Synthesis of Carbon Canotubes (CNTs) Grown Over Supported Catalyst and their Adsorption Properties

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Abstract

Hydrogen is considered as one of the renewable energy sources. The use of hydrogen as fuel particularly in automotives is hampered by the lack of a safe and economical storage medium. Materials with high hydrogen storage capacities are desirable for storage applications. Carbon based materials are well known for its capability as absorbents due to its adsorptive and large surface area properties. Thus, carbon nanotubes (CNTs) are considered to be a promising medium for hydrogen storage in hydrogen-based energy system. Since the pioneering report on the discovery of carbon nanotubes (CNTs) in 1991 by Iijima, scientists and researchers worldwide are very interested to investigate in depth this new family of carbon because of its myriad properties and potential applications. In this study, CNTs have been successfully synthesized by using catalytic chemical vapor deposition (CCVD) method. The as-synthesized CNTs were characterized using SEM/FE-SEM, EDAX, nitrogen adsorption (NA) and transmission electron microscope (TEM). The structures of CNT formed were dependent on the catalytic support used. The as-synthesized CNTs are expected to have good storage capacity for hydrogen in fuel cell application.

Keywords: Carbon nanotube (CNT); Catalytic chemical vapor deposition (CCVD); Hydrogen storage.

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1. Introduction

Today, 'nanotechnology' is a hot topic attracting scientists, industrialists, journalists, governments and even the general public. Nanotechnology is the creation of functional materials, devices and system through control of matter on the nanometer scale and the exploitation of novel phenomena and properties of matter (physical, chemical, biological, electrical, etc) at that length scale.

Carbon nanotubes (CNTs) is one of the key components of nanotechnology. Ever since the discovery of carbon nanotubes by Iijima in 1991 [1], it has captured the attention of researchers worldwide. Understanding their unique properties and exploring their potential applications have been a main driving force in this area [2-5].

Carbon nanotubes, having unique geometrical structure and stable mechanical and chemical properties are also an excellent source of hydrogen storage due to their relatively small surface and pore volume. Research findings have shown that carbon nanotubes are able to store hydrogen [6]. Its capability to absorb and release hydrogen under normal atmospheric pressure and moderate temperatures would be a major breakthrough for the fuel cell system.

The increasing demands for mass production of carbon nanotubes have resulted in the development of new methods to produce carbon nanotubes. Catalytic chemical vapour decomposition (CCVD) was found to be one of the promising methods for the synthesis of CNTs at low temperature and ambient pressure. Controlled synthesis involving CCVD has been studied as an effective strategy to order or pattern CNTs on a variety of surfaces. Metal and mixture of metals supported on oxides, clays and zeolites have been found to be active as catalysts in CCVD method [7]. In the field of heterogeneous catalysis, a number of oxides and mixed oxides have been used to disperse and stabilize metallic particles. Catalytic properties of these solids are known

to depend upon the interaction between the support and the metal particles, which in turn depends on their method of preparation [8]. The synthesis of CNTs is carried out in the temperature range of 500-1000 °C with a stream of hydrocarbon gas (methane, acetylene, etc.) diluted with inert compounds such as nitrogen, argon, etc. The dissociation of the gas occurs at the hot catalyst surface. The precipitation of carbon from the saturated metal particle leads to the formation of tubular carbon structures in the form of nanotubes or nanofibers [9].

In this work, we have attempted to synthesize CNTs over alumina and molecular sieve supported Fe, Co and Ni catalysts. The morphologies of the as-grown CNTs were analysed. In addition, the effects of different supported catalysts and their potential adsorption properties were also investigated.

2. Experimental

2.1 Catalyst Preparation

Alumina (Al_2O_3) and molecular sieve (MS) beads obtained from commercial sources were used as catalyst supports. Both the supports were dried to eliminate water vapour and impurities prior to the addition of catalysts. The catalysts were prepared by the impregnation method. The supports were immersed with metal salt solution until saturation and dried overnight. The prepared supported catalysts were then used in the synthesis of CNTs.

2.2 CNTs Synthesis

A simple and inexpensive thermal catalytic chemical vapour deposition system has been designed. The experiments to produce CNTs were carried out in a horizontal tube furnace at atmospheric pressure. The supported catalysts were placed inside a

quartz tube. Acetylene gas, C_2H_2 was passed through to react with the catalysts. The pyrolysis of C_2H_2 was carried out at temperature > 600 °C. Prior to sampling, the reaction chamber was cooled down to room temperature. The samples were collected as black powder on the catalyst.

2.3 Characterization

The surface morphology and elements present on the support and catalysts were investigated using Scanning Electron Microscope (SEM) and Energy Dispersive X-ray Analysis (EDAX) (XL 40, Philips). The quality and nature of the as-grown CNTs were observed using SEM.

