SYNTHESIS OF CARBON NANOTUBES VIA CATALYTIC DECOMPOSITION OF ACETYLENE ON BI-METALLIC SUPPORT INTERACTION OF CO-MO/MGO

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Abstract

The research work investigate the viable utilization of acetylene as the precursor for the synthesis of carbon nanotubes (CNTs) with the aid of bimetallic Co-Mo/MgO support catalyst via catalytic chemical vapour deposition (CCVD). The experimental results show the presence of nano sized and hollow core of the tubular carbon structure. An increase in the heat treatment temperature enabled Co-Mo/MgO catalysts in growing CNTs at higher yield, the results show an increase in the diameter when the treatment temperature is raised from 700°C-800°C.

Keywords: Synthesis, Bi-metallic alloy, Catalytic Chemical Vapour Deposition, Electron microscopy

1. INTRODUCTION

There have been rapid developments in the production of carbon nanotubes (CNTs) materials that lie within the nanometer scale from precursor materials since it was first discovered by Sumio Iijima in 1991(1). Carbon nanotubes are tubular in shape, made of graphite. The mind breaking interest in the carbon allotrope is attributed to their unique structural, mechanical, thermal, optical,chemical and electronic properties (2). These have drawn the attention and prompt most researchers in the field of science and technology to conduct research in this area of study, significant scientific studies have reveal the potential of CNT applications which include: super capacitors, reinforcements in high performance composites, hydrogen storage (3), catalyst support (4), selective adsorption agents (5) and field emission devices (6).

Till date, various methods have been developed to synthesis carbon nanotubes this includes arc-discharge (7), laser ablation(8) and chemical vapor deposition (9). Although arc-discharge is one of the earliest methods used in the production of CNTs, catalytic chemical vapour deposition (CCVD) has become the most promising and versatile method due to its large production capacity at an extremely low cost with high purity (10). Furthermore, CCVD also offers the opportunity to control and adjust multiple physico-chemical properties of the nanotubes. Properties such as morphology, diameter, length, surface structure and alignment of the CNTs have been synthesized (11).

Cobalt (Co), among transition metals from group VIII, was considered as a result of its ability to grow hollow and higher graphitized CNTs (12-13). Also the choice of Molybdenum (Mo) as the catalyst promoter to enhance the performance of the catalyst is due to its suitability to be paired with Co to form a bimetallic catalyst which is efficacious for high yield synthesis of CNTs of high quality (14-16).

Alkaline earth metal oxide (MgO), considering it's easily dissolution in mild acid, was chosen as t catalyst support in the research study. MgO has been reported to be a good support for bimetallic (Mo catalyst for the synthesis of high quality and yield CNTs (14, 17, 18). Numerous researches h been conducted in the production of viable CNTs from precursor. Yeoh et al. in 2013 (18) repor effective synthesis of carbon nanotubes via catalytic decomposition of methane on support interact of Co-Mo/MgO catalyst, Lee et al. in 2010 (19) conducted research on the optimization of car nanotubes synthesis via methane decomposition over alumina-based catalyst. Chai et al. in 2006 (reported the preparation of carbon nanotubes over cobalt-containing catalysts via catal decomposition of methane. The previous researches conducted make use of alkane in (methane) as precursor; this research is conducted to investigate the effect of alkene in (acetylene) as the precur on the synthesis of carbon nanotubes via catalytic decomposition on bi-metallic support interactio Co-Mo/MgO catalyst.

2. Materials and method

2.1. Materials

The material used for the investigation are Co $(NO_3)_2$*$6H_2O$ and Mo $(NO_3)_3$*$6H_2O$ as received fr Kem light lab. Mumbai India, distilled water from Dana Pharmaceuticals Co. Ltd Minna, MgO fr Kermel china and H_2SO_4 from Guangdong Guanglua Sci-Tech Co. Ltd (JHD), all with (9 chemically pure were procured.

