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Methane Adsorption on Planar WS_2 and on WS_2-Fullerene and -Nanotube Containing Samples

E.B. MACKIE
Department of Physics, Southern Illinois University, Carbondale, IL 62901, USA

D.H. GALVAN
Centro de Ciencias de la Materia Condensada-UNAM, Apartado Postal 2681, C.P. 22800, Ensenada, B. Mexico

A.D. MIGONE
Department of Physics, Southern Illinois University, Carbondale, IL 62901, USA

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Abstract. Adsorption-desorption cycles were measured for methane on non-irradiated WS_2, and on irradiated WS_2 (which contained, in part, WS_2 fullerenes and nanotubes). Both types of samples were further subdivided into three sets: one set received no further treatment, another set was heated under vacuum, and the last set was acid-treated and heated. The specific surface area was determined for each set; so was the presence or absence of a hysteresis loop in the adsorption-desorption cycles. The results of these two groups of measurements were correlated with the space available for adsorption. The implications of the results for the experimental determination of the dimensionality of gas adsorbed at the interior of nanotubes are discussed.

Keywords: adsorption, WS_2, nanotubes and fullerenes

Introduction

Nanotubes have very large aspect ratios: their diameters are several orders of magnitude smaller than their lengths (Ajayan and Ebbesen, 1997; Ijima, 1991). The nanotubes' centers are hollow. The ends of the tubes are capped by atoms having a different symmetry from those in the walls of the tubes (Ajayan and Ebbesen, 1997). The caps can be opened using specific treatments (Dillon et al., 1997; Tsang et al., 1993, 1994). Open-ended nanotubes offer a unique environment for adsorption.

Physical adsorption on planar substrates has long been used to produce effectively two-dimensional systems. Nanotubes used as substrates can, potentially, provide physical realizations of one-dimensional systems. Gas/nanotube systems, thus, have considerable fundamental appeal. Adsorption phenomena on nanotubes are of interest from a practical perspective, as well. Several possible applications have been suggested (e.g. using nanotubes for gas storage at room temperature (Dillon et al., 1997), a possibility that could make economically feasible the use of hydrogen to power automotive vehicles).

Aside from graphite and carbon, nanotubes have been produced from BN (Chopra et al., 1995), WS_2 (Tenne et al., 1992; Margulis et al., 1996; Galvan et al., 1998; Tenne, 1999), and MoS_2 (Margulis et al., 1993). All these materials have in common a bulk structure consisting of layers with strong interlayer couplings and weak intralayer bonds (Tenne, 1999). While production of carbon nanotubes generally requires extreme

environments (e.g., very high temperatures), it has been reported that WS_2 fullerenes (Margulis et al., 1999) can form under much milder conditions.

We present the results of an adsorption-desorption isotherm study of CH_4 on differently treated WS_2 substrates. Two main groups of WS_2 samples were used in the study: irradiated WS_2 samples (which are known to contain fullerenes and nanotubes) (Tenne et al., 1992; Galvan et al., 1998); and non-irradiated samples of WS_2. Each one of these two main groups of WS_2 samples were, in turn, subdivided into three sets which received different activation treatments (heating, and, acid treatment plus heating).

While the adsorption study on the unirradiated, untreated WS_2 samples was undertaken in order to provide a standard against which to compare results on samples which had undergone irradiation and treatment, the results are of interest in themselves. The isotherms show steps (see Figs. 1(a) and 2(a)). Step-wise isotherms are characteristic of high quality, smooth, homogeneous substrates. We are aware of no other reports in the literature of adsorption studies on planar WS_2.

Our aim in conducting the heating, and, acid plus heating activation treatments was to determine if either approach would result in the uncapping of the portion of tubes present in the irradiated sample. However, very recent TEM studies described elsewhere, have shown that the acid plus heating treatment used here resulted in the production of tubes on unirradiated samples (Mackie et al., 2000). As a consequence, the only sample that can be considered free from fullerenes and nanotubes is the un-irradiated, un-treated one.

