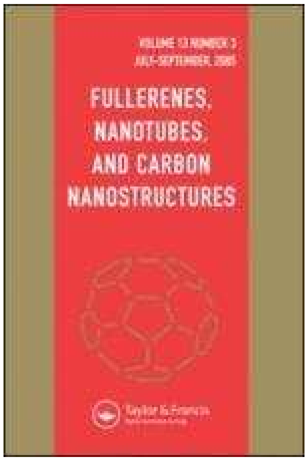

Carbon nanotube and nanofiber growth on Zn Based Catalysts

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CARBON NANOTUBE AND NANOFIBER GROWTH ON Zn BASED CATALYSTS

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ABSTRACT

In this study, acetylene gas was delivered to a catalyst network consists of NaCl-support and Zn nanoparticles in a temperature range of 500-700°C by means of a chemical vapor deposition (CVD). A principle feature that delineated this CVD study from prior studies lay, first in the method used to support the catalyst and secondly the choice of the catalyst metal. In particular, NaCl was deliberately retained and exploited in subsequent manipulations for the reason that it performed remarkably well as a support medium. The catalytic activity of Zn towards production of CNT/CNFs appeared to be promoted as a result of using molten ionic substrate.

Keywords: CVD, Zn catalyst, NaCl support, carbon nanotube growth.

1 INTRODUCTION

Carbon nanotube (CNT) and carbon nanofiber (CNF) production through CVD became a very intense research field because of its potential for scaling up the production and low cost (1). Recent developments showed that alignment, positional control on nanometer scale, control over the diameter, as well as the growth rate of the carbon nanotubes (CNT) and CNFs could be achieved by using CVD (2-4).

Many metal catalysts and catalyst supports were used previously for CNF and CNT production through CVD technique, all aiming for increase the yield of the process while controlling the properties such as diameter, length and morphology of the structures. In many studies silica (SiO_2) (5), alumina (Al_2O_3) (6), quartz (7), titania (TiO_2) or calcium oxide (CaO) (8) were used as the catalyst support because of their high surface area, chemical inertness and high-temperature resistance. However, all of these support materials require harsh chemical treatment i.e. concentrated bases (NaOH) or strong acids (HF) to remove them, and these reagents may also damage the carbon nanostructure. Additionally, strong acids and bases are less desirable for large-scale production due to environmental concerns.

In terms of the selection of the metal catalyst, Fe, Co and Ni were the active metals that were used the most previously in the catalytic CVD process for carbon materials production (9, 10). The reason for choosing these metals as catalyst for CVD growth of nanotubes was due to the fact that; carbon is soluble in these metals and this solubility leads to the formation of metal-carbon solutions and therefore the desired carbon nanomaterial formation nucleates (11). In this study, zinc based organometallic complex catalysts synthesized by a new approach of simultaneous synthesis of the support material and the catalyst. Therefore an easy production method for catalyst to use in CVD was developed by using only wet chemistry.

In this study we propose a very unusual catalyst system based on NaCl as the catalyst support which provides easy production and easy removal properties to the catalyst system and Zn used as the catalyst metal. NaCl was used as a catalyst support material previously in a few studies. Szabó et al.(12) used cobalt nitrate ($(Co(NO_3)_2).6H_2O$) as the catalytic precursor and NaCl powder as the support. However, this method was not satisfactory because of the low CNT production yield which is expected to be higher for Co catalyst systems, the volume of side-products such as carbon-encapsulated Co nanoparticles, and the presence of amorphous carbon (indicated by significant weight-loss at a temperature around 300 °C). Geng et. al. (13) made a progress on using the NaCl as a catalyst support by using nickel based catalyst systems only. Here we introduce a new approach for preparation of the catalyst system as simultaneous formation of support material during the synthesis of the Zinc based catalysts. Together with the exceptional characteristic of support material, the metal catalyst preparation step was differentiated from the conventional wet catalyst methods as well. In most of the studies catalysts were prepared in a liquid solution containing the catalyst in salt form is applied to the substrate via spray coating (14-16), spin coating (17-19), or micro-contact printing (20). Here we propose a very simple way to prepare catalyst in powder form and control of the catalyst size was obtained by mechanical activation using ball-milling technique. Our goal in synthesizing CNTs/CNFs is to achieve a control in tailoring the diameter, and morphology at the same time. We believe that understanding the chemistry involved in the catalyst and nanofiber growth process is the critical point to be able to produce property controlled CNTs/CNFs.

2 EXPERIMENTAL

2.1 Catalyst preparation

All reagents used were analytical grade without further purification. Zinc based catalyst precursors were prepared (tartrate, and oxalate) by starting from chloride forms by modifying the previously described methods (21). The pH of the solution was adjusted to 11 to 12 by addition of NaOH to the reaction solution. Presence of the chloride and sodium ions in the saturated solution resulted with production of the NaCl, as a side product of the reaction, Reaction 1.

