ADSORPTION CAPACITY AND ITS DYNAMIC BEHAVIOR OF THE HYDROGEN STORAGE ON CARBON NANOTUBES

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ABSTRACT

The potential of carbon nanotubes (CNTs) produced in our laboratory to be used for hydrogen storage was tested in this study. The test includes the determination of the hydrogen gas adsorption capacity and the dynamics of the adsorption and desorption of hydrogen on CNTs at isothermal temperature of $25^{o}C$ and pressures of 0–1,000 psia. A similar test was also conducted on commercial CNTs obtained from the Chinese Academy of Sciences for comparison. The results showed that the hydrogen adsorption capacity of the local CNTs is lower than that of commercial CNTs. At pressures around 960 psia, the adsorption capacities of local and commercial CNTs are 0.09% and 0.13% weight, respectively. In general, the hydrogen adsorption data of both the adsorbents can be represented well by the Langmuir model, with less than 3% absolute average deviation (AAD). The dynamics of adsorption and desorption can be represented well by the Gasem and Robinson model with less than 2% AAD. The adsorption and desorption processes on both local and commercial CNTs occurred very quickly. At the highest pressure (960 psia), the adsorption and desorption equilibriums on the local CNTs were reached in approximately 30 s, while on commercial CNTs, they were reached in 2 s. The rates of the adsorption equilibriums on both local and commercial CNTs increase at a higher pressure. In the desorption process, while the equilibrium time is reached slightly faster at a higher pressure on commercial CNTs, the time is almost similar at all pressures for local CNTs.

Keywords: Adsorption; Carbon nanotubes; Desorption; Dynamics of adsorption and desorption; Hydrogen

1. INTRODUCTION

The use of hydrogen as a substitute for fossil energy is quite promising. This is because hydrogen is a renewable and environmentally friendly energy. Abundant availability in nature, free from CO_2 emissions, and higher energy density make hydrogen a good choice for future energy resources related to the applications for a sustainable energy, as stated also in the blueprint of our national energy policy (Presidential regulation No 5 of 2006).

Despite its great potential, hydrogen also has some limitations in its application, especially in its transportation and storage. Therefore, the selection of a safe, cheap, and effective storage option will be very important for the use of hydrogen as an alternative future energy source.

Today, four kinds of hydrogen storage options have been introduced, i.e., liquefaction,

compression, metal hydride, and adsorption in porous materials. Liquefaction is a technique resulting in the highest capacity compared to other techniques; however, its operating cost is also very high to liquefy hydrogen up to -253°C. The compression of hydrogen requires very high pressure for storage and requires safety consideration. Using a metal hydride is relatively safer, but it is quite heavy and requires a higher temperature to release hydrogen, making it unsuitable for a vehicle fuel application. Adsorption on porous materials, such as carbon, seems to be the most suitable option for hydrogen storage. It is safe, easier to handle, and has a relatively low operating cost. The density of gas molecules stored in the adsorption state is close to the density in its liquid phase, which creates a higher storage capacity, at about half of that of the liquefaction method (Zhou & Zhou, 1998).

A hydrogen storage system using adsorption technology has been attracting many researchers. Carbon nanotubes (CNTs) are one of the materials with a good ability to adsorb hydrogen. Dillon et al. (1997) reported that CNTs have an extraordinary ability to adsorb hydrogen. His research showed that the capacity was 5–10% (weight). This number is even higher than the target stated by the US Department of Energy, which is a 6.5% hydrogen storage capacity. Liu et al. (1999) also reported that the capacity of CNTs to adsorb hydrogen was 4.8%. However, inconsistent results regarding the capacity of CNTs to adsorb hydrogen were also obtained by some researchers. This is probably due to the variety of the physical properties of the CNTs used in the experiment, such as geometrical structure, purity, size of the pore volume, specific surface area, etc.

Our previous research (Wulan et al., 2011) has succeeded in producing CNTs from a methane decomposition catalytic reaction using a multi-metal catalyst. However, the produced CNTs have not been tested for their ability to adsorb hydrogen gas. Therefore, in this study, the adsorption of hydrogen on the produced activated carbon is performed at 25°C and at pressures up to 1,000 psia. The adsorption of hydrogen on CNTs is performed using volumetric based on a mass balance method. The dynamic behavior during the adsorption and desorption processes, which is an important aspect in designing a hydrogen storage system, is also recorded in this study. CNTs from the Chinese Academy of Science are also studied for a comparison.

