SURFACE MODIFICATION OF CARBON MATERIALS FOR HYDROGEN STORAGE

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ABSTRACT

Hydrogen is a great energy carrier for both mobile and stationary power generation. However, the availability of hydrogen as a power source is hindered due to lack of cost, effectiveness and safe storage solutions. Thus, one of the key areas for commercialization of hydrogen-powered vehicles is the development of safe methods for hydrogen storage. Gas-on-solid adsorption presents itself as the safest method for hydrogen storage. It is a more energy efficient method than either chemical or metal hydrides as well as compressed gas storage. Much work has been done to study the hydrogen storage properties of high surface area carbon materials. In this work, the effect of pretreatment on activated carbons and graphite was studied. Both carbon materials were treated with 4 M hydrochloric acid and heat at 600 °C in an inert atmosphere condition respectively. The surface area and morphology of the treated samples were thoroughly investigated using nitrogen adsorption and scanning electron microscopy techniques. It was found that acid treatment increases the surface area of activated carbon due to the opening up of the internal surface area and widening of the pores. Graphite however, displayed a smaller surface area after acid treatment as a result of the disruption of the ordered lattice layer. An increase in the surface area was also observed for both carbon materials after heat treatment thereby enhancing their adsorption properties.

Keywords: pretreatment, activated carbon, graphite, surface area, adsorption

1. INTRODUCTION

Hydrogen will play a decisive role in the future energy system as fossil fuels become scarce, expensive and become unsuitable because of ecological reasons. Thus, an efficient and lightweight hydrogen storage method may find its use in systems such as fuel cell, which enables the development of zero-emission vehicles.

Hydrogen contains more chemical energy per unit weight than any other hydrocarbon fuels and it is also the lightest existing substance. Burning hydrogen in fuel cells is the most promising and clean way of releasing energy. The key technology to the development of hydrogen vehicles is therefore hydrogen storage [1, 2].

Hydrogen is very volatile and is difficult to store. Hydrogen can be stored in several different forms; gas, cryogenic liquid or adsorbed gas in solid materials. Due to its low

energy density per volume, hydrogen is normally stored under high pressure and low temperature. High pressures of ~ 700 bar and low temperatures of ~ 20K are prerequisite for reasonable hydrogen storage [3]. A promising method to store hydrogen safely is by gas-on-solid adsorption.

With the discovery of novel carbon nanotubes in the 1990s, efforts have been intensified towards the study of carbon nanostructures as hydrogen storage materials. Hydrogen storage in carbon-based materials offers significant advantages. The micropores of a porous material like carbon (~ 2 nm) have the potential to adsorbed gases onto the solid surfaces [4]. Some of these carbon materials have ordered structures such as fullerenes, carbon nanotubes and nanofibres as well as graphites. Carbon nanotubes can be described as a half fullerene. Single-walled nanotube are structures with only one graphite layer while that consisting of multiple concentric graphite layers are multi-walled nanotubes [5,6]. The cylindrical structure of carbon nanotubes and fullerenes increases the adsorption potential in the tube core leading to capillary forces and enhanced storage capacity [7]. Numerous studies have also been conducted on the feasibility of using carbon nanostructures as hydrogen storage materials. Table 1 reviews some of the cited results [12]:

Table 1. Some previous research on carbon nanotubes

	Adsorbent type	Hydrogen storage (wt%)	Temperature (K)	Pressure (MPa)
Darkrimet *et al.*	SWNT	11	80	10
Wang *et al.*	SWNT	2	80	10
Yin *et al.*	SWNT	6.5	300	16
Dillon *et al.*	SWNT	5–10	300	0.04
Ye *et al.*	SWNT	8	80	8
Dillon *et al.*	SWNT	10	300	0.04
Liu *et al.*	SWNT	4	300	12
Zhu *et al.*	MWNT	5	300	10
Wu *et al.*	MWNT	0.25	300	0.1
Chen *et al.*	Li doped MWNT	20	200–400	0.1
	K doped MWNT	14	300	0.1
Yang *et al.*	Li doped MWNT	2.5	200–400	0.1
Pinkerton *et al.*	K doped MWNT	1.8	300	0.1
Chambers *et al.*	GNF	65	300	12
Browning *et al.*	GNF	6.5	300	12
Gupta *et al.*	GNF	10	300	12

Activated carbons however, comprised of sets of graphite planes of various sizes forming a disordered and highly porous three-dimensional structure. Sorption studies on activated carbons have been carried out since 1960s. It was found that the adsorption amount for activated carbon reaches values of ~ 0.5 wt. % hydrogen at ambient temperatures and 60 bar pressure. This amount was found to increase under cryogenic conditions [8] since the binding forces between hydrogen molecules and carbon atoms

are weak, physisorption process at room temperature is low and for significant amount of hydrogen storage, the carbon samples have to be cooled [7].

