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SYNTHESES, CHARACTERIZATIONS AND TESTINGS OF CARBON NANOFIBRE FOR HYDROGEN ADSORPTION STUDIES

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ABSTRACT

Renewable energy (RE) has been declared as the fifth fuel of Malaysia in addition to oil, gas, coal and hydropower. One of REs which is hydrogen has become an alternative fuel for transportation to replace petroleum. For sufficient hydrogen storage, the system requires an inexpensive, safe, low weight tank, comparable in to a gasoline tank with capability of quick loading and unloading hydrogen fuel. Carbon nanomaterials have been nominated as one of the best medium to store hydrogen due to its light weight, low cost production depending upon types of synthesis methods, non-toxic and can be generated with improvement in its storage capacity. The research work focuses on the development of carbon nanofibers by using chemical vapor deposition method. The development of catalysts such as iron (III) oxide and nickel (II) oxide for the synthesis of carbon nanofibers (CNFs) has also been investigated. The capacity of the developed materials in hydrogen adsorption is tested at 298K and the pressure is up to 100 bar using gravimetric measurement technique. Sample imaging observations using field emission electron microscopy (FESEM) and transmission electron microscopy (TEM) indicate that the synthesized CNFs have both platelet and herringbone structure with little carbon nanotubes (CNTs). Iron-based catalyst CNF (Fe-C) samples have diameter size of 170 nm while nickel-based catalyst CNF (Ni-C) has diameter size of 200 nm. Specific BET surface area of Fe-C and Ni-C are 92.34 m²/g and 45.96 m²/g, respectively. Both analysis which are energy-dispersive X-ray (EDX) and thermogravimetric proved that purity of Fe-C is between 88% to 95% while purity of Ni-C is ranges from 95% to 97%. For iron-based catalyst CNF, the highest uptake is 0.46 wt % at 70 bar and for nickel-based catalyst CNF, the highest uptake is 1.76 wt % at 70 bar.

Keywords: Carbon nanofiber, hydrogen adsorption, gravimetric measurement

1. INTRODUCTION

Oil and gas are the resources of energy to supply the industrial sectors, transportation and electricity demand in Malaysia. These natural resources have contributed towards Malaysian development in their own ways. Based on Malaysia External Trade Statistics reported in July 2008, the total exports of crude petroleum, natural gas and refined petroleum products contributes 17.18% of Malaysia total exports or RM114.01 billion (Matrade, 2008). However, the extensive utilization creates problems such as air pollution and global warming. According to PETRONAS, Malaysia's crude oil reserves of 5.25 billion barrels will last for another 20 years at current rates of extraction (Ariff, 2007). It is very crucial to replace oil and gas with renewable energy sources such as solar, wind biomass, biodiesel, biogas and hydrogen in the future. Hydrogen is the most abundant of all elements in the universe and it is the lightest gas amongst all which present as free element with a capacity of less than 1 ppm by volume. Unlike coal, solar energy, biomass energy, wind energy, nuclear energy and geothermal energy, hydrogen is not a source of energy but rather a fuel (Tarara, 2001). Currently, global hydrogen production is 48% from natural gas, 30% from oil, 18% from coal and 4% from water electrolysis (National hydrogen association, 2009). There are two main uses of hydrogen that are fuel for transportation and for storing excess electricity. For sufficient hydrogen storage, the system requires an inexpensive, safe, low weight tank, comparable in to a gasoline tank with capability of quick loading and unloading hydrogen fuel. Hence, this research taking part on the development of hydrogen storage by developing the material for hydrogen storage which is carbon nanofiber (CNF) with iron (III) oxide, (Fe_2O_3) and nickel oxide, (NiO) as catalysts by using chemical vapour deposition method. The ability of CNF to adsorb hydrogen was also been investigated.

