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Hydrogen adsorption of carbon nanotubes grown on different catalysts

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ABSTRACT

Single wall carbon nanotubes (SWCNTs) were synthesized by catalytic chemical vapor deposition of C_2H_2 at 800 °C for 60 min. Catalysts were prepared by impregnation of transition metals (Fe, Co, Ni, V and bimetallic mixture of Fe–Co) on MgO powder substrate with a metal to MgO ratio of 5:100. After the synthesis, the samples were purified by liquid phase oxidation method with 1.5 M HNO_3 for 30 min at 210 °C. The samples were characterized by thermal gravimetric analysis, scanning electron microscopy, X-ray diffraction and Raman spectroscopy. The hydrogen storage capacities of purified SWCNTs were investigated by volumetric method. It was found that the hydrogen uptake was in the range of 2.76–5.25 wt% at cryogenic temperature and 100 bar pressure. The maximum capacity was obtained with purified SWCNTs produced on Fe catalyst whereas purified SWCNTs grown on Fe–Co catalyst had the minimum hydrogen uptake.

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Introduction

Use of hydrogen as a clean energy carrier becomes more important as it is required to limit the use of fossil fuels due to environmental issues and decreasing supply of fossil fuels. Due to the potential use of hydrogen, there is an increase in the demand of hydrogen production. However, the main problem in the use of hydrogen effectively is the lack of feasible hydrogen storage technologies. For this reason, the selection of the material as hydrogen storage medium becomes important as it is one of the key parameters affecting the efficiency of storage system. It has been studied that nanostructured carbon materials can uptake and release high amount of hydrogen [1]. Among these materials, carbon

nanotubes (CNTs) are good candidates for hydrogen storage as they have promising hydrogen storage capacity due to their tubular structure, large surface area, chemical stability and low weight; however, their storage capacities scatter over a range of magnitude [2–5]. Previously, Dillon et al. have demonstrated that the hydrogen storage capacity of SWCNTs may range from 5 to 10 wt% [3]. In another study, reported that hydrogen uptake of SWCNTs were in the range of 1.5–5% and were affected by the radius of the CNTs [2]. The hydrogen can be stored in CNT structure by physisorption and/or chemisorption mechanism. The hydrogen storage of CNTs were explained by three different mechanisms on the top of the carbon atom, in the middle of the C–C bonds, and in the hollow of the CNT structure [6]. There are a number of factors related to synthesis of CNTs affecting the hydrogen storage

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capacity of CNTs including synthesis conditions, purification methods, and impurity and catalyst contents [7]. The properties of CNT structure such as the diameter, tube length and spacing, porous structure and edge opening also affect the hydrogen uptake of CNTs [6,8]. It has been previously reported that catalysts affect the carbon yield hence the properties of CNTs, especially when synthesized by chemical vapor deposition (CVD) in which CNTs grow on a metal catalyst (Fe, Co, Ni, Pd etc.) dispersed on substrates having high surface area. Yurum et al. stated that the metal impurities in CNT structure can affect the adsorption capacity [1]. Recent studies aim to increase the hydrogen uptake of SWCNTs as the Department of Energy (DOE) of the United States targets 6.5 wt% of hydrogen uptake for storage systems. In previous studies, it has been reported that the hydrogen storage capacities of SWCNTs vary as a result of parameters affecting the properties of SWCNTs. It was stated that the purity of the CNTs and the functional groups formed as a result of purification increase the hydrogen storage capacity [8]. The effect metal loaded to the carbon structure has been investigated and it was concluded that the transition metals enhance the hydrogen storage capacity of the carbon structures as they dissociate the hydrogen molecule hence the hydrogen atoms bond the carbon structure easily [9]. It has been previously stated that V catalyst enhances the hydrogen storage capacity of CNTs due to the dissociation of hydrogen molecules via spill over mechanism [10].

