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In situ CVD of carbon nanofibers in a microreactor

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ABSTRACT

An in situ CVD method was developed in order to grow CNFs on Ni/alumina and nickel thin film catalyst coated inside a closed channel fused silica microreactor. By directly flowing reactant gases over a catalytic coating inside the microchannels, a mechanically stable and porous CNF-alumina composite was formed with high surface area (160 m^2/g). Effects of growth time, growth temperature and H_2 addition during pretreatment and deposition steps on the composite thickness and nanofibers diameter were investigated. Hydrogen addition increases the deposition rate and helps in producing a mechanically stable support in the microchannel.

1. Introduction

Carbon nanofibers (CNFs) are graphite materials which can be used as nanostructured catalyst supports in gas and liquid phase applications [1]. They form aggregates that have high porosity (macroporous structure) with minimized tortuosity so that mass transfer rates will be maximized in the liquid phase [2]. CNFs can be catalytically grown over transition metal surfaces such as (alloys of) iron, cobalt, nickel, chromium, vanadium and molybdenum employing methane, carbon monoxide, synthesis gas (H_2/CO), ethylene and ethane as the carbon source in the temperature range of 700–1200 K [2,3]. Main difficulties of using powder CNFs are agglomeration and filtration in slurry phase operations and high pressure drops in fixed-bed reactors [4]. Therefore, it is important to immobilize CNFs to structured supports in order to have easy operation by avoiding agglomeration and filtration problems, provide effective contact with reactants and create functionalized sites on the support. Thin layers of CNFs were grown on structured supports such as ceramic monolith [5] and metal foams [6] with the aim of achieving a new catalyst support with excellent properties for applications in liquid phase.

Recently, there has been a great interest in microreactors with fast heat and mass transfer characteristics for applications in chemical synthesis [7], kinetic analysis [8] and catalyst development [9]. As-grown carbon nanostructures in a microreactor can allow significant increase of the surface-to-volume ratio and favor contact surface between reactants. Moreover, decreasing linear dimensions into nanoscopic regime can lead to significantly higher heat-transfer coefficients and improved mass transport enabling better control of chemical process parameters. Ago and co-workers [10] incorporated Pt-modified carbon nanotubes (CNTs) into a microreactor. By fixing nanotubes inside the microchannel, difficulty in dispersing nanotubes in solvent can be avoided, interaction between reactants and the catalyst becomes larger and no filtration of nanotubes is required after a chemical reaction. Popp and Schneider [11] demonstrated use of a monolithic porous carbon nanotube structure as a chemical reactor. This chip-sized nanostructured chemical reactor design exhibited dramatic increase in surface-to-volume ratio of 5×10^6 to 2×10^7 m^2m^3 and possibility of performing catalytically driven chemical reactions on sub-μm to nm scale.

Microstructured multiphase reactors with high surface area CNFs as catalytic coating on the walls can serve as a tool to develop and study selective routes in the production of chemicals. They offer complete control at the catalytically active sites, with enhanced activity and selectivity, and therewith enable a size reduction of the equipment as well as reduction in waste products. The fixation of CNFs on the walls of microreactors provides an additional increase in surface-to-volume ratio, while deposition of active metals on CNFs leads to a fully accessible catalytic surface and avoids need of filtration after chemical processing. Moreover, it is easier to deposit and stabilize small metal particles on the graphene edges in the surface of CNFs, instead of basal plane of graphene on the surface of CNTs. However there is no effective method to incorporate CNFs in a closed channel microreactor. Therefore, we have developed in situ CVD method to grow mechanically stable CNFs on Ni/alumina catalyst inside fused silica microreactor. This method provides a facile bottom up way to

