

Atomic Hydrogen Storage in Carbon Nanotubes Promoted by Metal Catalysts

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Atomic hydrogen storage by carbon nanotubes (CNTs) at atmospheric pressure is studied using Pd and La catalysts for dissociation of H₂ into atomic hydrogen and formation of defects on CNT surfaces, respectively. The defect sites on CNTs as adsorption sites of atomic hydrogen are prepared by oxidation pretreatment using a La catalyst. Pd catalysts are then deposited on CNT surfaces for dissociation of H₂ into atomic hydrogen, which then spills over to the defect sites. In the best case, 1.0 wt % hydrogen is stored in the defective CNT with Pd particles at 1 atm and 573 K. The hydrogen desorption in temperature programmed desorption (TPD) experiments started at 700–900 K, which agreed with the annealing temperatures of CNTs prior to hydrogen storage. Also, the amount of hydrogen stored in CNTs decreased with increasing annealing temperature. These results are ascribed to the crystallization of the defective structure of CNT into graphitic structure. The activation energies of 46.6, 87.3, and 129.8 kJ/mol derived from the desorption peaks of hydrogen in the defective CNT with Pd particles vary from 46.6 to 129.8 kJ/mol, depending on the annealing temperatures at 523, 623, and 773 K, respectively. The difference in the activation energies is probably due to the energies required for the recrystallization of the defect sites into the graphite structure.

1. Introduction

Hydrogen is an ideal fuel because of its zero or low pollutant emission during combustion. For the utilization of hydrogen, hydrogen storage technology is necessary, in which light, environmentally friendly and cheap materials are required to be used. In recent years, carbon materials such as carbon nanotubes (CNTs), carbon nanofibers, and mechanically milled graphites have attracted attention owing to the availability of new carbon materials.^{1–11} However, most studies concerning hydrogen storage have been carried out at high pressures (1–16 MPa) and low temperatures (80–133 K) in order to store molecular hydrogen by physisorption. It has been often reported that hydrogen storage by physisorption remains less than 4 wt % at room temperature and at even high pressures.^{1,2} Although large hydrogen uptakes by CNTs have been reported,^{3,4} these results have not been easily reproduced. The hydrogen adsorption sites and the interaction between CNTs and hydrogen have not been well understood yet.

Recently, it has been reported that atomic hydrogen can be stored at defect sites on carbon materials.^{7–10} Orimo et al.⁷ have reported that nanostructured graphite can store hydrogen up to 7.4 wt % by ball milling under a hydrogen atmosphere. The large hydrogen uptake is regarded to be related to the defective structures produced by mechanical milling. It is expected that hydrogen storage capacity varies depending on the number of defects because the defects should have dangling bonds. The effective methods for preparing defects in carbon materials include mechanical milling,^{7,8} chemical oxidation using HNO₃, HCl, and H₂O₂,^{12–14} oxidation by O₂ at high temperatures above 800 K,^{15,16} and oxidation by alkali-metal addition.^{17–19} Hahn et al. have reported that addition of cesium to graphite promotes

the oxidation reaction in a localized region through formation of CsO and CsO₂ intermediates.¹⁹

One of the important applications of hydrogen storage is in a fuel cell system. Hydrogen is often used as an energy source of fuel cells. The catalysts in the fuel cell electrodes have been studied to find the best catalysts for H₂ dissociation on carbon materials. It is known that a minor amount (0.2–2 wt %) of a transition metal such as Pd or Pt dispersed in carbon could dissociate hydrogen molecules to hydrogen atoms.²⁰ We succeeded in producing the best performance at 0–600 mA/cm² with using Pt deposited CNT electrodes.^{21,22} The decoration of CNTs with metal for hydrogen dissociation is the common technique in not only hydrogen storage but also fuel cell catalysts^{21,22} and sensors.^{23,24}