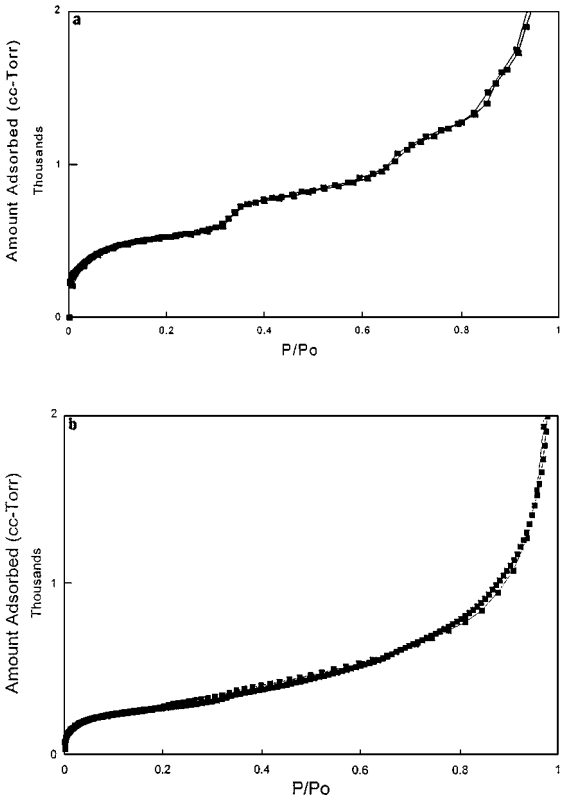

Figure 1. Adsorption-desorption cycles measured on samples of: (a) non-irradiated; and (b) irradiated material. The measurements were conducted at 88 K. The steps visible in the data, especially in 1(a) correspond to the successive formation of layers on the planar substrate. The amount of gas adsorbed is plotted in the Y-axis (in cc-Torr at 273 K, with 1 cc-Torr $= 3.54 \times 10^{16}$ molecules) as a function of the reduced pressure (the pressure scaled by the saturated vapor pressure). Note that the same choice of axes is made for the remaining figures. There is no hysteresis in the un-irradiated sample (1(a)), while there is a small amount of hysteresis on the irradiated sample (1(b)).

Samples

The structure of WS_2 and MoS_2 has a metal plane sandwiched between two S planes. These trilayer sandwiches are stacked in ABAB..... sequence (Wyckoff, 1963). The bonding between the metal and S planes is through strong covalent bonds, while adjacent S planes are held together by weaker van der Waals forces.

All the WS_2 samples used were obtained from Johnson Matthey. The irradiated samples were prepared by the group of Prof. Galvan in UNAM, La Ensenada. The WS_2 was subjected to electron beam irradiation from a van der Graaff generator (Galvan et al., 1998). The irradiation process was conducted under the following conditions: 1.3 MeV voltage, 5 microAmps, and a dose rate of 25 kGy/min.

The irradiated as well as the non-irradiated WS_2 samples were separated into three different sets. One set was used in as-received condition, without subjecting it to any further treatment (other than evacuation to a pressure of 1×10^{-6} Torr or lower, prior to the performance of the measurements). Of the other two sets, one was heated under vacuum to 700°C prior to utilization. The other set was soaked in nitric acid, filtered, rinsed, and then heated under moderate vacuum to 100°C prior to utilization.

Irradiation results in a number of structures appearing on the previously planar WS_2. Besides nanotubes, regions containing onion-like and worm-like structures are present in the irradiated samples (Galvan et al., 1998).

