



# Controlling the yield and structure of carbon nanofibers grown on a nickel/activated carbon catalyst

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## Abstract

Carbon nanofibers (CNFs) were grown via the chemical vapor deposition of C<sub>2</sub>H<sub>4</sub> on an activated carbon (AC)-supported Ni catalyst. The texture of the CNF/AC composites can be tuned by varying the growth temperature and by treatment in reducing atmosphere prior to C<sub>2</sub>H<sub>4</sub>/H<sub>2</sub> exposure. The Ni-catalyzed gasification of the AC support increases the microporosity of the composite and shown to be dominant throughout the composite synthesis especially during reduction, subsequent treatment in reducing atmosphere, and CNF growth at low temperatures. N<sub>2</sub> isotherm and scanning electron microscope were used to characterize the texture and morphology of the composites. Subsequent treatment in reducing atmosphere were shown to increase the Ni catalyst activity to grow CNFs. High resolution transmission electron microscope however did not reveal any microstructural difference for Ni catalyst with and without the subsequent reduction treatment. We propose in this paper that the carbon dissolutions during treatment of the catalyst might have an implication on the CNF growth.

## 1. Introduction

Carbon materials possess unique characteristics, as they can exist in different forms that exhibit various functionalities. These materials range from sp<sup>2</sup>-hybridized graphitic materials, such as graphite, carbon nanofibers (CNFs) and carbon nanotubes (CNTs), to turbostratic carbons consisting of sp<sup>2</sup> and sp<sup>3</sup> mixtures such as carbon black, soot and activated carbons, to the sp<sup>3</sup>-hybridized diamond. The different allotropes offer a broad range of physical and chemical properties.

Application of carbon materials as catalyst supports have been widely reported with a broad scope of reaction applications [1-22]. As a support, activated carbon (AC) has attracted much interest because it offers advantages such as high thermal stability, high surface area, and cheap and easy recovery of the metal catalyst by simple combustion. Carbon-carbon composites may represent combinations of carbons having different dimensions (nano with micro) and/or different orderings (graphitic or disordered). Su et al. has successfully synthesis CNFs on AC support

with Fe catalyst using C<sub>2</sub>H<sub>4</sub> as the carbon source [23,24]. Such composites have found applications both as adsorbents and in catalysis [3-22].

During the past several years, metal-free catalysts have attracted considerable interest, especially in industrial application. However, only graphitic nanocarbons exhibit excellent long-term stability and high catalytic activity [25,26]. On the other hand, the powdery form of nanocarbons makes them unsuitable for use in fixed-bed reactors on an industrial scale. The compactions of loose nanocarbons used in previous work, before being transferred into the reactor, were evidence of severe technical difficulties. Therefore, immobilizing the graphitic nanocarbons onto a carbon-based support allows for better reactants diffusion, and prevents hot spots, pressure drops and avoiding chemical discontinuities in such a carbon-carbon composite [27]. Considering the issues described above, mass production of immobilized nanocarbons on a carbon support is desirable for industrial applications in chemical reactors.

Filamentous carbon was already reported in the late 1960s as side products in the petroleum and nuclear indus-

tries, which caused severe technical problems. Various forms and microstructures of filamentous carbon were reported to deposit on metal surface after exposure to carbon-containing gases within a broad range of temperature from 323 to 1000°C. Thus the early works related to carbon filaments was to control their formation aiming to prevent the carbon deposition [28,29]. The characterization of the carbon filament and the quantification of both the solid and gaseous product under reaction condition were carried out by the pioneering work of Alstrup and Baker for the study of steam reforming catalysis and in situ TEM works respectively. Based on kinetics and microstructural studies, it was proposed that the growth of carbon filaments process via the diffusion of carbons in the bulk of catalyst particles due to thermal and/or concentration gradients [29-33]. The investigation of carbon filaments further attracts researchers with the advent of high-resolution microscopy followed by the discovery of CNTs by Iijima [34,35]. Thus numerous papers arise with respect to the synthesis and applications of filamentous carbon materials. The aim of the present article is the large-scale synthesis of CNFs via the catalytic decomposition of H<sub>2</sub> and C<sub>2</sub>H<sub>4</sub> over an AC-supported Ni catalyst. Nickel was selected as the catalyst due to its higher activity in producing filamentous carbon compared to Fe and Co as the classic catalysts for CNF and CNT synthesis [36]. Pham-Huu et al. [37,38] synthesized CNFs using both graphite felt and CNTs as supports. These works produced uniform CNFs with herringbone and a mixture of herringbone and platelet graphene arrangements for systems supported on graphite felt and CNTs, respectively. However, these expensive support materials limit their use for industrial application. Thus, natural AC is a good alternative due to its low cost, availability in several shapes, and potential for chemical modification.

## 2. Experimental

### 2.1. Catalyst impregnation

The AC was derived from palm kernel shell obtained from NanoC sdn bhd. Malaysia. The AC was previously treated with concentrated HNO<sub>3</sub> (70%, Sigma Aldrich) to eliminate inorganic impurities, such as Fe, that would lead to heterogeneity of the produced CNFs. Later in the text, AC is referred as the HNO<sub>3</sub>-treated support. The AC samples were ground and sieved to a ≤50 μm particle size before impregnated via the wet-impregnation method with Ni(NO<sub>3</sub>)<sub>2</sub> in an acetone solution to achieve Ni weight loading of 1%. The samples were further dried overnight at 40°C in static air.

