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Adsorption desulfurization and weak competitive behavior from 1-hexene over cesium-exchanged Y zeolites (CsY)

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ABSTRACT

The systematic research about the adsorption desulfurization and competitive behavior from 1-hexene over cesium-exchanged Y zeolites has been investigated. The structural properties of the adsorbents were characterized by X-ray diffraction (XRD), N_2 sorption (BET) and thermal analysis (TGA). The effects of calcination temperature, calcination atmosphere, and adsorption temperature were studied by the dynamic and static tests. The competitive adsorption mechanisms between thiophene and 1-hexene were studied by in-situ Fourier transform infrared spectroscopy (in-situ FTIR) and temperature-programmed desorption (TPD). CsY adsorbents exhibited high selectivity for thiophene even when a large amount of olefins exist. In-situ FTIR spectra of thiophene and 1-hexene adsorption indicated that both thiophene and 1-hexene were mainly adsorbed on CsY via π-complexation. The higher desorption activated energy and higher adsorption heat of thiophene than 1-hexene obtained by thiophene-TPD and hexene-TPD has revealed that thiophene is adsorbed more strongly in CsY adsorbents than 1-hexene.

1. Introduction

The removal of sulfur for ultra-clean transportation fuels has been mandated by governments all over the world because of the increasingly stringent environmental legislations, which has put forward a major operational and economic challenge for the petroleum refining industry [1–3].

Conventional hydrodesulfurization (HDS) is mature in the removal of reactive (di) sulfides using catalysts and H_2, but less efficient for refractory molecules such as thiophene (T), benzothiophene (BT), dibenzothiophene (DBT) and their derivatives [4]. Typical reactions were conducted at elevated temperatures (300–340 °C) and pressures (2.0–10.0 MPa) using Co-Mo/Al_2O_3 or Ni-Mo/Al_2O_3 as catalysts [5,6]. To meet the legislation specifications, a high investment cost for scaling up reactor volume and consuming more energy is needed, concomitantly resulting in a significant loss in octane number due to olefin saturation. Especially, thiophene and its derivatives are found to be particularly difficult to remove by hydrotreatment processes. So, looking for low cost and efficient methods has been the most important target. The selective adsorption desulfurization has received much attention due to the high capacity and selectivity in removing thiophenic sulfur compounds at room temperature and atmospheric pressure, with no need for hydrogen [7,8].

The key challenge of this approach is to explore an adsorbent that can selectively adsorb sulfur compounds but leave other compounds unchanged. Zeolites Y have been found to be promising materials for the adsorptive desulfurization. Yang and co-workers [9–12] reported that cation-exchanged Y zeolites, Cu(I)Y, AgY and NiY, can retain sulfur compounds in fuels by π-complexation bonds with the transition metal cations in the zeolites.

However, competitive adsorption of olefins inevitably affects the selective adsorption of sulfur compounds. King and Li [13] found that the adsorption capacity of thiophene over Cu(II)Y decreases substantially when olefins are present in the feed, suggesting that there are strongly competitive interactions of olefins and thiophenes toward the copper sites. Duan et al. [14] has focused on the effects of 1-octene on the performance of L-CeY zeolites for selective adsorption desulfurization. And it can be clearly seen that olefin component in model fuels can strongly affect the adsorption of thiophene sulfur compounds due to chemical adsorption. The adsorption capability for sulfur compounds decreases significantly as the concentration of olefins increases in model fuels. Wang et al. [15] 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.

Simultaneously, the acidity of adsorbents could also affect the selective adsorption of sulfur compounds. Researchers [16]

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Table 1. The component of mixtures.

Mixtures	Sulfur concentration (mg/L)	Mass fraction of 1-hexene (%)
M-1	746.46	0
M-2	748.06	4
M-3	732.17	6

demonstrated that the protonation of thiophene and cyclohexene was also detected on the Brönsted acid sites of LaNaY or Ce(IV)Y. Thiophene oligomerization, olefin oligomerization and thiophene alkylation with olefin could occur on the Brönsted acid sites, which resulted in the blockage of pores and the coverage of adsorption active centers, further inhibiting thiophene adsorption. Li et al. [17] utilized K cation to decrease the amount of Brönsted acid sites of NiY adsorbent. The results showed that protonation reactions were weakened and the negative effects of Brönsted acid sites were reduced. Thomas et al. [18] studied the adsorptive removal of dibenzothiophene, quinoline and naphthalene in hexadecane on the zeolites, NaY, NiY and CsY. Cs^+ was chosen due to its basicity.

However, among so many novel published works focusing on the adsorption desulfurization, adsorbents modified by alkali metals (K^+, Rb^+ and Cs^+) were rarely reported. Thus, the main objective of this study is to pick up the modified absorbent with best thiophene removal performance (CsY), and systematically find the adsorption conditions and the competitive adsorption mechanisms between thiophene and 1-hexene over CsY zeolites. The structural properties of the adsorbents were characterized by XRD, BET and TGA. The adsorption behaviors of thiophene and 1-hexene have been studied by the dynamic tests, static tests and in-situ FTIR spectroscopy. The desorption activated energy as well as the adsorption heat of thiophene and 1-hexene on adsorbents were determined by the temperature-programmed desorption (TPD).

