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CATALYTIC SYNTHESIS OF CARBON NANOTUBES FROM ACETYLENE USING Mm BASED C 15 TYPE AB_2 ALLOY HYDRIDE MATERIALS AS CATALYSTS AND THEIR HYDROGEN ADSORPTION STUDIES

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ABSTRACT

Synthesis of multi-walled carbon nanotubes (MWNTs) by the catalytic decomposition of acetylene over Mischmetal (Mm) based AB_2 alloy hydride catalysts is reported. Hydrogen decrepitation technique has been used to prepare the catalyst particles of these Mm based hydrogen storage alloys. The samples were purified by air oxidation and acid treatment and were characterized by XRD, SEM, TEM, HRTEM, and Raman spectroscopy. Hydrogen adsorption measurements were carried out for as- prepared and purified MWNTs at 125 K and 298 K using a high pressure hydrogen adsorption set-up. A maximum hydrogen storage capacity of 3.2 wt % at 60 bar is obtained at 125 K for purified CNTs prepared with $MmFe_2$ hydride catalysts.

Keywords: Carbon nanotubes; Hydrogen storage; Chemical vapour deposition

1. INTRODUCTION

The field of carbon nanotubes (CNTs) has been an explosive growth area ever since their discovery[1], because of their unique structure and excellent properties showing potential applications[2] as electronic devices, catalysts, sensors, field emission devices and hydrogen storage media. Recent reports of high and reversible adsorption of hydrogen in carbon nanotubes have initiated numerous studies, both experimental and theoretical [3,4]. Since the properties of carbon nanotubes are expected to be dependent on their diameters and helicity, considerable efforts have been made to study the synthesis and growth mechanism of CNTs[5]. CNTs are usually prepared by arc evaporation, laser ablation or metal catalysed chemical vapor deposition (CVD)[6]. Catalysts with large surface area having active catalytic centers are vital for the large-scale production of carbon nanotubes using CVD. In our recent work, the role of stability of Ni nanoparticles obtained *in situ* from the decomposition of Ni/Cr hydrotalcite –type anionic clay, on the growth of multiwalled carbon nanotubes (MWNTs) was studied[7]. In the present paper, we report the synthesis of MWNTs by the catalytic decomposition of acetylene using Mischmetal (Mm) based C 15 type AB_2 alloy hydride catalysts. Fine powders of $MmNi_2$ and $MmFe_2$ alloy hydrides were prepared by hydrogen decrepitation technique where in break down of particle size occurs due to plastic deformation during several cycles of hydrogen absorption and desorption. The presence of transition metals especially Fe and Ni and the hydrogen decrepitation method of powdering the above mentioned catalysts into fine particles in the presence of hydrogen, provide effective catalytic sites for CNTs growth. The as-grown and purified CNTs were characterized by X-ray diffractrion, thermogravimetric (TG) analysis, scanning electron microscopy (SEM), transmission electron microscopy (TEM), high resolution

TEM, and Raman spectroscopy. In addition, the hydrogen uptake properties of these samples were also investigated and are discussed.

2. EXPERIMENTAL

$MmNi_2$ and $MmFe_2$ hydrogen storage alloys were prepared by arc melting the constituent pure elements [Indian Misch metal (Nuclear Fuel Complex); Ce: 50 %, La: 35 %, Pr: 8 %, Nd: 5 %, Fe: 0.5 %, other mixtures: 1.5 %] in an arc furnace (CENTORR, USA) under argon atmosphere (99.995 % pure), in stoichiometric proportions. Each alloy was hydrogenated to a maximum storage capacity using a high pressure Seiverts apparatus[8]. Fine powders of alloys were obtained after several cycles of hydrogenation/ dehydrogenation. X –ray diffraction patterns of these catalyst precursors show the formation of single phase with a C 15 – type cubic structure.

