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中華民國 94 年
Abstract

In this study, carbon fibers were formed from acetylene decomposition on hydrogen-reduced Pd and Ni catalysts at 450-700 °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 °C; while a significant amount of carbon filaments were observed at 650 °C. In contrast, carbon filaments were found both at 450 and 550 °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 sp² structure) cm⁻¹. SEM results indicated the Ni could catalyze the C₂H₂ decomposition to form carbon filaments at a lower temperature than Pd. Furthermore, C₂H₂ was decomposed on Ni catalyst at 450 °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/synthesis 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$_2$O$_3$ surface at 650 °C, 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$_2$H$_4$ and C$_2$H$_2$ on MgO supported Fe surface by CVD at 500-850 °C. Growth conditions have included temperatures ranging from 500-1000 °C [9-10,12-13,19,22-23] and pressures ranging from several mTorr to one atmosphere pressure.

This study investigated the characteristics of C$_2$H$_2$ 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$_2$H$_2$ 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$_2$O$_3$. The Ni and Pd nitrate sol gels were prepared and coated on the Al$_2$O$_3$ film substrate-plate with a spin coater. Each catalyst-coated substrate-plate was calcined at 400 °C to remove impurities. Each calcined-plate was then reduced under a hydrogen atmosphere (170 ml min$^{-1}$ for 1h) at 300-450 °C 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 °C in 30 min with a C$_2$H$_2$/N$_2$ mixture flow rate of 1.83 l min$^{-1}$ (N$_2$ flow rate: 1.1 l min$^{-1}$; C$_2$H$_2$ 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-Ka radiation ($\lambda$=0.15406 nm) with a scintillation detector, scanning range10-70 (2 theta), 0.02 step, and 1 sec/step. The 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 °C; 50% of the C$_2$H$_2$ decomposed on the catalyst at 450 °C. Few carbon filaments were observed on the catalyst surface. Figure 1b exhibits the 1 hr Pd catalyst reduction in the hydrogen atmosphere at 400 °C; 40% of the C$_2$H$_2$ decomposed at 650 °C. 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 °C for 1 hr) surface at 450 °C. According to the study results, e Ni catalyzed the C2H2 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 CH4 on a Pd catalyst to form carbon nanotubes at 750 °C. Lee et. al. [16] used Co-Ni as seed particles to decompose C2H2 and form carbon nanotubes at 500-550 °C. In addition, Jeong et. al. [17] decomposed C2H2 on Ni film at 550-600 °C. These studies indicated the carbon source decomposition and nanotubes formation temperature was higher on Pd than on Ni.

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 sp² structure) cm⁻¹. The intensity ratio of the D-band and G-band was approximately 1.0 from 500 to 700 °C. 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 °C revealed a weak peak (R-breathing mode) in the vicinity of 300 cm⁻¹.

3 X-ray diffraction (XRD)
Figure 3 shows the C2H2 XRD spectra on the Ni catalyst surface. NiO and Al₂O₃ peaks were found on the catalyst surface before the reduction process. Curves B (T: 500 °C) and C (T: 600 °C) indicate the Ni, Al₂O₃ peaks on the catalyst surface

![Figure 1 SEM micrographs of carbon filaments on Pd and Ni catalysts](image1)

![Figure 2 Overview of Raman](image2)
after the reduction process. There are no significant carbon or graphite peaks on the curve. Curve D (T: 700 °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 °C and then C₂H₂ decomposed on the catalyst from 500 to 700 °C. There is no significant carbon diffraction peak at 500 °C. The graphite peaks were found at 600 and 700 °C. When the carbon fiber formation is compared at 300 and 450 °C it appears that the reduction temperature at 450 °C is more suitable than 300 °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 °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 °C is more suitable for carbon fiber formation than at 300 °C. Compared to other research, the C₂H₂ decomposition and carbon nanotubes production on a Ni catalyst at 450 °C is a relatively low temperature process.

1: Al₂O₃; 2: NiO; 3: Graphite
The 2θ peaks of Ni are at 44.497 and 51.851. Al₂O₃ are at 25.572, 35.146, 37.768, 43.346, 52.542, 57.491, 66.305, and 68.193. In addition, the graphite peaks are at 26.228 and 44.365.
References