The single point surface area was measured at 79K (-196 °C) using a Micromeritics Pulse Chemisorp 2705. The samples were outgassed using nitrogen gas for 1½ hour at 350 °C. The nitrogen adsorption-desorption was carried out in liquid nitrogen. The surface area measurement was repeated in triplicate and an average of the peak area was taken. Reproducibility of the peak area was within ± 0.02 units on the display meter. The BET surface area was therefore calculated as:

$$BET \text{ (surface area)} = Peak\ Area\ (m^2)\ /\ sample\ weight\ (g) \tag{1}$$

The same apparatus was also used to measure the desorption of hydrogen at ambient temperature and pressure. All samples were outgassed in nitrogen at 350°C for 3 hours before saturation of hydrogen takes place. Saturation was carried out at ambient temperature and pressure for 1 hour. The volume of gas desorbed was established using the loop-volume calibration of the apparatus. The volume of hydrogen desorbed corresponded to the peak area displayed.

3. Results and Discussion

The growth process of CNTs was found to be strongly dependent on the catalyst-support interaction [9]. In a similar work, it was reported that supports play an effective role in exposing the active sites on the catalyst metals for CNTs production. The metals also have some degree of affinity to the support [10].

The SEM images of the CNTs synthesized over different metal supported catalysts at specific reaction temperatures are shown in Figures 1 and 2. All of the as-grown CNTs were examined under the scanning electron microscope without any purification. Results obtained showed that the as-grown CNTs floss were in various forms and sizes. From Figures 1 (a)-(c), the growth densities of CNTs over monometallic alumina-supported catalyst were less dense as compared with bimetallic and trimetallic alumina-supported catalyst, Figures 1 (d)-(e). In the later cases, the Fe/Co- Al_2O_3 and Fe/Co/Ni- Al_2O_3 showed excellent activity in growing aligned CNTs floss. The density of the aligned CNTs was extremely high almost covering the surface of the supported catalyst.

Similar patterns in the growth of the CNTs were observed for CNTs floss grown over molecular sieve-supported catalysts. The as-grown CNTs were less dense and randomly grown on the surface of the MS support (Figures 2 (a)-(d)). It can also be observed that the CNTs floss grown over the MS-supported catalysts, showed white spots at most of their tubular tips, Figure 3. These white spots originated from the metal cluster [10]. This indicated that the CNTs were grown by the 'tip growth model' with weak catalyst-support interaction [11]. The necessary carbon feed stock supplied from the catalytic decomposition of acetylene dissolved in metallic species to form metastable metal carbide. This metastable metal carbide will dissolve more carbon resulting in an oversaturation of carbon. Subsequently, graphic-carbons will precipate to form CNTs by keeping metallic cluster at the tip of the tubes.
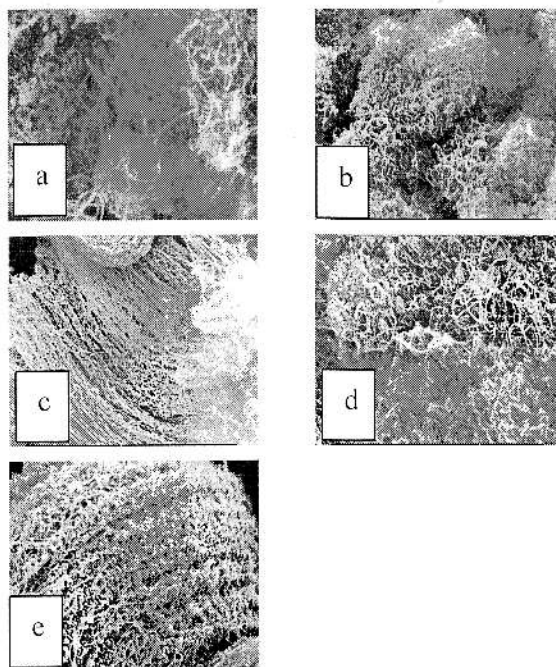
Fig. 1. CNTs grown over alumina supported catalysts (a) Fe-Al_2O_3; (b) Co- Al_2O_3;

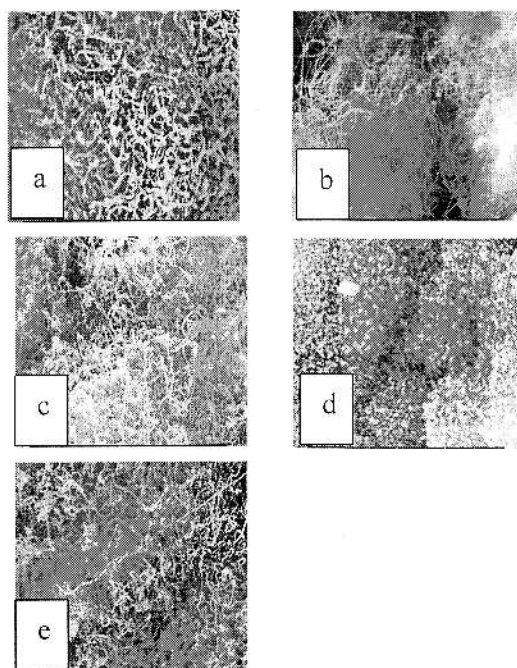(c) Fe/Co- Al_2O_3; (d) Ni- Al_2O_3; (e) Fe/Co/Ni- Al_2O_3