2. EXPERIMENTAL SETUP

2.1. Adsorption Test Equipment Preparation
The adsorption test equipment includes some parts, i.e., a dozing cylinder, a sampling cylinder, pressure transducers, needle valves, and pressurized gas cylinders. Each part is connected using a 1/8-inch stainless steel pipe. A dozing cylinder is used to measure the amount of gas injected, while a sampling cylinder is where the CNT is placed and where the adsorption occurs. The dozing cylinder and sampling cylinder are made of a ¼-inch stainless steel pipe with a volume ratio of 2:1. The volume in the dozing cylinder is 23 mL. The gas transfered from the dozing cylinder to the sampling cylinder is managed by a needle valve (valve 2). Calibrated pressure transducers are attached to both the dozing cylinder and the sampling cylinder and connected to the data acquisition (Advantech USB 4718) so that pressures in both compartments can be monitored and recorded at all times through a computer unit. All of the equipment is placed in the temperature controlled compartment. Figure 1 shows the adsorption equipment scheme.

2.2. Materials
CNTs produced in our laboratory are considered multi-walled CNTs, which still consist of a remaining catalyst, with an outer wall diameter of 50–100 nm and a specific surface area of 126 m^2/gram (Wulan et al., 2011). CNTs from the Chinese Academy of Science are also multi-walled with a purity of >95%, having an outer side diameter of 8 nm, an inside diameter of 2–5 nm, a length of 10–30 μm, and a specific surface area of 500 m^2/gram. The amount of CNTs

used for the adsorption test is about 2 grams. The CNTs are inserted into the sampling cylinder and heated to 50°C in a vacuum condition for 5 h to keep away from the water vapor trapped in the carbon.

High-purity helium and hydrogen (99.995%) from a commercial supplier were used in this experiment.
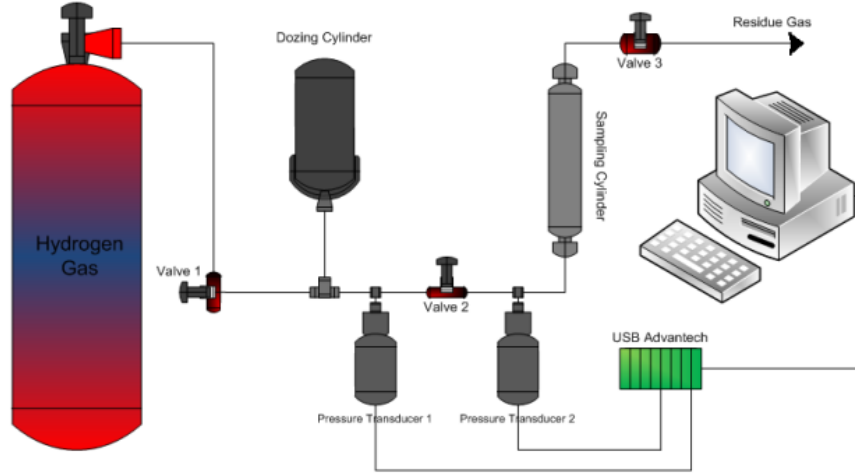

Figure 1 Scheme of adsorption test equipment

2.2.1. Adsorption and desorption tests

The void volume is determined by injecting helium gas from the dozing cylinder into the sampling cylinder at various pressures from 0–1,000 psia. The amount of helium injected can be determined if the initial (i) and final (f) conditions of the dozing cylinder are known, according to Equation 1.

$$n = \left(\frac{P_i}{Z_{Hei} RT_i} - \frac{P_f}{Z_{Hef} RT_f} \right) V_{dozingcylinder} \tag{1}$$

The void volume can be calculated according to Equation 2.

$$V_{void} = \frac{n_i Z_{He} RT_f}{P_f} \tag{2}$$

The void volume obtained from Equation 2 will be used to determine the amount of hydrogen gas adsorbed (Goodman et al., 2004).

The hydrogen adsorption test is conducted by injecting hydrogen gas from the dozing cylinder into the sampling cylinder at an isothermal temperature of 25°C and pressures vary from 0 to 1,000 psia, while the desorption test is conducted by releasing hydrogen gas from the sampling cylinder to the dozing cylinder after the adsorption test, with pressures varying from 1,000 to 0 psia. The number of moles of hydrogen adsorbed is determined using Equations 3 and 4 (Goodman et al., 2004).

