Raman and TEM Studies of Carbon Nanotubes Produced by Bimetallic Catalysts System

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ABSTRACT

Studies were carried out on the use of various bimetallic catalyst systems for the production of carbon nanotubes (CNTs) by thermal decomposition of acetylene (C_2H_2). The pyrolysis of C_2H_2 was carried out at 700 °C. The CNTs synthesized were examined by Raman spectroscopy and transmission electron microscopy (TEM). Both analyses confirmed the presence of multi-walled carbon nanotubes (MWNTs) for all the bimetallic catalyst systems investigated. Raman spectroscopy shows that the Co-Ni supported catalyst produced CNTs with the highest I_G/I_D value. TEM was conducted to investigate the quality and nature of the CNTs produced. TEM observations confirmed that the CNTs produced are multi-walled and the residual catalyst particles are located inside the tubes of the CNTs. Energy-disperse X-ray analysis (EDAX) confirmed that the residual catalysts in the CNTs are in the form of alloy.

Keywords: bimetallic catalyst, Raman spectroscopy, TEM, carbon nanotubes

INTRODUCTION

Carbon nanotubes (CNTs) are strongly related to other forms of carbon, especially to crystalline 3D graphite, and to its constituent 2D layers (where an individual carbon layer in the honeycomb graphite lattice is called a graphene layer). The synthesis of CNTs with different metal catalyst is an important issue. Previously, mixtures of catalyst such as Fe-Ru, Fe-Pt, Fe-Co have been investigated by other researchers [1-2]. The use of bimetallic catalysts was found to improve the production of CNTs compared to the single-metal catalysts. Shajahan *et al.* [3] investigated the C_2H_2 decomposition of CNTs over Co-Mo/MgO with different loading ratio of metal.

They found that the production of SWNTs and multi-walled carbon nanotubes (MWNTs) were highly dependent on the amount of metal loading. The studies indicated that catalyst is the crucial factor in influencing the production of CNTs.

Various techniques have been used to characterize the morphology, texture, and structure of CNTs such as scanning electron microscopy (SEM), Raman spectroscopy, transmission electron microscopy (TEM) etc. Raman spectroscopy has been widely studied for different types of carbon. In the case of CNTs, this technique has been very successful in providing information for both electronic and structural properties, mostly due to the resonance nature of the Raman scattering process involving the so-called one-dimensional (1D) van Hove singularities (vHSs) [4-5]. TEM investigation has been widely used to investigate the structure of CNT [2-3]. In the present study, we have performed Raman and TEM studies of CNTs grown on different bimetallic catalysts using acetylene as the carbon source.

EXPERIMENTAL

Three supported catalysts were prepared using wet-impregnation method. The detail procedure is based on a previous report [6].The prepared catalysts were then used for the synthesis of CNTs. The synthesis of CNTs was carried out in a fixed-bed reactor at 700 °C. A quartz boat containing catalyst is placed at the center of the tube furnace. Acetylene (carbon source) and nitrogen as the carrier gas were introduced to the system simultaneously. After the reaction, the deposited carbon (hereafter referred as as-grown CNT) was characterized by means of Raman spectroscopy and transmission electron microscope (TEM). Raman measurements were performed with Raman spectrophotometer (Jobin Yvon U-1000) using 10 mW of the 488 nm line of an Ar ion laser. For TEM (JEOL 2100) analysis, a suspension of carbon containing sample in ethanol was achieved by stirring the solid sample with ultrasound for 10 min. A few drops of the resulting suspension were then deposited on a grid and subsequently evacuated before the TEM analysis.

RESULTS AND DISCUSSION

In a catalytic chemical vapor deposition (CCVD) method at a fixed temperature, the properties and the morphologies of the as-grown CNTs mainly depend on the chemical nature of the catalyst used. Previous report [7] has shown that different

morphologies of CNT could be observed when different catalysts were used. Thick tubes (20 - 30 nm) could be seen in SEM micrographs (not shown), suggesting the formation of MWNTs. This deduction was further confirmed by Raman and TEM.

