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Adsorptive desulfurization of diesel oil using nickel nanoparticle-doped activated carbon beads with/without carbon nanofibers: Effects of adsorbate size and adsorbent texture

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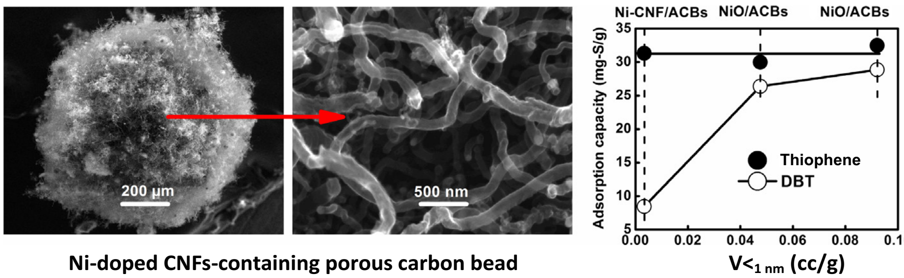
HIGHLIGHTS

- Efficient Ni-doped CNF-containing adsorbents were prepared for ADS of diesel oil.
- The adsorbate size and adsorbent textures influenced the adsorption capacity.
- Ni-CNF/ACBs showed higher adsorption capacity than Ni/ACBs in a commercial oil.

GRAPHICAL ABSTRACT



Ni-doped CNFs-containing porous carbon bead

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ABSTRACT

Nickel (Ni)-doped activated carbon beads (ACBs) with/without carbon nanofibers (CNFs) were synthesized for the efficient desulfurization of diesel oil by adsorption. The materials were characterized for their physico-chemical properties, using the BET, SEM, XRD, and TPD analysis. The in-situ dispersed Ni nanoparticles in the ACBs served the dual role of catalyzing the growth of the CNFs (average thickness c.a. 70 nm) across the ACB surface and the removal of S-containing compounds from the liquids. The adsorption capacity of Ni/ACBs (without CNF-containing adsorbents) was approximately 3.5 times higher than that of Ni-CNF/ACBs for the large sized dibenzothiophene molecules, because of the higher BET surface area and pore volume of the former adsorbent. On the contrary, the adsorption capacity of Ni-CNF/ACBs was higher than that of Ni/ACBs for the small sized thiophene molecules, despite the BET surface area and pore volume being smaller in the CNF-containing adsorbent, indicating that the π-complexion interactions were dominant over physisorption in the graphitic CNFs. The comparative adsorption data indicate that the adsorption capacities of the prepared Ni-containing adsorbents with/without CNFs in this study were greater than most of the adsorbents discussed in the literature. This study assumes significance from the perspective of selecting suitable adsorbents for the different sized-S-compounds in diesel oil.

1. Introduction

Diesel is one of the high energy density (42.5 MJ/kg) fuels commonly used in transportation vehicles, power generators, and industrial furnaces. During combustion of diesel, several air pollutants such as H_2S and SO_2 are emitted because of the

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decomposition of sulfur-containing aromatic compounds such as thiophene (TH), benzothiophene (BT), dibenzothiophene (DBT) and its alkyl-substituted derivatives. These compounds are inherently present in the fuel. The sulfur-containing compounds can also poison the catalyst of the catalytic converter in automobiles. Many countries have set strict regulations for the maximum amounts of sulfur in diesel. European standards organization has restricted the sulfur concentration below 10 ppm by weight (ppmw) in all fuels since 2009 [1]. In India, regulations have been set at 10 ppmw-sulfur in diesel oil from 2017 onwards [2].

Hydrodesulfurization (HDS) is commonly used for removing sulfur or sulfur-containing compounds from diesel by the catalytic hydrogenation. The method using Ni/Co/Mo-based catalysts requires relatively severe operating conditions (350–400 °C and 3–10 MPa hydrogen-pressure), and is considered to be effective for treating diesel containing sulfur over the 500–2000 ppmw-concentration range [1,3]. However, further reduction of sulfur in diesel by HDS may be ineffective, because the hydrogenation of aromatic hydrocarbons in the fuel is more reactive than that of the aromatic sulfur compounds [4]. In this context, adsorptive desulfurization (ADS) has gained much attention because of the required less severe operating conditions (<200 °C and 0.1–0.8 MPa) compared to conventional HDS processes. Furthermore, such processes do not alter the sulfur-free composition and physical properties of the fuel.

The ADS processes use different transition metals such as Cu, Ni, Ag, and Zn, which are dispersed in various inorganic supports, viz., molecular sieves, silica and activated alumina (AA). Transition metals have the capability to enhance the adsorption of sulfur compounds through π-complexation and/or metal-sulfur interaction [5]. Among the transition metals, Ni has attracted much attention for the ADS of diesel oils, with the adsorption capacity of the Ni-based adsorbents determined to be 0.2–16 mg-S/g over the sulfur concentration range of 14–700 ppmw and temperature range of 25–220 °C [6–8]. In particular, Liao et al. [5] evaluated the desulfurization performance of different transition metals supported in AA at room temperature (~30 °C) and found the adsorption capacities for TH in the following order: Ag > Ni > Cu > Zn. Similar comparative studies also showed the relatively superior performance of Ni-based adsorbents [7,9].