Our vision here of hydrogen storage is to adsorb atomic hydrogen at the defect sites of CNTs after dissociation of H₂ by Pd catalyst particles attached to the CNTs. La catalysts were also doped to CNTs in order to introduce the defect sites, which catalyze oxidation of CNTs by O₂. We used thick MWCNTs for atomic hydrogen storage, because the defect density on the wall of MWCNTs is expected to be much more than that on SWCNTs or thin CNTs and because MWCNTs can be obtained at low cost by catalytic decomposition of hydrocarbons as a mass production. The amount of hydrogen stored was exactly measured by thermal programmed desorption (TPD). We report here that atomic hydrogen can be stored in CNTs by modification with catalysts for defect making and the dissociation of H₂. The amount and desorption temperature of adsorbed hydrogen depend on the procedure of defect making.

2. Experimental Section

The CNTs (NanoTech. Co. Ltd. China) used in this study have been produced by catalytic decomposition of hydrocarbons. BET specific surface area of the CNTs was 98 m²/g with a

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length of 10 μm , outer diameter of 20–50 nm, inner diameter of 3–10 nm, and wall layers of 25–60. The synthesis catalyst particles contained in the CNTs were removed by washing in concentrated HNO_3 (14 N) at room temperature for 1 h followed by ultrasonication in concentrated HNO_3 . After subsequent washing with distilled water, the CNTs were dried at 373 K in air. La was doped to the purified CNTs as an oxidation catalyst by putting the CNTs in $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ solution dissolved in tetrahydrofuran (THF) followed by stirring at room temperature for 1 h. The THF solution was then evaporated to deposit La ion compounds on the CNT surface as confirmed by X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD). To generate the defects and to open the end of CNTs, the La-loaded CNTs were heated in a quartz tube reactor with flowing air (10 cm^3/min) to 873 K. After the oxidation in air, the La catalyst particles were removed by washing in concentrated HNO_3 at room temperature for 30 min followed by ultrasonication in concentrated HNO_3 for 30 min.

To dope the Pd catalysts, the oxidized CNTs were put into $\text{Pd}(\text{C}_5\text{H}_7\text{O}_2)_2$ solution dissolved in 30 mL of THF. After stirring the mixture at room temperature for 1 h, the THF solution was evaporated to leave Pd-doped CNTs.

Hydrogen storage by CNTs was carried out using the flow reactor connected to a gas chromatograph (GC) (Shimadzu, GC-8A). The Pd/CNTs were heated at 573 K for 3 h in helium with 99.99% purity (1 atm) to remove impurities on CNT surfaces. The reason for the low annealing temperature is to avoid significant recrystallization of the defective CNTs at higher temperatures above 600 K. Carboxyl groups, which are expected to be major impurities, can be removed by annealing at 373–673 K.³⁵ We thus chose the annealing temperature of 573 K. Then, hydrogen (99.99%) was let (30 mL/min) into the reactor at 1 atm and flowed at 573 K for 3 h. The amount of stored hydrogen and the desorption behavior were examined by temperature programmed desorption (TPD) experiments using the gas chromatograph, where N_2 (30 mL/min) was used as the carrier gas.

The prepared Pd/CNTs were characterized with transmission electron microscopy (TEM) (JEOL, JEM-2010F), thermal gravimetry (TG) and differential thermal analysis (DTA) (Seiko, EXSTAR6000 TG/DTA/DSC), Raman spectroscopy (Ar laser, 514.5 nm, Jasco, TRS-600), XPS (Vacuum Generator, Escalab 220i-XL), and XRD (Phillips, X'Pert MPD).

3. Results and Discussion

To generate defects by oxidation using air, La was doped to CNTs as a catalyst to promote the oxidation. The effect of La upon oxidation of CNTs was investigated by TG, Raman spectroscopy, and TEM.