### 2.2. CNF synthesis

For every composite synthesis, 5 grams of the fresh catalyst were calcined at 250°C with 5% O<sub>2</sub> in Ar for 1 hour

and reduced at 300°C under 5% H<sub>2</sub> in Ar for 1 hour. The temperature was then increased to the desired CNF growth temperature under Ar atmosphere. The CNF synthesis was carried out between 500°C and 850°C for 2 hours under a H<sub>2</sub> and C<sub>2</sub>H<sub>4</sub> gas mixture (7:1) with a total flow of 230 ml/minute. The calcination, reduction and CNT growth were carried out continuously in a single quartz tubular reactor. CNF/AC composites synthesized at 500°C, 550°C, 600°C, 700°C and 850°C from 1% Ni supported on AC were designated as NC500, NC550, NC600, NC700 and NC850, respectively (Table 1). Composites synthesized with a subsequent treatment in 5% H<sub>2</sub> at 500°C and 550°C for 1 hour prior to H<sub>2</sub> and C<sub>2</sub>H<sub>4</sub> exposure are designated NCT500 and NCT550, respectively.

### 2.3. Characterization methods

The textural properties of the AC support and CNF/AC composite were measured on the basis of the N<sub>2</sub> isotherm performed at 77 K with a Quantachrome instrument. Surface area and micropore volume were calculated using the Dubinin-Radushkevich (DR) equation. The mesopore volume was determined as the difference between the total pore and micropore volume. The morphology of the CNFs was studied with a scanning electron microscope (SEM) performed on FEI Quanta 200F SEM. The quality and microstructure of the CNFs was investigated with a high resolution transmission electron microscope (HRTEM) performed on a Philips TEM/STEM LaB6 and FEG microscope. The acceleration voltage was set to 200 kV. CNF and CNT average diameter was calculated after measuring 200 CNFs for every sample. The Ni particle size distribution was determined by counting 400 particles per sample. The temperature-programmed reduction (TPR) of the Ni/AC fresh sample was carried out under 5% H<sub>2</sub> in N<sub>2</sub> with a temperature ramping of 5°C per minute using a Netzsch TG/SDTA coupled with an MS quadruple Omnistar detector. The weight change after each treatment was calculated by comparing the final weight with the impregnated sample's weight after water removal.

## 3. Results and discussion

### 3.1. Texture and microstructure of the CNF/AC composites

The textural properties of the reduced Ni/AC samples and the CNF-AC composites produced at different temperatures are summarized in Table 1. In general, there is a gradual increase in the mesopore volume of the sample after reduction and after CNF growth. The N<sub>2</sub> isotherms in Figure 1 show the appearance of hysteresis after CNF growth over the whole temperature range. Such N<sub>2</sub> condensation at high relative pressure is assigned to the condensation in between the CNFs. Indeed, this observation is in

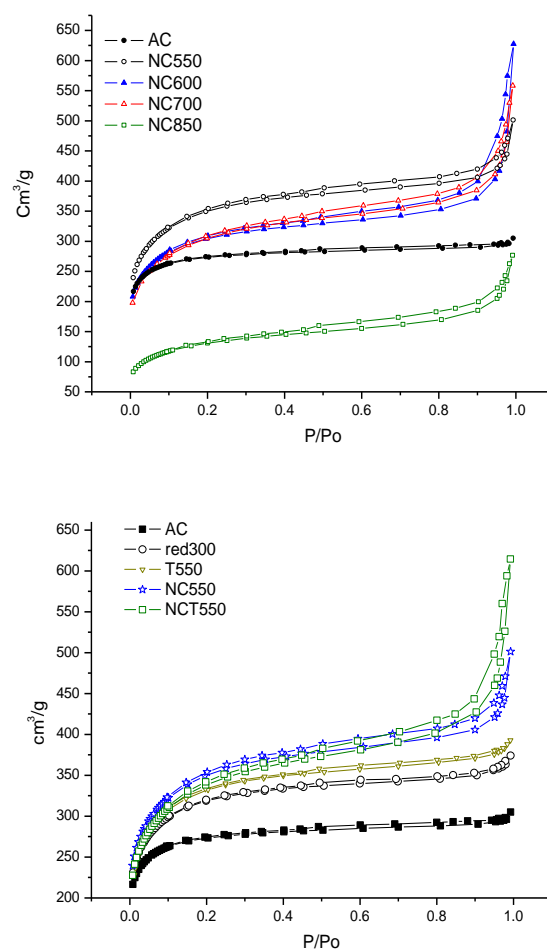
**Table 1.** Textural properties of CNF/AC composites

	Growth temp °C	Weight change% after CNF growth	DR Surface area m <sup>2</sup> /g	Micropore volume cm <sup>3</sup> /g	Total pore volume cm <sup>3</sup> /g	Mesopore volume cm <sup>3</sup> /g
AC	-	-	1233	0.438	0.455	0.017
Red 300	-	-21	1454	0.517	0.565	0.048
T550 <sup>a</sup>	-	-24.7	1485	0.527	0.585	0.058
NC500	500	-27	nd <sup>b</sup>	nd	nd	nd
NC550	550	-10.3	1588	0.56	0.659	0.099
NC600	600	-2.6	1135	0.494	0.645	0.151
NC700	700	16.2	1491	0.53	0.66	0.130
NC850	850	25	598	0.212	0.325	0.113
NCT500	500	-29	1347	0.479	0.55	0.071
NCT550	550	-20.2	1525	0.542	0.725	0.183