The formation of NaCl in the structure motivated us to use of NaCl as the support of the catalytic material. In order to keep the metal/support ratio in the range of 1/20 to 3/10, additional NaCl was added to the synthesis medium in the course of the synthesis of catalyst. The metal salt-sodium chloride mixture was exposed to vigorous mixing for 24 hours at room temperature, and then it was slowly evaporated at 50°C in 6 hrs. The final catalyst system was pulverized and mechanically activated in order to obtain further dispersion of the active metal precursor particles through the NaCl structure in a ball-mill for 24 hrs at 200 rpm.

2.2 Synthesis of carbon nanoproducts

CNF/CNT production was performed by using conventional tube furnace CVD set-up. The catalyst system was placed in to the quartz tube reactor with a diameter, Φ= 30 mm and length, L= 90 cm. For the calcination of the Zn tartrates and oxalates, the system was kept at 500°C under constant Ar flow for 30 mins. Then, hydrogen gas was passed through the tubular reactor in order to reduce the catalyst into the metallic form at same temperature. After the catalyst system was prepared in the reduced metal form, for the production of carbonaceous material, high purity acetylene was allowed to flow with a rate of 3 L/min for the formation of the carbon nanostructures while keeping the system between 500°C and 700 °C according to the previous optimization studies (22). After the CVD experiments were stopped the system was kept under vacuum until it reached to room temperature in 2 hours.

2.3 Carbon deposition

In order to give some quantitative characterization of catalytic decomposition of acetylene, an experimental work on the kinetics of the CNT/CNF growth was performed. In the kinetic experiments, the duration of the CVD reaction was taken as the time in between the acetylene flow started and ended. The boats in which the carbon deposition occurs were weighed both before and after the reaction. The yield of the reaction was calculated according to the equation 1.

$$\text{Carbon yield} = \frac{(W_f - W_c)}{W_c} \text{ x}100\% \qquad \text{Eq 1}$$

Where;

W_f = final weight of the product and catalyst together

W_c = weight of the catalyst after reduction step

2.4 Characterization Methods

The structural, thermal and chemical properties as well as the surface morphology and porosity of the catalysts have been investigated by using the following techniques;

X-ray diffraction (XRD) was performed by using a *Bruker aXS Diffraction Solutions D8 Advance X-ray diffractometer,* using monochromatic CuKα radiation within the 2θ angle range from 10° to 90° by rotating the samples at 10 rpm.

The microstructure of the catalyst systems and the CNF products were examined with a Leo G34-Supra 35VP scanning electron microscope (SEM) coupled with energy dispersive spectrometer (EDS) software. Before analysis, catalyst samples were coated with carbon by Emitech, T950x Turbo Evaporator. Imaging was generally obtained using an accelerating voltage in the 1 to 3 keV range using secondary electron and in-lens imaging techniques.

Thermal stability and decomposition characteristics of the catalyst samples were analyzed by using a Netsch 449C thermogravimetric analyzer (TGA). TGA analysis was done in the following manner; the catalyst samples were heated up to a temperature 700^{o}C with 10°C/min heating rate under nitrogen atmosphere and the mass loss of the samples was recorded against temperature.

The particle size of the metal catalysts and the size distribution of the metal particles were determined by using a Malvern Zetasizer Nano instrument. The solutions of catalyst systems having 2 g/L concentration were prepared in water. Since all the NaCl is expected to dissolve in this concentration, the measured catalyst sizes are representing only the size of Zn particles.

Elemental analysis of the catalysts was done using a Vista-Pro Axial; Varian Pty Ltd, Mulgrave, Australia, inductively coupled plasma optical emission spectrometer (ICP-OES) The catalyst samples were dissolved in 30 mins by using an acid mixture which consists of HNO_3:H_2O_2 (5:2) in a Mars Express, CEM Corp., Matthews, NC, USA microwave digestion system. Then the diluted samples were analyzed by ICP system. The percent metal and NaCl content of the catalysts was calculated according to the dilution coefficients individually.

3 RESULTS AND DISCUSSION

The catalyst precursor structures were investigated using XRD and TGA analysis, the hydroxide tartrate and oxalate structure formation was observed in these analyses. Prior to the carbon nanostructure deposition on the catalysts, the Zn catalysts first converted into oxide form during Ar treatment and following this the metallic Zn particles were formed during H_2 flow, Figure 1. The formation of those intermediates was observed with XRD measurements as well, Figure 2.