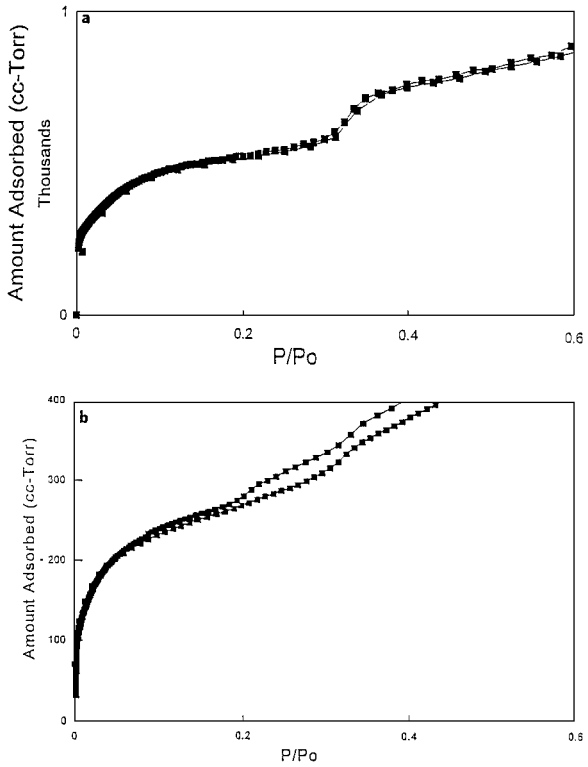

Figure 2. Expanded view of the data presented in Fig. 1 for a coverage region which corresponds to the first two layers; (a) non-irradiated; and (b) irradiated WS_2. The presence of a hysteresis loop in the irradiated sample (2(b)) is manifested clearly by the non-overlap of the adsorption (lower coverage) and desorption (higher coverage) data, and by the presence of an additional step in the desorption data which has no counterpart in adsorption.

Apparatus

Adsorption-desorption isotherms were measured in an in-house built automated apparatus (Shrestha et al., 1994). Low temperatures were attained with a ^{4}He closed-cycle refrigerator. The sample cell temperature was regulated with a two-stage temperature control set-up to within ± 0.005 K of the selected value throughout the adsorption-desorption cycle.

The gas handling system consists of computer-controlled valves, calibrated volumes, capacitance manometers, and a pumping station. The computer-controlled valves admit a pre-set amount of gas into the gas-handling system using a small dosing volume (approximately 0.5 cc). Gas is subsequently admitted into the sample cell by another electro-pneumatic valve. The gas to be admitted into the gas-handling system is stored in a low-pressure gas reservoir; the pressure in this reservoir (and the small $\sim$0.5 cc dosing volume) determine the minimum dose size (Shrestha et al., 1994). MKS Baratron capacitance manometers, with ranges of 1,10 and 100 Torr, were used for pressure measurement. In our setup we have a coverage resolution, in each individual dose, of better than 0.04 micromoles when using the 10 Torr gauge.

Results

We studied the adsorption of CH_4 on the different types of WS_2 substrates discussed above (activated as well as non-activated samples of both, irradiated and non-). The measurements were done at 88.0 and 90.5 K, in the vicinity of the bulk triple point of the adsorbate. For each one of the samples used we determined the specific surface area. We also established the presence or absence of a hysteresis loop in the adsorption-desorption cycles. In a companion study (Mackie et al., 2000), several of the samples investigated here were also examined by HRTEM.

The specific surface areas were determined from the BET equation as well as from the point B method (Gregg and Sing, 1982); both yield consistent results. The activation process can alter the surface of the sample in a number of ways, resulting in changes in the specific area. In the case of non-irradiated WS_2, it may create holes or defects; or, as we have recently found and report elsewhere (Mackie et al., 2000), it may result in the formation of tubes. For the samples where tubes are already present prior to activation (the case for the irradiated WS_2) the activation process can result in the opening of the capped ends of the tubes. When activation results in the uncapping of the tubes' ends, changes in the specific surface areas can be correlated to the surface area made available for adsorption at the interior of the tubes as a result of the treatment.

The adsorption-desorption isothermal cycles were undertaken in an attempt to determine experimentally the dimensionality of the gas adsorbed on the samples. The presence of a hysteresis loop in the adsorption-desorption data is a manifestation of capillary condensation (Gregg and Sing, 1982; Lowell and Shields, 1991). Capillary condensation is the formation of a condensed bulk phase, either solid or liquid, at pressures below the equilibrium saturated vapor pressure on pores and non-planar regions on the substrate (if there are nanotubes with open ends, it is possible for capillary condensation to occur in the hollow center of the tube).