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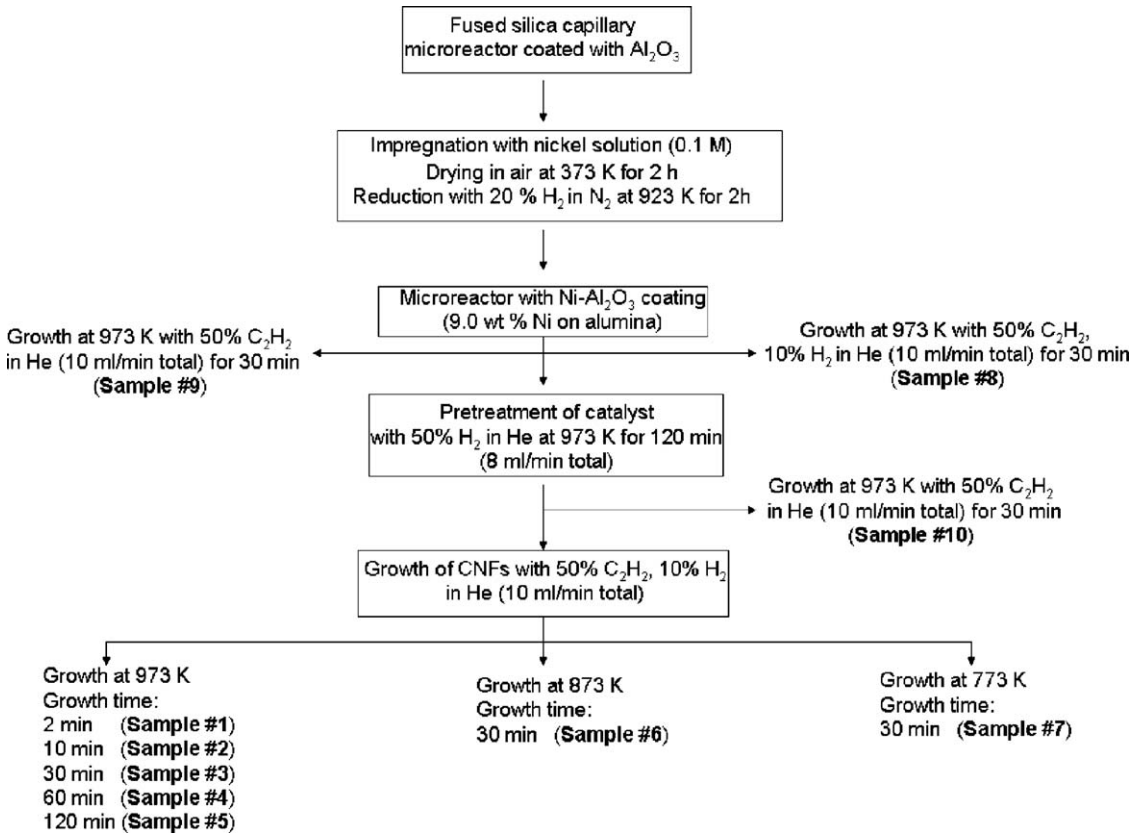

Fig. 1. Preparation scheme of samples.

increase surface-to-volume ratio of microreactors and good potential bringing high surface area nanoscopic catalyst support and catalyst itself into microreaction technology.

