行政院國家科學委員會專題研究計畫　期中進度報告

廢有機溶劑研製奈米碳材特性及應用研究(1/2)

計畫類別：個別型計畫
計畫編號：NSC94-2211-E-039-007-
執行期間：94 年 08 月 01 日至 95 年 07 月 31 日
執行單位：中國醫藥大學職業安全與衛生系

計畫主持人：江鴻龍
共同主持人：何詠碩
計畫參與人員：謝主信、黃堯聖

報告類型：精簡報告
報告附件：出席國際會議研究心得報告及發表論文
處理方式：本計畫可公開查詢

中　華　民　國 94 年 12 月 28 日

行政院國家科學委員會補助專題研究計畫 □ 成果報告 ■期中進度報告

廢有機溶劑研製奈米碳材特性及應用研究(1/2)

計畫類別：■ 個別型計畫　□ 整合型計畫
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中　華　民　國　94　年

行政院國家科學委員會補助專題研究計畫期中報告

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中文摘要

本研究以乙炔分解於氫還原之含 Pd 及 Ni 觸媒擔體，於 450-700 ^oC 溫度下，生成碳纖維。以 X-ray 繞射分析觸媒及碳纖維之結晶型態、SEM 分析其外觀特性、再利用 Raman 光譜分析碳纖維特性。目前初步結果顯示 450^{o}C 時，有少量碳纖維生長於 Pd 觸媒擔體上，而溫度需至 650^{o}C 以上，方有較大量之碳纖維生長。相對於 Ni 觸媒擔體則於 450 及 550 ^{o}C，即有碳纖維生長。顯示鎳觸媒可令乙炔於較低溫分解生成碳纖維。根據 X-ray 分析有碳及石墨結晶型態生成。萊曼光譜波峰則出現於 1290 及 1590 cm^{-1}。

關鍵詞：碳纖維、乙炔、氣相化學沉積、萊曼光譜

Abstract

In this study, carbon fibers were formed from acetylene decomposition on hydrogen-reduced Pd and Ni catalysts at 450-700 ^{o}C. X-ray diffraction (XRD) was used to examine the crystal characteristics of catalysts and carbon fibers. The carbon fibers were also examined by a scanning electron microscope (SEM) and Raman spectroscopy to define their appearance and structure. Small carbon fibers were found on the Pd catalyst surface at 450 ^{o}C; while a significant amount of carbon filaments were observed at 650 ^{o}C. In contrast, carbon filaments were found both at 450 and 550 ^{o}C on the Ni catalysts. According to the XRD spectrum, there was carbon and graphite present on the Ni surface. Raman spectroscopy revealed two peaks at 1290 (D band, disorder mode, amorphous carbon) and 1590 (G band, graphite sp^2 structure) cm^{-1}. SEM results indicated the Ni could catalyze the C_2H_2 decomposition to form carbon filaments at a lower temperature than Pd. Furthermore, C_2H_2 was decomposed on Ni catalyst at 450 ^{o}C; this is a relatively low temperature to form carbon nanotubes.

Keywords: carbon fiber, acetylene, chemical vapor deposition (CVD), Raman spectra

1. Introduction

Carbon nanotubes can be divided into two groups: single-walled (SWNT) and multi-walled nanotubes (MWNT). The differences in morphology are due to their different atomic structures [1]. The diameters of carbon fibers range from micrometric [2], submicron [3] and nanometric [4] depending on the various experimental conditions.

Carbon nanotubes were first discovered by Iijima [5]. Their unique properties and potential applications have created a great deal of interest [6-8]. Growth/syntheses methods, catalyst selection and preparation, carbon sources, atmospheric conditions (temperature and backup gas), and the properties of carbon nanotubes have been studied in recent years.

Growth/synthesis methods have included: Arc discharge, laser vaporization, pyrolysis, and plasma-enhanced or thermal Chemical Vapor Deposition methods (CVD). Carbon fibers formed by CVD have several advantages which include high purity, high yield, selective growth, and vertical alignment.

Various catalysts have been studied in CVD processing. These have included Fe [9-12], Co [13], Ni [14], other transition metals, noble metal [15] and alloys[16-18]. Interestingly, carbon nanotubes have also grown on an oxide surface, i.e. Bai [19] decomposed acetylene on an Al_2O_3 surface at 650 ^oC, forming coiled carbon structures.

