Ni Nanoparticles이 doping된 Multiwall Carbon Nanotubes의 수소저장 특성에 관한 연구

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Hydrogen Storage in Ni Nanoparticles-Dispersed Multiwall Carbon Nanotubes

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ABSTRACT

Ni nanoparticles이 표면에 분산된 mutiwall carbon nanotubes (MWNTs)의 수소저장 특성을 분석하였다. Metal nanoparticles의 분산 방법은 incipient wetness impregnation procedure을 사용하였는데, 이러한 Ni catalysts의 역할은 기존에 알려진 Li, K doping과 같은 개념으로 기상의 수소를 분해하여 carbon 표면에 chemical adsorption 시키는 역할을 하게 된다. 실제로 Ni nanoparticles이 6wt% loading된 경우에는 thermal desorption spectra를 분석한 결과 ~2.8wt% hydrogen이 ~340-520K의 온도범위에서 방출되는 것을 관찰할 수 있었다. Kissingers plot을 통해서 MWNTs와 hydrogen과 interaction energy를 구한 결과 ~31kJ/molH$_2$를 얻을 수 있었으며 이 값은 기존의 SWNTs에 hydrogen이 physi-sorption에서 실험적으로 얻을 수 있었던 값보다 1.5배 큰 값이라고 할 수 있다. 자세한 수소저장 기구를 분석하기 위해서 FT-IR분석을 한 결과 C-Hn stretching vibrations이 관찰되었으며 mono-hydride와 weak di-hydride sp^{3}가 형성된 것으로 해석될 수 있었다. 이와 같은 결과는 Ni nanoparticle들이 예상과 같이 hydrogen molecules을 dissociation하는 역할을 하는 것을 의미한다. 연속적인 thermal desorption 실험을 통해 가역성도 평가하였다.

주요기술용어 : Carbon nanotube(카본나노튜브), Hydrogen(수소), Ni-nanoparticles(Ni-나노 입자), Thermal desorption spectroscopy(열분석법)

1. Introduction

Since discovery of carbon nanotubes (CNTs)

in 1991 by Iijima[1], hydrogen storage in CNTs has shown great promise as high energy density absorbent[2,3]. In many theoretical and

empirical results, superior hydrogen gas absorbing property has been reported under high pressure and often at extremely low temperature[4-7]. The interaction mechanism between carbon and hydrogen has been attributed to physisorption of molecular hydrogen inside the tubes and interstitial sites in tube bundles. Recently, studies on hydrogenation under high pressure and at elevated temperature have shown the possibility that every carbon atom on CNTs could be a potential site for chemisorption of one hydrogen atom [8-10]. Since it needs ~440kJ/molH$_2$ to break H-H bond of H$_2$ molecules, the chemical adsorption is unlikely to occur in gas phase except for these special environments. Experimentally, the doping of dissociative catalyst such as alkali metals has also activated chemical adsorption process, resulting in much higher hydrogen storage capacity than physisorption mechanism [11,12].

However, these alkaline dopants have higher hydrogen affinity and lower hydrogen molecules dissociative activity than transition metals such as Ni, Co, Pt. Accordingly, it was difficult to conclude which is responsible for the improved storage capacity. For the better understanding of the role of dopants, it is necessary to investigate the relationship between hydrogen storage properties and the hydrogen molecules dissociative catalysts.

In this paper, we selected Ni as hydrogen molecules dissociative catalyst and employed incipient wetness impregnation method, which enabled nano-sized catalysts to be dispersed uniformly on carbon surface [13-14]. The hydrogen storage properties were evaluated by evolution temperature and quantity measured by thermal desorption technique. We also evaluated the possibility of chemical adsorption process assisted by Ni nanoparticles present on nanotube surface.

2. Experimental

The MWNTs were synthesized with microwave plasma enhanced CVD as presented in previous of our work[15-16]. Firstly, cobalt layer with a thickness of 50nm were deposited on p-type Si-substrate by rf magnetron sputtering at 100W rf power and the pressure was adjusted to 30mTorr by feeding Ar gas. Prior to the growth of CNTs in microwave PECVD, hydrogen was introduced and plasma treatment was conducted at 1100W microwave power for 90s. The plasma treated cobalt seeds were used as catalytic seeds for the growth of MWNTs. A mixture of H$_2$ (89.9%, vol.%), CH$_4$ (0.1%), and O$_2$(10%) was used as the gas source. The microwave power and working pressure during the growth of CNTs were 700W and 30Torr, respectively. The growth temperature was maintained at 750 °C using halogen lamp heating. No further process was performed to purify the soot or to open the tube end with as-produced samples. 0.005g of MWNTs was impregnated with 5, 10, 21, and 73mM Ni nitrate acetone solutions of 10ml. The metal loading amount was determined by concentration of the solution as reported by Joo et al. [14]. After immersion, black sample was dried in 60 °C and subsequently heat-treated in H$_2$ gas flow. To observe the hydrogen storage properties, hydrogen (99.999%) was charged under 4MPa at 400K for 2 hours in 0.002g MWNTs with nano-particles dispersion. The sample was placed in quartz reactor, which was surrounded

