

Adsorptive hydrogen storage in carbon and porous materials

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Abstract

The hydrogen adsorption and desorption isotherms of a highly pure single-walled carbon nanotube sample (SWCNT), a corresponding nitric acid-treated sample (A-SWCNT), two zeolites, and several kinds of activated carbon fibers (ACFs) were measured at 77 and 303 K over the hydrogen pressure range 0–3.5 MPa by using the high-pressure adsorption apparatus with sufficient accuracy. The amount of adsorbed hydrogen by weight depended on the micropore volume of the sample, except for the SWCNT and the A-SWCNT sample. The hydrogen storage capacity of A-SWCNT at a given micropore volume was higher than that of the zeolite and ACF samples. The specific surface area of micropore of A-SWCNT was 710 m²/g, whereas the theoretical surface area is 2630 m²/g. This finding suggests that the hydrogen storage capacity can be enhanced when the SWCNT has an ideal structure with a higher surface area.

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1. Introduction

Hydrogen storage on carbon materials has recently been attracting attention because of the importance of hydrogen as an ideal substitute for fossil fuels. Several research groups have reported that carbon nanotubes and nanofibers exhibit a high hydrogen storage capacity (>3 wt.% at ambient temperature) [1–4], and some theoretical researches by Monte Carlo simulation and other calculations have supported this finding [4–6]. However, other researchers were unable to reproduce these results experimentally and obtained storage capacities of less than 0.7 wt.% at ambient temperature and high pressure (10 MPa) [7–9]. The reasons for the discrepancy among recent reports with respect to hydrogen storage capacity of carbon materials can be considered to be the difference of evaluation technique, and experimental errors owing to the difficulty of evaluation. Since the amount of hydrogen adsorbed on carbon materials is much smaller than that of other gases such as methane and carbon dioxide, careful attention must be paid to experimental details, that is, the leak in the apparatus, control of temperature, time for equilibration of pressure, purity of gas and amount of

sample used, in order to obtain accurate results in the volumetric or gravimetric method. In a previous report [10], the purity of the sample was insufficient to obtain accurate values of hydrogen storage capacities. However, in recent years, techniques for the preparation of high-purity carbon nanotubes and nanofibers have been developed. In order to obtain accurate values of hydrogen storage capacities, the influence of structural changes resulting from pretreatment and metal catalyst contamination must be understood. Most of the previously reported values of hydrogen storage capacity of activated carbon are in agreement [11,12]. Thus, in evaluating the hydrogen storage capacities of carbon nanotubes or nanofibers, activated carbon can be used as a reference material to improve the accuracy of the experimental results. In addition, the mechanism of hydrogen storage and the interaction between the carbon surface and hydrogen are not adequately understood. Therefore, the hydrogen storage properties of carbon materials must be analyzed accurately by using well-characterized samples to evaluate the capacity and mechanism of hydrogen storage in carbon materials as well as to design an appropriate structure to enhance the storage capacity.

In this study, we made the high-pressure adsorption apparatus with sufficient accuracy, and measured the hydrogen adsorption and desorption isotherms of a single-walled carbon nanotube sample (SWCNT), a corresponding nitric

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acid-treated sample (A-SWCNT), two zeolites, and several kinds of activated carbon fibers (ACFs) at 77 and 303 K over the hydrogen pressure range 0–3.5 MPa. From these results, we determined the relationship between the storage capacity and the pore structures of the samples.

2. Experimental

2.1. Samples

The A-SWCNT sample was prepared as follows. A highly pure SWCNT sample (HiPcoTM, Carbon Nanotechnologies Inc., USA) was stirred in 4 M HNO₃ for 60 h at ambient temperature. The sample was then stirred in 5 M HCl for 24 h at ambient temperature, washed with pure water, and finally heated in a hydrogen flow at 973 K for 1 h.

H-Y-type (H-YZ) and H-ZSM-5 zeolites were obtained from the Catalysis Society of Japan. Four kinds of ACF (ACF-1000, ACF-1400, ACF-1800, and ACF-2300; all derived from phenolic resin) were used. ACF-1000 was oxidized with an (NH₄)₂S₂O₈ solution at ambient temperature for 48 h [13]. After oxidation, the sample was washed with pure water. The oxidized sample is designated O-ACF-1000.

