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Hydrogen Storage In Single-Walled Carbon Nanotubes Purified By Microwave Digestion Method

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***Abstract*—**The aim of this study was to synthesize the single walled carbon nanotubes (SWCNTs) and determine their hydrogen storage capacities. SWCNTs were firstly synthesized by chemical vapor deposition (CVD) of acetylene (C_2H_2) on a magnesium oxide (MgO) powder impregnated with an iron nitrate ($Fe(NO_3)_3{\cdot}9H_2O$) solution. The synthesis parameters were selected as: the synthesis temperature of 800°C, the iron content in the precursor of 5% and the synthesis time of 30 min. Purification process of SWCNTs was fulfilled by microwave digestion at three different temperatures (120, 150 and 200 °C), three different acid concentrations (0.5, 1 and 1.5 M) and for three different time intervals (15, 30 and 60 min). Nitric acid (HNO_3) was used in the removal of the metal catalysts. The hydrogen storage capacities of the purified materials were measured using volumetric method at the liquid nitrogen temperature and gas pressure up to 100 bar. The effects of the purification conditions such as temperature, time and acid concentration on hydrogen adsorption were investigated.

***Keywords*—**Carbon nanotubes, purification, microwave digestion, hydrogen storage

I. Introduction

HYDROGEN is considered to be a clean energy carrier. However, the most serious barrier to potential uses is the development of feasible hydrogen storage systems. The discovery of high hydrogen storage capacity of carbon nanotubes (CNTs) makes up alternatives for hydrogen storage systems. Since their identification in 1991, CNTs, especially SWCNTs, have attracted huge research interest due to their outstanding mechanical, electronic, optical, and thermal properties which provide large possible technological application fields. Although CNTs have a simple chemical composition and atomic bonding configuration [1], they have important structure and structure–property relations among nanomaterials. There are three common methods used to synthesize CNTs: 1) Laser ablation 2) Electric arc discharge 3) chemical vapour deposition. Chemical vapor deposition (CVD) synthesis method is an efficient method for large-scale production of high quality CNTs. Also this method provides control of the system parameters such as carbon source, catalyst, time, temperature etc. By this way in CNT synthesis system, product yield and quality are increased. CNTs are synthesized as multiwall and single wall depending on temperature and common carbon sources are hydrocarbons or carbondioxide. Also metal catalyst and support materials are varied in order to improve the CNT production. Mostly Fe, Co and Ni are used as the catalysts and MgO, SiO_2, Al_2O_3, and zeolite are used as the support materials. Regardless of the method to produce CNTs, there are always impurities present in the final product such as metal catalyst and carbonecous materials. It's important to reduce or completely eliminate these impurities in the as-grown CNTs. The purification had a large effect on the adsorption characteristics of the CNTs [2]. Several purification methods have been investigated to remove impurities. Purification methods can be varied depending on the application field that molecular electronics, chemical sensing, polymer composites and electrocatalysis, require the chemical functionalization of carbon nanotubes as an essential preparation step [3]. Chen et al. [4] reached the yield of 10-20 w% when they purified CNTs by oxygen at 530°C for 3 days. Rinzler et al. [5] refluxed SWCNTs in 2.6 M HNO_3 for 45 h. They had yield of 10-20 w%. Wang et al. [6] tried a new method to remove both of metal and amorphous carbon. They used an aqueous mixture of H_2O_2 and HCl at 40–70°C for 4–8h and the purification yield was significantly increased to 50 wt% and the purity was up to 96 wt%. Ye et al. [7] studied for tip opening and purification of MWCNT arrays was performed in an aqueous solution of 57% H_2SO_4 at room temperature. In their studies the results of inductively coupled plasma-mass spectrometry indicated that 98.8% of the Ni was removed after the electrochemical oxidation. Wang et al. [8] developed a three-step method to purify and cut SWCNTs synthesized by CVD. This method included refluxing in 2.6 M HNO_3 to remove metal particles, ultrasonication in acid solution (H_2SO_4/HNO_3, H_2SO_4/H_2O_2) to cut and polish the SWCNTs, and heat treatment in an NH_3 atmosphere to remove carbon impurities and heal structural defects. Also microwave-assisted digestion method provides effective and short-time purification. The method enables both to removes metal and amorphous carbon particles, and to increase the surface area. This is explained with the opening of the nanotube tips due to the removal of the embedded metal particles [2]. Geng et al. [9] studied on hydrogen storage capacity of multiwall carbon nanotubes at room temperature and under low pressure. They found 0.3wt% capacity after microwave digestion which is mostly attributed to the introduction of micropore surfaces.