The formation of carbon nanotubes and nanofibers with different morphologies was observed when using Zn based catalysts. Carbon nanostructures with various morphologies; tubular Figure 3A (Zn tartrate/NaCl catalyst), C (Zn oxide/NaCl catalyst and twisted Figure 3B Zn oxalate/NaCl catalyst), were obtained depending on the Zn catalyst precursor. The variation in the structures and the formation efficiency were similar to those catalyst metals such as Fe and Co which were accepted as good catalyst for CNT/CNF growth previously (11). Although there was not a detailed investigation on Zn as a catalyst material for the production of nanostructured carbon materials, it was accepted as a poor catalyst since some undesired carbon by-products were observed (23). However, the Zn based catalysts prepared in this study appeared to be very active towards the production of CNT/CNFs with uniform and narrow diameter distribution. The reason of this achievement considered to be related to the preparation method of the catalyst. In the previous studies Zn was used in a spray pyrolysis vapor-phase procedure in the form of either metallocene mixture ($(C_5H_5)_2M$) or metal chloride solution (MCl_x)(23), therefore, the growth process was realized in a fluidized bed system. On the other hand, in the present study, well dispersed solid state catalysts were used in a fixed bed reactor system. It was possible to adjust the particle size of the Zn particles starting from 15 nm to 200 nm depending on the catalyst precursor and the ball-milling conditions, i.e. the duration time, the size of the titania balls and the speed of ball-milling. From the carbon product formation point of view, which was summarized in Table 1, our process seemed that the diffusion of carbon atoms took place more effectively than fluidized growth. The smallest particle size was obtained by using hydroxide type precursor having an average particle size of 22 nm, Figure 4. The average particle size of the Zn catalyst with tartrate and oxalate precursors was 110 nm and 230 nm respectively. This significant difference between the size of the catalyst lead to the formation of different type of carbon nanoproducts.

The most important criteria of CNF/CNT production are (A) Homogeneity and quality of the carbon nanoproduct (B) Yield of the product. Using the NaCl as the catalyst support gives many advantages for the former criteria. In comparison to typical silica and alumina-based support media, a non-porous sodium chloride medium clearly revealed major operational advantages in the matter of fabricating carbon species such as nanofibers and nanotubes. In particular, pyrolysis could be conducted at temperatures spanning 500°C to 700°C without observing any agglomeration and subsequent sintering of the catalyst. The main cause of the high stability of these catalytic nanoparticles was not elucidated conclusively but it appeared to be related to the segregating effect of the support matrix, which could arise initially by the direct interaction between mobile chloride ions and the catalyst surface, and subsequently via encapsulation of each catalyst particle, by the growing polymeric species. High catalytic activity appeared to be promoted by the fact that the sodium chloride matrix became mobile, since its melting temperature is 810°C. This mobile phase is acetylene-permeable at elevated temperatures, the most important evidence originating from electron micrographs, which clearly indicated carbon-coated catalysts enclosed entirely in sodium chloride. Therefore, both the catalyst and the support materials were considered as they have met the criteria of homogeneity and quality of the carbon nanoproduct, Figure 3 and Figure 7. It is very clear from these figures that zinc hydroxide precursor with its smaller size led to the formation of bamboo-like MWNTs with an average diameter of 20 nm, while the tartrate and oxalate type precursors formed CNFs with an average diameter of 100 and 200 respectively with different morphologies.

In addition to the studies based on understanding the formation of different morphological structures, the carbon deposition yield was investigated by using Equation 1 and the results were summarized on Table 1. The graphical representation of the data obtained from the analysis of the carbon deposition/kinetics study was given in Figure 5. The catalyst system used in the kinetic study part was Zn tartrate/NaCl system, therefore the main carbon species produced was CNFs with an average diameter of 60 nm. From the temperature dependent kinetic analysis, it is clearly seen that the carbon nanoproduct formation produced a peak around 500°C, hence the most efficient temperature for the formation of CNFs was accepted as 500°C, Figure 5A. Therefore time dependent studies were performed at 500°C. On the other hand, after 500°C the catalyst system started to lose its activity which was considered as a result of NaCl becoming to melt and the porous structure of catalyst system collapsed after 600°C. Two main results were achieved in the time dependent studies; first one is that the increase in the yield of CNF formation during the 20 min interval of CVD formation and from that point forward the formation rate does not change, second one is that there is stability in terms of product yield at this temperature which showed in the rage of 40% to 100%. Actually the yield of the CNF/CNT deposition for Zn tartrate found was comparable to the well-known catalysts such as Fe and Co (24, 25). Thus this is another decision on Zn as an effective catalyst for CNF/CNT formation through CVD. The similarity between the binary phase diagrams of Co-C system and Zn-C system can be accepted evidence on these results as well, Figure 6. Zinc is known to have limited carbon solubility in the range of 1 at% in the solid solution, and able to form few stable carbide phases usually at higher temperatures than Co, Fe or Ni forms similar meta-stable carbides (26). However our suggestion for the increased activity of the Zn based catalyst at lower temperatures then must have been originated from the metal-support interaction. Under CVD conditions, just before carbon deposition on the catalyst particles started to take place, NaCl formed an ionic media, which might have enhanced the catalytic activity of the metals towards CNT/CNF formation. In fact in heterogeneous catalysis, support-catalyst interactions are known in ionic media and can give rise to catalyst activation (27). While C atoms have certain solubility in Zn already, the mobile NaCl matrix with enhanced permeability at elevated temperatures help the diffusion of C atoms in to the Zn particles.