The pore structures of the samples were estimated from the nitrogen adsorption isotherms at 77 K by using the α_s plot. The change in the structure of the SWCNT sample after treatment with nitric acid was analyzed by using a transmission electron microscope (TEM; JEM-2000EXII, JEOL) and Raman spectrometer (Ramanor T-64000, Jobin Yvon).

2.2. Measurement of hydrogen adsorption isotherms

Hydrogen adsorption isotherms at 77 K up to a hydrogen pressure of 0.1 MPa were measured by using the volumetric apparatus (BELSORP 28SA, BEL Japan) after pretreatment at 393 K and 1 Pa for 12 h. High-purity hydrogen (99.99999%) was used in this study.

Hydrogen adsorption isotherms at 303 K over the hydrogen pressure range 0–3.5 MPa were measured by using the manually-controlled apparatus for high-pressure adsorption. The following procedures ensured accuracy of the experimental results: (1) The principal part of the apparatus was held in an air thermostat to keep its temperature at 303 ± 0.1 K. (2) We determined that no hydrogen adsorbed onto the sample cell walls and that the apparatus was leak-free for at least 2 h at each step of equilibration. (3) The time adopted for equilibration was 30 min at each step. (4) Approximately 1.0 g of sample was placed in the sample cell. Prior to measurement, the cell was heated at 393 K for 24 h. (5) The amount of hydrogen sorption for LaNi₅ that was measured with this apparatus (1.42 wt.%) agreed with that previously reported [8]. (6) The desorption isotherm was measured to confirm the accuracy of the results.

3. Results and discussion

The TEM images of both SWCNT and A-SWCNT show a bundle structure consisting of single-walled carbon nanotubes (Fig. 1), indicating that the nitric acid treatment used in this study did not break the tube structure. However, upon acid treatment, part of the bundle structure was released, and the diameter of the bundle decreased. Acid treatment also resulted in fewer dark spots, corresponding to Fe catalyst particles, in the TEM images. The diameter of the tubes in the SWCNT and A-SWCNT samples was estimated to be 0.9–1.3 nm from the TEM images. In Raman spectra of SWCNT and A-SWCNT, the positions of peaks, assigned to the radial breathing mode (RBM) in the 100–300 cm⁻¹ region, remained unchanged before and after the treatment with nitric acid. The diameter of the tubes in SWCNT and A-SWCNT estimated from the RBM frequency was 0.9–1.3 nm, and agreed with that estimated from the TEM images.

Table 1 lists porosity parameters for the samples used in this study. The α_s plot can provide the information about the micropore and the external surface containing the mesopore and macropore. The specific surface area of the micropore (S_{micro}) was linearly related to the micropore volume (V_{micro}). For SWCNT, the external surface area (S_{ext}) was larger than S_{micro} , whereas for the zeolites and ACFs, S_{ext} was much smaller than S_{micro} . The S_{micro} value of A-SWCNT was more than twice that of SWCNT, whereas S_{ext} of A-SWCNT was 1.3 times as large as that of SWCNT. The average micropore widths (W_{ave}) of SWCNT and the zeolites were estimated from S_{micro} and V_{micro} by assuming a cylinder-shaped pore. The diameter of the tubes in SWCNT estimated from the TEM images and Raman spectra did not agree with W_{ave} . This result can be explained by assuming that the interstitial space between the tubes acts as a site for adsorption, in addition to the inner walls of the tubes. Values of W_{ave} for ACFs were estimated by assuming a slit-shaped pore.

Fig. 2 shows the hydrogen adsorption isotherms of the SWCNT, A-SWCNT, zeolite and ACF samples at 77 K

Table 1
Porosity parameters for the samples used in this study

Sample	S_{micro}^a (m ² /g)	S_{ext}^b (m ² /g)	V_{micro}^c (cm ³ /g)	W_{ave}^d (nm)
SWCNT	320	460	0.12	0.76
A-SWCNT	710	590	0.25	0.71
H-YZ	710	60	0.27	0.75
H-ZSM-5	330	50	0.15	0.92
ACF-1000	980	20	0.38	0.77
ACF-1400	1380	30	0.53	0.77
ACF-1800	1810	40	0.72	0.79
ACF-2300	2250	70	1.04	0.92
O-ACF-1000	840	20	0.27	0.65

^a Specific surface area of micropore.

