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Carbon fiber formation on Pd and Ni catalysts by acetylene decomposition

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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 both by scanning electron microscopy (SEM) and Raman spectroscopy to define their appearance and structure. Little amount of 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 comparison, more carbon filaments were observed on the Ni catalysts at 450 °C. According to the XRD spectrum, there was carbon and graphite present on the Ni surface. Raman spectroscopy revealed two peaks at 1290 cm^{-1} (D band, disorder mode, amorphous carbon) and 1590 cm^{-1} (G band, graphite sp^2 structure). 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 °C; the formation of carbon nanotubes by decomposing C_2H_2 on Ni at 450 °C was a relatively low temperature.

Keywords: Carbon fiber; Acetylene; Chemical vapor deposition (CVD); Raman spectra

1. Introduction

Carbon nanotubes can be divided into two groups: single-walled nanotubes (SWNT) and multi-walled nanotubes (MWNT). The differences in morphology are due to their different atomic structures [1]. The diameters of carbon fibers ranging from micrometric [2], submicron [3], and nanometric [4] can be controlled through 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 and alloys [15–17]. Interestingly, carbon nanotubes have also grown on an oxide surface, i.e., Bai [18] decomposed acetylene on an Al_2O_3 surface at 650 °C, forming coiled carbon structures.

Carbon sources are a key factor in the growth of carbon nanotubes. CH_4 [10,12,18–19], ethanol [13], aromatic gases (benzene [17] and toluene [20]), and polyethylene [21] have commonly been used to form carbon nanotubes; i.e., Li et al. [22] investigated the potentials of CH_4, C_2H_4 and C_2H_2 on MgO supported Fe surface by CVD at 500–850 °C. From the literatures [9,10,12,13,18,21,22], the growth conditions of carbon fiber have included temperatures ranging from 500 to 1000 °C and pressures ranging from several mTorr to 1 atm 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 physicochem-

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ical properties of carbon fibers. The characteristics of the carbon fibers formed on the Ni or Pd surface were compared. Furthermore, the temperature effect of carbon fiber formation was also investigated.

2. Experimental

2.1. Carbon fiber preparation

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

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 ($\lambda = 0.15406$ nm) with a scintillation detector, scanning range 10–70° (2θ), 0.02 step, and 1 s/step. The morphology of the carbon nanotubes was examined with a scanning electron microscope (SEM, XL-40FEG, Philip). A Micro-Raman System (Jobin Yvon) using He–Ne laser beam with a wavelength of 632.8 nm was used in analyzing the microstructure of the nanotubes. The quality was identified by Raman spectroscopy using the 514 nm line of an argon laser operated at a laser power of 50 mW.

3. Results and discussion

3.1. SEM micrograph

Fig. 1 shows SEM micrographs of carbon filaments on the Pd and Ni catalysts. Fig. 1(a) displays little carbon filaments were observed on the catalyst surface. Fig. 1(b) exhibits more carbon filaments were observed at 650 °C. The diameter of the carbon filaments in Fig. 1(b) ranged from tens to hundreds nanometers.

Fig. 1(c) shows the carbon filaments formation at 450 °C on Ni substrate. Fig. 1(d) displays huge and more carbon filaments formation at 550 °C. According to these figures, Ni catalyzed the C_2H_2 decomposition and formed carbon filaments at a lower temperature than Pd.

According to Massalski et al. [23] Ni–C and Pd–C phase diagrams, reaction temperatures of Ni and carbon are lower than those of Pd and carbon. 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. [19] decomposed CH_4 on a Pd catalyst to form carbon nanotubes at 750 °C. Lee

