Fixed bed adsorptive desulfurization of thiophene over Cu/Ni-dispersed carbon nanofiber
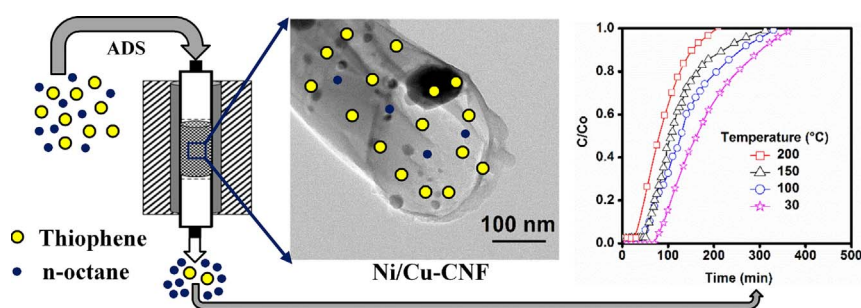
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GRAPHICAL ABSTRACT

ARTICLE INFO

ABSTRACT

Adsorptive desulfurization (ADS) of thiophene containing n-octane at low S-concentrations (≤ 70 ppmw) was performed under dynamic (flow) conditions in a fixed bed of Cu/Ni nanoparticles (NPs)-dispersed carbon nanofibers (CNFs). Briefly, Cu-CNFs were prepared using chemical vapor deposition with acetylene as the carbon source and the Cu NPs as the catalyst. The metal NPs also served as a support for the CNF-growth. The Ni/Cu-CNFs of different particle sizes (0.20, 0.35 and 0.50 mm) were synthesized by impregnating the heat treated Cu-CNF with Ni salt, pelletizing it using the phenolic resin binder, followed by calcination, H_2-reduction, and pulverization to the required particle sizes. The adsorbent showed the BET surface area of $\sim 350\,\mathrm{m^2/g}$, metal nanoparticle-size of 5–25 nm, and thermal stability over 30–900 °C. The prepared adsorbent material was easily pelletized to the cylindrical shape, with the pellet showing high mechanical strength (~ 1900 kPa). Breakthrough experiments showed the adsorbent to be capable of suppressing concentrations at or below 1 ppmw-S, with the breakthrough and saturation capacities determined to be 0.25 and 0.60 mg-S/g-adsorbent, respectively at 30 °C and 35 ppm (w/w) S-concentration, which were comparable with those of adsorbents discussed in literature for the ADS of lean sulfur containing fuels.

1. Introduction

Sulfur is the third most abundant element found after carbon and hydrogen in petroleum feedstock, and its content varies from less than 0.05% to 14% (w/w) or greater in petroleum [1]. Increasing number of automobiles worldwide has resulted in significant emissions of SOx,

NOx, and particulate matter into atmosphere. Stringent environmental regulations have been imposed to reduce sulfur level in fuels including diesel and gasoline. At present, maximum 50 ppmw-sulfur containing diesel and gasoline fuels are being supplied for transportation vehicles in India. As per the new regulation, the maximum S-content in such fuels should be decreased to 10 ppmw by 2020 [2]. Applications such as

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fuel cells require S-content in the fuels even lesser than 1 ppmw [3]. Conventional hydrodesulfurization (HDS) process uses H_2 and a heterogeneous catalyst, e.g., Al_2O_3-supported Ni(Co)/Mo(W), however, at high temperatures and pressures [4]. Therefore, the HDS processes may not be economical for deep desulfurization because of severe operating conditions and the requirement for highly active catalysts.

Adsorptive desulfurization (ADS) is one of the non-conventional routes to the desulfurization of fuels, requiring mild operating conditions. One of the main advantages of the ADS process is that quality of the processed fuels is retained, which may be altered otherwise during HDS because of the prevalent severe operating conditions [5]. Therefore, development of efficient adsorbents is critical to removing sulfur compounds from the fuels, especially at low S-concentrations.

Various transition metals such as Cu, Ni, Ag, and Zn dispersed in various substrate materials have been studied for ADS under low to moderate temperature and pressure conditions [6–8]. The transition metals bind with sulfur compounds via direct metal-sulfur interaction and/or π-complexation [9]. Use of Ni as an active metal for ADS has gained attention because of its relatively better performance in removing sulfur compounds from fuels. In particular, Bhandari et al. [10] studied the desulfurization of diesel oil using ion-exchanged zeolite. Among the four different metals, namely, Fe, Ni, Cu, and Zn, the Ni-dispersed zeolite showed the highest adsorption capacity (~ 42 mg-S/g). Liao et al. [11] studied the ADS of thiophene (TH) over the γ-Al_2O_3-supported metals (Ag, Ni, Cu, and Zn) at room temperature. The adsorption capacity of the adsorbents was measured to be increasing in the following order of the active metals: Zn < Cu < Ni < Ag. Ma et al. [12] studied the ADS of commercial gasoline over the silica-alumina supported Ni and Cu (I) Y-zeolite at room temperature (~ 30 °C) and 200 °C. Under the identical experimental conditions, the Ni-based adsorbent showed higher adsorption capacity compared to the Cu(I) Y-zeolite. A comparative literature data show the adsorption capacity of various Ni-based adsorbents at 25–200 °C in the range of 0.2–133 mg-S/g corresponding to the sulfur concentration range of 10–1200 ppmw [8,10–14].

