$CaCO_3$ Supported Co-Fe Catalysts for Carbon Nanotube Synthesis in Fluidized Bed Reactors

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DOI 10.1002/aic.11403

The synthesis of carbon nanotubes (CNTs) on a cobalt-iron (Co-Fe) catalyst supported on a calcium carbonate ($CaCO_3$) substrate, contained within a fluidized bed was investigated for the first time. $CaCO_3$ supported catalysts, prepared using traditional wet impregnation techniques result in a soft and sticky powder requiring special arrangements to ensure satisfactory fluidization. A modified method developed using citric acid complex resulted in $CaCO_3$ supported catalysts that can be classically fluidized without special arrangements. The issue of Fe^{3+} (aq) hydrolysis above its critical pH of $\sim$3.5 was also addressed. A carbon yield consistently greater than 10 times the weight of the catalyst metal loading was obtained. Thermogravimetric analysis coupled with mass spectrometry showed a single peak centered on 575°C, with no peaks below 400°C, indicating that an insignificant quantity of amorphous carbon was present. Transmission electron microscopy verified that the products contained a large proportion of CNTs. © 2008 American Institute of Chemical Engineers *AIChE J*, 54: 657–664, 2008
Keywords: deposition methods, particle technology, fluidization

Introduction

Carbon nanotubes (CNTs) are a form of crystalline carbon with extraordinary properties, making them potentially valuable in a wide range of applications.[1] They have been studied intensively for the past decade, with the aim of elucidating their intrinsic properties, and perhaps most importantly, their mechanism of growth.[2] However to date, the use of CNTs in commercial applications has been restricted by low production capability.[3] Recently, researchers have reached a consensus that chemical vapor deposition (CVD) is the most viable technique for producing CNTs on a truly large scale,[4–6] which we define as being of the order of 10,000 tones per plant per year.[7] From a macro perspective, CNT synthesis via CVD is simply a dehydrogenation reaction over transition metal catalysts, for example, iron, cobalt, or nickel, where the transition metal is usually supported on a substrate, most often alumina or silica. When using an unsupported catalyst, for example, an aerosol-based technique, volatile organometallic precursor catalysts, co-fed with the carbon feedstock, decompose into nanosized metal particles, catalyzing CNT growth.[8–10] However, particle coalescence at high precursor concentrations suggests that the overall efficiency is limited to dilute conditions.[10–12] This is evidenced by the fact that quantitative measures of carbon yield are rarely reported for unsupported CVD reactions. In the two articles where yield is reported, for example, 0.5 g/h[8] and 0.1 wt % conversion of feedstock to CNTs,[13] the results do not appear to substantiate claims that the technique is suited to large-scale, economic CNT synthesis.

Although research into CNT synthesis via catalytic CVD has advanced tremendously in recent years,[14,15] much of the focus has been on the development of catalysts supported on insoluble alumina and silica substrates because their surface area, porosity, and pore structure can be easily tuned.[16] In addition, substrates stabilizes metal nanoparticles and prevent their coalescence, which enables a higher metal loading to be

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used, for example, 60 wt % relative to silica.[17] Thus, the large-scale production of high quality nanotubes via CVD is only restricted by the requirement to separate the CNTs from both the catalyst and its substrate. To achieve this, product purification is usually undertaken using multistep processes involving (i) the controlled oxidation of amorphous carbon, followed by (ii) removal of catalyst particles with mineral acids.[18] However, the removal of "insoluble" alumina or silica substrates is required, typically via physical (e.g., sedimentation and centrifugation) or chemical (e.g., dissolution in hydrofluoric acid) means. These processes have been shown to have a detrimental effect on the quality of the nanotubes.[19,20] Although much effort has been dedicated to CNT purification,[21–25] we contend that the less purification needed the better. To this end, a reduction in product purification is attainable by (i) improving the selectivity of the synthesis process, and/or, (ii) using a soluble substrate material. Consequently, researchers have revived the idea of using soluble catalyst support materials, for example, carbonate minerals, thereby negating the need for complicated and expensive purification processes.

