

# Structure and catalytic activity relationships of Fe/Co supported on resistance different sources of Al(OH)<sub>3</sub> in the production of multiwall carbon nanotubes by catalytic chemical vapour deposition method

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## ABSTRACT

Al(OH)<sub>3</sub> from different sources has been used as supports for a mixture of Fe/Co salts and employed in the synthesis of Multiwall Carbon nanotubes by Catalytic Chemical Vapour Deposition method. These supported-catalysts have been characterized by Scanning Electron Microscopy, Powdered X-ray diffraction, and Thermo gravimetric studies. Surface area was determined by N<sub>2</sub> adsorption technique. Carbon nanotubes synthesis reactions have been conducted at 700 °C using acetylene as the hydrocarbon source in N<sub>2</sub> atmosphere. The quality and quantity of Multiwall carbon nanotubes depend not only on the carbon source, the textural & structural properties of the support and also their interactions with the active components available on the surface. Copyright © 2012 VBRI Press.

**Keywords:** Catalysts; multiwall carbon nanotubes; supports; catalytic chemical vapor deposition.



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National & International conferences held in India and abroad.

## Introduction

Several attempts have been made to synthesize carbon nanotubes, in large quantities & in large quantities & in the process several methods are developed. Carbon nanotubes are novel isomorphous forms of elemental carbon, discovered in the year 1991 by Japanese scientist S. Iijima. Carbon nanotubes are low in weight, have high strength and a high aspect ratio i.e. long length compared to a small diameter [1-3]. There are mainly two types of carbon nanotubes Single wall (SWNTs) and Multiwall (MWNTs). One of the promising methods used in the synthesis of carbon nanotubes is catalytic chemical vapor deposition (CCVD) of hydrocarbons over supported metal catalysts [4]. In CCVD, the peculiar ability of metals dispersed in support to promote carbon nanotubes (CNTs) growth is related to their catalytic activity for the decomposition of hydrocarbon source, which precedes the CNTs growth. The role of support material is to disperse the active metal species, provide porous structured, prevent sintering, improve mechanical strength and promote catalysis [5]. In the case of supported catalysts, the interactions between the support and the catalyst nanoparticles have to be taken into account. There are several factors which affect the growth of carbon nanotubes in CCVD such as size of catalyst (metal) particles, their electronic structures, crystallographic orientations, method of preparation of catalysts-supports, dispersion of catalyst nanoparticles in support, the nature of catalysts support interactions etc. Although these properties have been partially investigated, the concept about the support and the active metal species interactions is not yet clearly understood, as the different results are observed with different supported materials. Alumina and Aluminium hydroxide have been recently reported as very effective catalytic supports for CNTs preparation [6, 7].

Several scientists have studied alumina as a support in different forms such as, micro sized powders [9], aero gels [10], membranes [11], disc type pellets [12] and as layered double hydroxides [13] and obtained different results. Some of the methods adopted to prepare alumina catalyst composites are: Sol gel, Impregnation, Co-precipitation, Super critical drying, annealing and Mechanical mixing [14-19]. The metals that are used in the alumina-catalyst composite preparation include Fe, Co, Ni, Mo, Cu and their binary mixtures [6, 20-21]. By using these catalysts - alumina mixtures, different kinds of carbon nanotubes such as SWNTs, MWNTs, DWNTs and also carbon fibers are obtained. A very few have used  $\text{Al}(\text{OH})_3$  as the support for Fe/Co(22) in the production of MWNTs by CCVD. Further, using  $\text{Al}(\text{OH})_3$  as support for Fe and Co seems to be interesting to study their catalytic activity in the production of MWNTs by CCVD. In this work Fe/Co supported on  $\text{Al}(\text{OH})_3$  procured from different sources were used to investigate the production of MWNTs by CCVD.

## Experimental

Five different samples of  $\text{Al}(\text{OH})_3$  were procured from different sources and used as supports for Fe and Co.

Ferric nitrate [ $\text{Fe}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ] and Cobalt nitrate [ $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ] were used as the precursor for Fe and Co catalysts respectively.