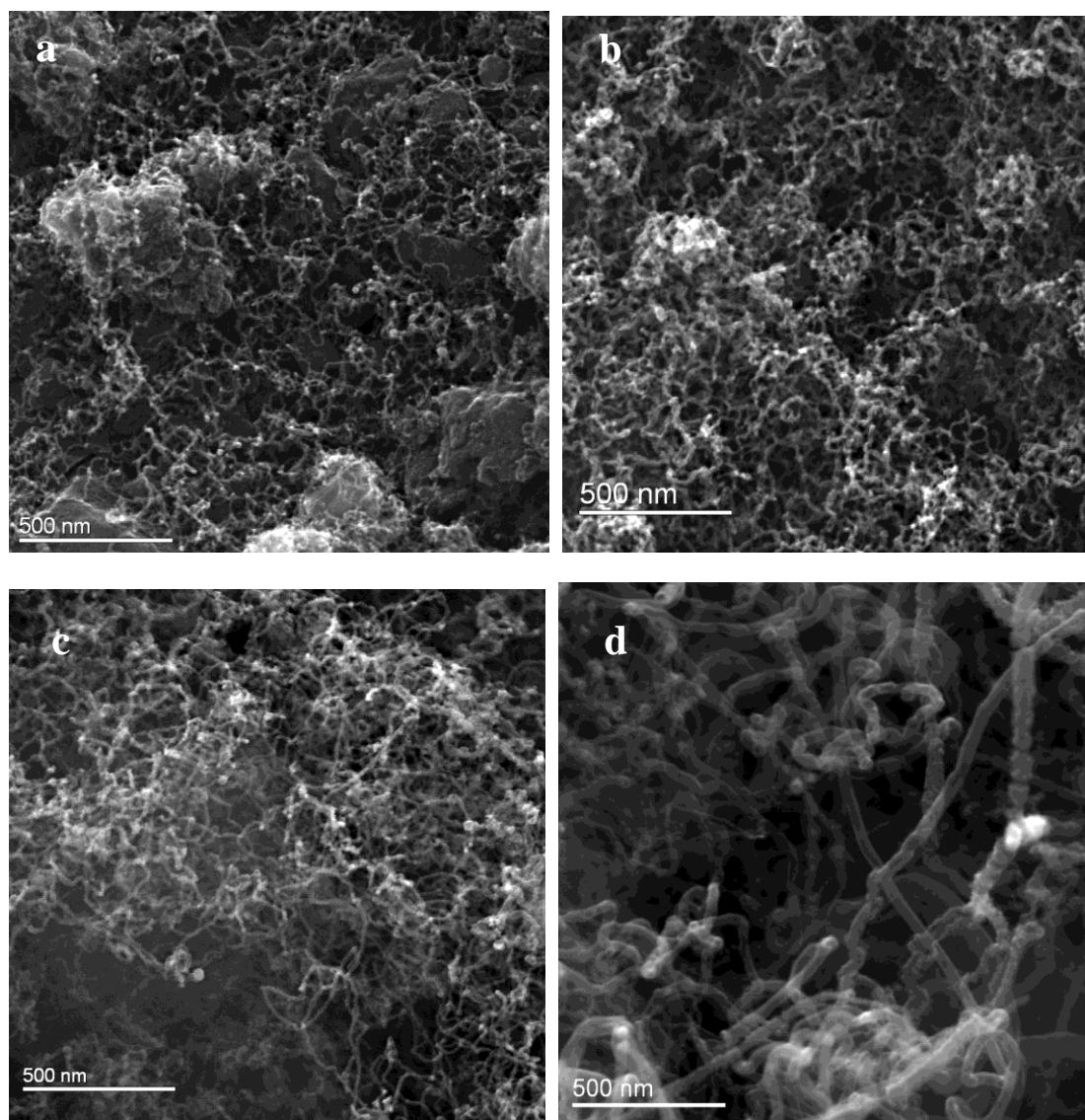
<sup>a</sup>Subsequent reduction at 550°C for 1hour 5% H<sub>2</sub>/Ar after reduction at 300°C<sup>b</sup>Not determined

agreement with our SEM images in Figure 2, which shows that the as grown CNFs are highly entangled, providing spaces for N<sub>2</sub> molecules to condensate at high relative pressure. The NC500 sample showed no observable formation of CNF by SEM.

For composites synthesized at 550°C (NC550) and 600°C (NC600), there is a positive relationship between the mesopore content and weight change (after CNF growth) (Table 1). At higher temperatures, however, the mesoporosity of the composites depended less on the CNF growth. This is mostly due to different level of CNF entanglement that occurs at different growth temperatures. CNFs grown at higher temperatures tend to give straighter filaments (Fig. 2d), most likely due to better graphene stacking of the CNF (Fig. 3). From HRTEM investigation presented in figure 3, for CNF grown at 550°C the microstructure shows a poorly defined or hydrogenated amorphous carbon. Similar hydrogenated carbon filaments for growth at low temperature has been reported previously [39,40]. The CNF microstructures give defective platelets and more graphitic platelets when grown at 600°C and 700°C respectively. CNFs with parallel graphene wall perpendicular to the filament axis with hollow channel were observed for growth at 850°C. NC850 give straight CNF morphology (Fig. 2d) showing less entanglement as featured in the N<sub>2</sub> isotherm at a higher relative pressure (Fig. 1). The variation of the graphitic character of the samples under study was investigated by X-ray powder diffraction (Fig. 4). The X-ray diffraction patterns did not show sharp graphite (002) and (100) signals for composites synthesized at low temperatures. Only the composite synthesized at 850°C showed appreciable intensity for the (002) diffraction signal, which might reflect the additive effect of both the improved graphitic character and the higher fraction of CNF (Fig. 3d and Table 1). None of the diffractograms of the composites



**Fig. 1:** N<sub>2</sub> isotherm of the CNF/AC composites synthesized at different temperatures (a) and the effect of reduction and subsequent treatment to the to the N<sub>2</sub> isotherm of Ni/AC catalyst and CNF/AC composites (b).