2. Experimental

Fig. 1 shows preparation scheme of samples. The microreactor is a commercial fused silica capillary (HP-porous-layer open-tubular Al_2O_3 column, "S" deactivated) with an inner diameter of 0.53 mm and coated with Al_2O_3. Microchannel was flushed continuously for 1 h with distilled water to dissolve the deactivating agent (Na_2SO_4), free liquid was removed and the samples were dried at 373 K for 1 h, followed by heating in flowing air (5 K/min) at 923 K to remove polyimide coating outside the capillary. Nickel was deposited on the alumina coating by adsorption from a pH-neutral nickel solution (0.1 M). The solution containing 29 g of $Ni(NO_3)_2{\cdot}6H_2O$, 80 g NH_4NO_3 and 4 ml of ammonia solution (25 wt.%) per liter was injected into the capillary for 2 h. Excess liquid was removed by forcing air through it. Sample was dried overnight at room temperature and then heated to 373 K for 2 h, followed by reduction in flowing 20% hydrogen in nitrogen (5 K/min) at 923 K for 2 h. An attempt has also been made to deposit nickel thin film inside capillary microreactor with an in situ atmospheric pressure chemical vapor deposition method. Nickel acetylacetonate was used as the source material. Solid nickel acetyl acetonate was heated at a temperature of 493 K and formed gas was introduced into the microreactor with helium as carrier gas (10 ml/min) and hydrogen as reducing gas (10 ml/min). During growth of the nickel film, microreactor was heated to 573 K. The microreactor was fitted in a metal block heated with a cartridge heater capable of supplying 100 W and type K thermocouples were put next to capillary to measure the temperature. CNF growth was carried out in situ by flowing reactant gases through the microchannel. Initially, the catalyst was reduced (pretreatment step) with 50% hydrogen in helium at 973 K for 120 min (total flow rate 8 ml/min) then temperature was set (5 K/min) to CNF growth temperature. When the growth temperature was reached, gas mixture was switched to 50% ethylene, 10% hydrogen in helium (total flow rate 10 ml/min). Amount of carbon deposited into the microreactor was determined from the difference between the weight of the capillary before and after deposition. Nickel loading on alumina coating was measured with a Philips X-ray fluorescence spectrometer (PW 1480). Morphology of CNFs was studied with scanning electron microscopy (SEM) (LEO 1550 FEG SEM) equipped with EDX analysis, and high resolution transmission electron microscopy (HRTEM, Philips CM300ST-FEG microscope). HRTEM analyses were performed by mounting samples on a carbon supported copper grid. The BET surface area, pore volume and pore size distribution were measured by N_2 adsorption–desorption at 77 K using an ASAP 2400 (Micromeritics) instrument. Error margin of surface area is around 10% due to low amounts of CNFs used in the analysis

3. Results and discussion

Fig. 2a shows fused silica capillaries coated with Al_2O_3 and Ni loaded Al_2O_3 (Ni–Al_2O_3). Alumina has been commercially used as an effective gas solid chromatography porous layer sorbent for separations of hydrocarbons and other organic molecules. Here, alumina coating in the column capillaries has been used as an amorphous and porous support for nickel loading in order to represent an easy geometry to support a uniform catalyst layer for CNF deposition in a microreactor. Ni–Al_2O_3 catalyst layer after calcination is shown in Fig. 2b. Layer thickness is around 8 μm. Nickel concentration in the alumina along the microchannel was found to be constant within 3% according to XRF analysis. SEM-EDX