Fig. 1. CNTs grown over MS supported catalysts (a) Fe-MS; (b) Co-MS; (c) Fe/Co-MS;

(d) Ni- MS; (e) Fe/Co/Ni- MS

In the case of the CNTs grown over alumina-supported catalysts, the tips of the CNTs floss possess less visible white spots. The CNTs were probably grown by 'base growth model' in which the catalysts have a strong catalyst-support interaction, which enhanced the growth of aligned CNTs.
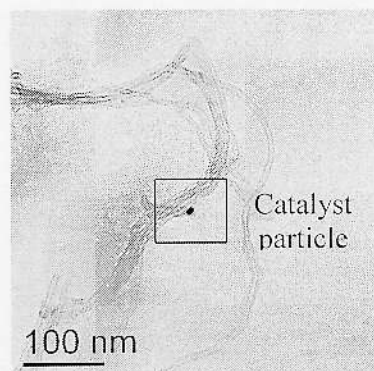

Fig. 3. TEM of as-grown CNTs

Table 1

Analytical and desorption data of as-synthesized CNTs grown over alumina (Al_2O_3)-supported catalysts.

Alumina-supported catalysts	[a] Carbon Composition (%)	[b] Surface Area (m^2/g)	[c] Volume of H_2 gas Desorped (mL/g)
Ni-Al_2O_3	30	73	94
Fe-Al_2O_3	39	90	43
Co-Al_2O_3	41	78	19
Fe/Co-Al_2O_3	64	83	184
Fe/Co/Ni-Al_2O_3	53	68	65

Table 2

Analytical and desorption data of as-synthesized CNTs grown over molecular sieve

(MS) - supported catalysts.

MS-supported catalysts	[a] Carbon Composition (%)	[b] Surface Area (m^2/g)	[c] Volume of H_2 gas Desorped (mL/g)
Ni-MS	59	12	41
Fe-MS	45	22	23
Co-MS	40	16	25
Fe/Co-MS	45	63	71
Fe/Co/Ni-MS	42	63	65

[a] : EDAX, [b] : NA (Nitrogen Adsorption), [c] : H_2-TPD

The EDAX data from Tables 1 and 2 indicated that all the supported catalysts were successful in producing CNTs. The key to obtaining high yields of pure CNTs is achieving hydrocarbon decomposition on catalyst sites alone and avoiding spontaneous pyrolysis [12]. Alumina materials were reported to be a good support owing to their strong metal-support interaction, which allows high metal dispersion and, thus, a high density of catalytic sites. Such interactions prevent metal species from aggregating and forming unwanted large clusters that lead to graphite particles or defective CNTs. These facts explained that all the supported catalysts were effective catalysts for CNTs production, with Fe/Co on alumina supported catalyst giving the best yield of CNTs.

The BET surface area in Tables 1 and 2 showed that alumina supported catalysts gave larger surface area than MS supported catalysts. The CNTs grown over bimetallic and trimetallic supported on both alumina and molecular sieve gave the highest volume of hydrogen desorped relative to the CNTs grown over monometallic supported catalysts. This correlation between surface area and sorption properties is in agreement with the work done by Zuttel *et al*, who found that reversible hydrogen sorption process takes place via physisorption in nanostructured carbon and the amount of hydrogen

adsorbed was found to be proportional to the BET surface area of the nanostructured carbon [13-15].

From these sorption studies, we have come to a hypothetical statement that the hydrogen molecules is probably bonded physically onto the. aligned and orderly arranged CNTs structures, retained and sufficiently released when heat is introduced to the hydrogen storage materials.

Hence it may be possible to yield better quality and quantity of CNTs using alumina supported catalysts as good adsorbent material for hydrogen storage.

4. Conclusion

Carbon nanotubes (CNTs) were successfully grown over alumina and molecular sieve supported catalysts by decomposition of C_2H_2. It was observed that the yield of CNTs highly depended upon the catalyst-support interaction. However, the use of bimetallic and trimetallic supported catalysts gave the best quality yield with high density of CNTs. Fe/Co on alumina recorded the highest volume of desorped hydrogen making it a potential candidate as hydrogen storage material. Based upon these preliminary findings, a more conclusive studies at different temperatures and pressures of adsorption and desorption will be carried out to yield more significant results.

Acknowledgement

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