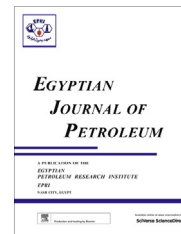




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FULL LENGTH ARTICLE

Study of the productivity of MWCNT over Fe and Fe–Co catalysts supported on SiO₂, Al₂O₃ and MgO



S.A. Shokry ^a, A.K. El Morsi ^{c,*}, M.S. Sabaa ^b, R.R. Mohamed ^b,
 H.E. El Sorogy ^a

^a Science and Technology Center of Excellence, El Salam City, Cairo, Egypt

^b Department of Chemistry, Cairo University, El Giza, Egypt

^c Department of Process Development, Egyptian Petroleum Research Institute, Egypt

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Abstract In the present study, multi-walled carbon nanotubes (MWCNT) were prepared in good quality and quantity, MWCNT were produced using the catalytic chemical vapor deposition (CCVD) technique and the carbon source was acetylene. Different catalysts were synthesized based on iron and a mixture of iron and cobalt metal supported on SiO₂, Al₂O₃ or MgO. The effect of parameters such as iron concentration, support type, bimetallic catalyst and the method of catalyst preparation has been investigated in the production of MWCNT. The quality of as-made nanotubes was investigated by the high-resolution transmission electron microscopy (HRTEM) and thermogravimetric analysis (TGA). The best yield of MWCNT was 30 times of the amount of the used catalyst. The high yield of MWCNT was gained by 40 wt.% Fe on alumina support which was prepared by the sol–gel method. TEM analysis was done for the carbon deposit, which revealed that the walls of the MWCNT were graphitized, with regular inner channel and uniform diameter. It reflected a reasonable degree of purity. The TGA showed that MWCNT was decomposed at 635 °C by a small rate indicating a high thermal stability and well crystalline formation of the produced MWCNT.

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* Corresponding author.

E-mail address: drakilakamel158@yahoo.co.uk (A.K. El Morsi).

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1. Introduction

The new techniques for large scale production of MWCNT were catalytic chemical vapor deposition using high-pressure carbon monoxide process, arc discharge [1,2], and laser ablation [3]. CCVD involved catalyst assisted decomposition of hydrocarbons (commonly benzene, ethanol, acetylene, propylene, methane, ethylene, CO, etc.) and growth of MWCNT over

the catalyst (usually transition metals such as Ni, Fe, Co, etc.) at reaction temperature ranging from 300 to 1200 °C. Good alignment [4] as well as positional control on a nanometric scale [5] could be achieved by using a CCVD.

The nature of the supporting materials such as Al₂O₃, SiO₂, or MgO and the method of dispersion of the transition metal particles could influence the production of carbon nanotubes [6]. The use of MgO minimized the formation of amorphous carbon (AC) as the main impurity [7], deterred the metal particles from aggregating, while it could be dissolved from the synthesized MWCNT using low concentration acid solutions (e.g. HCl), leaving the structural characteristics of MWCNT almost intact. Furthermore, it had been reported that the use of MgO increased the yield of the synthesized MWCNT compared to other support materials like alumina or silica [8]. On the other hand, the use of bimetallic systems of transition metal oxides gave higher yields of synthesized MWCNT, since the synergistic action of the two metals enhanced the total catalytic activity [9,10].

Because the CCVD process seemed to be the most fitted method for producing large scale MWCNT, research on new effective catalysts was essential. The methods used to prepare catalyst nanoparticles were sol-gel (SG), coreduction of precursors, impregnation, incubation, ion-exchange precipitation, ion-adsorption precipitation, reverse micelle method, physical deposition, etc. [11]. The SG method seemed to be a very appropriate way to synthesize catalyst supports because it yielded high surface area supports with high porosity, properties that facilitated the high dispersion of metal particles during the later impregnation step [6]. Furthermore, the SG method permitted metal-supported catalyst synthesis in one step. This meant that the dispersion of metal precursors took place during the support synthesis by SG [12].

At the present study, a series of Fe-catalysts were prepared trying to study the effect of different Fe concentrations and bimetal catalysts (Fe-Co) over various supports as SiO₂, Al₂O₃ and MgO on the yield and morphology of the MWCNT using acetylene as carbon source. Multi-walled carbon nanotubes were synthesized over different catalyst samples obtained by SG and impregnation methods.