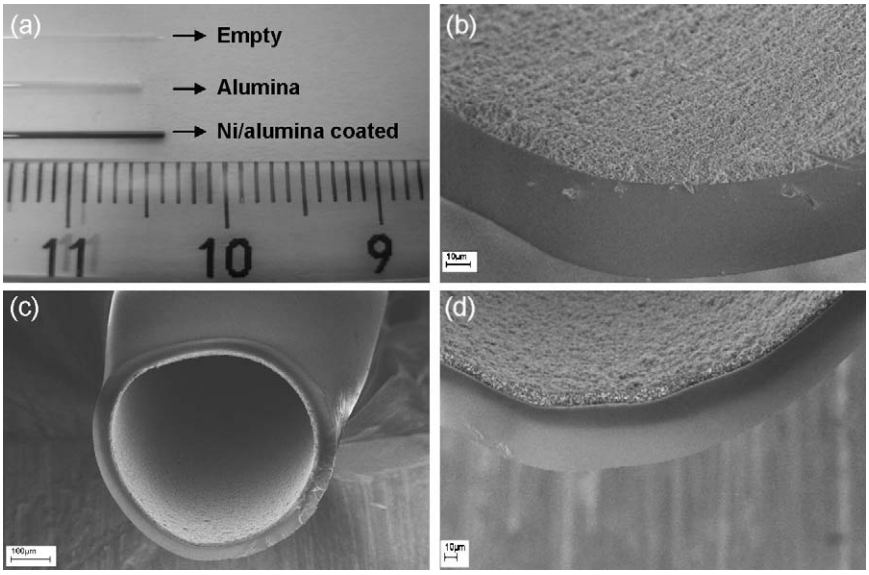

Fig. 2. (a) Fused silica capillaries coated with Al_2O_3 and Ni loaded Al_2O_3 (Ni–Al_2O_3), (b) SEM image of cross section of Ni–Al_2O_3 layer, (c) and (d) SEM cross sections of capillaries after in situ growth of CNF at 973 K for 120 min.

analysis of Ni concentration profile at a cross section of Ni–Al_2O_3 layer (Fig. 2b) indicates that Ni is evenly distributed in the alumina layer. Ni loading is found to be 9.0 wt.% on alumina. Specific surface area of the catalyst layer is around 310 m^2/g and total pore volume 0.29 cm^3/g with an average pore size of 37.3 nm. Fig. 2c and d shows SEM cross sections of microcapillaries after in situ growth of CNF at 973 K for 120 min. CNFs have been successfully grown on porous Ni–Al_2O_3 layer with a uniform coating thickness of 9.5 μm along the microchannel wall. A highly dense, homogenous and porous CNF-alumina composite was formed with a thin layer of CNFs at its outside (Fig. 2d). It is observed that the apparent thickness of the Ni–alumina layer increased due to high fragmentation and expansion during CNF deposition. BET surface area of the composite is found to be 160 m^2/g and pore volume is 0.17 cm^3/g with an average pore size of 42.5 nm. It can be seen from Fig. 1d that a bulk nanofiber layer filled the voids and covered the alumina fragments. CNFs are densely packed providing a high surface area for the deposition of catalytically active metal particles in the microchannel. Decrease in pore volume shows that part of the mesopores in the alumina is filled or even destroyed by fragmentation.

To investigate the growth of CNF layer on alumina support inside the microreactor, we analyzed variations with growth time, growth temperature, H_2 flow and pretreatment step. Table 1 presents synthesis conditions, average composite thickness and nanofibers diameter range. Thickness of CNF-alumina composite and diameter of the fibers along the microchannel increased with increasing deposition time (Samples 1–4). Carbon deposition led to fragmentation of alumina layer and as CNFs continued to grow, total composite thickness increased. It is known that [2,12–14] larger Ni particles cause slow formation of CNFs and this fact explains the observation of thicker nanofibers in the composite with longer deposition times. To study the influence of temperature on the deposition, CNFs were also grown at 873 K and 773 K (Samples 6–7). Thinner nanofibers were grown on alumina at 773 K compared to the fibers grown at 973 K. At lower temperatures, agglomeration and surface migration of Ni nanocrystal particles are reduced and smaller Ni particles would give thinner nanofibers on the alumina layer. Critical role of hydrogen during pretreatment and deposition is evident for CNF synthesis as it increased the yield and thickness of the CNF composite (Table 1, Samples 8–10).

Structure of the fibers after different deposition conditions was studied with HRTEM and SEM. TEM analyses show that primary structure of all CNFs are fishbone-type (not shown). Fig. 3a is a typical TEM micrograph of a Ni catalytic nanoparticle at the tip of a single nanofiber with a diameter of 30 nm taken from Sample 5. Inset of Fig. 3a shows that interplanar spacing of Ni nanoparticle is 2.8 Å, which corresponds to that between (1 1 1) planes of the cubic unit cell [15].

Time evolution of CNFs growth on alumina in the microreactor was studied and is shown in Fig. 3b–e. Fig. 3b shows surface of Ni/alumina catalyst after 5 s of deposition at 973 K. This is the initial growth stage with many nano-islands as nucleation sites which are considered to play an important role in nanofiber formation. Catalyst particles were reported to have hemispherical geometry

Table 1
Characterization of CNF coating in the microreactor at different conditions.