We have previously reported that fluidized bed chemical vapor deposition (FBCVD) is potentially suited to large-scale CNT synthesis.[7] There are several advantages that arise when using fluidized beds for this reaction, namely, good heat and mass transfer and the ability to handle powders continuously.[18,26–28] Consequently, a uniform bed temperature is achievable, which in turn, is critical for the control of nanotube quality. In this work, we investigate the use of calcium carbonate ($CaCO_3$) as a substrate material for CNT synthesis using a 0.5 kg/h fluidized bed CVD reactor. $CaCO_3$ was chosen because it has been investigated previously in fixed bed reactors and is easily dissolved using dilute mineral acids at room temperature.[29–33] The ease of removal of the substrate during the purification process is especially advantageous for large-scale CNT synthesis, as the cost of purification is a major component of the overall process cost. Although the end results from fixed bed studies reported in the literature are promising, there has been no discussion concerning how Fe^{3+} (aq) hydrolysis above pH $\sim$ 3.5, was prevented. In addition, the use of <1 g of catalyst material makes it difficult to gauge whether the technique is viable for large-scale CNT synthesis.

$CaCO_3$ is regarded as a "soft and sticky" material, but even so, depending on the particle size, classical fluidization is still possible. For example, we observed that $CaCO_3$ particles with a mean diameter of 130 μm undergo bubbling fluidization at ambient temperature and pressure, confirming that $CaCO_3$ particles in this size region are "well-behaved" Geldart Group B solids. However, shear forces within the bed (e.g., particle interaction with the reactor wall and particle–particles interactions) during fluidization can lead to particle attrition with a reduction in the mean particle size and increase in the breadth of the particle size distribution. With 50-μm $CaCO_3$ particles, $CaCO_3$ behaves like Group C powders. When this occurs, the bed material ceases to fluidize normally and channels are formed, with a significant proportion of the gas bypassing the particle bed. Whilst the increase in surface area that results from particle attrition is potentially advantageous in heterogeneous reactions, the fluidization of $CaCO_3$ powders in this size region typically requires the application of external forces, for example, mechanical vibration, to ensure satisfactory mixing; this increases the complexity and cost of the reaction system considerably. Our experiments at ambient temperature and pressure suggest that the time required to attrite the $CaCO_3$ particles is significantly much greater than 12 h, which is considerably greater than typical batch processing times ($\sim$1 h) for CNT synthesis.

Despite the successful assisted fluidization of Group C powders being reported in the literature,[34–39] we feel it is more attractive to develop a catalyst that is easily fluidized, rather than to deal with the complexities of designing large scale assisted fluidized reactors, none of which are in commercial use. Applying $CaCO_3$ directly into acidic salt solutions during catalyst preparation would eventuate in acid–base reactions, leading to substrate size reduction and other implications, for example, metal (ion) hydrolysis. We have addressed these issues using a novel catalyst preparation method, loosely based on impregnation and sol-gel auto-combustion.[16,40] We also demonstrate here for the first time, the synthesis of CNTs using a soluble $CaCO_3$ substrate contained within a fluidized bed reactor.

Experimental

Supported catalyst preparation

Traditional catalyst preparation by wet impregnation usually involves mixing the substrate with a solution of the active metal (e.g., in ethanol), followed by drying and calcination. In this work, a modified wet-impregnation technique was developed that we report here for the first time. $CaCO_3$ powder with a mean particle size (d_{50}) of 130 μm supplied by Omya Australia Pty Ltd (99% purity) was used as the catalyst substrate. It was isolated from a large batch by sieving between 75 and 250 μm. When fluidized at ambient temperature and pressure, it had a minimum fluidization velocity (U_{mf}) of 0.014 $\pm$ 0.002 m/s. The catalyst materials, iron nitrate (Aldrich, 99.99%) cobalt nitrate (Aldrich 99.99%), citric acid (Science Supplies Australia, 98%), and ammonia solution (Aldrich, 28 wt %) were used as received. The $CaCO_3$-supported catalyst, containing 0.5968 mmol % iron and 1.139 mmol % cobalt, was prepared by mixing 15 ml of deionized water into 2.4 g of iron nitrate, 3.3 g of cobalt nitrate, and 3.3 g of citric acid. Ammonia solution was added dropwise until a neutral pH was obtained and then this solution was allowed to stand for 6 h, resulting in a reddish brown solution with no precipitate. 100.0 g of $CaCO_3$ was then stirred into this solution to form a dry slurry, which was then left to stand overnight. The resulting powder was calcined at 500°C between 2 and 12 h in a muffle furnace. The U_{mf} value of the resulting catalyst was similar to that of the virgin $CaCO_3$.