2. Experimental

2.1. Preparation of support

SiO₂, Al₂O₃ and MgO were obtained from different salts. Alumina was prepared by the sol-gel method from aluminum triisopropoxide (ATIP) or through impregnation by hydrolysis of ATIP [13]. These alumina supports were known as Al₂O₃ (SG) and Al₂O₃I, respectively. Silica supports used were either prepared by sol-gel method of tetraethyl orthosilicate (TEOS) or obtained from a commercial source (silica-60). These silica supports were represented as SiO₂ (SG) and SiO₂I, respectively. MgO was either prepared from Mg(NO₃)₂; MgO(SG) or by precipitation method; MgOI.

2.2. Catalysts preparation

The catalysts were prepared using two methods. The first method used was the SG method. Silica-supported catalysts

had been prepared by a method similar to that reported in Ref. [14]. Tetraethyl orthosilicate was mixed with iron nitrate and cobalt nitrate aqueous solution and ethanol by magnetic stirring for 20 min. A few drops of concentrated hydrogen fluoride (0.4 ml) were then added, and the mixture was stirred for another 20 min. The mixture was then poured into a borosilicate glass plate. Gelation and xerogel formation processes were dried at 80 °C overnight to remove the excess of water and ethanol. After that, the substrates were fired at 450 °C for 10 h in air. Alumina-supported catalysts have been prepared as indicated in Ref. [6]. The mass ratio of Fe:Co:Al₂O₃ was 10:0:90, 40:0:60 and 6:4:90. ATIP support precursor was dissolved in water in a proportion of 100:1 and the solution was stirred for 1 h. Then, a 1.5 M aqueous ammonia solution was added under stirring until the pH of the resulting solution reached a value of 10. The metal precursor(s), previously dissolved in acetone, was then added to the first solution. The volume of acetone was calculated so that $V_{\text{acetone}} = 1.1 \times (V_{\text{water}} + V_{\text{ammonia}})$, where V_{water} was the volume of water in the Al(C₃H₇O)₃ solution and V_{ammonia} was the volume of 1.5 M ammonia solution. This final solution was stirred for 4 h at 50 °C and then aged for 15 h in a closed flask at ambient temperature. The flasks were then opened and held at ambient temperature for 3 days then dried at 150 °C for 24 h. The catalysts were then calcined in an oven with natural air circulation at 500 °C for 1 h. Each catalyst was crushed and kept in a closed flask. MgO supported catalysts was prepared following the method previously reported in Ref. [15]. A mixture of Fe(NO₃)₃, Co(NO₃)₂ and Mg(NO₃)₂ was dissolved in distilled water to prepare catalysts with a mass ratio of Fe:Co:MgO = 10:0:90, 40:0:60 and 6:4:90. Citric acid three times the weight of the catalyst, was added to the mixture that was continuously stirred and heated around 90 °C for 1 h until it became a gel. The gel was baked at 120 °C overnight and then ground into fine powder. The resulting powder was calcined at 550 °C for 2 h in air. The second method was the impregnation method. The support-catalyst mixtures were prepared by an impregnation method [16]. A calculated quantity of the metal salt was ground into a fine powder and dispersed in a few drops of water. A required amount of the support material was added to the metal salt paste and mixed well to get a homogeneous mixture of the support and the metal salt paste. This mixture was dried in an oven at 120 °C for 12 h, cooled and ground well to obtain a fine powder of the support-catalyst mixture. Hence the support-catalyst mixture was represented simply as the catalyst.

2.3. Production of nanotubes

About 0.05 g of the catalyst, spread on an alumina boat was introduced into a horizontal furnace with a diameter of 2.5 cm and a length of 60 cm preheated to 500 °C. Reduction of the catalyst was carried out by flowing hydrogen and nitrogen gas mixture in a ratio of 1:1 and a total flow rate of 80 ml/min. After 30 min the temperature was raised to 900 °C, after 10 min the furnace was cooled to 700 °C. MWCNT synthesis reactions were carried out using a mixture of nitrogen gas (100 ml/min) and acetylene gas (35 ml/min) flowing on the catalyst for 60 min. The hydrocarbon gas flow was stopped; the product on the alumina boat was cooled to room temperature while nitrogen flow was on. The weight of the carbon

