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DESORPTION BEHAVIOR OF GASEOUS MOLECULES ON SINGLE-WALLED CARBON NANOTUBE BUNDLES

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Abstract. Temperature programmed desorption (TPD) technology was used to examine desorption activation energies (E_d) of O_2, N_2 and Ar on single-walled carbon nanotube (SWCNT) bundles. The SWCNT bundles obtained from Carbon Nanotechnologies Inc. were prepared by high-pressure CO (HiPco) disproportionation process, and had diameters of approximately 0.8 nm. The results show that the temperatures at which the maximum desorption rates of O_2, N_2 and Ar on SWCNTs are all below 200 °C, and the corresponding E_d values are 209, 192 and 188 meV, respectively. The E_d values are very close to the isosteric heat of adsorption (q_{st}) obtained from our previous studies, implying that these gases are physisorbed onto SWCNTs.

1. INTRODUCTION

Carbon nanotubes (CNTs) have a high specific surface area and a nano-scale structure that provide plenty of sites at which gases can react. Thus, they exhibit very good gas adsorption properties [1-3] and are suitable for various applications [4-6]. Several researchers have studied the gas adsorption behavior of CNTs, including the amount adsorbed, the isosteric heat of adsorption (q_{st}), the binding energy (ε), and variations of the electronic properties during gas adsorption [7-11]. However, other basic adsorption properties, such as desorption activation energy (E_d) and adsorption activation energy (E_a), have not yet been determined in detail, although such information is of fundamental interest and will yield further important information on the applications of CNTs.

Our previous results [12] disclosed the values of q_{st}, ε and the amounts of O_2, N_2 and Ar absorbed on SWCNTs at ambient temperature. The ε values of these gases were greater for HiPco SWCNTs than that of planar graphite ones, as determined by adsorption isotherm measurements. In order to understand the adsorption of gas molecules on CNTs, the desorption activation energy (E_d) and the adsorption activation energy (E_a) of gaseous molecules were determined by temperature programmed desorption (TPD) method in this study. TPD is a highly effective method to study both adsorption and desorption rates. Using the TPD method, A. C. Dillon *et al.* [13] demonstrated that the E_d value of H_2 on single-walled carbon nanotubes (SWCNTs) was 19.6 kJ·mol^{-1}. W. Teizer *et al.* [14] also studied the desorption behavior of ^{4}He and Ne on SWCNT bundles at T>14K. They found that these adsorbates were described approximately as one-dimensional adsorption, and that the He and Ne atoms were of ideal size for physisorption interactions on SWCNTs.

In this paper, the TPD method is used to investigate the desorption behavior of O_2, N_2 and Ar on HiPco SWCNT bundles in a vacuum at a controlled temperature and various heating rates (β). The E_d values of these gases were calculated from the measured