Sample number	Growth temperature (K)	Growth time (min)	H_2 flow in deposition (sccm)	H_2 flow in pretreatment (sccm)	Composite thickness (μm)	Nanofiber diameter (nm)
1	973	2	1	4	7.7	10–20
2	973	10	1	4	7.7	10–30
3	973	30	1	4	7.7	10–30
4	973	60	1	4	9.4	10–30
5	973	120	1	4	9.5	10–60
6	873	30	1	4	8.1	10–30
7	773	30	1	4	7.5	10–20
8	973	30	1	0	7.4	10–20
9	973	30	0	0	6.6	10–20
10	973	30	0	4	7.7	10–20

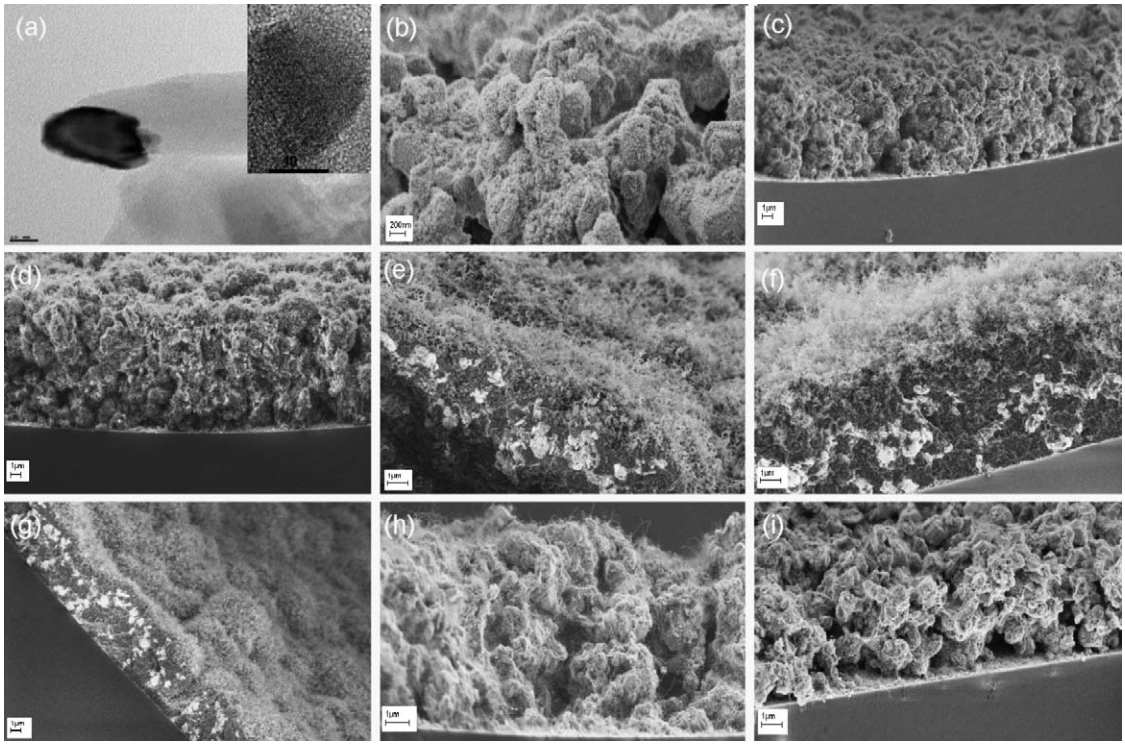

Fig. 3. (a) TEM micrograph of Ni catalytic nanoparticle at the tip of a single nanofiber with a diameter of 30 nm, taken from Sample 5. The inset shows the interplanar spacing of a Ni nanoparticle, which is 2.8 Å, (b) surface of Ni/alumina catalyst after 5 s of deposition at 973 K, (c) after 2 min, (d) after 10 min, (e) after 2 h, (f) 30 min deposition at 873 K, (g) 30 min deposition at 773 K, (h) CNF layer grown at 973 K for 30 min without hydrogen pretreatment and (i) without hydrogen during the deposition.