In order to obtain the information regarding the crystallinity of the entire CNTs, Raman spectroscopy was used. Raman spectra of CNTs grown on Co-Ni/Al_2O_3, Fe-Co/Al_2O_3 and Fe-Ni/Al_2O_3 catalysts are displayed in Figure 1. All Raman spectra show mainly two peaks. These peaks are the typical feature for MWNTs. Generally, a peak centered at 1605 cm^{-1} is called the G-band, which indicates ordered structure in MWNTs while a peak centered at 1370 cm^{-1} is called the D-band, indicating the defect structures. The G-band is attributed to the movement of carbon atoms in apposite direction along the surface of a tube as in 2D-graphite [8].

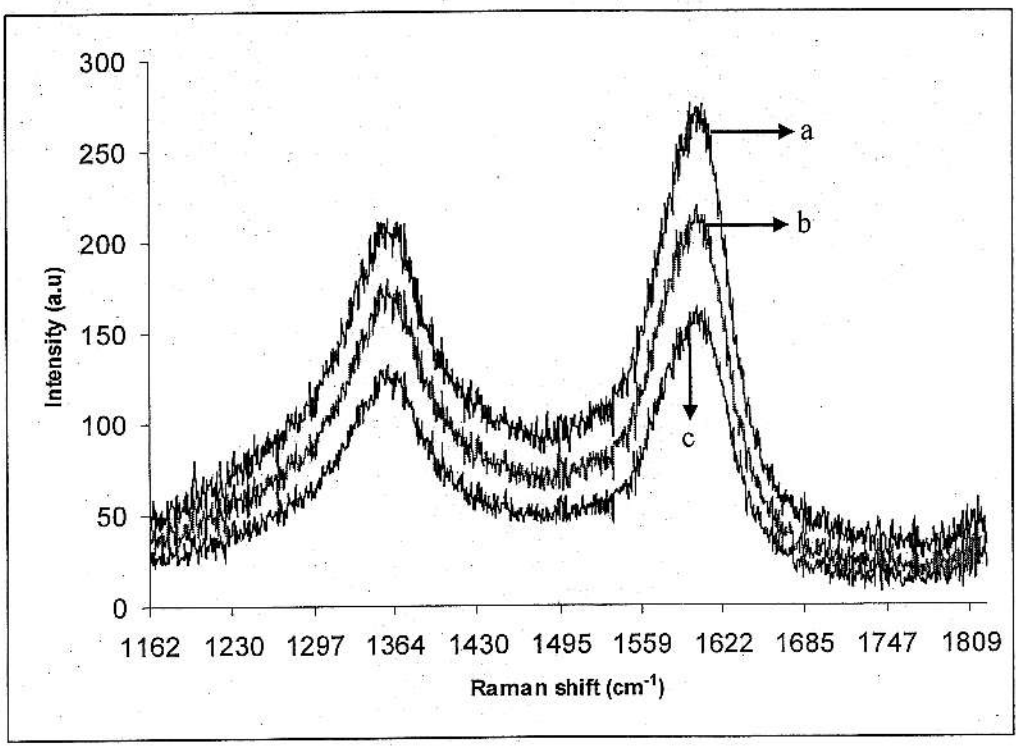

Figure 1: Raman spectra of MWNTs grown on (a) Co-Ni/Al_2O_3 (b) Fe-Co/Al_2O_3 and (c) Fe-Ni/Al_2O_3 catalysts.

For MWNTs grown on Co-Ni/Al_2O_3 and Fe-Co/Al_2O_3 catalysts, the intensity of the G-band becomes stronger than MWNTs grown on Fe-Ni/Al_2O_3 catalyst. The relative intensity of G-band to D-band (I_G/I_D) can be regarded as an index for the crystalline order of graphite [9]; i.e the degree of graphitization of carbon is higher with larger I_G/I_D value. The I_G/I_D values for MWNTs grown on Co-Ni/Al_2O_3, Fe-Co/Al_2O_3 and Fe-Ni/Al_2O_3 catalysts are 1.58, 1.50 and 1.30, respectively. This indicates that the degree of long range ordered crystalline perfection would be higher for MWNTs grown on the Co-Ni/Al_2O_3 catalyst compared to those grown on the other two catalysts. There is no observable peak at low frequency region (100 - 300 cm^{-1}) which indicates the absence of single-walled carbon nanotube (SWNTs). This observation also confirmed by TEM investigations.