Figure 1 shows the TG and DTA results of CNTs and La/CNTs oxidized in O_2/air . It is shown in Figure 1a that CNT without La is burned out in O_2 at 730–800 K with a peak of heat production around 790 K. However, for the La/CNTs shown in Figure 1b, the oxidation started at lower temperatures (650–750 K), indicating that the oxidation of CNTs is catalyzed by La. La can be regarded as an oxygen reservoir by forming LaO , where O_2 molecules dissociate on the LaO surface to atomic oxygen. The atomic oxygen or LaO probably migrates during oxidizing carbon.^{30,31}

Figure 2 shows the Raman spectra of CNTs, oxidized CNTs, and oxidized La/CNTs. Two peaks at 1580 and 1350 cm^{-1} are called the G and D bands, which can be assigned to the active E_{2g} vibration of graphite and disordered structures, respectively.²⁵ It is known that the intensity ratio of the D and G peaks

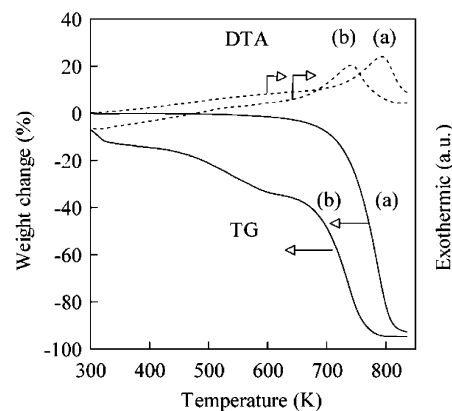


Figure 1. TG and DTA profiles of (a) CNTs and (b) La/CNTs.

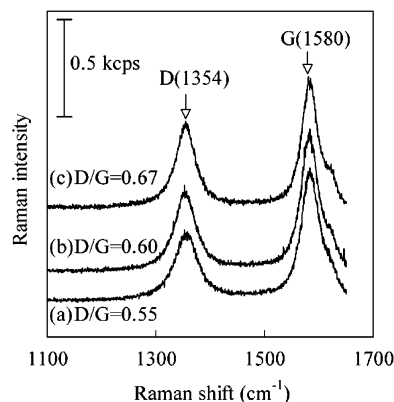


Figure 2. Raman spectra and intensity ratio of D and G band peaks of CNTs. (a) CNTs before oxidation. (b) CNTs after oxidation. (c) La/CNTs after oxidation.

(I_{1350}/I_{1580}) gives information on the degree of disorder of CNTs.²⁶ We found that the intensity ratio of I_{1350}/I_{1580} increased by oxidation of the La-doped CNTs, indicating the creation of defects at the CNT surface.

Figure 3 shows the TEM images of CNTs treated by nitric acid and La/CNTs after oxidation at 650 K. Figure 3a reveals that catalysts for CNT synthesis with the tip mechanism³² were removed and the tube ends were opened by sonication with nitric acid. As shown in Figure 3b, the partial oxidation of La/CNTs by air brought about opening of the tube ends and creation of the defects at the outer walls. The defects at the outer walls can be observed by the magnified TEM images shown in Figure 3c. It was found that the layers of a tube were partially etched and holes of 10–30 nm size were formed. On the basis of the results, we can conclude that the La catalyst promotes oxidation of CNTs by a cycle of LaO formation and oxygen supply from the LaO . The La compounds were not observed in TEM images, probably due to small particles. We thus consider that the holes and the defects after oxidation provide the pathway and the adsorption sites of atomic hydrogen, respectively.¹⁰ Figure 3d shows the TEM image of a Pd-deposited CNT. We found that Pd particles of 5–30 nm size were deposited on the CNT surfaces. Although not shown in this paper, TEM results showed that Pd particles with average size of 2 nm were deposited on the CNT surface. The amount of Pd was roughly estimated to be 2.5 wt % by XPS.

