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Evaluation of catalyst ball-milling process on growth and diameter of carbon nanotubes on iron nanoparticles

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ABSTRACT

In this study, we describe the growth of carbon nanotubes on commercial iron nanoparticles without carbon shell (Fe (nm), size <60 nm) andiron nanoparticles with carbon shell (Fe* (nm), size <60 nm) as catalysts by chemical vapour deposition method. In order to investigation of supports effects, preparation of catalyst nanopowders (Fe* (nm)/Al_2O_3 and Fe* (nm)/MgO) was carried out by mixing commercial Fe* nanoparticles (as catalyst) with Al_2O_3 and MgO powders (as supports)by using ball-milling method. The results show in spite of the fact that ball-milling process can have negative effects on diameter and morphology of synthesized CNTs at 925 ˚C, but it could increase the range of growth temperature from 865 ˚C to 975 ˚C.

Keywords: *Ball-milling; Carbon nanotubes; Catalyst nanoparticles; Chemical vapor deposition.*

INTRODUCTION

In recent years, carbon nanotubes (CNTs) were investigated extensively because of their several unique properties, such as chemical stability, favorable thermal conductivity, high aspect ratio and excellent mechanical strength[1, 2].They have many potential applications such as catalysis, composites, batteries and field emission display sensors [3, 4]. Many experiments were performed toward controlling the growth of carbon nanotubes [5-7]. Among the conventional methods in the synthesis of carbon nanotubes, chemical vapour deposition (CVD) method is more appropriate due to its low cost, large quantity, good quality, and high degree of control of the CNTs can be obtained by the catalytic CVD techniques. In CVD method, various parameters can be effective on the growth characteristics of the nanotubes. Studies shows that in synthesis of CNTs by CVD method, a variety of porous supports such as MgO, Al_2O_3, SiO_2 and zeolite can be used [8-10].

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Depending on the catalysts preparation process, the interaction between supports and catalyst nanoparticles can influenced by parameters such as type of catalyst and support, shape and particle size, which are playing important roles in nanotube growth process [8, 11]. Interactions between catalyst nanoparticles and supports can be either chemical or physical. In the case of chemical process, the interaction between catalyst particles and supports occurs during the process of catalyst formation [12]. However, physical interactions, the catalyst particle size can be controlled by the presence of porosity on the supports [9]. Thus to achieve proper results, control over the nanotube growth process would be very important.

According to above points, in this study we describe the effect of ball- milling process on Fe* nanoparticles, supported by MgO andAl_2O_3 powders, on growth temperature, diameter and morphology of carbon nanotubes. The aim was to enhance CNTs productivity and controlling their growth temperature and diameters. The prepared catalyst and carbon nanotubes were characterized by X-ray diffraction (XRD, GBC, Cu (K_α) radiation, $\lambda = 1.54$ Å), and the resulting carbon nanotubes were characterized by scanning electron microscopy (SEM, Philips, MAG 15kV, 30000X, SE) and transmission electron microscopy (TEM, LEO 912 AB, 120 KV).

EXPERIMENTAL

Materials

In this research, the following materials were used: MgO and Al_2O_3 powders as a support raw material, iron nanoparticles (Merck, capsulated with carbon shell, purity>99%) with dimensions less than 60 nm and average size 26 nm. CVD system equipped with ethylene as feed gas and Ar as carrier gases for synthesis of CNTs.

Preparations of Catalyst nanoparticles

Fe* (nm)/Al_2O_3 and Fe* (nm)/MgO nanopowders, was carried out by direct combination of commercial iron nanoparticles with Al_2O_3 and MgO powders. Commercial iron nanoparticles (Fe (nm) and Fe* (nm)) with dimension of less than 60 nm have been used as catalyst. For Preparing Fe* (nm) /supports, commercial iron nanoparticles with 10% was mixed with support powder ethanol under ultrasonication process for 15 minutes. To achieve a uniform distribution and smaller size of catalyst nanoparticles, the dried powders were ball-milled with 500 rev per min in an iron jar, for 2h.The ball radius was 2 mm and the weight ratio of ball to powders was 1/5.