MWNTs were synthesized by the decomposition of acetylene over $MmNi_2$ and $MmFe_2$ hydride powders using a fixed- bed catalytic reactor[8]. About 250 mg of the hydride powder was taken in a quartz boat that was inserted into the center of a quartz tube (30 mm inner diameter and 500 mm long). The quartz tube was mounted in a furnace and was heated to 500 $^{\circ}$C in argon atmosphere (200 sccm). Subsequently hydrogen (50 sccm) was introduced into the quartz tube for 1 h. The synthesis of CNTs was performed at 700°C and for 30 min with an acetylene flow of 70 sccm. Argon flow was maintained through out the experiment until the furnace was cooled to room temperature. The purification of the collected sample was carried out with conc nitric acid[9]. The crystallinity and purity of the samples were obtained by XRD (Cu-K_α radiation) and TGA measurements (10°C/min). The samples were characterized using SEM, TEM, HRTEM and Raman spectroscopy measurements.

3.0 RESULTS AND DISCUSSION

$MmNi_2$ and $MmFe_2$ alloys, after several hydrogenation and dehydrogenation cycles, were found to be finely powdered to about 5- 10 μm. These novel hydride catalysts prepared using hydrogen decrepitation technique, provides fresh surfaces with large surface area, free from getting oxidized which further increases the catalytic sites for the formation of CNTs. High hydrogen absorption, large decrepitation and low cost make these hydrides better catalysts for large-scale production of CNTs. In our experiment, with a reaction time of 30 min, the carbon deposit was found to have a mass gain of about 0.7 g. The yield of the carbon deposit formed during the reaction was calculated as follows: Carbon yield (%) = 100 $(m_{tot} - m_{cat}) / m_{cat}$, where m_{cat} is the initial amount of catalyst and m_{tot} is the total weight of the sample after reaction.

Fig. 1 a shows the XRD pattern of as- prepared CNTs using $MmNi_2$ hydrides as catalysts. The peaks are indexed to the reflections of hexagonal graphite. Few peaks corresponding to the catalytic impurities are also seen while the removal of metallic impurities is clearly shown in Fig. 1 b for purified CNTs prepared with $MmNi_2$ hydrides. Fig. 2 shows the TG curves of as-grown and purified MWNTs prepared by the catalytic decomposition of acetylene over $MmNi_2$ hydride catalysts. A slight weight gain is observed below 200°C for the as-grown sample, which is due to the oxidation of catalytic metals[9], while burning of amorphous carbon results in the weight loss up to 500°C. Weight loss between 500 – 700°C is assigned to the burning of MWNTs Final residual weights of 54.6 % and 9.1 % were obtained for as-grown and purified MWNTs respectively revealing a purity of about 90 % for the purified sample. The variability of oxygen exposure of the samples during the initial oxidative heat treatment could also retain the catalytic impurities[10]. In the present work, the yield of MWNTs is defined as the ratio of weight loss between 500 $^{\circ}$C and 700 $^{\circ}$C to the weight remained at 850 $^{\circ}$C, both measured from

TGA. This is a measure of the ratio of the weight gain by MWNTs to the weight of the catalytic powder. The yield of MWNTs was estimated to be ~ 60 % from the TG curves[11].

SEM images of purified CNTs prepared with $MmNi_2$ hydride catalysts and as –grown CNTs synthesized with $MmFe_2$ hydride catalysts are shown in Fig. 3 a, b respectively. The SEM images indicate that a large quantity of carbon nanotubes are seen. While the as-grown sample shows the presence of traces of catalytic particles and amorphous carbon, the purified sample is seen to be free from these impurities. TEM images of as-grown and purified CNTs prepared with $MmFe_2$ and $MmNi_2$ hydride catalysts are shown in Fig. 4. The inner diameter of the nanotube is about 16 nm and the outer diameter is around 80 nm on average. CNTs were almost unaffected by the acid and oxidation treatment, because of higher thermal stability of MWNTs. However, the tips of purified MWNTs were opened after purification process, as shown in Fig. 4 b. A typical HRTEM image of a purified MWNT, with the graphite layers clearly seen, is shown in Fig. 4 c. Fig. 5 shows the Raman spectra of purified MWNTs prepared with $MmNi_2$ hydride catalysts. The spectrum shows two strong peaks at 1365 cm^{-1} and 1590 cm^{-1} . The peak at 1590 cm^{-1} (G-band) correspond to the Raman allowed optical mode E_{2g} of 2- dimensional graphite, while the peak at 1365 cm^{-1} (D-band) is mainly derived from disordered carbon defects of the MWNTs[12]. The growth process of carbon nanotubes by CVD with catalyst is proposed to include three steps; (i) dissociation of hydrocarbon gas on the surface of the catalyst, (ii) diffusion of carbon atoms on the surface or through the bulk of the catalyst and (iii) growth of nanotubes[6]. It has also been proposed that the form of graphite that is produced is closely related to the physical dimensions of the metal catalyst particles and the most effective metals have been shown repeatedly to be iron, nickel and cobalt[13]. In the present study, as the size of the alloy hydride particles are seen to be in the range of 5 – 10 μm, we propose that each alloy hydride particle would be composed of a number of catalytic centers, which could act as nucleation sites for the growth of carbon nanotubes. There could be a further reduction in the catalyst particle size during the hydrogen treatment before the carbon deposition. This also accounts for the high yield of carbon deposit we obtained for a reaction time of 30 min. Further, the nickel or iron particles are well interspersed in the alloy, allowing better dispersion of the active catalytic sites. This would further result in lesser sintering of the particles.

