Carbon 95 (2015) 794–801

Contents lists available at ScienceDirect

Carbon

journal homepage: www.elsevier.com/locate/carbon

Iron oxide-functionalized carbon nanofilaments for hydrogen sulfide adsorption: The multiple roles of carbon

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ARTICLE INFO

Article history:
Received 29 April 2015
Received in revised form
29 August 2015
Accepted 31 August 2015
Available online 4 September 2015

ABSTRACT

Iron-functionalized carbon nanofilaments (Fe–CNF) have been tested as sorbents for low-temperature (T) gas desulfurization. This patent-pending material has a high hydrogen sulfide (H_2S)-removal capacity while allowing for low-H_2S breakthrough at the exit gas. CNF were produced by a patented ethanol dry reforming process, then acid-treated prior to Fe functionalization through a wet impregnation-calcination protocol. Desulfurization tests were performed with 35- to 95-mg samples and gas flow of 500 ppm H_2S in helium. To understand the desulfurization process, fresh and used Fe–CNF were analyzed thoroughly by X-ray absorption near-edge spectroscopy and X-ray photoelectron spectroscopy. The results show that carbon (C) has 2 important roles in this Fe–CNF sorbent: it acts both as sulfur adsorbent and nanometric support which disperses Fe efficiently in oxide form, enhancing the H_2S capture rate and efficiency. As well, iron oxide has 2 roles in the sorbent: at low T (100 °C), it acts as adsorption catalyst for H_2S-dissociative oxidation, and at higher T (300 °C), it reacts with H_2S to form iron sulfide. At the higher T tested, sulfidation occurred in parallel with C adsorption.

1. Introduction

Demand for desulfurization of gases at levels below 1 ppm for diverse applications, such as fuel cell feed or syngas in chemical synthesis, is a driving force behind the development of new sorbents [1,2]. There is a need for materials with high hydrogen sulfide (H_2S) capture capacity, low breakthrough concentrations, relatively low cost and optimized for a large range of operating conditions.

Metal oxides are generally employed at mid to high temperature (T) ranges (300–800 °C) [3,4]. The general equation (1) for this desulfurization shows the reaction of H_2S with metal oxide and metallic sulfide formation [4]:

$$MeO_x + xH_2S \leftrightarrow MeS_x + xH_2O \quad (1)$$

Various types of activated carbon (AC) are often used at low T: RT (room temperature) to 100 °C [5,6]. Adsorption is enhanced by caustic or oxidation treatment [7,8]. The reported prevailing mechanism includes dissociative adsorption and H_2S-derived species oxidation on the adsorbent's surface.

Carbon nanofilaments (CNF) are attractive as supports for sorbents and heterogeneous catalysts because of their morphological properties and surface chemistry [9,10]. In addition, they are good candidates because they are similar to the usual carbon (C)-based sorbents [11] and are characterized by significant advantages over AC: their small (nanometric) dimensions and high aspect ratio morphology contribute to the acceleration of low mass transfer rates usually encountered in highly-specific surface but complex internal pore structures such as AC. Thus, as opposed to AC, CNF have much larger specific external surfaces [12], which is why functionalized C and nanocarbon materials are being studied for general adsorption applications [13,14] and desulfurization applications [15–18]. In particular, Kovalenko et al. [13] obtained higher capacity for desulfurization of diethanolamine using carbon nanofilaments then activated carbons.

There are numerous methods for carbon nanofilaments metal functionalization, the most common being electrochemical deposition, chemical vapor deposition and impregnation [19–22].

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http://dx.doi.org/10.1016/j.carbon.2015.08.117
0008-6223/

Impregnation has the advantages of simplicity and large scale applicability [22].

The impregnation is generally preceded by a surface treatment, in order to incorporate oxygenated group which decrease the hydrophobicity of the carbon nanofilaments or carbon nanotubes [23].

Nitric oxide is often used for the pre-treatment step since it allows for an efficient oxidation of the carbon nanofilaments surface [24,25]. In addition, surface oxygen species as well as gas humidity are known for their role in H_2S adsorption. Chen et al. [17] tested Na_2CO_3-treated CNT to increase their alkalinity for oxidative adsorption of H_2S. They obtained sulfur (S) retention capacity at saturation up to 186 g H_2S/100 g sorbent, measured when outlet concentration reached 1000 ppm of entering gas. The presence of Na_2CO_3 provided the necessary alkalinity for H_2S dissociation.

In the present work, we propose the combination of C and metal oxide properties to develop a functional H_2S sorbent for a large range of T. CNF were chosen because of their low fabrication cost and their relatively large external surface area. They were oxidized by nitric acid before metal impregnation. More details about the preparation protocol of this new iron (Fe)–C material for H_2S adsorption have been presented in Ref. [26]. Differences were seen in metal dispersion as function of 2 nitric acid treatment protocols, but adsorption capacities proved to be similar with both preparation methods. The objective of our work is to understand the adsorption mechanism as function of operating T, including the important roles of C in adsorption.

Different species before and after adsorption were analyzed by X-ray adsorption near-edge spectroscopy (XANES) and X-ray photoelectron spectroscopy (XPS) in H_2S adsorption experiments. XPS identified C and S species, and XANES assessed Fe oxidation state, complementing S analysis.