with a finite contact area with the substrate surface [16]. As graphite layers precipitated out of the catalyst nanoparticles, graphite nano-islands were formed as shown in Fig. 3b. Range of nanofiber diameters grown on alumina in the microreactor depends on that initial stage with varying size of Ni nanoparticles. After 2 min (Fig. 3c), a thin layer of CNFs was formed on the surface of alumina particles in the microchannel. These are nanofibers rapidly grown from small Ni particles. CNF-alumina composite thickness and nanofiber diameter increased after 10 min of deposition, as shown in Fig. 3d. It turns out that fragmentation of support layer had already started due to the fact that some of the thicker nanofibers fill the pores of the alumina. Fig. 3e shows the CNF-alumina composite layer formation after 2 h of deposition. Alumina layer was completely fragmented and a dense carbon layer filled the voids of the fragments. A homogeneous and thin layer of CNFs can be seen at the outside of the composite. The composite is mechanically stable showing no cracks or detachment from the glass microchannel wall. Similarly, packed nanofibers with much denser deposit under loosely grown surface CNFs layer can be seen in Fig. 3e. Fig. 3f and g shows the composite layers grown at 873 K and 773 K, respectively. Similar to 973 K, CNFs grown at these temperatures also produce stable and dense layers. Fig. 3h and i shows the CNF layer grown without hydrogen

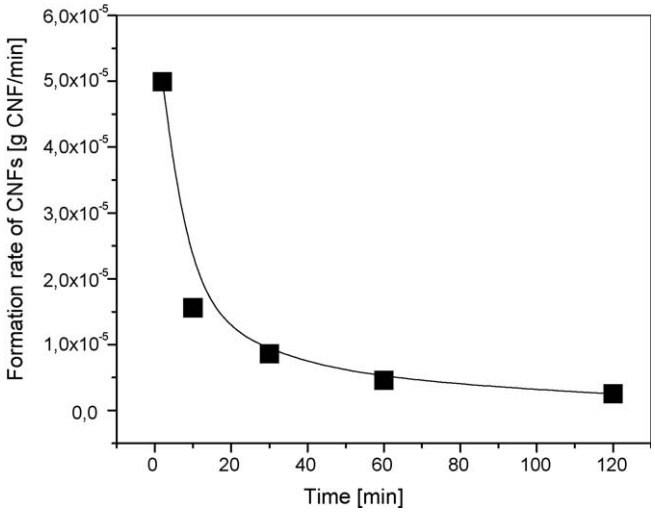

Fig. 4. Change of formation rate of CNFs with time.

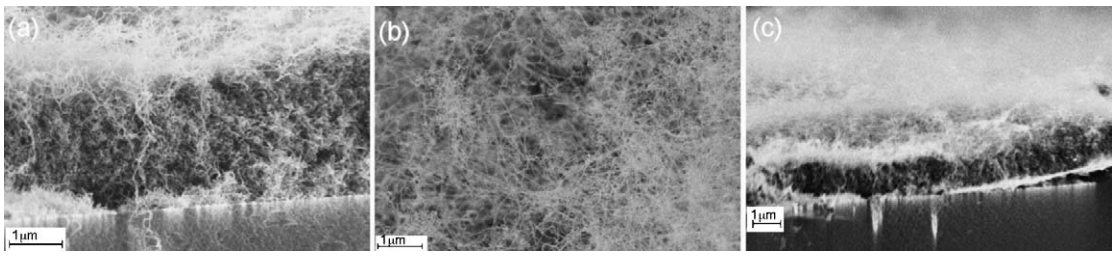

Fig. 5. CNFs growth inside the microreactor on nickel thin film at 973 K for 30 min.

