

CHARACTERIZATION OF ADSORPTION ON CARBON NANOTUBES USING A PULSE MASS ANALYZER

Edward W. Bittner, Milton R. Smith, and Bradley C. Bockrath
National Energy Technology Laboratory
US Department of Energy
Pittsburgh, PA 15236

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INTRODUCTION:

In addition to their other special properties, carbon nanotubes also have excited considerable interest because of their potential to serve as hydrogen storage materials [1]. Several groups have reported [2-4] large values for hydrogen uptake by single walled nanotubes. Molecular simulation studies were used to identify critical structural properties that are important for development of an effective material for hydrogen storage [5]. A list of critical properties culled from the experimental and theoretical results includes the diameter of the tube, the relative number of tubes with open ends, the ease of penetration of the pore mouth to the interior of the tube, the ease of entrance into the extra-tubular space typically found between the single tube strands of rope-like structures, and the interaction potential between hydrogen and the carbon surface. In the work described below, a pulse mass analyzer similar to that originally developed to investigate the kinetics of coke deposition on cracking catalysts [6] was used to evaluate novel materials for storage potential. Direct measurements were made of weight changes in a packed bed of storage material caused by changes in the gas stream or by injection of small samples of volatile organic compounds. The amount of weight change found after injection of the samples and the "retention" time of the adsorbed material provided useful information on the characteristics of various nanotube samples. The method holds promise as an additional tool for characterization of adsorbents and storage materials.

EXPERIMENTAL:

Materials. The single wall nanotubes were obtained from Rice University (Tubes@Rice). "Fullerene Nanotubes" were used after grinding in a ball mill for ease of introduction into the sample holder, and are referred to below as raw Rice tubes. According to the analysis provided the average tube diameter is 1.36 nm. TGA analysis gave a residue weight after combustion corresponding to the expected amount of catalytic metals reported as incorporated during the synthesis. Analysis of the TGA residue by ICP led to the determination of 3.7 % nickel, 3.5 % Co, and 0.44 % Fe in the original material.

Equipment: Figure 1 is a block diagram for the apparatus including the pulse mass analyzer (PMA1500) manufactured by Rupprecht and Pataschnick. The PMA1500 is a mass measuring device that employs a tapered glass element that is stimulated to vibrate at its natural frequency. The element is made up of a long narrow hollow quartz glass tube that opens at the bottom to a 0.100 cc volume into which the sample is placed. Quartz wool and a retaining cap hold the sample in place. The element is mounted vertically in a holder in a stainless steel vessel. Carrier gas flows through the sample bed providing excellent contact. The frequency of vibration of the element is monitored via an optical system. With appropriate calibration the frequency changes are recorded as mass changes within the reactor using Equation 1. A stream of purge gas sweeps out carrier gas and other components once they have passed through the sample bed. In addition, a valve/loop injector allows pulses of reactant gases to be introduced into the carrier gas upstream of the sample chamber. Injection of volatile organic liquids was made by syringe through a heated injection port. Mass flow controllers (Brooks, 5850E) were used to regulate the flow of both carrier and purge gases. The instrument is able to work at pressures from 1- 60 atmospheres (Brooks backpressure regulator, 5866E) and at temperatures up to 700 C.

$$\Delta m = k / (1/f_1^2 - 1/f_2^2) \quad (1)$$

To determine k the instrument was equilibrated at a set temperature with no sample or sample-retaining cap and with flow rates of carrier and purge gases at nominal values. After the frequency of the vibrating element was recorded the sample-retaining cap of known mass was placed on the element and the frequency was measured a second time. Thus, k is established for the particular set of pressure, flow and temperature settings used. The constant k has a strong temperature dependency and re-calibration must be done when the temperature is varied.

Additional information was obtained from a quadrupole mass spectrometer (Ametek MA 100M) that sampled the exit gas stream through a 6-meter length of a capillary GC column. This detector was especially useful with the PMA in pulse mode. When a significant portion of an injection was not retained by adsorption on the sample the pulse of material passing through the bed was observed by the mass spectrometer. Materials that were retained and then slowly

bled from the sample remained below the detection limit and were not observed. The use of a capillary column as transfer tube provided an additional means to discriminate between compounds by observing the transit time between PMA and the spectrometer. For example, the transit time for ethanol was 3.5 min. while that for 2-propanol was 5.0 min.

Gas Density Experiment

The frequency of vibration depends on the mass of the tapered element and its contents, including the weight of the gas contained within the tapered element. For example, when the carrier gas was switched from nitrogen to helium a change in mass occurred due to the change in gas density inside the element. Cycling back and forth showed reproducible gas density changes (Figure 2). Because of this, the changes in mass due simply to changes in gas density must be taken into account when the results from adsorption experiments are considered.