The study of actual mechanism of carbon nanotube growth over alloy hydride catalysts through a detailed understanding of the surface and bulk reactions involving the carbon nucleation and the alloy – carbon interactions is in progress. Hydrogen adsorption measurements were performed for the as- grown and purified samples at 298 K and also at 125 K for the purified samples. Fig. 6 a, b show the hydrogen adsorption isotherms of carbon nanotubes synthesized with $MmNi_2$ and $MmFe_2$ hydride catalysts respectively. The hydrogen molecules could be physically adsorbed on the external nanotube walls and also could condense inside the cavity of the tubes[14]. ysts.

The hydrogen storage capacities of the purified MWNTs are found to be higher than that of as-prepared one, showing the necessity of purification process for better storage capacities of CNTs. The purification process could open the ends of CNTs effectively, as revealed from the TEM image (Fig. 4 b) and hydrogen molecules could have entered the inner cavities through these ends, leading to increase in hydrogen adsorption capacities. The disordered layers of the MWNTs would also act as adsorption centers and provide the access for hydrogen to be stored between these layers[3]. Our previous studies[15] on hydrogen adsorption measurements revealed an increased storage capacity of 3.3 wt % for the purified CNTs prepared with Mm based AB_5 alloy hydride catalysts. The amount of adsorbed hydrogen correlates with the specific surface area of the sample[16]. In our samples, the increased surface area upon purification, due to the removal of catalytic impurities from the tips of CNTs, and the amorphous carbon and

nanospheres adhered on the surface of the tubes, is responsible for the increased storage capacity of hydrogen.

The further increase in hydrogen storage capacity at 125 K could be attributed to the larger condensation of hydrogen molecules inside the cavities, as low temperature reinforces the effect of gas- adsorbent attractive interactions[4]. However, we could not find large difference in storage capacities upon purification. Since the aspect ratio of the CNT is usually up to 10^4~10^6, it is very unlikely that hydrogen inside the CNTs are accommodated exclusively by the capillary effect through the open-ends. Hence the possibility of hydrogen insertion through the tube wall by flip-in and kick-in mechanism[17], preserving the wall stability of nanotubes, could account for our experimental findings. We presume that higher adsorption capacities could still be achieved with complete removal of impurities and amorphous carbon and with better alignment of CNTs.

4. CONCLUSIONS

CNTs with about 90 % purity with an yield of ~ 60 % have been obtained by the pyrolysis of acetylene over $MmNi_2$ and $MmFe_2$ hydride catalysts, prepared by hydrogen decrepitation method. Due to the high hydrogen intake capacity, large hydrogen absorption, large decrepitation and low cost, these alloy hydrides are suitable catalysts for large-scale production of CNTs. The hydrogen adsorption studies of as- grown and purified MWNTs show that the hydrogen adsorption capacity can be increased with purification. Maximum hydrogen storage capacities of 2.8 wt % at 95 bar and 2.7 wt % at 81 bar have been obtained at 298 K for the purified CNTs synthesized with $MmNi_2$ and $MmFe_2$ hydride catalysts respectively, while a hydrogen storage capacity of 2.3 wt % at 59 bar and 3.2 wt % at 60 bar have been obtained at 125 K respectively for purified CNTs prepared with $MmNi_2$ and $MmFe_2$ alloy hydride catalysts.