2. METHODOLOGY

2.1 Synthesis of catalyst

Fe_2O_3 catalyst was prepared by dissolving 7 g amount of iron (III) nitrate nonahydrate, $Fe(NO_3)_3.9H_2O$ (purity 99.99+%, CAS number 7782-61-8, manufactured by Fisher Scientific) into 100 cm^3 of distilled water. The solution was stirred at room temperature until all the transition metal salts had completely dissolved and were precipitated in 2 M ammonia solution. The dark brown precipitate was filtered and washed for several times with distilled water at room temperature until it became nitrate-free. The precipitate of hydroxides was dried over night at a temperature of 80°C in oven and was calcined at 400°C in the furnace oven at atmospheric pressure for 4 hours. After calcinations, the developed Fe_2O_3 was ground into fine powder using mortar and pestle. For the synthesis of nickel (II) oxide (NiO), 7 g of nickel nitrate hexahydrate, $Ni(NO_3)_2.6H_2O$ (purity 99.999%, CAS number 13478-00-7, and manufactured by Sigma Aldrich) was dissolved into 100 cm^3 of distilled water before it is mixed with 2 M of ammonia solution. However, unlike iron solution, the nickel salt solution was stirred at temperature of 250°C using magnetic stirrer until paste was formed. Later, the precursor which was in the form of thick green paste was dried overnight at temperature of 400°C. It was then calcined at a specific temperature for 4 hours before it was ground into fine powder until no lumps were observed.

2.2 Synthesis of graphitic nanofiber CNF

The quartz boat was filled with 0.05 g of catalyst and was placed in a 45-mm inner diameter and 1200-mm length of tube furnace. There were three gas lines (H_2, N_2 and C_2H_4) controlled by the mass flow controller. Initially, the system was filled with N_2 at 1000 ml/min. At equilibrium temperature, the reaction began by flowing C_2H_4/H_2 mixture into the reactor for specific period of time. Table I shows parameter value in developing the CNF.

Table 1 Parameter in synthesizing CNF

Catalyst	Calcination time (hours)	Calcination temp (^oC)	C_2H_4/H_2 flowrate (ml/min)
Fe_2O_3	4	700	50/450
NiO	2	600	240/60

2.3 Hydrogen adsorption

The hydrogen adsorption measurement was carried out using magnetic suspension balance (MSB). It was conducted to measure hydrogen adsorption at a high pressure of 100 bar or more in room temperature

3. RESULTS AND DISSCUSSION

3.1 Catalyst Study

The developed catalyst was characterized using surface area analyzer to determine its pore size distribution and specific BET surface area. Figure 1 and 2 below shows pore volume (cm^3/g.Å) versus the pore width (Å) of Fe_2O_3 and NiO. For Fe_2O_3, pore volume is highly dominated by pore width of 273 Å which covers pore volume of 0.0013 cm^3/g.Å. It shows that the Fe_2O_3 catalyst is mesoporosity adsorbent with size of 27.3 nm. BET surface area of Fe_2O_3 catalyst is 36.56 m²/g. The average yield of the Fe_2O_3 and NiO is 37.43% and 82.37%, respectively.Pore volume of NiO is highly dominated by pore width of 83.75 Å which covers pore volume of 0.00064 cm^3/g.Å. It shows that the NiO catalyst is mesoporosity adsorbent with size of 8.375 nm. BET surface area of NiO catalyst is 32.78 m²/g. The reaction yield of the developed catalyst was calculated based on the number of mol of the catalyst metal using the following formula:

$$\text{Catalyst yield} = \frac{\text{mol of product}}{\text{mol of limiting reactant}} \times 100\%$$

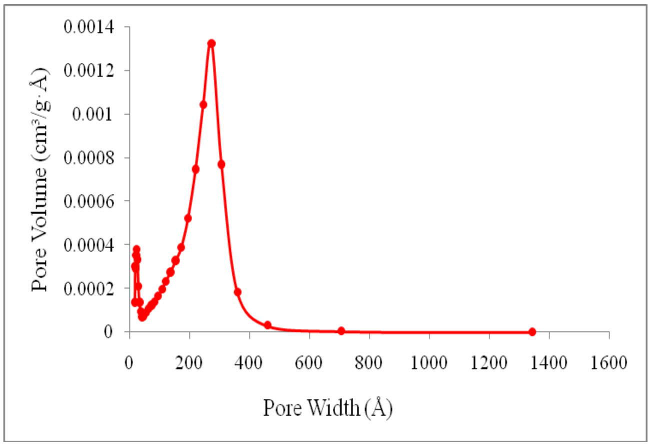


Figure 1 Pore distribution of Fe_2O_3 catalyst.