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In this study, the hydrogen adsorption on single-walled carbon nanotubes (SWCNTs) purified by microwave digestion method was investigated. SWCNTs were firstly synthesized by chemical vapor deposition (CVD) method and purification process was fulfilled by microwave digestion at three different temperatures (120, 150 and 200 °C), three different acid concentrations (0.5, 1 and 1.5 M) and for three different time intervals (15, 30 and 60 min). Nitric acid (HNO_3) was used in the removal of the metal catalysts. The hydrogen storage capacities of the purified materials were measured using volumetric method at the liquid nitrogen temperature and gas pressure up to 100 bar and the effects of the purification conditions such as temperature, time and acid concentration on hydrogen adsorption were investigated.

II. Experimental Study

A. Synthesis of Carbon Nanotubes

Carbon nanotubes were synthesized by the fluidized-bed CVD synthesis of acetylene (C_2H_2) on a magnesium oxide (MgO) powder impregnated with an iron nitrate ($Fe(NO_3)_3 \cdot 9H_2O$) solution. The CVD apparatus consists of a vertical furnace and a quartz glass tube with a diameter of 3 cm in which in the middle a quartz filter (Fig. 1). A magnesium oxide (100 $m^2 \cdot g^{-1}$) supported iron oxide powder produced by impregnation in an iron nitrate ethanol solution is used as precursor powder. To get a precursor with a MgO to Fe weight ratio of 5%, MgO were suspended in ethanol and iron nitrate ($Fe(NO_3)_3 \cdot 9H_2O$) previously dissolved in 100 ml ethanol was stirred together and sonicated for 20 min in order to homogenize the mixture. Afterwards the precursor was dried and grinded into a fine powder.

For one deposition, typically 0.75 g of precursor powder was filled in the quartz tube and the atmosphere was purged with argon for 5 min. Then the furnace was heated to the synthesis temperature (800 °C). By heating up the precursor powder iron oxide clusters were formed due to the thermal decomposition of the iron nitrate at 125°C. The synthesis was started with the introduction acetylene mixed with argon for 45 min. After synthesis, the SWCNTs were cooled in inert gas (argon). The total experimental time varied from 2 to 3 h with duration of actual growth stage 45 min.

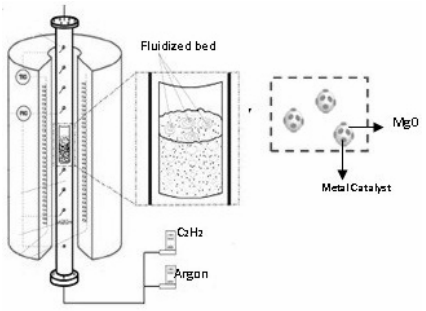


Fig. 1 Schema of the fluidized-bed reactor

A. Purification Procedure

As mentioned above, synthesized SWCNT materials contain mainly metal catalysts of iron, and magnesium particles and amorphous carbon. The synthesized or as-grown samples were purified by applying microwave digestion method to investigate the influence of purity of SWCNT material on hydrogen adsorption. Sample was weighted and placed in TFM vessels made of Teflon. The power of microwave was set at 500 W and at first step temperature ramped up to setting temperature. The second step was carried out at setting temperature for 15, 30 and 60 min. Nitric acid (HNO_3) in different concentrations (0.5, 1 and 1.5M) was used in the removal of the metal catalysts from the synthesized SWCNT material. Possible effects of different concentration (0.5, 1 and 1.5M), time (15, 30 and 60 minute) and temperature (120, 150 and 210°C) to the purification steps were investigated. The purified samples were washed with distilled water until pH was reached to ~ 7, and then dried in an oven at 105°C for 48 h.