**Fig. 2:** SEM images of the CNF/AC composites: NC550 (a), NC600 (b), NC700 (c) and NC850 (d).

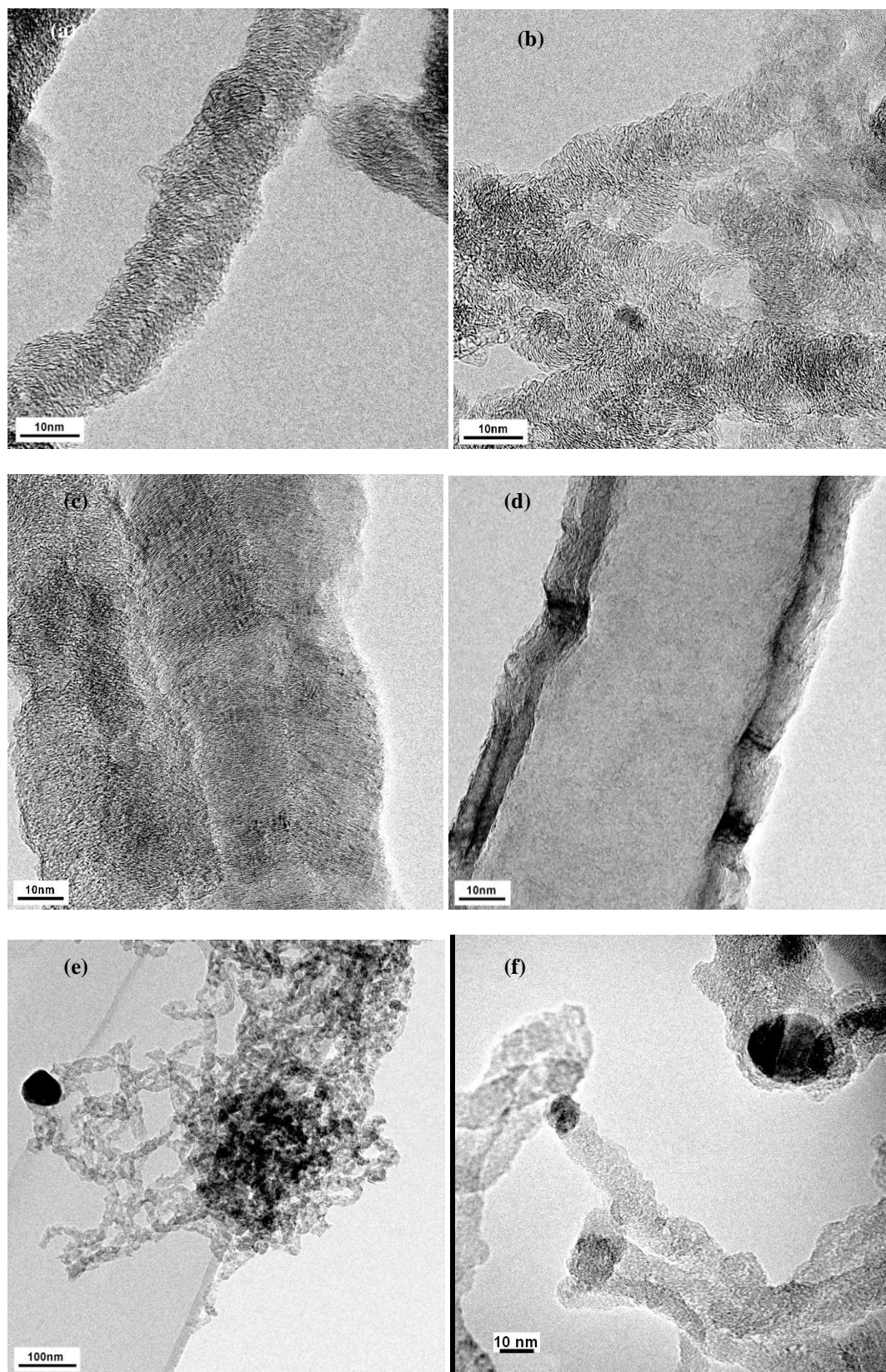
showed the presence of Ni metal or Ni carbide, possibly due to the low percentage of Ni in the composites.

The average CNF diameter in the composites was shown to increase with the synthesis temperature (Fig. 5). The increase may be primarily due to sintering of the Ni particles facilitated by the surface modifications (surface functional groups decomposition) of the AC supports. The average CNF diameter increased dramatically for composites synthesized at 850°C. This behavior may also be due to the change in the growth mode from a mixture of octopus and single directional CNFs grown at 550-700°C to preferentially single direction CNFs for composite grown at 850°C (Fig. 3e and f). The octopus CNFs are mostly observed from bigger Ni particles, which is in agreement with previous studies [38,41-47]. Several effects, such as particle size, surface reconstructions, exposed facets and rate of ethylene decomposition, were proposed to explain the CNF growth preferences [48-51].