deposited along with the catalyst was noted. The percentage of carbon deposit was determined in each reaction according to the following equation:

$$C\% = \frac{w_2 - w_1}{w_1} \times 100$$

where w_1 was the weight of the catalyst after reduction and w_2 the weight of the carbon deposit and the catalyst. The weight of the catalyst at the reaction temperature was less than the weight taken initially. In order to find this decrease in weight of the catalyst at the reaction temperature, about 0.05 g of exactly weighed catalyst was reduced at the temperature and time of the reaction under N_2 and H_2 flow. From the weight of the catalyst after reduction the loss of weight was calculated. The structure and morphology of the synthesized MWCNT were characterized using transmission electron microscopy (TEM). Selected MWCNT specimens were studied by high-resolution TEM (HRTEM, from JEOL, JEM2100, operated at 200 kV and equipped with a Gatan's high resolution CCD camera with special resolution reaching 0.14 nm). Thermogravimetric profiles of the as prepared MWCNT were recorded on TA instrument – Q500. Samples of approximately 5 mg in weight were heated in nitrogen atmosphere from 25 °C to 800 °C, at a rate of 10 °C/min.

3. Results and discussion

3.1. Physical appearance and the percentage yield of the as synthesized carbon deposit on different supports

Table 1 showed that the deposited carbon on catalysts C2, C5, C7, C8, C9, C10 and C12 appeared spongy and that on catalysts C6 and C11 showed soft and spongy material. The soft and spongy material indicated a high yield of carbon nanotubes. The physical appearance of the deposited carbon on catalysts C1, C3 and C4 was fine powder. This indicated a low yield of carbon nanotubes. In general, it was observed that when the carbon deposit appeared spongy or soft and spongy, the used catalyst was active for MWCNT production. These results are consistent with previous findings [16].

Reaction conditions: acetylene flow 35 ml/min; nitrogen flow 100 ml/min; time of the reaction 60 min and reaction temperature 700 °C.

3.2. Parameters affect the yield of carbon nanotubes

As shown in Table 1, carbon was deposited on all surfaces of the catalysts, but the yield was distinctly different. The following sections describe the effects of the used twelve catalysts that were selected according to type of support, iron concentration, bimetallic and method of preparation of catalyst on the yield of MWCNT.

3.2.1. Effect of substrate type

The initial observation indicated that the support played an important role in the catalytic activity of metal particles deposited on it. One of the major factors influencing the activity was the nature of distribution of the metal(s) particles on the support. The state of the distribution of metal(s) on a support depended on the type of metal–support interaction which in turn depended on the nature of the support. An attempt was

executed to find out the effect of the nature of the support on the catalytic activity of metal(s) in the production of nanotubes. The results in Table 1 indicated that metals supported on MgO have higher catalytic activity than those supported on SiO_2 and Al_2O_3 . According to previous results [17], the growing of MWCNT on a metal particle mainly depended on the dispersion of the metal particles on the support. This indicates a better mixing and homogeneous distribution of metals on MgO than that on SiO_2 or Al_2O_3 . Thus MgO support seems to be the best candidate as a support for 10 wt.% metal(s) catalyst preparation.

3.2.2. Effect of iron catalyst concentration

When we compared the MWCNT grown by using alumina and silica supports with different iron concentrations (Table 1), it was evident that the less iron present the lower the carbon deposited. The percentage of carbon deposited on alumina and silica was directly proportional to the catalyst concentration. Catalysts loaded with 40 wt.% Fe on alumina exhibited the highest carbon deposit (more than 2900%) as detailed in Table 1. The lower carbon deposition yielded on Cata-1 and Cata-5 was due to the lack of sufficient Fe clusters to catalyze the growth of the MWCNT, whereas at higher concentrations of iron, the enhancement of carbon yield was caused by the higher catalytic activity of the larger Fe particles.

It was also observed that the lower activity of higher concentration of Fe supported on MgO support indicated that the size of the metal particles produced was somewhat larger than the average nanometer scale clusters [18] required for producing MWCNT. The lower concentration of Fe had good distribution especially on MgO support.

Therefore, higher Fe concentrations provide better conditions for the growth of MWCNT on alumina and silica supports. Fe particle catalysts and the alumina support were probably behaving in a symbiotic manner for the increase in yield of the MWCNT.