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FIGURES

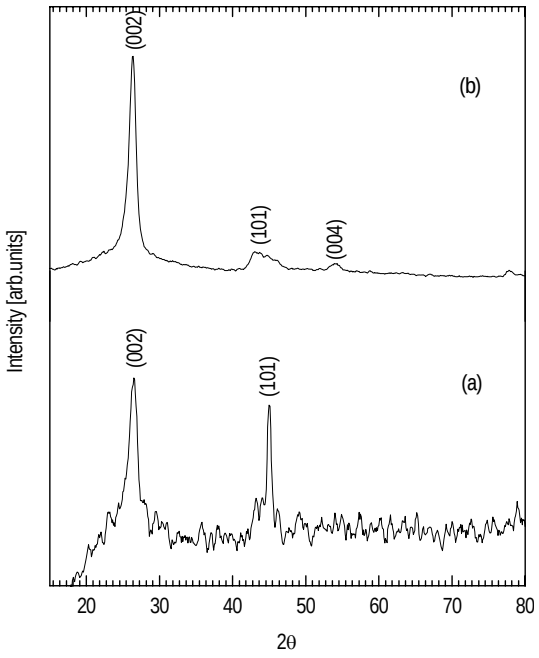

Fig. 1 Powder X- ray diffraction pattern of (a) as-grown and (b) purified MWNTs synthesized by the decomposition of acetylene over $MmNi_2$ hydride catalysts

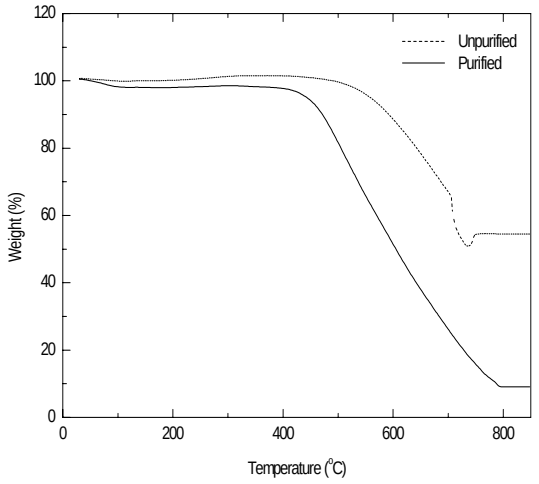

Fig. 2 Thermogravimetry (TG) curves of carbon nanotubes grown over $MmNi_2$ hydride catalysts.

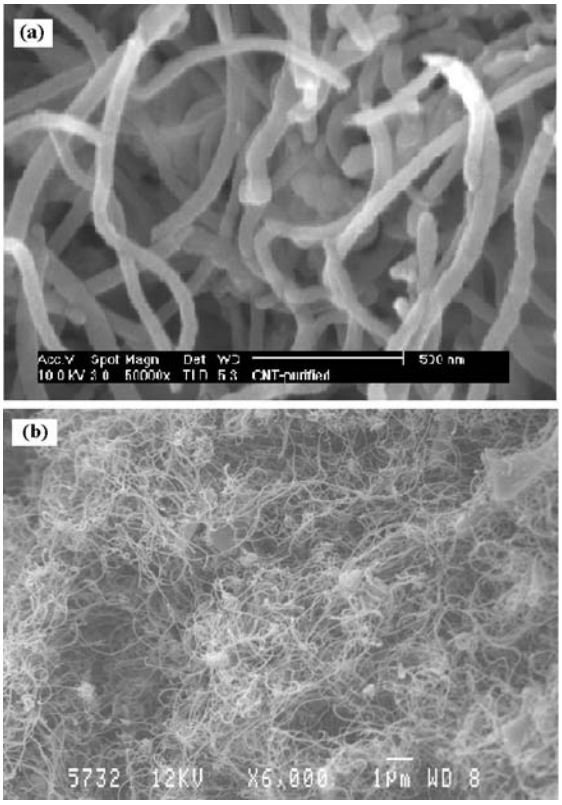

Fig. 3 SEM image of as-grown carbon nanotubes obtained from decomposition of acetylene over (a) $MmNi_2$ hydride catalysts (b) $MmFe_2$ hydride catalysts.