Table 1. Surface area and hysteresis comparison of WS_2.

	Irradiated	Non-irradiated
As produced	2.76 m^2/g	1.59 m^2/g
	Small hysteresis	No hysteresis
Heated to 700°C	3.05 m^2/g	2.66 m^2/g
	Large hysteresis	Small hysteresis
Nitric acid + Heat	1.73 m^2/g	1.39 m^2/g
	Large hysteresis	Small hysteresis

Table summarizes the results of our measurements. The columns correspond to results on irradiated and non-irradiated samples. Each row corresponds to additional activation treatment applied to the samples. For each entry, i.e. for each combination of treatments, we provide the specific surface area and information on the presence and size of hysteresis loops in adsorption-desorption data.

Capillary condensation is a 3-D phenomenon. The presence of hysteresis loops in adsorption-desorption data in an open nanotube substrate would indicate that the material adsorbed in the interior of the tubes is behaving three-dimensionally. The hysteresis, however, may originate in pores or defects on the outer surfaces of the tubes, not just at the interior of open-ended tubes, so that its presence cannot, by itself, rule out 1-D behavior at the interior of the tube. To try to determine whether the hysteresis in the adsorption-desorption data originated at the interior or the exterior of the tubes, we compared isothermal cycles measured on samples subjected to different treatments.

Table 1 presents a summary of our observations. The differences in the data obtained on samples subjected to the various treatments are evident in these results.

The as-received sample, not subjected to any treatments, was studied as a standard against which to compare the effects of the various activation treatments on the WS_2. The as-received WS_2 has a specific surface area of 1.59 m^2/g (all specific surface areas reported were obtained from the BET equation). The adsorption-desorption data shows no evidence of the presence of a hysteresis loop. The mass of the sample used was 1.4 grams. For a planar substrate, as is the case for the non-irradiated WS_2 in its as-received condition, the absence of a hysteresis loop is an indication that there are no pores present in the substrate. Data corresponding to this sample is given in Figs. 1(a) and 2(a).

The steps present in Fig. 1(a) correspond to the formation of successive layers of methane on the planar WS_2 substrate. A step-wise adsorption isotherm is clear indication that the substrate is of high quality; steps occur on substrates with sufficiently large crystallites, and, a high degree of adsorption energy homogeneity.

Figure 2(a) shows in greater detail the adsorption desorption data measured in a coverage region corresponding to the first two layers on the substrate. There is excellent overlap between the adsorption and desorption branches, confirming the absence of hysteresis. TEM micrographs found the planar structure of this WS_2 sample unaltered.

Data for the irradiated sample which was subjected to no additional post-production treatments is displayed in Figs. 1(b) and 2(b). The specific surface area for this sample is larger, 2.76 m^2/g. A small hysteresis loop is present in the adsorption-desorption data for this sample. The mass of the sample used was 0.43 grams. The hysteresis loop is barely visible in Fig. 1(b). In the expanded view of the data presented in Fig. 2(b), however, this feature can be resolved. A characteristic signature of a hysteresis loop is the presence of an additional step in the desorption data (Gregg and Sing, 1982). This additional step can be seen at a relative pressure $\sim$0.2 in Fig. 2(b).

Since this sample was subjected to no additional treatment beyond irradiation, and since the TEM photographs show no evidence of uncapping of the fullerenes present on the sample, the most likely explanation is that the hysteresis loop in data is the results of the introduction of defects on the WS_2 during the irradiation.

The behavior of films adsorbed on irradiated and on non-irradiated samples which were subjected to heat treatment under vacuum at 700°C is displayed in Figs. 3 and 4. Data for both groups shows an increase in specific surface area (a modest fractional increase, to 3.05 m^2/g for an irradiated for a 1.7 gram sample; and, a much larger fractional increase to 2.66 m^2/g for a 0.41 gram non-irradiated sample). The size of the hysteresis loop in the adsorption-desorption data depends on whether the sample had been irradiated or not. There is a very noticeable hysteresis loop in the data measured on the heated, irradiated sample (Figs. 3(b) and 4(b)). By contrast, there is only a small hysteresis loop in the heated, non-irradiated sample (Figs. 3(a) and 4(a)).

