Synthesis of Single-Walled Carbon Nanotubes by Decomposition of Methane on CoMo/MgO Catalysts Prepared by a Combustion Method

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Introduction

Single-walled carbon nanotubes (SWNT) have attracted considerable attention in recent years due to their remarkable physical and chemical properties. However, scalability of production methods yielding nanotube samples of uniform quality is still an issue. Catalytic Chemical Vapor Deposition of carbon-containing molecules shows potential as a cost-effective technology for SWNT production of reproducible quality [1]. In particular, CoMo catalysts supported on SiO_2 have been extensively studied in our group [2, 3].

In this contribution we present the results of systematic studies of production of SWNT by decomposition of methane using CoMo catalysts supported on MgO, prepared by a combustion method using citric acid as a fuel. The effects of methane partial pressure, time on stream, reaction temperature and catalyst reduction temperature on the SWNT structure and quality were analyzed, by using a combination of Raman spectroscopy, optical absorption, temperature-programmed oxidation (TPO) and electron microscopy techniques.

Materials and Methods

The catalyst used for this study (which has a composition $Co_{0.0075}Mo_{0.0025}Mg_{0.99}O$) was prepared by the combustion method using citric acid as the fuel [4]. The metal precursors used for the preparation are $Mg(NO_3)_2.9H_2O$, $Co(NO_3)_2.6H_2O$ and $(NH_4)_6Mo_7O_{24}.4H_2O$. The decomposition of methane was carried out in a vertical bed reactor, with varying temperatures (800-950ºC), reaction times (10-120 min) and feed compositions (6-50 mol% CH_4 in H_2 mixtures). The catalyst structure and changes upon reduction were investigated by X-Ray Diffraction (XRD) and Temperature-Programmed Reduction (TPR). The as-produced carbon nanotubes were studied by Raman spectroscopy, optical absorption, TPO and transmission electron microscopy (TEM). The purification of the samples was performed by a combination of gas phase treatments (oxidation / hydrogenation / annealing) and liquid-phase treatments (attack by acid solutions).

Results and Discussion

The preparation of the catalyst using the combustion method usually leads to a highly porous material. The BET surface area of the as-prepared catalyst is 134 m^2/g. Peaks in the XRD diffraction pattern are those corresponding to the MgO rocksalt structure. The temperature programmed reduction profile indicates an optimum reduction temperature of 500ºC. Reaction runs without a previous reduction showed lower quality of SWNT as seen in their Raman spectra and electron micrographs.

The time on stream has a considerable effect on the quality of the as-produced carbon nanotubes. Longer reaction times usually result in an increase in the disorder-induced Raman band (D band, around 1340 cm^{-1}), which is indicative of the presence of sp^2 hybridized disordered carbon materials; and an increase of the D/G ratio, where G is the Raman band assigned to the tangential C-C stretching modes of SWNTs. Increases in reaction temperature and hydrocarbon concentration in feed also result in lower quality materials as shown by Raman spectroscopy and electron microscopy techniques. In order to investigate the nature of this increase in D band, several gas-phase treatments were tried after reaction. Figure 1 shows the effect of oxidizing the as-produced sample in air at 250ºC for 20 minutes. This treatment burns mostly amorphous carbon, and results in a considerable decrease in the D/G ratio in the final sample, suggesting that the D band might arise mainly due to amorphous carbon deposition on the support.

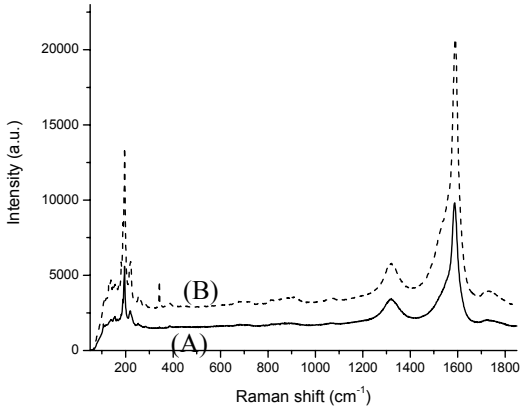

Figure 1. Raman spectra of as-produced carbon nanotubes showing the effect of oxidative treatment in air at 250ºC for 20 min. A) original sample, B) oxidized sample.

Significance

The methane decomposition reaction to form SWNTs on CoMo/MgO catalysts was systematically studied. A variety of characterization techniques were used to correlate the effect of reaction conditions and purification treatments with the structure of the produced SWNT. A protocol yielding samples of high quality was developed for this system.

References

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