two interpretations suggest that the mechanism of the effect of olefin on adsorption desulfurization may be complex.

In our previous work [18], zeolites NaY and LaNaY were used as adsorbents for removing sulfur compounds from model gasoline with and without toluene, and an improved adsorption capacity for thiophene removal from solutions containing large amount of aromatics over LaNaY was ascribed to the direct S–La^{3+} interaction suggested by FT-IR studies. The present work mainly focuses on the effect of olefin on thiophene removal over NaY and LaNaY zeolites by adsorption experiments that were carried out in stirred batch reactor at room temperature. The mechanisms of the effect of olefin on adsorption desulfurization were elucidated by FT-IR, gas chromatograph–sulfur chemiluminescence detector (GC–SCD), ultraviolet–visible (Uv–vis) spectra and gas chromatograph–mass spectroscopy (GC–MS) technologies.

2. Experimental

2.1. Adsorbents and MG preparation

The starting material used in this study was NaY zeolite ($SiO_2/Al_2O_3 = 4.67$). Adsorbent LaNaY was prepared by a liquid-phase ion exchange method according to the process reported previously [18]. Thiophene, cyclohexene (CHE) and cyclohexane were employed to be the model components for sulfur compound, olefinic compound and saturated hydrocarbon in gasoline distillate, respectively. Several model gasoline fuels (MG1 to MG5) containing ca. 100 mg S/L were prepared, in which the molar ratios of CHE to thiophene were 0:1, 1:1, 10:1, 100:1 and 500:1, respectively. MG6 containing high concentration of thiophene, as well as MG7 and MG8 using 3-methylthiophene (3-MT) and 2,5-dimethylthiophene (2,5-DMT) as model sulfur compounds, was also prepared for different purposes. The detailed compositions of the model fuels were summarized in Table 2.

2.2. Adsorbent characterizations

The XRD patterns for the adsorbents were collected in the 2θ range of 5–40° using a Rigaku.D/Max-RB diffractometer with Cu K_α radiation ($\lambda = 1.5418$ Å), operated at 40 kV and 200 mA. Elemental analysis for adsorbents NaY and LaNaY was achieved by SRS-3400(BRUKER) XRF. N_2 adsorption–desorption isotherms of NaY and LaNaY zeolites were measured on an ASAP-2020 apparatus at −196 °C. Prior to the measurements, the samples were evacuated at 300 °C for 3 h. The pore volumes were analyzed by Horvath–Kawazoe (HK) method, and the surface areas were determined by BET method. The acidic property of NaY and LaNaY was measured by FT-IR, using pyridine as probe molecule. IR spectra were recorded on Nicolet Impact 410 FT-IR spectrometer by scans of 64 with a resolution of 4 cm^{-1}.

2.3. IR study on the interaction between adsorbent and adsorbate

IR spectra of thiophene or CHE adsorbed over NaY and LaNaY zeolites were obtained on Nicolet Impact 410 FT-IR spectrometer by scans of 64 with a resolution of 4 cm^{-1}. The samples were pressed into a self-supporting wafer (10–15 mg) and placed in a quartz IR cell with CaF_2 windows. Then it was purged with N_2 flow at 350 °C for 1 h and subsequently cooled down to RT for thiophene or CHE adsorption. The IR spectra of the samples before thiophene or CHE adsorption were recorded at different temperatures, and after adsorbing for 10 s, the samples were purged with N_2 flow to higher temperatures at a heating rate of 10 °C/min. Then the IR spectra of thiophene or CHE on samples were recorded at different temperatures. All the spectra given in this work were difference spectra.

2.4. Adsorption desulfurization

Prior to desulfurization experiment, the adsorbents were dried in oven at 120 °C overnight in order to remove the physically adsorbed water. The adsorption experiment was carried out in a batch system at RT and atmospheric pressure. The dried adsorbents (0.25 g) were mixed rapidly with 5 mL of MG (MG1 to MG5) in flasks to adsorb thiophene for 3 h. The adsorption time was determined by monitoring the variance of sulfur content of MG with time, and the results showed that a period of 3 h was enough for the adsorption to achieve equilibrium. The desulfurized MG was separated by filtration, and the sulfur content of MG before and after adsorption was analyzed by microcoulometry. The sulfur removal (R%) was calculated according to the following formula:

$$R\% = \frac{c_0 - c_e}{c_0} \times 100\%$$

Table 2
The compositions and proportions of model gasolines.

Model gasoline	Sulfur content (mg/L)	Compositions	n_{CHE}/n_{Thio}	vol.% of CHE
MG1	94.5	Thiophene/cyclohexane	0	0
MG2	97.5		1	0.0315
MG3	99.0		10	0.315
MG4	96.4	Thiophene + cyclohexene/cyclohexane	100	3.15
MG5	94.7		500	15.76
MG6	1038.9		10	3.15
MG7	104.6	3-methylthiophene/cyclohexane	0	0
MG8	90.9	2,5-dimethylthiophene/cyclohexane	0	0