The prepared catalysts were characterized using scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX). Figure 1a shows a low magnification SEM image showing the typical discrete particle size of the prepared catalysts. The virgin $CaCO_3$ and the prepared catalyst exhibited similar particle size distributions, typically between 110 and 250 μm, which indicates that minimal size reduction occurred during catalyst preparation. The high magnification image in Figure 1b further shows the general

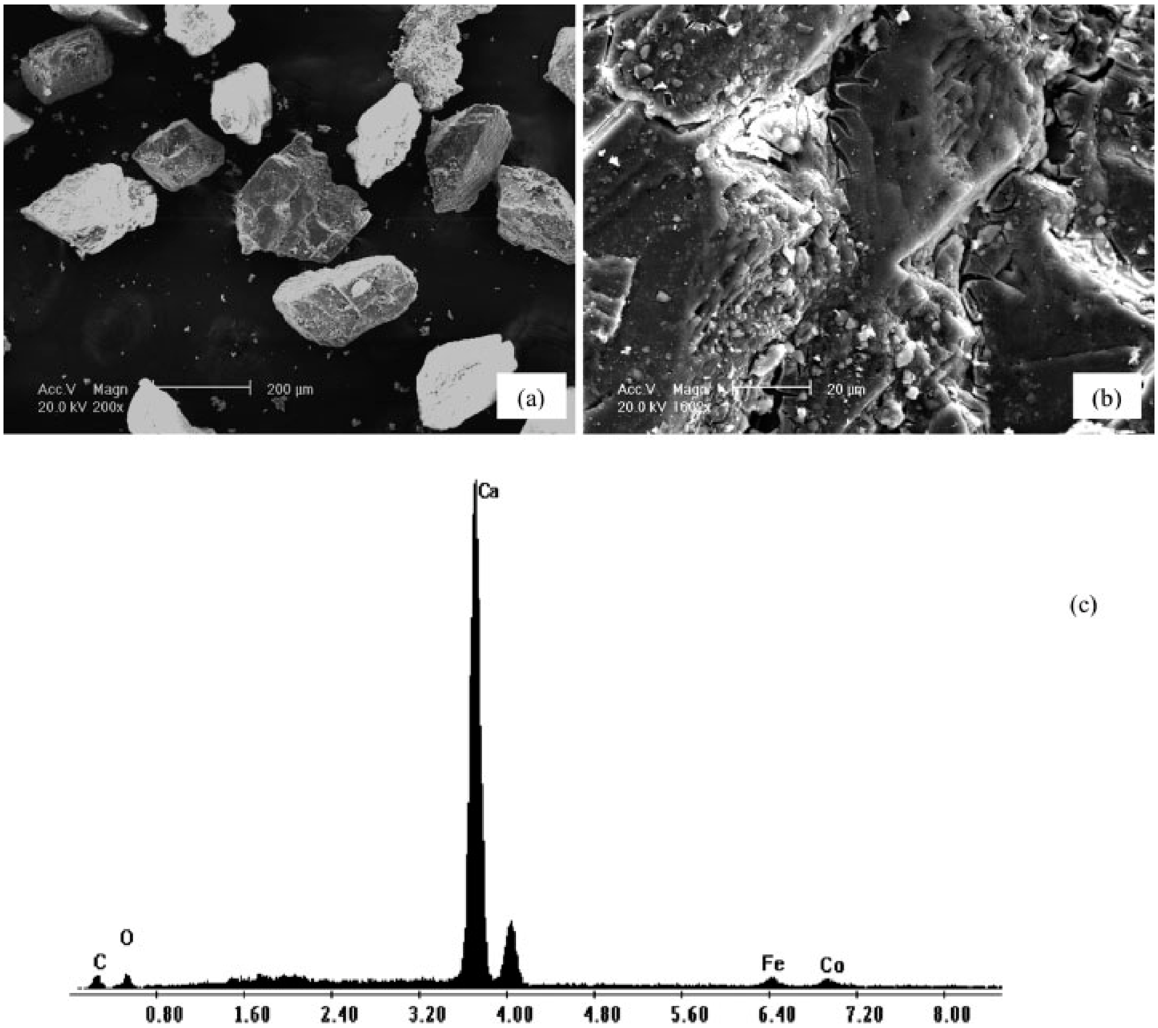

Figure 1. SEM image, high magnification image, and EDX spectrum.