The high activity attained by the use of Zn based catalysts might initiate a discussion on the purity of the catalyst. Therefore, the purity of the Zn based catalysts were analyzed by ICP if there is any contamination in the catalysts by iron, nickel or cobalt which are known to be active catalysts for formation of CNT/CNF production. Table 2 summarizes the ICP elemental analysis of the tartrate based catalysts. The Zn catalyst seems not contaminated by other metals which proves that our claim on preparation of Zn catalyst which is active for CNT/CNF production. Furthermore, the lower concentration of the oxide catalyst in comparison with the tartrate and oxalate species can be the reason for smaller sized ZnO particle formation.

Concerning the preparation method of the catalyst it was found that those results were promising for the production of carbon nanomaterials with specific properties. By using catalyst and support in the solid-state we managed to produce CNFs and MWNTs on Zn based catalysts selectively depending on the catalyst precursor and pre-treatment of the catalyst. These investigations also showed that support material could play a very important role on the yield of CNF/CNT deposition rate. The support already has critical functions on the production of CNF/CNTs including inhibit the formation of larger metal catalyst clusters and the contribution of the substrate material on the formation of specific morphologies such as CNFs, SWNT or MWNTs (6, 28). In our case, the support material has functioned in other ways too by means of promoting the catalytic reaction by supplying a mobile phase which increases the diffusion of carbon atoms in to the Zn catalyst particles.

4 CONCLUSIONS

The subject of this research was developing a new type of catalyst and investigating conditions to tailor the CNF/CNT growth through CVD. It was managed to prepare a nano-sized metallic catalyst while keeping the catalyst size uniform only by using wet and basic chemistry. Catalyst systems were found have high purity and do not contain any other effective metal catalysts. The particle size of the catalysts was determined by DLS method and it was found that catalysts have clusters in the NaCl matrix and it was possible to adjust the particle size of the Zn particles starting from 15 nm to 200 nm by choosing the catalyst precursor and adjusting the ball-milling conditions. Various carbon nanostructures were obtained depending on the catalyst precursor composition. Tartrate and oxalate precursors resulted with catalysts with relatively high particle size, therefore led to CNF formation. On the other hand, the hydroxide precursors formed smaller diameter particles with an average of 22 nm and led to formation of bamboo-like CNT formation. All carbon nanoproducts showed uniformity by means of morphology and microstructure. The supercapacitor and composite applications studies of these structures which will point to the mechanical and electrical properties will be presented as a separate communication.

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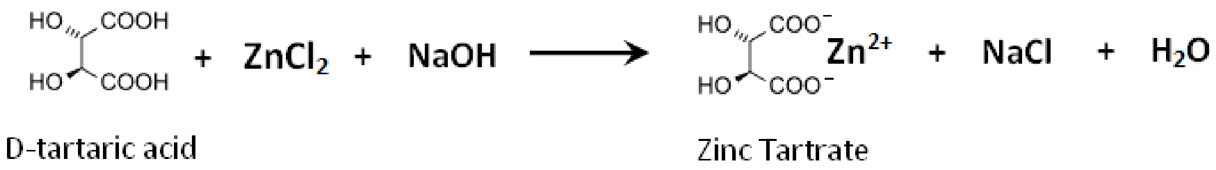
List of Figures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COOH
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+
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NaCl
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H_2O
D-tartaric acid
Zinc Tartrate

Reaction1.