Synthesis of carbon nanotubes

Carbon nanotubes were synthesized by the catalytic decomposition of ethylene at different temperatures (865°C– 975°C) over catalysts, using CVD method at atmospheric pressure. While keeping constant Ar carrier gas flowing at 150 sccm in the quartz reaction tube (120 cm length, 5 cm diameter), the temperature of the furnace was raised to the suggested value for the growth of carbon nanotubes. Then 500 mg of catalyst powder was dispersed uniformly on a quartz boat, placed directly in the middle of the furnace. Synthesis of carbon nanotubes was carried out by pyrolysis of ethylene feed (flow rate of 15 sccm) for 20 min. After synthesis of carbon nanotubes, the reactor was cooled down to room temperature under Argon atmospheric pressure. In order to remove some carbon impurity, the as-produced carbon nanotubes were heated in a horizontal furnace under air flow at 480 ºC for 2 h.

RESULTS AND DISCUSSION

In order to obtain the optimum temperature for growth of carbon nanotubes, the experiments were done on iron nanoparticles without any carbon shell (Fe (nm)) at different temperatures from 865 °C to 975 °C. Figure 1 shows the SEM images of aggregated commercial iron nanoparticles without carbon shell (Figure 1a),and carbon products at three different temperatures of 865 °C, 925 °C and 975 °C(Figures 1b, 1c and 1d). At 865 °C, all products were carbon impurities which covered the catalyst's surface and no carbon nanotubes were seen in scanning electron microscopy images (Figure 1b). This indicates that Fe nanoparticles are not active for growth of carbon nanotubes at 865 °C. The existence of carbon nanotubes in Figure 1c, illustrates that 925 °C is the appropriate temperature for catalytic activity of Fe(nm) for decomposition of ethylene molecules [13]. The produced carbon nanotubes have long length and are intervened together. The diameter distribution of carbon nanotubes is in the range of 60-130 nm and the average diameter of them is about 90 nm. By increasing temperature to 975 °C (Figure 1d), however, the amount of synthesized carbon nanotubes are low and most products are carbon impurities. An important reason why nanotubes are not grows in this temperature is that catalyst nanoparticles are adhered together and form bigger clusters. As the diameter of iron catalyst particles increase, the catalytic activity reduces and their capsulation by carbon atoms results in amorphous carbon formation from pyrolysis of hydrocarbon gas. Another reason would be the fact that most of the thermal decomposition of ethylene gas is composed of soot which prevents the diffusion of carbon molecules into the surface of catalyst for growth of CNTs [14].

