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The carbon nanotubes growth study under catalytic decomposition of ethylene over F_2O_3/Al_2O_3 catalyst

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ABSTRACT

In this study, F_2O_3/Al_2O_3 catalyst was prepared by using co-precipitation method. This catalyst was used to grow carbon nanotubes (CNTs) bundles by catalytic decomposition of ethylene in a floating catalytic chemical vapor deposition reactor. It was noticed that nanotubes yield increased with an increase in F_2O_3/Al_2O_3 weight. The carbon yield obtained with different weights of F_2O_3/Al_2O_3 was ranging from 68-93%. However, the surface defects in the grown tubes were also increased with an increase in the catalyst weight. High yield with the low surface defects and impurities was found for 0.3 g catalyst. The formation of CNTs bundles was attributed to the well-dispersed Fe particles at the catalyst surface. These Fe particles were acting as nuclei for the CNTs growth. The van der Waals forces were acting between the as-grown individual CNTs. These forces make them to grow in the same direction in the form of bundles.

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INTRODUCTION

Hollow carbon fibers have been known for many decades (Monthioux and Kuznetsov 2006) but it was the ground-breaking report by Iijima (1991), who discovered the ever demanded CNTs. The considerable interest in CNTs is due to their exclusive characteristics and applications (Grobert 2007). Since their discovery, CNTs have remained the main subject of most of the research investigation. These can be treated as a wonderful material with super electrical, chemical, thermal and mechanical properties.

Different methods have been used to produce carbon nanotubes such as arc discharge (Hutchison *et al*. 2001), laser ablation (Chen *et al*. 2005), solar energy furnace (Laplaze *et al* 1998) and catalytic chemical vapor deposition (CCVD) (Shukrullah *et al*. 2014). CCVD has been identified as the most promising large-scale synthesis route toward CNTs (Shukrullah *et al*. 2014). The CCVD method consists of the decomposition of a hydrocarbon precursor and deposition of the carbon on a solid or powder catalyst in a hydrogen rich environment. The CCVD process appears to be the easiest method to scale-up the production capacity at reduced cost (Shukrullah *et al*. 2014). However, regardless of these advantages, selection of an appropriate catalyst for bulk CNTs production still remains a challenge for researchers and producers.

Many complementary material-characterization techniques are then routinely used in all laboratories for the diagnostics of the CNTs. All characterizations are aimed at the optimization of the preparation method (Wang *et al*. 2006; Shukrullah *et al*. 2014). Requirements on the microstructure of CNTs may even significantly differ depending on the specific application field. In view of the industrial use, the high yield seems to be one of the most pressing demands for large-scale CNTs production. Usually, Mo has been reported to present synergism when combined with other transition metals in bimetallic catalysts, having a drastic effect in both the yield and the morphology of the as-grown CNTs bundles, which was thought that Mo is absolutely necessarily for the preparation of CNTs bundles. Tang *et al*. (2001) had systematically investigated the influence of the different ratio of Mo and Co on the synthesis of CNTs. The addition of Mo to Co/MgO obviously increased the yield of CNTs. Molybdenum is known to be a catalytic center for promoting the aromatization of methane (Tang *et al* 2001; Wang *et al*. 2009). Metal catalysts with Mo, such as $MgMoO_4$, Ni–Y/Mo, $Mg_{1-x}Fe_xMoO_4$ and Ni/Mo/MgO (Wang *et al*. 2006; Shukrullah *et al*. 2014; Tang *et al* 2001; Wang *et al*. 2009; Kadlecˇı´kova *et al*. 2007) were used to prepare CNTs bundles by catalytic chemical vapor deposition (CCVD) method with methane as carbon source. Mo has been reported to have a drastic effect on both the yield and the morphology of the CNTs bundles and to be necessary for their preparation.

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In the present case, F_2O_3/Al_2O_3 catalyst was prepared by using co-precipitation method without use the transition metal Mo. In later stage, CNTs bundles were grown by using FCCVD reactor at 800°C reaction temperature. Ethylene was used as a carbon precursor and argon as a carrier gas. Hydrogen gas was also added in reaction to act as a supporting gas. The grown CNTs bundles were further characterized for study of the catalytic effects on product yield, type and diameter. For this purpose, Field emission scanning electron microscopy (FESEM) was introduced to characterize the prepared CNTs bundles.

Research Methodology:

Schematic of the FCCVD reactor used for synthesis of the CNTs is given in Fig. 1. The steps involved in obtaining the catalyst to CNTs and their characterization have been explained in next sections.

There are many methods to prepare the catalyst such as sol gel, impregnation method and co-precipitation method. Here in, we prepared the F_2O_3/Al_2O_3 catalyst by using co-precipitation method. A rotary evaporator was also used for this purpose. Thereafter, the catalyst was dried at 150°C in oven for 12 hours. The fully dried catalyst was sieved by using a 63 microns sieve.