Carbon sources are a key factor in the growth of carbon nanotubes. CH_4 [10,12,19-20], ethanol [13], aromatic gases (benzene [18] and toluene [21], polyethylene[22] have commonly been used to form carbon nanotubes; i.e. Li et al [23] investigated the potentials of CH_4, C_2H_4 and C_2H_2 on MgO supported Fe surface by CVD at 500-850 ^oC. Growth conditions have included temperatures ranging from 500-1000 ^oC [9-10,12-13,19,22-23] and pressures ranging from several mTorr to one atmosphere pressure.

This study investigated the characteristics of C_2H_2 decomposition on Ni and Pd catalyst substrates and the formation of carbon fibers by the CVD method. In addition, SEM, Raman spectroscopy, and XRD were used to examine the physicochemical properties of carbon fibers. The characteristics of the carbon fibers formed on the Ni or Pd surface were compared. Furthermore, the temperature effect of C_2H_2 decomposition was also investigated.

2. Experimental

2.1 Carbon fiber preparation

Fe-Cr-Al alloy plates (Fe-20Cr-5Al) were used as substrates and coated as a film on Al_2O_3. The Ni and Pd nitrate sol gels were prepared and coated on the Al_2O_3 film substrate-plate with a spin coater. Each catalyst-coated substrate-plate was calcined at 400 ^oC to remove impurities. Each calcined-plate was then reduced under a hydrogen atmosphere (170 ml min^{-1} for 1h) at 300-450 ^oC in a CVD furnace. Acetylene was selected as the carbon source and was decomposed on the Pd and Ni catalysts. Carbon filaments were formed at 450-650 ^oC in 30 min with a C_2H_2/N_2 mixture flow rate of 1.83 l min^{-1} (N_2 flow rate: 1.1 l min^{-1}; C_2H_2 flow rate: 0.73 l min^{-1}).

2.2 Structure and morphological analysis

The identification of the crystalline phases was made through an X-ray diffractometer (XRD, Bruker D8, Germany) using Cu-Kα radiation (λ=0.15406 nm) with a scintillation detector, scanning range10-70 (2 theta), 0.02 step, and 1 sec/step. **T**he morphology of the carbon nanotubes was examined with a scanning electron microscope (SEM, XL-40FEG, Philip). The quality was identified by Raman spectroscopy using the 514 nm line of an Argon laser operated at a laser power of 50mW. The laser beam was focused by a 60×objective onto the surface with a beam size of approximately 10μm in diameter.

3.Results and Discussion

3.1 SEM micrograph

Figure 1 shows SEM micrographs of carbon filaments on the Pd and Ni catalysts. Figure 1a displays a 1 hr Pd catalyst reduction in the hydrogen atmosphere at 400 ^oC; 50% of the C_2H_2 decomposed on the catalyst at 450 ^oC. Few carbon filaments were observed on the catalyst surface. Figure 1b exhibits the 1 hr Pd catalyst reduction in the hydrogen atmosphere at 400 ^oC; 40% of the C_2H_2 decomposed at 650 ^oC. There were a lot of carbon filament formations on the catalyst surface. The diameter of the carbon filaments in Fig. 1b ranged from tens to hundreds of nm.

Figures 1c and 1d show the carbon filament formation on the Ni catalyst surface. The carbon filaments were formed on the Ni catalyst (reduction in the hydrogen atmosphere at 300 or 400 ^oC for 1 hr) surface at 450 ^oC. According to the study results, e Ni catalyzed the C_2H_2 decomposition and formed carbon filaments at a lower temperature than Pd. According to Massalski et al. [24] Ni-C and Pd-C phase diagrams, Ni and carbon reaction temperatures are lower than Pd and carbon reaction temperatures. Therefore, this may be the reason that carbon filaments can be formed on a Ni surface at lower temperatures than on a Pd surface. Wong et al. [20] decomposed CH_4 on a Pd catalyst to form carbon nanotubes at 750 ^oC. Lee et. al. [16] used Co-Ni as seed particles to decompose C_2H_2 and form carbon nanotubes at 500-550 ^oC. In addition, Jeong et. al. [17] decomposed C_2H_2 on Ni film at 550-600 ^oC. These studies indicated the carbon source decomposition and nanotubes formation temperature was higher on Pd than on Ni.