The effect of the Pd and La catalysts upon hydrogen storage by CNTs was examined by TPD measured with GC, where hydrogen was adsorbed at 1 atm and 573 K for 180 min. Curves a, b, and c of Figure 4 show TPD results of H_2 desorption from CNTs without Pd and La, Pd/CNTs, and Pd/(La)/CNTs,

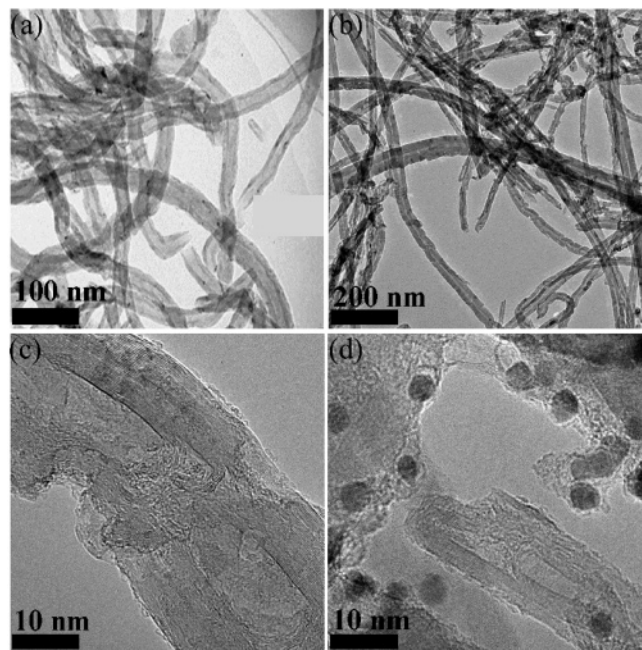


Figure 3. TEM images of CNTs. (a) CNTs after HNO_3 treatment. (b) La/CNTs after air oxidation. (c) Typical defects of La/CNTs created by air oxidation. (d) Pd nanoparticles on (La)/CNTs.

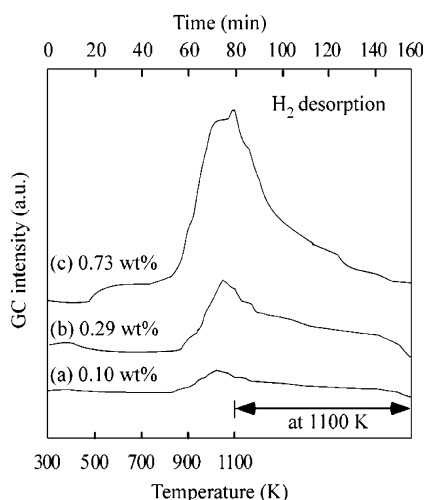


Figure 4. TPD of hydrogen. (a) CNTs, (b) Pd/CNTs, and (c) Pd/(La)/CNTs.

respectively. Since we could not heat the reactor over 1100 K, we once stopped heating at 1100 K during TPD experiments and kept it at 1100 K to measure the amount of stored hydrogen. The amount of hydrogen storage was estimated from the peak area to be 0.10, 0.23, and 0.73 wt % for CNTs, Pd/CNTs, and Pd/(La)/CNTs, respectively. However, the desorption temperature starting at 800 K is so high that atomic hydrogen should be chemisorbed on the dangling bond of the defect site. We accordingly conclude that H_2 should be dissociated by the Pd catalyst and the hydrogen atoms spill over to defect sites on CNTs.^{20,27} We thus propose a new strategy for the hydrogen storage by CNTs using both La and Pd catalysts for the reaction of defect sites by oxidation and hydrogen dissociation, respectively.