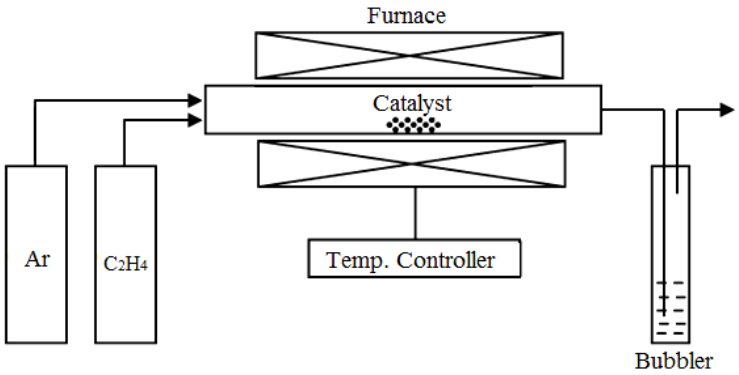

Fig. 1: Schematic of the FCCVD reactor.

The FCCVD reactor (OTF-1200-80mm) was composed of a quartz tube with horizontal heating zones. The tube was 80 mm in outer diameter, 72 mm in inner diameter and 1000 mm in length. The temperature of zones was set and controlled by temperature controller. The quartz tube was connected to a gas mixer and the flow rates of argon, hydrogen and ethylene were controlled by flowmeters. Initially, the quartz boat containing 0.1 g Al_2O_3/iron nitrate catalyst was placed in temperature zone where CNTs were formed due to reaction of catalyst with carbon precursor. In CNTs growth process, firstly, the argon gas (100 sccm) was flushed into the system and waited unless the reaction temperature reached to 800°C with ramping rate of 10°C per minute. At this stage, ethylene and hydrogen gases were also introduced into the reaction chamber with flow rate of 50 and 100 sccm, respectively. After one hour, the gas supply was stopped and the furnace was allowed to cool down at the room temperature. The CNTs were taken out from the quartz tube and stored in dust and moisture free environment. The similar process was taken in account by varying the catalyst alumina/iron nitrate weight from 0.1 to 0.5 g. Finally, morphology, type and diameter of the synthesized CNTs bundles were studied through SEM micrographs obtained at different resolutions.

Results and Discussion:

In order to investigate the effect and role of the catalysts on CNTs growth, the carbon yields was obtained by using different catalyst weights and compared by using the following equation:

$$Carbon\ yield = [\frac{M_{total} - M_{catalyst}}{M_{catalyst}}] \times 100\%$$

Where, M_{Total} is the total mass obtained at the end of the process and $M_{Catalyst}$ is mass of the used catalyst.

The carbon yield obtained with different weights (0.1-0.5 g) of F_2O_3/Al_2O_3 catalyst can be depicted in Fig. 2. It has been noticed that M_{total} was increasing linearly with an increase in catalyst weight from 0.1-0.5 g. However, the carbon yield, initially, showed a concomitant increase with an increase in catalyst weight from 0.1 to 0.3 g, thereafter, reached to a steady state. After 0.3 g, the catalyst weight did not show significant authority on the carbon yield. The overall increase in the carbon yield was remained in the range of 68-93%.

The morphology of the grown CNTs, their dimensions and orientation was revealed by using FESEM micrographs. The FESEM illustration of the MWCNTs bundles has been given in Fig. 3. It can be seen that CNTs grown with 0.1 g and 0.2 g catalyst were low in yield, highly curved, randomly oriented and tangled with varying diameters. They were bending and growing in random directions in bundles. However, the growth rate

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and carbon yield were low due the least availability of the catalyst particles required to react sufficiently with the carbon source gas.

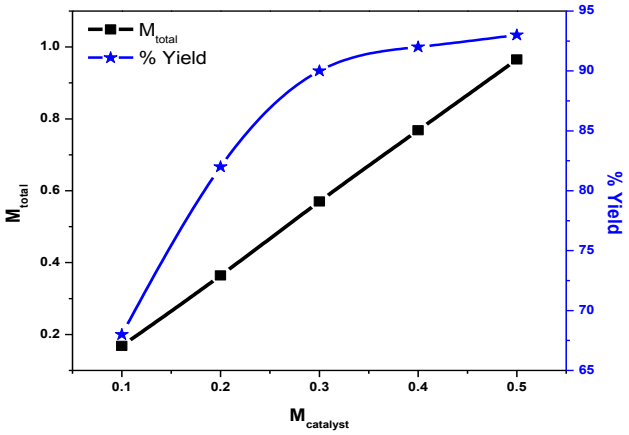

Fig. 2: Carbon yield obtained with different weight of F_2O_3/Al_2O_3 catalyst.

