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Efficient solvent regeneration of Basolite C300 used in the liquid-phase adsorption of dibenzothiophene

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HIGHLIGHTS

- The spent C300 adsorbent can be regenerated by washing with alcohols.
- Initial adsorption capacity of the fresh C300 can be recovered after regeneration with methanol.
- After three desulfurization–regeneration cycles the adsorption capacity remain constant.

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ABSTRACT

The metal–organic framework (MOF) Basolite C300 displays excellent performance for the removal of dibenzothiophene (DBT) in a model system consisting in DBT in a mixture of 2,2,4-trimethylpentane (TMP). With the aim to exploit this property in a continuous operation, it is imperative to develop a simple and effective regeneration procedure. Our previous work (Fuel 105 (2013) 459–465) demonstrated that there is only partial thermal regeneration of this system at 473 K, which makes this approach of limited value. In the present work, we developed a significantly more effective regeneration procedure in which the DBT-saturated MOF C300 system was washed with polar solvents, such as methanol, ethanol and isopropanol. It was found that regeneration using methanol as a solvent at temperatures near ambient (304 K) is highly effective and allows for the recovery of the initial adsorption capacity. After several regeneration cycles, both the crystallinity and the initial sorption capacity of the C300 system are essentially unchanged.

1. Introduction

In recent years, sulfur removal from hydrocarbon fuels, such as diesel and gasoline, has resulted in a global effort to prevent air pollution that includes the deactivation of exhaust catalysts [1,2]. Mandatory environmental fuel specifications introduced by the European Standards Organization (CEN) and the federal government of the United States (EPA) require that refineries reduce the levels of sulfur in gasoil for heating purposes and in marine diesel to 1000 ppmw by 2008 and 2010, respectively. Additionally, there is a demand for ultra-low-sulfur fuel (preferably down to 0.1 ppmws) [3].

In the petroleum industry, low-sulfur fuels are often obtained through hydrocracking or hydrotreating processes (HDS) [4]. The organic S-compounds are converted to H_2S and the corresponding hydrocarbon. These reactions are conducted under high hydrogen pressure (typically 40 bar) and at temperatures around 670 K in refinery units using Ni(Co)–Mo(W) sulfide phases that are deposited on alumina substrates. Although current HDS processes are highly efficient and technologically important, they do not appear to be suitable for the production of ultra-clean fuel. While they efficiently eliminate aliphatic and alicyclic sulfur compounds and thiophenes, they are much less effective at removing the more sterically hindered benzothiophene (BT), dibenzothiophene (DBT), and 4,6-dimethyldibenzothiophene (DMDBT) fuel contaminants due to the sterically hindered adsorption of these compounds on the catalyst surface [5]. Among the novel technologies proposed for deep fuel desulfurization, adsorption appears to be a soft technology for sulfur removal because hydrogen is not required, and the process operates under mild conditions [6–8].

The ability to use the adsorption process at ambient temperature and pressure would be a major advance in the petroleum refinery industry. One of the challenges of the adsorptive desulfurization process is that the sorbent material should remove only the sulfur compounds without adsorbing the other aromatics and olefins in the fuel. For on-board or onsite fuel cell applications,

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the adsorptive desulfurization should be performed at near ambient temperatures. It is also mandatory that the adsorbent material be regenerable to reduce costs.

Several sorbents have been previously studied: zeolites, silica, carbon, alumina [9,10] and metal–organic frameworks (MOF) systems [1,11–14], with the latter being the most promising candidate. Metal–organic frameworks are crystallized hybrid porous solids built up from inorganic subunits (clusters, chains, or layers) that are connected through organic linkers, such as carboxylates or phosphonates [15]. They are composed of metal ions and organic linkers, the latter of which act as bridging ligands between the metal ions to form highly ordered frameworks. They exhibit a huge variety of structures that sometimes have very large pores and high surfaces areas, which are qualities that lead to excellent adsorption.

We recently reported the use of MOF systems as sorbents for organosulfur compounds present in transportation fuels and showed that this system is an efficient complement to the conventional hydrodesulfurization process [12]. However, the thermal regeneration of this sorbent results in a partial recuperation of the original adsorption capacity [16]. Part of this incomplete regeneration can be attributed to the limited regeneration temperature, as the adsorbent is not stable at high temperatures. The aim of this work is to study the regeneration of a MOF (BASF C300) used in the adsorptive desulfurization of fuels via solvent washing.

2. Experimental section

2.1. Materials

Solvents, dibenzothiophene and the Basolite C300 [$Cu_3(C_9H_3O_6)_2$] metal–organic framework were purchased from Sigma–Aldrich and used without further purification.

