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Study of Hydrogen Adsorption by Spiral Carbon Nano Fibers Synthesized From Acetylene

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A spiral carbon nanofiber of 30 to 40 nm diam and 20 μm average lengths has been synthesized by catalyst chemical vapor deposition method using Ni or Fe-Ni alloy as catalyst. The purpose of synthesis of carbon nano fibers was to use it for hydrogen adsorption. Catalysts used affected the morphology of carbon nano material (CNM) where as purification and ball milling of CNMs affected the hydrogen adsorption. The hydrogen adsorption is found to be 0.296 wt% and 0.334 wt% at hydrogen pressure of 11 Kg/cm^2 with as grown and purified CNMs with nitric acid respectively. After the ball milling of CNMs, their hydrogen storage capacity decreased to 0.222 wt%.

Keywords acetylene, CNMs, hydrogen adsorption, spiral carbon nanofiber, ball milling, CCVD process

INTRODUCTION

The depletion of energy resources and maintenance of environmental pollution are essential problem that are closely related to the sustainable development of human society and demand for prompt solution. A fuel cell to combat this problem has drawn the attention of many workers. Hydrogen is regarded as one of the most fascinating candidates for the fuel cell because end product is non-polluting water.[1] Due to difficulties in storing hydrogen, its application as fuel has been limited. The discovery of carbon nano tubes (CNTs)[2] in 1991 has opened a Pandora box of its various applications. This has created the necessity to develop economical process to synthesize CNMs. Arc discharge[3,4] and laser ablation[5] are principle methods for obtaining high quality CNMs of various forms such as CNTs, carbon nanofiber(CNFs), carbon nanobeads (CNBs), single-walled carbon nanotubes (SWCNTs), multi-walled carbon nanotubes (MWCNTs). But chemical vapor deposition (CVD) process[6–10] seems to have become plausible method for large-scale production of CNTs. Sharon and his group have developed a method for large-scale production of CNMs by the catalyst chemical vapor deposition (CCVD) process[11] from natural sources. One dimensional nano carbon including CNFs,[12,13] MWCNT,[14] SWCNT[15–17] and CNMs obtained from natural source[11] have been reported to be promising candidates for hydrogen adsorption. In this paper the effect of acid treatment and ball milling of spiral carbon nano fibers (SCNF) synthesized from acetylene by CCVD process to store hydrogen is reported.

EXPERIMENTAL

Synthesis of CNMs

For the synthesis of carbon nanomaterial, it is necessary to use a catalyst particle of nanosize range. For this purpose we adopted the method discussed elsewhere.[18] The catalyst i.e., Ni or Fe-Ni alloy was prepared by urea decomposition procedure (Figure 3f). In conventional production method of CNMs, aromatic compound mainly benzene are used as the carbon source.[19–22] Acetylene is also a source of carbon for nano fiber production.[23–25] The CCNFs was prepared from acetylene by CCVD process. The pyrolysing apparatus was same as described earlier[26] and presented in Figure 1. In this method one-meter long quartz tube kept inside the

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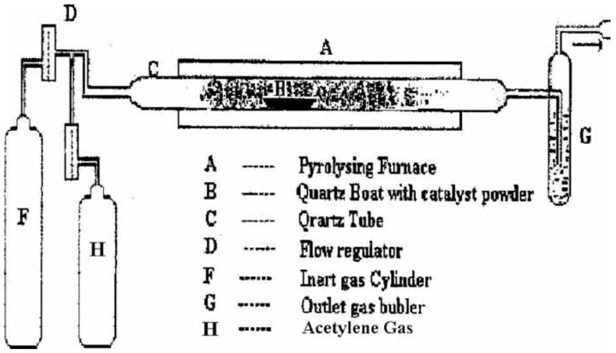

FIG. 1. Schematic showing the apparatus for the preparation of CNMs using CCVD.

furnace has been used. Ni or Fe-Ni alloy particle was kept in quartz boat and placed inside the tube furnace. Hydrogen gas was passed in to the furnace tube at the flow rate of 0.4 or 0.6 cc/min. to create inert atmosphere. After 5 min. of passing gas the pyrolysis was tried at 750 °C and 850 °C. As soon as the temperature reached, the acetylene gas was allowed to pass very slowly at a flow rate of 0.4 cc/min. for 1 h. and heating was continued for 2–3 h. At constant set temperature in an inert atmosphere of hydrogen. The furnace was allowed to cool down to room temperature, and then the pyrolised material was collected from the furnace.