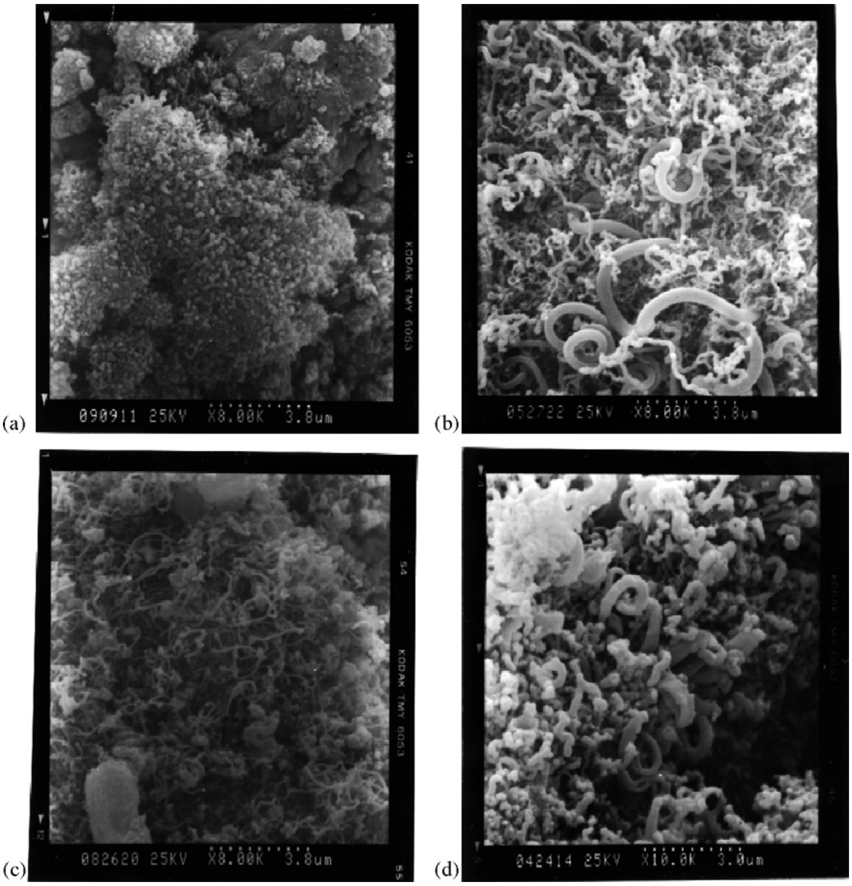

Fig. 1. SEM micrographs of carbon filaments on Pd and Ni catalysis: (a) hydrogen reduction temperature: 400 °C; C_2H_2: 50%; decomposition temperature: 450 °C on the Pd substrate; (b) hydrogen reduction temperature: 400 °C; C_2H_2: 40%; decomposition temperature: 650 °C on the Pd substrate; (c) hydrogen reduction temperature: 300 °C; C_2H_2: 50%; decomposition temperature: 450 °C on the Ni substrate; (d) hydrogen reduction temperature: 300 °C; C_2H_2: 50%; decomposition temperature: 550 °C on the Ni substrate.

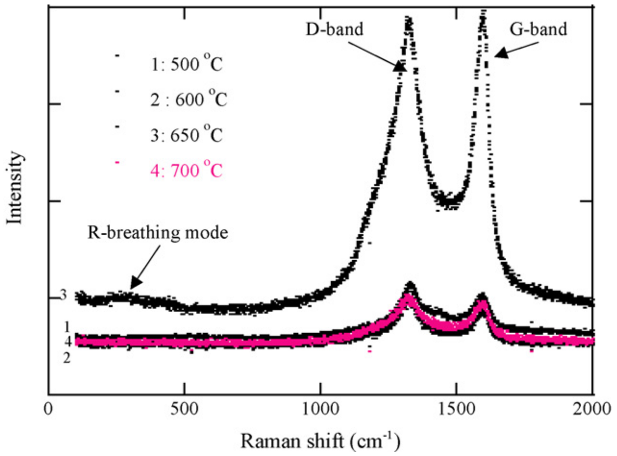

Fig. 2. Overview of Raman.

et al. [15] used Co–Ni as seed particles to decompose C_2H_2 and form carbon nanotubes at 500–550 °C. In addition, Jeong et al. [16] decomposed C_2H_2 on Ni film at 550–600 °C. These studies could be indicated the carbon source decomposition and nanotubes formation temperature was higher on Pd than on Ni.

3.2. Raman spectra

The D band, G band, and the R (R-breath mode) in the Raman spectrum were investigated. 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 (100–300 cm^{-1}), and a G′ band (2600 cm^{-1}) in Raman spectra.