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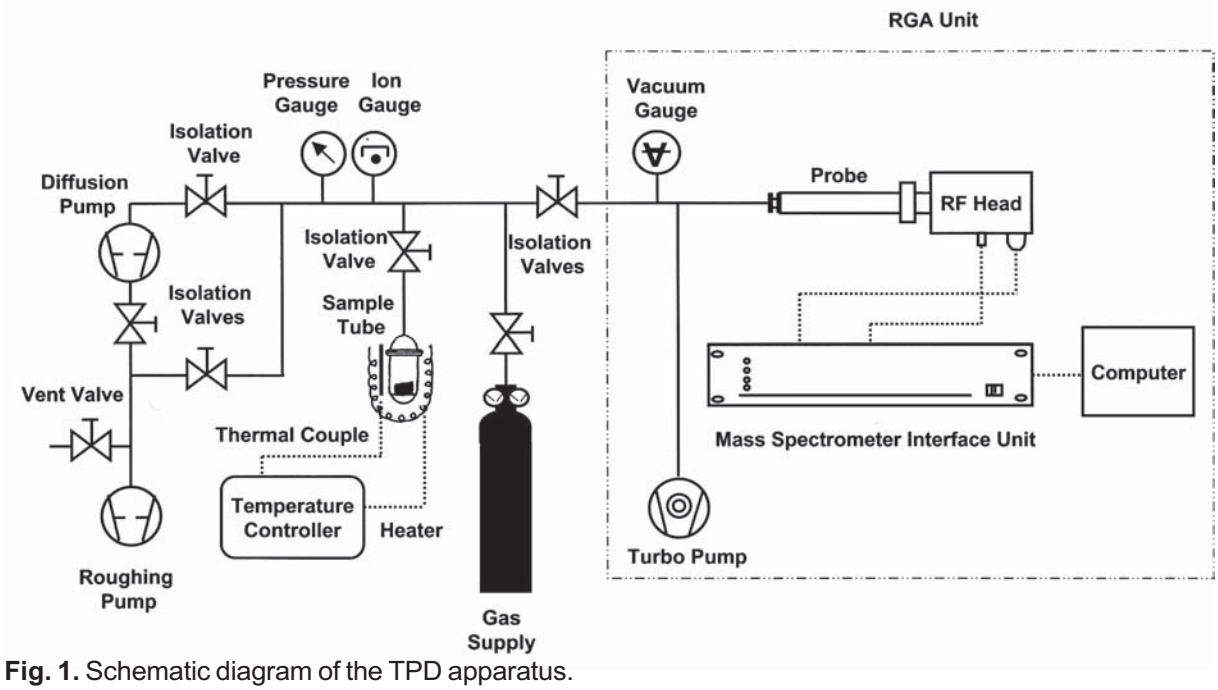

Fig. 1. Schematic diagram of the TPD apparatus.

temperatures (T_m), T_m is a temperature at which maximum desorption rates occurs during TPD heating interval, and will used to compare with the q_{st} values from previous reports [12,15].

2. EXPERIMENTAL

The gas-desorption properties were investigated using a home-build TPD system. The O_2, N_2, and Ar gases of 99.99 % purity and SWCNTs samples of 10 mg are used in this experiment. Fig. 1 depicts the TPD experimental apparatus that is comprised primarily of a sample chamber, a gas supply, a vacuum system and a residual gas analyzer (Hiden HALO 301 RGA). They were connected each other via individual valves. During heating, the desorbed gases were simultaneously analyzed by RGA, which displayed curves of the intensity of mass signals versus time. A heating zone of about 5 cm was maintained at a constant temperature to within ±1 °C, using a precision temperature controller.

The HiPco SWCNTs were produced by high-pressure CO disproportionation [12,16], with diameters of around 0.8 nm and 90% purity, were bought from Carbon Nanotechnology Inc. (CNI). The SWCNTs were placed in an U-shape Pyrex sample tube that was connected to a Pyrex vacuum system. At the beginning of each TPD experiment, the sample chamber and vacuum tubing were evacuated to about 10^{-5} Torr, at which pressure they were maintained for at least 2 hours. The SWCNTs were then heated in a vacuum at a rate of 10 °C/min to 500 °C, at which temperature they were held for 2 hours. Subsequently, the sample was cooled to room temperature. After pre-treatment of SWCNTs at 500 °C in a high vacuum, the adsorbates of the gas were introduced into the sample chamber until the pressure reached 760 Torr at which it was held for 30 minutes to let the gas adsorption on SWCNTs. Then, the sample chamber was evacuated again for 30 minutes to ensure that the low coverage of the adsorbates on SWCNTs could be achieved. Before the TPD signals were measured, we close the valves that connect the Pyrex vacuum system with the sample chamber, and open the isolation valves to connect the RGA analyzer with the sample chamber to perform a TPD measurement. The β of the TPD test used herein was 10 to 30 °C/min and the temperature increased from 40 °C to 500 °C.