The octopus CNFs are beneficial for establishing a bulk macroscopic structure due to entanglement from multiple directions for each catalyst particle [43,46].

### 3.2. The catalytic gasification of AC support by Ni catalyst

Ni catalyzes the gasification of carbon supports under hydrogen [1,3,28,52-65]. As shown in Table 1, the weight changes after growth indicate the extent of gasification during both reduction and CNF growth. The gasification is so dominant that the supported catalyst loses 20% of its mass after reduction. Figures 6a and b show the evolution of gaseous products from the Ni/AC catalyst during heating under inert gas (Ar) and 5% H<sub>2</sub>/Ar respectively. In both cases the surface functional groups present on AC



**Fig. 3:** Microstructure of CNF in NC550 (a), NC600 (b), NC700 (c), NC850 (d), octopus (e) and single directional CNF (f) typically present in CNF/AC composites.

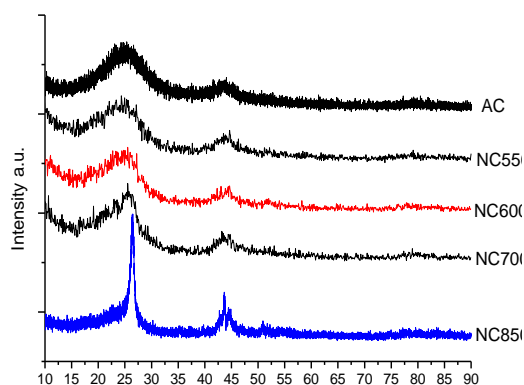


Fig. 4: XRD patterns of the AC and CNF/AC composites.

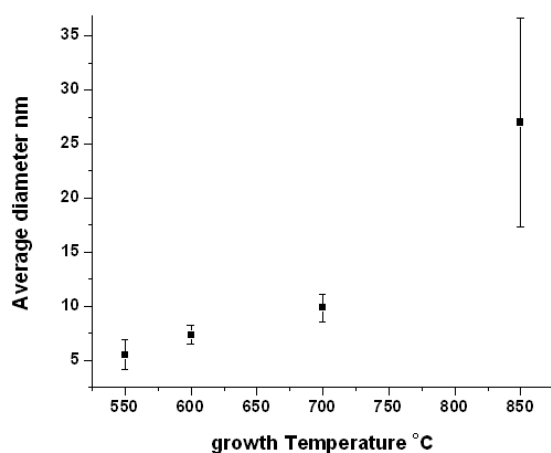


Fig. 5: Average diameters of CNF grown at different temperatures.

support decompose during heating [1,3,66]. Methane was only detected when the Ni/AC catalysts were heated under reducing atmosphere. It is still unclear whether the catalytic gasification proceeds via spillover of hydrogen and/or gasification of carbon on the Ni surface as a result of carbon atoms diffusing from the metal-carbon support interface [3,52,56].

Figure 6b shows that methane starts to evolve at around 250°C, which indicates the presence of Ni metal available to provide active hydrogen to gasify the AC support. The reduction process increases the micropore volume by 20% and gives a 3-fold increase of the mesopore volume (Table 1). The knee broadening in the  $N_2$  isotherm at  $P/P_0 < 0.2$  indicates broadening of the pore size distribution towards bigger pores, which could be explained by the catalytic gasification of the supports creating new pores and/or enlarge existing ones in the dimension of the Ni particle sizes (Fig. 1b). Because AC is microcrystalline curved graphite with possible cross-linking between the graphite microcrystals, the catalytic gasification is likely to occur in three dimensions of the carbon matrix, creating voids thus

