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SYNERGISTIC EFFECT IN HYDROGEN UPTAKE BEHAVIOR OF CARBON NANOTUBES AND COPPER NANOPARTICLES CATALYST

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The synergistic effect in hydrogen uptake behavior of carbon nanotubes and copper nanoparticles catalyst was investigated with H_2 adsorption apparatus. The multi-walled carbon nanotubes [MWNTs] were synthesized by a pyrolysis method. The structure and phase composition of the nanotubes and the catalyst were investigated with transmission electron microscopy (TEM) and X-ray diffraction (XRD). We found the outside diameter and inner diameter of the synthesized carbon nanotubes to be in a range of 200–500nm and 80-120nm respectively. The P–C–T curve of H_2 adsorbing of the MWNTs with and without the catalyst was measured up to 12 MPa pressure at room temperature. The hydrogen uptake behavior of the sample without catalyst is caused mainly by physical adsorption whereas the one with catalyst is both physical and chemical adsorption occur. MWNTs with the catalyst were found to adsorb up to 3.07 wt% H_2 at 12 MPa. Heat treatment was found to increase the H_2 storage capacity from 0.91 % at 200 °C to 1.42 % at 600 °C. H_2 uptake rate was found to increase with increasing H_2 pressure in the range of 0.2 to 0.6 MPa at room temperature.

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Keywords: Carbon nanotubes; Hydrogen storage; Copper catalyst

1. Introduction

Developing cost-effective, safe, and practical method of hydrogen (H_2) production is crucial for the advancement of using H_2 as a fuel and for fuel-cell technologies [1-3]. The current state-of-the-art is at an impasse in providing any material that meets a storage capacity of ≥6 wt% of that required for practical applications [4]. The interest in research on H_2 storage in carbon nanotubes has increased recently [5-7]. Compared to carbon nanotubes, the H_2 storage capability of metals such as cobalt, nickels, and copper is low (approximately 1.4 wt.%) [8,9], however, it has an obvious plateau, and the plateau pressure is relatively low [10]. Here, we report on the investigation, preparation conditions, and H_2 adsorption of multi-walled carbon nanotubes [MWNTs] produced by the pyrolysis method using copper particles as a catalyst.

2. Experimental

2.1 Procedure

Carbon nanotube were synthesized by the pyrolysis method using copper nanoparticles (size: 500–1000 nm) as a catalyst. First, the particles were loaded into a quartz tube reactor and

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heated in a furnace with N_2 as the pretreatment gas for 30 min, followed by H_2 treatment at a flow rate of 50 ml/min at 550 °C for 30 min. Next, acetylene and H_2 mixture (2:1 or 1:1) was introduced and passed over the catalyst for 30 min at a flow rate of 50 ml/min (or 25 ml/min) in acetylene and 25 ml/min in H_2 atmosphere at 700 °C. The upper part of the product in the quartz tube, which was composed mainly of carbon nanotubes, was taken as a sample for examination. The lower part of the product was removed because it had a few residual catalyst particulates that did not react completely.

2.2 Characterization

An X-ray diffraction (XRD) with Cu (Kα) radiation was used to identify the phase and crystal structure. The micro-structure of carbon-coated iron nanoparticles was observed using transmission electron microscope (TEM; JEM-2010 HR) operating at 200 kV. Fracture surfaces of the samples were examined with scanning electron microscope (SEM; PHLIPS 515, Holland). The surface functional groups were tested by FTIR (EQUINOX55, HITICHI, Japan). H_2 uptake experiments were performed with gas adsorption apparatus.

3. Results

3.1. Structure and morphology of carbon nanotubes and catalyst

Based on the SEM observation (Fig.1), we found that the diameters of the copper particles used as catalyst to synthesize carbon nanotubes were approximately 1000–1500 nm. After the reaction the diameters of copper catalyst reduced to 80-120 nm (Fig. 2). We inferre that the copper catalyst have been broken during the reaction. The TEM images of the samples indicate that the samples have a form of hollow tubes with an inner diameter of 80–120 nm and the outside diameter is in the range of 200-500nm. As observed in the figures, most catalyst particles are located at the end of the carbon nanotubes, however, some catalyst particles are also located in the middle of the carbon nanotubes, indicating that the growth mode of these nanotubes is complicated and diverse.

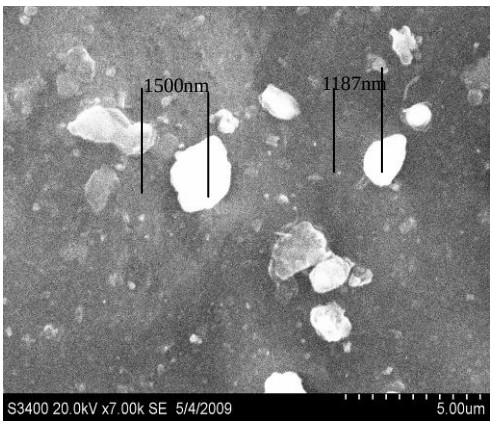

Fig. 1(a) SEM image of copper particles (catalyst)