^b Specific external surface area.

^c Micropore volume.

^d Average micropore width.

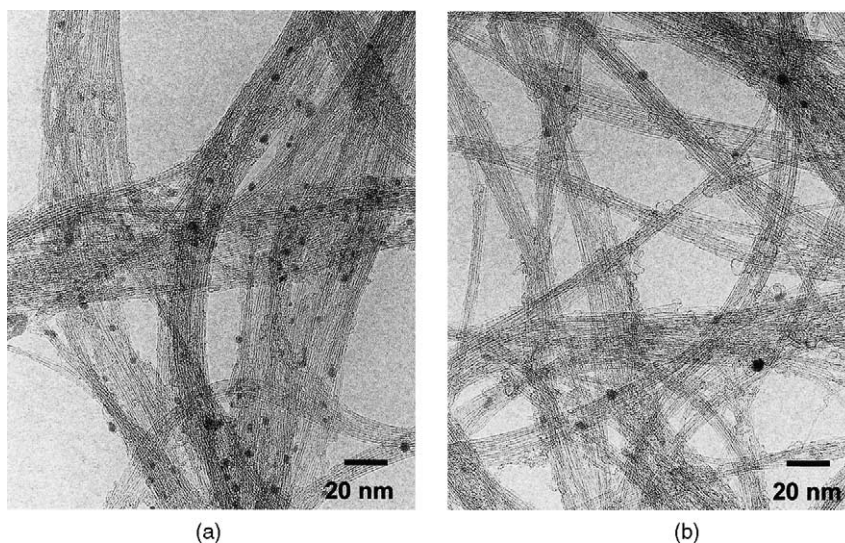


Fig. 1. TEM images of: (a) SWCNT; (b) A-SWCNT.

over the hydrogen pressure range 0–0.1 MPa. The adsorption isotherms agreed with desorption isotherms, and hysteresis was not observed. Elemental analysis indicated that SWCNT and A-SWCNT contained 11 and 9 wt.% of metal, respectively. Therefore, the amount of hydrogen adsorbed on SWCNT and A-SWCNT was expressed by weight, exclusive

of metal. The amount of hydrogen adsorbed on SWCNT, 0.8 wt.% at 0.1 MPa, was smaller than the amount of hydrogen adsorbed on the ACF samples. However, the amount of adsorption increased remarkably upon treatment with nitric acid and reached 1.8 wt.% at 0.1 MPa. The amount of hydrogen adsorbed on the zeolite samples was smaller than that adsorbed on the ACF samples. For the ACF samples, hydrogen uptake increased with increasing surface area and reached 2.3 wt.% at 0.1 MPa for ACF-2300. The amount of hydrogen adsorbed on O-ACF-1000 was smaller than that adsorbed on ACF-1000.

Fig. 3 shows the hydrogen adsorption isotherms of the SWCNT, A-SWCNT, zeolite and ACF samples at 303 K over the hydrogen pressure range 0–3.5 MPa. The agreement between the adsorption and desorption isotherms indicates that the data are sufficiently accurate and that the adsorption process is completely reversible. The amounts of hydrogen adsorption at 303 K were approximately one-tenth as large as those at 77 K. The amount of hydrogen adsorbed on ACF-2300, 0.26 wt.% at 303 K and 3.1 MPa, was the largest of all the samples used in this study, but did not reach the DOE target, 6.5 wt.%.

