

Multiwalled Carbon Nanotubes by the decomposition of acetylene using Co Catalysts

Binod Kumar Singh, Hojin Ryu, Soo Jin Park, Seok Kim and Jae Rock Lee

Advance Materials Division, Korea Research Institute of Chemical Technology (KRICT)

Abstract

Catalytic performance of Co catalysts supported on MgO for the formation of multiwall carbon nanotubes (MWCNTs) having 40–60 nm in diameter has been investigated through acetylene decomposition at 600°C. Scanning electron microscopy measurements show that the nanotubes are chain and coiled structures whereas x-ray diffraction patterns indicate the formation of MWCNTs with Co nanoparticles. In addition Raman spectra confirms the formation of MWCNTs due to presence of characteristic radial breathing mode along with D and G bands.

1. Introduction

Carbon nanotubes and nanorods have attracted significant attention not only because of their small dimensions and unique morphological properties, but also for their potential applications in various technologies [1] due to their high mechanical strength [2], capillary properties [3] and remarkable electronic structures. Different methods were employed for the synthesis of CNTs that include electric arc discharge in the absence or presence of metal [4], laser vaporization of a metal-graphite composite target [5], chemical vapour deposition (CVD) [6–8], and plasma-enhanced CVD [9,10]. Among these methods, CVD is the most commonly employed technique for laboratory scale and commercial purpose. To grow multi-walled carbon nanotubes (MWCNTs), alumina, zeolite, MgO and graphite supports with different hydrocarbons, as a source has been the locus of many investigations.

In the present study, we have synthesized MWCNTs using acetylene as the carbon source and Co-MgO as catalysts. Different characteristic of CNTs were studied using X-ray diffraction (XRD), scanning electron microscopy (SEM) and Raman spectra analysis.

2. Experimental

The carbon nanotubes are synthesized through CVD by Co-MgO catalyst in presence of H_2/C_2H_2 gas flow. First, we have prepared Co/MgO catalysts by impregnation method at different percentage. In this case the loading ratio of Co:MgO (wt.%) was varied from 1 - 75% of cobalt on MgO support. $Co(NO_3)_2 \cdot 6H_2O$ and $Mg(OH)_2$ were used as a starting materials for the preparation of the catalyst. Stoichiometric amount of $Co(NO_3)_2 \cdot 6H_2O$ and $Mg(OH)_2$ were stirring in ethanol with an agate mortar and then mixture was dried at 100°C for 10 hrs in an oven. This dried mixture powder was used as a catalyst and H_2/C_2H_2 gaseous mixture was used as a carbon source for synthesis of CNTs. Catalyst powder of 0.1 g of was uniformly dispersed in the base area of alumina boat and placed in the central region of horizontal quartz tube having inner diameter of 4.5 and a length of 100 cm. Then this quartz tube placed inside a furnace. Argon gas was then flown inside the furnace and the temperature was raised up to 600°C with a heating rate of 10°C/min. At the desired temperature, H_2 gas was introduced in the furnace at the flow rate of 100 ml/min for 30 minutes to generate active Co catalyst on MgO support. After maintaining the hydrogen stream for desired period, C_2H_2 and H_2 gas was flown through the furnace for 1 hr at a flow rate of 15 ml/min to produces CNTs. We have synthesized CNTS over three catalysts under these experimental conditions. Carbon yields were

calculated by weighing the sample after the reduction process using the equation: CNTs yield (wt.%) = $[(M_f - M_i)/M_i] \times 100$.

Where M_f is the total weight obtained after synthesis and M_i is the weight of catalyst utilized for synthesis. CNT's samples were characterized using XRD (Rigaku D/Max-2200V equipped with CuK_α radiation, $\lambda = 1.5418\text{\AA}$), the morphological and structural changes of the CNTs samples has been investigated by SEM (Jeol JSM 6700F), BET surface area analysis (Micromeritics ASAP-2400) and Raman spectra were recorded under ambient conditions using a Bruker FRA106 FT Raman spectroscope (excitation source 1064 nm) maintaining constant and optical power of 10 mW at the sample position.

3. Results and Discussion

Fig. 1 shows the XRD patterns of as synthesized CNTs after the catalytic decomposition of acetylene over Co/MgO at different loading. The XRD pattern reveals graphite like peaks in the sample. The graphite (002) and (004) reflections are distinct at 26° and 54° . The cobalt (111) and (220) peaks are prominent corresponding to 44.3° and 51.5° in the spectra of 25 and 75% samples [11]. The comparison of intensity patterns for cobalt peaks for three samples indicates that 50% sample possesses highly dispersed Co particles in the MgO matrix along with the flattening of MgO phase. It implies that at this composition, the distribution of Co nano particles is uniform with particles size of about 18.8 nm as derived from the Scherrer equation. Moreover, such a finely divided Co particles on MgO support is found to be responsible for the better yield of CNT's thus produced. In addition to these features, there is either absence of peaks with reduced intensity corresponding to oxide phase to metallic cobalt is optimum and may be attributing for the efficient growth of CNT's. Thus, Co particle catalysts and the MgO support are probably behaving in symbiotic manners that increase the yield of the product. However, the sharpening of the graphite peak takes place as the cobalt loading is increased implying the enhanced crystallinity of this phase.

