

Studies on the Adsorption of Organic Materials Inside Thick Carbon Nanotubes

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We clarified the adsorption sites inside the single-wall carbon nanohorns (SWNHs), a type of single-wall carbon nanotubes having thick diameters of 2–5 nm, through the thermogravimetric analysis of the desorption of xylene and benzene from SWNHs. The influence of the sizes of holes piercing through the SWNH walls was also examined. Three types of adsorption sites were found inside the SWNH tubes, which were assigned to the tube tips, the sidewalls, and central regions of the hollow spaces. The experimental results also suggested that the adsorbed xylene and benzene were stabilized mainly by weak self-interactions at the central regions and their quick desorption was caused by the weak self-interactions.

Introduction

The single-wall carbon nanohorn (SWNH) is a type of single-wall carbon nanotube (SWNT). SWNHs are horn-shaped with large diameters of 2–5 nm, and they form spherical aggregates with diameters of 80–100 nm (Figure 1, bottom panels).¹ The tube walls of the SWNHs have defects at the tips and kinks where holes can be opened by local combustion at high temperatures between 350 and 600 °C.^{2,3} These holes let various molecules and particles enter the SWNH tubules.^{2–9} Methods of incorporation at room temperature in the liquid phase have been established by our group,¹⁰ and potential applications for material storage extend to various fields, including drug delivery systems.¹¹ The storage of materials inside SWNHs has been achieved with size selectivity,² site selectivity,^{2,6,8} and affinity selectivity.¹⁰ These selective actions depend on the hole diameters² and chemical groups at the hole edges.¹² For practical use, the stored materials must be released in a controlled manner.¹¹ To achieve this, it is necessary to study and understand the storage states, for example, how strongly the stored materials are bound to the graphene walls of the SWNHs.

In this report, we compare the desorption of xylene and benzene from SWNHs whose structures were changed step-by-step through localized combustion of the defect sites.

Experimental Section

Aggregates of the SWNHs having a dahlia-like morphology were obtained by CO₂ laser ablation of graphite in a 760-Torr Ar atmosphere at room temperature.¹ They were formed without using metal catalysts. The purity of the SWNHs was approximately 85%. The 15% of impurities consisted of particles of amorphous carbon, bud-type aggregates of SWNHs, graphitelike particles, and a small amount of fullerenes.¹⁴ To remove the fullerenes, we heat-treated the SWNHs in a vacuum (1×10^{-5} Torr) at 1200 °C for 2 h.

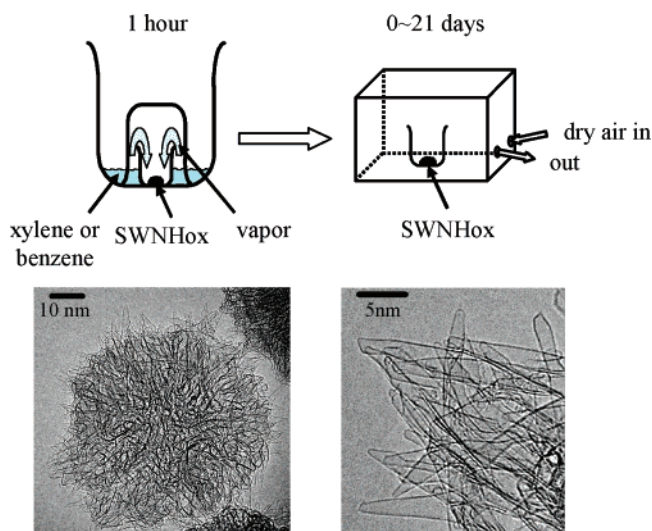


Figure 1. Schematic drawings of adsorption and desorption methods (top) and transmission spectroscopic images of SWNHs (bottom).

Holes were pierced through SWNH tubule walls made of single-graphene sheets by means of local combustion in hot oxygen gas.^{2,3} The temperature of the oxygen gas was between 350 and 620 °C, and the combustion duration was 10 min.