2.2. Method

2.2.1. Preparation of Co-Mo/MgO Catalyst

The bimetallic Co-Mo/MgO Catalyst was prepared by conventional impregnation method, with we ratio set at 54.5:3.4:42.1. The right amounts of Co $(NO_3)_2$ $6H_2O$ and Mo $(NO_3)_3$ $6H_2O$ were disso in distilled water and then the solution was impregnated onto MgO. The impregnated samples w stirred using magnetic stirrer for 20 minutes at the speed of 1500 rpm for 12 hours at the temp of 1 in an oven. The dried samples were ground and calcined in air at 700°C for 5hours. The prep catalysts were then used without a prior hydrogen reduction (19).

2.2. Synthesis of CNTs

CNTs were synthesized by the decomposition of acetylene in a chemical vapour deposition (C reactor. The synthesis was carried out in a horizontal quartz reactor (with length and diameter I mm and 65 mm, respectively) at an atmospheric pressure. The catalyst (bi-metallic Co-Mo catalys MgO support) was placed on a quartz boat (100×50×50 mm length, width and depth respectiv located at the middle of the reactor. Acetylene and nitrogen play the role of carbon precursor and gas respectively (19). Acetylene gas was used as a carbon precursor due to its stability at temperatures, which can avoid self-pyrolysis that causes the formation of amorphous and graphitic carbon (21). After the reaction, the reactor was cooled down to ambient temperatu nitrogen atmosphere. The ceramic boat was then removed and weighed to determine the quanti CNTs produced (19).

2.3. Characterization

The as produced carbon nanotubes deposit were characterized by XRD (Panalytical X'Pert Pr Kα radiation, λ = 0.1789 nm) at 40 KV and 30 mA. The XRD patterns were measure in 2θ ra from 10° to 9° with a step of 0.02° and measuring time of 2 sec per point. SEM images in SE were taken with a Zeiss Supra 35 field emission SEM equipped with energy dispersive X-ray (analyzer. Samples for transmission electron microscopy were prepared by dispersing pow

ethanol, placing in an ultrasonic bath, and then putting droplets onto 3 mm copper grids coated with amorphous carbon film and drying in air at room temperature. High-resolution TEM (HRTEM) images were obtained using a 200 kV JEOL JEM-2100F transmission electron microscope, equipped with a field emission gun and EDX analyzer (22).

3. Result and discussion

3.1. TEM analysis

The TEM representative image of the carbon nanotubes deposits is presented in Fig. 1 and 2. From the TEM images, it is observed that clusters of rope like carbon nanotubes structures were grown on the catalyst. The carbon nanotubes structures possessed appreciable hollow cores which indicate that the structures are carbon nanotubes and not fibres. This confirms that CNTs can be synthesized using acetylene as the precursor material and metal support interaction of Co-Mo/MgO Catalyst. The synthesis calcined at 700°C produced a CNT with narrow diameter distribution and further increases in heat treatment temperature to 800°C lead to an increase in the diameter of the CNTs distribution.

Fig. 3 and 4 shows the EDX spectrum of the CNT synthesized, this reveals the presence of Mg, O_2, C, S and Co as the constituents of the CNT produced. The peaks of Co and Mg elements are from the catalysts while the peak of O element is probably from the dissolution of H_2O, H_2SO_4 and the catalyst MgO. The Sulfur peak could be attributed to the presence of H_2SO_4.