According to the Claye et al. [24] study, the R-breath mode within the 100–300 cm^{-1} band is characteristic of SWNTs in Raman spectra. Other peaks such as D (disorder mode, amorphous carbon) and G (graphite sp^2 structure) bands center at 1350 and 1590 cm^{-1}, respectively, and can be used to evaluate the purity of carbon tube products.

Fig. 2 indicates the Raman spectra curves. A weak peak (R-breathing mode) in the vicinity of 300 cm^{-1} at 650 °C. It need further study to clarify the R-breath mode formation mechanism in the case. Raman spectra revealed two peaks at 1290 cm^{-1} (D band) and 1590 cm^{-1} (G band). The intensity ratio of the D and G bands was approximately 1.0 from 500 to 700 °C. In general, the D and G band intensity ratio indicated the purity of the carbon nanotubes. In this study, the value of the D and G band intensity ratio indicated impure carbon content in the carbon nanotubes.

3.3. X-ray diffraction

Fig. 3(a and b) shows the XRD spectra of the C_2H_2 decomposed on the Ni catalyst surface reduced at 300 and 450 °C, respectively. For catalyst substrate without H_2 reduction, only NiO and Al_2O_3 peaks were found on XRD spectra as curve A in both Fig. 3(a and b). When substrate reduced at 300 °C, i.e., Fig. 3(a), only Ni and Al_2O_3 diffracted peaks were noticed, and no graphite peak was observed in curves B (500 °C) and C (600 °C). But in curve D (700 °C) noticeable graphite peaks were found. For substrate reduced at 450 °C, similar XRD spectra were observed in Fig. 3(b) except the curve C (C_2H_2 decomposed at 600 °C). Graphite diffracted peaks (2θ at 26.228 and 44.365) were observed at substrate with C_2H_2 decomposed at 600 °C. This indicated that carbon nanotubes can be formed at even lower temperature when the catalyst substrate was reduced at higher temperature, i.e., 450 °C. It appears that the reduction temperature at 450 °C is more suitable than 300 °C.

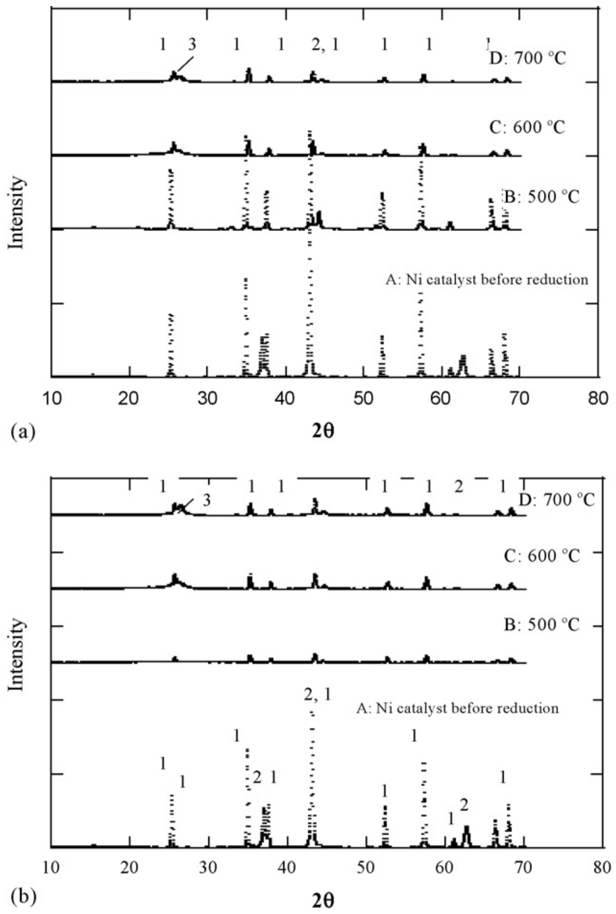

Fig. 3. XRD spectra: (1) Al_2O_3, (2) NiO, and (3) graphite. The two peaks of Ni are at 44.497 and 51.851; Al_2O_3 are at 25.572, 35.146, 37.768, 43.346, 52.542, 57.491, 66.505, and 68.193. In addition, the graphite peaks are at 26.228 and 44.365. (a) 300 °C hydrogen reduction; (b) 450 °C hydrogen reduction.

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