Note that hydrogen started to desorb around 773 K, which was close to the He treatment temperature of 773 K. It is suggested that the defects created by the oxidation are recrystallized to graphite by annealing at high temperatures.^{28,33} To examine the effect of annealing temperature upon hydrogen

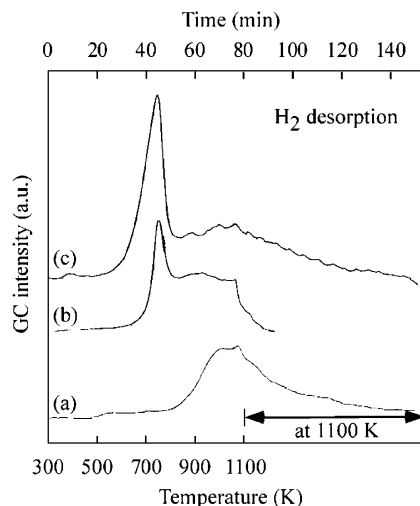


Figure 5. TPD of hydrogen from Pd/(La)/CNTs depending on thermal pretreatment temperatures at (a) 773, (b) 623, and (c) 523 K.

desorption, we carried out TPD of H_2 from Pd/(La)/CNTs annealed at different temperatures in He prior to hydrogen adsorption. Figure 5 shows the TPD profiles of H_2 from Pd/(La)/CNTs for pretreatment temperatures of 523, 623, and 773 K. As for He treatment at a lower temperature of 523 K, it is clear that hydrogen started to desorb at a lower temperature around 600 K. The annealing at 623 K resulted in the shift of the peak top to 760 K. Further annealing at 773 K caused the peak top to shift to 1000 K. These results in Figure 5 with good reproducibility suggest that crystallization to graphite by heating significantly influences hydrogen storage.

For the annealed CNT samples, the amount of hydrogen storage was estimated from the peak areas to be 0.73, 0.60, and 1.00 wt % for curves a, b, and c, respectively, of Figure 5. Here, we stopped heating at 1100 K during TPD experiments and kept it at 1100 K until hydrogen desorption was completed as shown in Figure 5a,c, while in Figure 5b we stopped heating at 1100 K and then cool to room temperature. Therefore, the real hydrogen storage of Figure 5b would be higher than 0.60 wt %.

It is thus considered that the hydrogen desorption temperature and the amount of hydrogen stored strongly depend on the thermal treatment. Furthermore, the sharp desorption peak observed at 740 K in Figure 5 is similar to that reported for nanostructured graphite by Orimo et al.,⁷ who attributed it to CH_3 species with sp^3 hybridization located at defective structures of the nanostructured graphite.³⁴ Zhong et al.⁹ also reported that hydrogen desorbed from nanosized nickel (or cobalt)/graphite at temperatures similar to that of the first desorption peak in Figure 5. They reported that hydrogen is stored in nanosized nickel (or cobalt)/graphite by formation of CH_2 species as measured by IR. We have preliminary IR data for significant hydrogen storage by Pd/CNTs (above 4.0 wt %), showing that the asymmetric and symmetric CH stretching peaks of CH_2 species appeared at 2930 and 2850 cm^{-1} , respectively. However, the CH stretching peak of CH_3 species was sometimes observed at 2964 cm^{-1} . These three peaks disappeared after annealing at about 900 K. We thus consider that the peak at 600–800 K corresponds to the CH_2 or CH_3 species, while the assignment of the higher temperature peak is not clear from the present IR result.

We also estimated the activation energy for the hydrogen desorption by analyzing leading edges of the desorption peak.²⁹ Figure 6 shows the Arrhenius plots for hydrogen desorption

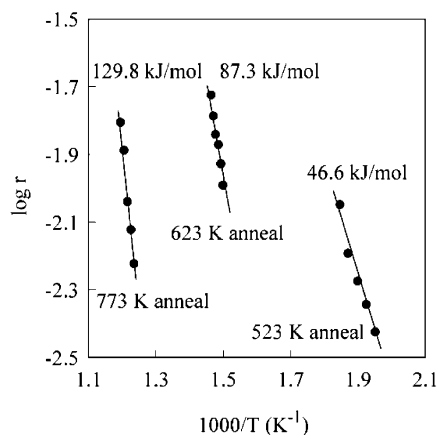


Figure 6. Arrhenius plots of leading edges for desorption peaks of hydrogen from Pd/(La)/CNTs pretreated at different temperatures shown in Figure 5.