3.2.3. Effect of bimetallic catalyst

The results represented in Table 1 showed that the yield of MWCNT of bimetallic catalysts, Cata-3 and Cata-7, were less than that of monometallic catalysts, Cata-1 and Cata-5, respectively. Iron alone either on alumina or silica showed higher activity than Fe/Co catalyst on alumina or silica.

The deposited MWCNT obtained by Cata-11 (bimetallic catalyst) is higher than that obtained by Cata-9 (monometallic catalyst). So, the addition of Co significantly enhanced the catalytic activity of Fe on MgO support for the growth of MWCNT. The major factor influencing the activity of bimetallic catalyst toward carbon deposition is the highly dispersed metal particles along with the flattening of the MgO phase [19]. However, the activity of bimetallic, Fe–Co, catalysts on MgO support for the growth of MWCNT was much better than that of bimetallic on alumina and silica supports. This provides an appreciation of the selectivity of the catalyst–support toward carbon nanotube formation.

3.2.4. Effect of method of catalyst preparation

All the catalysts were reduced before the passing of the carbon source. The reduction of iron oxide phase to metallic iron was optimum and contributed to the efficient growth of MWCNT. It was evident that the method of preparation of the catalyst

Table 1 The catalysts used, the physical appearance and yield (wt.%) of the as synthesized carbon deposit in CCVD of acetylene.

Symbol	Catalyst	Method of catalyst preparation	Appearance of the carbon deposit	Weight % yield of carbon deposit	Density of MWCNT deposit
Cata-1	(10% Fe-SiO ₂)	Sol-gel	Fine powder	279	Low
Cata-2	(40% Fe-SiO ₂)	Sol-gel	Spongy	759	Good
Cata-3	(6% Fe/4% Co-SiO ₂)	Sol-gel	Fine powder	136	Low
Cata-4	(10% Fe-SiO ₂)	Impregnation	Fine powder	253	Low
Cata-5	(10% Fe-Al ₂ O ₃)	Sol-gel	Spongy	819	Good
Cata-6	(40% Fe-Al ₂ O ₃)	Sol-gel	Soft and very spongy	2974	Very good
Cata-7	(6% Fe/4% Co-Al ₂ O ₃)	Sol-gel	Spongy	764	Good
Cata-8	(10% Fe-Al ₂ O ₃)	Impregnation	Spongy	571	Good
Cata-9	(10% Fe-MgO)	Sol-gel	Very spongy	1393	Very good
Cata-10	(40% Fe-MgO)	Sol-gel	Spongy	646	Good
Cata-11	(6% Fe/4% Co-MgO)	Sol-gel	Soft and very spongy	2552	Very good
Cata-12	(10% Fe-MgO)	Impregnation	Very spongy	1056	Very good

Table 2 The diameter of the carbon nanotubes obtained by different catalysts.

	Cata-1	Cata-2	Cata-5	Cata-6	Cata-9	Cata-10
Mean inner diameter	11	8.3	5.4	5.8	8.5	7.7
Mean outer diameter	35	30.3	25.7	36.3	27.8	30
No. of walls	42	39	36	54	34	39

and hence its nature greatly influenced the yield of the carbon deposit. MWCNT growth on Cata-4, Cata-8 and Cata-12 compared to Cata-1, Cata-5 and Cata-9 showed a visible decrease in carbon yield. Catalysts obtained by the sol-gel method showed higher activity in the formation of NTs than that obtained by the impregnation method. This was probably due to the fact that the sol-gel method resulted in the distribution of metal ions in a highly homogeneous manner [18]. Lower activity of SiO₂I and Al₂O₃I compared to MgOI supported metal indicated that the size of the metal particles produced in the former as somewhat larger than the average.

3.3. TEM analysis

TEM analysis of the as synthesized carbon deposit from different catalysts confirmed our preliminary observations that all the catalysts were active in the formation of MWCNT when using the CCVD method. HRTEM images indicated that the MWCNT obtained by the different catalysts were multi-walled. Taking into consideration, 0.34 nm as the interlayer spacing, the diameter of carbon atom (0.22 nm), the thickness of MWCNT, the average number of walls of the carbon nanotubes was calculated previously [20–23] and number of walls of the synthesized carbon nanotubes was summarized at Table 2.