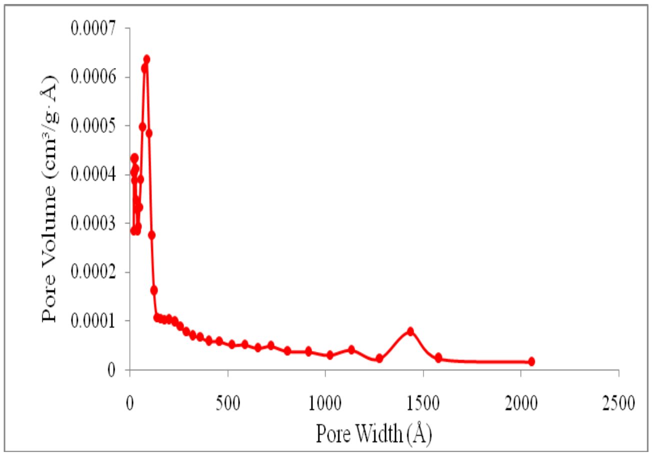


Figure 2 Pore distribution of NiO catalyst.

3.2 Carbon Nanofiber (CNF) study

BET surface area of iron-based catalyst CNF (Fe-C) and nickel-based catalyst CNF (Ni-C) were found to be 92.34 m²/g and 45.96 m²/g, respectively. BET surface area of the latter is low since some of the developed in CNF was capsulated by nickel catalyst. Due to the capsulation, nitrogen could not being adsorbed into the pores which led to lower surface area. Both of Fe-C and Ni-C were highly dominated by pore width 2.2 nm. The size is larger than what recommended by Rzepka et al. (Rzepka et al., 2005) that is 0.7 nm for optimum pore size for hydrogen adsorption.

For TGA analysis, the sample was running under the air at initial temperature of 50^{o}C. Then the sample was being heated up to 1100^{o}C with heating rate of 10^{o}C/min. It can be seen from the derivative graph that at initial stage which between 50^{o}C to 510^{o}C, adsorption and desorption happened. The weight percentage of Fe-C fluctuates from initial to 50 minutes due to oxidation of iron catalyst. The desorption starts at 510°C to 740°C. The total weight loss from sample was about 88.03% indicates the purity of CNF while the balance is weight percent of metal which is 11.97% of Fe in CNF.

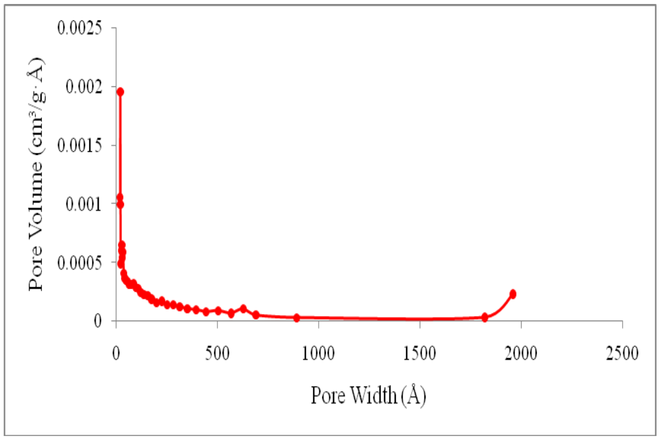


Figure 3 Pore distribution of FeC

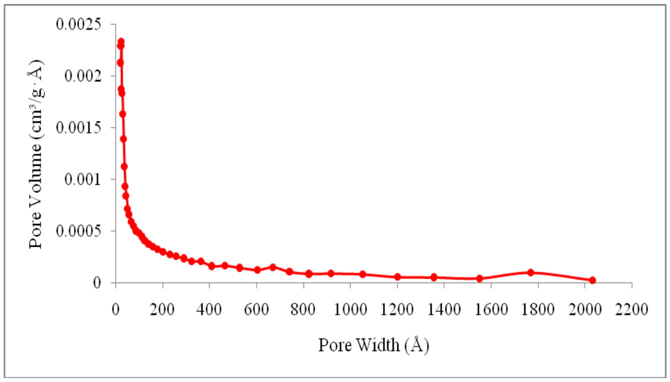


Figure 4 Pore distribution of NiC

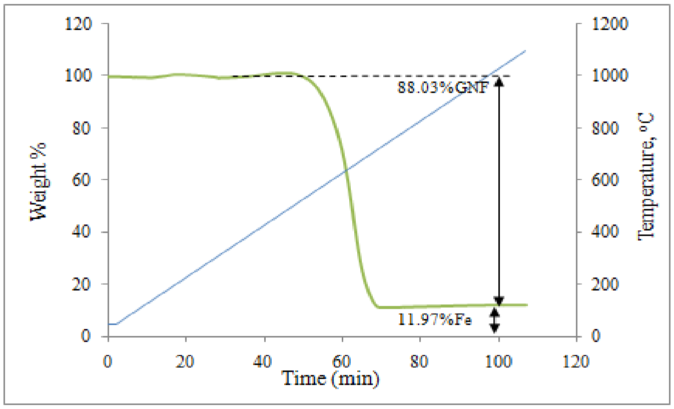


Figure 5 TGA analysis of FeC.

