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Effects of Catalyst Ball-Milling Process and Support on Synthesis of Carbon Nanotubes Over Fe Commercial Nanoparticles

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This research was carried out to determine the growth of carbon nanotubes (CNTs) on Fe nanoparticles without carbon shell [Fe (nm), size < 60 nm], Fe nanoparticles with carbon shell [Fe* (nm), size < 60 nm], Fe* (nm)/Al_2O_3 and Fe* (nm)/MgO catalysts by chemical vapour deposition (CVD) method. Preparation of supported nanoparticles for growth of carbon nanotubes was carried out by mixing commercial Fe* nanoparticles (as catalyst) with Al_2O_3 and MgO powders (as supports) using ball-milling method. The quality of carbon nanotubes grown was compared using scanning electron microscopy (SEM) images and scanning electron microscopy patterns. Results indicated that, the preparation of nanoparticles/supports by ball-milling method could increase the range of growth temperature from 865-975 ºC. In addition, it can also have negative effects on diameter and morphology of synthesized carbon nanotubes at 925 ºC.

Key Words: Catalyst nanoparticles, Ball-milling, Carbon nanotubes, SEM, XRD, CVD.

INTRODUCTION

In recent years, carbon nanotubes 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 is more appropriate due to its high production yield and possibility of growth as well as the desired economic justifications. In chemical vapour deposition method, various parameters can be effective on the growth characteristics of the nanotubes. Studies indicate that in synthesis of nanotubes by chemical vapour deposition method, a variety of porous supports such as MgO, Al_2O_3, SiO_2 and zeolite can be used[8-10]. Depending on the context, the interaction between supports and catalyst particles can be affected by parameters such as particle size and shape, which are playing important roles in nanotube growth process[8,11]. Interactions between catalyst nanoparticles and supports can be either physical or chemical. In physical interactions, the catalyst particle size can be controlled by the presence of porosity on the supports. However, in case of chemical process, the interaction between catalyst particles and supports occurs during the process of catalyst formation[12]. Thus to achieve proper results, control over the nanotube growth process would be very important.

In this research, we report the effect of ball- milling process on Fe* nanoparticles, on growth temperature, quality and morphology of carbon nanotubes, in which MgO and Al_2O_3 powders were used as catalyst supports.

EXPERIMENTAL

In this research, the following materials were used: magnesium oxide and alumina 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 chemical vapour deposition system equipped with ethylene and Ar as feed and carrier gases respectively for synthesis of carbon nanotubes. The prepared catalyst and carbon nanotubes were characterized by X-ray diffraction (XRD, GBC, CuK_α radiation, $\lambda = 1.54$ Å) and the resulting carbon nanotubes were characterized by scanning electron microscopy (SEM, Philips, MAG 15kV, 30000X, SE).

Catalytic support preparation: Fe* (nm)/Al_2O_3 and Fe* (nm)/MgO catalysts, was carried out by direct combination of commercial iron nanoparticles with alumina and magnesium oxide powders. Iron nanoparticles commercial [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 min. The mixture was then dried on a hot plate in order to remove ethanol from the sample. Finally, to achieve a uniform distribution and smaller size of catalyst nanoparticles, the prepared powders were ball-milled with 500 rev per min in an iron jar, for 2 h. 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 (865-975 ºC) over catalysts, using chemical vapour deposition 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 865-975 ºC. Fig. 1 shows the scanning electron microscopy images of carbon products at three different temperatures of 865, 925 and 975 ºC. At 865 ºC, all products were carbon impurities which covered the catalyst's surface and no carbon nanotubes were seen in scanning electron microscopy images (Fig. 1a). This indicates that Fe nanoparticles are not active for growth of carbon nanotubes at 865 ºC. The existence of carbon nanotubes (Fig. 1b), illustrates that 925 ºC 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 20-90 nm and the average diameter of them is *ca.* 60 nm. By increasing temperature to 975 ºC (Fig. 1c), however, the amount of synthesized carbon nanotubes are low and most products are carbon impurities. An important reason why nanotubes growth is not happening in this temperature is that catalyst nanoparticles are adhered together and form bigger clusters[14]. 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 carbon nanotubes[15].

