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Carbon nanofibers grown on metallic filters as novel catalytic materials

P. Tribolet, L. Kiwi-Minsker *

Ecole Polytechnique Fédérale de Lausanne (EPFL), LGRC, CH-1015 Lausanne, Switzerland

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Abstract

Carbon nanofibers (CNF) were synthesized on sintered metal fibers (SMF) filters of nickel and Ni-containing alloys (Inconel, stainless steel (SS)) by thermal chemical vapor deposition of ethane in the presence of hydrogen at ~660 °C. The CNFs were formed directly over the SMF filters without deposition of metal particles. The catalytic active sites leading to the CNF formation were attained by oxidation–reduction of the SMF filter. The CNFs present platelet morphology as determined by X-ray diffraction and transmission electron microscopy. The CNF/SMF composites have thin carbon layer in the microns range strongly anchored to the metal surface. The initial open structure of SMF filters is preserved. Scanning electron microscopy together with temperature programmed oxidation suggests the formation of uniform CNFs deposits on $\mathrm{SMF_{Inconel}}$ with fiber's diameters in the range of 70 nm. Carbon deposits with a different nature were observed over $\mathrm{SMF_{Ni}}$ and $\mathrm{SMF_{ss}}$.

The CNF/$\mathrm{SMF_{Inconel}}$ composites have high specific surface area due to mesopores of CNFs, high thermo-conductivity and open 3D macrostructure. This is advantageous for catalytic applications, especially during the catalysis of highly exo/endothermic reactions in reactors with structured catalytic bed.

Keywords: Carbon nanofibers; Sintered metal fiber filters; Carbon/metal composites; Structured catalyst

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1. Introduction

Carbon nanofibers (CNF) are novel carbon compounds, which have unique mechanical, electronic, chemical and physical properties [1–3]. They are also used as catalyst and catalytic supports [4,5]. Compared to activated carbons, CNFs offer high specific surface area due to meso-pores without micro-porosity, thus preventing internal diffusion limitations. In addition, their graphitic structure leads to specific metal–support interactions, which improves the catalytic activity/selectivity. Thus, CNF supports have been reported to induce an increase in the catalytic performance of nickel nanoparticles during hydrogenations of 1-butene, 1,3-butadiene [6] and crotonaldehyde [7]. Other reports have shown advantageous properties of CNFs catalytic supports [8–10].

The CNF synthesis involves supporting of metallic (Ni, Fe, or alloys) particles on oxides or other materials for carbonization of gaseous precursor by catalytic pyrolysis (thermal CVD synthesis). Due to the reaction of active metallic particle with precursor gases, several vapor-grown CNFs were obtained with different crystalline orientation. The majority of the synthesis requires considerable post-processing involving further CNFs purification with final product in the form of fine powders. For several applications like electrode materials, absorbent media for filtration, and catalytic materials, the CNFs have to be reattached on the support with suitable macro-structure. To avoid this operation, one approach is the CNFs synthesis directly on the support material. Vieira et al. proposed to grow CNFs on graphite felt [11]. Other groups have synthesized nano-carbons directly on monoliths [12,13], carbon blacks [14] and on a large area of sodalime glass by CVD synthesis of acetylene [15]. But achieving stable anchoring and uniformity of CNFs still remains a challenge, especially on metallic surfaces.

In this work, we propose the use of sintered metal fibers (SMF) filters as catalysts and supports for the growth of CNFs. Sintered metal fibers filters have uniform micron size filaments sintered into a homogeneous 3D structure. They are characterized by porosity up to 80–90%, large

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* Corresponding author. Tel.: +41 21 693 3182; fax: +41 21 693 3190.
E-mail address: lioubov.kiwi-minsker@epfl.ch (L. Kiwi-Minsker).

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permeability and excellent filtrating properties with a low pressure drop through the bed during reactor operation. Fibers made of special alloys (stainless steel, Inconel, Fecralloy) exhibit high mechanical strength, chemical and thermal stability. High thermal conductivity of the metal fiber matrix provides a radial heat transfer coefficient two-fold higher compared to randomly packed catalytic beds [16]. This results in nearly isothermal conditions when used as catalytic materials for highly exo/endothermic reactions. This fibrous matrix acts also as a static micromixer avoiding channeling.

This study addresses the effect of the SMFs composition and the necessary pre-treatment/activation steps for CNF growth directly from the support surface. The gas's concentrations, temperature and time of the CVD synthesis were also studied regarding the CNF morphology, graphitic structure, density and uniformity of metal surface coating by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction and temperature programmed oxidation (TPO) methods.