B. Characterization of Materials

The synthesized and purified SWCNTs were characterized by by transmission electron microscopy (TEM) -FEI-Tecnai-G2 F-20 instrument, raman spectroscopy-Horiba Jobin-YVON HR 800UV instrument and thermogravimetric analyzer (TGA)-TA-Q600 SDT instrument.

C. Hydrogen Storage Mesurement

The hydrogen storage capacities of SWCNTs were measured with HPVA-100 series of gas adsorption analyzer from TA Instruments (VTI Corporation). About 0.2 g sample was filled into the sample chamber. In order to remove adsorbed gases and moisture, the sample has been heated under vacuum at 300 °C for ~24 h until a pressure of better than 2×10^{-6} mbar was achieved. After out gassing, helium and hydrogen gases were fed into the system. Helium was used to calibrate sample cell and to measure the pressure steps. For measurements at liquid nitrogen temperature, the whole measuring system was immersed in a temperature-controlled liquid nitrogen bath to keep the temperature constant at -196 °C. Equilibrium time was selected as 10 minutes and experiments in the range of 0.1 to 100 bar pressure were carried out. During the experiment, all steps were monitored by computer program.

D. Electrical Conductivity Measurement

Electrical conductivity measurement of prepared samples was performed by electrometer of Keithley 6517A. The measurement was achieved at 20°C temperature under 1 V electrical current. Thickness of the samples was measured by digitally micrometer.

III. Results and Discussion

A. Structure Characterization of SWCNTs

TEM image of the yield is shown in Figure 2. TEM, being the highest resolution technique, is typically capable of imaging CNT samples up to atomic resolution. It is evident

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that the structures synthesized by chemical vapor deposition method are CNTs. The dark side of the figure is thought to be due to the impurities existing within the sythesized material. TEM images of the samples indicate that single wall carbon nanotubes were synthesized at 800°C.

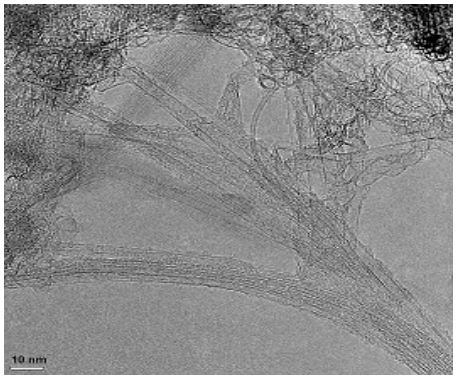


Fig. 2 TEM image of SWCNTs synthesized at 800 °C

Raman spectroscopy is a powerful technique for the characterization of the structure of carbon nanotubes. Fig. 3 shows Raman spectra for the synthesized carbon nanotubes excited by 633 nm laser. Two different spectra of SWCNTs were observed at the G band (around 1580 cm^{-1}) and D band (around 1350 cm^{-1}). As shown in Fig. 3 that the intensity of the G band is considerably higher than D band. The intensity ratio of D and G band (I_D/I_G) express the quality of SWCNTs. The higher ratio explains the higher amorphous carbon content and defect formation. The intensity ratio of D and G band of the synthesized SWCNT sample was found as 0.31. This observation leads to a conclusion: SWCNTs have the low amorphous carbon content. As seen from Fig. 3, the spectrum in RBM band, which is a characteristic of SWCNT, was observed in the sample. The reason of this spectrum is that the tube diameter is below 2 nm and this result is consistent with other studies found in literature [10]. If nanotube diameter is greater than 2 nm, RBM spectrum becomes difficult to be observed.

