Effect of catalyst and substrate on growth characteristics of carbon nanofiber onto honeycomb monolith

Soraya Hosseini [a], Suraya Abdul Rashid [b], Ali Abbasi [c], Farahnaz Eghbali Babadi [b], Luqman Chuah Abdullah [a], Thomas S.Y. Choong [a,*]

[a] Department of Chemical and Environmental Engineering, Universiti Putra Malaysia, 43400 Selangor, Malaysia
[b] Materials Processing and Technology Laboratory, Institute of Advanced Technology, Universiti Putra Malaysia, 43400 Serdang, Selangor, Malaysia
[c] Faculty of Chemical Engineering, Universiti Teknologi Malaysia, Skudai 81310, Johor, Malaysia

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ABSTRACT

Carbon nanofiber coated monolith with a homogeneous and consistent layer was prepared by catalytic decomposition of benzene on iron catalyst. A comparative study was carried out on carbon nanofiber growth onto bare monolith, acid modified monolith and wash-coat alumina monolith. The catalyst was prepared by dip-coating the monolith into an iron-salt solution with different concentrations (0.1–0.3 g/mL), dried, and calcined at 500 °C. It was found that the concentration of catalyst controlled Fe particles dispersion, which in turn was responsible for the catalytic activity. Lower iron concentration loaded monolith showed higher bulk density of nanofibers growth compared with higher concentration of iron solution used. The results demonstrated that after treatment with nitric acid, the surface area of cordierite monoliths could be increased to values as high as 30.6 m^2/g. Intertwined bundles of carbon nanofibers grown by this pre-treatment formed of a wide range of diameter sizes with tree like morphology. In addition, wash-coat materials such as alumina, utilized to increase the specific surface area and to distribute the catalyst on the surface of the monolith. The deposition of alumina wash-coat layer caused the iron (Fe) to appear more homogeneously distributed after drying and calcination, indicating Fe-0.2–Al_2O_3/monolith to be a superior support to grow CNFs compared to other substrates.

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1. Introduction

Carbon nanofibres (CNFs) are extensively applied in numerous industries due to their fascinating characteristics such as: high strength and tensile modulus, high chemical stability in acidic and basic media, high thermal and electrical conductivity, low density, high corrosion resistance, and excellent creep resistance [1,2]. CNFs form aggregates with high surface areas, high mesopore volumes and low tortuosity. These fibers are promising materials for liquid phase reactions due to their mesoporous structure without microporosity, resulting in the lack of mass transfer limitations [3].

The wider use of CNFs in powder form is hampered due to some drawbacks including high-pressure drop, plugging and flow mal-distribution for fixed bed operation as well as agglomeration and difficulty in filtration because of fines formation for slurry operation [4–6]. To circumvent these drawbacks, CNFs' growth on macro-structured supports has been suggested. The synthesis of the nanofibers directly on such substrates can efficiently improve their

performance in a variety of applications, especially as catalyst supports, by increasing the surface area. The role of the support is not only to disperse catalysts' active phase, but also more importantly to prevent metal nanoparticles from aggregation into larger clusters. Spreading the metal phase on a support results in the formation of small crystallite sizes on the surface which is desirable for CNF growth [7]. The growth of CNFs on metallic filters, foams, silica gel beads, carbon felts and ceramic supports has been reported. Recently monolithic materials have attracted a good deal of attention due to their applications in a wide variety of processes.

In separation and purification applications, monolith is preferred since a single-piece permeable mass can separate species better than a cluster of packed particles [8,9]. The application of a catalyst in the form of a honeycomb structure with a system combining liquid, gas and solid phases is known to decrease the mass transfer limitations between the phases due to the hydraulic regime developed inside the capillary channels of the monolith [10,11]. Despite the advantages of monolithic cordierite such as high void fraction, uniform flow distribution, large geometric surface area, low pressure drop and thermal shock resistance, the use of cordierite as a catalyst support is limited due to the fact that this material has a low specific surface area

(0.02–0.5 m^2/g) and weak metal–support interactions [12]. Therefore, two different treatments including wash coating [13] and acid modification [14] have been developed to increase the specific surface area.

According to the literature, CNFs can be synthesized directly on monolith as substrate either by adding a catalyst such as ferrocene in the feed or by impregnation of metal (Fe, Ni, Co) over alumina through wash coating [15,16]. Jarrah et al. reported the synthesis of CNF coated monolith by using CH$_4$ as carbon source and Ni deposited thick alumina layer (8–17 μm) as catalyst and used the samples for enzyme immobilization [17]. Furthermore, uniform layers of carbon nanofibres appeared on Ni catalyst on alumina wash-coated monoliths *via* thermocatalytic decomposition of C$_2$H$_6$:H$_2$ by Garcıa-Bordeje et al. [18]. Afterward, they extended their work by changing the growth conditions such as the reaction temperature, the thickness of the alumina wash-coated layer and the type of carbon source [19]. They concluded that the growth conditions and the properties of the catalyst are the parameters affecting the properties of synthesized CNF–monolith composite. Ulla et al. deposited a zeolitic layer onto cordierite monolith in order to have the sufficient number of cationic exchange sites to anchor cobalt as an active catalyst metal. By using the prepared surface for CNF formation and acetylene as carbon source, carbon nanofibers grew over the cordierite monolith [20]. The effect of oxidation treatment of CNF-coated monolith was studied by Armenise et al. [21]. The treatment with concentrated acid (HNO$_3$ and H$_2$O$_2$) created oxygen functionalities on the fibers. The growth of CNFs on monolithic structure using Ni–Cu alloy as catalyst and C$_2$H$_4$ as carbon source has also been reported by Yan-Li et al. [22]. They concluded that the addition of Cu to Ni can inhibit the over-growth of metal particles in order to improve the growth rate of CNTs at high temperatures.

