# Effect of addition of Ni metal catalyst onto the Co and Fe supported catalysts for the formation of carbon nanotubes

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**Abstract**

Production of novel porous material is a major target in current material science research due to its wide applications. As carbon nanotube (CNTs) is a one dimensional hollow structure it is also one of the promising materials in applications ranging from electronics to hydrogen storage medium. Catalytic chemical vapor deposition (CCVD) is a method whereby CNTs can be produced in large amount. Thus, in this work, we have synthesized CNTs via pyrolysis of acetylene using various supported transition-metal catalysts in a fixed-bed reactor. Scanning electron microscope (SEM) and transmission electron microscope (TEM) were used to investigate the CNTs structure. The structures of nanotubes formed by acetylene pyrolysis were dependent on the catalysts used. It was found that alumina supported Ni/Fe catalyst inhibited the formation of CNTs growth while alumina supported Ni/Co catalyst gave high density of CNTs. However, nanotubes grown over alumina supported Ni/Fe catalyst were less dense due to the deactivation of the catalyst at the early stage of the pyrolysis process.

*Keywords: carbon nanotubes, supported catalysts, SEM, TEM*

## Introduction

Carbon nanotubes (CNTs) are currently the focus of intense research in nanotechnology due to their unique properties and potential to impact broad areas of science and technology. Knowing its wide-ranging applications, a variety of synthesis methods have been explored. Catalytic Chemical Vapor Deposition (CCVD) has been chosen to be one of the promising methods for the synthesis of CNTs at low temperature and ambient pressure (1). Controlled synthesis involving CCVD has been studied as an effective strategy to order or pattern CNTs on a variety of surfaces. Metal and mixture of metals supported on oxides have been found to be active as catalyst in CCVD methods (1,2). The role of the support materials in supported catalyst is to disperse the active phase, control the porous structure, prevent sintering, improve mechanical strength and assist catalysis.

Almost all of the supported catalyst mixtures were found to be active in the formation of different forms of CNTs. The quantity and quality of the CNTs produced over different supported catalyst were however, significantly different. Therefore, one of the active fields of research in the area of CNTs technology at present is synthesis, characterization and applications (3-5). Several supports and transition metal/s combination have been investigated for their activity in the synthesis of CNTs under different experimental conditions (6,7). A wide variety of conditions have been used to condition the supported catalysts and subsequently grow CNTs. Therefore, a synthesis study on the combinations of mixed metal/s supported catalysts influences the formation CNTs was examined. In the present work, we describe the effect of monometallic and bimetallic supported catalyst on alumina towards the growth of the CNTs.

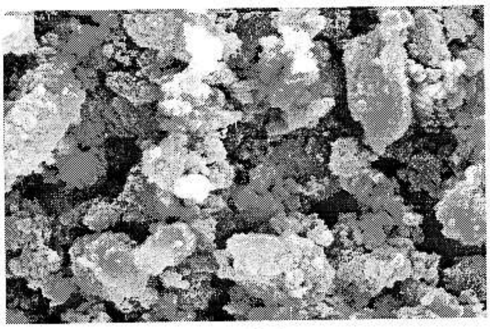
## Experimental

The catalysts used in this work were prepared using a wet impregnation method and the procedure is based on a previous report [8]. In this work, we used Ni, mixture of Ni-Co and Ni-Fe as catalysts instead of Co-Fe catalyst. The CVD growth of CNTs catalyzed by different catalysts was carried out using acetylene as carbon reactant. The procedure of the synthesis is described in detailed elsewhere [8]. Briefly, the catalysts were located at the center of the reactor furnace and acetylene ($C_2H_2$) and nitrogen ($N_2$) gases were introduced into the tube reactor simultaneously. The morphological structures of the products were examined by scanning electron microscope (SEM) and transmission electron microscope (TEM).

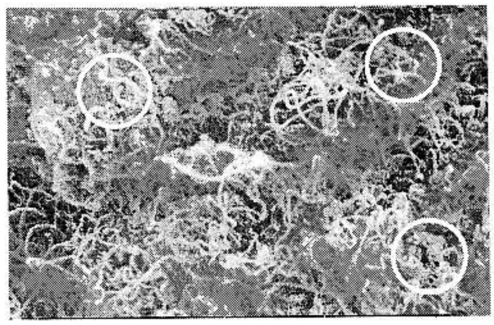
## Results and Discussion

Three metal species Co, Fe, and Ni were chosen in this work to explore the effect of different metal-support interactions upon the growth of CNTs. The as synthesized carbon deposit obtained was black in colour. The SEM micrographs in Figure 1 showed that the CNTs grown over the alumina supported catalysts were mostly in the form of tubular CNTs which grew in bundles.