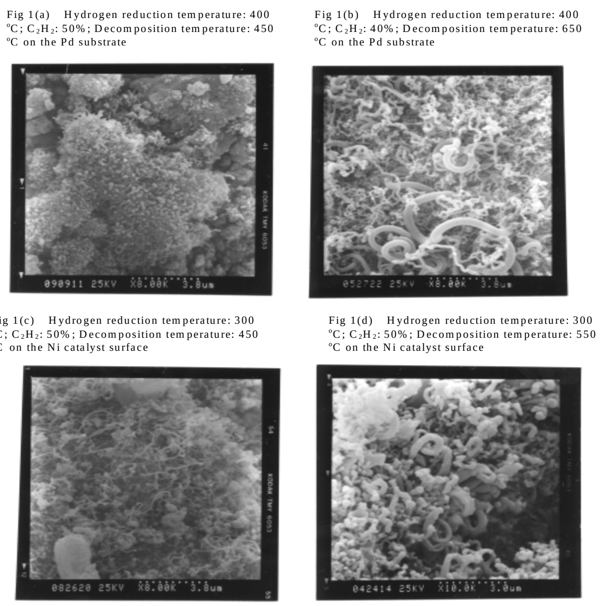

Figure 1 SEM micrographs of carbon filaments on Pd and Ni catalysts

3-2 Raman spectra

Carbon nanotubes have four main spectra regions which include a high-frequency tangential mode (1500-1600 cm^{-1}), an intermediate-frequency Z-breath mode (300-1100 cm^{-1}), a low-frequency R-breath mode (140-300 cm^{-1}), and a G' band (2600 cm^{-1}) in Raman spectra.

According to the Claye et al. [25] study, the radial breath mode within the 100-300 cm^{-1} band is characteristic of SWNTs in Raman spectra. Other peaks such as D and G bands center at 1350 and 1590 cm^{-1}, respectively, and can be used to evaluate the purity of carbon tube products.

Figure 2 indicates the Raman spectra curves. Raman spectra revealed two peaks at 1290 (D band, disorder mode, amorphous carbon) and 1590 (G band, graphite sp^2 structure) cm^{-1}. The intensity ratio of the D-band and G-band was approximately 1.0 from 500 to 700 ^oC. In general, the D band and G band intensity ratio indicated the purity of the carbon nanotubes. The value of the D and G band intensity ratio indicated impure carbon content in the carbon nanotubes. In addition, one sample Raman spectra at 650 ^oC revealed a weak peak (R-breathing mode) in the vicinity of 300 cm^{-1}.

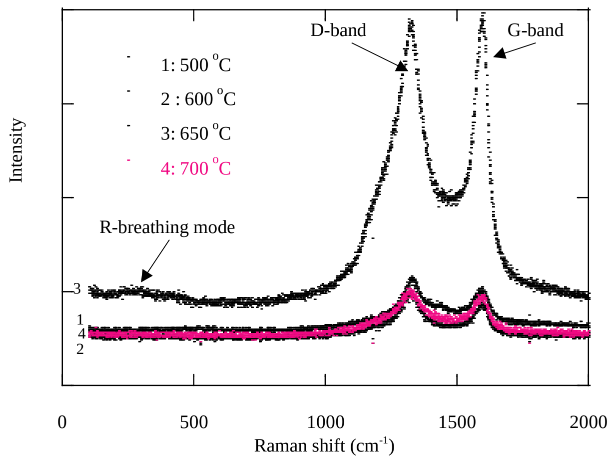

Figure 2 Overview of Raman

3-3 X-ray diffraction (XRD)

Figure 3 shows the C_2H_2 XRD spectra on the Ni catalyst surface. NiO and Al_2O_3 peaks were found on the catalyst surface before the reduction process. Curves B (T: 500 ^oC) and C (T: 600 ^oC) indicate the Ni, Al_2O_3 peaks on the catalyst surface after the reduction process. There are no significant carbon or graphite peaks on the curve. Curve D (T: 700 ^{o}C) represents the graphite peaks at 26.228 and 44.365. Figure 3(b) reveals the XRD spectra of the Ni catalyst which was reduced in the hydrogen atmosphere at 450 ^{o}C and then C_2H_2 decomposed on the catalyst from 500 to 700 ^{o}C. There is no significant carbon diffraction peak at 500 ^{o}C. The graphite peaks were found at 600 and 700 ^{o}C. When the carbon fiber formation is compared at 300 and 450 ^{o}C it appears that the reduction temperature at 450 ^{o}C is more suitable than 300 ^{o}C.