The adsorption-desorption results obtained in the un-irradiated heated samples (Fig. 4(a)) are very similar to the hysteresis loops obtained on the un-heated irradiated sample (Fig. 2(b)). This suggests that the capillary condensation present in both substrates originates from the same type of structures. Since the nanotubes which are present in the un-irradiated heated sample

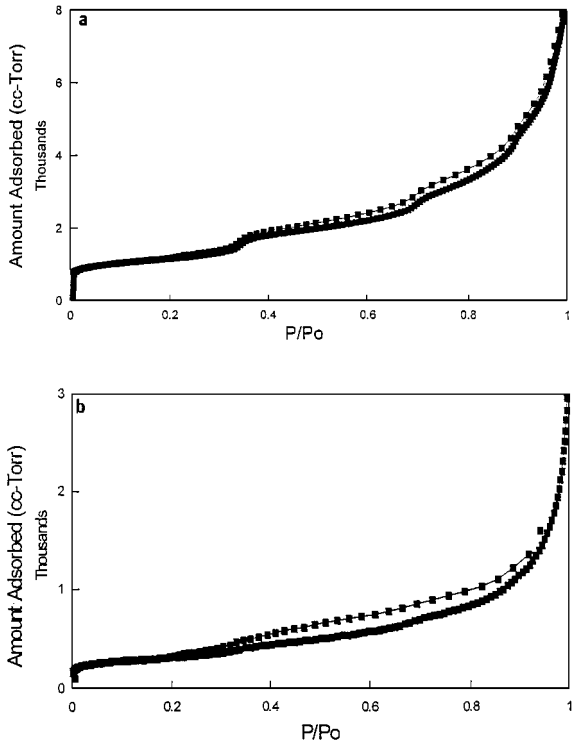

Figure 3. Adsorption-desorption data measured on WS_2 samples, after heating under vacuum to 700°C; (a) non-irradiated; and (b) irradiated WS_2. A much more noticeable hysteresis loop is visible in the data for the irradiated sample (3(b)). A smaller hysteresis loop is present in the data for the non-irradiated sample (3(a)). The hysteresis loop for the non-irradiated samples (3(a)) is comparable to that displayed for the irradiated, non-heated, substrate (Fig. 1(b)). The adsorption-desorption cycle presented was measured at 88.0 K.

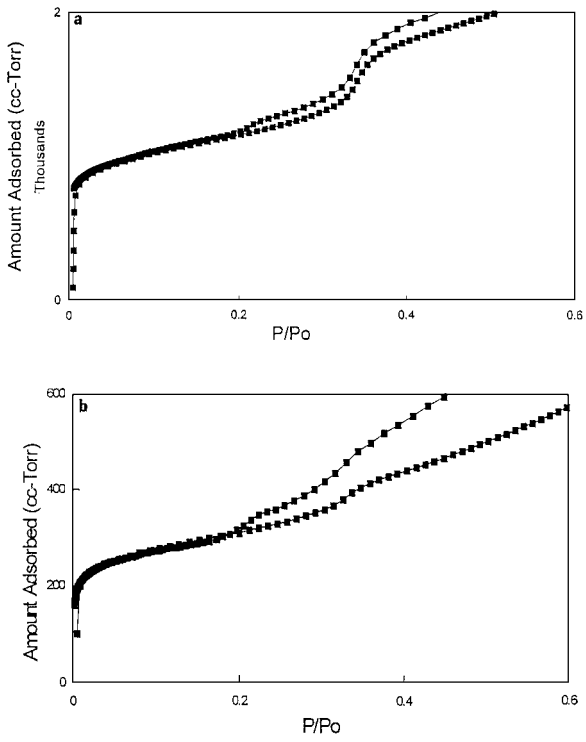

Figure 4. Expanded view of the data presented in Fig. 3 corresponding to coverages in the first two layers. As before, (a) corresponds to non-irradiated, while corresponds (b) irradiated material. Additional steps on desorption are visible in both sets of data. The hysteresis loop in 4(b) is clearly larger.

are capped, we speculate that the capillary condensation in both cases is taking place on defects and pores in the outer surface of the tubes.