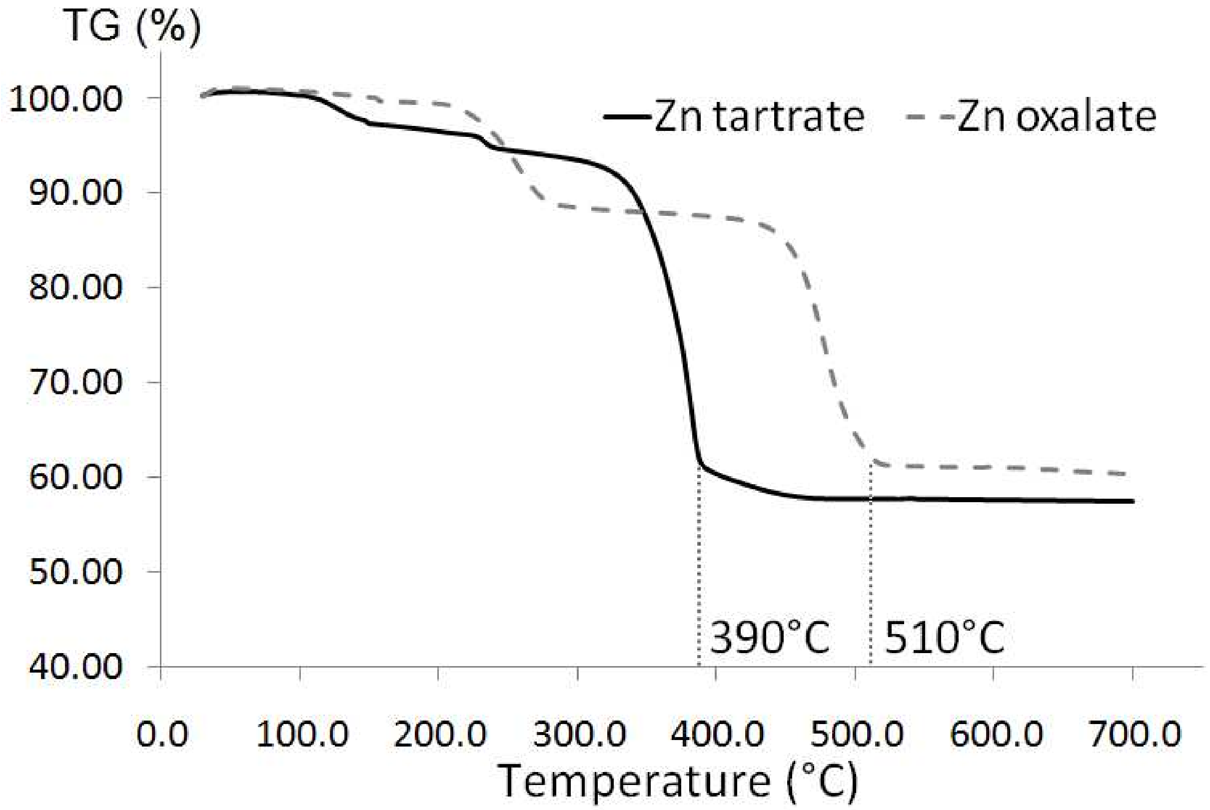

Figure 1. TGA thermogram of Zn oxalate /NaCl and Zn tartrate /NaCl systems

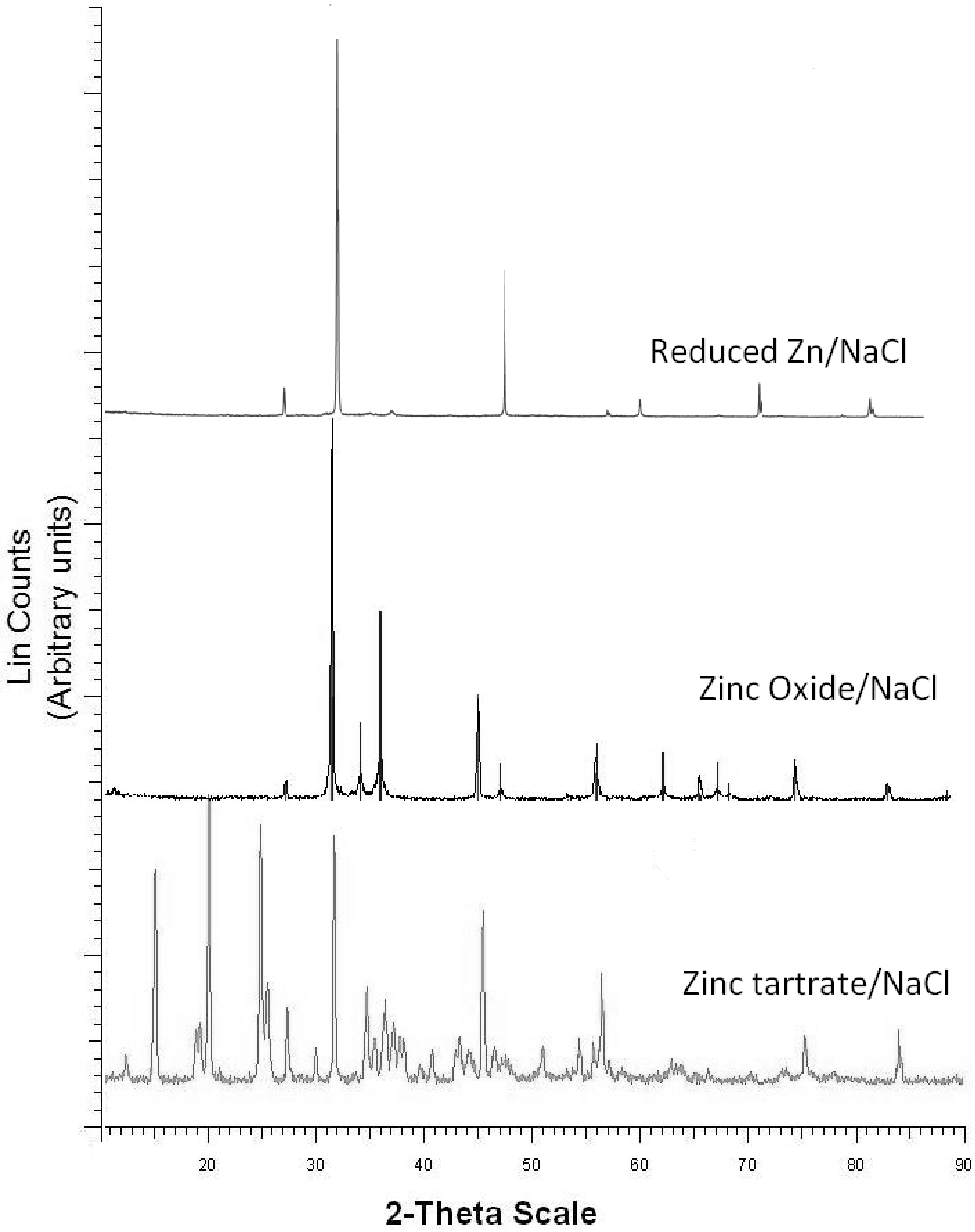

Figure 2. XRD diffractograms of Zn tartrate/NaCl system, as produced, after calcination and after reduction processes.