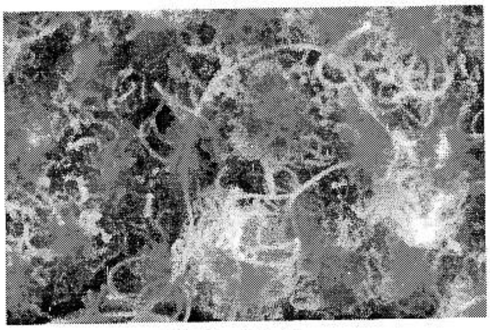
The transformation of the CNTs structures were clearly seen from the SEM micrograph in Figure 1, when Ni was introduced onto the Fe- $Al_2O_3$ and Co- $Al_2O_3$ catalysts system. Comparison between micrographs of as grown CNTs over respective supported catalyst showed that CNTs bundles grown over Ni- $Al_2O_3$ were highly dense with many white spots at the tips of CNTs floss. These white spots originated from the metal clusters (9,10) which indicated the occurrence of weak support-catalyst interaction. FE-SEM micrograph in Figure 2a supported the occurrence of the white spots at the tip of the slightly wavy tubular CNTs which can be clearly seen in the white circulated area an the SEM micrograph.



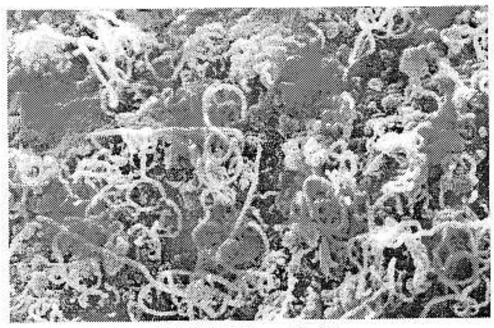
(a) $Al_2O_3$



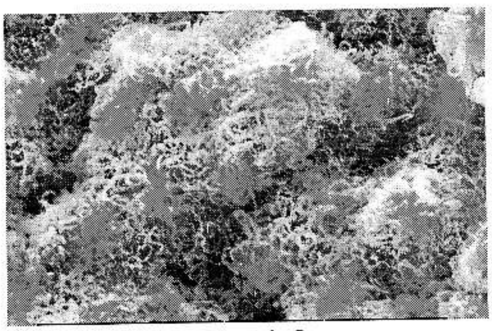
(b) Ni-$Al_2O_3$



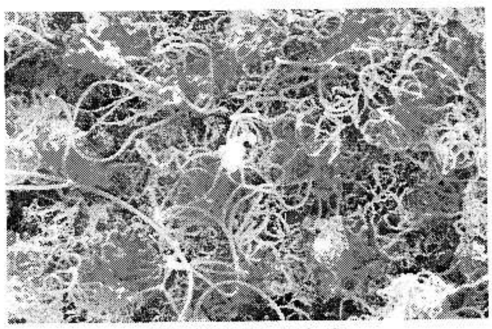
(c) Fe-$Al_2O_3$



(d) Ni/Fe-$Al_2O_3$



(e) Co-$Al_2O_3$

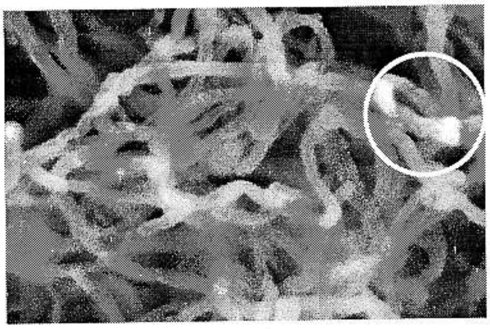


(f) Ni/Co-$Al_2O_3$

**Figure 1** : SEM Images of as-grown CNTs over alumina-supported catalysts (10,000 x magnification)

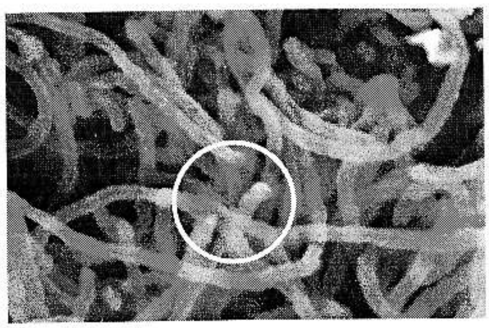
On the other hand the SEM micrograph of CNTs grown over Ni/Fe- $Al_2O_3$ showed less dense CNTs bundles without white spots. From this observation it can be inferred that the supported-catalyst interactions in the Ni/Fe- $Al_2O_3$ system were stronger. FE-SEM micrograph in Figure 2b showed that the CNTs grown over Ni/Fe – $Al_2O_3$ have opened end tubular structure with non uniform tubular sizes and many CNTs tubular structure.

However, the SEM micrograph of CNTs grown over Ni/Co- $Al_2O_3$ (Figure 1) revealed a highly dense CNT bundles with very little white spots. The Co- $Al_2O_3$ FE-SEM in Figure 2 (c ) has proven that by introducing Ni, high quality and purity of as grown CNTs was produced. The FE-SEM micrograph showed uniformity of the tubular sizes as well as many CNTs tubular structure which support the statement made earlier.