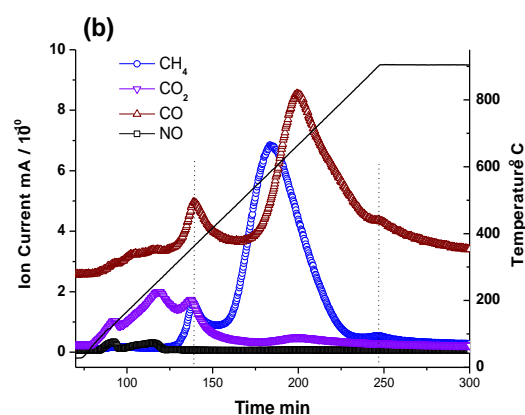
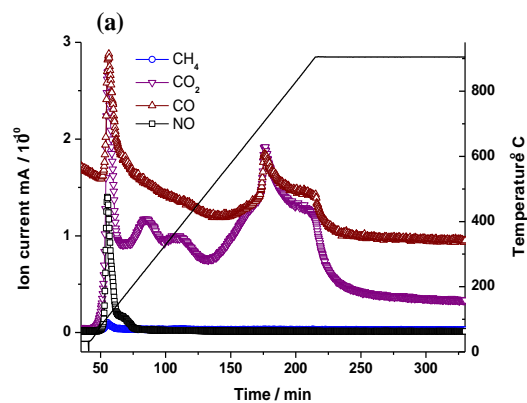
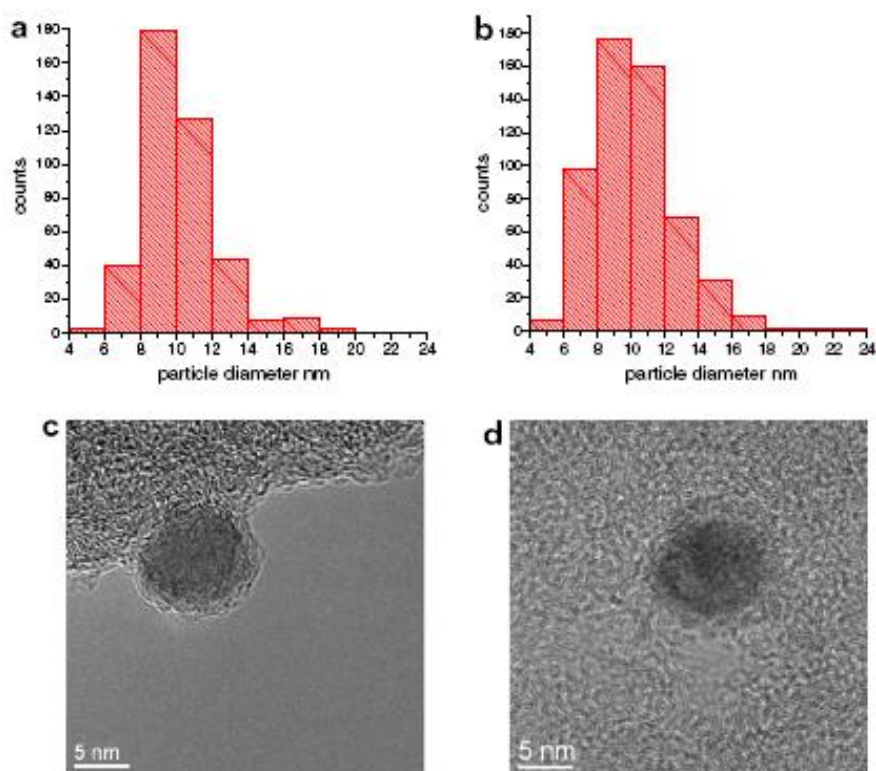


Fig. 6: Gases evolved during the heat treatment in argon (a) and 5%  $H_2$  in argon (b) of 1wt% Ni/AC

increasing the porosity. Such gasification is different from that of graphite that forms two-dimensional channels in certain directions [57-59,60,62,67]. Figure 1b also shows that catalytic gasification remains a dominant process even after CNF growth, especially for composite grown at 550°C. The preservation of microporosity in the composites, even after CNF growth for 5 hours, suggest that Ni catalysts of the micropores dimension ( $\sim 2$  nm) may be inactive under these conditions. In fact, no filaments of  $\sim 2$  nm in diameter were observed in the TEM images for any of the composites. Another possible scenario is that these Ni nanoparticles sinter to form bigger particles during the gasification prior to the growth of CNFs. Indeed, the catalyst size distributions measured for samples after reduction (red300) and after subsequent treatment at 550°C (T550) show a shift towards a higher value, indicating a tendency for the Ni particles to sinter after treatment at 550°C (Fig. 7). In an earlier study on Ni-catalyzed carbon gasification Tomita et al. reported the gradual increase of Ni particle size after the gasification in hydrogen atmosphere [54].

Gasification produces two prominent  $CH_4$  peaks, the first at the low temperature region with a peak maximum at 300°C and a second peak with higher intensity and a maximum around 670°C. The methane production is strongly correlated with the surface functionalities of the carbon



**Fig. 7:** Particle size counts and HRTEM for the Ni/AC catalyst after reduction (Red300) (a, c) and after subsequent treatment (T550) (b, d).

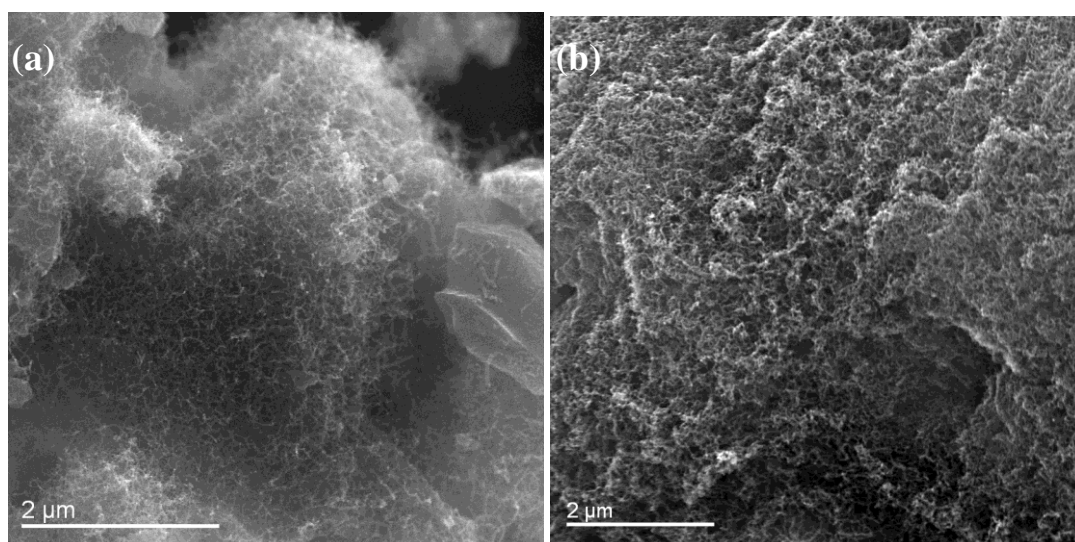
support [54]. Figure 6b shows the overlapping CH<sub>4</sub> and CO peaks at the low temperature region and deviated from the overlaps for the second methane peak at the higher temperature region. Note that CO<sub>2</sub> evolution under reducing atmosphere was suppressed dramatically at the high temperature region. CH<sub>4</sub> production decreased at around 750°C, as shown in Figure 6b. The minimum is also illustrated in the N<sub>2</sub> isotherms after reduction at 300°C and subsequent treatment at 550°C in Figure 1b. The isotherms show a more moderate increase in micropore adsorption for samples after subsequent treatment at 550°C when compared with that after reduction at 300°C. Several arguments have been proposed from earlier studies to explain the catalytic gasification deactivation, which includes catalyst encapsulation by carbon, H<sub>2</sub> diffusion problems, and catalyst-carbon surface contact loss [52,54,56,63]

