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Fast carbon nanofiber growth on the surface of activated carbon by microwave irradiation: A modified nano-adsorbent for deep desulfurization of liquid fuels

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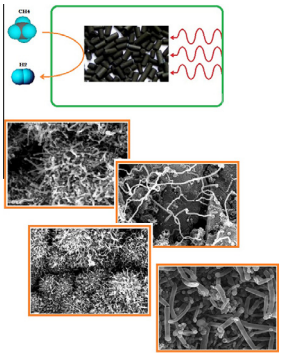
HIGHLIGHTS

- Fast growth of carbon nanofibers on the surface of activated carbon was performed.
- Microwave assisted chemical vapor deposition was successfully implemented.
- Methane and ethane were studied as carbon sources, comparatively.
- Efficient performance of the material was observed in desulfurization liquid fuel.
- Modified AC showed 87% higher efficiency in sulfur removal rather than regular AC.

GRAPHICAL ABSTRACT

Synthesis of carbon fibers was carried out by chemical vapor deposition of methane and ethane on the surface of activated carbon. Methane/ethane decomposed by microwave radiation and the carbon fibers were grown faster in presence of Ni catalyst. Those fibers made from ethane were thicker than the others made by methane.



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ABSTRACT

Carbon nanofibers were fabricated on the surface of regular activated carbon (AC) by microwave-assisted chemical vapor deposition (CVD) method. Methane and ethane were comparatively used as the source gases to figure out the textural and particulate properties and efficiency of the produced nano-adsorbents in sulfur adsorption from a fuel model. AC granules were firstly impregnated with nickel and exposed to a flow of hydrocarbon–nitrogen mixture through a stationary bed. A 900 W household microwave apparatus was used as the energy source to decompose the hydrocarbon and grow up nanofibers on the surface. Effect of catalyst fraction, radiation time and inlet gas flow rate were studied as the influential synthesis parameters. The 0.5 wt% Ni-impregnated AC was exposed to equal mole fraction of N_2–hydrocarbon mixture with WHSV of 6.7 ml/g min and the result revealed the highest yield of nanofibers growth on the surface. The diameter of nanofibers made from ethane was almost twofold over the diameter of nanofibers made from methane. Thiophene and dibenzothiophene removal were comparatively investigated by a series of batch adsorption experiments with a model fuel comprising *n*-octane. The sulfur removal efficiency was improved up to 87% compared with the original AC. During two hours contact time, the sulfur content of solution was decreased from 290 to 45 ppm by the modified AC surface.

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1. Introduction

Nowadays regarding to the emergency situation of highly polluted environment tough regulations are demanded to lower sulphur content as a perilous component in hydrocarbon fuels. A 15 parts per million (ppm) sulphur specification, known as Ultra Low Sulphur Diesel (ULSD), was phased in for highway diesel fuel from 2006 to 2010 by united state environmental protection agency [1]. Also Environment Protection Agency (EPA) allows refiners to produce gasoline with a range of sulfur levels as long as their annual corporate average does not exceed 30 parts per million (ppm) [2]. As it is the main concern in recent decade, different methods like hydrodesulfurization [3,4], oxidative desulfurization [5,6], biodesulfurization [7,8], adsorption [9–11] and etc. [12] have attracted more attention to approach deep desulfurization of fuels.

Among all above-mentioned strategies, adsorption is a promising trend with regard to its safe operational process, less side effects on the fuel properties, less expensive facilities and lower operational costs to approach deep desulfurization condition. Adsorption techniques are highly dependent on the properties of adsorbents. Recently, new carbonic materials are fabricated and suggested for deep desulfurization process [13].

Carbon fibers and nanofibers are the carbonic materials with high porosity and high specific surface area, which can be used as appropriate materials for the adsorption of sulfur-containing compounds such as multi-ring thiophenic families [14].

AC is by far one of the most common types of adsorbent which is frequently used for the adsorption of organic materials; however surface improvement of the ACs may increase the specific surface area and consequently sulfur adsorption capacity. Physical and chemical methods are implemented for the modification and improvement of ACs surface properties [15–17,18]. However chemical treatments of AC confront environmental restrictions and consume chemical materials.

Among various methods which have been proposed for the synthesis of carbon nanofibers [19–21], chemical vapor deposition is still the dominant method for the production of large amounts of nanofibers [22,23]. Decomposition of a hydrocarbon at high temperature can cause the nanofibers grow and extend the surface area on a stationary carbonic basis. Using AC substrate for growing nanofibers prevents agglomeration of the fibers due to the porous structure of the substrate. Vapor deposition can be implemented with either thermal or catalytic cracking process; however catalytic vapor deposition can be more appropriately controlled than the thermal deposition for the faster and more controllable growth of fibers [24].