2. Experimental

2.1. Adsorbents preparation

The starting material was NaY zeolite in powder form, which was kindly provided by Huahua Co. Ltd., Wenzhou city, Zhejiang Province, China. The alkali mental cation-exchanged zeolites (K^+, Rb^+ and Cs^+) were prepared by liquid ion exchange using 0.1 M aqueous solution of the corresponding metal salt (chloride) at 80 °C for 6 h. After exchange, the adsorbents were filtered under vacuum, rinsed thoroughly with deionized water and dried at 120 °C overnight.

2.2. Feedstocks

Thiophene, 1-hexene and n-octane were employed to be the model components for sulfur compound, olefinic compound and saturated hydrocarbon in gasoline distillate, respectively. The adsorbents were tested with different mixtures, which were denoted as M-1, M-2, and M-3. The detailed compositions of the mixtures are described in Table 1.

2.3. Adsorption experiments

2.3.1. Dynamic tests

Dynamic tests were carried out to evaluate the adsorption desulfurization of the adsorbents in a fixed bed flow reactor at room temperature (25 °C) and atmosphere pressure (0.1 MPa), with weight hourly space velocity (WHSV) of 5 h^{-1}. First, 0.89 g of adsorbent samples were packed into a quartz column (length: 500 mm; internal diameter: 9 mm; bed volume: 1.25 cm^3). Then the adsorbents were loaded in the middle of the reactor and the spare spaces were filled with quartz sand (20–40 mesh). Prior to the adsorption measurement, in-situ calcination at 350 °C for 4 h in N_2 atmosphere was necessary, in order to ensure elimination of water and any other substances that could have been previously adsorbed. The fuel was pumped into the fixed-bed flow reactor with a flow rate of 6 mL/h. Sulfur content of the effluent was sampled at different operating time and analyzed by TS-3000 fluorescence sulfur tester. The adsorbents were penetrated until the outlet concentration of sulfur is more than 10 mg/L.

2.3.2. Static tests

Static tests were carried out to evaluate the capacity of the adsorbents for sulfur removal. Adsorbent (0.1 g) was added to a 10 mL mixture sample in an airtight container operating at room temperature for 12 h. Then the concentration of sulfur was analyzed by TS-3000 fluorescence sulfur tester. The sulfur capacity of the adsorbent was calculated as follow:

$$\text{Sulfur capacity}(\text{mg}_S/\text{g}_{\text{adsorbent}}) = (C_0 - C_t)V/m \tag{1}$$

where C_0 is the initial concentration of sulfur (mg/L), C_t is the final concentration of sulfur (mg/L), V is the volume of the mixture (L), m is the mass of the adsorbent (g).

2.4. Characterization of adsorbents

2.4.1. X-ray diffraction

X-ray diffraction analyses of all the adsorbents in the powder state to characterize the crystal structure were carried out using a Siemens Model D-500 X-ray diffractometer equipped with Ni filtered Cu KR radiation (40 kV, 100 mA). The patterns were recorded over a range of 2θ angles from 5°–80° in steps of 0.02°/s.

2.4.2. N_2 adsorption–desorption

The BET surface area and pore volume were obtained from nitrogen isotherms determined at liquid nitrogen temperature on JW-BK200C. Before testing, the samples were degassed under vacuum condition for 90 min at 150 °C. The specific surface area was calculated by Brunauer–Emmett–Teller (BET) method. The pore volume was estimated from the last point of the isotherm.

2.4.3. X-ray fluorescence analysis

The chemical composition was determined by X-ray fluorescence spectrometry (XRF-1800, Shimadzu Corporation, Japan). The quantitatively results of samples were used to analyze elements contents and their percentages.

2.4.4. Thermal analysis

Thermo-gravimetric (TGA) curves were obtained using a TA Instruments thermal analyzer. The samples were exposed to an increase in temperature of 10 °C/min up to 800 °C while the nitrogen flow rate was held constant at 100 mL/min.

2.4.5. Temperature-programmed desorption of thiophene and 1-hexene

Thiophene-TPD and hexene-TPD were conducted on Auto Chem 2910 (Micromeritics, USA). Approximately 100 mg of adsorbent was taken in a custom-made vertical stainless steel tube and pretreated at 500 °C in nitrogen flow for 60 min. When the temperature was cooled down to 30 °C, thiophene and 1-hexene was injected in pulse to the sample until saturation respectively. After that, thiophene-TPD and hexene-TPD were carried out from 30 to 500 °C at different heating rates of 6–12 °C/min. Component and composition of the effluent was analyzed by the TCD. TPD without the adsorbent was also carried out under identical experimental conditions in order to find the effect of the adsorption of the adsorbates on the column walls. This was found to be very small and could be neglected.

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