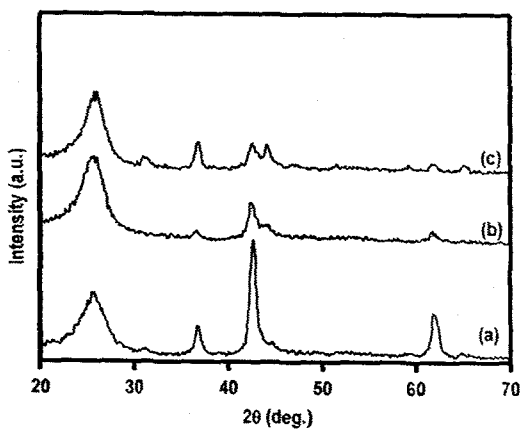


Fig. 1. X-ray diffraction pattern of CNTs synthesized using (a) 25% Co (b) 50% Co and (c) 75% Co on MgO support under acetylene-hydrogen mixture for 1 hr.

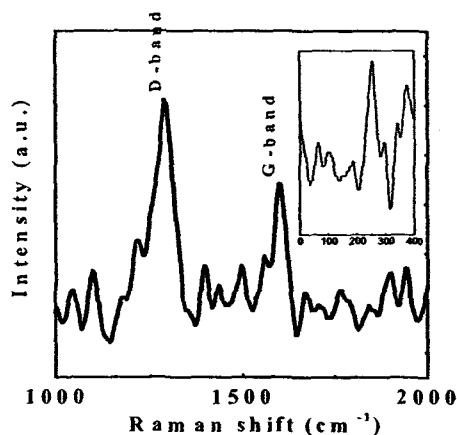


Fig. 2. Raman spectrum of the as synthesized MWCNTs by catalytic decomposition of acetylene using 50% Co loading on MgO support. Inset figure depicts the radial breathing mode (RBM) for the same.

Fig. 2 shows the Raman spectrum of the synthesized CNT's with 50% cobalt loading on MgO support. The first order Raman spectrum typically between $1000 - 2000 \text{ cm}^{-1}$ is composed of two main well-known peaks D and G at around 1300 cm^{-1} and 1600 cm^{-1} [12] respectively. The former band corresponds to the defect-induced Raman band and is known as the defect mode, associated with vibrations of carbon atoms with dangling bonds in plane terminations of disordered graphite or glossy carbon. The latter peak represents the Raman-allowed E_{2g} mode of graphite and is related to the vibration of sp^2 bonded carbon atoms in a two-dimensional hexagonal lattice, such as in graphite layer [11]. Nanotubes with

multiwalled layers of hexagonal carbon lattice display the similar vibrational modes. Also close to G-band, there is small intensity peak around 1673 cm^{-1} , usually recognized as D' probably arising out of maximum in the phonon density of states. The D and D' peaks correlate with the size of the crystal, i.e., a smaller crystal would give rise to a larger peak [13]. The intensity of D-band of our sample is higher than G-band displaying the disordered phase, however, it is plausible that such highly intense band may also be due to the polarization effects occurring within aligned nanotube bundles.

The radial breathing mode (RBM) of CNT' s detected in the low-frequency domain (Fig. 2 inset). They are seven components at 62.7, 101.5, 185.9, 253.6, 295.3, 341.8 and 378.8 cm^{-1} respectively. The diameter of CNTs were calculated from the radial breathing mode (RBM) signal using the relation; $\nu(\text{cm}^{-1}) = 9 + 235/d(\text{nm})$ [14]. It can be seen from this data that the inner wall diameter ranges from 0.6 - 1 nm while the outer diameter is found to be 1.5 - 4 nm. It is observed from SEM and Raman spectra that the diameter distributions are quite different from each other, which indicates the structural characteristic the formation of CNT' s are between SWNTs and MWNTs.

The specific area measurements of as synthesized CNT' s were carried out and the results are given in table 1 in order to understand the effect of cobalt content on the surface area of the supported catalysts. The tabulated values show that increase in cobalt concentration lead to enhancement in the surface area up to 50% and then remain constant. It implies that beyond 50% loading of cobalt, the CNTs size becomes smaller due to segregation of bigger sized MgO particles. It may be due to non-covalent interaction between MgO and cobalt oxide moieties at higher concentrations. And even the interaction within the MgO lattice may not be sufficient enough to expel CoO grains at boundaries in the lattice due to reduction of the cohesive force of MgO. It is significantly to be noted that the surface area of the CNT' s prepared in the present investigation ($150 - 184\text{ m}^2/\text{g}$) is considerable higher than those reported for MWNT' s from different catalytic processes [15], which can be attributed to symbiotic feature of Co nanoparticles. Overall it signifies the dispersibility of Co nanoparticles on the MgO catalysts matrix, which is responsible for growth and morphology of CNT' s thus synthesized.