Purification

The crude product (CNMs) obtained from acetylene contained amorphous carbon and metal particles as impurities. To remove the impurities the crude product was soaked in either conc. Nitric acid or conc. HCl for 3 h. The CNM was then washed with water till neutral pH. Finally it was rinsed with acetone to remove the traces of water and then dried in an oven at 150 °C. The purified sample was heated up to 700 °C in hydrogen atmosphere for 2 h to oxidize the amorphous carbon. The product was characterized by using SEM, TEM and XRD studied for its hydrogen adsorption capacity.

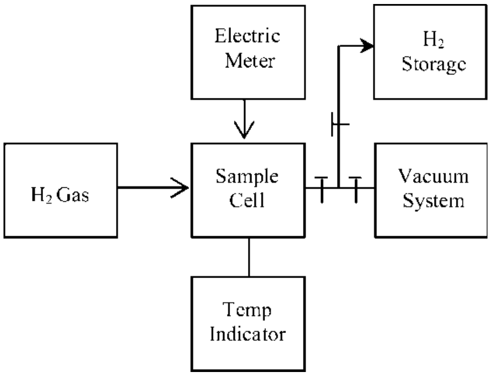

FIG. 2. A schematic diagram showing the measurement of hydrogen absorption.

Ball Milling

CNM, were cut to smaller sizes using centrifugal ball milling. CNM was Ball Milled in Zirconia jar using Zirconia balls of weight 3.36 g for 1 h at 300 rpm. Weight ratio of CNM to ball was 1 : 5.

Characterization by SEM, TEM and XRD

Scanning Electron Microscope (SEM) observation was conducted on FEI quanta 200, Transmission Electron Microscope (TEM) observation conducted on a Philips CM200 and XRD study conducted on a Philips Panalytical Xpert.