### 3.3. The effect of the subsequent treatment to the CNF/AC composite

Interestingly, the CNF growth increased dramatically with subsequent treatment at 500°C (NCT500) or 550°C (NCT550), compared if composites were synthesized without the treatment (NC500 and NC550) as represented in the SEM images shown in Figure 8. CNF was not observed under SEM analysis for sample grown at 500°C without the subsequent treatment (NC500). The effect of the treatment is reflected in the increased weight change, the develop-

ment of the hysteresis in the N<sub>2</sub> isotherm and thus higher mesoporosity after CNF growth (Table 1 and Fig. 1b).

In an attempt to understand the improved activity after the treatment at 550°C, TEM investigations were carried out for Ni/AC samples after reduction at 300°C (Red 300) and after subsequent treatment at 550°C (T550) for their catalyst size distribution and microstructure (Fig. 7). Both size distributions and microstructure of Ni particles failed to show significant differences after either treatment. Within the resolution of the HRTEM used, the d spacing of the Ni particles show values assign for Ni<sup>0</sup> with fcc structure. Albeit a small shift in the catalyst size distribution after the subsequent treatment, it is unlikely that such small difference can cause the dramatic activity for CNF growth. However, we have yet to take into consideration that the shape of Ni particle may changes after each treatment. Pioneering works with controlled atmosphere electron microscope (CAEM) by Baker in the 70s clearly showed the mobility of metal particles on graphite under different atmospheres [28,57,62,67-69]. Later on equipped with better resolution, Anton [64,65] also reported the liquid-like mobility of Ni nanoparticles on thin amorphous carbon films subjected to heating in inert and reducing atmospheres under in situ TEM observations at temperatures similar to the current study. The mobile Ni particles were observed to wet the carbon surface and spread out randomly leaving behind graphitic tracks. Thus, reshaping the Ni particles during reduction and subsequent treatment is very likely to occur in the current study. To elucidate on the mobility of



**Fig. 8:** SEM images of CNF/AC composites synthesized after treatment in 5% H<sub>2</sub>/Ar for 1 hour at 500°C (NCT500) (a) and 550°C (NCT550) (b).

catalyst metal particles, Baker has shown the relationship between mobility of metal particles on graphite surface with the Tamman temperature ( $0.5T_{\text{melting}}$ ) of the metal. For 10 nm size Ni metal particles it was observed that the mobility starts at 640°C under hydrogen atmosphere [62,67,69]. The temperature is lower than that expected from the current investigation where the gasification and the increase of porosity were observed. This may be due to the smaller average size of Ni particle size (fig 7) and the nature of carbon support, which is less graphitic and more functionalized in the current study [52,54,56]. In addition the catalyst surface could be at a higher temperature due to the heat released from the gasification. Thus there is every reason to believe that the mobility will have a pronounced effect in the orientation and size distribution of the metal particles on the carbon surface.

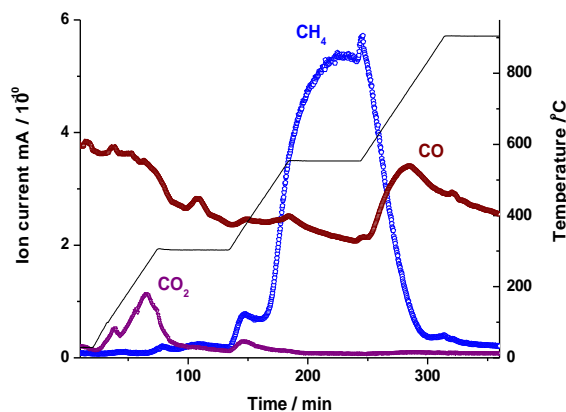
In the previous *in situ* TEM study of Ni-catalyzed amorphous carbon gasification, Ni particles encapsulated with several graphitic layers were also observed. Indeed earlier works have shown under inert atmosphere iron and nickel supported on amorphous carbon films precipitated graphite films after heating [70,71]. However Ni particles encapsulated by graphitic layers or carbon layers were not observed by our HRTEM investigation of samples in the current study.