Dry impregnation method was adopted to prepare the catalysts. The support and metal salts were mixed such that the weight % of the support was 95 and that of the each metal was 2.5. Calculated amounts of the metal salts was ground into fine powder and dispersed in a few drops of water. Required quantity of  $\text{Al}(\text{OH})_3$  powder was added to the metal salts paste; mixed well to get a homogeneous mixture and dried in an air oven at  $120^\circ\text{C}$  for 24 hr to obtain the final catalyst. Thus prepared catalysts are abbreviated as: Cata-AC, Cata-MK, Cata-SD, Cata-LB and Cata-Al. The first four samples were prepared using different commercial samples of  $\text{Al}(\text{OH})_3$  as the support whereas for the last one the support was prepared from aluminium nitrate using liquor ammonia as the precipitating agent.

### Characterization of catalysts

The catalysts were analyzed for their surface and bulk properties. The BET surface area was measured using NOVA (Ver 3.7) by purging nitrogen gas at 77K. Powder XRD patterns were recorded in the range of 4 to 60 degrees on a Phillips, Belgium X-ray diffractometer with  $\text{Cu K}\alpha$  radiation ( $1.542 \text{ \AA}$ ). SEM images of the catalysts were taken using Philips Belgium instrument. TGA/DSC graphs were recorded on NETZSCH STA, Belgium in the temperature range 40 to  $1000^\circ\text{C}$  with a heating rate of  $10^\circ\text{C}/\text{min}$  in the presence of Helium.

### Production of carbon nanotubes

Acetylene was used as the sources of carbon. Pyrolysis of hydrocarbons acetylene at  $700^\circ\text{C}$  was carried out in a horizontal furnace to produce MWNTs, at atmospheric pressure in the presence of nitrogen as the carrier gas ( $300 \text{ ml}/\text{min}$ ). The rate of flow of the hydrocarbon was  $30 \text{ ml}/\text{min}$ .

In a typical MWNTs synthesis experiment, about 1 gram of accurately weighed catalyst was spread over a quartz plate as a thin layer and placed inside the furnace which was pre-heated to  $700^\circ\text{C}$ .  $\text{N}_2$  gas was purged for ten minutes followed by acetylene for one hour. Later the reaction vessel was cooled to room temperature and the weight of the carbon deposited on the catalyst was found out. The percentage of carbon deposit was calculated by considering the weight loss of the catalyst at the synthesis temperature [23].

## Results and discussion

### Surface area

The catalysts exhibited distinctly different surface area values in the range of 1.5 to  $75 \text{ m}^2/\text{g}$ . This is an indication that the size and the porosity of the catalyst particles are different. The surface area indicated mesoporous/microporous nature of the catalyst particles. It is noteworthy that Cata-Ac and Cata-Al exhibited very low surface area and hence larger particles associated with low porosity. The decreasing order of the surface area of

the catalysts is: Cata-MK > Cata-SD > Cata-LB > Cata-AL > Cata-AC. The surface area values of different catalysts used are given in **Table 1**.

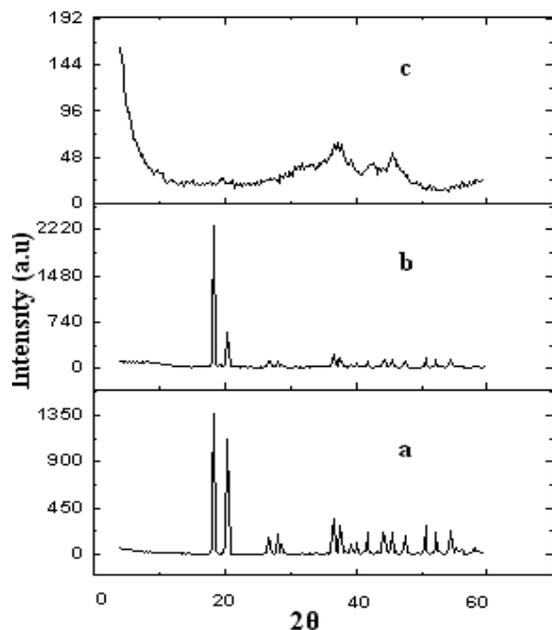
**Table 1.** The Fe/Co catalysts supported on different Al(OH)<sub>3</sub> support and their surface area in m<sup>2</sup>/g.