Carbon-based materials such as activated carbon (AC), activated carbon fibers (ACFs), carbon nanotubes, carbon nanofibers (CNFs), and aerographite contain large BET surface area. The materials are stable under severe acidic and basic conditions, and are also amenable to surface modifications, which make them a suitable candidate for various applications [15–23]. A literature review also corroborates the superior ADS performance of AC-based adsorbents than the other supports including Al_2O_3, silica, and zeolites [24–27].

CNF-based materials have been used for several potential applications including catalyst support [28], adsorption of heavy metals [29], H_2 storage [30], and energy [31]. However, their applications in ADS have not been studied in details. Kim et al. [32] synthesized ZnO/CNFs using electrospinning method. The synthesized material was used as an adsorbent for H_2S under flow conditions. The maximum breakthrough time was reported to be 530 min/g-adsorbent for 761 ppmw of inlet H_2S concentration, with the corresponding breakthrough capacity of the material measured to be ~ 114 mg-S/g-adsorbent. Bigdeli and Fatemi [33] synthesized CNFs over the Ni-AC support using chemical vapor deposition (CVD) technique. The Ni-AC-supported CNFs were used as the adsorbent for TH and dibenzothiophene (DBT) in n-octane under batch conditions. The adsorption capacity of the 0.5% (w/w) Ni containing sample was measured to be ~ 1.98 and ~ 2.17 mg-S/g-adsorbent for TH and DBT having initial concentrations of 448 and 998 ppmw, respectively. In a recent study, CNFs were grown over the porous carbon beads, using CVD, and the CNF-decorated beads were used for the ADS of TH and DBT over the concentration range of 350–1200 ppmw-S in diesel [14]. The data showed that the activated carbon beads without CNFs were suitable for adsorbing large sized (4.93 Å × 9.87 Å) DBT molecules, whereas the beads with CNFs were suitable for the small sized (4.7 Å × 4.7 Å) TH molecules. The study clearly showed the significance of the microporous graphitic CNFs in the enhanced adsorption of small sized S-compounds via the formation of π-complexation and/or metal-sulfur interaction, and therefore, the suitability of the CNF-based adsorbents for the ADS of the small sized solutes (viz. thiols and sulfides) containing commercial diesel oils.

Despite CNFs or Ni-impregnated CNFs indicating a strong desulfurization potential for the S-containing species, one of the drawbacks of such materials is their application as adsorbents in a large scale packed bed under flow conditions. Flow through powdery or micro-nano sized materials is prone to maldistribution or channeling which often undermines the performance of the material and impacts its adsorption efficiency. Therefore, adsorbent materials are used in extrudate or pelletized forms. It is important to mention that in the previous studies [14,33,34], CNFs grown over a carbon support (viz. AC or ACF) were detached from the support in an ultrasonication step. In the present study, the Ni NP-doped CNFs were grown using CVD, with Cu NPs serving as the CVD catalyst. Notably, the CNF-growth did not require any carbon support (ACF or AC). Rather, the Cu NPs simultaneously served as the support. The synthesized Cu-CNFs were doped with Ni NPs and pelletized using the phenolic resin binder. The prepared Ni-Cu/CNF pellets were used as an adsorbent for the ADS of TH at low concentrations (35, 45 and 70 ppmw-S) in n-octane under flow conditions in a fixed bed adsorber. This is the first study on the synthesis of the Ni NP-doped pelletized CNFs for the efficient ADS of low S concentration-fuels under flow conditions in a packed bed adsorber.

2. Experimental

2.1. Materials

Potassium sodium L (+) tartrate (purity 99%) and n-octane (99%) were purchased from SDFCL, Mumbai (India). TH (99%) was purchased from Avra, India. Nickel nitrate hexahydrate ($\geq 98\%$), cupric chloride (99%), and ethyl alcohol (99%) were purchased from Merck, Mumbai (India). Zero grade gases were purchased from Sigma Gases and Services, New Delhi (India).

2.2. Preparation of copper tartrate

Fig. 1 shows a schematic diagram of the synthesis steps for the Ni/Cu-CNF adsorbents. Copper tartrate was synthesized using precipitation method. Approximately 100 mL aqueous solutions of cupric chloride (0.1 M) and potassium sodium tartrate (0.1 M) were separately prepared. The cupric chloride solution was slowly mixed into the potassium sodium tartrate solution under vigorous stirring. Stirring was continued for 0.5 h. The produced precipitate of copper tartrate was collected and washed with Milli-Q® water until chloride ions were completely removed from the precipitate. The precipitate was washed with ethanol and dried at 110 °C for 12 h in an oven.

2.3. Synthesis of Cu-CNFs

Approximately 1 g of copper tartrate powder was placed in a crucible boat and heated in a horizontal furnace. Temperature of the furnace was increased 5 °C/min to 280 °C. During heating, H_2 gas was flowed over the powder at 100 standard-cc/min (sccm) using a mass flow controller (Eureka MFC). The H_2 flow was continued for another 1 h at 280 °C. The C_2H_2 gas was flowed at 40 sccm to the furnace for 2 h. The gas flow was switched off and the furnace was cooled to room temperature. The prepared sample is referred as Cu-CNF for the reference purposes in this study. The prepared Cu-CNFs were heat treated at 800 °C for 1 h under 100 sccm of N_2 flow. The heat treatment removed stickiness of the material, and also, increased its BET surface area, discussed later. The heat treated sample is referred as Cu-CNF (HT).