3. RESULTS AND DISCUSSION

3.1. Cleaning of the SWCNTs surface

In this study, each raw SWCNT was pre-treated in a vacuum at 500 °C for 2 hours before the TPD test to clean the surface of the SWCNTs. Figs. 2a-2c present the mass spectra of HiPco SWCNTs during

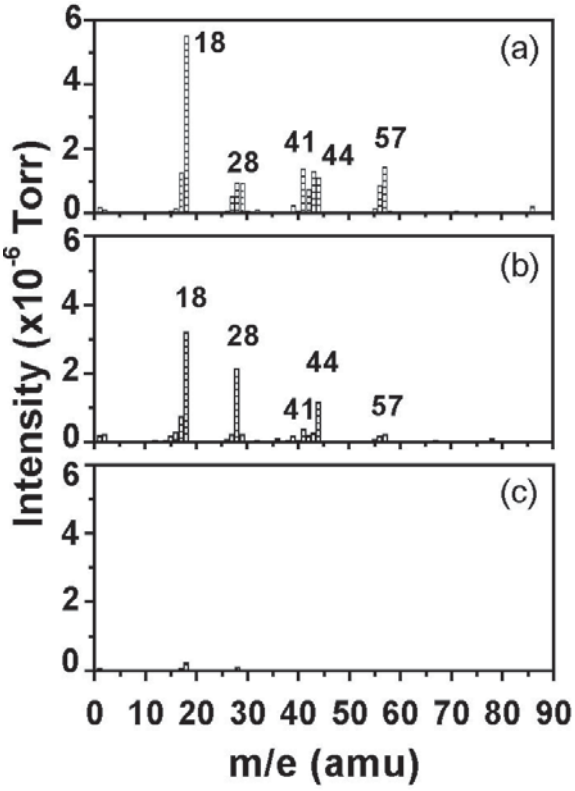

Fig. 2. TPD mass spectra of HiPco SWCNTs desorption (a) at 240 °C, at which maximum desorption occurs, (b) at 500 °C, and (c) after isothermally holding at 500 °C for 1 hour. The lack of signals in the spectrum (c) indicates the complete desorption of adsorbed species and impurities.

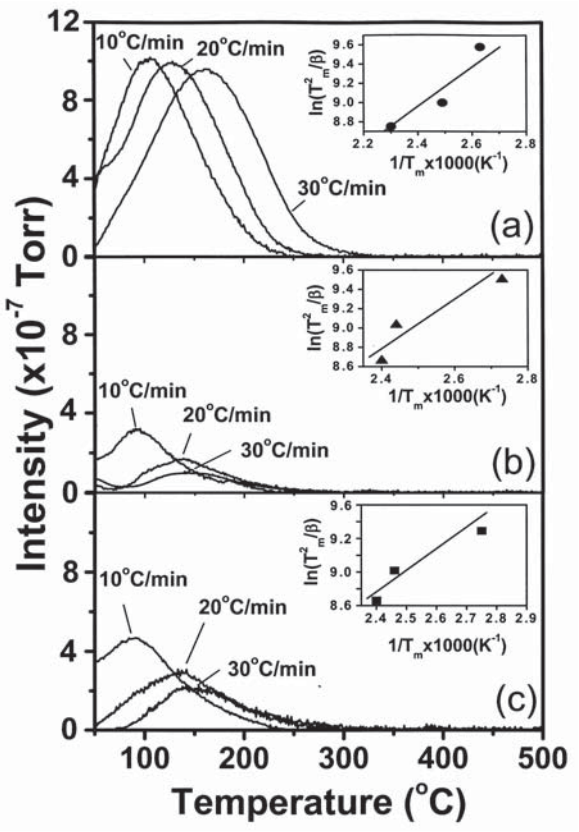

Fig. 3. TPD profiles of HiPco SWCNTs after (a) O_2, (b) N_2, and (c) Ar exposure; inset plots $\ln(\beta/T_m^2)$ against $1/T_m$ for β from 10 to 30 °C/min. The activation energy of desorption, E_d, is determined from the slope.

the TPD heating process at a rate of 10 °C/min. For comparison, the Y-axes in Figs. 2a-2c have the same scale for both 240 °C and 500 °C. The results show that some desorbed species are obtained from the HiPco SWCNTs, such as m/e=18, 28, 41, 44, and 57 amu, during heating from 40 °C to 500 °C. The desorption spectra show that the temperature at which maximum desorption amount occurred is about 240 °C (see Fig. 2a). The amounts of desorbed species are noticeably decreased by heating to 500 °C (see Fig. 2b). Fig. 2c shows no obvious desorption signal after isothermal heat treatment at 500 °C for 1 hour. Thus, the pre-treatment of SWCNTs of the each TPD test at 500 °C for 2 hours is required to clean completely the surface of the adsorbent.