Catalysts abbreviations	Surface area in m <sup>2</sup> /g
Cata AC	01.50
Cata MK	74.26
Cata SD	55.41
Cata LB	16.30
Cata AL	04.46

#### Powder X-ray diffraction patterns

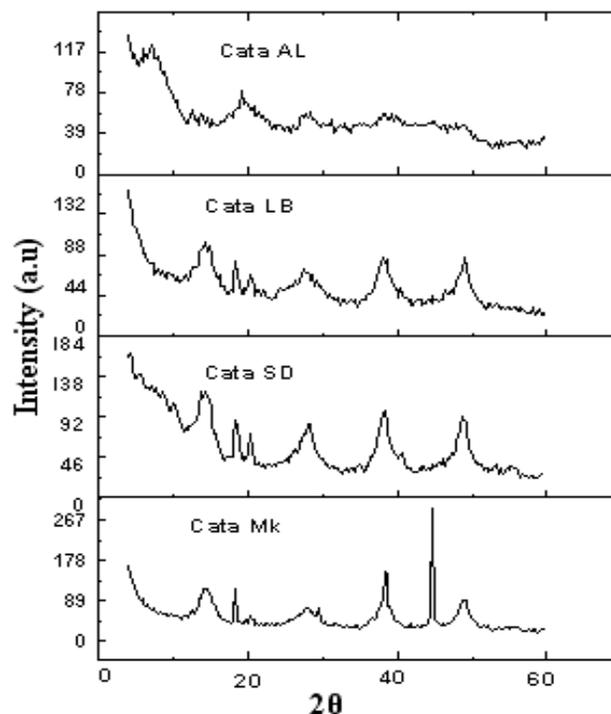
PXRD results on the catalysts provided interesting and useful information on the textural difference of the support material and hence explain the difference in their activity for the production of different quantities and quality of CNTs.

The PXRD patterns of Al(OH)<sub>3</sub> support that was used to prepare Cata-AC was found to be crystallized and exhibited diffraction patterns characteristic of bayerite [ $\beta$ -Al(OH)<sub>3</sub>] phase as (**Fig. 1**) [24]. It is interesting to note that when this support is dry impregnated with Fe and Co metal salt solutions the intensity of the diffraction peak at  $2\theta = 21^\circ$  of the original hydroxide has significantly decreased with a corresponding increasing in the peak intensity at  $2\theta = 19^\circ$  (**Fig. 1**). This is a clear indication of a possible metal - support interaction. Bayerite phase seems to be involved in enhancing the activity of Fe and Co metal ions in the production of MWNTs, because as is evident later that Cata-AC is the one that produced highest quantity amount of MWNTs.



**Fig. 1.** PXRD patterns of a) Support Al(OH)<sub>3</sub> b) Catalyst AC and c) Calcined support Al(OH)<sub>3</sub>.

It was noticed that the pure Al(OH)<sub>3</sub> support completely lost its crystallinity on calcinations to 700 °C as evident by its PXRD given in **Fig. 1**. This observation indicates that the Bayerite ( $\beta$  Al(OH)<sub>3</sub>) phase that existed initially collapsed at higher temperatures resulting poorly crystallised ( $\eta$ ,  $\gamma$ ,  $\theta$ ) phases of alumina.