Adsorption Experiments

The sample bed was packed with the carbon nanotube sample and heated using helium as carrier gas and nitrogen as purge gas both at 50 cc/min. All of the experiments were performed at atmospheric pressure. Each sample was pre-treated in situ by heating to either 200 C or 700 C for 4 hours before adsorption measurements were made. Then the temperature was set for the adsorption experiment (30 C, 100 C, or 200 C) and the PMA was allowed to equilibrate for about an hour. Organic compounds (typically 1.0 or 2.0 μ l as liquids), were injected into the pre-heated port (200 C) of the PMA where they vaporized rapidly in the carrier stream; the mass responses were recorded. For a carrier flow of 50 cc/min, a mass response was seen within 6 seconds, the time taken by the vaporized sample to reach the fixed bed. The mass changes were recorded as a function of time. For those compounds poorly adsorbed only a very small and transient change in mass was observed. For those strongly adsorbed, a large, rapid increase in mass was observed followed by a gradual decrease as the retained compound slowly desorbed. The gravimetric decay curve had a long tail resembling that associated with a poorly performing chromatographic column. Strongly adsorbed species took hours to desorb completely.

RESULTS:

Effect of adsorbate structure.

Hydrogen, carbon dioxide, and organic compounds were injected at 30 C, 100 C, and 200 C.

30 C. The sample holder was packed with 80.0 mg of raw Rice tubes and heated to 200 C in a stream of helium at 50.0 cc/min. with a purge gas of nitrogen at 50.0 cc/min. Following this pretreatment, the temperature of the PMA was equilibrated at 30 C for one hour. Individual pulses of hydrogen gas (3.90 mg., 1.95 mmoles) were introduced through the loop injector valve. A small peak was formed equivalent to a mass gain of 20- 25 μ g that returned to the baseline in a matter of seconds, indicating that only a small fraction of hydrogen injected was adsorbed then rapidly desorbed under these conditions. Pulses of CO₂ (12.8 mg., 0.291 mmoles) had a similar appearance. As typical of poorly retained compounds, hydrogen and carbon dioxide peaks appeared in the mass spectrometer following these injections and were of comparable size to those following injections into an empty reactor. Experiments conducted at a later time confirmed that little or no hydrogen adsorption occurred at 30 C by this sample, even under 27.0 atmospheres of hydrogen pressure flowing at 50 cc/min. for 3 hours. In these experiments the raw Rice tubes did not adsorb hydrogen or CO₂ to any significant extent at 30 C.

100 C. As before, pulses of hydrogen and carbon dioxide passed through the sample without significant adsorption. A series of organic compounds with similar boiling points, methanol (65.0 C), tetrahydrofuran (64.5 C), and n-hexane (68.0 C) was injected. Injections of methanol (2.0 μ l.) gave reproducible changes of 1.0 mg. corresponding to 63% of the material adsorbed. A small peak for methanol was also observed by the mass spectrometer, consistent with a partially or poorly adsorbed compound. THF was adsorbed more strongly than methanol. Duplicate injections gave 86 % and 89 % of the THF retained and each injection took approximately 60 minutes to desorb. The most strongly held compound of the series was n-hexane. Of two injections, 91% and 88% were retained and it required several hours at 100 C followed by heating to 200 C to remove it completely.

200 C. At 200 C another series of compounds of disparate polarity and structure but similar boiling points was used. These were ethanol (78.5 C), 2-propanol (82.0 C), 2-butanone (79.6 C), cyclohexane (81.0 C), cyclohexene (83.0 C), and benzene (80.0 C). Figure 4 shows the PMA responses and the data are summarized in Table 1. The most striking feature of Figure 4 is the wide range of retention. Alcohols are hardly retained. For ethanol, the amount adsorbed after each 0.790 mg. (1.0 μ l) injection was 0.230 mg, only 29 % of the mass injected. Desorption of the ethanol occurred within 30 seconds. About 55 % of the 2-propanol injected was retained and also desorbed rapidly. Markedly more of the cyclohexane (92 %) and cyclohexene (88 %) were

retained and each desorbed slowly. Among the three cyclic compounds, cyclohexene and benzene desorbed much more slowly than cyclohexane. The times required for the weight gain to diminish by one half (Table 1) were taken as a rough measure of relative retention.