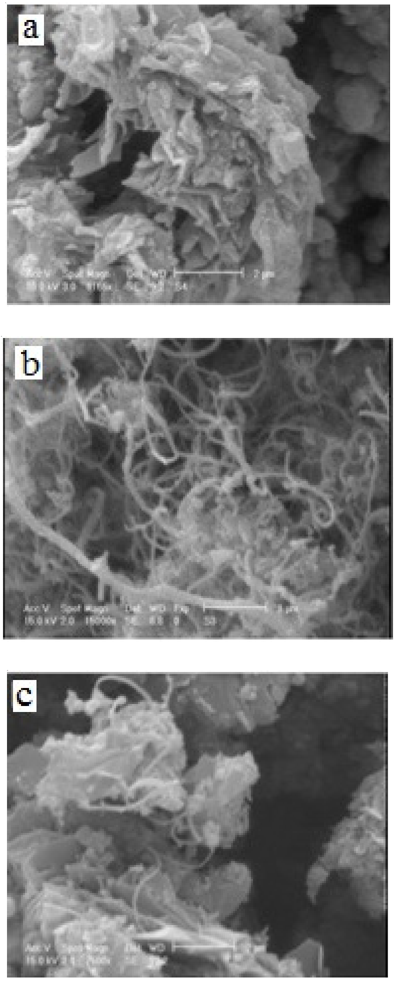

Fig. 1. SEM images of catalytic decomposition of ethylene on Fe nanoparticles without used supports at; (a) 865 ºC, (b) 925 ºC and (c) 975 ºC

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 (Fig. 2). According to the ones from Fe nanoparticles before nanotubes synthesis (Fig. 2a), peaks in 2θ = 37.7, 42.8, 43.4, 44, 45.9, 54.3, 58.1 and 82.2º are related to Fe nanoparticles. Picks with different intensities in scanning electron microscopy patterns after synthesis of nanotubes are also observable, (Fig. 2b) are related to X-ray diffraction from iron carbide nanoparticles and graphite sheets regarding nanotubular structures. Peaks in 2θ = 26.5, 42.6 and 77.5º are due to graphitic structures in nanotubes resulting from X-ray diffraction from (002), (100), (110) graphite sheets[16]. The ones in 2θ = 33.2, 35.7, 39, 43.1, 44.16, 52.4, 69.4, 72.6 and 84.9º are related to iron carbide with crystal structure of bcc and chemical formula of Fe_3C[16,17].

The Fe (nm) catalyst used for the synthesis of nanotubes is the reason for existence of peaks 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[18].

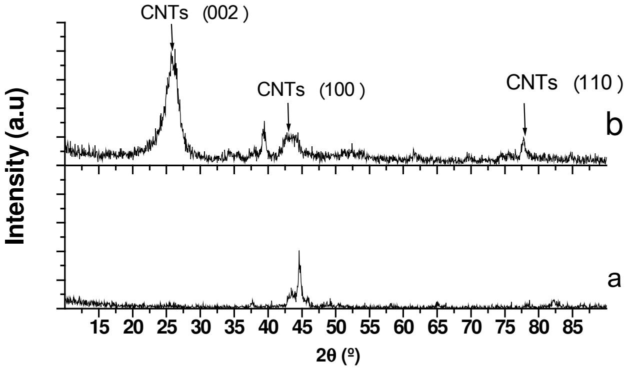

Fig. 2. XRD Patterns of Fe nanoparticles powder without any support (a) and CNTs synthesized on Fe catalyst in 925 ºC (b)

In the next experiment, we used commercial iron nanoparticles encapsulated with carbon shell [Fe* (nm)] as catalyst for synthesis of carbon nanotubes. Fig. 3, shows the scanning electron microscopy images of catalytic decomposition of ethylene on Fe* (nm) in 925 ºC without support. Scanning electron microscopy 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 carbon nanotubes do not occur.

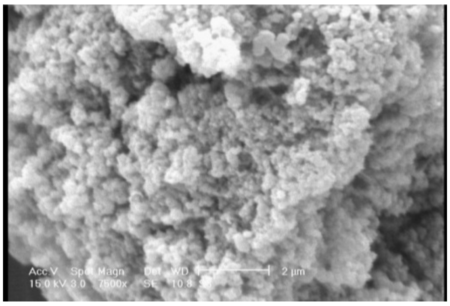

Fig. 3. Synthesis of carbon soot on surface of Fe* (nm)

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 (Figs. 4 and 5) studies reveal that, carbon nanotubes were produced from Fe* (nm)/Al_2O_3 and Fe* (nm)/MgO, prepared under experimental conditions cited above. At 865 ºC, with exception of some tubular structure, most products are carbon impurities that cover the surface of catalyst nanoparticles (Figs. 4a and 5a). This result indicates that, Fe* nanoparticles supported by Al_2O_3 and MgO, are not active for growth of carbon nanotubes at 865 ºC. However, synthesis of carbon nanotubes on Fe* (nm)/Al_2O_3 and Fe* (nm)/MgO catalysts happened at 925 ºC (Figs. 4b and 5b). 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, respectively. By increasing temperature to 975 ºC (Figs. 4c and 5c), 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 ºC with those at 975 ºC, 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[19,20].