2.2.2. Model development for hydrogen adsorption and desorption

The adsorption model used in this study is the isothermal Langmuir model given in Equation 5 (Yang, 1987).

$$n_{H_2\,ads} = n_{H_2,i} - n_{H_2\,unads} \tag{3}$$

$$n_{H_2\,ads} = \left[\left(\frac{P_i}{Z_{H_2,i}RT_i} - \frac{P_f}{Z_{H_2,f}RT_f}\right)V_{dozing\,cylinder}\right] - \left[\frac{P_fV_{void}}{Z_{H_2,f}RT_f}\right] \tag{4}$$

$$n_{ads}^{abs} = n_{maks}\frac{bP}{1+bP} \tag{5}$$

The deviation of the experimental data and the Langmuir model are expressed in % absolute average deviation (AAD). By minimizing the % AAD, the Langmuir model constants (b and n_{maks}) can be obtained.

The adsorption and desorption dynamic models are derived from the model proposed by Gasem and Robinson (2001), as shown in Equations 6 and 7.

$$\theta = \frac{\beta t^{(ap^2+bp+0.5)c}}{1+\beta t^{(ap^2+bp+0.5)c}} \tag{6}$$

$$n_{t\,model} = \theta(n_f - n_i) + n_i \tag{7}$$

Theta (θ) is a fraction of adsorbed gas, while β, a, b, and c are the adsorption equilibrium constants. The amount of gas adsorbed at any time (n_t) is calculated from the amount of gas adsorbed at the initial adsorption (n_i) up to the final adsorption (n_f). The deviations of the experimental data and the dynamic model are expressed in % AAD. By minimizing the % AAD, the dynamic model constants β, a, b, and c can be obtained.

3.   RESULTS AND DISCUSSION

3.1.   Adsorption and Desorption of Hydrogen

The results of the hydrogen adsorption and desorption tests are presented in Figure 2, which shows that the hydrogen adsorption capacity of the CNTs from the Chinese Academy of Science (commercial CNTs) is higher than that of the CNTs produced in our laboratory (local CNTs).
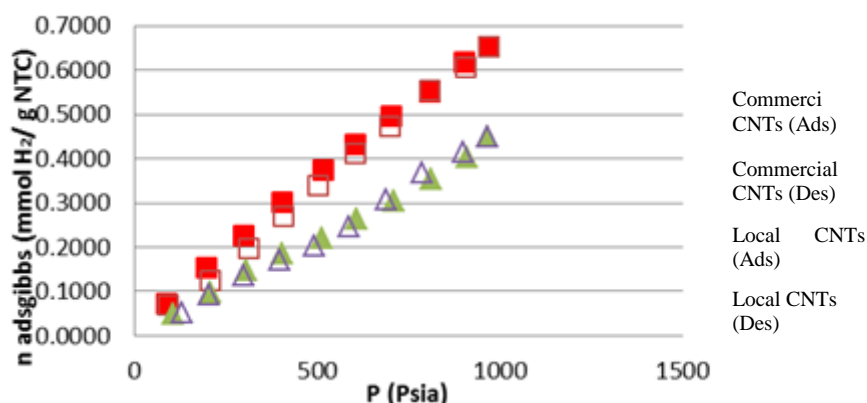

Figure 2 Hydrogen adsorption and desorption results

At the highest pressure (about 960 psia), the commercial CNTs were able to adsorb as much hydrogen as 0.65 mmol/g or 0.13% weight, while the local CNTs only adsorb as much as 0.44 mmol/g or 0.09% weight. The lower adsorption capacity of the local CNTs is probably because of the lower purity, as the remaining metal catalyst might hinder the hydrogen gas to be adsorbed in porous sites. Besides, a higher diameter and lower surface area of the local CNTs might also affect the interaction of the carbon atom and hydrogen molecules, and that can lower the adsorption capacity.

Figure 2 also shows that the number of hydrogen molecules adsorbed is increased by increasing pressures. The higher the pressure, the higher the number of hydrogen molecules, resulting in a higher driving force of the molecules diffusing to the surface and entering the pores of the CNTs. This results in an increase in the capacity of adsorption. The hydrogen adsorption on CNTs tends to remain increased when the pressure is increased, even at more than 960 psia.

The typical adsorption on both CNTs follows the adsorption isotherm type I, based on the Bruneur classification. This type is also called the Langmuiric isotherm, where the adsorption mechanism can be represented by one-layer adsorption, which is usually obtained for adsorption on micro-porous materials. The same type of adsorption for hydrogen was also obtained in the experimental results reported by Zhou et al. (2004).