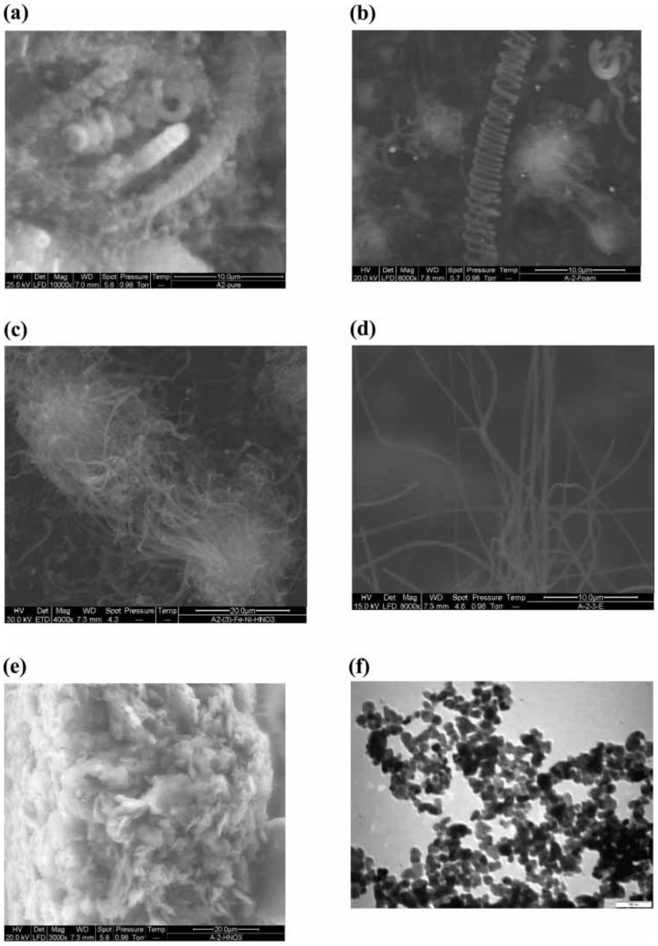

FIG. 3. (a) SEM photograph of as grown CNTs obtained from acetylene at 750 °C over Ni catalyst; (b) SEM photograph of purified CNTs with conc. HCL obtained from acetylene at 750 °C over Ni; (c) SEM photograph of as-grown CNTs obtained from acetylene at 750 °C over Fe-Ni catalyst; (d) SEM photograph of purified CNTs with HNO_3 obtained from acetylene at 750 °C over Fe-Ni catalyst; (e) SEM photograph of purified CNTs with HNO3 by refluxing at 150 °C obtained from acetylene at 750 °C over Fe-Ni catalyst; (f) SEM photograph of Ni catalyst obtained by urea decomposition method.

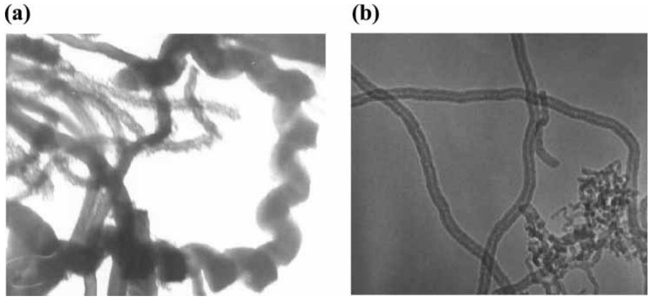

FIG. 4. (a) SEM photograph of purified CNTs with HNO_3 obtained from acetylene at 750 °C over Ni catalyst; (b) TEM photograph of purified CNTs with HNO_3 obtained from acetylene at 750 °C over Fe-Ni catalyst.

Measurement of Hydrogen Adsorption

Hydrogen adsorption study was carried out with an apparatus shown in Figure 2. This apparatus enabled us to calculate the hydrogen adsorption capacity of CNMs by measuring the decrease in hydrogen pressure. Since volume of the container was fixed (470 cc) this decrease in pressure was used as the quantity of hydrogen adsorbed by the CNMs. For each experiment, 5 g samples were used in a sample cell.

A leak test of apparatus was done before starting each experiment. For this purpose, the sample cell holder was evacuated and then left overnight to see whether there was any leakage. Then hydrogen gas was filled in the sample cell at the desired pressure and left over night to measure whether there was any decrease in the pressure. Two sets of hydrogen adsorption were done: one was blank where sample did not have any CNMs and the other was sample cell loaded with purified CNMs. Both these experiments confirmed that there was no leakage.

The sample cell was then filled with hydrogen at 11.0 Kg/cm^2. The change in the pressure of hydrogen was then measured as rise in temperature of the sample cell. This was achieved by heating the sample cell. This rate of change in hydrogen pressure with temperature was used as a blank experiment. Then 5.0 g of CNFs was placed inside the sample cell. The sample cell was heated up to 150 °C for degassing under vacuum, and left over night. Next day the sample cell was filled with hydrogen at 11.0 Kg/cm^2 left for 2 h to observe whether there was any change in hydrogen pressure at room temperature. Then the sample cell was gradually heated up to 170 °C and the change in hydrogen pressure with temperature was noted. A graph was plotted between the changes in pressure of hydrogen (i.e., when the carbon sample was present in the pressure vessel and when there was no carbon sample in the pressure vessel) at various temperatures. The difference in pressure was then plotted against temperature.