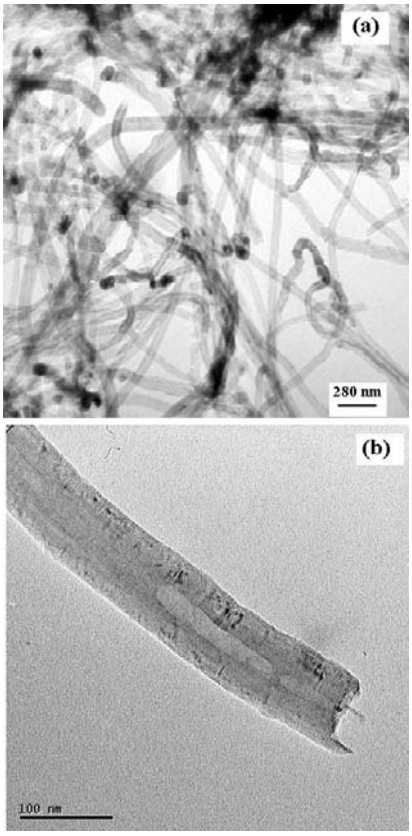

Fig. 4 TEM image of (a) as-grown and (b) purified MWNTs synthesized by the decomposition of acetylene over $MmFe_2$ hydride catalysts, MWNT synthesized by the decomposition of acetylene over $MmNi_2$ hydride

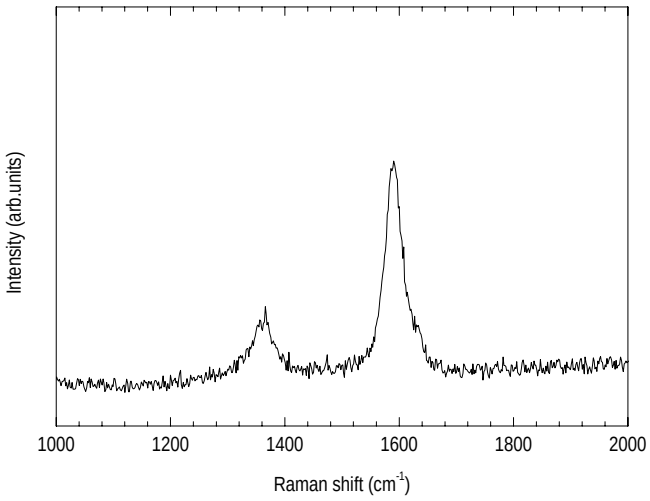

Fig. 5 Raman spectra of carbon nanotubes grown over $MmNi_2$ hydride catal

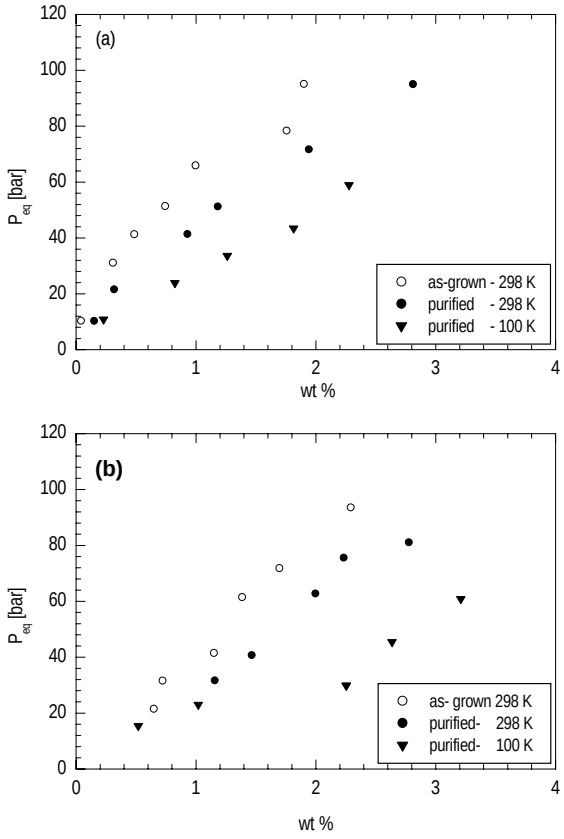

Fig. 6 Hydrogen adsorption isotherms of MWNTs synthesized by decomposition of acetylene over (a) $MmNi_2$ and (b) $MmFe_2$ hydride catalysts.