Using microwave is a fast, easy and energy-efficient approach, which provides significant amounts of energy and high temperatures within a few seconds. Many studies have been performed on the fabrication of carbon fibers under microwave irradiation [25,26]. Zou et al. [25] have prepared vapor grown carbon fibers without any catalyst by microwave pyrolysis. Xieet al. [27] made an attempt to synthesize coiled carbon fibers using acetylene as the carbon source at 700 °C by microwave technique. They had used silicon carbide as substrate due to its affinity to absorb microwaves which was firstly seeded with Ni catalyst. The microwave system was composed of a switching power supply, which derived a 3 kW magnetron.

In this work, formation of carbon nanofibers upon the surface of regular AC is proposed to modify AC morphology and enhance its adsorptive capacity. This task is implemented using methane and/or ethane as the feed source by taking advantage of the fast microwave irradiation technique. In addition, the application of the modified AC is investigated for deep desulfurization of liquid fuels.

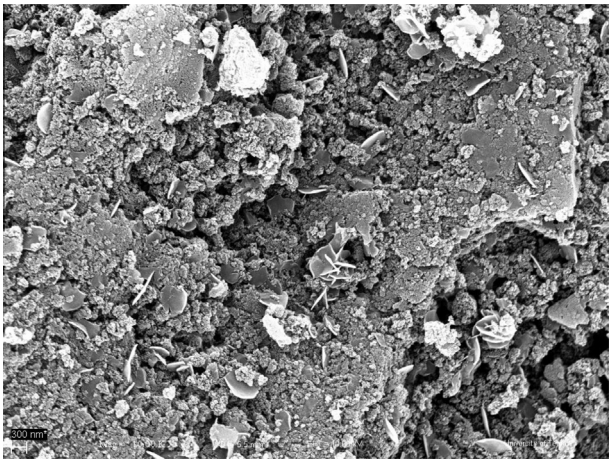

Fig. 1. SEM image of the raw AC substrate (magnification 10,000).

2. Experimental

In this study commercial activated carbon granules were purchased from Norit Company. The SEM image of the surface is observed in Fig. 1. Nitric acid solution (65 wt% pure) and Ni $(NO_3)_2$·$6H_2O$ powder were purchased from Merck Co. Acetone (99.8 wt%) and distilled water were prepared from domestic companies. Solutions with different concentrations of 0.01 wt%, 0.5 wt%, 1 wt% and 1.5 wt% of Ni $(NO_3)_2$·$6H_2O$ in acetone were prepared for different impregnation tests. Methane (99.9%) and ethane (99.9%) were used as carbon source gases and nitrogen (99.99%) as the carrier gas. For the sulfur adsorption tests, the fuel model solutions were prepared from two kinds of sulfur-containing compounds; thiophene and dibenzothiophene in *n*-octane (99%) solution.

The set up was a U-tube shape reactor made of quartz with internal diameter of one centimeter, which was placed inside a household microwave apparatus. Two separate gas inflow lines were equipped with mass flow controllers; one for the carbon source gas and another for the inert gas, nitrogen. Two kinds of activated carbon were prepared as the support for fiber growth; AC with Ni catalyst and AC free catalyst. AC granules were placed inside the tube and installed in the microwave. An infrared thermometer with precision of 1 °C was used for sensing the temperature of the reactor surface at the end of each experiment. The process of chemical vapor deposition was assisted by a household microwave with 900 W power supply in the described set up as shown in Fig. 2.

The process of nanofiber growth was consisted from three steps. Firstly pretreatment of ACs was carried out by washing with nitric acid (65 wt%), and drying at 105 °C. Secondly impregnation with Ni catalyst was performed using Ni $(NO_3)_2$ solution by ultrasonic bath (only for the catalytic samples). Finally the reaction was implemented by heating the samples inside the U-tube quartz reactor in the microwave oven accompanied with hydrocarbon–nitrogen flowing through the bed.

2.1. Synthesis parameters

Methane and ethane were used as the hydrocarbon sources separately to find out the yield, quality and morphology of the synthesized nanofibers. The fibers were grown on two different pretreated surfaces; AC free catalyst and AC impregnated with Ni catalyst. In each experiment 1.5 g of the AC was used for CVD process. Good results were obtained after different trials in order to have a homogenous microwave irradiation over the entire filled