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Hydrogen Sorption Capacity of as-grown Multiwalled Nanotubes (MWNTs)

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In this work, Multiwalled Carbon Nanotubes (MWNTs) have been synthesized as hydrogen storage material for use in a proton exchange membrane fuel cell system. The carbon source used is a cheap feedstock (acetylene) mixed with an inert gas, nitrogen. The production of MWNTs was carried out in a furnace chamber at atmospheric pressure and has relatively low energy requirements. The gas feedstock, acetylene, was passed over the catalysts at temperatures between 600-800°C and carbon nanotubes were collected as black powder on the catalysts. The MWNTs produced were then characterized for their purity through FE-SEM and TEM. The as-grown MWNTs were found to be 90 % high in purity.

The MWNTs produced have 11 concentric walls with diameters between 4 and 11.6 nm with the distance between layers being 0.345 nm corresponding to the lattice layers of graphite. As a result, better hydrogen adsorption characteristic was observed between the graphitic layers of the MWNTs. Due to the high purity of the as-grown MWNTs, no complex purification process will be required. The as grown MWNTs showed high volume of adsorption at 77K and room temperatures and this indicated that hydrogen gas was sufficiently adsorbed in the MWNTs via physisorption

1. Introduction

The discovery of carbon nanotubes (CNT) by Sumio Iijima [1] in 1991 has attracted many researchers to study and explore the material. The unique characteristics that carbon nanotubes possess include excellent properties for energy production and hydrogen storage. Researchers found that carbon nanotubes have the potential to adsorb hydrogen due to their low density, high strength, and hydrogen adsorption characteristics.

Among methodsof storing hydrogen, physisorption method is said to be the most promising for fuel cell powered vehicle [2, 3]. The storage of hydrogen can rely on physisorption because the adsorbed gas can be released (the process is reversible) [4]. However, a detailed understanding of the hydrogen storage mechanism and the effect of materials processing on this mechanism is still needed. Researchers have studied different mechanisms that affect the gas adsorption on CNT, such as CNT geometries [5,6], surface area of CNT [7], methods to open the tubes [8,9] and the purification of the adsorbent [10].

In spite of various model calculations [2,11-13] that have been carried out using a variety of computational techniques, the actual mechanism of the hydrogen storage in CNT is still unknown [14]. Although interest in applications of artificial neural network (ANN) in chemistry has increased tremendously [15], it has not been employed comprehensively in hydrogen desorption studies in CNT.

2. Experimental/Materials and methods

2.1 Materials

As synthesized MWNT samples for this study was synthesized by catalytic decomposition (CCVD) of acetylene over supported metal oxide catalyst. Two types of supports were used i.e. alumina and molecular sieve (MS) supports. Details of the synthesis are described elsewhere [3]. The commercial MWNT samples were purchased from Sun Nanotech Co. Ltd. (SUNNANO) with a purity > 80 %, < 10 % amorphous carbon, 1.61% Fe, 1.04 % Ni, 0.115% Al and 0.55% Si as specified by the manufacturer. The commercial SWNT was procured from Shenzhen Nanotech Port Co., China with a purity of around 50~80 %, < 5% of amorphous carbon and 1 ~ 2 wt % of ash.

2.2 Temperature-Programmed Desorption Analysis (TPD) Analysis

The hydrogen sorption properties of the nanotube samples were investigated by means of a temperature-programmed desorption (TPD) using a Micromeritics Pulse Chemisorbed 2705. Prior to hydrogen saturation, sample pretreatment was carried out by heating the samples in vacuum at 350 °C for 3 hours at ambient pressure so as to remove contaminants and moisture from the sample. Saturation was carried out for 1 hour at three different temperatures i.e. room temperature, 77K and 70 °C while hydrogen desorption was carried out at fuel cell temperature, 70 °C. 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.

2.3 Single Point Surface Area (BET, Brunauer-Emmett-Teller surface area)

The single point surface area was measured with a Micromeritics Pulse Chemisorbed 2705, where a constant flow (16-18 cm^3 N_2 min^{-1}) of nitrogen gas was adsorbed at liquid nitrogen temperature, 77 K. Single point measurements were accomplished using a mixture of 30 % N_2 / 70 % He gas. The samples were out-gassed using nitrogen gas for 1½ hour at 350 °C. The surface area measurement was carried out in triplicate and an average 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 (surface area) = Peak Area (m^2) / sample weight (g)

3. Results and discussion

Sorption characteristics of carbon nanotubes

Table 1 *
Summary of samples and experimental conditions of the sorption study

Sample	BET Surface area (m^2/g)	Saturation temperature (°C)	H_2 desorped per gram (ml/g)
C-MWNT	119.56	Room Temperature	17.45
		Liq. N_2 (77K)	19.55
		70	19.05
C-SWNT	204.36	Room Temperature	16.97
		Liq. N_2 (77K)	13.66
		70	13.82
AS-MWNT1 (Alumina support)	119.79	Room Temperature	17.71
		Liq. N_2 (77K)	16.02
		70	19.50
AS-MWNT2 MS support	103.02	Room Temperature	17.12
		Liq. N_2 (77K)	25.58
		70	16.43

** The saturation time was fixed at 1 hour under ambient pressure. Desorption was carried out at 70 °C.*
MWNT – multi walled carbon nanotube; SWNT – single walled carbon nanotube; CNT – carbon nanotube; MS – molecular sieve

Table 1 gives a summary of the sample and experimental conditions of the sorption study. In terms of BET surface area, the C-SWNT exhibited he highest surface area compared to the other samples.