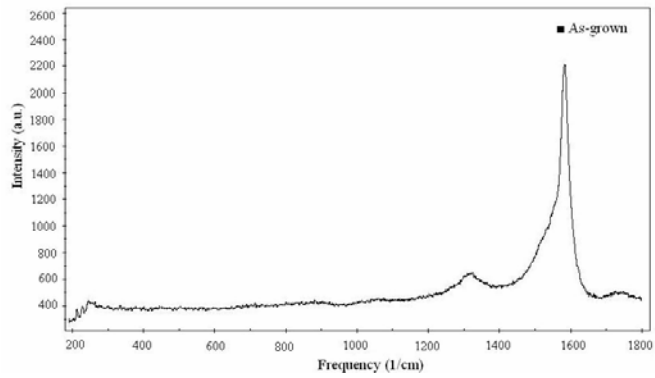


Fig. 3 Raman spectra of SWCNT

RBM band has an another property that can be used to calculate the mean diameter of SWCNTs by the equation (1);

$$\omega(cm^{-1}) = A / dia(nm) + B(cm^{-1}) \quad (1)$$

where; A and B are constants (A= 223 cm^{-1}/nm, B=10 cm^{-1}) and d is the diameter of SWCNT [11]. The calculated mean diameter of the synthesized SWCNT sample was found as 0.94 nm.

Thermogravimetric (TG) analysis is used to characterize the total carbon loading and determine the residual metallic catalyst. The amorphous carbon is completely oxidized at temperatures below 350 °C and graphite burns above 750 °C. The oxidation temperatures of the SWCNTs depend on the nanotube type and SWCNTs is generally oxidized at the temperatures above 400 °C. In this study, the TG analysis of synthesized SWCNTs was conducted in air atmosphere with a ramp of 5 °C/min between 25 and 800 °C. The yield was defined as the relative weight loss due to the oxidation of the carbon and the result of this analysis is shown in Fig. 4. As shown in this figure, carbon nanotube sample has high metal content (about 74%). Moreover, Derivative Thermogravimetric Analysis (DTG) of the sample was accomplished and the result is also given in Fig. 4. The derivative curves directly reflect the variation in the weight as a function of temperature by occurrence of thermal events (such as the onset of burning). It can be seen from Fig. 4 that maximum weight loss of SWCNTs was occurred at 590°C (DTG_{max}). Especially, it is observed that DTG curve of the sample has only one peak which belongs to SWCNTs. This is the also evidence of low amorphous carbon content of the sample. Similar situation is reported on the other studies in literature and oxidation of amorphous carbon below 400 ^{0}C is mentioned [12].

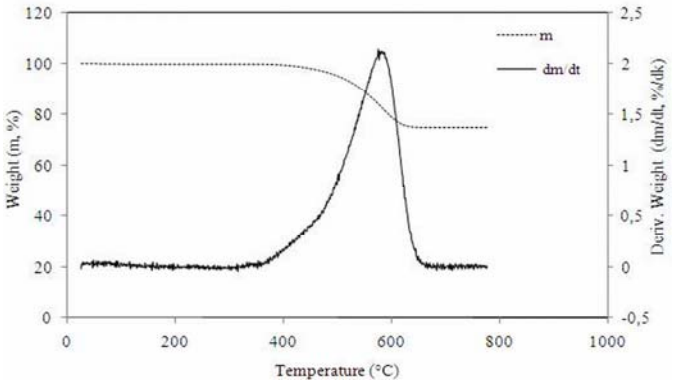


Fig. 4 TG and DTG curves of SWCNT synthesized at 800 °C

B. Purification of SWCNTs

In order to investigate the influence of product purity which is provided by microwave digestion method on hydrogen adsorption properties SWCNTs synthesized at 800°C were purified by HNO_3. TG analyses of the purified samples were performed in air atmosphere with a ramp of 10 °C/min between 25 and 800 °C. The results are shown in Table 1. Purification yield was calculated according to the following equation (2):

$$\text{Purification yield (\%)} : (w_0 - w_t) / w_0 * 100 \quad (2)$$

where w_0 is the metal content of as-grown SWCNT (%) and w_t is the metal content of purified SWCNT (%).