Fig. 1. TEM and HRTEM pictures of the MWNTs grown using $CH_4/H_2/O_2$ reaction gases. The scale bars indicate (a) 500nm, (b) 100nm, (c) 50nm, and (d) 10nm, respectively.

by liquid nitrogen cooled cryostat and wound by heating element with a programmable power supply. The injection port of gas chromatograph was connected directly to the reactor and high purity Ar(99.999%) of 1atm was used as carrier gas. Hydrogen evolved from MWNTs was probed with gas chromatograph equipped with TCD (thermal conductivity detection method) and the selected capillary column (CARBOXEN 1006PLOT). Temperature scanning range and the rate were set to 280–673K and 1.5–4.5K/min, respectively.

Gas chromatograph separated one gas species and insured that only hydrogen is involved in desorption peak. The reference hydrogen peak enabled the precise calculation of evolved hydrogen amount by integration of peak area. The activation energies for desorption was estimated with the aid of Kissingers method[17]. In order to analyze chemical bonds in CNTs before and after hydrogenation, Fourier– transform infrared (FTIR) studies of MWNTs were performed on spectrometer with MCT–b detector. The MWNTs samples were prepared by mixing of 0.001g MWNTs with 0.1g KBr powder and pressing into transparent pellet. Approximately 32 scans

Fig. 2. TEM pictures of MWNTs coated with Ni nanoparticles;the loading amounts are (a) 40wt%, (b) 13wt%, (c) 6wt%, and (d) 3wt%.

were collected.

3. Results and Discussion

As shown in Fig. 1(a)-(d), the pristine MWNTs grown using $CH_4/H_2/O_2$ reaction gas have the aligned structure with less defective graphene layer. The nano-holes in MWNTs were not the closed structures such as bamboo-type. HRTEM images of tube end parts reveal that most tubes are open state. Through a detailed analysis of numerous different TEM images, the outer and inner diameters are estimated to be about 20nm and 8nm, respectively. Fig. 2(a)-(d) show the morphologies of the MWNTs after Ni nanoparticles impregnation by wetting in nitrate solutions of various concentrations. The loading amount of metal particles varied depending on the concentration of precursor solution [14]. As concentration increases from 5 to 73mM, more metallic Ni particles are coated on MWNTs surface between 3-40wt%. When 40 and 13wt% Ni loaded, the agglomerated Ni particles of ~10nm are scattered on the whole carbon surfaces. MWNTs covered with 6wt% Ni particles show highly uniform dispersion of Ni particles as small as ~1.2nm, and only some Ni islands are observed on carbon surface after less than 3wt% loading. As

shown in Figure 3, in closer observation of MWNTs containing 6wt% Ni, the black spots

Fig. 3. HRTEM picture of MWNTs containing 6wt% Ni nanoparticles; a number of dark spots on graphite wall are identified as the dispersed metallic Ni particles.

identified as metallic Ni by E.D.S analysis were distributed widely over CNTs surface.

Fig. 4 displays the hydrogen thermal desorption spectra of nanoparticles-dispersed MWNTs. Hydrogen evolution occurred at slightly higher temperature between 330K and 520K, where the released hydrogen amount corresponded to approximately 2.8wt%. As reported elsewhere [4,18-19], physically adsorbed hydrogen molecules by weak van der Waals force in curved carbon structures mostly released at sub-ambient temperature. On contrary, as shown in temperature desorption spectra results, the adsorbed hydrogen with the assistance of highly dissociative catalyst could be more stable even at elevated temperature range. The hydrogen desorption activation energy was calculated by Kissingers method. Generally, the gas evolution temperature (T_C) changes with variation of temperature scanning rate (=1.5~4.5K/min), and Kissigners plot was shown in Fig. 5. The
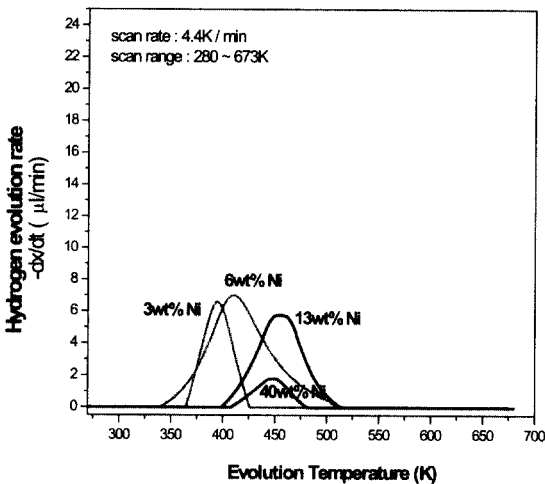