The hysteresis loops are larger for the irradiated and heated sample (see Figs. 3(b) and 4(b)), than for either of the two cases discussed in the previous paragraph (unheated-treated and untreated heated). We conclude that in this case there were additional capillary condensation sites made available as a result of the treatment. It is reasonable to interpret the presence of a much larger hysteresis loop on data for this sample as resulting from adsorption occurring inside the tubes. The additional adsorption surface area is made available by the open-ended tubes resulting from heating the irradiated WS_2. This interpretation is supported by some TEM evidence, as well.

Our interpretation suggests that the behavior of the adsorbed gas inside of the nanotubes is not 1D-like. We note that differences in the effective dimensionality of matter adsorbed at the interior of a nanotube as a function of the nanotube's diameter has been observed in computer simulations for Ar and N_2 on 5.4 and 1.3 nm diameter carbon nanotubes (Maddox and Gubbins, 1995). A hysteresis loop was present in the simulated adsorption-desorption data for larger diameter tubes (i.e., matter in this tube displayed 3D behavior), while none was present in the simulated data for the smaller diameter tubes (l-D behavior) (Maddox and Gubbins, 1995). We note that some of the tubes present in this sample were found, in the TEM study, to have diameters well in excess of 10 nm.

An estimate of the degree of reproducibility of the adsorption/desorption data can be obtained by comparing adsorption to desorption data in the lower pressure region, below $P/P_0 = 0.2$ (i.e. below where the desorption data has the additional step). As can be seen in Figs. 2 and 4, the data fail to overlap by a coverage amount on the order of 1 micromole.

We have also studied the behavior of both the irradiated and non-irradiated WS_2 subjected to an activation which consisted of soaking in nitric acid, filtering and then heating under moderate vacuum to 100°C. Both the irradiated and non-irradiated WS_2 had a relatively small decrease in effective surface area as a result of the nitric acid treatment. A decrease from 1.59 m^2/g to 1.39 m^2/g resulted when the non-irradiated WS_2 was given the nitric acid treatment and the irradiated WS_2 displayed a decrease to 1.73 m^2/g from 2.76 m^2/g as a result of the same treatment. The decrease in surface area is most likely due to residual contamination by nitric acid which our very moderate heat treatment and evacuation was not able to remove.

A hysteresis loop is resolvable in the adsorption-desorption data for these two sets. Similar to the difference in the size of the hysteresis loop of the irradiated and non-irradiates WS_2 subjected to the heat treatment, there is a difference in the size of the hysteresis loop resolvable for both samples subjected to the nitric acid treatment: the non-irradiated WS_2 has a smaller hysteresis loop than that of the irradiated WS_2 sample. It is likely that the explanation of this difference is the same than that which we have suggested for the previous case, namely that the larger hysteresis corresponds to capillary condensation occurring at the interior of tubes open as a result of the activation.

Conclusions

We have studied adsorption and desorption of CH_4 near its bulk triple point on samples of planar and tubular WS_2 which were subjected to various activation treatments, and to no treatment at all. We have investigated the effect of activation on the specific surface area of the samples, and on the presence and size of hysteresis loops in data for adsorption-desorption cycles.

Our results show that samples of irradiated WS_2, which possess nanotubes, experienced a marked increase in the size of the hysteresis loop present in adsorption-desorption cycle data as a result of being subjected to heating under vacuum at 700°C, or to acid treatment plus heating. Our interpretation of this result is that activation treatment results in the uncapping of the ends of the nanotubes in the irradiated WS_2, and that the increased hysteresis loop is the result of capillary condensation taking place at the inside the tubes. The presence of capillary condensation in these data is an indication that the material inside the tubes is not behaving in 1-D fashion.

Our measurements provide a way for the experimental determination of the lower limit of diameters above which matter inside a tube behaves as if it were three dimensional.

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