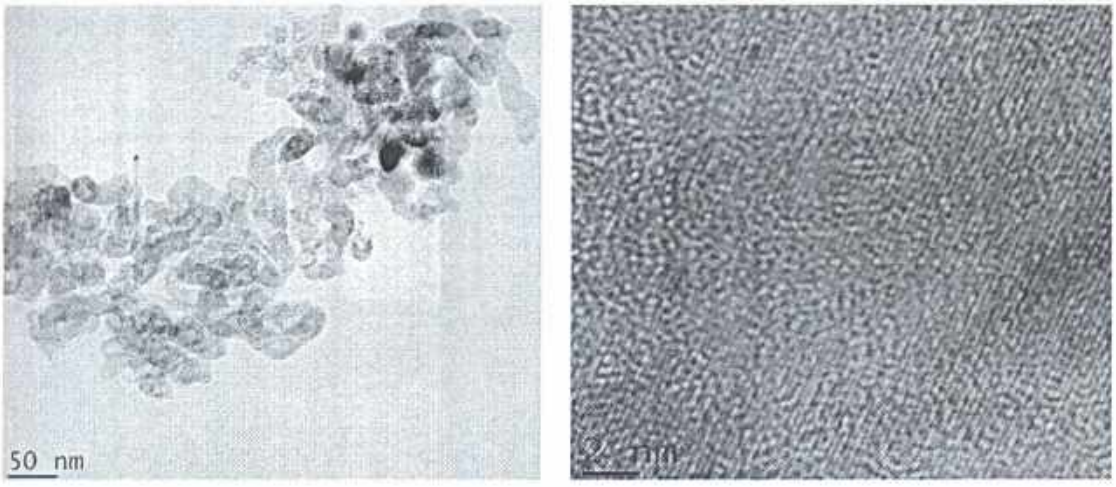

Figure 1 TEM images of the as-synthesized CNTs at 700°C

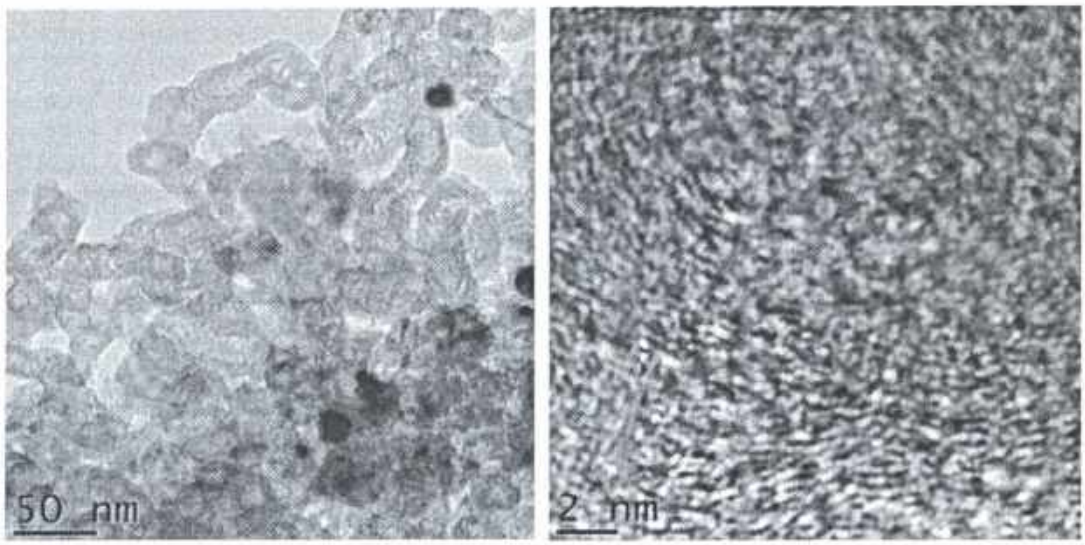

Figure 2 TEM images of the as-synthesized CNTs at 800°C

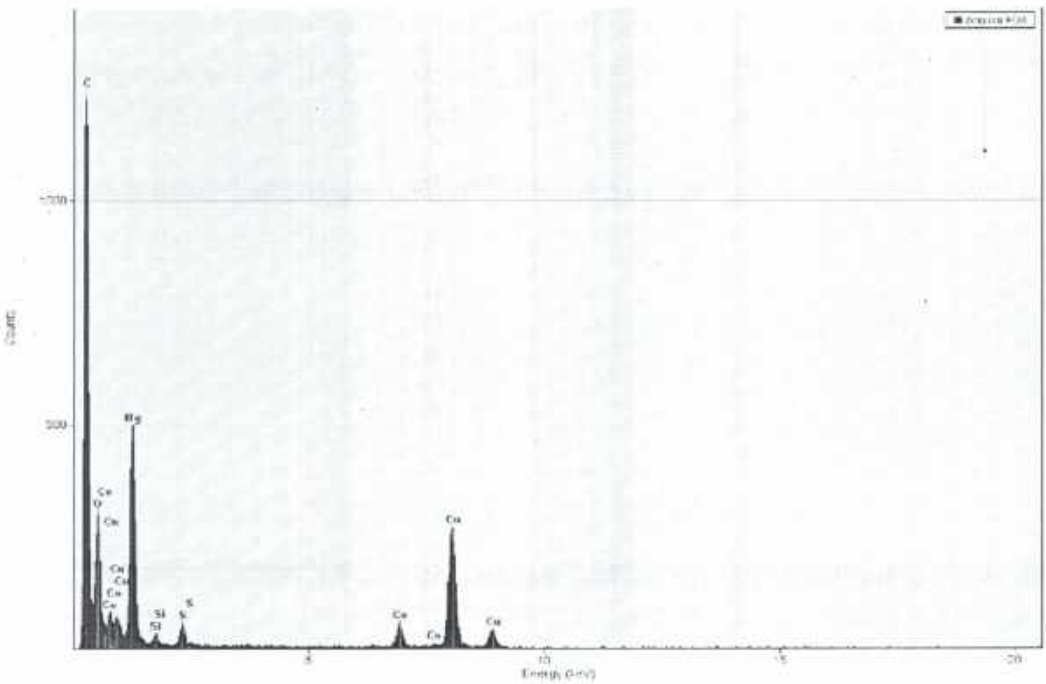

Figure 3 EDS of CNTs at 700°C

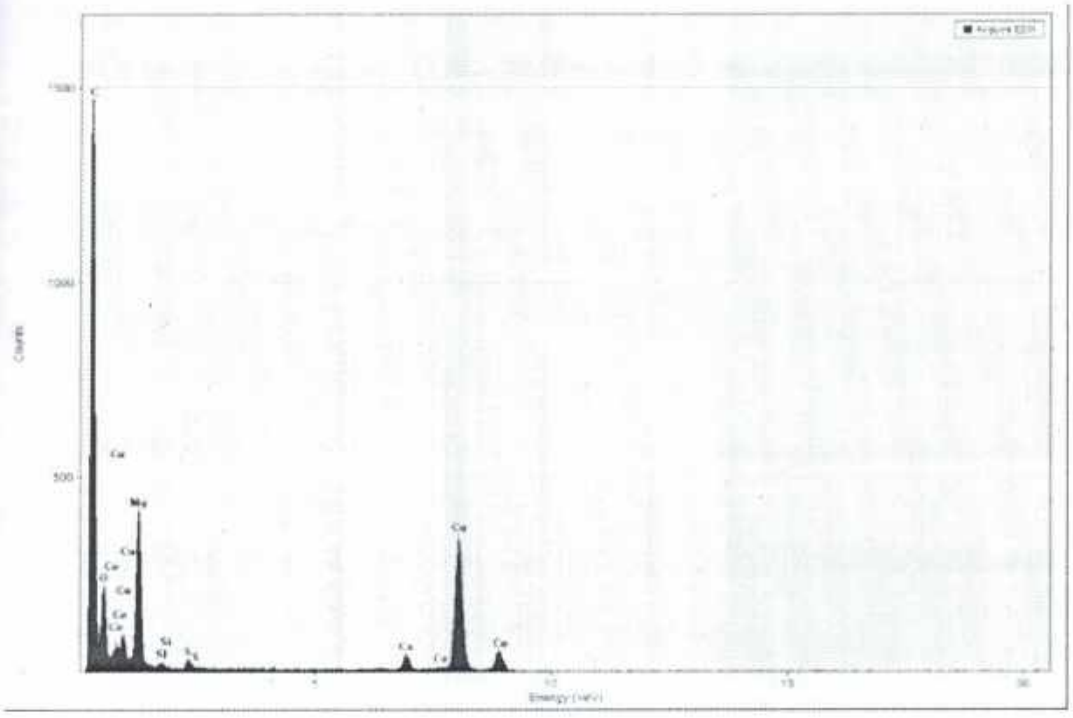

Figure 4 EDS of CNTs at 800°C

3.2. SEM Analysis

Figure 5, 6 and 7 shows a SEM image of the as-synthesized CNTs in the catalytic chemical decomposition reaction of Co-Mo/MgO. The obtained carbon nanotubes are formed as a network of rope like structure with different densities. CNTs diameters can be estimated as between 10 and 120 nm and length up to 10 μm. The figure shows a SEM image of the CNT surfaces, fairly homogeneously distributed.