Fig. 4. Comparison of hydrogen thermal desorption spectra of nanoparticles-dispersed MWNTs (3, 6, 13, and 40wt%Ni loading).
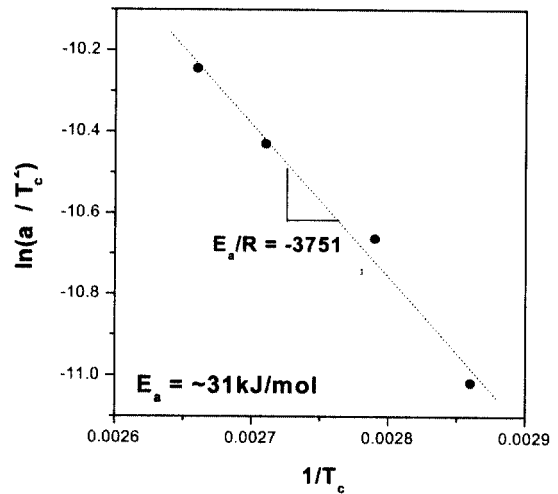

Fig. 5. Hydrogen desorption energy of MWNTs with Ni nanoparticles (TC = desorption peak temperature, α = scanning rate, R = gas constant).

(a) pristine MWNTS

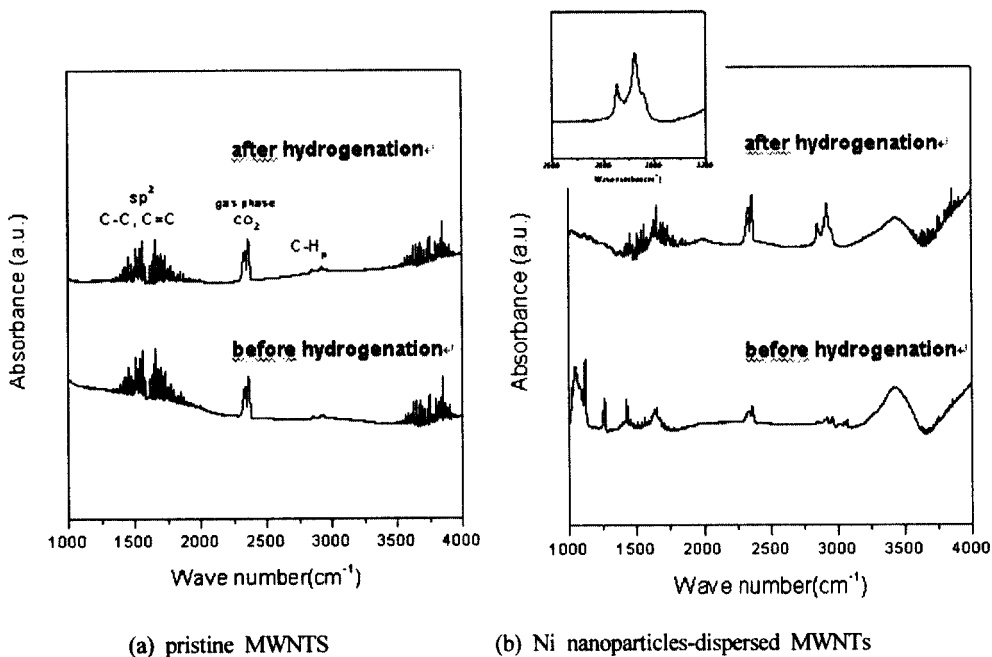(b) Ni nanoparticles-dispersed MWNTs

Fig. 6. FTIR spectra before and after hydrogenation of (a) pristine MWNTS, and (b) Ni nanoparticles-dispersed MWNTs. Inset is the magnified spectra in the range of 2600-3200cm-1.

desorption activation energy is measured to be ~31kJ/molH$_2$, which is higher value than the estimates in pure SWNTs[20], and thus implies that the hydrogen storage mechanism is closely associated with chemical interaction between hydrogen and carbon.