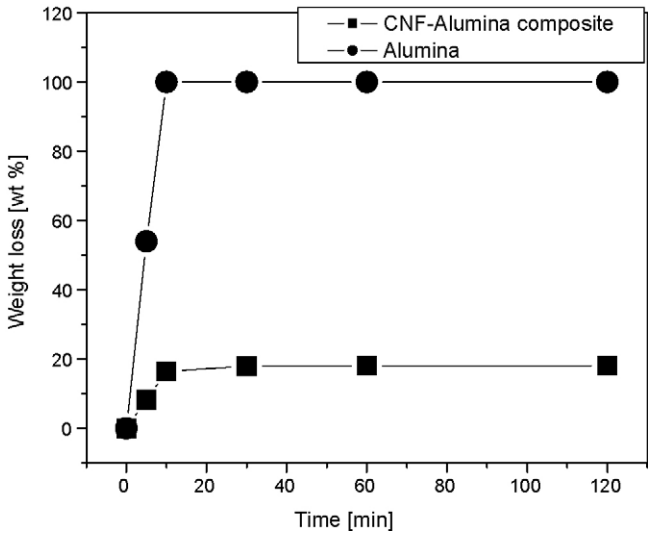

Fig. 6. Mechanical stability test based on weight loss of alumina and CNF-alumina composite coating in the microreactor during the maltreatment of the sample with 40 kHz ultrasound in pure water.

pretreatment and without hydrogen during the deposition, respectively. Yield of the growth and thickness of the composite decreased in both cases and the composite layer showed some detachments from microchannel walls and remained mechanically unstable after the deposition. This indicates that hydrogen addition during pretreatment and deposition increases CNFs formation rate so that a stable composite layer can be obtained. Additionally, microplasma activation of the catalyst using hydrogen and helium mixture in the microreactor is demonstrated for nanofibers synthesis and will be published elsewhere [17]. CNFs growth rate on Ni–Al_2O_3 in the microreactor was determined by amount of carbon, calculated from the weight increase. Deactivation of the catalyst resulted in decrease in formation rate and complete deactivation was observed after 2 h, as can be shown in Fig. 4. Deactivation can occur when carbon encapsulates the surface of nickel particles [18].

As an alternative approach to high surface area Ni loaded alumina, Ni thin film is utilized as catalyst for CNFs synthesis in the capillary microreactor. Maruyama and Tago [19] obtained polycrystalline nickel films by hydrogen reduction of the raw material by low-temperature atmospheric pressure chemical vapor deposition method. Using the same method, a nickel film was grown by the hydrogen reduction of nickel acetylacetonate in the microreactor. The film was translucent with a thickness of 25 nm and the surface looked like a shiny mirror. Fig. 5a–c shows CNF growth at 973 K for 30 min on a nickel thin film. Complete coverage of the inner surface of the microchannel with a 2 μm thick CNF film was obtained. However, in situ CVD process led to detachment of nickel thin film due to thermal stress, as is shown in Fig. 5c. To solve this delamination problem, an adhesion layer such as tantalum is proposed in order to produce a stable layer of CNFs in the future.

Stability and attachment of CNF-alumina composite and its comparison with an alumina layer on the surface of the microchannel wall were tested by determining the weight loss during the maltreatment of the sample with 40 kHz ultrasound in pure water. Fig. 6 indicates that the alumina layer was completely removed after 10 min. However, in the case of CNF-alumina composite, about 18% of the composite was removed and it remained stable after 2 h showing that CNF incorporation resulted in mechanical stability of catalyst support layer in the microchannel.

4. Conclusion

In situ CVD of CNFs was carried out by flowing reactant gases through a Ni/alumina coated fused silica capillary microreactors. A homogeneous and thin layer of highly porous and mechanically stable CNF-alumina composite was formed with high surface area (160 m^2/g). The thickness of CNF-alumina composite and the average diameter of the fibers increase with increasing deposition time. Hydrogen addition during pretreatment and deposition steps is important to increase growth yield and to produce a mechanically stable composite support in the microchannel.

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