The isotherm desorption on each CNT almost exactly follows its adsorption line, as presented in Figure 2. This phenomenon demonstrates that the adsorption of hydrogen gas on CNTs is a physical adsorption process. Some previous research results also agree with our results. However, some other researchers, such as Ioannatos et al. (2010), argued that the adsorption process on CNTs does not fully follow the physical adsorption process, as it also slightly follows the chemical adsorption process. In the physical adsorption process, hydrogen molecules weakly interact with the carbon atom, resulting in an easier release of the hydrogen molecules. Therefore, the adsorption line will be close to the desorption line.

The hydrogen adsorption capacity obtained in this study is still far lower than that from the value targeted by the DOE USA, which is a 6.5% weight.

3.2.   Langmuir Model Representation

A comparison of the adsorption experimental data and the Langmuir model is presented in Figure 3. In general, the adsorption experimental data can be represented very well with the Langmuir model within 3% AAD, as shown in Figure 3. The Langmuir model parameters are obtained, as presented in Table 1. The value of n_{maks} for the local CNTs is higher than that for the commercial CNTs (3.255 mmol/g compared to 2.704 mmol/g). However, the value of b for the local CNTs is lower than that for the commercial CNTs (0.0001 compared to 0003). This implies that the higher adsorption capacity in commercial CNTs is more affected by the interaction between the hydrogen molecules and carbon atoms than the specific surface area of the CNTs.
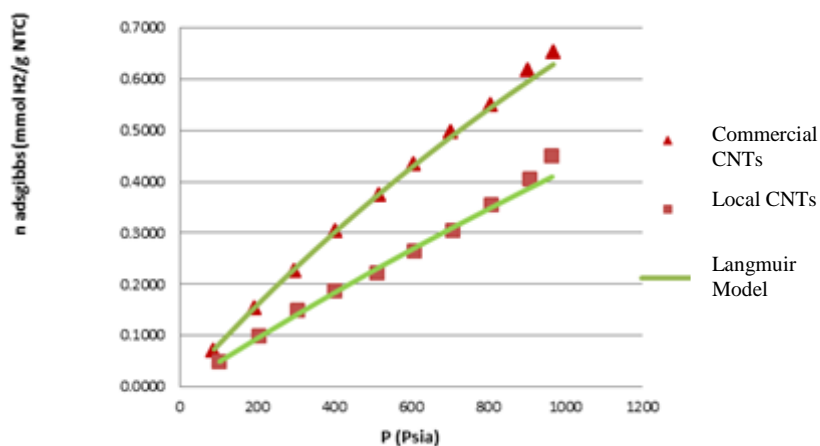
Figure 3 Comparison of the adsorption data and Langmuir model

Table 1 Langmuir Model Parameters

CNT	n_{maks}	b	% AAD
Local	3.255	0.0001	3.00
Commercial	2.704	0.0003	1.68

3.3. Representation of Adsorption and Desorption Dynamic Behavior

The adsorption and desorption dynamic processes can be represented quite well with the Gasem–Robinson model, as shown in Figures 4–7. In general, the deviation between the experimental data and the model is no more than 2% AAD.
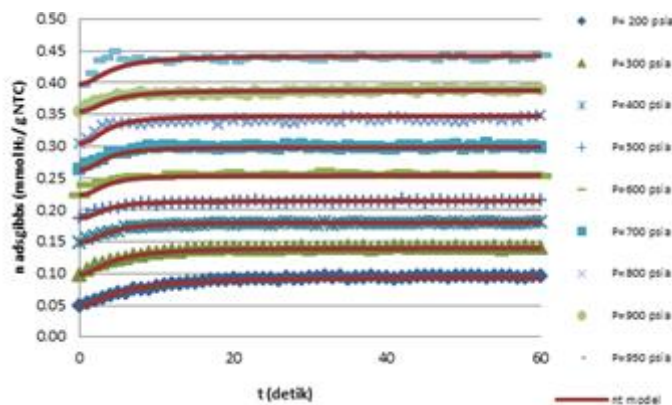