3.2. Measurements of the gas-desorption properties of SWCNTs

Figs. 3a-3c plot the TPD profiles of O_2, N_2 and Ar, respectively, at various heating rates (β). Since desorption is a thermal activation process, a larger β corresponds to a higher temperature (T_m) at which the maximum intensity occurs; while the intensities can be considered as desorption rates during TPD heating. In this study, the desorption activation energies (E_d) are determined from these TPD results. It has been discussed in detail elsewhere that the relationship between T_m and E_d for a uniform surface may be expressed in the following relationship [17], $\ln(T_m^2/\beta) = E_d/RT_m$, where R is the universal gas constant; T_m is measured at β between 10 and 30 °C/min. Hence, E_d can be determined from the slopes of the plots of $\ln(T_m^2/\beta)$ against $1/T_m$, as plotted in the insets of Figs. 3a-3c.

Interesting results can be found from comparing E_d of gas desorption obtained from the TPD data (Table 1), with the q_{st} values from references [12,15] (Table 2). The E_d values shown in Table 1 for O_2, N_2, and Ar on the SWCNTs are 209, 192, 188 meV, respectively. Table 2 indicates the results on q_{st} measure by B. J. Wei *et al.* [12] for O_2, N_2, and Ar

Table 1. Temperatures of maximum desorption rate and desorption activation energies of O_2, N_2, and Ar from HiPco SWCNTs at various heating rates.

Adsorbate	*Heating rate* β (°C/min)	*Temperature of maximum desorption rate* T_m (°C)	*Activation energy of desorption* E_d (meV)
O_2	10	107	209
	20	129	
	30	162	
N_2	10	93	192
	20	136	
	30	143	
Ar	10	91	188
	20	133	
	30	143	

on HiPco SWCNTs as approximately 210, 203 and 197 meV, respectively. These values are very close to those obtained using pulsed-laser vaporized SWCNTs by D. H. Yoo *et al.* [15]; the authors determined q_{st} values for N_2 and Ar to be 183 and 180 meV, respectively,

With respect to the potential energy of adsorbate molecules, the relationship between E_d, q_{st}, and E_a is $E_d = q_{st} + E_a$ [18], where E_a is the activation energy of adsorption. E_a represents the activation energy of chemical adsorption of a gas molecule onto an adsorbent, while E_a is less for physical adsorption. Tables 1 and 2 reveal that the values of q_{st} are very close to those of E_d measured by TPD, resulting in E_a values less than 11 meV. E_a values are low indicating that O_2, N_2, and Ar gases are physically adsorbed on SWCNTs. This is consistent with the results of J. Zhao *et al.* [19]. Our results also resemble those of A. C. Dillon *et al.* [13], they showed that E_d is equivalent to q_{st} for H_2 that physically adsorbs on SWCNTs.

Table 2. Comparison of isosteric adsorption heats of O_2, N_2, and Ar on SWCNTs.

Adsorbent	*Isosteric heat of adsorption* q_{st} (meV)		
	O_2	N_2	Ar
HiPco SWCNTs [12]	210	203	197
Pulsed-laser vaporization SWCNTs [15]	–	183	180

4. CONCLUSION

This study has demonstrated that the TPD method provides a simple and elegant method for measuring desorption properties of O_2, N_2, and Ar on SWCNT bundles. The temperatures (T_m) at maximum desorption rates are determined for different gases using the TPD desorption spectra. The results of T_m are used to calculate the E_d of each gas.

The TPD results show that the T_m values of O_2, N_2, and Ar for SWCNTs are all below 200 °C. Moreover, the E_d values of O_2, N_2, and Ar for SWCNTs are 209, 192 and 188 meV, respectively. The E_d values are very close to their isosteric heats of adsorption (q_{st}). These results imply the physical adsorption behavior of these gases on SWCNTs below 200 °C.

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