4. Conclusion

From this study, we found that carbon filaments seem to be more easily formed on a Ni surface than on a Pd surface at 450 ^{o}C. Raman spectroscopy shows two absorption peaks about 1300 and 1600 cm^{-1} that is the D-band and G-band, respectively. Furthermore, XRD spectroscopy shows the graphite structure formation at high temperature. In addition, the Ni catalyst reduced by hydrogen at 450 ^{o}C is more suitable for carbon fiber formation than at 300 ^{o}C. Compared to other research, the C_2H_2 decomposition and carbon nanotubes production on a Ni catalyst at 450 ^{o}C is a relatively low temperature process.

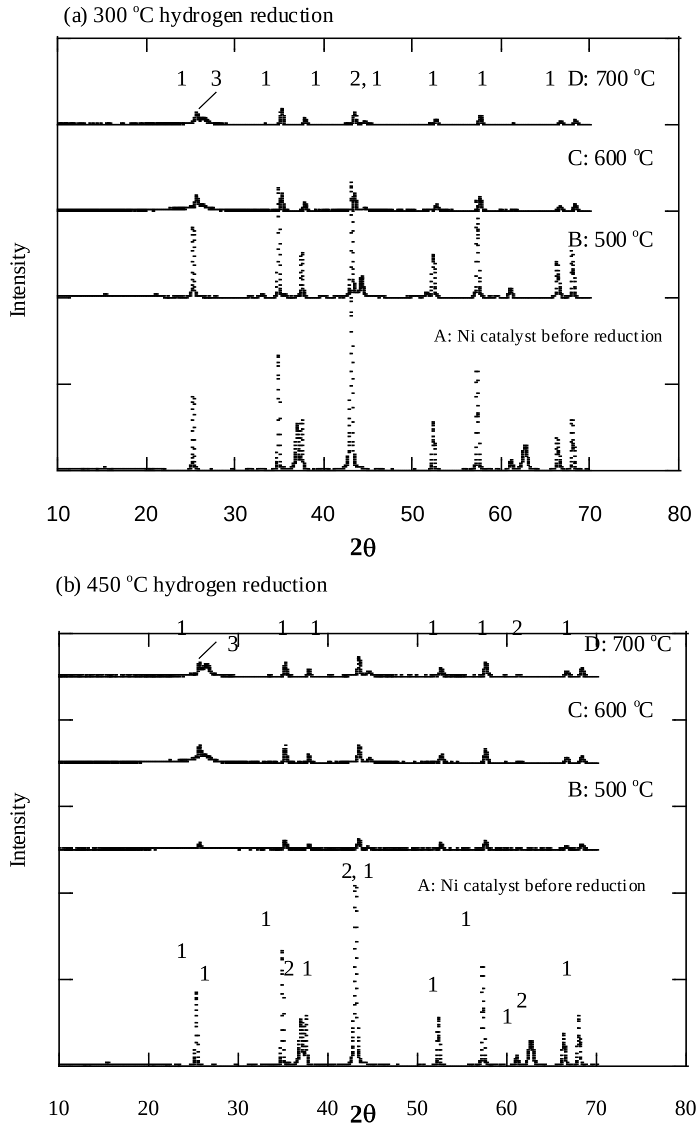

Figure 3 XRD spectra

1: Al_2O_3; 2: NiO; 3: Graphite
The 2θ peaks of Ni are at 44.497 and 51.851. Al_2O_3 are at 25.572, 35.146, 37.768, 43.346, 52.542, 57.491, 66.505, and 68.193. In addition, the graphite peaks are at 26.228 and 44.365.

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