Program settings of TGA for Ni-C are similar as Fe-C where the initial temperature is 50°C. Desorption starts at 450°C and ends at 650°C. The total weight loss from sample was about 97.2% indicates the purity of CNF while the balance is weight percent of metal which is 2.8% of Ni in CNF. Ni-C has 9.17% higher purity compared to iron-based catalyst Fe-C.

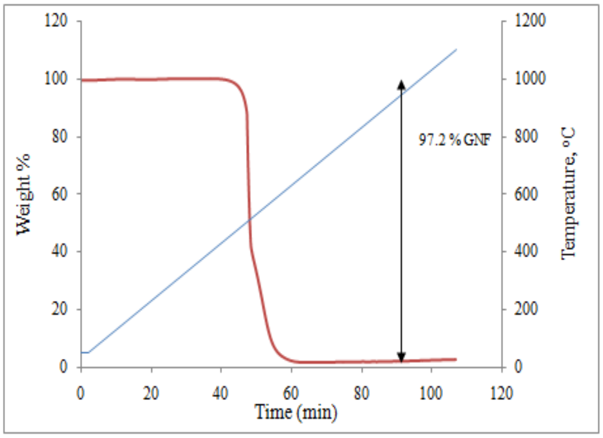


Figure 6 TGA analysis of NiC

Based on the FESEM imaging, it can be noticed Fe-C and Ni-C has herringbone structure as in Figure 7(a) and (b), respectively. Meanwhile as in Figure 8, it also can be observed that Ni-C has platelet structure. It means that Ni-C has mixture of herringbone as well as platelet structure. NiC has diameter size distribution of approximately 200 nm while for Fe-C the diameter size is 170 nm.

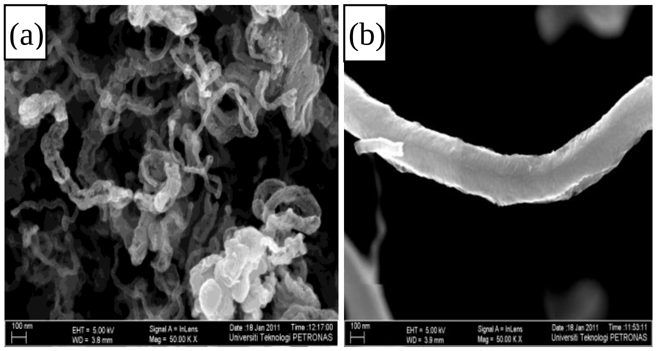


Figure 7 FESEM imaging shows (a) Fe-C at magnification of 50kX; and (b) Ni-C at magnification of 50kX

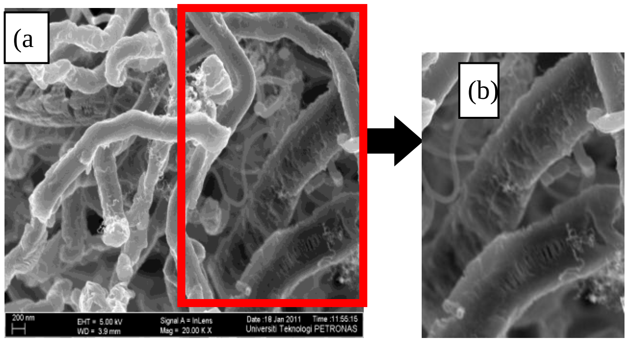


Figure 8 FESEM imaging of platelet structure of NG.

Fig. 9(a) and 9(b) shows that Fe-C and Ni-C were fully developed since long strand of nanofibers can be observed. This proved that the reaction conditions being set are sufficient enough to enable complete CNF formation.