The diameter of the carbon nanotubes greatly depends on the size of metal particles. Large inner diameter of MWCNT as shown in Table 2 attributed to that some nanoparticles of catalysts had agglomerated in the reduction process.

The quality of the tubes formed differed from one another to a large extent. In general, the MWCNT were not straight and they were usually more or less covered with AC on the outer layer. The observations deduced from TEM on carbon nanotubes growth using 10 and 40 wt.% Fe as catalysts were summarized as follows:

Fig. 1(a) indicated that most of MWCNT obtained by Cata-1 (CNT-1) were closed at the end with a fullerene-like

structure but there are no iron nanoparticles encapsulated in that end. This is the Yarmulke mechanism proposed by Dai et al. [24] and indicated that the base-growth mode prevails in agreement with a strong interaction between the catalyst particle and the support. This strong interaction is due to the chemical affinity between the iron nanoparticle precursor and the SiO₂ matrix. The outer region (i.e. tube wall) is constructed with many layers of carbon with graphite-like platelets (multi-walls), external and internal diameters values are summarized in Table 2. Multi-wall carbon nanotubes show “bamboo-like” defects [25] associated with the inner shells. These results attributed to a strong interaction between the catalyst particle and the support, therefore the bamboo-like structure was frequently observed for the MWCNT formed by Yarmulke mechanism [26]. This phenomenon can be clearly seen in Fig. 1(b). The carbon nanotubes that were obtained by Cata-2 (CNT-2) resulted in ramification as shown in Fig. 1(c), the length reached upto several microns and the bamboo-structure was absent in this sample.

The carbon nanotubes obtained by Cata-5 (CNT-5) and -6 (CNT-6) are straight or curved with no embranchments (Fig. 2(a) and (b)). Both of their walls are well graphitized and the inner channel is very regular (nanotubes are of regular turbostratic structure). The walls of CNT-5 were mostly crystalline with a very low content of AC adhered on the external surface to provide high purity. The outer diameter of CNT-6 (high Fe catalyst concentration) was higher than that obtained by lower Fe concentration (CNT-5) [27].

A closer examination of nanotubes' structure indicates that non-crystalline carbon is deposited on the nanotube's surface in the form of nanoparticles that cover the surface. As the catalyst concentration is increased; however, many catalyst particles grow to exceed the threshold for MWCNT formation, leading to increased non-MWCNT contamination in the sample [28]. Their appearance is darker in the picture as seen circled in Fig. 2(b).