Effect of pre-treatment temperature

After completing the adsorption experiments above, the raw Rice tubes were heated to 700 C to explore for effects due to the pretreatment temperature. This seemed appropriate because evidence has been presented [2,7] that functional groups are removed from tube openings by high temperature treatments, thus allowing for greater access to the interior of the tubes. The results show that the retention time increased significantly for some of the organic compounds compared with those found after pretreatment at 200 C (Table 1). For example, the retention time for cyclohexane doubled from 33 to 67 minutes. In general, the desorption curves for strongly retained compounds have long tails. Kinetic data from material pretreated at 200 C do not appear to obey a simple rate law. In contrast, the decay curves for all of the hydrocarbons sorbed onto nanotubes activated at 700 C were well described over the first 400 seconds by a second order rate law (eg. Figure 5). For comparison, the half lives were calculated in seconds for 1.0 mg starting weights of each as: cyclohexane (46), cyclohexene (88), benzene (89), and hexane (205). The result shows an increase in retention on introduction of one degree of unsaturation from cyclohexane to cyclohexene, but no further change on going to the aromatic compound benzene. A much greater increase was seen with n-hexane, the calculated half-life being nearly 4 1/2 times that of its cyclic counterpart. This remarkable difference may be due to the ability of n-hexane to flex and bend to accommodate maximum interaction with the nanotube surface. This flexibility may allow either stronger binding to the exterior surface or alternatively, a greater tendency to be trapped within the tube. At present it seems unlikely that the desorption process can be successfully interpreted in terms of a single, well-defined adsorption site. Further studies with linear and branched hydrocarbons are needed to gain better insight into the adsorption process.

Table 1^a
Raw Rice Tubes, Pre-treated at 200 C and 700 C

COMPOUND	BP (C)	Den. (g/ml.)	Halfwidth ^b	Halfwidth ^c
			Sec.	Sec.
ETOH	78.5	0.789	13, 13	13
I-PROH	82.0	0.780	13, 13	15, 15
CYCLOHEXANE	81.0	0.779	33, 33	67, 67
BUTANONE	79.6	0.805	40, 40	-----
CYCLOHEXENE	83.0	0.811	67, 67	133, 133
BENZENE	80.0	0.880	77, 77	107
n-HEXANE	68.0	0.659	-----	313

a) 1.0 µl injections at 200 C, helium carrier 50 cc./min. nitrogen purge 50 cc./min., duplicates shown. b) Raw Rice tubes, pretreatment 200 C. c) Raw Rice tubes, pretreatment 700 C.

CONCLUSIONS:

The interactions of hydrogen and carbon dioxide as well as several organic compounds with carbon nanotubes were investigated with a pulse mass analyzer. The pulse mass analyzer proved to be a useful tool for elucidation of structure/adsorptivity relationships in these systems. Our findings indicate that neither hydrogen nor carbon dioxide has a great affinity for these materials as compared to the organic compounds tested. Within the organic sequences, we find that alcohols are not retained as well as hydrocarbons. Moreover, unsaturation may be beneficial for adsorption in some cases (cyclohexene versus cyclohexane), but in another case (hexane) the enhanced flexibility associated with saturation of the carbon chain perhaps leads to an even greater affinity for nanotubes.

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DISCLAIMER:

Reference in this work to any specific commercial product is to facilitate understanding and does not necessarily imply endorsement by the United States Department of Energy.