Activated carbon (AC) is widely recognized as a versatile material having potential to act as an adsorbent, catalyst, and support to metal catalysts, attributed to its relatively large BET area, amenability for surface functionalization, and stability in acidic medium [10]. In the present context of desulfurization also, ACs have recently gained considerable attention [11–16]. Among the salient studies performed in this area, Xiao et al. [11] investigated the comparative effects of AC and Na^+/Y zeolite (without metal) for the removal of BT and DBT from *n*-octane at 30 °C. The ACs showed relatively higher adsorption capacity for both sulfur compounds, attributed to the relatively larger pore size of the adsorbent *vis a vis* the molecular size of the solutes, and a strong interaction between carbon and the BT and DBT molecules. Muzic et al. [12] investigated the performance of AC and zeolite for the ADS of commercial diesel at different temperatures ranging from 30 to 70 °C. The adsorption capacity of AC was determined to be approximately three times higher than that of zeolite. Hernandez and co-worker [13] compared the performances of the Ni-dispersed AA-SiO_2 composite with that of AC with and without Ni for the ADS of different model oils containing BT, DBT and 4,6-DMDBT. Interestingly, the data showed that the adsorption capacity of AC without Ni was higher than that of all AA-SiO_2-supported Ni materials synthesized in the study. The inclusion of Ni into AC showed even higher adsorption capacity. Similar results have been reported for the ADS of commercial as well as synthetic diesel containing DBT and DMDBT [14–16]. The adsorption capacity of AC was found to be higher than that of the metal-dispersed SiO_2/AA/zeolite/molecular sieves.

From the overview of the aforesaid studies, it is evident that Ni dispersed-carbons are potentially efficient materials for the ADS of diesel. Extending along the theme of those studies, this paper describes the development of the Ni-containing spherical activated carbon beads (~0.8 mm) having different textural properties for the ADS of diesel. The transition metal-dispersed porous carbon beads have been found to exhibit significantly large adsorption capacity for a number of pollutants in water, such as arsenic, fluoride, vitamin B-12, and Cr(VI) [17,18], and are the focus of the present study on desulfurization. Such materials (beads) can also be packed in a tubular adsorber and efficiently used under flow conditions without maldistribution or channeling of the liquid to be treated.

The present study investigates the ADS performance of the Ni/NiO-doped porous carbon beads decorated with/without carbon nanofibers (CNFs). The effects of textural properties (BET area, pore volume, pore size distribution (PSD), metal and graphitic contents) of the prepared materials on desulfurization are investigated using two different organosulfur compounds, namely, TH and DBT, which are different in molecular size. Several salient studies have been recently geared in this direction and are revisited in details later in the context of discussing the adsorption mechanism for desulfurization [19–24]. This study shows that suitable textural modifications to the adsorbent materials are required for the efficient desulfurization of diesel oil, depending upon the type of target compound to be removed.

2. Materials and methods

2.1. Chemicals

Phenol (>99.5%), formaldehyde (37–38%), hexamethylenetetramine (HMTA, 99%), triethylamine (TEA, 99%), polyvinyl alcohol (PVA) (MW = 95,000), nickel nitrate hexahydrate (>98%), and *n*-octane (>99%) were purchased from Merck Germany. The TH (99%) and DBT (98%) sulfur-containing compounds were purchased from Alfa Aesar and Spectrochem Pvt. Ltd. Mumbai, respectively. Commercial diesel (~115 ppmw-S) was purchased from a local market. All gases used in this study were zero grade and purchased from Sigma Gases India.

2.2. Synthesis and heat treatment of Ni-doped polymeric beads

The Ni-doped phenolic precursor-based polymeric beads were synthesized according to the procedure described in the previous study [17]. The in-situ Ni-doped polymeric beads were pre-oxidized by air (100 standard cubic centimeter per min (sccm)-flow rate) at 350 °C for 1 h in the horizontal stainless steel (SS) tubular reactor mounted in a tubular furnace. The temperature of the reactor was increased at a rate of 5 °C/min to 950 °C. The oxidized beads were carbonized under N_2 flow (100 sccm) for 1 h and then activated at the same temperature for another 1 h, using a mixture of N_2 (100 sccm) and steam (0.3–0.5 g per min). After activation, the furnace was allowed to cool to room temperature under N_2 flow. Next, the Ni-containing porous carbon beads were calcined at 450 °C for 4 h under 100 cc/min of N_2 flow to convert Ni-nitrate into NiO. Such samples were termed as NiO/ACB for the reference purposes in this study. The reduction of NiO into Ni^0 was carried out at 600 °C for 2 h, using H_2 as a reducing agent at 100 sccm-flowrate. These samples were termed as Ni/ACB. Next, CNFs were grown over Ni/ACBs, using CVD with acetylene gas (30 sccm) as the carbon source. The dispersed Ni^0 in the beads catalyzed the growth of the CNFs. The CVD was carried out at 600 °C