We investigated the adsorption of benzene and *m*-xylene by the SWNHs and by the SWNHs with holes (SWNHox) by exposing them to benzene vapor (benzene/SWNHox) or xylene vapor (xylene/SWNHox) for 1 h in closed containers (Figure 1, top panels). To determine the weight-loss profile resulting from the desorption of benzene or xylene from SWNHox as the temperature was increased (5 °C/min), we placed approximately 1 mg of benzene/SWNHox or xylene/SWNHox on a Pt pan set in a thermogravimetric (TG) analysis system where He gas flowed at a rate of 100 mL/min. Before starting the heating, we ensured that the gas flow was steady by allowing He gas to flow for approximately 30 min. To clarify the adsorption stability, benzene/SWNHox ($T_{\text{ox}} = 450$ °C) and xylene/SWNHox ($T_{\text{ox}} = 550$ °C) were placed in a dry-air flow for 1–21 days before the measurement in He.

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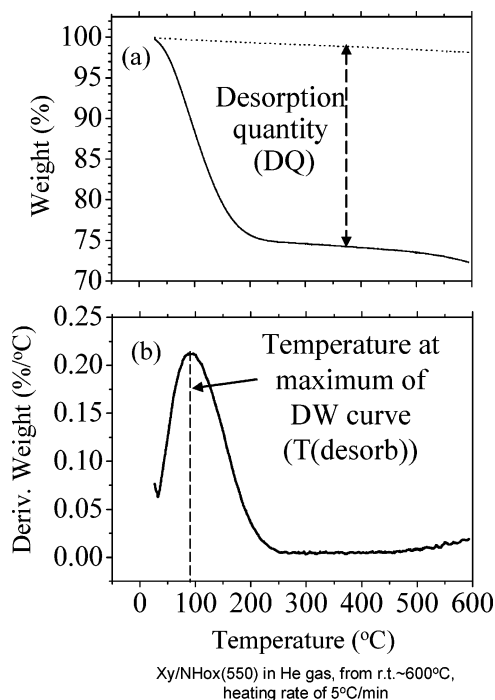


Figure 2. Thermogravimetric analysis of xylene/SWNHox. (a) The weight of xylene/SWNHox in O_2 decreased as the temperature increased. The weight loss at approximately 300 °C (DQ) corresponded to the quantity of xylene desorbed from SWNHox. (b) The derivative curves of weight changes (DW) have maxima at the temperatures of $T(\text{desorb})$. Period(air) was 0 days for part a experiments. SWNHox was prepared by local combustion of defects in O_2 at 550 °C. The dotted curve in part a indicates the baseline.

Results

Desorption of Xylene from SWNHox. The desorption of xylene was monitored by weighing the specimens. Typical results are shown in Figure 2. We defined the desorption quantity (DQ) and desorption temperature ($T(\text{desorb})$), which is the maximum temperature obtained by differentiating the weight–temperature curve (DW) with respect to temperature (Figure 2b). In this figure, DQ was approximately 25%, and $T(\text{desorb})$ was about 85 °C.

The desorption of xylene from the SWNHox changed greatly with the local-combustion temperature T_{ox} (Figure 3a). The DW profiles were asymmetrical (Figure 4), suggesting that the desorption mechanism was not simple. To make it easier to understand this complex desorption process, we show deconvoluted DW curves below.

From the deconvolution of DW profiles of xylene/SWNHox, we found three peaks (X, Y, and Z) in Figure 4. Interestingly, peak Z was small and disappeared at and above $T_{\text{ox}} = 580$ °C. The validity of the deconvolution was confirmed by the good agreement between the experimental DW curves (black lines) and the summations of the deconvoluted peaks (red lines). The $T(\text{desorb})$, full width at half-maximum (fwhm), and area under the peaks obtained from Figure 4 were plotted against T_{ox} (Figure 5a). Here “quantity” indicates the quantity of desorbed xylene per 100 g of SWNHox, which was calculated from the areas in Figure 4.