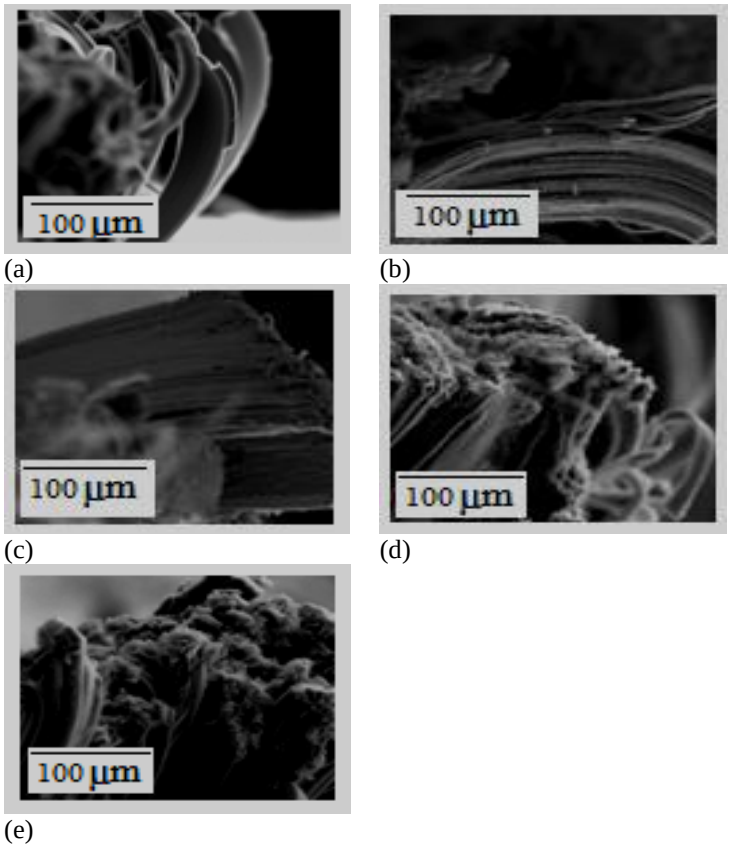

Fig. 3: FESEM images of CNTs grown with; (a) 0.1 g, (b) 0.2 g, (c) 0.3 g, (d) 0.4 g and (e) 0.5 g of catalyst.

It was a kind of evidence of low reactivity of the catalyst and consequently, the low carbon yield with very less amorphous carbon. In contrast, CNTs produced by 0.3 g catalyst were relatively thicker with a large wall numbers and also in bundle-type as shown in. Fig. 3c. Similar kind of results was obtained even for increased catalyst weight (0.4 and 0.5 g). The carpet like areas with bundle-type CNTs with certain large flakes and many large particles were also spotted in the CNTs which were attributed to Fe-doped alumina particles. Nevertheless, the dense networks of CNTs with relatively low impurity level and iron content were evident in the case of 0.3 g catalyst.

The growth of CNTs bundles has also been reported elsewhere (Wang *et al*. 2006; Tang *et al* 2001; Wang *et al*. 2009; Kadlecˇı´kova *et al*. 2007). Wang *et al*. (2006) used MgO as a carrier and methane as a carbon precursor. They also used the transition metal Mo along with other transition metals to form bimetallic catalysts.

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These catalysts were having drastic effects on both; morphology and yield of CNTs (Tang *et al* 2001; Wang *et al*. 2009; Kadlecˇı´kova *et al*. 2007). They anticipated that Mo was a necessary part of the catalyst for growing CNTs bundles. Contrarily, in the present case, CNTs bundles have been grown in CCVD reactor without introducing Mo in the catalyst formulation. Unlike others, only F_2O_3/Al_2O_3 was used to break the C_2H_4 chains and to grow CNTs bundles. This catalyst leads to the dense growth of CNTs in the form of bundles. The formation of CNTs bundles was attributed to the well-dispersed Fe particles at the catalyst surface. These Fe particles were acting as nuclei for the CNTs growth (Shukrullah *et al*. 2014). The van der Waals forces were acting between the as-grown individual CNTs. These forces make them to grow in the same direction in the form of bundles. Wang *et al*. (2009) also obtained the bundles of CNTs having good microstructure and high purity as in the present case.

Conclusions:

In this detailed note, CNTs bundles were grown by using FCCVD reactor at 800°C reaction temperature. Different weights of F_2O_3/Al_2O_3 were used as a catalyst, ethylene as a carbon precursor and hydrogen-argon mixture as a carrier gas. The synthesized CNTs were characterized by using FESEM techniques. It was noticed that dense and bundled growth of CNTs can be achieved by the decomposition of ethylene even in the absence of transition metal of Mo in the catalyst. The bundled grow was happening due the existence of van der Waals forces between the individual CNTs. The comparative studies of different amounts of the catalyst revealed that the carbon yield increases with increase in catalyst weight. High yield with low surface defects and impurities was obtained with 0.3 g catalyst. Furthermore, some of the grown CNTs were found defective in case of others samples. These surface defects were increased with an increase in the catalyst weight.

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