**Fig. 2.** PXRD patterns of Cata AL, LB, SD and MK obtained from different commercial Al(OH)<sub>3</sub> sources.

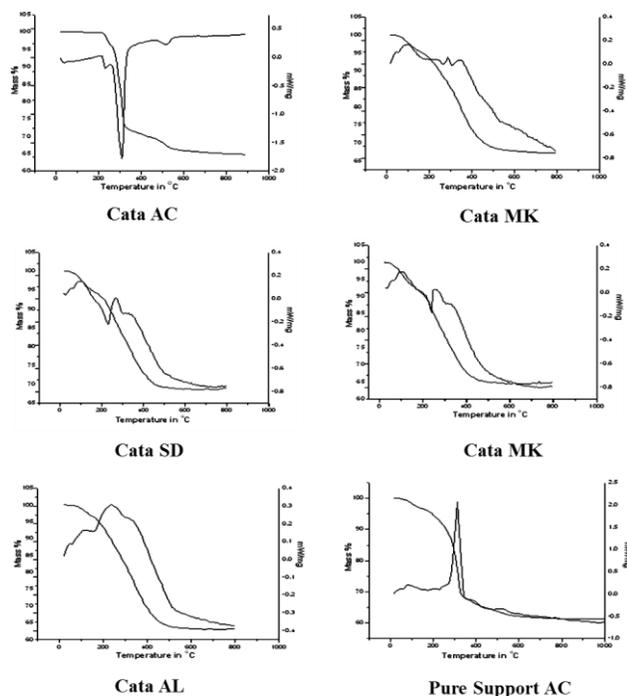
The PXRD patterns of the other commercial samples of Al(OH)<sub>3</sub> and also those of the catalysts prepared using them were recorded & shown in **Fig. 2**. All of them exhibited very weak x-ray diffraction patterns indicating predominantly amorphous nature of the original catalysts. The peaks can not be assigned to any particular phase of aluminium hydroxide. These observations indicated that the particles size in the original catalyst AC -catalyst is larger when compared to those in the others samples, correlating the observed low surface area of Cat-AC.

Further, the absence any characteristic diffraction peaks corresponding to the oxide phases of Fe and Co in the XRD spectra of the catalysts indicated that the transition metal ions did not form any crystallites of their oxides whose size correspond to the X-ray coherence length. As it is known that a certain periodicity in the samples (10 nm) is needed to produce diffraction patterns of sharp peaks by x-ray diffraction, the metal ion species may suppose to be distributed on the support surface as nanoparticles.

#### TG and DSC studies

The TG/DSC profiles of all the catalysts are given in **Fig. 3**. The TG/DSC studies were conducted to identify the change in phase that the catalyst would undergo when subjected to heat treatment in the temperature range 40 °C

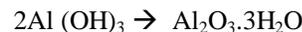
to 1000 °C. It is noteworthy that different catalysts exhibited different behavior when subjected to heat treatment.



**Fig. 3.** TG and DSC curves of different Fe/Co supported on  $\text{Al}(\text{OH})_3$  catalysts and pure AC Support.

The TG patterns of Cata MK, Cata SD, Cata LB and Cata AL are almost similar to one another in the sense that all these catalysts showed a gradual decrease in the weight loss up to about 450 °C. The total weight loss that occurred when these catalysts were heated to this temperature was about 32.5% of their initial weight. This weight loss may be attributed mainly to the decomposition of the metal nitrates and the loss of physically adsorbed water molecules. In Cata AC however, the weight loss occurred in two steps. A sharp first step at 315 °C and a gradual second step in the range 315 °C to 450 °C which accounted for 27.5 % and 5.0% weight loss respectively. These results indicate that the textural properties of the former set catalysts are different from the later.

The DSC patterns of Cata MK, Cata SD, Cata LB and Cata AL are significantly different from each other and also from that of Cata AC. The former catalysts did not exhibit any significant exotherm or endotherm when subjected to thermal treatment as shown by the Cata AC. The differences in DSC profiles observed among the catalysts other than Cata AC, also indicates that the processes such as dehydration/ phase transition/ crystallisation that might have occurred in these catalysts during heat treatment are different from one another as well as from that of Cata AC. The DSC studies in the case of the pure support used for the preparation of Cata AC, exhibited a sharp exotherm at 315 °C (**Fig. 3**) indicating a possible phase transition accompanying crystallization at this temperature. This may involve probably the conversion of the hydroxide form of the support into the hydrated oxide form.