2. Experimental

2.1. Materials

Three types of commercially available sintered metal fiber filters were used as catalysts and catalyst supports during this study:

- Stainless steel (SS), sintered AISI 316L (composition: Cr: 16.5%; Ni: 12%; Mo: 2.5%; Mn: 2%; Si: 1%; P: 0.05%; S: 0.03%; C: 0.03%; Fe: balance), 32 μm fiber diameter, 0.3 mm thickness (Southwest Screens & Filters, Belgium)
- Inconel 601, Bekipor ST20AL3 (composition: Ni: 60.5%; Cr: 23%; Al: 1.25% Cu: 1%; Mn: 1%; Si: 0.5%; C: 0.1%; S: 0.015%; Fe: balance), 8 μm fiber diameter, 0.49 mm thickness (Bekaert Fibre Technology, Belgium)
- Nickel; 12 μm fiber diameter, 0.1 mm thickness (Bekaert Fibre Technology, Belgium)

The filters were used as received. The Ar, H_2, C_2H_6, N_2 were >99.995% purity (supplied by Carbagas, Switzerland) and used as received. Nickel nitrate ($Ni(NO_3)_2 \cdot 6H_2O$, p.a.), methanol and ethanol (both p.a.) were purchased from Fluka, Switzerland. Water was distilled before the use.

2.2. Growth of carbon nanofibers

Carbon nanofibers were grown on SMF filters by catalytic pyrolysis (chemical vapor deposition, CVD) of ethane in the presence of hydrogen. The synthesis was carried out in a tubular quartz reactor with 24 mm internal diameter posed in a tubular furnace. The SMF filters were cut in 24 mm diameter round slices and one piece was placed perpendicularly to the flow of reagents, at about two-third of the reactor length, ensuring a thermal equilibrium of the gases. The synthesis temperature was monitored by a thermocouple inserted into the reactor within a quartz pipe in contact with the surface of the SMF filter.

All SMF filters were first oxidized in air: SMF_{Ni}, at 550 °C for 1 h; SMF_{SS} filter, at 550 °C for 3 h; and $SMF_{Inconel}$, at 650 °C for 3 h.

Ni° nano-particles were deposed in some cases on SMF filters by impregnation. The filters were dipped in an aqueous solution of nickel nitrate for 5 min, dried in air during 1 h and subsequently in oven at 125 °C for 1 h. The concentration of the Ni-solution was calculated based on the SMF wetness capacity of ~23% to attain Ni° concentration on the SMF filters between 0.2 and 7 wt.%.

Before the synthesis of the CNF, the SMF filters were reduced in hydrogen (120 ml (STP)/min). The temperature was increased 10 °C/min and held at 600 °C for 2 h. Then, the reactor was heated up to the synthesis temperature between 630 and 705 °C, and the CVD mixture was introduced. Standard CNF synthesis mixtures of $C_2H_6:H_2 = 15:85$ (flow 120 ml (STP)/min), or of $Ar:C_2H_6:H_2 = 80:3:17$ (flow 600 ml (STP)/min) were used. The synthesis time was varied between 15 min and 4 h. A flow of H_2 (120 ml (STP)/min) was used after processing to prevent the CNF oxidation during the cool down. Reactor pressure was kept at 1.25 bar during the whole process. The carbon yield is defined as the mass of carbon formed on the SMF filter divided by the mass of metal support.

2.3. Characterization of CNF/SMF composite materials

The attrition resistance of the carbon nanofibers over filter material was tested using an ultrasonic bath (Bransonic ultrasonic cleaner, HF-output power nom. 30 W, Branson Ultrasonics Corp., USA). The standard procedure after the CNF synthesis was to treat the resulting CNF/SMF composite by ultrasound in methanol during 5 min. All other characterizations were carried out after this step.

The specific surface areas (SSA) of the carbon based composites were measured using N_2 adsorption–desorption at 77 K by a Sorptomatic 1990 instrument (Carlo Erba). Pieces of 100 mg (stainless steel and inconel based composites) or 50 mg (nickel based composite) were cut into 3 mm × 3 mm slices and placed in the reactor for measurement. The SSA was calculated employing the BET method. To estimate the SSA of CNF synthesized, the SSA of SMF filters was neglected. The BET surface measured for the composite was attributed to the carbon calculated from difference between the mass of the SMF filter and the mass of the resulting CNF/SMF composite. The Dollimore/Heal approach was applied to calculate the pore volume and the pore's size.

The surface morphology of the samples was investigated by scanning electron microscopy, using a JSM-6300F, JEOL. The thickness of the CNF layer on the metallic fibers was estimated by subtraction of the metallic fiber diameter from the CNF/fiber diameter measured on the SEM image.