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TABLE I
THERMOGRAVIMETRIC ANALYSIS RESULTS OF THE PURIFIED SWCNTS

Code	Concentration (M)	Time (min)	Temperature (°C)	Purification Yield (%)
1	0.5	30	210	93.16
2	1	30	210	95.72
3	1.5	30	120	94.46
4	1.5	30	150	94.02
5	1.5	15	210	96.31
6	1.5	30	210	98.40
7	1.5	60	210	98.77

As it is seen from the results, SWCNTs have been successfully purified by high efficient microwave digestion purification method. In this method nitric acid absorb microwave energy rapidly and dissolve metal efficiently. Purification conditions (temperature, time and acid concentration) also affect on the yields of SWCNTs. Time is one of the important parameters. As shown in Table I, the residual catalyst content of different digestion time ranges from 15 to 60 min at the temperature of 210 °C. It is obviously that the content suddenly falls to 3.69% only in 15 min digestion. With increasing purification time, the catalyst contents slowly decrease to 1.60 and 1.23% of 30 and 60 min treatments, respectively. The reason might be that of most particles were removed within the first few minutes. So, it is not a genius way to increase the digestion time, but to reduce the diameter of CNTs. The efficiency of microwave digestion could be increased if the diameter of CNTs is small and uniform.

From chemical kinetics, temperature is largely responsible for the speed and completeness of the impurity dissolution reactions [13]. Experimental support for purification temperature dependency is shown in Table I, which displays a general upward trend in both impurity removal efficiency and impurity weight loss as a result of increased temperature. The optimum temperature for purification was determined to be 210 °C.

Another important parameter in purification is acid concentration. As shown in Table I, the residual catalyst content of different nitric acid digestion concentrations ranges from 0.5 to 1.5M at the temperature of 210 °C and time of 30 min. It is obviously that the content suddenly falls to 6.84% only in 0.5 M acid digestion. With increasing acid concentration, the catalyst contents slowly decrease to 4.28 and 1.60% of 1.0 and 1.5M acid treatments, respectively.

TG curves of SWCNTs that were purified by microwave digestion are shown in Fig. 5. The lines reflected the weight loss upon heating and their shape were dependent on the composition and the oxidative stability of the sample components. A final temperature of 800 °C was sufficient for complete burning of the nanotubes and carbon impurities such as graphite and amorphous carbon that were completely burned at the temperatures of 625-660 °C. The residual weights (%) after the heating process showed the presence of metallic impurities.

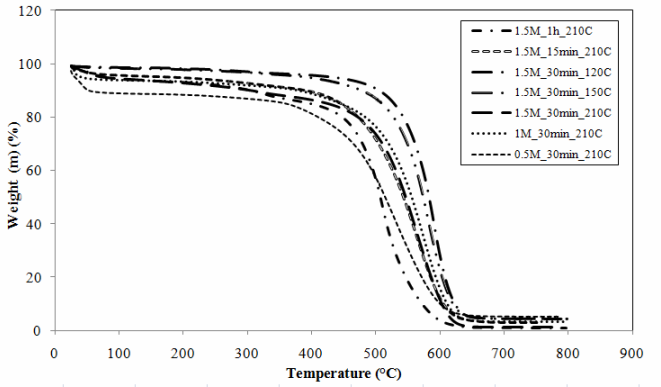


Fig. 5 TGA curves of SWCNTs purified by microwave digestion

DTG analysis of the samples was also accomplished and the results are shown in Fig. 6. DTG curves consist of broad peaks in different positions, suggesting an influence of the purification treatments on the thermal stability. The maximum weight losses of SWCNTs purified by different microwave digestion temperatures at 120, 150 and 210°C for 30 min and 1.5 M HNO_3 concentration were occurred at 577, 567 and 545 °C, while the maximum weight losses of SWCNTs purified by 0.5, 1 and 1.5M HNO_3 at 210°C for 30 min were 514, 558 and 545°C, respectively. DTG curves clearly demonstrate that oxidation temperatures of the purified samples are lower than that of the as-grown sample (590°C).