Figure 4 Representation of the hydrogen adsorption dynamic behavior on local CNTs
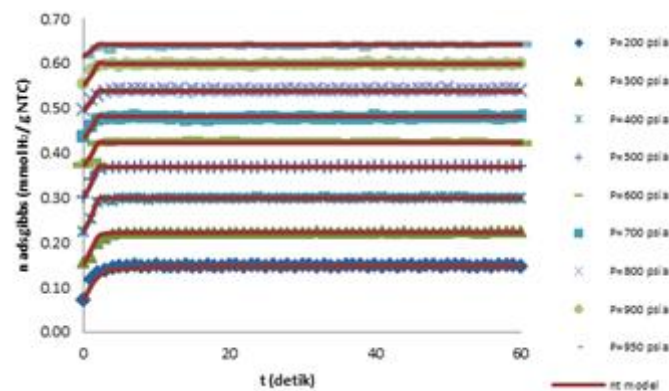
Figure 5 Representation of the hydrogen adsorption dynamic behavior on commercial CNTs
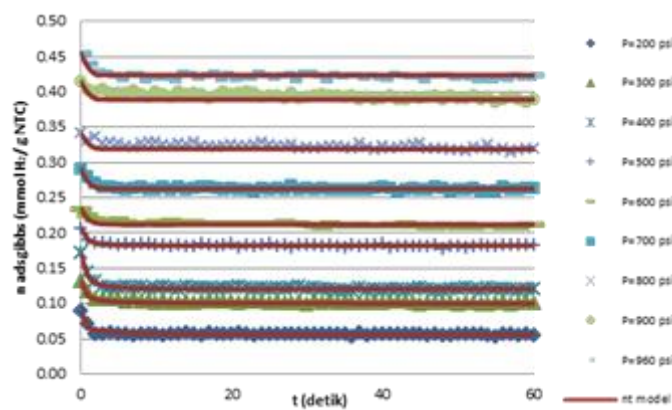

Figure 6 Representation of the hydrogen desorption dynamic behavior on local CNTs
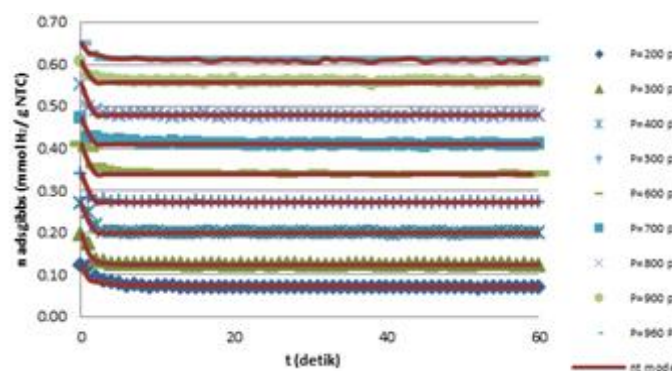

Figure 7 Representation of the hydrogen desorption dynamic behavior on commercial CNTs

The local CNTs have lower constant values of β and a than the commercial CNTs for the adsorption process. This result implies that the adsorption equilibrium is slower in local CNTs than in commercial CNTs. In the desorption process, a constant value of β is almost the same for both CNTs, but the constant value of a is higher in commercial CNTs than in local CNTs. This result shows that even though the desorption time in both CNTs is almost the same, the

amount of hydrogen desorbed is higher in the commercial CNTs. The results also indicate that the local CNTs have a more complex geometric structure than the commercial CNTs, where a more complex structure will produce a longer path and more obstacles during the diffusion process. This effect is commonly called the tortuosity factor.

Beta (β), as shown in the Gasem–Robinson model, has a similar physical meaning to b in the Langmuir model, where b represents the ratio of the desorption rate constant to the adsorption rate constant. In this study, the value of β is higher in the desorption process than in the adsorption process. This agrees with the theory that the desorption process is faster than the adsorption process.

The adsorption process at higher pressures is faster than that at lower pressures. This might be due to the slower effective diffusion affected by Knudsen diffusion at lower pressures. The same characteristic is also obtained in the desorption process.

In general, the adsorption and desorption processes occur very quickly (in seconds). This result indicates that the in-charging and discharging processes in this study are mostly affected by the adsorption and desorption processes and not much affected by the fluid mechanism along the piping and tube storage system.

4. CONCLUSION

The hydrogen adsorption capacity of the CNTs from the Chinese Academy of Science (commercial CNTs) is higher than that of the CNTs produced in our laboratory (local CNTs). This is probably because of the lower purity, higher diameter, and smaller surface area of the local CNTs. Hydrogen adsorbed is increased by increasing the pressure. In general, the adsorption experimental data can be represented well with the Langmuir model within 3% AAD. In general, the adsorption and desorption processes occur very quickly (in seconds). A quick process of adsorbing and desorbing hydrogen on CNTs is very useful for storing fuel hydrogen. The adsorption and desorption processes at a higher pressure are faster than that at a lower pressure, and the adsorption and desorption dynamic processes can be represented quite well using the Gasem–Robinson model with a deviation of no more than 2% AAD.

5. ACKNOWLEDGEMENTS

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