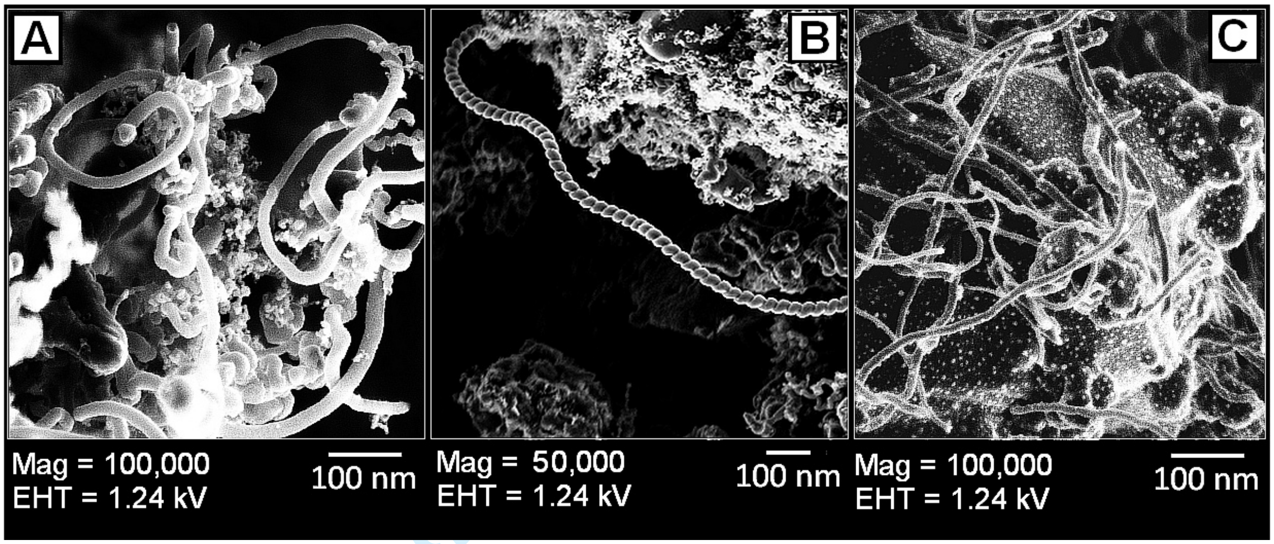

Figure 3 SEM micrographs of the carbon nanostructures produced by using Zn based catalysts

A) Zn tartrate/NaCl catalyst B) Zn oxalate/NaCl catalyst C) Zn oxide/NaCl catalyst