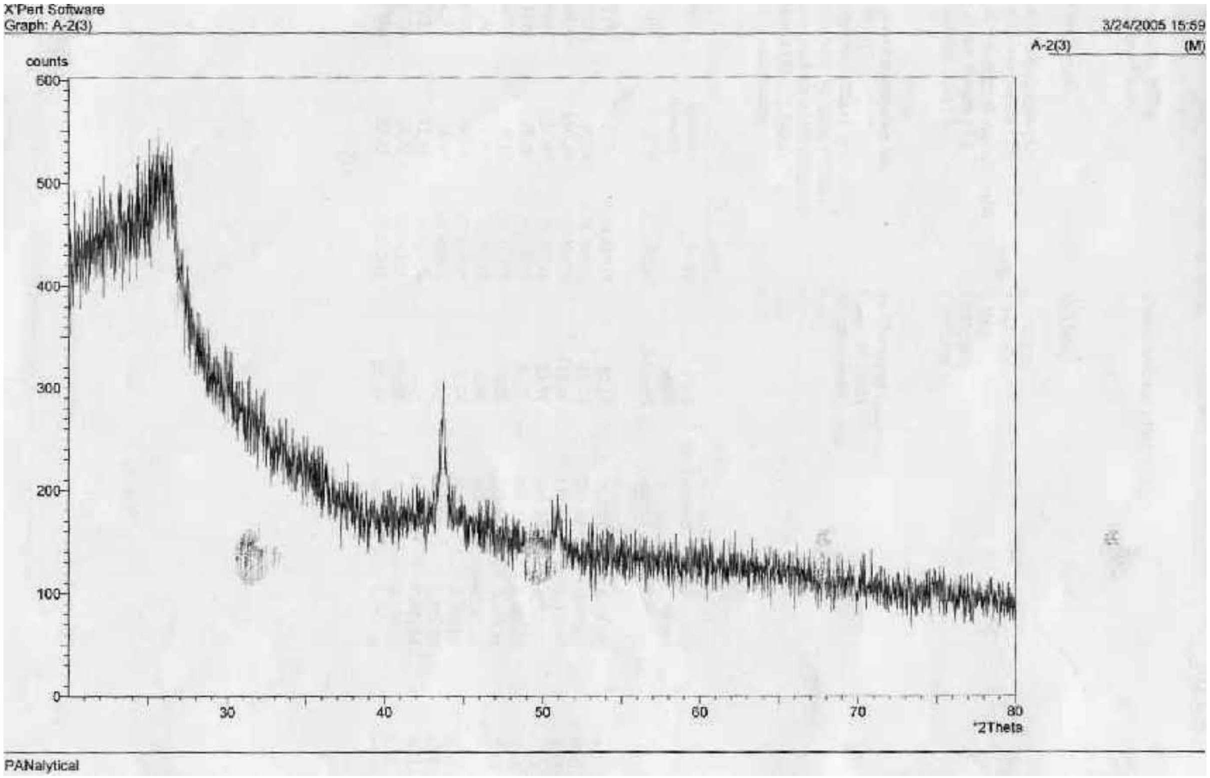

FIG. 5. XRD of CNMs obtained from acetylene purified with HNO_3 acid obtained from acetylene at 750 °C over Fe-Ni catalyst.

RESULTS AND DISCUSSION

Urea decomposition procedure for nano size catalyst preparation yielded nano sized (40–60 nm) Ni or Fe-Ni alloy. These catalysts have been successfully used by the Sharon group.[26,18] Acetylene introduced into the furnace at a flow rate of 0.4 cc/min. was found to yield higher amount of CNMs when it was run for 30 minute. This procedure yielded 4 g of CNMs per liter acetylene. An increased flow rate 0.6 cc/min. was not only decreased amount of CNMs but also produced more amorphous carbon. In trial, the acetylene flow rate was kept constant at 0.4 cc/min and hydrogen flow rate was decreased. But this also could not increase the yield; rather it showed more deposition of amorphous carbon in quartz boat. This suggests that the residence time of the acetylene in the reactor is controlling the amount of disorganized carbon coatings. It was found that a large amount of tar-like liquid by-product was being condensed on the cooled part of the furnace outlet. This might be due to a part of acetylene feed getting converted in to higher hydrocarbons by the catalytic action of nickel or Fe-Ni alloy as reported by Soneda et al.[27]