2. Experimental

2.1. Preparation of metal-functionalized CNF

CNF were produced according to a patented [27] ethanol/CO_2 dry reforming reaction-based process, with a near-zero internal porosity (2D) surface-oxidized steel catalyst. CNF production was done in a tubular quartz reactor of 10 cm diameter placed in a tubular oven. Eight rectangular sheets of catalyst (25 mm × 20 cm, 0.79 mm width) were pretreated over industrial argon (Ar) blanket gas containing 1% air for 90 min at 800 °C in the reactor. Oven T was decreased to 570 °C for the CNF production step. The flow rate of reactants at operating conditions was 2800 ml/min with a 1.4 M ratio of CH_3CH_2OH/CO_2. About 50 g of CNF were produced and collected over a 9 h run. More details on the CNF production and characterization methods have been presented previously [28].

CNF were functionalized using a 2-steps optimized methodology: 1) acid treatment and 2) metal addition by wet impregnation. For acid treatment, CNF were suspended in 10 M nitric acid aqueous solution for 5 h, at a ratio of 1 g CNF in 20 ml of nitric acid solution, at RT. At the end of acid treatment, the CNF suspensions were filtered, washed to neutral pH and dried overnight at 105 °C. Metal was added by wet impregnation with $Fe(NO_3)_3 \cdot 9H_2O$ solution (98.0–101.0% from Alfa Aesar) in distilled water. The nitrate mass was measured to obtain 20% w/w of metal loading in the final Fe–CNF product as H_2S sorbent. The nitrates were dissolved in sufficient water to allow good suspension (low agglomeration) of CNF, which was found to be 20 ml of solution per g of CNF. The suspension was stirred at room T for 1 h and heated afterwards under the same stirring conditions until complete water evaporation. The Fe–CNF so-obtained were, then dried overnight at 105 °C.

2.2. H_2S adsorption coupled with XANES

2.2.1. H_2S adsorption

4 mg of Fe–CNF were mixed with boron nitride and pelletized in a 6-shooter sample holder placed inside a quartz tube with 2 Kapton windows. First, they were oven heated in the set-up under Ar at 350 °C, and cooled to RT. H_2S adsorption followed, with a mixture of 500 ppm in helium (He), and gas hourly space velocity (GHSV) around 50,000 $ml_{gas}/h/g_{Fe\text{-}CNF}$, at 300 °C, for 2 h. After the adsorption step, the samples were quenched to RT under He for XANES.

2.2.2. XANES

XANES spectra of the Fe K-edge and S K-edge were acquired via Soft X-ray Microcharacterization Beamline from Canadian Light Source Inc. (http://www.lightsource.ca/). First, after H_2S adsorption in the set-up and without contact with air, Fe spectra of the material were acquired in transmission mode. Next, the samples were transferred to an inert environment to minimize oxidation for fluorescence measurements of S K-edge spectra.

2.3. H_2S adsorption coupled with XPS

2.3.1. H_2S adsorption

H_2S adsorption was performed in a Chemisorb 2750 unit from Micromeritics. The samples were placed on quartz wool, in a quartz tube of 1 cm diameter. 35- to 95-mg Fe–CNF samples were tested in a 2–3 mm high bed. H_2S exit concentrations were monitored by GasAlertQuattro gas detector (from BW Gas Monitors) equipped with an electrochemical sensor possessing 0.1 ppm resolution and 0–200 ppm range of detection. The detector was coupled with the Chemisorb unit at the exit.

Fe–CNF were first calcined in inert atmosphere, with Ar flow of 30 ml/min at 350 °C for 30 min at a 5 °C/min increasing ramp rate, and subsequently cooled to RT. After the calcination step, the samples were heated under He flow to the desired T. H_2S adsorption followed, with a mixture of 500 ppm in He and gas flow rate of 30 ml/min. GHSV varied with the different masses used, from 25,000 to 95,000 $ml_{gas}/h/g_{Fe\text{-}CNF}$, at operating conditions. Two different Ts were tested: 100 °C and 300 °C. The samples were quenched to RT in inert atmosphere.

The experiments were stopped at different exit concentrations with corresponding time on stream (TOS), to collect samples for XPS and follow the evolution of captured S species with time. Different TOS with 0 ppm exit concentrations in tests at 300 °C were compared with those performed at 100 °C which showed lower H_2S capture capacity. Table 1 lists these experiments. It can be seen that samples "1" and "7" have similar TOS, with different exit concentrations due to differences in operating conditions. Adsorption capacities were calculated by integrating the breakthrough curves, and normalized the mass of S per mass of functionalized CNF. The adsorption capacity ratio was calculated from mass after calcination. Since the adsorption tests were usually conducted directly after the calcination step, mass was estimated in a series of calcination tests. With the adsorbent labeled as containing 20% w/w Fe (20Fe–CNF), 13% loss was confirmed by calculation based on the nitrates added.

2.3.2. XPS

The samples were transferred and prepared for analysis in Ar atmosphere, in a glove box, to minimize oxidation by exposure to air. XPS was undertaken in an Axis Ultra DLD from Kratos Analytical Equipment with Al Kα monochromatic X-ray source at 225W. The Kratos charge neutralizer system was used on all specimens, and the charging effect was corrected with the binding energy (BE) of