Although no special changes appeared in the quantity and temperature of xylene desorption when xylene/SWNHox samples were left in flowing dry air for certain periods (period(air)) (Figure 3b), curious behaviors were revealed by the deconvolution of the DW profiles (Figure 5b). The changes in peaks Y and Z were reasonable (Figure 5b). However, the $T(\text{desorb})$ and

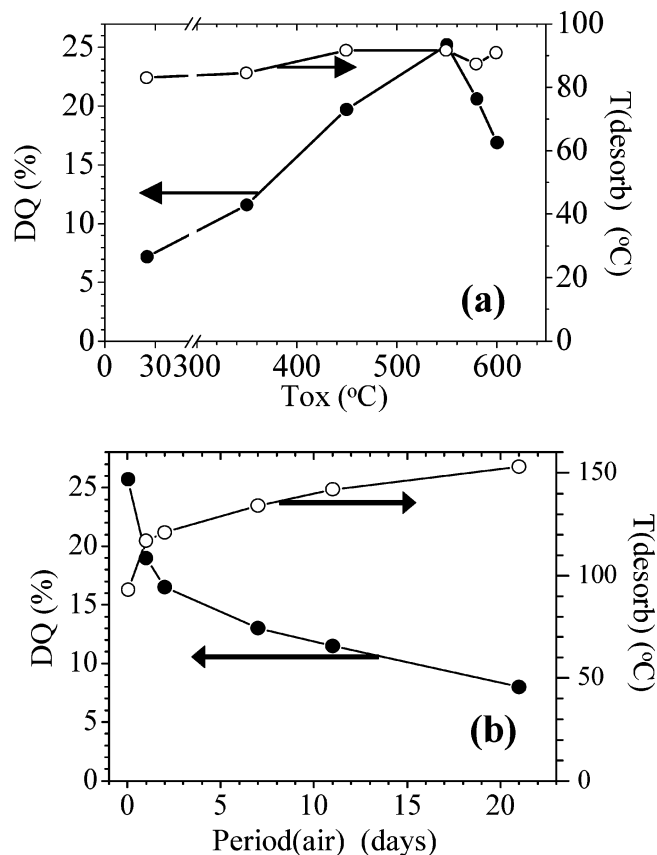


Figure 3. $T(\text{desorb})$ and DQ of xylene/SWNHox versus (a) defect combustion temperature (T_{ox}) and (b) the time spent in flowing dry air (Period(air)).

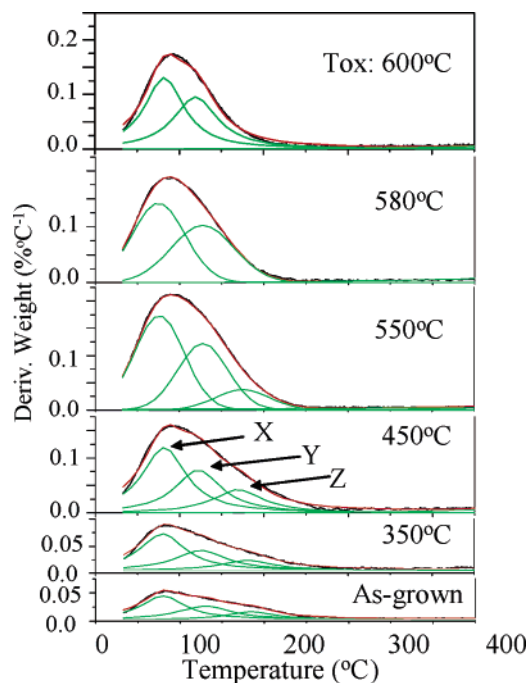


Figure 4. Derivative curves of weight–temperature (DW) profiles of xylene/SWNHox deconvoluted into three components (green curves): X, Y, and Z. Experimental curves (black) fit well with the summation (red) of the deconvoluted peaks.

fwhm of peak X varied with period(air), and peak X disappeared (i.e., its quantity became zero) in a short period(air) of 11 days (Figure 5b). These results may indicate that adsorption sites corresponding to peak X had small adsorption energies that were