The objective of this study is to investigate the influence of catalysts (Fe, Co, Ni, V, Fe–Co), on the hydrogen storage capacity of SWCNTs which were synthesized by catalytic decomposition of C_2H_2 on transition metals (5:100 weight ratio) impregnated on MgO substrate. The hydrogen storage capacities were measured with High Pressure Volumetric Analyzer (HPVA). Thermal stability of SWCNTs was determined by thermal gravimetric analysis (TGA). The structural and morphological investigations were carried out by X-ray diffraction (XRD), scanning electron microscopy (SEM), and Raman spectroscopy.

Materials and methods

Catalyst preparation

The catalysts were prepared by impregnating MgO with transition metals (Fe, Co, Fe–Co, Ni, and V). The process was carried on by mixing MgO with $Ni(NO_3)_2 \cdot 6H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$, $Co(NO_3)_2 \cdot 6H_2O$ and V_2O_5 in separate processes for each catalyst.

The metal and MgO were mixed with a weight ratio of 5:100 in ethanol solution by ultrasonic homogenizer. The prepared solution was carefully mixed for 30 min and then dried in the oven at 80 °C for 18 h. The catalyst was then ground to avoid any agglomeration that may affect the interaction between source gas and the surface of catalyst negatively.

SWCNT synthesis

SWCNT was synthesized by CVD on a fluidized bed system. The catalyst was placed in the middle of the reactor on a nano-

porous silica disc that only allows gas flow. Ar was used as carrier gas and C_2H_2 was used as a carbon source. SWCNTs were synthesized at 800 °C for 60 min. After the synthesis, Ar flow continued until the temperature was dropped below 300 °C. The synthesized SWCNTs were purified by liquid phase oxidation method with 1.5 M HNO_3 for 30 min at 210 °C.

Characterization

TA Q600 SDT was used for the thermal analysis (TGA) of SWCNTs in a dry air atmosphere with an increasing temperature rate of 10 °C/min from 25 to 800 °C. TGA and DTG data were used to calculate the carbon yield and measure the maximum oxidation temperature of the SWCNTs. The scanning electron microscopy (SEM) images of SWCNTs were collected on Leo G34-Supra35 VP. Raman spectra of the samples purified with nitric acid were investigated with Renishaw inVia Reflex Raman microscope with 532 nm laser. The XRD analysis of the samples were conducted using 0.15406 nm Cu $K\alpha$ radiation on a Bruker AXS diffractometer fitted with a Siemens X-ray gun and the data analyzed with Bruker axS Diffrac PLUS software. The patterns were set in the range of 2θ from 2° to 90° and the X-ray generator, to 40 kV at 40 mA.

Hydrogen storage

Hydrogen storage capacities of the SWCNTs were measured with HPVA-100 series of gas adsorption analyzer from TA Instruments (VTI Corporation). The samples were outgassed at 300 °C for 16 h. The hydrogen uptakes of the outgassed samples were measured at cryogenic temperature up to a pressure of 100 bar. The hydrogen adsorption and desorption data were collected during the measurements.

Results and discussion

Structure of SWCNTs

MgO peaks for XRD patterns of all unpurified SWCNTs on Fe, Co, V, Ni, Fe–Co catalysts were observed at $2\theta \approx 37^\circ$ (111), 43° (200), 62.5° (220), 75° (311), and 78° (222) as shown in Fig. 1. Although, the characteristic peak of highly ordered pyrolytic graphite (HOPG) at $2\theta \approx 26^\circ$ (002) was observed in the XRD patterns, the intensities of MgO peaks were much stronger than the graphite peaks due to the high content of MgO in as-synthesized CNTs. SWCNTs synthesized on Co–MgO and V–MgO catalysts had a lower degree of graphitization, whereas the intensity of graphite peaks for SWCNTs synthesized on the Fe–Co–MgO and Ni–MgO catalysts were slightly higher than that of Co–MgO and V–MgO. This result can be explained with the fact that the intensity of HOPG peak (002) is connected to the degree of graphitization and existence of this peak refers to the multilayered graphite structure around the catalyst particles for SWCNTs [11].

SEM images of SWCNTs grown on all catalysts show that SWCNTs grown on the catalyst systems have typical bundled structure. As it is seen in Fig. 2, the SWCNTs has grown via tip growth which occurs due to the low interaction between the metal and the surface of the substrate, resulting with C_2H_2

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