The data indicated that the amount of hydrogen desorped depends on the type of CNTs and the saturation temperature. All samples showed similar amount of hydrogen desorped when saturation was performed at room temperature. The AS-MWNT2 showed the highest volume of hydrogen desorped when saturation was performed at liquid nitrogen temperature (77 K). At a saturation temperature of 70°C, the C-SWNT showed lowest amount of hydrogen desorped. However, both the C-MWNT and AS-MWNT1 showed relatively high volume of hydrogen desorped

at this saturation temperature. It is also interesting to note that the C-SWNT samples showed relatively low volume of hydrogen desorped under the conditions studied.

It is claimed that MWNTs synthesized by catalytic decomposition of acetylene is a promising adsorbent for hydrogen [4]. The high volume of hydrogen desorped by AS-CNT2 at is supported by reports that at a saturation temperature of 77 K the amount of adsorbed hydrogen is about one order of magnitude higher than saturation at 300 K (room temperature) [5]. The low temperature reinforces the effect of gas-adsorbent attractive interaction. The high amount of hydrogen desorped by the AS-CNT2 samples in this study when hydrogen saturation was at 77 K indicates that reversible physisorption takes place between hydrogen and carbon [6], [7],[8].

Studies has indicated that hydrogen gas was efficiently adsorbed in multi walled carbon nanotubes materials [9] at room temperature and that hydrogen storage in CNTs at room temperature is most likely to be physisorption rather than chemisorption, since both C and H are stable under that condition [10], [11]. This supports the significant volume of hydrogen desorped by the samples when saturation was carried out at room temperature. Several authors have postulated that the interplanar spacing between the adjacent platelets in MWNTs can accommodate a considerable amount of molecular hydrogen, and the adsorption mechanism was explained by chemisorption, physisorption, and a combination of these two processes. Additionallly, the hydrogen storage capacity should increase with their surface area, whereas in the present study they are inversely proportional to the specific surface area. This is agreeable with suggestions by several authors that hydrogen not only adsorbed on the surface, but also stored in the interplanar spacing between the adjacent platelets in MWNTs.

The as synthesized samples used in this study were prepared using supported metal oxide catalyst. Two types of support were used i.e. alumina and molecular sieve supports. The AS-MWNT2 gave better hydrogen desorption (25.58 ml/g) when hydrogen was adsorbed at 77 K than the AS- CNT1 samples. SEM micrographs of the samples showed that that the AS-MWNT2 contain a larger amount of metallic cluster at the tip of the carbon nanotubes than the AS-CNT1. The presence of these residual catalyst might enhanced the adsorption and desorption properties of the nanotubes. It has been reported [10] that the metal content in CNTs, such as Fe, may have a significant influence on the storage and release of hydrogen, even with small amount of metal. The hydrogen storage on multiwalled CNTs has also been shown to be dependent on the degree of catalyst removal whereby, the residual catalyst participates in the hydrogen adsorption [12]. Since the catalyst used in the synthesis is not completely removed as evidenced from EDAX analysis, this supports the higher amount of hydrogen desorped in the two AS-MWNT2 samples.

It is observed that the narrow pore size distribution of SWNT make it favorable as high adsorptive material properties [9]. Hydrogen can be stored in bundles of SWNTs, space between SWNTs separating the intertube distances. Physisorption of hydrogen to the SWNT is expected because chemisorption to SWNT surfaces appears to be stable at least up to T = 1000 K. Furthermore, physisorbed H_2 molecules preferentially sit outside the SWNTs.[13]. However,the C-SWNT samples investigated showed relatively low volume of hydrogen desorped under the conditions studied. This can be explained based on the low purity of the samples used i.e. 50~80 %. Studies have shown that high purity SWNT samples can store significant amount of H_2 near liquid N_2 temperature [14]. Hence, the low amount of hydrogen desorped can be attributed partly to the low purity of the samples.

4. Conclusion

The study indicated that the amount of H_2 desorbed is affected by the adsorption temperature and the type of carbon nanotubes. In general, the commercial MWNT sample showed relatively higher amount of hydrogen desorbed per gram sample under the adsorption temperatures studied compared to the commercial SWNT and the as synthesized CNT's. However, at the adsorption temperature of 77 K, the as synthesized CNT showed the highest amount of hydrogen desorped. The studies also indicated that there is no direct correlation between the amount of hydrogen desorped and surface area of the CNT's under the conditions studied.

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