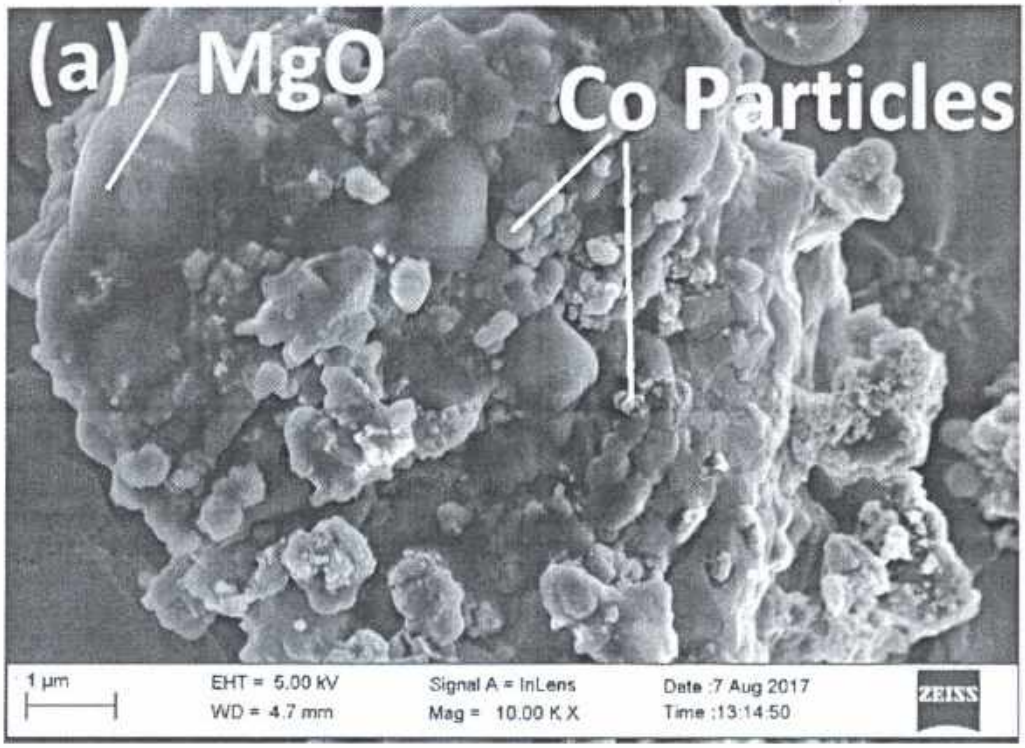

Figure 5 SEM images of the as-synthesized CNTs showing Co and MgO catalytic support