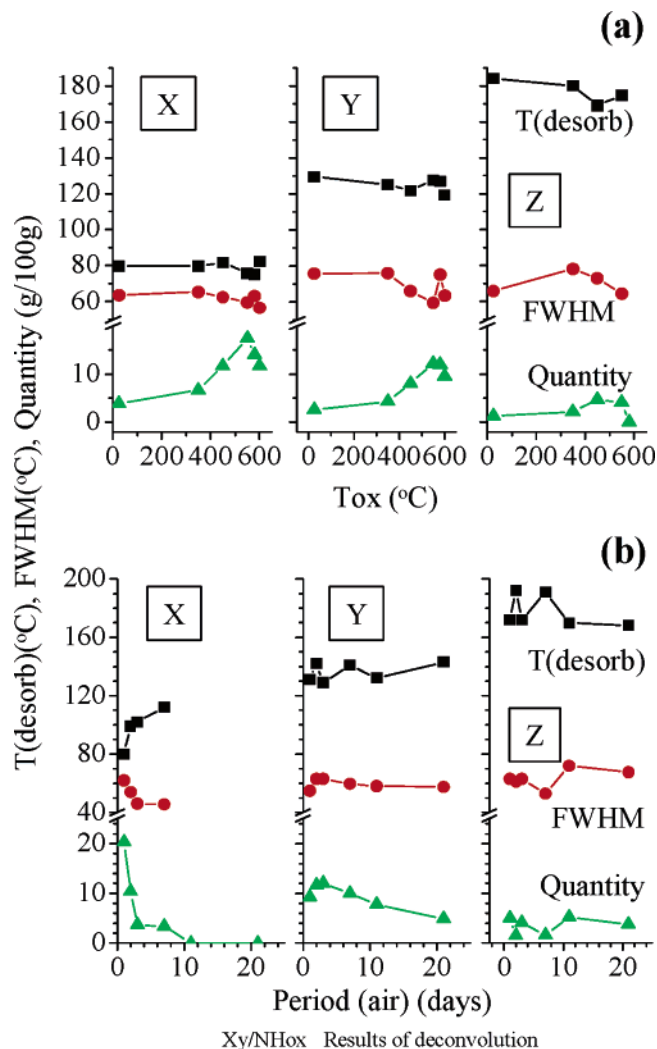


Figure 5. $T(\text{desorb})$, full width at half-maximum (fwhm), and quantity of X, Y, and Z peaks as functions of (a) T_{ox} and (b) period(air). Here, period(air) was 0 days for the part a experiments. SWNHox used in the part b experiments was prepared by defect combustion in O_2 at 450°C .

spread over a wide energy range. However, adsorption sites corresponding to peaks Y and Z had energetically distinct adsorption sites.

Desorption of Benzene from Benzene/SWNHox. Similar measurements and analyses were carried out for benzene/SWNHox (Figures 6 and 7). The differences between benzene/SWNHox and xylene/SWNHox were clarified through deconvolution of the DW profiles. Only two peaks appeared for benzene/SWNHox, one large peak (Y) and a rather small peak (Z) (Figure 7). The changes in these peaks with T_{ox} (Figure 7a) were similar to those of peaks Y and Z of xylene/SWNHox (Figure 5a). However, $T(\text{desorb})$ changed for Y and Z, and even fwhm changed for Z, when the samples were left in air (Figure 7b). This means that benzene molecules were weakly adsorbed and the adsorption energy was spread over a wide range; in other words, the density of adsorption sites as a function of adsorption energy had smaller peaks at lower temperatures for benzene than for xylene.

Changes in DQ and $T(\text{desorb})$ with T_{ox} and period(air) for benzene/SWNHox (Figure 6) showed the same tendencies as those of xylene/SWNHox (Figure 3) but with smaller values of DQ and $T(\text{desorb})$.