2.2. Adsorbent characterization

The thermogravimetric analyses of the used MOFs were performed with a Perkin-Elmer TGS2 instrument using a heating rate of 10 K min^{-1} under a nitrogen flow (60 mL min^{-1}).

The X-ray diffraction (XRD) patterns of the fresh and used C300 samples were recorded using a Seifert 3000P vertical diffractometer and nickel-filtered Cu Kα radiation (λ = 0.1538 nm) using the standard powder diffraction procedures. A standard glass slide was used for the background corrections. The crystallinity of the C300 MOF system in both the fresh and the used samples was studied to detect any possible deterioration of the crystalline structure when used in the adsorption experiments. The crystallinity percentage was determined using the ratio of the sum of the relative intensity of the five most intense peaks, according to the following equation:

$$\%\,crystallinity = \frac{\sum_{i=1}^{5} I_{relsample}}{\sum_{i=1}^{5} I_{relsample}} \times 100 \quad (1)$$

In this calculation, the fresh C300 sample was taken as the standard (100% crystallinity).

The textural properties were determined using the adsorption–desorption nitrogen isotherms recorded at 77 K with a Micromeritics TriStar 3000. The specific area was calculated by applying the BET equation to the values of the nitrogen adsorption isotherms within the relative pressure (P/P^0) range from 0.03 to 0.3 and using a value of 0.162 nm^2 for the cross-section of an adsorbed nitrogen molecule at 77 K. The pore size distributions were computed by applying the Horvath-Kawazoe model to the desorption branch of the nitrogen adsorption–desorption isotherms.

X-ray photoelectron spectra (XPS) were acquired with a VG Escalab 200R spectrometer equipped with a hemispherical electron analyzer utilizing a Mg Kα ($h\nu$ = 1253.6 eV) non-monochromatic X-ray source. The samples were degassed in the pretreatment chamber at room temperature for 1 h prior to being transferred into the instrument's ultra-high vacuum analysis chamber. The high resolution Cu2p, O1s, S2p and C1s spectra were scanned several times at pass energy of 20 eV, to obtain good signal-to-noise ratios. The binding energies (BE) were referenced with respect to the BE of the C1s core-level spectrum at 284.9 eV. The invariance of the peak shapes and widths at the beginning and end of the analyses indicated a constant charge across all of the measurements. The peaks were fitted using a non-linear least square fitting routine after background subtraction and a properly weighted sum of Lorentzian and Gaussian component curves. The surface atomic ratios were estimated from peak areas, normalized to silicon, and corrected using the corresponding sensitivity factors [17].

2.3. Adsorption measurements

A model diesel fuel (MDF) was prepared for the adsorption experiments. This fuel contained a molar concentration of dibenzothiophene (DBT) in a mixture of 2,2,4-trimethylpentane (TMP). Prior to use, the MOF samples were degassed under vacuum to remove any adsorbed water or solvents. Both fresh and regenerated MOF C300 sorbents (see below) were tested in a liquid-phase glass batch reactor operating at atmospheric pressure with constant stirring. The procedure involved suspending 1 g of C300 in 100 g of a solution of the sulfur compound (DBT) in TMP. This mixture was kept at 304 K with vigorous stirring for 72 h to reach the thermodynamic equilibrium of adsorption. The sorbent saturated with the organosulfur compound was then separated from the liquid phase via filtration for subsequent characterization, while the liquid phase was analyzed by GC-FID to evaluate the sulfur compound concentration. All measurements were performed at least three times for reproducibility test.

2.4. Regeneration treatment

The regeneration of the used MOF was accomplished using the following procedure: the saturated adsorbent was put in contact with the solvent with vigorous stirring at 304 K for 72 h. The solid was then recovered by filtration and dried at 373 K to remove any adsorbed solvent or water.

3. Results and discussion

We began the study with fresh C300 samples because these samples were used in the adsorption of DBT in a model system consisting in DBT in a mixture of 2,2,4-trimethylpentane (TMP), under the conditions selected in our previous works [12,16]: a temperature of 304 K, an initial S-concentration of 1 wt%, and a time period of 72 h. Under these conditions, the adsorption equilibrium is reached with an adsorption capacity of 58.1 g S/kg sorbent.

Attempts were made to regenerate the spent C300 sample by washing the adsorbent with three different polar solvents: methanol, ethanol and isopropanol (50:1 solvent:sorbent). The solvents were selected based on their Hildebrand solubility factors (Table 1) [18,19], as the higher polarity helps to remove the sulfur compounds. Consequently, solvents with a δ value higher than 22 are expected to be good candidates for the extraction of these compounds (Table 1). After regeneration, the samples were reused for the adsorption of DBT. The results shown in Table 2 indicate that the extraction efficiency depends on the polarity of the solvent. The adsorption capacity for fresh samples and samples