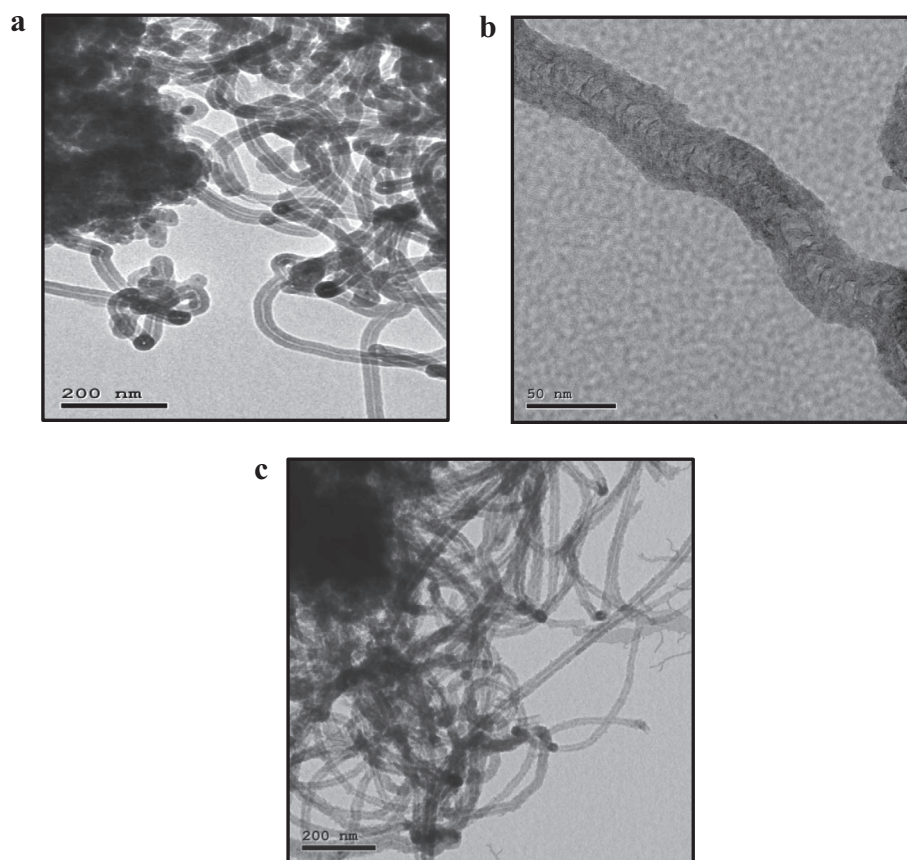


Figure 1 TEM images of MWCNT produced on SiO_2 supported catalysts (a) Cata-1 and (b) Cata-2.

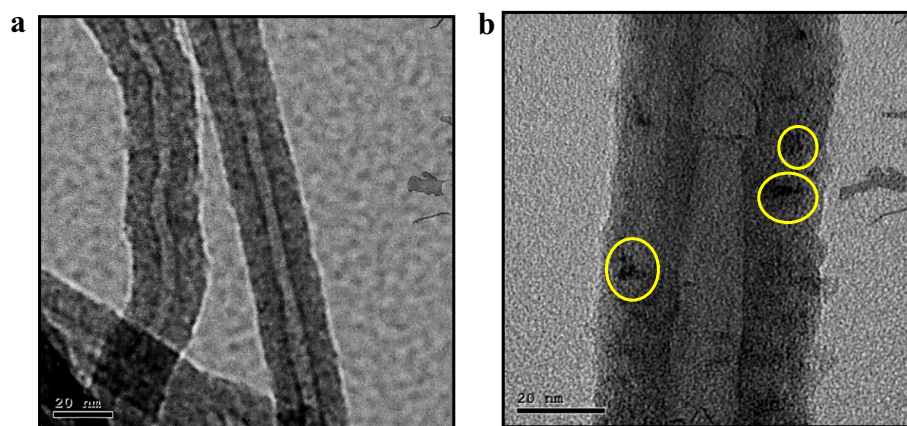


Figure 2 TEM images of MWCNT produced on Al_2O_3 supported catalysts (a) Cata-5 and (b) Cata-6.

In general, the MWCNT grown on Cata-9 (CNT-9) are not straight and have good graphitic walls as shown in Fig. 3(a). There were small defects presenting at the shells and the central core, which may result from the lower catalyst concentration with the CCVD method [28]. MWCNT grown on the catalyst surface of Cata-10 (CNT-10) are closed at the end but there are no iron nanoparticles encapsulated in that end (base-growth mode). As shown in Fig. 3(b) MWCNT appeared with regular inner channels (turbostratic structure) with a wide range of outer diameter. CNT-10 has a very low amount of AC,

indicating reasonable purity and MWNTs have uniform diameter but are curved because of the longer length.

3.4. TGA characterization

From the TGA curve the degradation temperature of MWCNT could be defined and measured precisely providing a good estimation of their overall quality. Higher degradation temperatures are always associated with purer, less defective and highly crystalline MWCNT [29]. The TGA thermograms

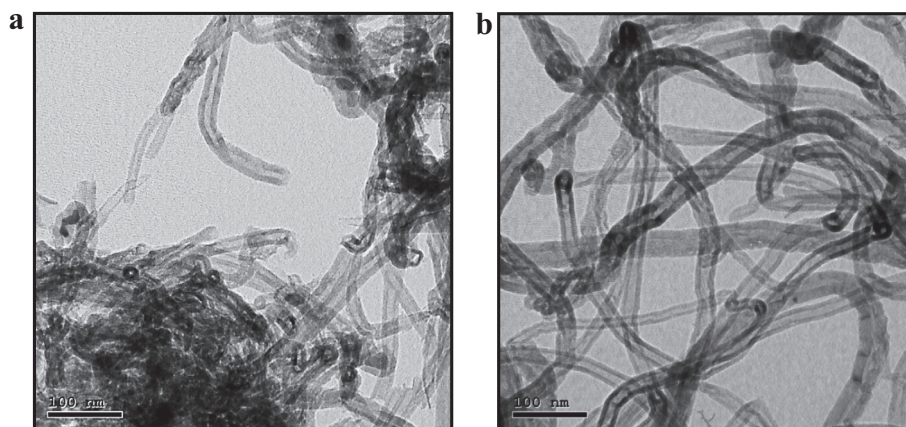


Figure 3 TEM images of MWCNT produced on MgO supported catalysts (a) Cata-9 and (b) Cata-10.