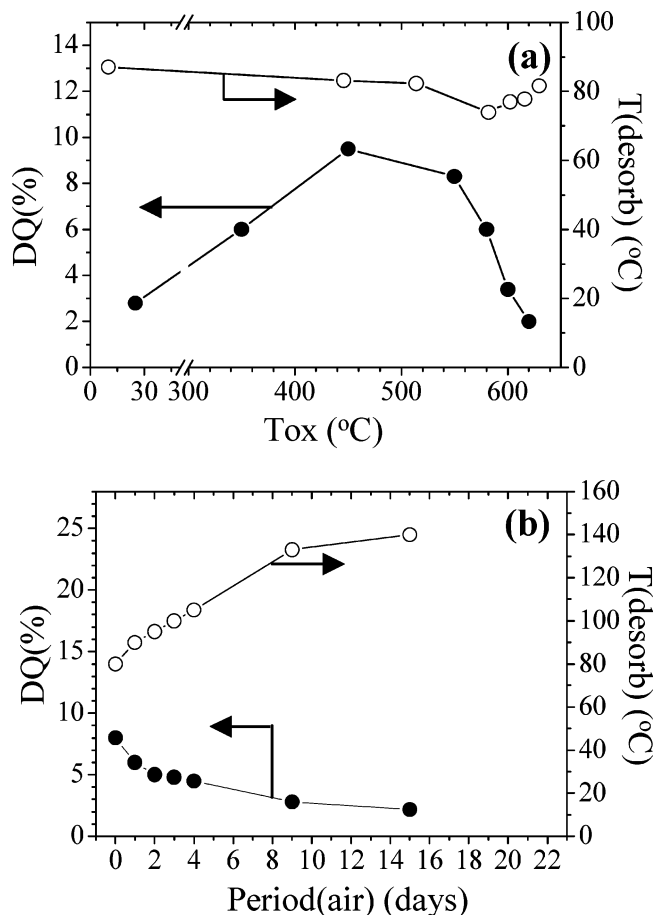


Figure 6. $T(\text{desorb})$ and DQ of benzene/SWNHox versus (a) T_{ox} and (b) the time spent in flowing dry air.

Discussion

Judging from the SWNH shapes¹ and from earlier studies,¹⁴ we believe there are three adsorption sites inside the SWNHs. The energetically deepest sites are on the inside walls at the tips and convex parts whose large curvatures led to greater contact areas with adsorbed molecules. In reference to our previous study, the second deepest sites are on the other parts of the wall surfaces away from the tips and convex parts, and the energetically shallowest sites are in the central region of the hollow spaces inside the SWNHs. The latter two sites were found in our previous study of nitrogen adsorption by SWNHs.¹⁴

The adsorption quantity (in moles) and $T(\text{desorb})$ of xylene and benzene were similar at sites Y and Z, as shown in Table 1. We think that site Z corresponds to the inside walls at tips and convex parts, because its $T(\text{desorb})$ is the highest (Figures 5 and 7). The actual loss of tips and convexes (i.e., hole opening) caused by combustion at approximately 570°C has been observed with a transmission electron microscope.⁶

It was not easy to find site Z through a gas-adsorption study. As a matter of fact, the loss of site Z (i.e., tips and convex parts of the SWNHs) could barely be detected by measurements of nitrogen adsorption at 77 K ; only a small decrease in the adsorption was seen at a pressure ratio P/P_0 of 10^{-4} to 10^{-5} (P , N_2 pressure; P_0 , 760 Torr) when SWNHox was treated at $T_{\text{ox}} > 500^\circ\text{C}$, meaning that micropores with diameters of 1 nm or less were lost. This subtle change might correspond to the loss of site Z, but the evidence is not clear.

We assigned site Y to the inside surface of the SWNH walls, except where site Z was assigned (at the tips and convex parts).