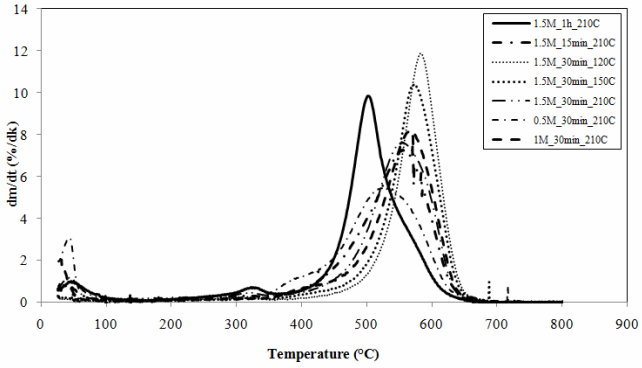


Fig. 6 DTG curves of SWCNTs purified by microwave digestion

Fig. 7 shows Raman spectra of the sample purified by microwave digestion which is obtained as the optimum conditions (at 210°C for 30 min. and 1.5 M HNO_3 digestion). The strong peaks observed at nearly 1590 cm^{-1} on G band were attributed to typical peak of SWCNTs. The peaks at around 1300 cm^{-1} on D band indicates the presence of amorphous carbon and defect formation. Because D band indicates disordered sp^2 hybridized carbon atoms and G band reflects the structural integrity of the sp^2 hybridized carbon atoms of the nanotubes. The intensity ratio of D and G band of the purified SWCNT sample was higher than as grown sample and found as 0.40. The reason might be that SWCNTs have defects formations which were occurred in purification. The higher amount of defects at lower might also indicate that the CNTs are grown with amorphous carbon structure which

content very low amount in agreement with the results of TGA given in Figure. 4.

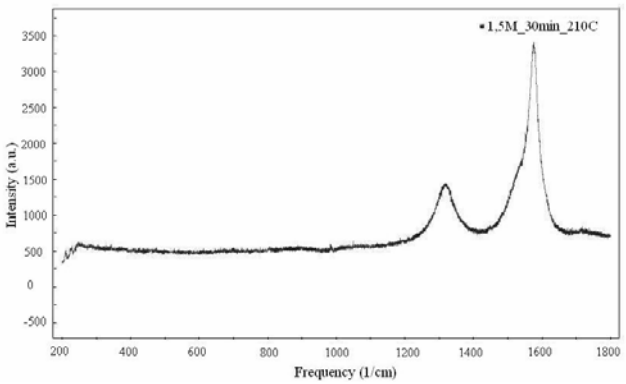


Fig.7 Raman spectra of SWCNTs purified by microwave digestion

C. Hydrogen Storage

The hydrogen storage capacities of SWCNTs purified by microwave digestion method were determined by volumetric method up to 100 bar at liquid nitrogen temperature (– 196 °C) and the results are given in Table 2. In Figures 8 and 9, we also show plots of hydrogen adsorption versus pressure for the various purified SWCNTs studied by us. It is seen from this table and figures that the hydrogen gas pressure has a great influence on hydrogen adsorption in SWCNTs, that is, the hydrogen storage capacity of SWCNTs increases with increasing hydrogen pressure in the range of 0-100 bar. A linear dependence was observed for all samples. While only a small amount of H_2 (less than 1 wt %) could be stored at low pressure (1 bar), hydrogen storage could be reached up 3.70 wt % at high pressure (100 bar).