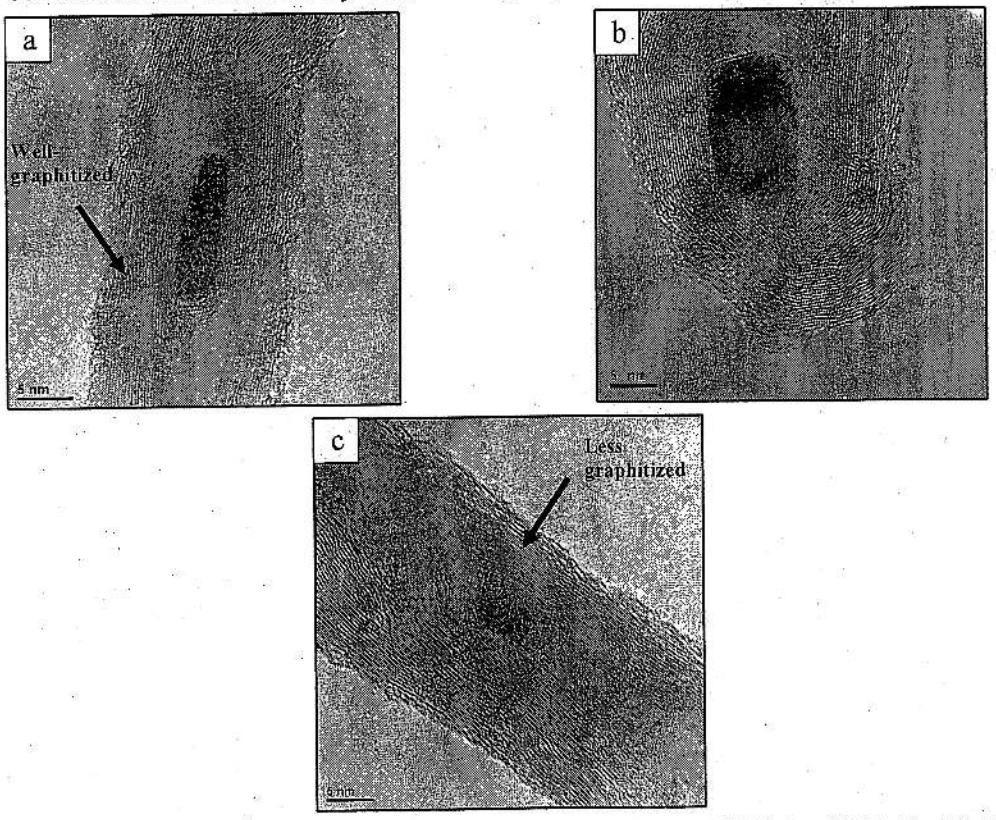

Figure 2: TEM micrographs of MWNTs grown on (a) Co-Ni/Al_2O_3 (b) Fe-Co/Al_2O_3 and (c) Fe-Ni/Al_2O_3 catalysts.

TEM micrographs revealed that the CNTs produced are MWNTs in nature. High resolution TEM (HRTEM) micrographs for the MWNTs grown on Fe-Co/Al_2O_3, Fe-Ni/Al_2O_3 and Co-Ni/Al_2O_3 catalysts were taken in order to determine the effect of catalyst on the crystallinity of the MWNTs produced. From these micrographs, one clearly sees that the catalytic metal exists at the close end of the tube or in the middle of the tube, which indicates 'tip growth' mechanism [10]. It suggests that the metal particles are responsible for the nucleation of the MWNTs. The residual metal particles are in the form of alloy as confirmed by EDAX analysis. The MWNTs are formed by many graphitic layer, which is separated by 0.34 nm. As shown in Figure 2, the outer graphitic layers are usually less crystalline than the inner graphitic sheets.

At 700 °C, the MWNTs produced on Co-Ni/Al_2O_3 were the best quality, i.e they posses well-crystalline graphitic layers. The average inner and outer diameters of these MWNTs were found to be in the range of 4-5 nm and 13-15 nm, respectively. The HRTEM micrographs reveal that the crystallinity of MWNTs follows a sequence of Co-Ni > Fe-Co > Fe-Ni. This result is in a good agreement with Raman spectra in Figure 1.

CONCLUSION

Raman and TEM studies showed that the CNTs produced are MWNTs. In this study, we presented the effect of bimetallic catalyst on the nature and the crystallinity of the MWNTs. Different catalysts gave different quality of MWNTs. Co-Ni/Al_2O_3 catalyst is the best catalyst to produce well-graphitized MWNTs. The detailed explanation of the quality of CNTs formed based on the metal-support interaction awaits further investigation.

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