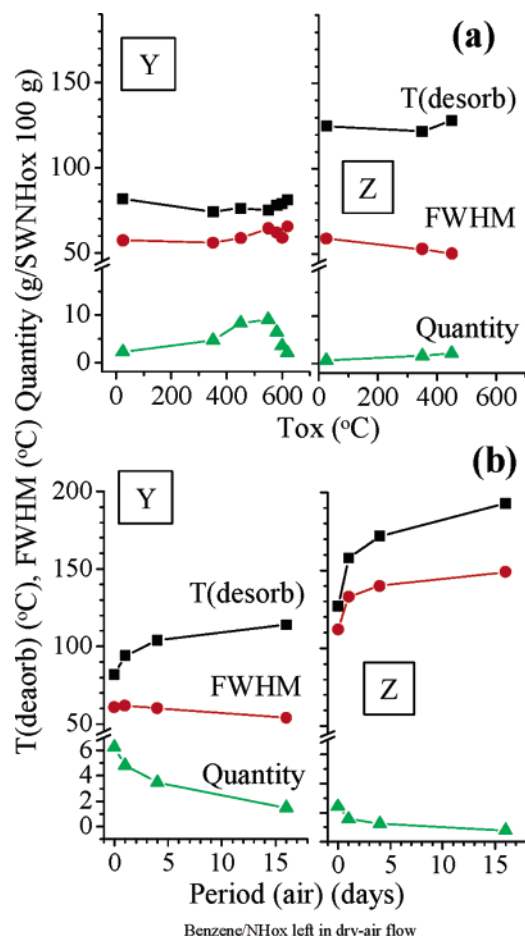


Figure 7. $T(\text{desorb})$, full width at half-maximum (fwhm), and quantity of peaks Y and Z versus (a) T_{ox} and (b) period(air).

TABLE 1: Desorption Quantities and Temperatures for Three Sites X, Y, and Z, Estimated from TG Profiles of Xylene/SWNHox and Benzene/SWNHox through Deconvolutions

sites		X	Y	Z
xylene/ SWNHox	desorption quantity (mol/SWNHox(100 g))	0.17	0.11	0.046
	desorption temp (°C)	75	120	170
benzene/ SWNHox	desorption quantity (mol/SWNHox(100 g))	not detected	0.12	0.026
	desorption temp (°C)	not detected	80–110	130–190

This assignment should be correct because the results presented in Figures 5a and 7a verified two assumptions made for the assignment, (1) the adsorption/desorption quantity at site Y must be considerably larger than that at site Z, and (2) the desorption temperature at site Y should be lower than that at site Z because the contact area between xylene or benzene and the SWNH walls at site Y is smaller than that at site Z.

$T(\text{desorb})$ from sites Y and Z did not change with the time the sample was left in air (Figure 5b) in xylene desorption but increased in the case of benzene desorption (Figure 7b). The interaction between benzene and the SWNH walls was probably weak enough to differentiate the subtle structure change of the surface of the inside walls. Xylene would be expected to interact with the SWNH walls more strongly because its electrical polarizability is at least 20% higher than that of benzene.¹⁵

The differences between xylene and benzene were more explicitly revealed at site X, which was found in xylene/SWNHox (Figure 5) but not observed in benzene/SWNHox

(Figure 7). This suggests that xylene and benzene were not bound to the SWNH walls. That is to say that the adsorption/desorption at site X was mainly controlled by self-interaction among the xylene or benzene molecules rather than by the interaction with SWNH walls. We assigned site X to the central region of the inner hollow space.¹⁴

Xylene desorption from site X was unique, exhibiting the largest quantity (Table 1), swift desorption (Figure 5b), and changes in $T(\text{desorb})$ with period(air) (Figure 5b). These observations suggest that the area/volume of site X was larger than those of sites Y and Z and that the xylene–xylene interaction was weaker than the interaction between xylene and SWNH walls. We think that the reason we did not observe benzene desorption from site X was that its desorption finished during the 30-min wait for steady He flow conditions before we began the TG measurements.

We previously reported that an antiinflammatory glucocorticoid, dexamethasone (DEX), was incorporated into SWNHox. The incorporated DEX was released, and its biological function was confirmed using biological cells.¹¹ The DEX release from SWNHox was interesting, exhibiting both slow and fast processes. We think that the fast process corresponded to the release from site X and the slow process to release from site Y. Here, SWNHox did not have site Z, because the SWNHs were locally combusted at 580 °C. For drug delivery, slow release is preferable, so the fast release from site X should be suppressed. It should be possible to obtain sustained release of DEX from site X by increasing the stability of DEX, for example, by incorporating molecules that associate with DEX. We are currently studying the effect of incorporation and will report our results elsewhere soon.

Conclusion

We could easily identify three adsorption sites inside SWNHs by observing the desorption processes of organic materials with conventional thermogravimetric measurement systems and using the results to control the structure of SWNHs, i.e., by removing defect sites step-by-step through heat treatment in oxygen gas. The deepest sites were on the inside surface of the walls at tips and convex parts, the second deepest sites were on other wall surface regions, and the shallowest sites were in the central region of the hollow space inside the SWNHs. Comparing the desorption of benzene and *m*-xylene, we found that they were bound to the SWNH walls at the first and second deepest sites, but they condensed through self-interaction at the shallowest site.

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