TABLE II
HYDROGEN STORAGE CAPACITIES OF SWCNTS

Code	Hydrogen adsorption (wt %)	
	P=1 bar	P=100 bar
1	0.68	1.64
2	0.84	3.31
3	0.79	3.49
4	0.74	3.49
5	0.73	3.70
6	0.62	2.97
7	0.41	2.90

Purification is important in the hydrogen adsorption process and caused a shortening of SWCNTs. Because, the purification process could open the ends of CNTs effectively and hydrogen molecules could have entered the inner cavities through these ends, leading to increase in hydrogen sorption capacities. Among all purified samples, the highest hydrogen storage capacity was obtained for SWCNTs purified by 1.5M HNO_3 for 15min at 210°C as 3.70 wt% and the nearest value belongs to SWCNT purified by 1.5M HNO_3 for 30min at 120 and 150°C was 3.49 wt%. Although maximum purification yields were provided by 1.5M HNO_3 for 30 and 60 min at 210°C, their hydrogen storage capacities are lower than the sample purified by 1.5M HNO_3 for 15 min at 210°C. This could be explained as follows: after 15min of acid treatment, CNTs can be damaged and decomposed. These changes in the CNT structure could reduce the hydrogen adsorption.

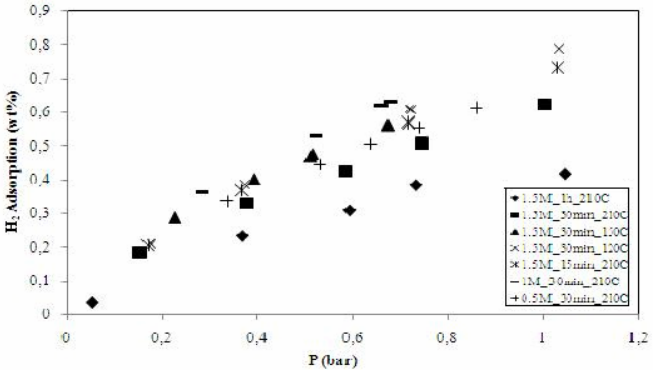


Fig. 8 The amount of hydrogen adsorbed in wt % as a function of pressure up to 1 bar for the purified samples by microwave digestion

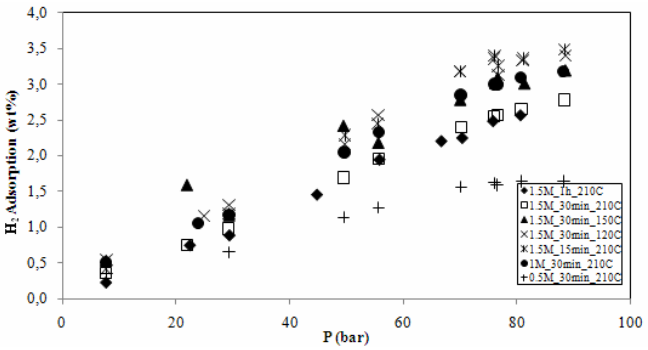


Fig. 9 The amount of hydrogen adsorbed in wt % as a function of pressure up to 100 bar for the purified samples by microwave digestion

IV. CONCLUSIONS

The present study has shown that metallic catalysts in SWCNTs were highly removed by microwave digestion acidic procedure. The advantages of this method are high efficient, easy to operate, short in time, free of damage on CNTs and little consumed in reagents. The results show that the purification efficiency increases with temperature, acid concentration and time. This study also indicates that CNTs can be used for adsorption of hydrogen. It was observed that the hydrogen adsorption capacities of the synthesized and purified samples were changed within the range of 0.41 to 3.70 wt%. Although the highest hydrogen adsorption capacity of 3.70 wt% was achieved at low temperature of -196 °C and high pressure at 100 bar, some further studies for increasing the hydrogen storage capacity of the samples are still carried out for achieving the value of 6.5 wt% which is the DOE's

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gravimetric hydrogen storage target for the transportation applications.

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