(a) SEM image of the prepared $CaCO_3$ supported Fe-Co catalysts. The typical particle size range from 110 to 250 μm. (b) An enlarged image of the prepared catalysts showing the rough textural morphology of the particle surface. (c) The EDX spectrum verified that both iron and cobalt were present on the surface of the catalyst particles.

rough texture of the particle surface. EDX was used to qualify the presence of metal catalysts on the surface of the $CaCO_3$ substrate. A typical EDX spectrum, shown in Figure 1c, indicates that both iron and cobalt were present on the surface of the $CaCO_3$ support.

CNT synthesis

A reactor setup similar to that reported by Harris et al.[41] was used for all experiments. This comprised a 52-mm internal diameter, 1000-mm long cylindrical Inconel reactor, encased within a high temperature furnace. An expansion section, with an internal diameter of 100 mm and a height of 500 mm was attached to the top of the reactor to minimize fine particle elutriation. The bed temperature was measured through a sampling port 30 mm above the distributor plate. The off-gases were passed through a particle filter, followed by a water trap before being released to atmosphere. The gases, ethylene (BOC, 99.95% purity), hydrogen (BOC, 99.999%), and nitrogen (BOC, 99.9995%) were supplied to the fluidized bed using mass flow controllers.

For each experiment, 70 g of the prepared catalyst and 40 g of pure $CaCO_3$ (to make up the bulk) was loaded into the reactor under 0.047 m/s of nitrogen. The flow rate of nitrogen was gradually reduced until the superficial gas velocity was between 0.8 to 1.2 × U_{mf} (measured at ambient temperature and pressure), as the temperature was increased to 600°C. The total gas flow rate was kept constant thereafter. Reduction of the bed mixture was carried out using 50% hydrogen in nitrogen for 1 h at 600°C. The gas was then switched to pure nitrogen and purged for 10 min before changing the temperature to the desired synthesis temperature, between 600 and 850°C. The synthesis gas mixture containing ethylene, hydrogen, and nitrogen in the ratio of 50:1:450 was introduced for 60 min.

CNT characterization

The reaction products were quantitatively analyzed using thermogravimetric analysis coupled with a mass spectrometer (TGA-MS), and qualitatively via transmission electron microscopy (TEM). For TEM analysis (Philips CM120, 120 kV), ~10 mg of the as-synthesized product was ultrasonically dispersed in 50 ml of ethanol, before being loaded onto a copper TEM grid. Before TGA analysis, the as-synthesized product was treated with dilute nitric acid (between 1 and 3 M) at ambient temperature to remove the calcium carbonate/oxide substrate and some of the active metal. The mixture was then washed with distilled water until neutral pH, filtered, and dried in an oven at 45°C for 24 h before analysis. It was necessary to remove any remaining $CaCO_3$ before TGA because $CaCO_3$ thermally decomposes (to give CO_2) at ~700°C and would have therefore skewed the measurement of carbon dioxide using the mass spectrometer. The purified product was analyzed using TEM and TGA, as above.

Results and Discussion

Catalyst development

Using a soluble compound as a support material is not a new idea. Calcium carbonate[29,32] and magnesium oxide[42,43] substrates have both been investigated for CNTs synthesis in traditional, small-scale (i.e., a few grams of catalyst), fixed bed reactors. In these studies, the yield and selectivity to CNTs were similar to that synthesized using standard alumina and silica support materials, for example, Kathyayini et al.[30] reported carbon yields of greater than 300% of the active catalyst weight, with little or no amorphous carbon, when $CaCO_3$ was used as a support material. Whilst the end results from these studies are promising, the authors[29,30,32] neither elaborate on the catalyst preparation method used, which we believe is not a simple impregnation process as reported, nor do they use large quantities of catalyst (i.e., more than a few grams per experiment). Hence, it is not possible to gauge whether the technique is viable for large-scale CNT synthesis.

Wet-impregnation is typically used for catalyst preparation, especially for large-scale production because of its simplicity. However in the work of Kathyayini et al.,[30] Couteau et al.,[29] and Cheng et al.,[32] where acidic impregnation solutions were used, the calcium carbonate substrate should have quickly dissolved in the acidic solution, reducing the substrate particle size considerably. For example, using iron nitrate as the transition metal source[30] leads to an acidic solution when dissolved in either water or ethanol. This solution will react with the basic $CaCO_3$ powder as follows:

$$Ca^{2+} + 2NO_3^- \rightarrow Ca(NO_3)_2 \tag{1}$$

$$(CO_3)^{2-} + 2H^+ \rightarrow CO_2 + H_2O \tag{2}$$

$$Fe^{3+} + 3(OH)^- \rightarrow Fe(OH)_3 \tag{3}$$

$$2Fe(OH)_3 \text{ in air} \rightarrow Fe_2O_3 + 3H_2O \tag{4}$$

Depending on the ratio of iron nitrate to calcium carbonate, iron hydroxide will be precipitated when the pH of the solution rises above its critical pH of ~3.5. Iron hydroxide oxidizes relatively rapidly in air to form the oxide species. A calcination step is then applied to form the final catalyst powder. There is uncertainty in the work of Kathyayini et al.,[30] Couteau et al.,[29] and Cheng et al.[32] as to whether the iron oxide is "impregnated" onto the calcium carbonate/oxide support or formed in situ within the solution. Consequently, we envisage that it is difficult to control both the resulting substrate particle size and active metal crystal size using the wet impregnation technique detailed in these studies.[29,30,32] Possibly, a combination of impregnation and precipitation reactions occurred. More importantly, when using a fluidized bed, the substrate size reduction that will occur (as the substrate is dissolved) is detrimental, since assisted fluidization would then be required. One way to circumvent this issue, and maintain the original substrate particle size, is to prepare a complex metal solution stable at neutral pH values. To this end, we have developed a method based loosely on impregnation and sol-gel auto-combustion.[16,40]

We found that when citric acid was added to iron nitrate in ~1:1 molar ratio, the addition of ammonia solution did not precipitate iron hydroxide, even at neutral pH. This applies also to binary iron/cobalt nitrate solutions. No precipitate was observed even after leaving the solution to stand overnight. The addition of this pH neutral solution to the $CaCO_3$ substrate did not result in the release of carbon dioxide, and the particle size of the substrate was maintained. Thus, the formation of the ammonium–metal–nitrate–citrate complex is crucial in maintaining the solubility of Co^{2+}(aq) and Fe^{3+}(aq) above its critical pH without precipitating metal hydroxides and hence, maintaining its composition before the calcination and synthesis reactions.

CNT characterization and results

During CNT synthesis, the plenum pressure in the fluidized bed was measured to monitor the quality of the fluidization.[44,45] A typical pressure profile is shown in Figure 2a. Spectral analysis was conducted using Welch's method, and the spectral density is plotted in Figure 2b. This plot shows a dominant characteristic frequency of ≈0.7 Hz, indicative of a bubbling fluidization regime. These results clearly suggest that the particle bed remained sufficiently fluidized throughout the duration of an experiment.

Figure 3 shows representative TEM images of multiwalled CNTs (MWCNTs) from the raw (unpurified) bed material (a and b) and the nitric acid washed samples (c–f) synthesized using the proposed method outlined in section 2. The TEM images show that the products contain a large proportion of MWCNTs. No "large" calcium carbonate particles [substrate particles shown as black fringes in (a)] were observed in the purified sample. More importantly, this shows that the facile purification step to remove the substrate did not significantly influence the morphology of the CNTs, for example, we did not observe any cutting or dislodging of the nanotube layers. The high magnification image in (f) shows the typical tubular wall structure of MWCNTs formed. From the TEM images, we observed that the MWCNTs produced were mostly around 10–20 nm in diameter and >0.5 μm in length. Carbon nanofibers were also observed. The CNTs were strongly agglomerated, especially in the purified sample where no support was present to keep them apart.

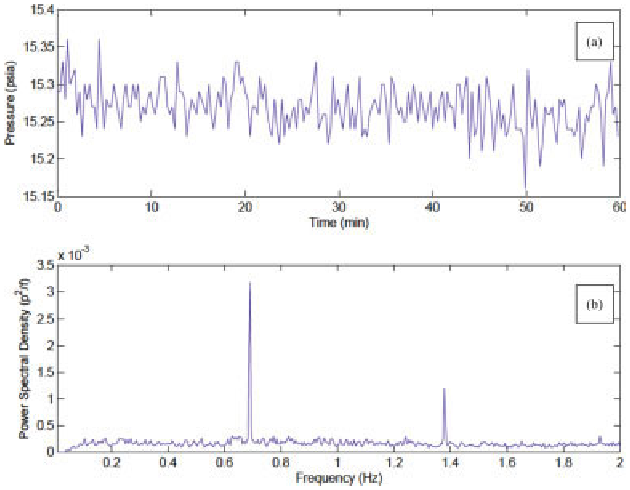

Figure 2. Pressure profile and spectral analysis.