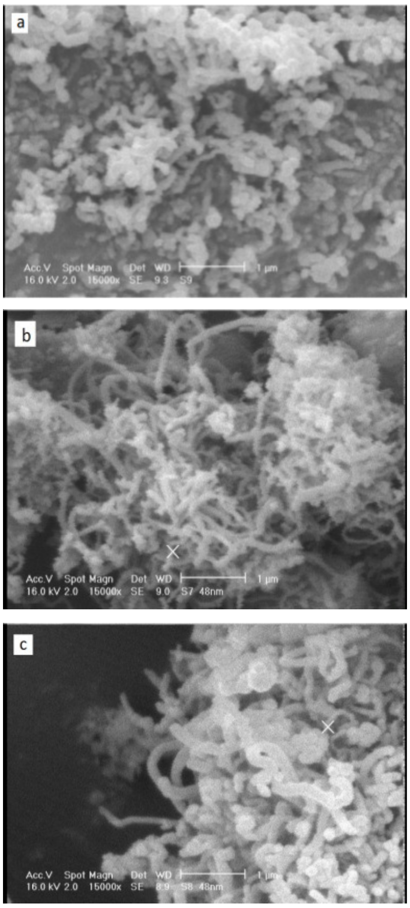

Fig. 4. SEM images of synthesized carbon nanotubes on Fe* (nm)/Al_2O_3 under different growth temperatures; (a) 865 ºC, (b) 925 ºC and (c) 975 ºC

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

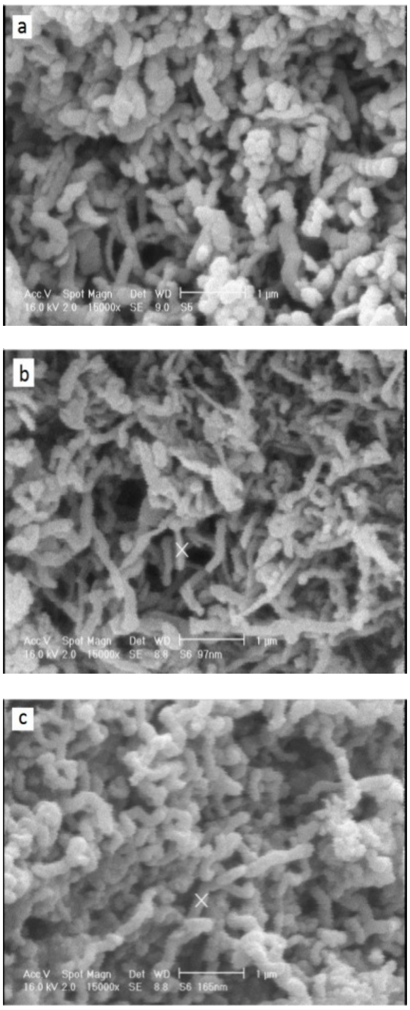

Fig. 5. SEM images of synthesized CNTs on Fe* (nm)/MgO under different growth temperatures; (a) 865 ºC, (b) 925 ºC, and (c) 975 ºC

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 *i.e.*, 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.

Conclusion

We observed a significant influence of the carbon shell on surface of iron nanoparticles and effect of ball-milling process on synthesis and quality of the carbon nanotubes. Also, the diameter and density of synthesized carbon nanotubes is adjustable by choosing the corresponding temperature and type of support. For Fe nanoparticles without carbon shell, the best condition for growth of carbon nanotubes is obtained at 925 ºC, when a simple method for dispersing nanoparticles on quartz substrate was used. However, in case which Fe nanoparticles with carbon shell was used under similar conditions, no CNT growth happened. This is because of the existence of carbon shell, which prevents carbon molecules reach the surface of catalyst. But using ball-milling method with alumina and magnesium oxide as supports changed catalytic activity of Fe* nanoparticles.

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