The amounts of hydrogen adsorbed at 77 K and 0.1 MPa (Fig. 4) and 303 K and 3.1 MPa (Fig. 5) seemed to be linearly correlated with the micropore volume. However, for a given micropore volume, the hydrogen uptake by the SWCNT and A-SWCNT samples was higher than the hydrogen uptake by the other samples. As shown in Table 1 and Figs. 2 and 3, the treatment with nitric acid enhanced the hydrogen uptake of SWCNT as well as S_{micro} . This result suggests that the increase in the number of sites with high interaction potentials for hydrogen adsorption was due to the nitric acid treatment. The TEM images and Raman spectra of the SWCNT and A-SWCNT samples showed that part of the bundle structure was released, but that the tube structure was not broken and the tube diameter was unchanged after the

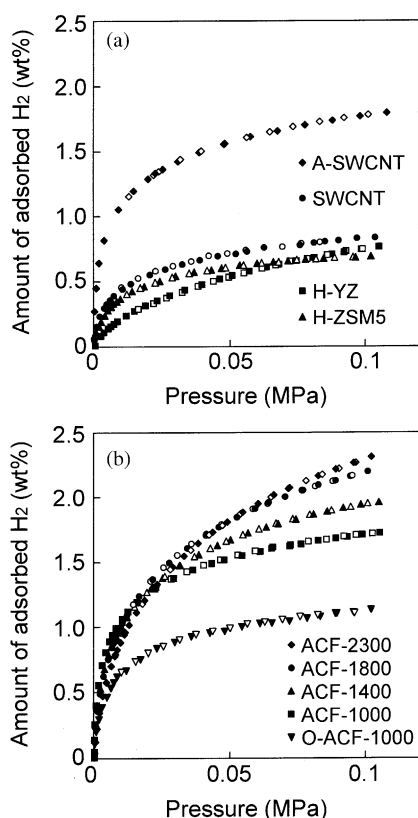


Fig. 2. Hydrogen adsorption isotherms at 77 K over the hydrogen pressure range 0–0.1 MPa: (a) SWCNT samples and zeolites; (b) ACFs. Filled symbols, adsorption; open symbols, desorption.

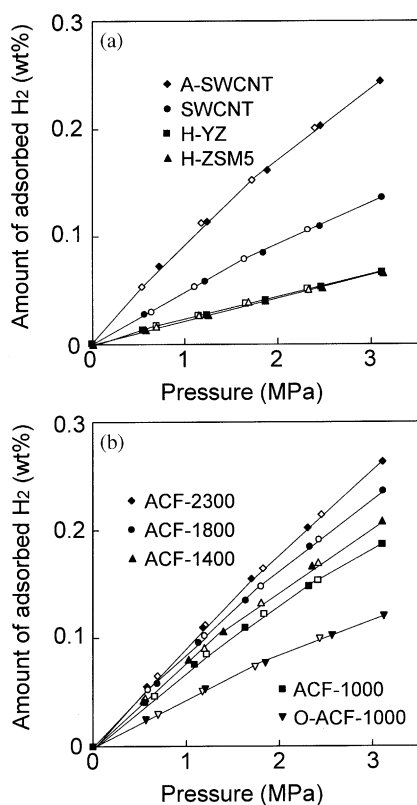


Fig. 3. Hydrogen adsorption isotherms at 303 K over the hydrogen pressure range 0–3.5 MPa: (a) SWCNT samples and zeolites; (b) ACFs. Filled symbols, adsorption; open symbols, desorption.

treatment. Therefore, the increase in the hydrogen uptake after treatment with nitric acid can be explained as follows: (1) The inside of the tubes came to act as sites for hydrogen adsorption as a result of removal of the terminal structures of the tubes. (2) More sites with high interaction potentials were created in the interstitial space between the tubes when the bundle structure was released. The specific surface

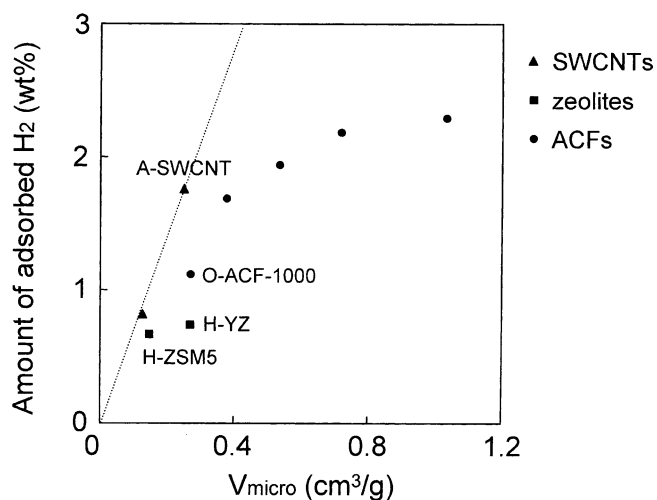


Fig. 4. Amount of adsorbed hydrogen at 77 K and 0.1 MPa vs. the micropore volume of the sample.