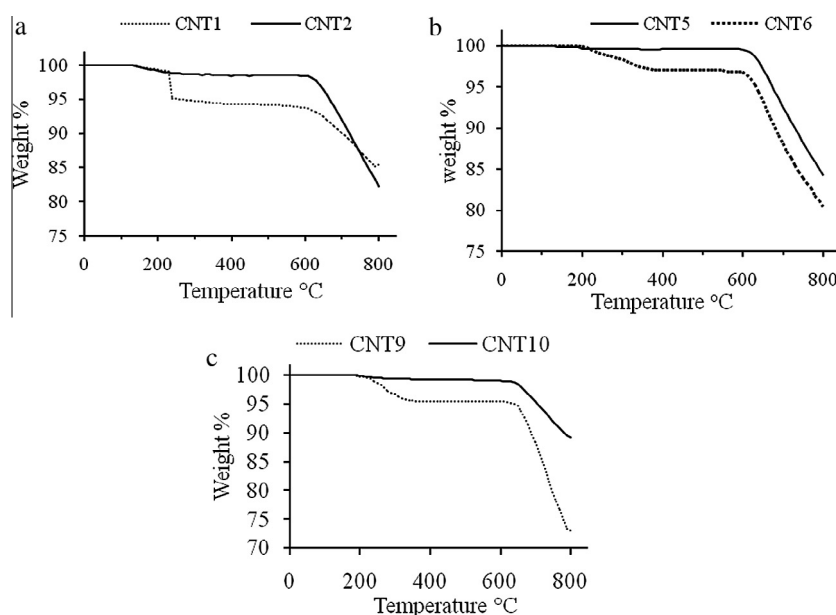


Figure 4 TGA of MWCNT produced on SiO₂ supported catalysts (a) Cata-1 and (b) Cata-2.

are divided into two stages, the first (lower temperature stage) corresponds to the degradation of AC and the second broad degradations (higher temperature stage) related to the thermal decomposition of the MWCNT. TGA results estimate the effect of catalyst loading on the thermal stability of the MWCNT and the amount of AC. The TGA results indicated that the amorphous carbon of CNT-1, CNT-2, CNT-9 and CNT-10 was 5.01, 0.74, 4.5 and 0.71 wt.%, respectively. A low amount of amorphous carbon was formed on the surface of the MWCNT grown on high metal concentrations that agrees with TEM analysis. As shown in Fig. 4(b), the AC of MWCNT grown on the Cata-5 (CNT-5) was of small significance (about 0.3 wt.%). The MWCNT grown on the Cata-10 (CNT-10) that was decomposed at 635 °C at a small rate indicates that the MWCNT grown over this catalyst present the highest resistance to decomposition, since the recorded decomposition temperatures were 635 °C. The higher thermal stability of CNT-10 implies extended crystallinity in the

synthesized MWCNT. The TGA results further indicated that pure and well-crystallized MWCNT were grown on Cata-10.

4. Conclusion

It is concluded from the gained results that: except MgO support, the catalytic decomposition of acetylene increased when the concentration of Fe is raised from 10% to 40%. A comparison of catalytic activity of Fe and Fe/Co supported on SiO₂, Al₂O₃ or MgO (supports obtained by different methods) indicated that the best yield of MWNTs is resulted on alumina prepared by the sol-gel method and containing 40 wt.% Fe. This indicates that the method of preparation of the catalyst and its nature greatly influenced the yield of the carbon deposit. Analysis of the carbon deposit by TEM indicated that the walls of CNT-6 and CNT-10 are well graphitized, regular inner channels and uniform diameter (turbostratic structure) and CNT-10 has a very low amount of AC, indicating reasonable purity.

TGA showed that CNT-10 has a small amount of AC and MWCNT was decomposed at the highest temperature at a small rate indicating well-crystallized MWCNT.

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