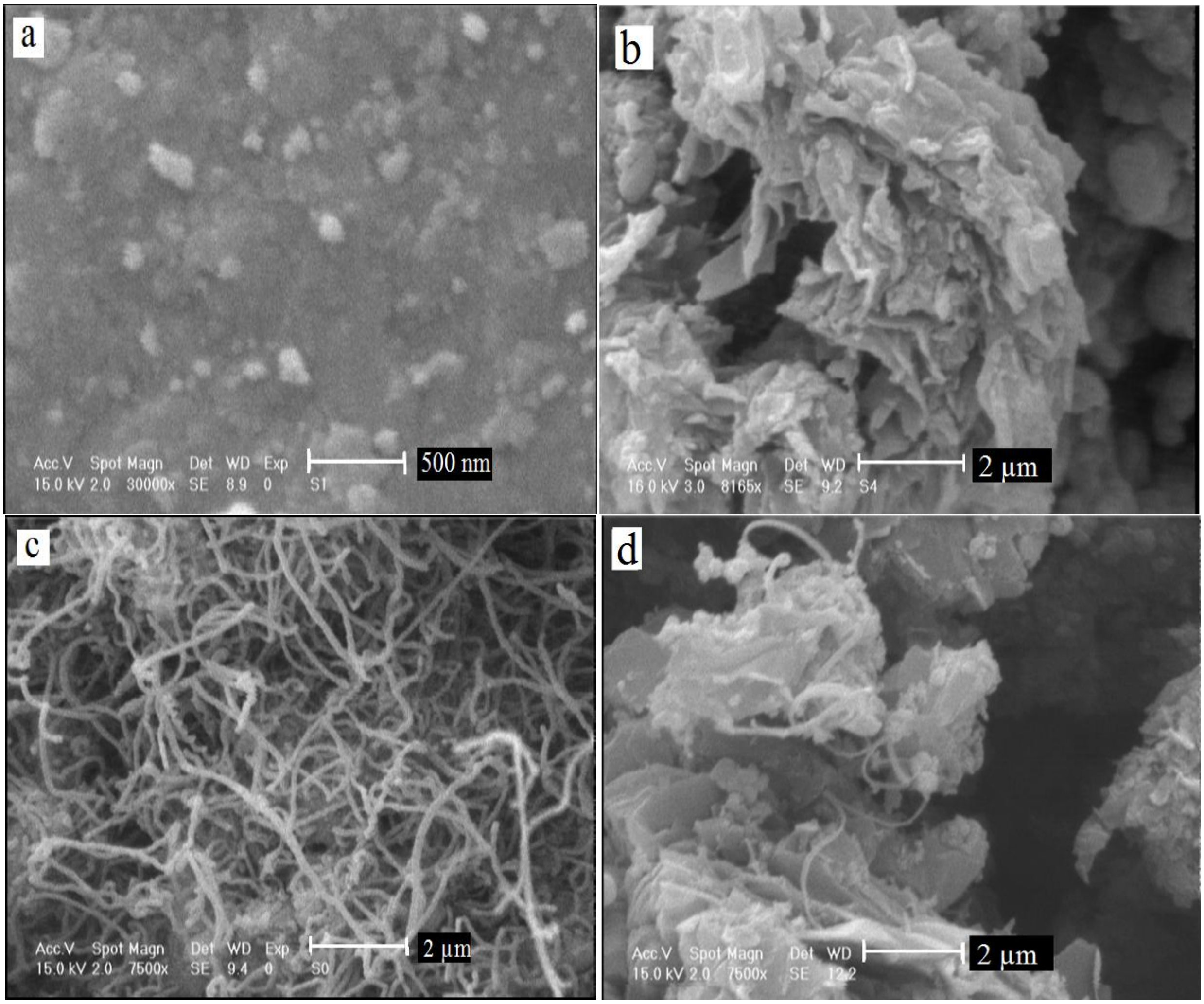

Fig. 1. SEM images of;commercial iron nanoparticles without carbon shell (a), catalytic decomposition of ethylene on Fe nanoparticles without used supports at 865˚C(b), 925˚C (c) and975˚C (d).

In Figure 2, the TEM image of CNTs grown on Fe (nm)at 925˚C,and their histogram diameter distribution are show. Their quality was high and they showed smooth walls with low impurity on sidewall. CNTs morphology seemed to be mainly different along their length. In addition, most of CNTs (%70) have diameter in range of 80 nm -100 nm (Figure 2b).