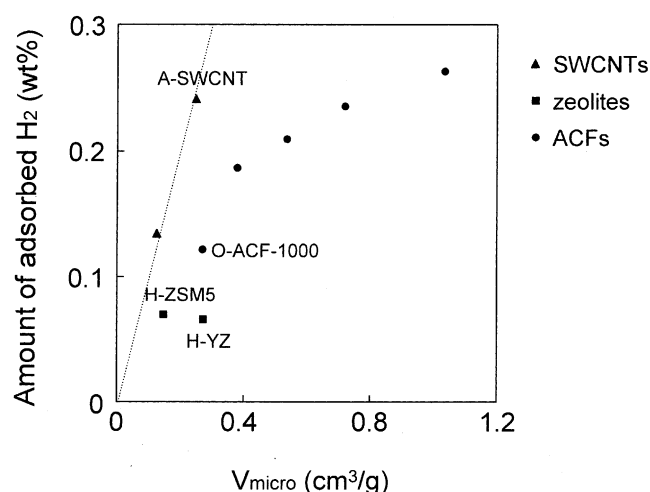


Fig. 5. Amount of adsorbed hydrogen at 303 K and 3.1 MPa vs. the micropore volume of the sample.

area of micropore of A-SWCNT was $710 \text{ m}^2/\text{g}$, whereas the theoretical surface area is $2630 \text{ m}^2/\text{g}$. This finding suggests that the hydrogen storage capacity can be enhanced when the SWCNT has an ideal structure with a higher surface area.

As shown in Figs. 4 and 5, the amount of hydrogen adsorbed on ACF-1000, ACF-1400 and ACF-1800 was linearly related to the micropore volume, but the amount of hydrogen adsorbed on ACF-2300 was smaller than that expected from the gradient of other ACFs. The average pore diameter of an activated carbon is known to increase with the progression of the activation. This pattern was observed in this study: the W_{ave} value of ACF-2300, 0.92 nm , was larger than that of any other ACF used. It was reported that the optimum pore diameter for adsorbing hydrogen was approximately 0.7 nm [14]. Thus, the smaller than expected amount of hydrogen adsorbed on ACF-2300 can be attributed to the diameter of the pores in the ACF-2300 sample. Oxidation of ACF-1000 resulted in a $>30\%$ decrease in hydrogen uptake. It was reported that the surface area and micropore volume decreased owing to the introduction of oxygen functional groups into the inside or entrance of pores [13]. Thus, the reduced hydrogen uptake of O-ACF-1000 relative to other ACFs can be explained by assuming that the number of pores with high interaction potentials for adsorption, that is, those with a diameter of approximately 0.7 nm , was decreased by the introduction of oxygen functional groups.

4. Conclusion

The hydrogen adsorption and desorption isotherms of SWCNT, A-SWCNT, two zeolites and several ACFs at 77 and 303 K over the hydrogen pressure range 0–3.5 MPa were measured by using the high-pressure adsorption apparatus

with sufficient accuracy and the following conclusions were obtained:

- (1) The amount of adsorbed hydrogen by weight both at 77 and 303 K seemed to be linearly related to the micropore volume of the sample. However, for a given micropore volume, the hydrogen uptake by SWCNT and by A-SWCNT was higher than that by any other sample in this study. The oxidation of ACF decreased the amount of hydrogen adsorbed owing to the introduction of oxygen functional groups into the inside or entrance of pores.
- (2) The amount of hydrogen adsorbed on the SWCNT sample increased remarkably upon treatment with nitric acid. TEM images and Raman spectra of the SWCNT samples showed that part of the bundle structure was released, but that the tube structure was not broken and the tube diameter was unchanged after the treatment. Therefore, acid treatment resulted in an increase in the number of sites with high interaction potentials for hydrogen adsorption, and these sites can be considered to be the inside of tubes or the interstitial space between the tubes.

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