Table I: Yield and surface area of CNTs synthesized using 0.1 g of Co-MgO catalyst at 600°C under $\text{H}_2/\text{C}_2\text{H}_2$ mixture for 1 hr.

Co loading (%)	Wt. of CNTs (g)	Yield ($\text{g g}^{-1}\text{ catalyst h}^{-1}$)	Surface area ($\text{m}^2\text{ g}^{-1}$)
25	0.2049	4.098	150
50	0.3943	7.880	180
75	0.3094	6.188	184

The morphology of the as-synthesized carbon nanostructures was investigated at different % of Co loading as shown by SEM in figure 3. It shows the presence of a homogeneous distribution of carbon nanotubes covering MgO-based catalyst surface in a web-like network. It is note worthy mentioning that no purification was conducted before imaging which qualitatively indicates that the carbon filaments have high yield. SEM also suggests that carbons deposited over the catalyst surface grow with a filamentous as well as chain like structures and the diameter ranges seem to be relatively uniform at different Co loading. Bright spots on the tip of the carbon tubes probably reveal the presence of Co nanoparticles and their diameters are similar to that of the corresponding tube thus corroborating the results obtained from the XRD studies on as-synthesized carbon nanotubes. It is quite likely that Co metal with diameters from 10 - 30 nm are responsible for the preferential growth of carbon nanotube through catalytic decomposition of acetylene at 600°C while those larger than 30 nm or smaller than 10 nm seem to be inactive for the formation of CNTs. The qualitative estimation of the average length and diameter of as-synthesized CNTs indicates that chain like structure (length $\sim 3.5 - 5.32\text{ }\mu\text{m}$) is predominant with 50% Co loading while coiled nature (length $\sim 0.34 - 0.42\text{ }\mu\text{m}$) is found to be present for 75% Co. On the other hand, lower Co loading produces both chains and coils indicating that the morphology of the CNTs specifically depends on the Co concentrations. Moreover, there exists inverse correlation between average diameter of nanotubes and cobalt loading with the formation of smaller

sized carbon tubes at high Co concentration. It probably stems from the fact that large amount of precursor carbon atoms are developed at the catalyst surfaces which eventually builds the nanotubes as a consequence of formation of large number of Co metal islands on the surfaces of MgO. These metal islands have high surface area and high activity for carbon nanotubes formation. With low Co loading, e.g. 25%, less number of the precursor carbons are generated leading to decreased yield while they can produce tubes with maximum width. The selective growth of carbon nanotubes requires a perfect balance between the rate of carbon supply and that of solid carbon precipitation otherwise amorphous carbon can build-up on the catalyst surface leading to deactivation and the formation of impurities.

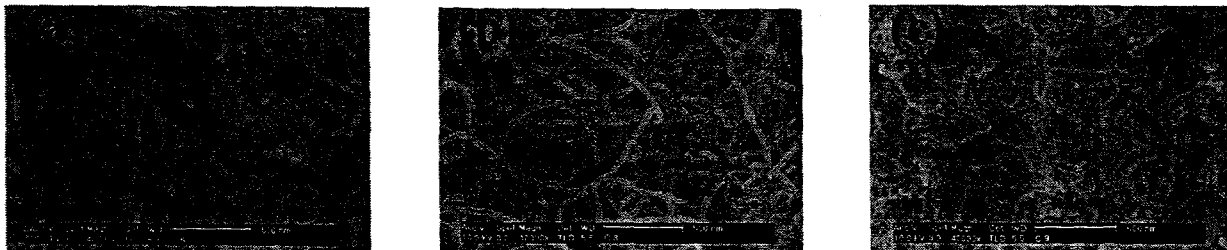


Fig. 3. SEM images of as-synthesized CNTs using (a) 25% Co (b) 50% Co and (c) 75% Co loading on MgO support.

4. Conclusion

The multiwalled carbon nanotubes are efficiently formed in large amounts at low-temperature decomposition of acetylene over Co/MgO catalyst. The overall yield of the MWCNTs increases with concomitant increase in Co loading indicating that the synthetic conditions are appropriately modulated by proper dispersion of Co nanoparticles in the MgO matrix. The XRD measurements of the as-synthesized MWCNTs indicate the presence of graphite like structure along with the formation of Co nanoparticles. It indicates that these active centers are uniformly distributed over MgO support thus affecting the morphology and orientations of carbon nanotubes. Based on the Raman spectroscopy, preferential growth of multiwalled carbon tubes is observed suggesting the selectivity of the catalytic system employed in the present investigation. Moreover, there seems to be beneficial effect of Co loading on the yield as well as the morphology of the MWCNTs as evidenced from the presence of different structural patterns from the SEM measurements.

Acknowledgment

One of the authors (Binod Kumar Singh) is grateful to Korea Federation of Science and Technology societies (KOFST) for the fellowship under Brain Pool Program.

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