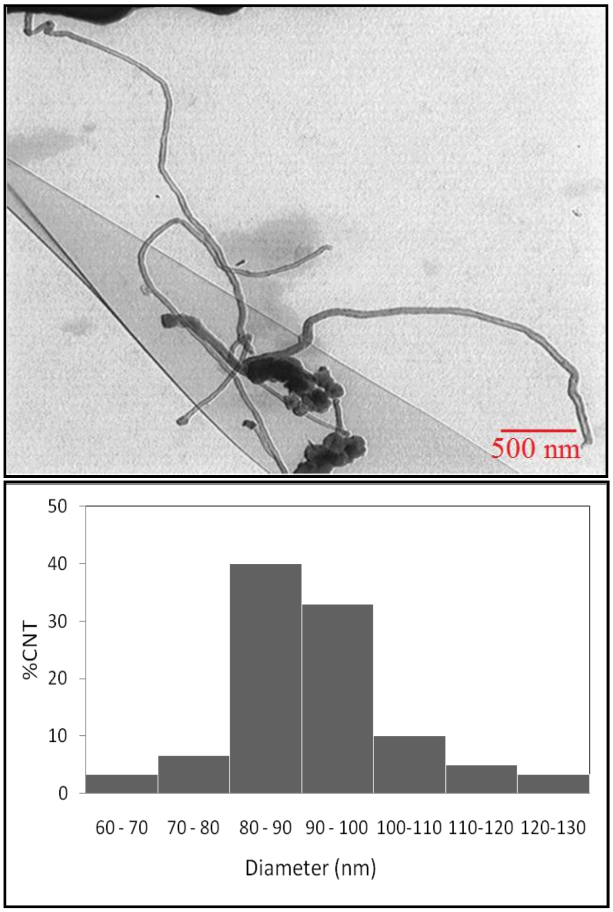

Fig. 2. TEM image and histogram of diameters distributionof CNTs grown on Fe (nm) at 925˚C.

In order to have a precise study on synthesis process of carbon nanotubes, X-Ray diffraction patterns were provided from conventional Fe nanoparticles and synthesized nanotubes (Figure 3). According to the ones from Fe nanoparticles before nanotubes synthesis (Figure 3a), intense picks are related to pure commercial iron nanoparticles. Picks with different intensities in SEM after synthesis of nanotubes are also observable,(Figure 3b)which are relate to X-Ray diffraction from iron carbide nanoparticles and graphite sheets regarding nanotubular structures. The diffraction patterns normally present sharp, graphitic (0 0 2) reflections at about 26.5˚, indicating a high degree of structural order of CNTs. The other peaks are always broad which might contain the overlapped diffractions of C structure, or possible are related to iron carbide with crystal structure of bcc and chemical formula of Fe_3C [15,16].The Fe(nm) catalyst used for the synthesis of nanotubes is the reason for existence of picks in X-Ray diffraction regarding iron carbides that can be explained by VLS mechanism. According to this mechanism for nucleation and growth of nanotubes, after decomposition of ethylene at surface of Fe nanoparticles, diffusion of carbon atoms into catalyst nanoparticles and metal carbide formation until saturation is necessary [17].

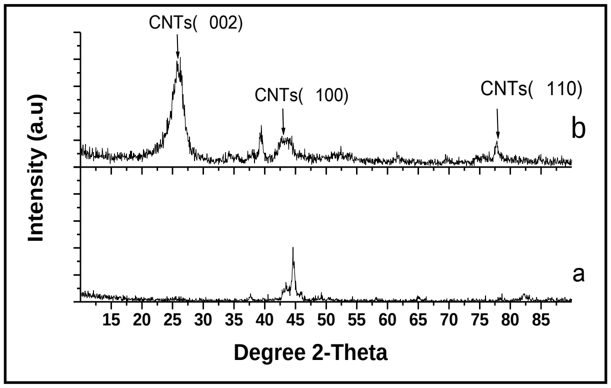

Fig. 3. XRD Patterns of Fe nanoparticles powder without any support (a), and CNTs synthesized on Fe catalyst in 925 ˚C (b).

In the next experiment, we used commercial iron nanoparticles encapsulated with carbon shell (Fe* (nm)) as catalyst for synthesis of carbon nanotubes. Figure 4, shows the SEM images of catalytic decomposition of ethylene on Fe* (nm) in 925˚Cwithout support.SEM images reveal that in synthesis which Fe* (nm) catalyst is used, there are no carbon nanotubes. This is because of the presence of carbon shell on the surface of iron nanoparticles. This carbon shell prevents hydrocarbon molecules reach the surface of catalyst. Therefore, catalytic decomposition and diffusion of carbon atoms into catalyst and growth of CNTs do not occur.

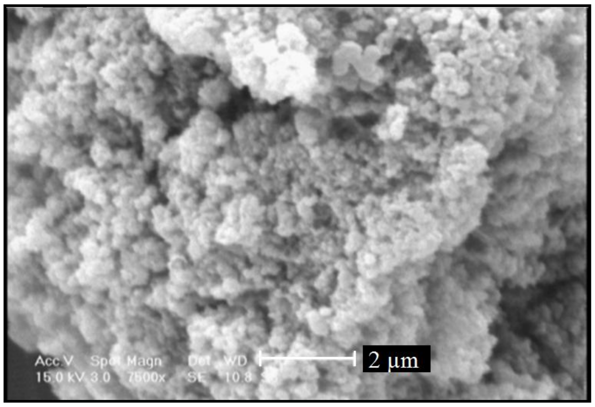

Fig. 4. Synthesis of carbon soot on surface of Fe* (nm).