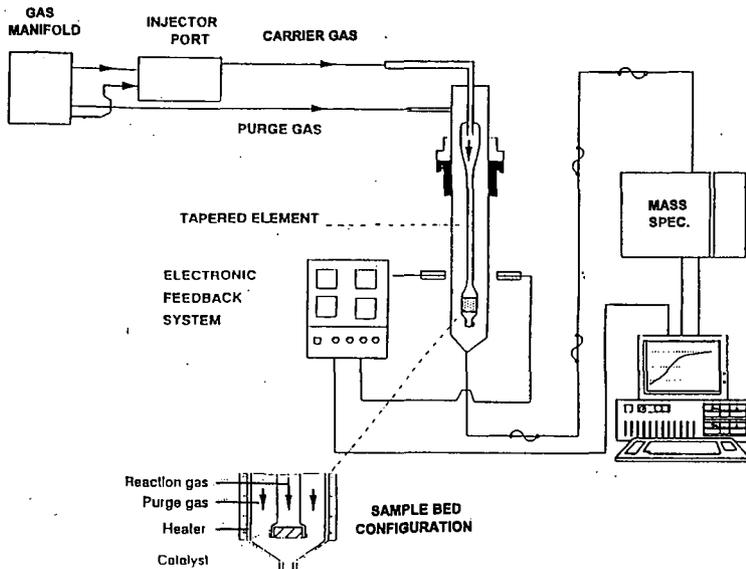


Figure 1 Block Diagram of the PMA1500

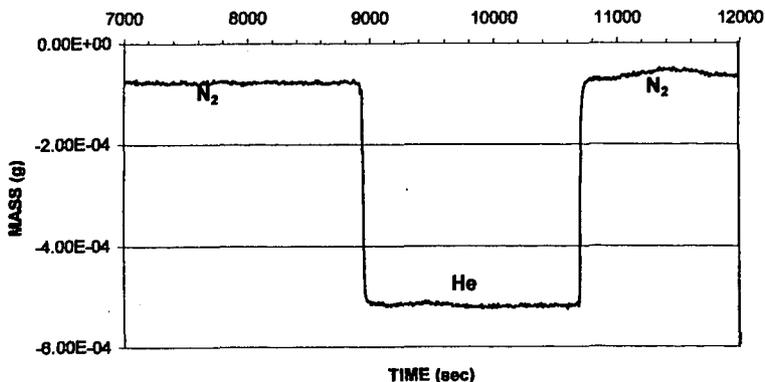


Figure 2 Gas Density Experiment, empty reactor, 30 C. carrier switch from 50cc/min N_2 to 50cc/min He to 50cc/min N_2 .

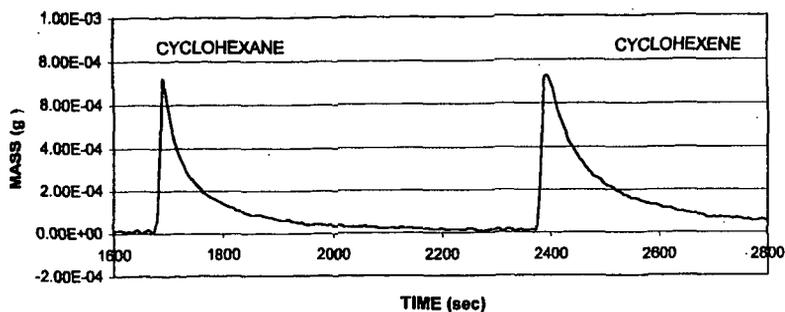


Figure 3 Raw Rice tubes at 200 C, 50 cc/min He carrier with 1.0 ul. Injections of cyclohexane and cyclohexene, pretreated at 200 C

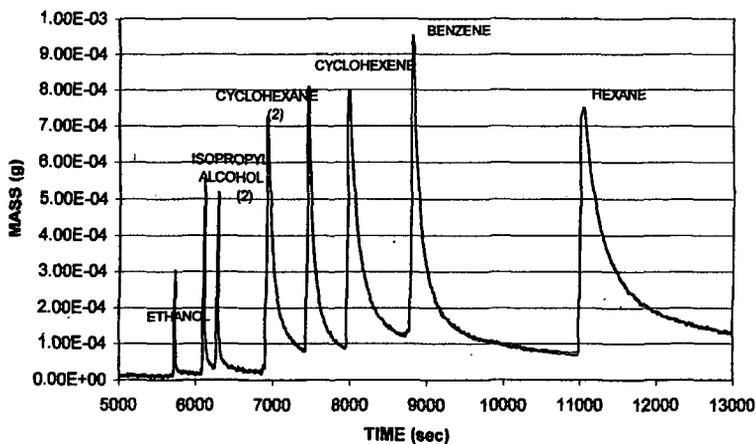


Figure 4. Raw Rice tubes at 200 C, helium carrier 50 cc./min., pre-treatment at 700 C, 1.0 ul. Injections

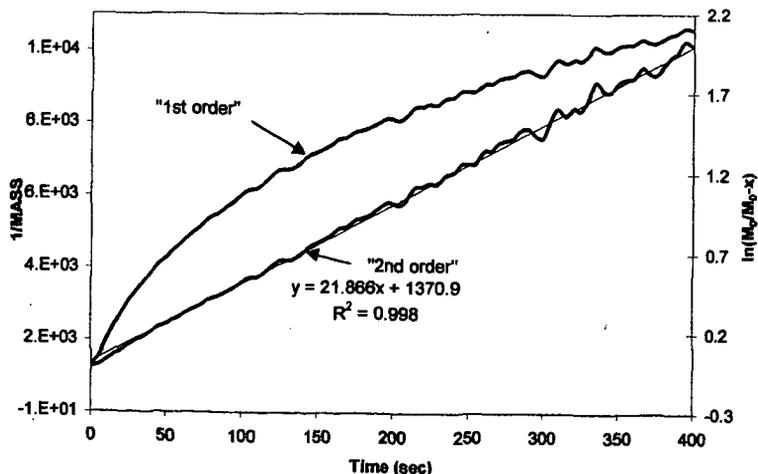


Figure 5. Rate dependence for loss of cyclohexane at 200 C (see Figure 4)