Fig. 6(a) and (b) show FTIR spectra of MWNTs with and without Ni nanopaticles dispersion, respectively. All of them have the distinct absorption bands corresponding to sp^2 C-C and C=C (aromatic and olefinic) stretching vibrations in the range of 1395-1620cm^{-1} [21]. As shown in Fig. 6(a), in case of as-produced MWNTs, the weak absorbance between 2850-3300 cm^{-1} consistent with C-Hn stretching vibration is observed and remains unchanged after hydrogenation. On contrary, the Ni particles-dispersed

MWNTs storing hydrogen shows prominent increase of C-Hn stretching vibration peak compared to the spectrum before hydrogen absorption(Fig. 6(b)), which further supports that Ni nanoparticles play an important role in hydrogen dissociative adsorption on carbon atom. The inset of Fig. 6(b) indicates the enlarged spectra around C-Hn stretching vibrations. The strong absorbance around 2915 cm^{-1} and relatively weak band at 2854 cm^{-1} are shown. Some matching C-H bond configurations are indicated in Table I[22]. The observed frequency around 2915cm^{-1} could be assigned to sp^{3}CH, which implies that the sp^2 nature of nanotube wall partially changes into single hydrogen bonded sp^3 configuration upon H$_2$ adsorption. These findings are consistent with the theoretically expected tendency
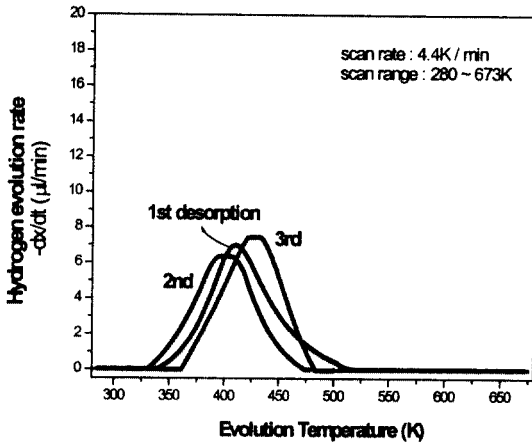
Fig. 7. Cyclic hydrogen desorption spectra of Ni nanoparticles-dispersed MWNTs.

Table 1. Various C-H stretching vibration bands[22]

Configuration	Predicted frequency (cm^{-1})
sp^2CH_2 (olefinic)	3020
sp^2CH (olefinic)	3000
sp^3CH_3 (asymmetric)	2960
sp^2CH_2 (olefinic)	2950
sp^3CH_2 (asymmetric)	2925
sp^3CH	2915
sp^3(symmetric)	2870
sp^3CH_2 (symmetric)	2855

for sp^2-sp^3 rehybridization by Tada et al.[23]. Another absorbance around 2854cm-1 corresponds to dihydride bond state (sp^3CH_2) and it is considered that some hydrogen atom preferentially adsorb on dangling bonds of amorphous carbon or nanotube edge rather than graphite surface in the form of tetrahedral dihydride configuration.

A reversibility of hydrogen absorption and desorption was also tested. Figure 7 shows the thermal desorption spectra during cyclic hydrogenation. The hydrogen desorption amount is maintained in the similar temperature range (320-520K). As a result, the chemical H adsorption and desorption using Ni nano-catalyst could be considered as potential reversible process. The MWNTs used in this experiment show the aligned open structure so that Ni nano-catalyst probably exist uniformly both inside and outside CNTs. Unlike alkali metals such as Li and K, metallic Ni just acts as active hydrogen dissociation catalyst without forming stable hydride, which indicates that hydrogen atom is mainly bound to carbon atom with higher interaction force

than physi-sorption and released reversibly upon heating.

4. Conclusions

When Ni nanoparticles are impregnated on MWNTs surfaces homogeneously. A high hydrogen uptake up to 2.8wt% has been achieved under moderate temperature and pressure. As expected hypothetically, the transition metal catalysts allow hydrogen molecules to dissociate and adsorb on carbon structures with higher interaction energy than physisorption. In the detailed analysis on the adsorbed hydrogen configurations using FTIR, the strong mono-hydride and weak di-hydride sp^3 bonding were observed. Accordingly, it is proved that the sp^3 transition occurs clearly while the dissociated hydrogen interact with carbon atom on tube wall, and the dangling bonds of amorphous carbon and graphite edges is possibly another stable hydrogen storage

site. Consequently, the chemical hydrogen adsorption and desorption process using nano-sized transition metal catalyst could be suggested as one of prospective hydrogen storage methods in multiwall carbon nanotube.

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