(a) Pressure time series data measured in the plenum of the fluidized bed during CNT synthesis. (b) Fourier transform was used to measure the typical characteristic bed frequency (~0.7 Hz), indicative of the bubbling fluidization regime, that is, the bed was sufficiently fluidized. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Substrate removal is necessary before TGA analysis because of the overlapping $CaCO_3$ decomposition and CNT oxidation temperatures. Approximately 2 mg of the purified sample was heated in a platinum pan at a heating rate of 5°C/min, with 50 ml laboratory air as the purge gas. The weight loss profile obtained from TGA coupled with mass spectrometry can quantitatively determine the total amount of carbon in the sample. The thermal stability of a sample can also be observed. According to the literature, amorphous carbon typically oxidizes in air at temperatures below 400°C,[46] whereas CNTs oxidize at higher temperatures (up to 800°C).[47,48] The oxidation profile is also strongly influenced by the heating rate. Generally, higher heating rates lead to higher burn-off temperatures. In this work, we used a heating rate of 5°C/min following Arepalli et al.[49] Although the range of burn-off temperatures between 400 and 800°C is usually associated with CNTs, we note that the oxidation of carbon fibers (CNFs) typically also occurs at the lower bound. Hence, it is difficult to quantitatively distinguish between CNFs and CNTs, as is often the case in the literature.[33,50] Most often researchers use TEM images to identify the presence of CNFs in a sample. In this work, TEM analysis showed that the majority of carbon was present as CNTs and hence we have referred to carbon products exhibiting burn-off temperatures between 400 and 800°C as CNTs.

A typical weight loss profile, as a function of temperature, is shown in Figure 4. The derivative weight loss shows a main peak at ~560°C and a slight shoulder at ~630°C. No peaks below 400°C were observed, indicating that an insignificant quantity of amorphous carbon was present in the sample. Mass spectrometry verified the evolution of carbon dioxide (m/e 44) from ~350 to 680°C, which corresponded to the weight loss obtained from TGA. In conjunction with the TEM and MS analysis, the weight loss centered at 560°C can be attributed to the oxidation of MWCNTs. The peak at 630°C is possibly due to other crystalline material, for example, graphitic soot. The results in Figure 4 agree well with previously reported literature.[51]

The weight loss profile shows that ~90% of the purified sample are carbon products. About 80% weight loss corresponds to the derivative peak at 560°C, and 10% weight loss to the shoulder peak. With the assumption that no carbon material was removed from the raw sample during the purification step, that is, there was no chemical oxidation because of the dilute acid used, the selectivity to CNTs is very high, at 89%, for a fluidized bed process. The 10% residual mass is most likely metal oxides (the removal of metal catalysts encapsulated with carbon has been reported to require harsh chemical treatment)[21–25] and/or calcium oxide that were not dissolved by the purification step. The oxygen content of the cobalt and iron oxides (assumed to be in the form CoO and Fe_2O_3) is ~20 and 30%, respectively. Therefore, assuming that the residue is entirely metal oxide, the carbon yield obtained per unit mass of metal is ~1100%.

To calculate the overall carbon efficiency, defined as the total amount of carbon deposited per unit mass of catalyst used, 20.0 g of the as-synthesized product was treated to remove the $CaCO_3$ substrate as outlined. Without taking into account mass transfer losses during purification, 0.60 g of dry purified sample was obtained. On the basis of the TGA results (7.6% metal), 0.55 g of the purified product would be carbon. Assuming that there is no mass loss during the calcination step, then 0.195 g of metal catalyst is present in the sample. Hence, the overall carbon efficiency of the system is 280%. Since the carbon efficiency is less than the carbon yield, it suggests that not all the catalyst particles were active in synthesizing CNTs, for example, not all were exposed to synthesis gas, which suggests that a more vigorous fluidization regime may be required (e.g., using higher superficial gas velocities) to ensure good contact between catalyst and carbon source. More research is required to optimize this system.