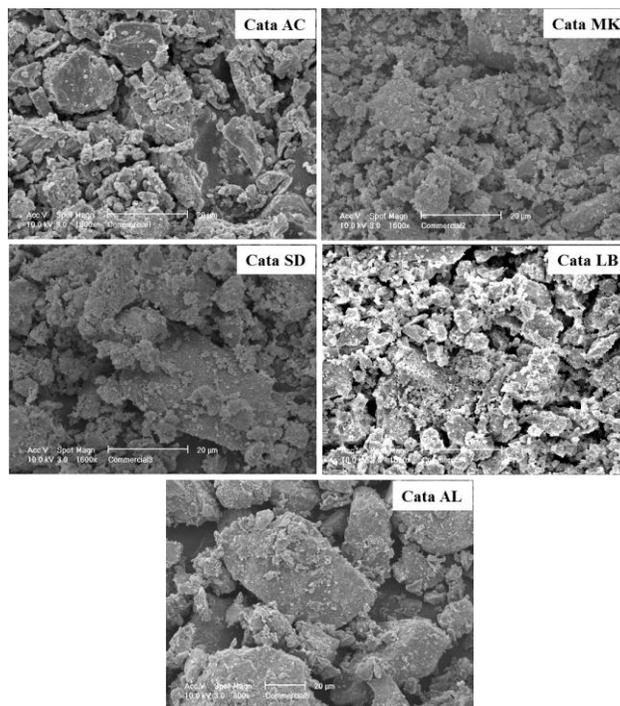


This temperature also corresponds to the transition temperature of the more crystalline bayerite into poorly crystallized phases of  $\text{Al}_2\text{O}_3$ .

On the other hand in the case of Cata AC, the DSC pattern exhibited at the same temperature an endotherm in place of exotherm as noticed with the pure support. This indicates in the presence of Fe/Co salts the transition from the hydroxide phase to hydrated oxide phase has been probably affected. Thus DSC analysis of the pure support provided useful information on the nature of the phase transition and the type the particles undergoing this change. DSC analysis also provides some information on the physical composition of the catalyst particles. The single sharp endotherms in the case of Cata-AC indicated more homogeneous nature of the crystallites present in the sample, than the particle in the other catalysts which exhibited multiple and broad DSC curves. This probably account for the significant difference in the catalytic activity associated with catalyst as explained later in this chapter. Thus TGA and DSC studies on the selected catalysts have clearly indicated that each of the five catalysts used in this investigation is found to be different from one another in the nature and homogeneity of the physical state of the particles associated with them.

#### Scanning electron micrographs of catalysts

It is noticed from the Scanning electron micrograph images of the catalysts that they exhibited distinctly different texture. SEM images of the catalysts (**Fig. 4**) indicate different morphology of the particles associated with the catalysts.



**Fig. 4.** SEM images of uncalcined catalysts AC, MK, SD, LB and AL.

These images supplemented the observed low surface areas of Cata-AC and Cata-AL samples had larger particles. Cata-AC also appears to be more crystalline than the other catalysts. The catalyst particles of Cata - Mk, Cata - SD and Cata - LB probably smaller and may form aggregates with support material.

**Table 2.** The percentage of carbon deposit obtained using acetylene as the carbon source.

Catalysts Abbreviation	% of carbon deposit using acetylene
Cata AC	334.71
Cata MK	149.90
Cata SD	142.90
Cata LB	124.33
Cata AL	106.00