Much work has been done to study the relationship between surface area of the carbon materials and their ability for adsorption [6,8]. Zuttel *et al* in his work has found that reversible hydrogen sorption process takes place via physisorption in nanostructured carbons. The amount of hydrogen adsorbed was found to be proportional to the BET surface area of the nanostructured carbon [9, 11]. Strobel *et al*, also studied the influence of surface area on activated carbons and found that there is a correlation between surface area and hydrogen adsorption for activated carbons. It was observed that a high surface area per unit mass will result in a large adsorption of energy [8]. Data simulated through several simulation works [7, 10} have also shown evidence that hydrogen adsorption can be optimized by varying the sizes of nanotube diameters and of the spaces between the nanotubes bundles [12].

As a result, surface modifications of carbon materials have generated a great interest in producing high surface area and porous structure that can adsorb gases with great ease. Several approaches have been employed to modify the surface area of carbon including oxidation with acid, burning in air/oxygen or acid oxidation followed by high temperature treatment in an inert condition. Research have shown that these treatments resulted in an increase in the purity of the carbon materials and enhances their adsorption capacity [13, 14, 15]

The objective of this work is to compare the different treatment methods on the surface area and adsorption properties of activated carbon, synthetic graphite and commercial carbon nanotubes. The data represented in this paper represents preliminary results of the undergoing study of hydrogen sorption properties of selected carbon materials.

2. MATERIAL AND METHODS

Two types of carbon materials were subjected to pretreatment. Activated carbon (100 mesh) was supplied by Aldrich and synthetic graphite, KS 44, was supplied by Timcal. Heat treatment was carried out in a horizontal tube furnace at a temperature of 600°C for 8 hours in a nitrogen atmosphere. Acid treatment was carried out by soaking the carbon samples in 4 M hydrochloric acid for 24 hours. The samples were then thoroughly washed in distilled water and dried at 100°C overnight to remove the residual water. Samples that were heat-treated were also subjected to acid treatment. The surface area and desorption properties of commercial carbon nanotubes were also analysed. Table 2 gives the types of treatment for both carbon samples.

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 by using equation (1).

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

Table 2. Carbon samples and their treatments

Samples	Treatment
Activated carbon, AO	None
A1	Heat/600°C/8 hrs/N₂
A2	HCl Acid/4M/24hrs
A3	Heat/Acid
Graphite KS44, K0	None
K1	Heat/600°C/8 hrs/N₂
K2	HCl Acid/4M/24hrs
K3	Heat/Acid
MWNT	Supplied by NTP, China
SWNTP	Supplied by NTP, China
SWNTNS	Supplied by NanoScape, Germany

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.

The surface morphology was analysed by using Scanning Electron Microscopy (SEM) on a Philips XL40 Scanning Electron Microscope and the percentage of carbon content was evaluated using Energy Dispersive X-Ray Analysis (EDAX).

3. RESULTS AND DISCUSSION

The carbon content of all samples after treatment remained high as seen from the EDAX data in Table 3. This indicated that the purity of all samples did not change significantly with treatment. Surface morphology of the graphite samples upon treatment did not show significant changes as illustrated in Figure 1a and 1b of their SEM. While a widening of the pores took place in the activated carbon samples, Figure 1c and 1d which corresponded to an increase in their BET surface area too. The surface area of activated carbon samples indicated that they are highly porous structures with large internal surface area. Acid treatment has further increase the surface area. This has resulted in an increase capability to adsorb hydrogen molecules as seen by the volume of hydrogen being desorped from Table 2. The desoption studies also showed that sample A2 gave the highest volume of hydrogen desorped for activated carbon. However, desorption occurs immediately upon adsorption indicating low retention time to hold hydrogen in the macro pores as observed from the peak area reading of the TPD instrument.

It has been found that structural imperfections such as sp^3-hybridized carbon atoms, edge atoms and carbon chains are present in non-treated carbons [16]. These imperfect structures are significantly removed during oxidation treatment such as heat and acid treatment.
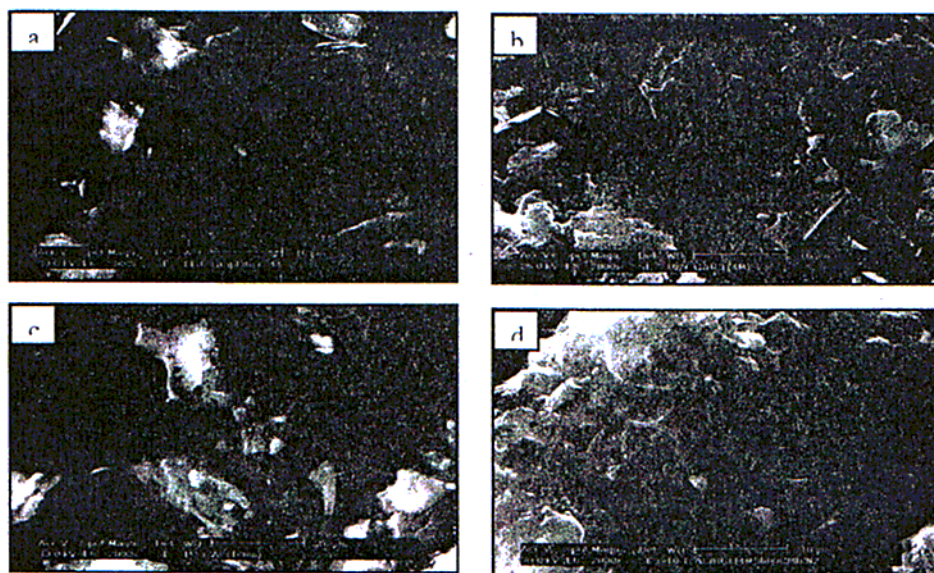
Figure 1 a. KO (no treatment) b. K2 (acid) c. AO (no treatment) d. A3 (acid)
(2000X magnification)