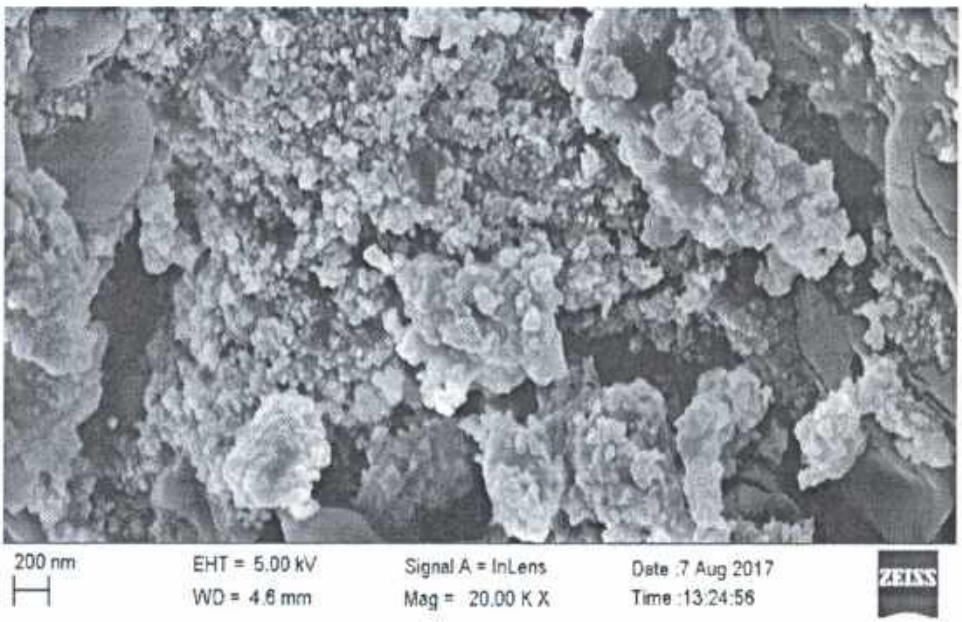

Figure 6 SEM images of the as-synthesized CNTs at 700℃

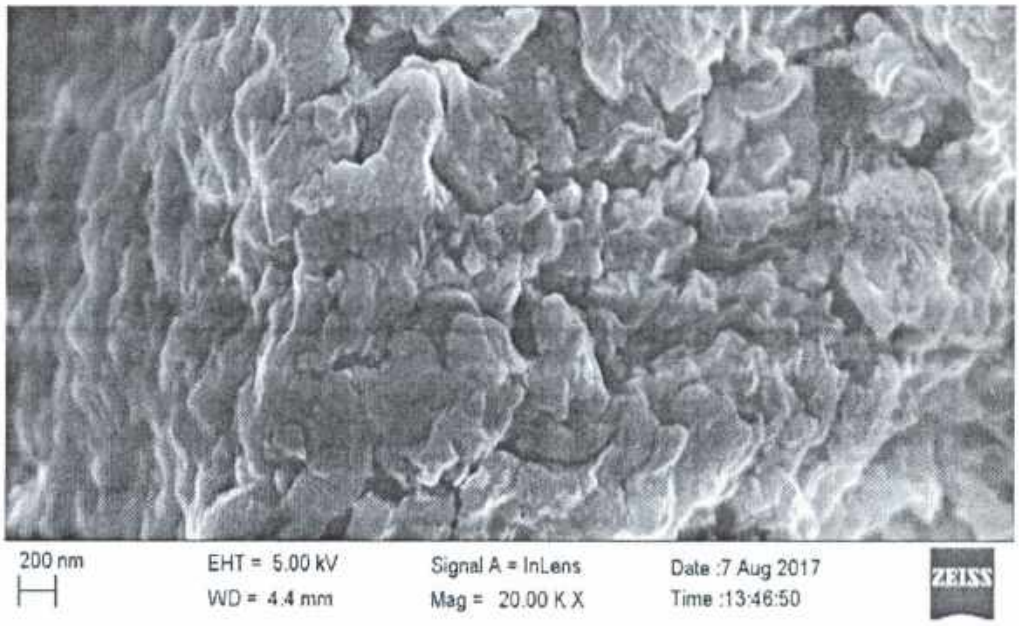

Figure 7: SEM images of the as-synthesized CNTs at 800°C

3.3. XRD analysis

From the XRD spectra as shown in Fig. 8, the emergence of diffraction peaks of CoMgO, CoO and MgO compound in the diffraction pattern of the CNTs produced. Heat treatment conducted at high temperatures healed the defect of crystals, giving the catalyst compounds of better crystallinity. $MgMoO_4$ and $CoMoO_4$ are thermally stable compounds up to 1000°C, and have the same role as MoO_3 for the prevention of extensive agglomeration of CoO species on the catalyst support (23).

Relatively to that was the decrease in MgO and CoO species content in the catalyst due to the incorporation of both MgO and CoO species into $MgMoO_4$ and $CoMoO_4$, respectively.