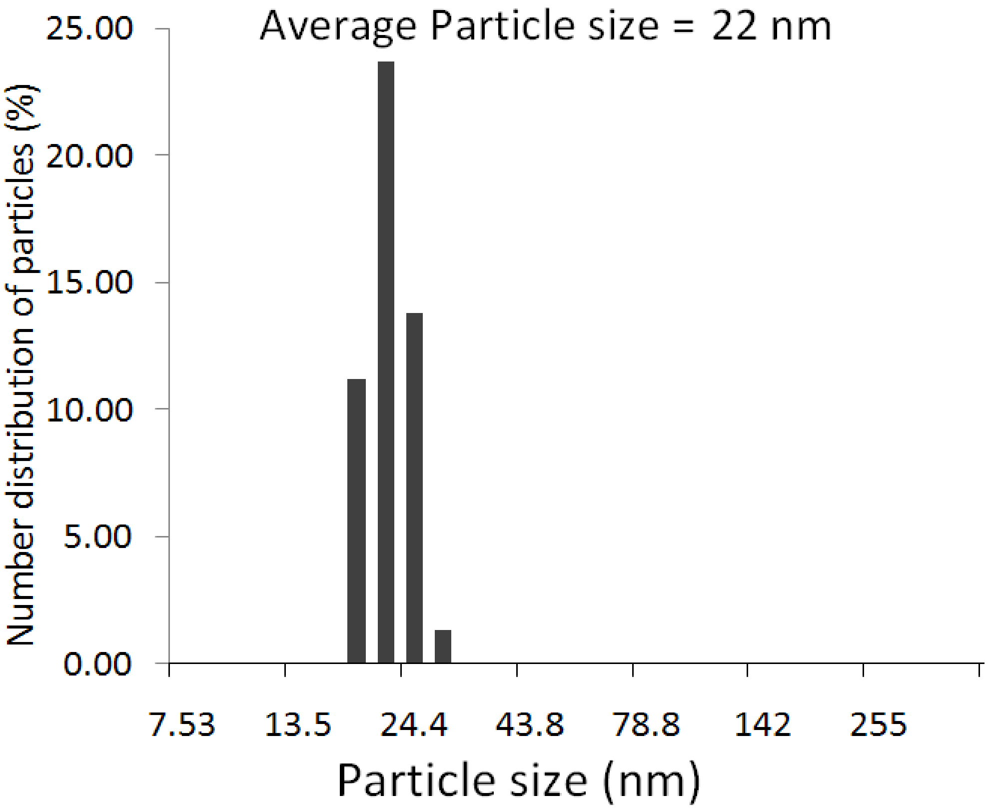

Figure 4 DLS particle size distribution graphs for the tartrate based catalysts zinc hydroxide ball-milled for 24 hrs at 200 rpm

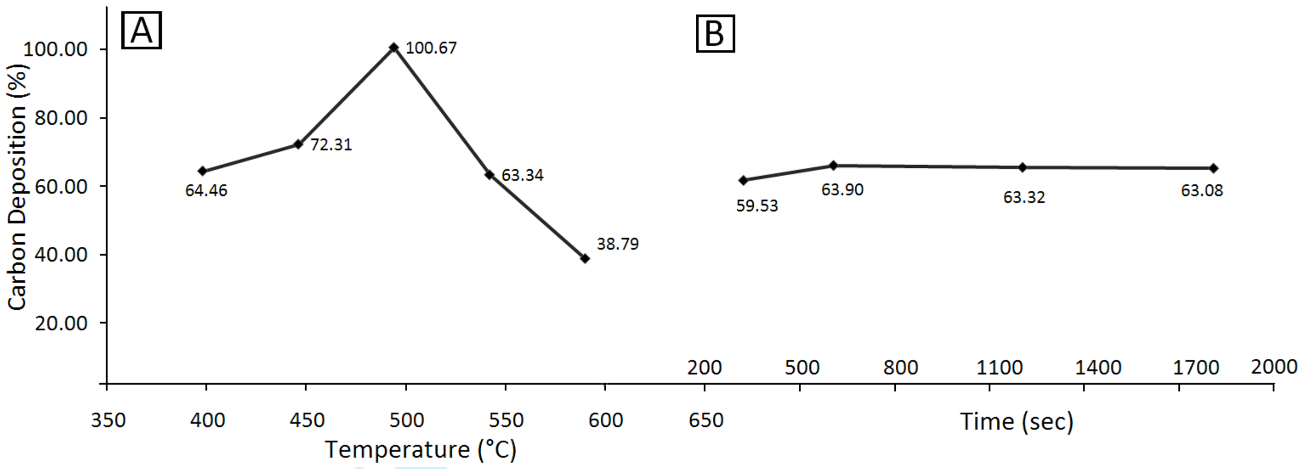

Figure 5 Carbon deposition study of CNT/CNF formation with respect to A) temperature and B) time (at 500°C)

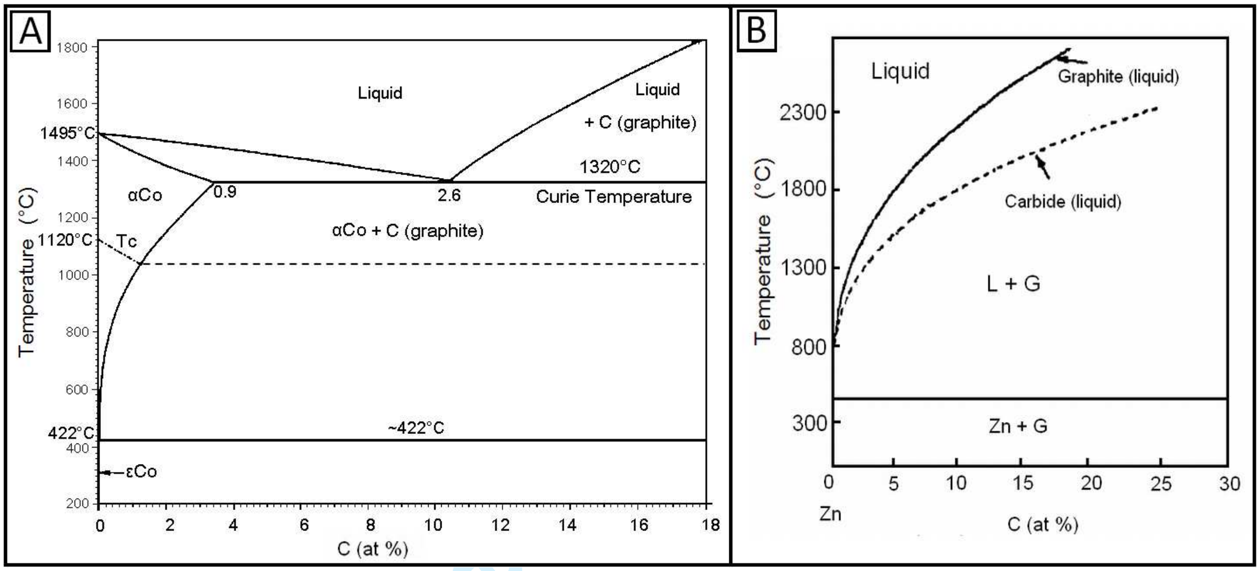

Figure 6 A) Binary phase diagram of Co-C system (29) B) The calculated binary phase diagram of Zn-C system adapted from (30)