Table 3. Results of the surface area and hydrogen desorption data for all samples.

Samples	BET surface area, m²/g	Hydrogen desorped, ml/g	Percentage of Carbon, %
A0	644.87	0.088	98.34
A1	736.94	0.029	92.03
A2	853.80	0.639	91.45
A3	735.95	0.193	90.22
K0	7.96	0.051	99.44
K1	6.92	4.69	99.41
K2	4.54	0.69	99.38
K3	8.28	0.29	90.55
MWNT	119.68	0.15	> 80% purity
SWNTP	410.70	20.98	50 -- 80% purity
SWNTNS	204.36	0.98	~ 70% purity

There is no correlation between surface area of the graphite samples with the volume of desorbed hydrogen was observed from the results in Table 2. However, the surface area of graphite K2, decreases with acid treatment due to the agglomeration of the graphite planes. Due to the slit-pore shaped nature of the graphite as see in the isotherm, Figure 2, the true value of the surface area is not being observed with nitrogen surface analysis. Furthermore this behaviour can be explained by the assumption that during the BET surface area measurement, nitrogen condensation does not reach the same surface area like hydrogen does [8].
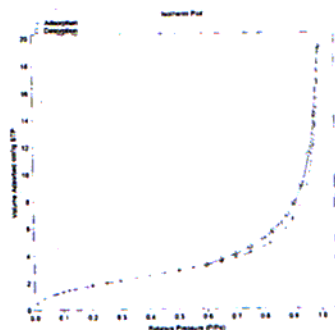
Figure. 2 Isotherm of KS44 graphite

It was also observed that heat treatment also improves the crystallization of the graphite structures whereby regular stack of graphene layers are formed. This has resulted in an enhanced hydrogen storage capacity for the graphite samples. The volume of hydrogen desorped for K1 showed a significant increase. This can be attributed to the capability of the graphite structure to better retain the hydrogen molecules in between the interstitial layers of the ordered graphite planes upon heat treatment. The heat treatment has resulted in a more ordered structure for the graphite planes, which enables more hydrogen molecules to adsorb [3]

All the graphite samples showed longer retention time for hydrogen as compared to activated carbon samples. Pretreatments such as acid and heat oxidation helps to enlarged the spaces between graphene layers in the graphite structure as well as formation of micropores which resulted in an increase in the number of sites for high interaction potentials for hydrogen adsorption [17]. Figure 3 depicts the SEM morphology of the carbon nanotubes analysed.
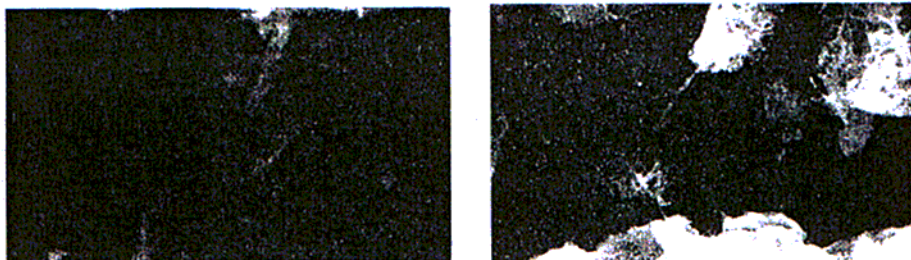

Figure 3 a. MWNT (Magnification 20000X)   b. SWNTP (Magnification 10000X)

All the carbon nanotube samples showed considerable amount of desorption of hydrogen. SWNTP gave the highest desorped value which is in agreement with Seung *et al* who reported that SWNTs are better material for hydrogen storage as compared to MWNTs [10]. A linear correlation was observed between the surface area and the desorption data for the carbon nanotubes. It is thus expected that a larger surface area carbon nanotube will result in an increase in the adsorption rate of hydrogen.

4. CONCLUSION

Surface studies have shown that both heat and acid treatment significantly changes the surface structure. Heat treatment has resulted in a more orderly stacking of the graphene sheets. Acid treatment however, may have disrupted these orderly structures. As for activated carbon, both acid and heat treatment have increased the pore sizes on the surface. The desorption studies of activated carbon, graphite and carbon nanotubes, were determined at ambient room temperature and pressure. SWNTP recorded the highest volume of desorbed 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.

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