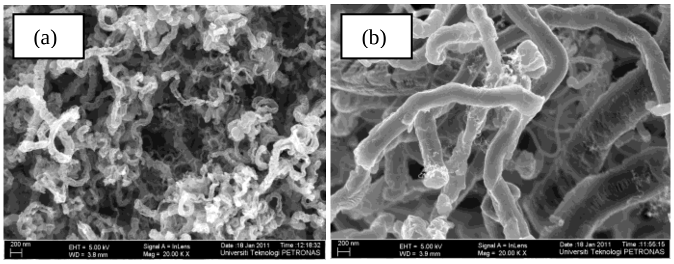


Figure 9 (a) Fe-C at magnification of 20kX; and (b) Ni-C at magnification of 20kX.

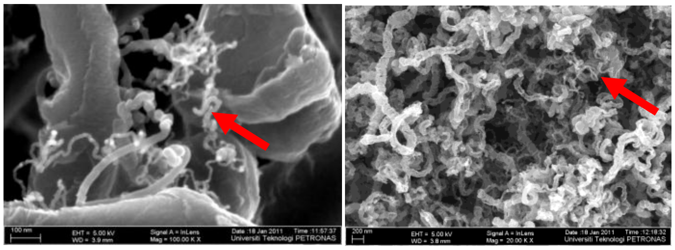
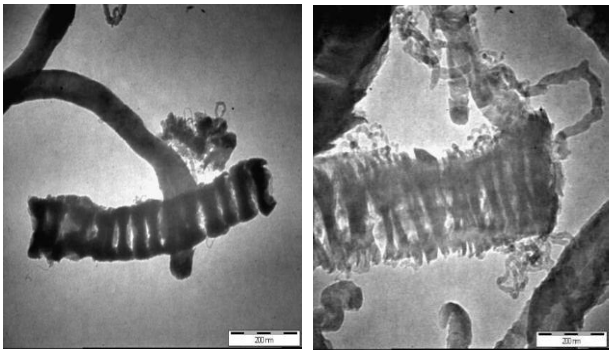


Figure 10 FESEM imaging shows (a) Ni-C; and (b) Fe-C at magnification of 100kX.

Throughout FESEM imaging, it can be observed that there were developments of carbon nanotubes in the sample. Existence of carbon nanotubes is depending upon experimental conditions. CNT images also could be clearly detected through TEM imaging which is in the next section. EDX analysis shows that iron-based catalyst CNF composed of 95.85% carbon, 3.38% oxygen and 0.76% iron while for nickel-based catalyst CNF composed of 94.46% carbon, 5.19% of oxygen and 0.34% nickel. EDX detects additional one element which is oxygen. Unconverted Fe_2O_3 and NiO catalyst led to oxygen production. The purity of CNF detected by EDX is comparable to TGA results where the purity of Fe-C is between 88% to 95% while purity of Ni-C ranges from 95% to 97%, respectively. The bright field TEM images reveal the internal carbon structure of CNF as herringbone and platelet. The herringbone structure consists of graphene planes at the angle of 45^{o} to the carbon filament axis while platelet structure consist of graphene planes is perpendicular to the carbon filament axis. Figure 11 proved that nickel-based catalyst GNF has herringbone structure and there is formation of corrugated on the surface that is known as corrugated carbon nanofibers (C-CNFs). The growth mechanism of C-CNF has been described in several literatures (Koizumi et al., 2006; Wang et al., 2006). Basically, when the surfaces of catalyst particles absorb carbon source gas, they maintain the state of absorption until the particles become saturated with the gases. As a result, the particles burst out all the gases uncontrollably and produce high density carbon disc (refer to Figure 11 and 12). Later, since all the carbons have been discharged, the absorption takes place again. At this time while waiting for the catalyst to become saturated again, low density of carbon discs are grown before the catalyst particles burst out the carbon to form high density carbon discs. These processes are repeated for number of times. Thus, the nanofiber formed a corrugated shape as seen in Figure 11.