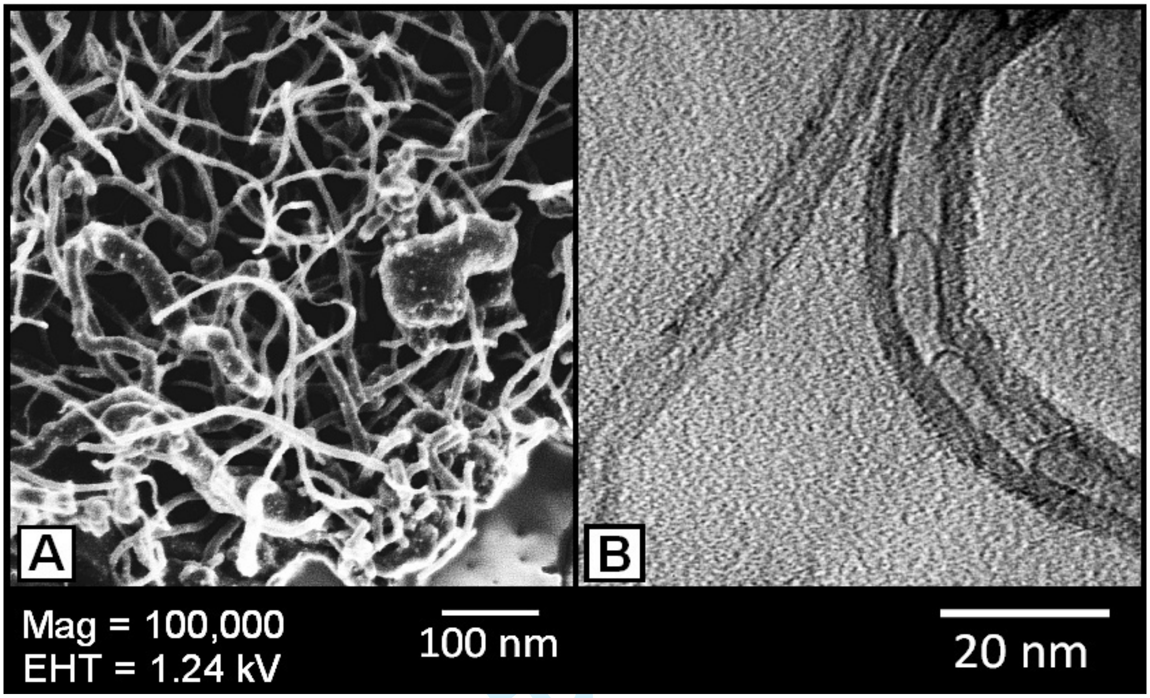

Figure 7 A) SEM and B) TEM micrographs of the carbon nanostructures produced by using Zn based catalysts Zn oxide/NaCl catalyst

Table 1 Carbon deposition yield values for Zn tartrate/NaCl catalyst in carbon nanotubes synthesis with respect to time and temperature

Catalyst	t (sec)	Temperature (°C)	$m_{catalyst}$ (g)	$m_{catalyst+product}$ (g)	Carbon Deposition (wt %)	Yield/catalyst (wt %)
Zn tartrate /NaCl (5%Zn by weight)	320	500	0.1858	0.2964	59.53	1190.53
	605	500	0.1942	0.3183	63.90	1278.06
	1204	500	0.1775	0.2899	63.32	1266.48
	1809	500	0.1617	0.2637	63.08	1261.60
	1822	400	0.1739	0.2860	64.46	1289.25
	1873	450	0.1300	0.2240	72.31	1446.15
	1833	500	0.1950	0.3913	100.67	2013.33
	3438	550	0.1743	0.2847	63.34	1266.78
	1806	600	0.1601	0.2222	38.79	775.77

Table 2 ICP Analysis results of the tartrate based catalysts

Sample	**Co (%)**	**Cu (%)**	**Fe (%)**	**Mn (%)**	**Mo (%)**	**Na (%)**	**Ni (%)**	**Pb (%)**	**Zn (%)**
Zn tartrate	0.002	-0.011	-0.010	0.000	0.000	45.90	-0.002	-0.001	**3.527**
Zn oxalate	-0.001	-0.002	-0.000	0.000	0.000	43.35	-0.002	0.000	**4.556**
Zn oxide	0.000	-0.001	0.000	0.000	0.000	42.73	-0.011	-0.002	**2.886**