Choice of substrate material

Product purification is usually undertaken using a multistep process, comprising harsh chemical and physical treatments. In this work, the use of an easily removed calcium carbonate substrate was advantageous because the mild purification conditions employed did not appear to influence the quality of the CNTs (Figures 1c–f). $CaCO_3$ was chosen primarily because it is easily dissolved in dilute nitric acid (e.g., 0.05 M) or even carbonated water (forming soluble calcium hydrogen carbonate). Work is currently in progress on the latter. It would also be possible to use other earth oxides (e.g., magnesium oxide) as the substrate material. However, in this work, calcium carbonate was chosen because magnesium oxide erodes more easily than $CaCO_3$ in a fluidized bed system, and therefore generates more fine particles in a shorter period of time.[52] In a batch fluidized bed system, this is detrimental because a significant amount of material would become entrained with the off-gas prior to the CVD reaction commencing. In addition, the fast attrition rate would lead to a bed material with a smaller average diameter, eventually leading to defluidization unless appropriate measures (and their attendant challenges) were employed. Furthermore, hav-

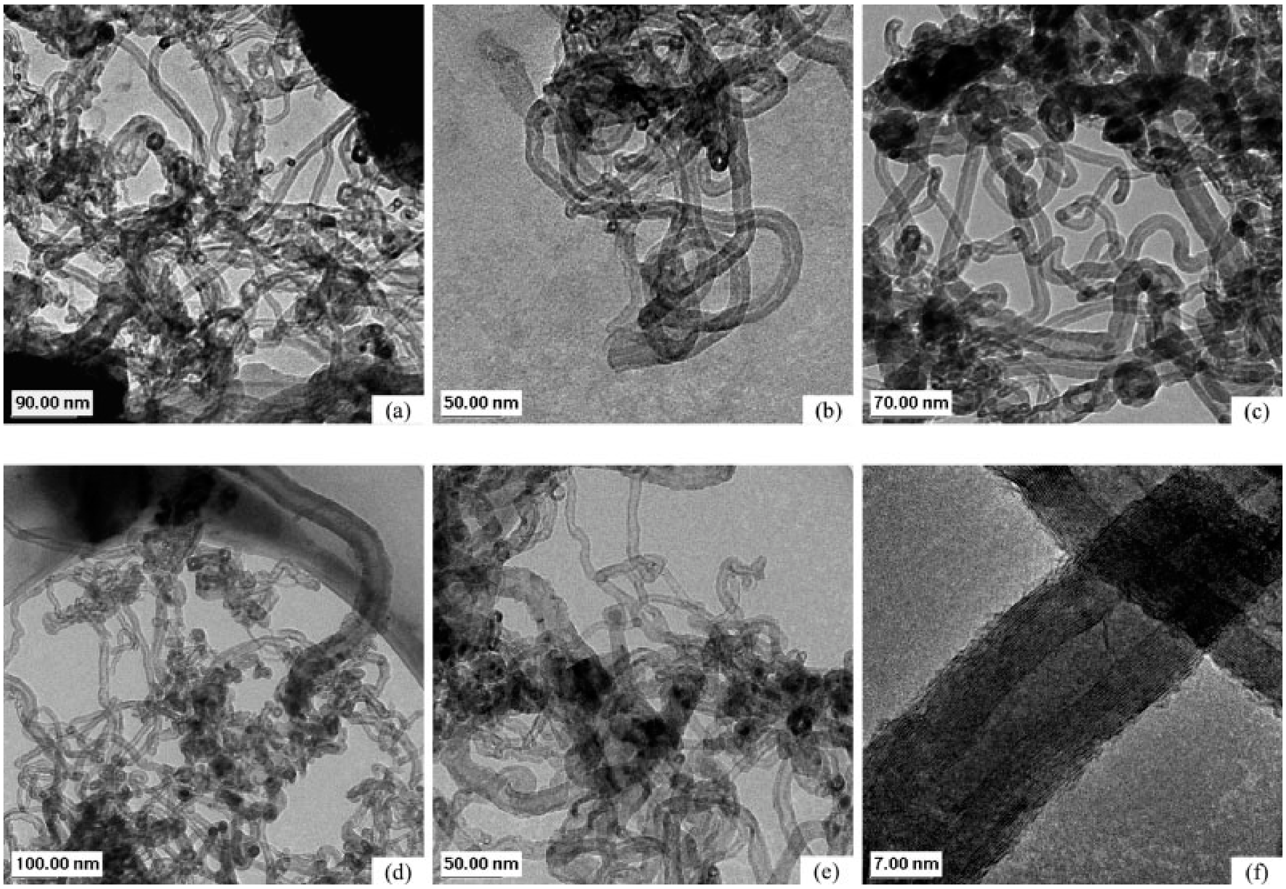

Figure 3. Representative TEM images (from top left to bottom right) showing MWCNTs synthesized using a soluble $CaCO_3$ substrate via FBCVD.