In the following, to verify the effect of support on catalyst activity, synthesis of nanotube can be re-examined by using alumina and magnesium oxide as supports. For Fe* (nm)/Al_2O_3 and Fe* (nm)/MgO catalysts, scanning electron microscopy (Figures 5, 6) studies reveal that, carbon nanotubes were produced from Fe* (nm)/Al_2O_3 and Fe* (nm)/MgO, prepared under experimental conditions cited above. In 865 ˚C, with exception of some tubular structure, most products are carbon impurities that cover the surface of catalyst nanoparticles (Figures 5a and 6a). This result indicates that, Fe* nanoparticles supported by Al_2O_3 and MgO, are not active for growth of carbon nanotubes at 865 ˚C. However, synthesis of carbon nanotubes on Fe* (nm)/Al_2O_3 and Fe* (nm)/MgO catalysts happened at 925 ˚C (Figures. 5b and 6b). Comparing these results with those synthesized on Fe* (nm) without any support, the change of catalyst activity of Fe* (nm) after ball-milling process can be explained. In fact, ball-milling process might be able to remove the carbon shell from surface of Fe* (nm) nanoparticles by collision of balls with high kinetic energy. Therefore, by removing carbon shell, hydrocarbon molecules can reach the surface of catalyst, catalytic decomposition and diffusion of carbon atoms which then leads to carbon nanotubes growth happens, respectively. By increasing temperature to 975 ˚C (Figures 5c and 6c), however, for Fe* (nm)/MgO catalyst, the tubular products are small with large diameters, they are large with wide distributions when grown on Fe* (nm)/Al_2O_3. Comparing nanotubes grown at 925 ˚C with those at 975 ˚C, it can be concluded that lower temperature corresponds to thinner and less impure structures, while high temperatures result in thicker diameter carbon nanotubes with more impurities. This was due to the increase in size of nanoparticles and faster reaction rate. The amount of carbon nanotubes reduced attributed to the catalyst partial surface deactivation. These results are in accordance with those reported by other researchers [14, 18].

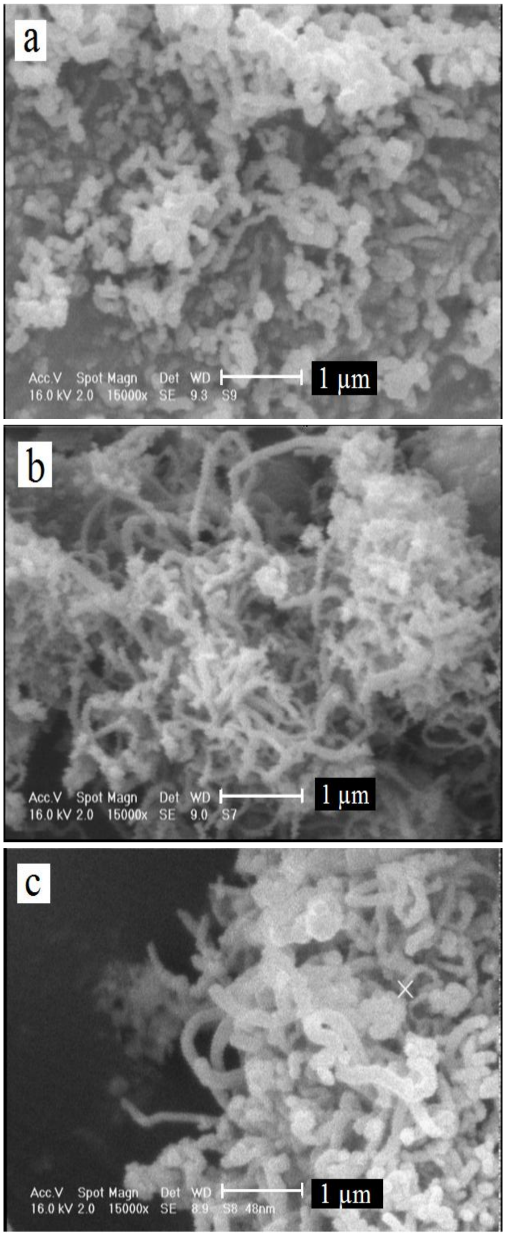

Fig. 5. SEM images of synthesized carbon nanotubes on Fe*(nm)/Al_2O_3 under different growth temperatures; a) 865°C, b) 925°C,and c) 975°C.