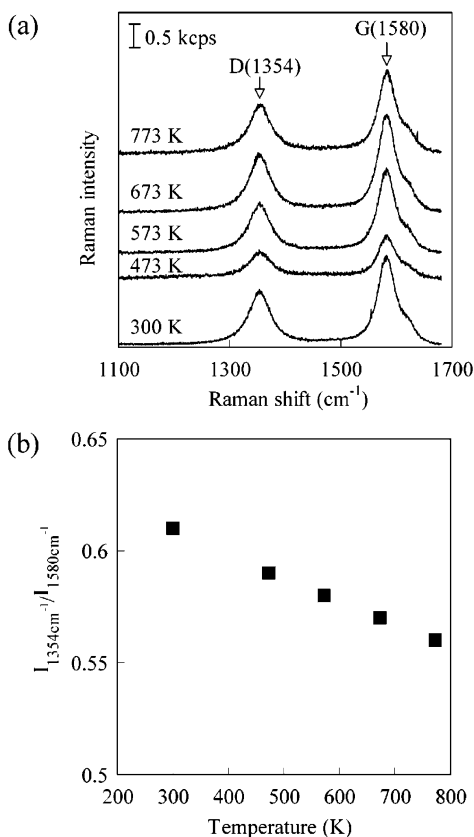


Figure 7. Raman spectra (a) and intensity ratio of D and G band peaks (b) for CNTs annealed at 300, 473, 573 K, 673, and 773 K.

from the Pd/(La)/CNTs heated at 523, 623, and 773 K in He. The activation energies were estimated to be 46.6, 87.3, and 129.8 kJ/mol for the He treatment temperatures 523, 623, and 773 K, respectively. The significant difference in the activation energies is probably due to the contribution of energy in the recrystallization of defective CNTs.

To examine the recrystallization of the defective CNTs, we measured the Raman spectroscopy of the CNTs oxidized by air as a function of annealing temperature. After oxidizing the CNTs at 800 K by air, the oxidized CNTs were heated at 473–773 K for 3 h in N₂ (30 cm³/min). Figure 7a shows the Raman spectra of the CNTs after annealing at different temperatures. The intensity ratio of the D and G peaks (I_{1354}/I_{1580}) was shown in Figure 7b as a function of the annealing temperature. We found that the intensity ratio of the D and G peaks decreased

with increasing annealing temperature. This indicates that the defective CNTs are recrystallized by annealing, leading to significant changes in the properties of hydrogen storage by CNTs. If one can try atomic hydrogen storage by CNTs, efforts should be made to keep the defective CNTs.

We have repeated the H₂ uptake–release cycle. In the second cycle, the amount of hydrogen storage decreased from an initial 1 wt % to 0.2 wt %, which was due to the recrystallization of the defective CNTs upon releasing hydrogen by heating to 1100 K. We are currently trying to decrease the desorption temperature of hydrogen.

4. Conclusion

The atomic hydrogen storage at the defect sites of CNTs by doping La and Pd catalysts was investigated at atmospheric pressure by TG, Raman spectroscopy, TEM, and TPD. The formation of defects on CNTs promoted by the La catalyst was clearly confirmed by TG, Raman spectra, and TEM. The introduction of the Pd catalyst for the dissociation of H₂ increased the amount of hydrogen storage up to 1 wt %. Two desorption peaks of hydrogen appeared around 700 and 1000 K, where the lower temperature peak shifted depending on the annealing temperature of CNTs. The activation energies for hydrogen desorption derived from the leading edges of TPD also varied depending on the annealing temperature. This was considered to be due to the crystallization of defect sites into graphitic structure as Raman spectra suggested.

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