As mentioned above, CNMs synthesized from SEM, TEM and XRD characterized acetylene by CCVD process for quality, structure and nature of carbon deposited on metal

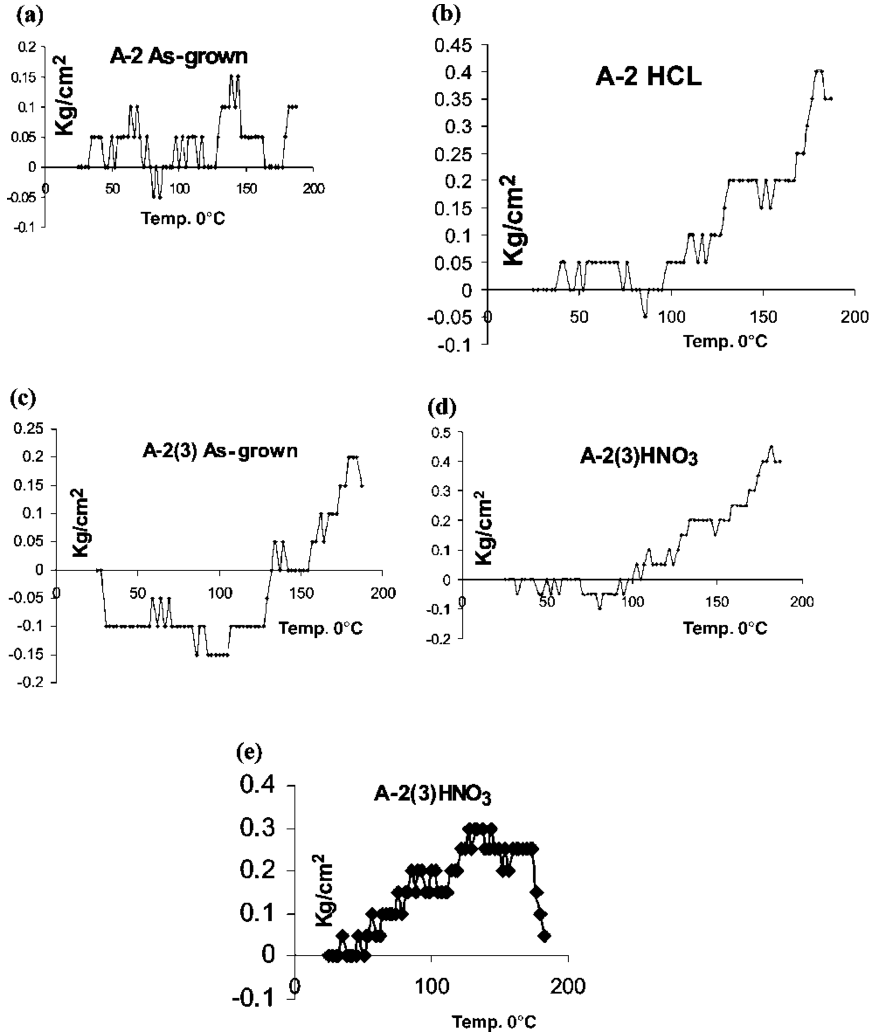

FIG. 6. (a) Variation of change in pressure vs. temperature for adsorption/desorption of as-grown CNTs obtained from acetylene at 750 °C over Ni catalyst; (b) Variation of change in pressure vs. temperature for adsorption/desorption of purified CNTs with conc. HCL obtained from acetylene at 750 °C over Ni catalyst; (c) variation of change in pressure vs. temperature for adsorption/desorption of as-grown CNTs obtained from acetylene at 750 °C over Fe-Ni catalyst; (d) variation of change in pressure vs. temperature for adsorption/desorption of purified CNTs with HNO_3 obtained from acetylene at 750 °C over Fe-Ni catalyst; (e) variation of change in pressure vs. temperature for adsorption/desorption of purified CNTs with HNO_3 obtained from acetylene at 750 °C over Fe-Ni catalyst and ball milled for 2 hrs.