(a, b) are of as-synthesized samples whereas (c–f) have been treated with dilute HNO_3 to remove the $CaCO_3$ substrate. The images show little difference in CNT morphology between the as-synthesized and purified sample, indicating that the facile treatment removed the $CaCO_3$ substrate without significantly damaging the CNT product. (f) The high magnification image shows the typical tubular wall structure of MWCNTs formed.

ing an easily removed substrate would eliminate a bottleneck currently limiting the large-scale production of CNTs. On the basis of the preliminary results reported here, dilute HNO_3 purification gave a product containing ~90% CNTs. Consequently, we believe that the use of $CaCO_3$ as a substrate material is advantageous for large-scale CNT synthesis, especially when coupled with a suitable technique, for example, FBCVD.

Finally, it is appropriate to discuss the influence of alkaline earth metals (AAEM) on the overall reactions involved in the synthesis of CNTs via CVD. AAEMs are known to influence the rate of gasification and oxidation of carbon materials; especially calcium oxide.[52–54] The thermal decomposition of $CaCO_3$ at the temperatures used in this work will have formed calcium oxide, which may in turn, have increased the rate of carbon gasification in the reactor. It is well documented that CNTs are more thermally and chemically stable compared to amorphous carbon material.[46] Hence, there is a higher probability that amorphous carbon will gasify under the reducing environment than CNTs, leading to a higher selectivity of CNT product. Depending on the coverage of the metal catalyst on the substrate, that is, on the surface, within the pores, and the "thickness" of the catalyst, porous calcium oxide particles may provide a larger surface area for these desirable heterogeneous reactions to take place. More work is necessary to investigate the chemical reactions and catalyst relocations that occur during both the catalyst preparation and synthesis processes.

Conclusions

We have explored, for the first time, the technical viability of using $CaCO_3$ as a soluble support material for the synthesis of CNTs via FBCVD and have shown that MWCNTs of similar quality to those synthesized via traditional CVD techniques using insoluble alumina or silica substrates, can be synthesized, in bulk. On the basis of TGA results, the carbon yield per unit weight of catalyst obtained was ~1100% and the overall carbon efficiency was calculated to be 280%. Of the carbon products, ~89% was MWCNTs between 10 and 20 nm in diameter. The calcium carbonate substrate from the as-synthesized product was easily removed using dilute nitric acid at ambient temperature and pressure, without visibly affecting the morphology of the CNTs. More research is necessary to (i) understand the chemical reactions that actually take place during the synthesis process, (ii) investigate the

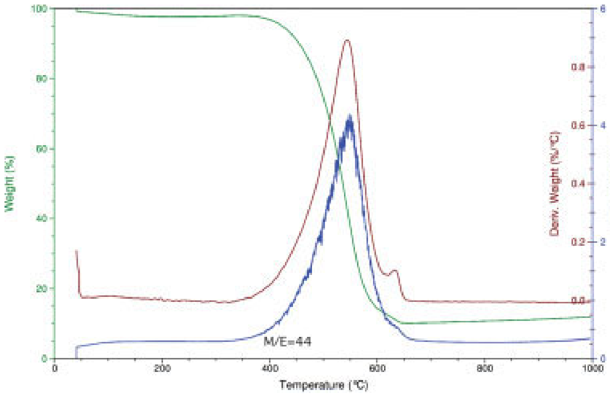

Figure 4. Weight loss and differential weight loss profiles for the dilute HNO_3 purified sample heated at 5°C/min in air.

The CNTs were synthesized on a $CaCO_3$ substrate with 1 wt % metal loading. The major derivative peak at 560°C is most likely representative of MWCNTs, while the shoulder peak is possibly due to other crystalline carbon material. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

influence of process parameters on the yield and characteristics of CNTs, and (iii) investigate the fluidization characteristics of the reactive system.

Acknowledgments

The authors are grateful to T. Romeo from NANO-MNRF Australia for assistance with electron microscopy. C.H.S. gratefully acknowledges the financial support of the Commonwealth of Australia and the University of Sydney for providing the Endeavour International Postgraduate Research Scholarship and International Postgraduate Award respectively. They thank Omya Australia Pty Ltd for providing them with the $CaCO_3$ substrate material.

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Manuscript received July 12, 2007, and revision received Nov. 9, 2007.