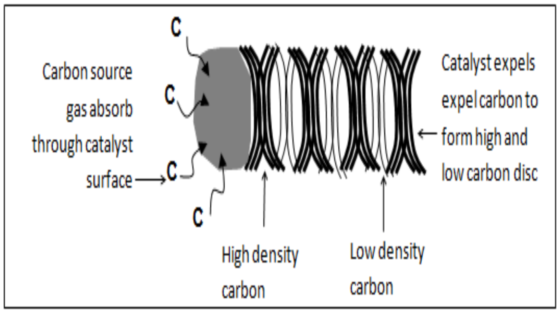


Figure 12 Formation of corrugated shape of CNF

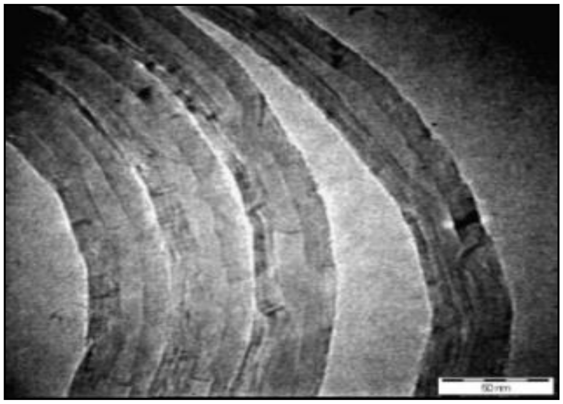


Figure 13 Hollow core in Fe-C.

Some CNFs has hollow core as in Figure 13. This is due to different particle size of catalyst which resulted in different inner diameter of CNFs. Figure 14 shows where nickel-based catalyst CNF developed on the surface of catalyst caused the catalyst particle remains trapped in the CNF. CNFs will be continuously formed a long straight nanofibers if the precipitation of carbon from all faces is identical (Rodriguez et al., 1995). Unfortunately, any perturbation in this behavior will results in abnormalities of fiber conformation. Thus, coiled and helical (or spiral) perturbations are likely to form. The coiled structure of CNF as in Figure 15 and 16 proved that carbon nanotubes developed in nickel-based catalyst CNF.

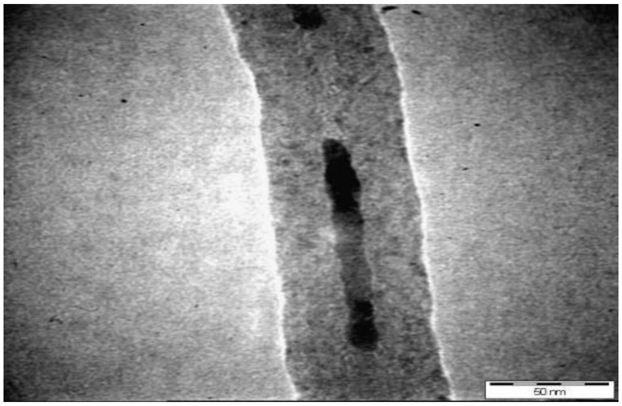


Figure 14 A TEM image of a catalyst confined in Ni-C

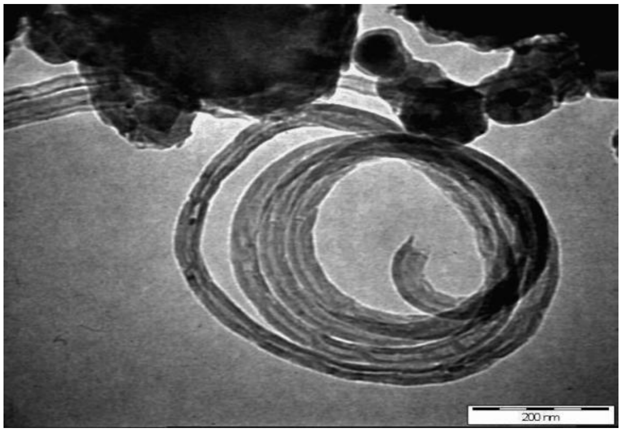


Figure 15 Coiled structure of Fe-C

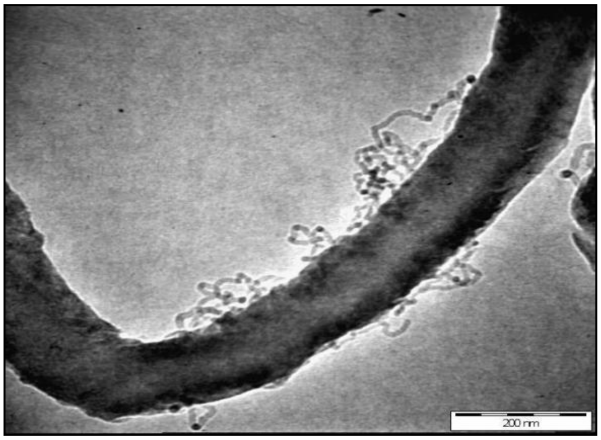


Figure 16 CNT images in Ni-C

3.3 Hydrogen adsorption

The hydrogen adsorption measurement was carried out using magnetic suspension balance (MSB) up tp 100 bars at 298 K. Ni-C achieved 1.3% higher hydrogen uptake compared to Fe-C. Highest hydrogen uptake by Fe-C and NiC occurred at 70 bar which equals to 0.46 wt% and 1.76 wt%, respectively.