**Table 3.** TEM observation of carbon deposit obtained using acetylene as hydrocarbon source from different catalysts.

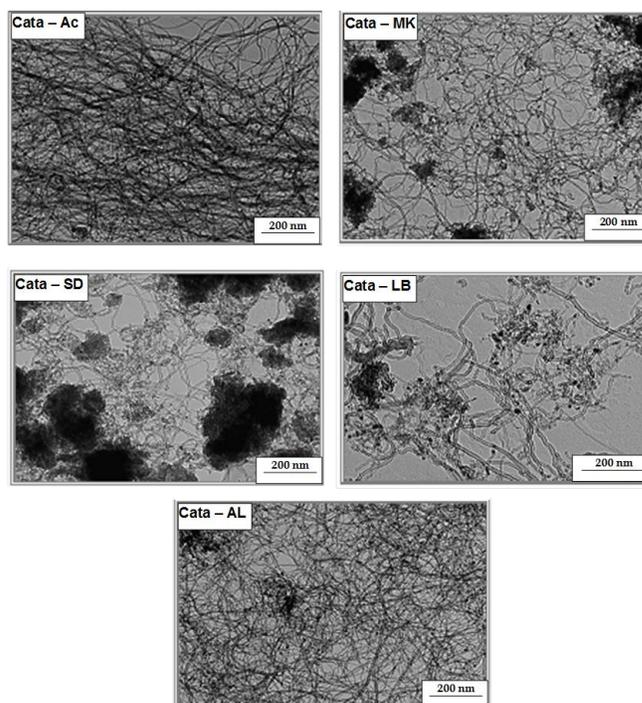
Catalyst	TEM observation of carbon deposit obtained using acetylene as hydrocarbon source from different catalysts
Cata - AC	Very good density of even size MWNTS, and few thick tubes without any particles inside the tubes and very clear tubes were observed.
Cata - MK	Many black spots, very few thin tubes, MWNTs appeared emerging from black spots. Few fibers or bamboo shaped tubes were seen.
Cata - SD	Only black spots and very few not well grown tubes are observed. Looks like some defects are seen.
Cata - LB	Very thick black spots and more of amorphous carbon were observed. The tubes were not at clear
Cata - AL	At very low magnification, nature of MWNTs was very clear and it is like quasi aligned form. Good density of MWNTs was observed with particles inside.

#### Analysis of the carbon deposit

It is interesting to note that all the catalysts have exhibited catalytic activity for the pyrolysis of acetylene carbon deposit. The percentage of carbon deposit obtained from Cata AC, Mk, SD, LB and AL are given in the **Table 2**.

TEM analysis of the carbon deposit produced over the different catalysts also showed that the MWNTs associated with it were distinctly different. A few representative low resolution TEM images of the carbon deposit are given in the **Fig. 5**. The density of the MWNTs produced is much higher on Cata-Ac and Cata-AL. It is to be recalled here that these are the catalysts prepared from aluminum hydroxide support which exhibited much lower surface area and diffraction patterns characteristic of crystalline materials; compared to the other catalysts. This

collaborates the fact that the surface properties of the support and the crystallographic orientation of the catalysts deposited over it plays a significant role on the growth of MWNTs in CCVD of hydrocarbons. Thus the support in Cata-AC provides the particles with right orientation for the Fe and Co to exhibit their catalytic activity in the growth of MWNTs. The crystallographic phase of  $\text{Al}(\text{OH})_3$  particles that seems to be having favorable orientation for Fe and Co catalysts is Bohemite. Hence this material produced very high percentage of carbon deposit which also had good density of MWNTs. From the amount of carbon deposit obtained, it is clear that the textural properties of the support exhibit a promising effect on the catalytic activity of Fe and Co in the production of MWNTs in CCVD. The carbon deposits obtained from different catalysts were analyzed for the density and nature of MWNTs associated with. The as made observation during TEM analysis of the samples obtained by CCVD methods using acetylene at different spots, on different carbon deposits are given in the **Table 3**.



**Fig. 5.** TEM images of carbon deposit obtained from acetylene source.

#### Conclusion

MWNTs have been synthesized using Fe/Co catalyst mixture supported on Aluminium hydroxide procured from different sources. The results clearly demonstrated that the nature and the amount of carbon nanotubes synthesized in CCVD method depend greatly on the surface properties of the support. The difference in the surface structure of the support significantly influence the nature of its interaction with the active component (metal species) deposited on it. It is noticed that not the high surface area of the catalyst that plays an important role in deciding its catalytic activity but the nature of the support surface that favor the conditions for the active components

available for MWNTs, is important. Thus a commercial sample of crystalline  $\text{Al}(\text{OH})_3$  with low surface area and porosity has been found to be a good support for iron and cobalt salts to obtain good quality MWNTs in large scale by CCVD method.

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