(a) Ni-$Al_2O_3$

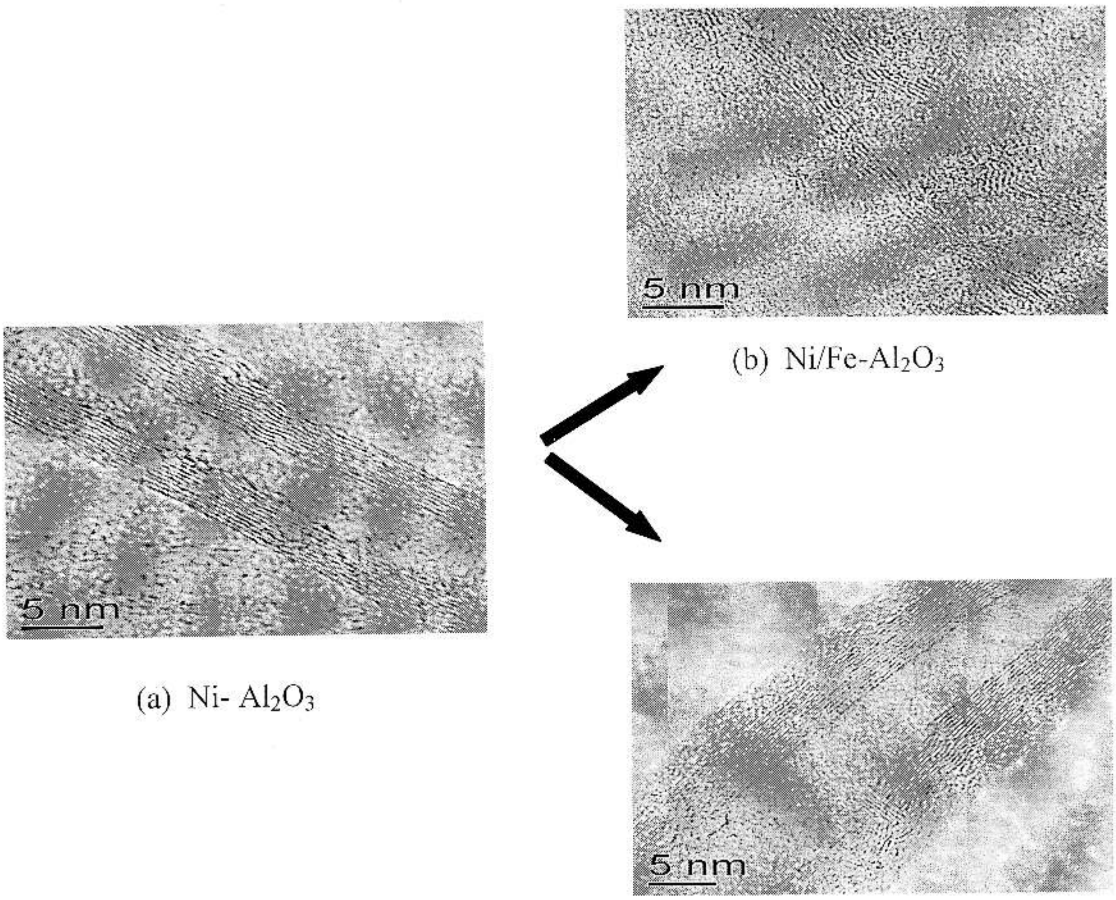
(b) Ni/Fe-$Al_2O_3$



(c) Ni/Co-$Al_2O_3$

**Figure 2** : FE-SEM Images of as-grown CNTs over alumina-supported catalysts

TEM analysis of all the synthesized CNTs was depicted in Figure 3. The results showed that the as-synthesized CNTs obtained in this work are multiwalled in nature, with the number of layered walls between 10-12. However, the walls are not concentric. The weak inner and outer diameters of the tubes were between 4.8 nm to 8.5 nm. The interlayer spacing between the graphene sheets is ~ 0.34 nm, which corresponded to the actual distance between the lattice layers in the graphite structure. TEM images for as-grown CNTs over Ni/Co-$Al_2O_3$ appeared to be high quality MWNTs as seen in Figure 3c, where the occurrence of almost straight-line layered walls. It should also be noted from the TEM images the amorphous carbon deposition presence was from the early stage of the pyrolysis process. TEM results for as-grown CNTs over Ni/Fe- $Al_2O_3$ also revealed that the quality of the MWNT's obtained is very poor.




(a) Ni- $Al_2O_3$

(b) Ni/Fe-$Al_2O_3$

(c)Ni/Co-$Al_2O_3$

**Figure 3** : TEM Images of as-grown CNTs over alumina-supported catalysts

These results suggested that the Ni/Co- $Al_2O_3$ supported catalysts gave the best yield of MWNTs, showing that interaction occurred between the catalysts and the support (11). This interaction can later affect both the crystallography and electronic structures of the supported catalysts and consequently affect the yield, morphology and structure of the as-grown CNTs.

## Conclusion

Combination of the metal catalyst and supporting substrate greatly affect CNTs yield, uniformity, purity and structure. In this work, we have demonstrated that the presence of Ni in the Fe- $Al_2O_3$ and Co-$Al_2O_3$ supported catalysts system have greatly influenced the quality and structure of as-synthesized CNTs formed. From the SEM and

TEM results obtained, we can conclude that the presence of Ni onto the Co-$Al_2O_3$ system gave the best form of MWNTs with high purity and quality.

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