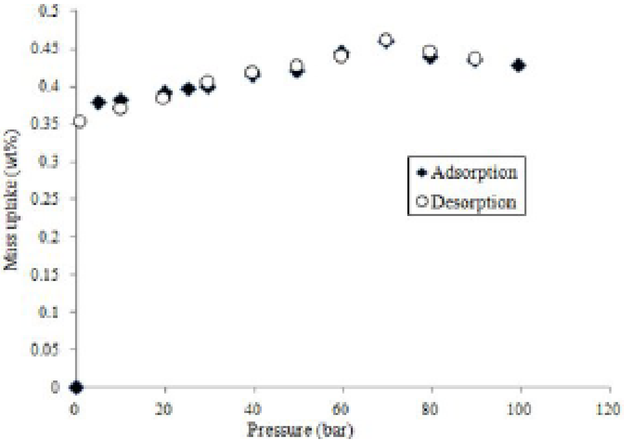


Figure 17 Hydrogen adsorption-desorption hysteresis of Fe-C at 298K and 100 bar

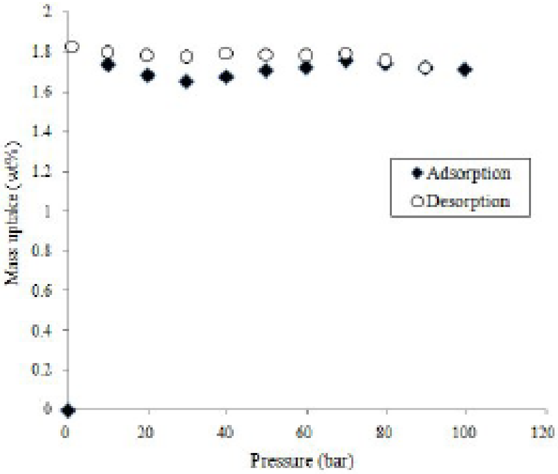


Figure 18 Hydrogen adsorption-desorption hysteresis of Ni-C at 298K and 100 bar

Based on the mass uptake, Fe-C achieved lower hydrogen uptake, although its surface area is higher than Ni-C's. It is thought that the higher the surface area, the higher the amount of hydrogen could be adsorbed since there would be more adsorption sites and higher interaction between hydrogen molecules and the surface of the carbon (Sufian, 2010). However, hydrogen adsorption does not follow the predicted behavior as some nanopores are unseen by nitrogen molecules during surface area measurement (Proirier, et. al. 2001). Thus, surface area (measured using nitrogen) is not one of the factors that affect the hydrogen uptake.

4. CONCLUSION

The research work has proved that Fe-C and Ni-C have effectively act as adsorbents for hydrogen adsorption. The highest adsorption uptake achieved by both adsorbents is at 70 bar with 0.46 wt% and 1.76 wt% for Fe-C and Ni-C, respectively. Specific BET surface area does not influence the amount of hydrogen adsorbed as Ni-C which has lower surface area than that of Fe-C exhibits better hydrogen uptake.

REFERENCES

Ariff, M. 2007. Need for new resources, The Star.

Koizumi, N., Minorikawa, Y., Yakabe, H., Kimura, H., Kurosu, T., Iida, M. 2006. Finding growth regions for carbon nanofibers and tubes under different growth conditions using simplified hot filament chemical vapor deposition, apanese Journal of Applied Physics 45 (8A): 6517-6523.

MATRADE, Malaysia External Trade Statistics, Department of Statistics Malaysia, 2011.

National hydrogen association, 2009, Global hydrogen production.

Proirier, E., Chahine, R., Bose, T.K. 2001. Hydrogen adsorption in carbon nanostructures, International Journal of Hydrogen Energy 26(8): 831-835.

Rodriguez, N.M., Chambers, A., Baker, R.T.K. 1995. Catalytic engineering of carbon nanostructures, Langmuir 11: 3862-3866.

Sufian, S. 2010. Synthesis, characterization and testing of graphitic nanofiber for hydrogen adsorption study, Universiti Teknologi PETRONAS, Malaysia.

Tarara, R. 2001. Hydrogen: A key component of energy in the future.