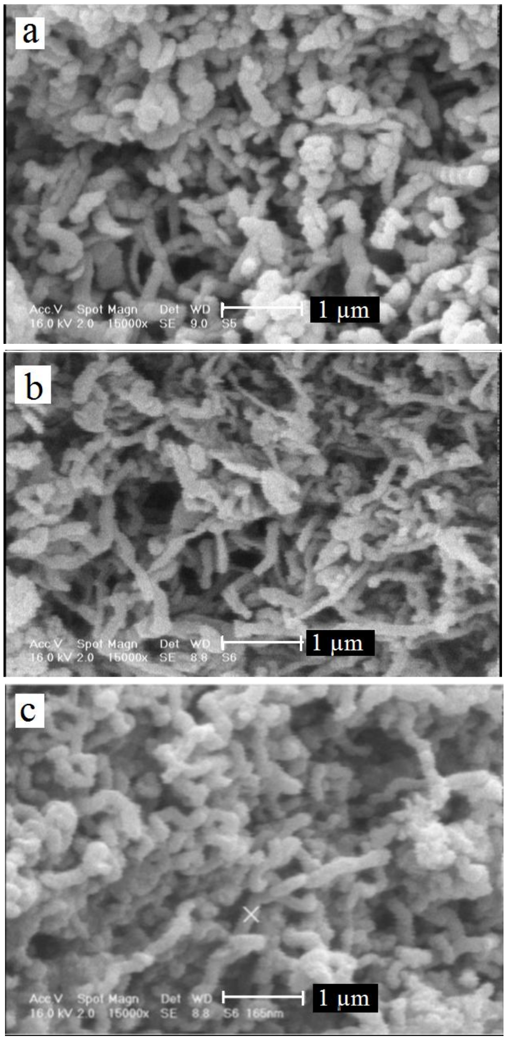

Fig. 6. SEM images of synthesized CNTs on Fe*(nm)/MgO under different growth temperatures; a) 865°C, b) 925°C,and c) 975°C.

Now we can have a comparison between the effect of alumina and magnesium oxide supports on growth of carbon nanotubes. In case which alumina powder is used as support, better conditions for synthesis of nanotubes revealed , temperature interval of growth process in vicinity of Fe* (nm) catalyst was also changed. However, in case which Magnesium oxide is used, improper situation appeared. Regarding the ball-milling method in which the catalyst nanoparticles and support were mixed together, the reaction taking place between them is just physical. Better synthesis yield for alumina compared to that of magnesium oxide can be explained by stronger chemical interactions taking place between alumina support and Fe* nanoparticles during the ball-milling process. Besides better conditions for nanoparticles with or without carbon shell during synthesis process when support is not used can be explained by two main purposes: chemical interaction between Fe* nanoparticles and surface of the quartz boat in high temperatures can probably be the first one because using support in this case avoids contact and therefore formation of the chemical bond between nanoparticles and quartz substrate. Second reason would be, when there is not a carbon shell ethylene molecules are able to reach the surface of catalyst.

CONCLUSIONS

In this work, we studied ball-milling process of commercial iron nanoparticles on growth, morphology and diameter of CNTs in the CVD reactor. We compare this new process with conventional method for synthesis of CNTs. In case which Fe nanoparticles with carbon shell was used, no CNTs growth happened at 925 ˚C. This is because of the existence of carbon shell, which prevents carbon molecules reach the surface of catalyst. However, using ball-milling method with alumina and magnesium oxide as supports changed catalytic activity of Fe* nanoparticles.

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