The aim of the present work is to study the effect of various monolith substrates for growing CNFs and to compare the growth yield and morphology of the obtained fibers. Here, we studied the initial catalyst deposition, CNF formation and its growth. Carbon nanofibers (CNFs) were grown over structured substrate consisting of honeycomb ceramic monoliths by catalytic chemical vapor deposition (CVD). The CNFs' synthesis mechanism involved the decomposition of benzene/H$_2$ as carbon source and use of various metallic surfaces as catalyst. Iron was selected as catalyst layer and was coated on different pre-treated surfaces. The catalyst layer was prepared by dip-coating of the monolith into an iron-salt solution with different concentrations (0.1–0.3 g/mL). Iron was coated over three various types of monoliths including unmodified, acid modified, and alumina wash-coated and then, the coated substrates were subjected to benzene/H$_2$ as carbon source to grow carbon nanofibers. Moreover, the effect of three various temperatures of 700, 800 and 900 °C on CNT growth and morphology was studied.

2. Chemicals and materials

Cordierite monoliths (2Al$_2$O$_3$•5SiO$_2$ 2MgO) with cell density of 400 cells per square inch and the size of 25(L) × 20(D) mm^2 were cut from a commercial sample (100 mm length) supplied by Beihai Haihuang Chemical Packing Co. Ltd., China, and used as substrate. The physical specification of monolith is summarized in Table 1. KOH, Fe(NO$_3$)$_3$•9H$_2$O, Al$_2$(SO$_4$)$_3$•16H$_2$O, sodium dodecyl sulfate (SDS) and benzene were obtained from Sigma-Aldrich, Malaysia. Purified gases of Ar (99.99%) and H$_2$ (99.99%) were supplied by The Linde AG Company.

2.1. Catalyst preparation

Three various catalyst-coated substrates were prepared to grow carbon nanofibers. In the first method, three various concentrations

Table 1
The specification of bare monolith.

Specification of monolith	
Monolith	
Cross-section	Circular
Diameter	2.50 ± 0.02 mm
Length	2.50 ± 0.02 mm
Surface area	1 cm^2/g
Cells	
Channel	Square
Cells	400 (cpsi)
Width	1.02 ± 0.02 mm
Wall thickness	0.25 ± 0.02 mm
Chemical compositions	
SiO$_2$	50.9 ± 1.0%
Al$_2$O$_3$	35.2 ± 1.0%
MgO	13.9 ± 0.5%
Others	<1%

of 0.1, 0.2, and 0.3 g/mL of iron solution were used to coat the unmodified monolith in order to study the effect of catalyst concentration. The iron deposited on monolith substrates acts as the catalyst for CNF growth. To increase the surface area, the monolith was pre-treated using 2 M HNO$_3$ solution in the second procedure before being coated with iron solution. In the third procedure, the monolith substrates were wash-coated with an alumina solution and afterwards impregnated with iron solution.

2.1.1. Coating over bare monolith

10 g Fe(NO$_3$)$_3$•9H$_2$O was mixed with 0.2 g sodium dodecyl sulfate (SDS) and 100 mL distilled water under agitation for 30 min. The bare monolith was soaked into the solution and heated at 100 °C for 6 h. Afterward, to avoid channel blockage or iron agglomeration, the excess solution trapped inside the monolith channels was purged using pressurized air. The orange colored monolith was then soaked in 1 M, KOH solution for 4 h in order to convert iron ions to Fe(OH)$_3$ according to the given equation.

$$Fe(NO_3) + 3NaOH \rightarrow Fe(OH)_3 + 3NaNO_3$$

The brown colored monolith was washed several times with distilled water to remove excessive basic solution. Initially, the monolith was dried at room temperature. During the slow drying at ambient temperature, the humidity gradient along the channels' lengths was lower and the formed particles were more homogeneously distributed. The iron-coated monolith was then dried in an oven at 110 °C for 24 h. Consequently, the monoliths were calcined under air atmosphere at the temperature up to 500 °C for 2 h with heating rate of 10 °C/min. Three iron solution concentrations of 0.1, 0.2 and 0.3 g/mL were individually used in the coating procedure of the catalyst on the monolith surface. The samples were labeled as Fe-0.1/monolith, Fe-0.2/monolith and Fe-0.3/monolith. The iron loading was determined by weighting monolith and was about 1.5, 2.8 and 4 wt% of the bare monolith for 0.1, 0.2 and 0.3 g/mL solutions, respectively.

2.1.2. Coating over acid modified monolith

The bare monolith was first modified through soaking in 2 M, HNO$_3$ (250 mL) solution for 24 h on a shaker at 30 °C. The treated monolith was then rinsed with distilled water until acquiring neutral pH. 0.3 wt% weight loss was reported by weighting modified monolith after acid treatment. The acid modified monolith was then dried at 110 °C for 24 h in an oven. Afterward, 20 g Fe(NO$_3$)$_3$•9H$_2$O was mixed with 0.2 g sodium dodecyl sulfate (SDS) and 100 mL distilled water under shaking for 30 min and the acid modified monolith soaked into the iron solution (0.2 g/mL). The pervious procedure was repeated to obtain iron coated acid modified monolith. The sample was labeled as Fe-0.2/acid modified monolith.