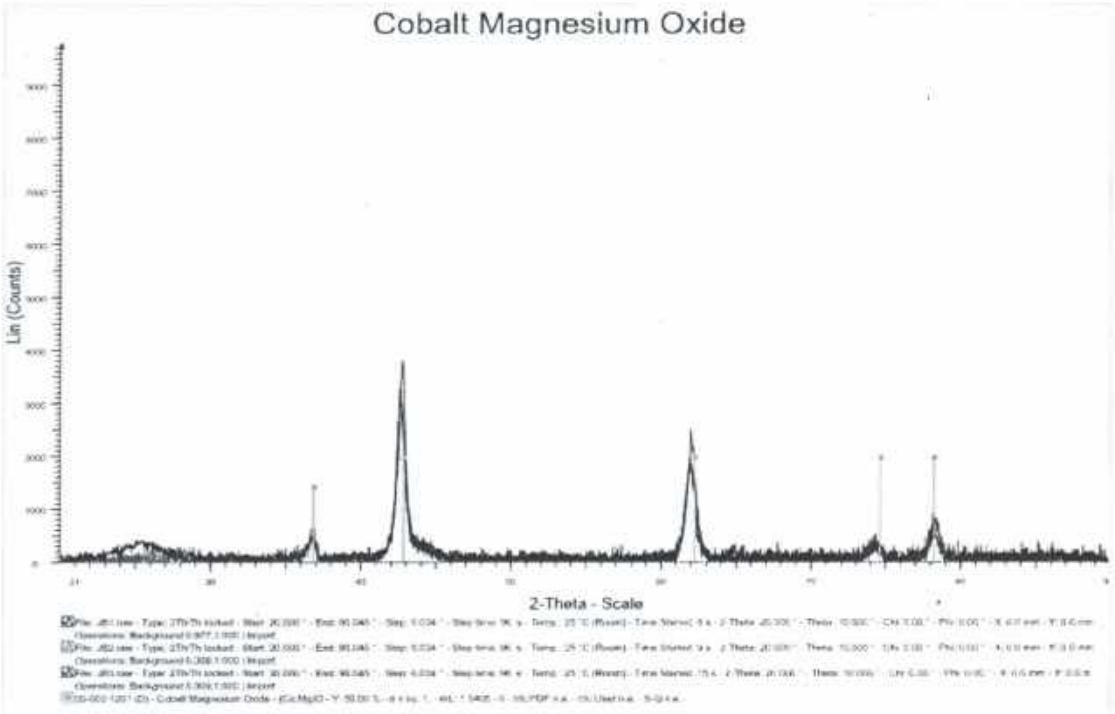

Fig. 8a. XRD spectra of as-synthesized CNTs revealing CoMgO

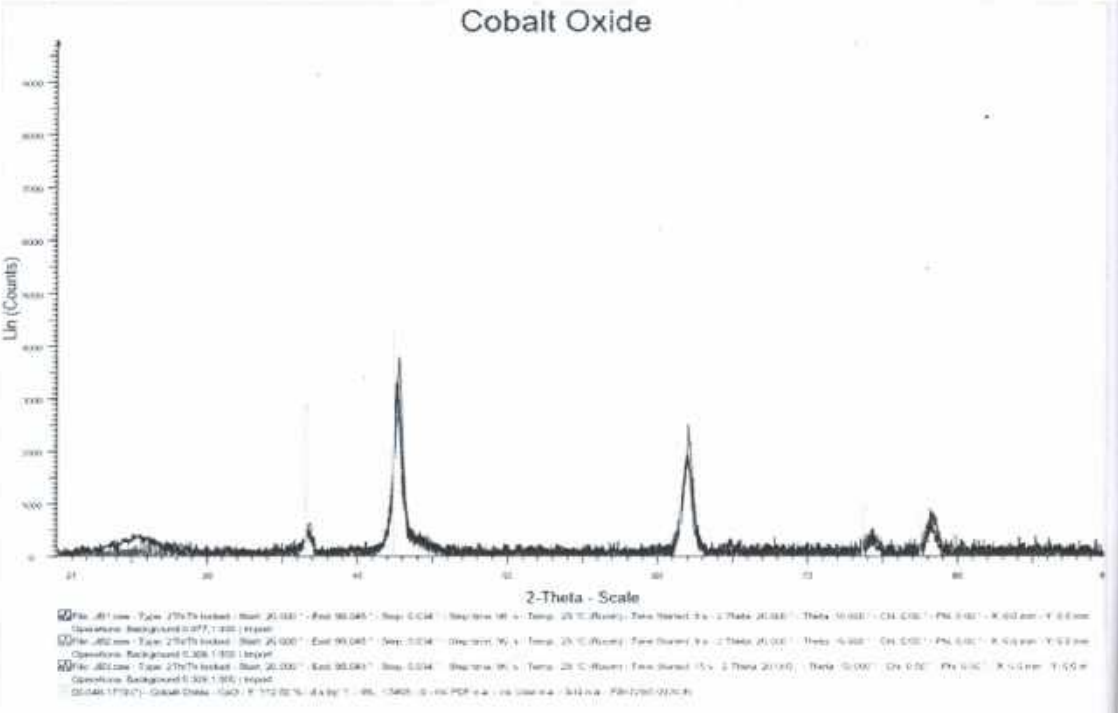

Fig. 8b. XRD spectra of as-synthesized CNTs revealing CoO

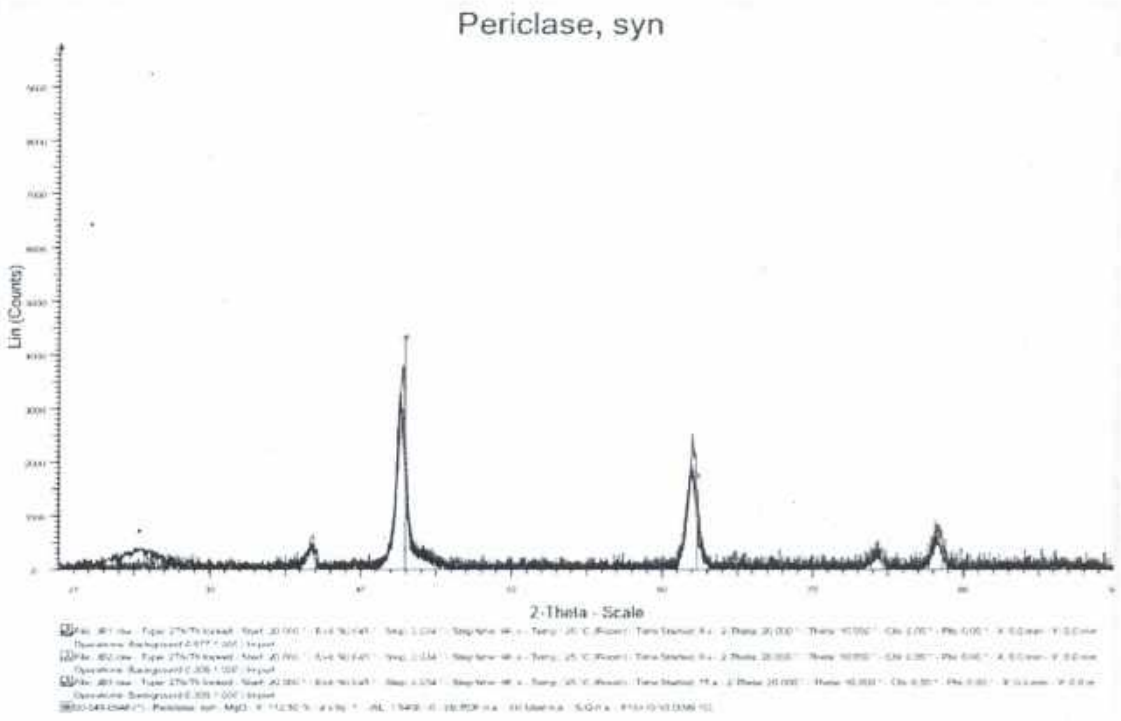

Fig. 8c. XRD spectra of as-synthesized CNTs revealing MgO

The catalytic performance is dependent on the strength of interaction between active metal and the support. The mobility of active metal on its support is governs by the metal-support interaction (MSI) of catalyst and this directly affects the agglomeration tendency of the active metal at elevated process temperature (24). In accordance to this, bimetallic Co-Mo/MgO catalyst with strong MSI will enhance the dispersion of CoO species on MgO for preventing its extensive agglomeration at 800°C during the CCVD process.

4. Conclusions

The research shows that acetylene can be utilized as precursor in the production of CNT via chemical vapour deposition as demonstrated in this work. This involves the production of the catalyst follow by the synthesis of the CNT using acetylene as the material in the CVD.

Need for further research

There will be need for further research in this area to know the amount and diameter of the CNT produced at various calcination temperatures.

Also there will be need to conduct the research at various calcination temperature and examine the phases of the CNT formed.

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