In addition, there is also a possibility for surface reconstruction of the Ni catalyst to occur due to the adsorption-desorption dynamics of CH<sub>4</sub> and CO molecules during the two treatments [72-75]. The CO profile changed dramatically when the atmosphere was changed from Ar to 5% H<sub>2</sub>/Ar, which strongly suggest that CO molecules interact with the Ni catalyst. TPR was carried out in a temperature program to simulate the reduction at 300°C and subsequent treatment at 550°C under 5% H<sub>2</sub>/Ar atmosphere (fig. 9). The subsequent treatment at 550°C produced a significantly higher CH<sub>4</sub> peak. Nevertheless, the catalyst particles are still in a metallic state after subsequent reduction at 550°C,

and no Ni carbide phase was evident in the HRTEM images (Fig. 7c and d). The absence of carbide phase is expected, as Ni carbide is not stable at 550°C [76]. Similarly the presence of metallic state and the absence of carbide phase of Ni catalyst were previously reported after deactivation from the catalytic carbon support gasification, after graphitization of the amorphous carbon film, and during and after CNT growth [44,63,65,77-81]. Catalytic gasification, CNT and CNF growth, and catalytic graphitization presumably involve a similar general mechanism of carbon atoms dissolutions, diffusion and precipitation from the catalyst Ni particles [56,65]. However, several works have claimed the presence of dissolved carbon [44,82] or carbide-like compounds [81] in Ni catalyst particles after CNF growth. Such dissolved carbon or carbon contamination has also been reported in works involving metal catalyst supported on non-graphitic carbons [1,83,84]. Gandia and Montes [85] reported the influence of carbon contamination of the carbon-supported Ni catalyst on the hydrogenation of acetone after thermal treatments in inert and H<sub>2</sub> atmospheres.

Based on the TPR profiles in Figures 6b and 9, CH<sub>4</sub> and CO evolution may be interdependent on the surface of the Ni catalyst. Indeed, several surface carbon species have been identified from the CO hydrogenation reactivity of Ni catalysts at conditions similar to those in the current study [86]. Such surface carbons or surface carbide species that may be present in the current study may cause electronic perturbations [74,87] and geometrical modifications [73,88], and thus affecting the activity of the Ni catalyst. Based on the literature mentioned above, we suggest the possibility of dissolved and/or surface carbons in the bulk and/or surface of Ni particles after reduction and/or after the subsequent treatment that may contribute to the Ni catalyst activity for CNF growth.





**Fig. 9:** Gasses evolved during TPR experiment under 5% $H_2$ /Ar simulating reduction at 300°C and subsequent treatment at 550°C.

Bengaard et al [89] demonstrated that certain facets or orientations in Ni particles are energetically more favored for carbon deposition. Based on earlier studies of metal catalyst on carbon support under heating and different gaseous environments, it is reasonable to believe that shape and/or orientation of the Ni catalyst particles in our study may change [28,60,62,64,65,67,69,78,90]. However, no conclusive differences were observed by standard HRTEM characterization in the current study for samples after reduction at 300°C and after subsequent treatment at 550°C. (fig 7c and d). The respective temperature and gas atmosphere conditions can give significant differences between the standard and the environmental TEM observations.

Metal catalysts supported on disorder carbon were shown to give lower activity than metal catalyst supported on graphitic carbons. In one of the early application of CNFs as catalyst support Rodriguez et al. have clearly shown the superiority of graphitic filament over disordered carbon support [5]. Various arguments were proposed previously to explain the intrinsic activity difference between metal catalyst supported on disordered and graphitic carbon. They include carbon contaminations, carbon encapsulation and faceting of the catalyst particles. Savva et al [91] reported that Ni supported on CNTs showed activity for CNF production with  $C_2H_4$  at 400°C, whereas Otsuka et al [92] showed that Ni supported on carbon fiber could grow herringbone CNFs after exposure to  $C_2H_4$  at 500°C. Other authors have also reported the production of CNFs by Ni supported on various carbon supports with  $C_2H_4$  in similar temperature ranges as those used in our study [51,57]. Pham-Huu et al [38] reported that CNF-supported Ni catalysts could grow CNFs with  $C_2H_6$  in similar temperature ranges.

In the current study, 550°C was the lowest temperature where CNFs can be observed with electron microscope after 1 hour reduction at 300°C. In addition to the already complicated dynamics of the catalyst for CNT and CNF synthesis, the fact that Ni may be supplied with carbon from three different sources ( $C_2H_4$ , carbon support and CO from the surface functionalities) further complicates the process. There are still no conclusive arguments for how gasification and/or carbon support contamination can change the catalyst activity to grow CNFs. Nevertheless, we showed experimentally that subsequent treatment of Ni/AC under reducing atmosphere for 1 hour prior to  $C_2H_4$  and  $H_2$  exposure increases the ability of the system to grow CNFs significantly.

We suggest several possible scenarios to explain the additional activity of the Ni catalyst after the subsequent treatment process: the presence of dissolved carbon, surface carbon, surface carbide, catalyst faceting and reconstruction, which may all contribute to the increase in Ni catalyst activity in growing CNFs under the current conditions. Such activity enhancement may also be relevant for the study of other reactions involving CO and/or hydrocarbons.

#### 4. Conclusions

CNFs and CNTs have been synthesized using a Ni/AC catalyst. By varying the growth temperature, the microstructure and the texture of the CNF/AC composite have been successfully controlled. Catalytic gasification was experimentally shown to change the texture of the CNF/AC composites via the development of microporosity. For composites synthesized at low temperatures, the activity of the Ni/AC catalyst was increased significantly after treatment with 5%  $H_2$ /Ar prior to  $C_2H_4$ / $H_2$  exposure. However, the particle size distribution and the microstructure of the Ni catalyst after the treatment did not show appreciable changes.

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