particles. The SEM images of Acetylene pyrolised on Ni particle show large quantity of SCNFs as well as CNTs. Figures 3a and 3b are SEM of SCNFs before and after purification, whereas acetylene pyrolised on alloy (Fe-Ni) showed comparatively more amount of CNTs than SCNFs in both unpurified and purified samples (Figures 3c and 3d). These results were consistent in all the trials.

TEM of purified CNMs presented in Figure 4 shows that Ni as a catalyst could produce more SCNFs (Figrue 4a) Whereas CNMs deposited on Fe-Ni alloy shows large quantity of CNTs (Figure 4b). Characterization using XRD was done to confirm the structure of pyrolysed CNMs. As it can be seen from Figure 5 there is a diffraction peak at 26.4°, which is corresponding to the diffraction peak of graphite.

CNMs prepared using catalyst Ni or Fe-Ni alloy were assessed for their ability to adsorb hydrogen. The hydrogen adsorption of as-grown SCNFs sample obtained from acetylene on Ni particle at 750 °C in hydrogen atmosphere at low hydrogen pressure (11 kg/cm^2 at 300 k) is 0.191 wt% and after purification with concentrated HCl it is 0.296 wt%, which is almost 55%, increased in the adsorption capacity.

As-grown CNTs obtained from acetylene on Fe-Ni alloy at 750 °C in hydrogen atmosphere shows 0.148 wt% hydrogen adsorption at low hydrogen pressure (11 kg/cm^2 at 300 K). After purification of CNMs with concentrated Nitric acid the hydrogen adsorption markedly increased at same hydrogen pressure (11 kg/cm^2 at 300 K) to 0.334 wt%, i.e., it doubled the hydrogen adsorption capacity. It can be concluded that purified CNMs synthesized in the presence of Fe-Ni alloy produces a better quality of CNMs so far as hydrogen adsorption capacity is concerned.

It has been found that hydrogen adsorption capacity decreased after the ball milling of CNMs for 2 h to 0.222 wt% (Figure 6e) at low hydrogen pressure. Ball milling for a short period may not be enough for the formation of thin graphitic sheets. The structure gets destroyed if the ball milling is done for a very long time. The detail of the formation of nanotubes and nanofibers in the ball mill carbon samples is being investigated.

To calculate the hydrogen adsorption, pressure vs. temperature graphs were plotted (Figure 6a–6e). When there was adsorption change in hydrogen pressure, a positive value was obtained and when there was desorption the change in pressure was negative. As grown SCNFs obtained on nickel particles (Figure 6a) and treated with concentrated HCl (Figure 6b) shows improvement in the hydrogen adsorption. As-grown CNTs obtained on Fe- Ni alloy (Figrue 6c) and purified with concentrated Nitric acid (Figure 6d) shows the increase in hydrogen adsorption capacity.

CONCLUSION

Both Ni and Fe-Ni alloy were found to be good catalysts for preparation of SCNFs and CNTs respectively using acetylene as precursor in CCVD method. And 0.4 cc/min flow rate of acetylene was found to be more suitable for synthesis of CNM as it yielded 4 g of CNTs per gram of acetylene. Better purification of as-grown CNFs was achieved when they were soaked in nitric acid. Moreover purified CNMs showed more hydrogen adsorption capacity. However ball milling of CNMs to smaller unit decreased their capacity to adsorb hydrogen.

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