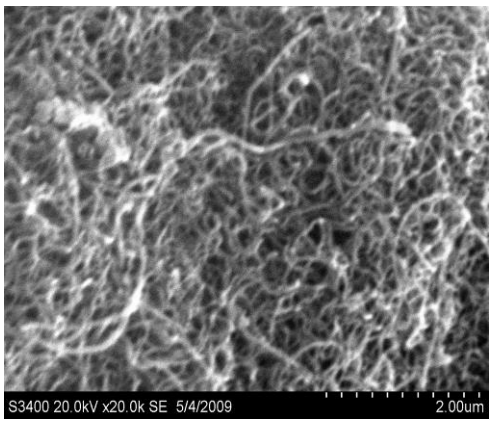

Fig.1 (b) SEM image of carbon nanotubes synthesized with copper particles

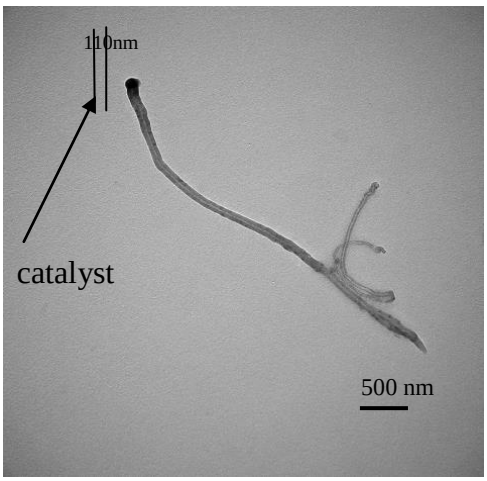

Fig.2a) TEM of the carbon and catalyst (end)

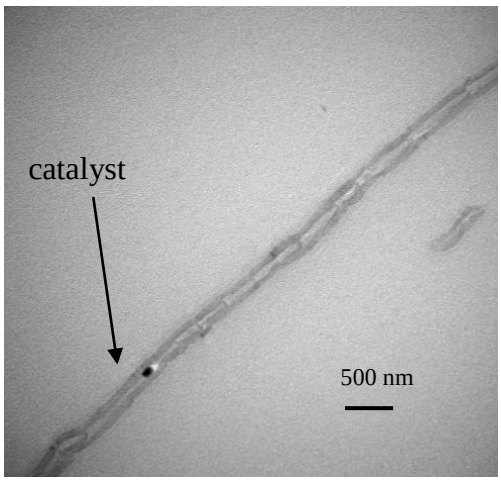

Fig.2b) TEM of the carbon nanotube and catalyst (middle)

3.2 Phase and the crystal structure of carbon nanotubes

The XRD patterns of the carbon nanotubes synthesized using copper nanoparticles as a catalyst are shown in Fig. 3. The patterns of the samples prepared at different ratios of acetylene and H_2 reaction gases are compared. While 'a' is the copper catalyst, 'b' and 'c' are the carbon nanotubes prepared at different ratio of acetylene to H_2. We found that the yield of carbon nanotubes was greater at higher ratio of acetylene to H_2. However, the XRD patterns of the samples obtained at the different ratios of reaction gases are very similar. Both the pattern show a typical amorphous peak, implying that the carbon atom in the carbon nanotubes is in an amorphous form. On the other hand, the Cu peaks in the XRD pattern of the copper catalyst particles are very clear, but they are fairly weak in samples "b" and "c".

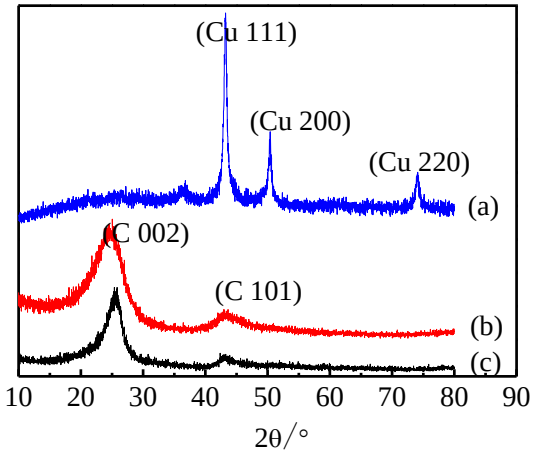

Fig. 3 XRD patterns of copper catalyst and carbon nanotubes synthesized by pyrolysis method at different gas atmospheres.
a) copper catalyst, (b) acetylene: H_2 (1:1), and (c) acetylene: H_2 (2:1).

3.3 Comparison of H_2 adsorption of MWNTs without and with copper catalyst

H_2 adsorption experiment was performed under an ambient condition of 290 K and in a pressure range of 0–12 MPa, which is suitable in the future application of electrical vehicles such

as large capacity H_2 electric cell [11,12]. We have tested the hydrogen adsorption of carbon nanotubes without copper catalyst (copper catalyst was removed by nitric acid) and the carbon nanotubes with copper catalyst.

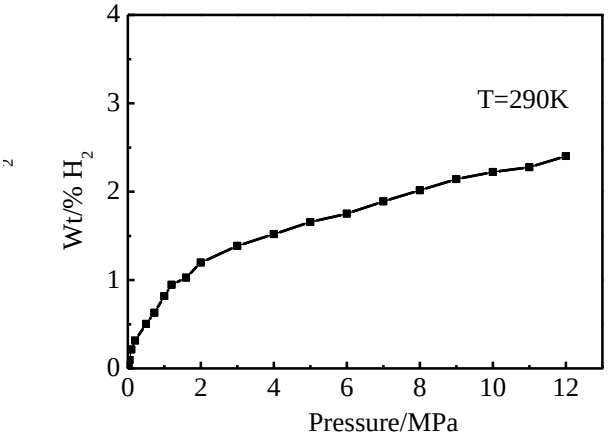

Fig. 4（a）H_2 adsorption on the carbon nanotubes without copper catalyst (at 290 K)

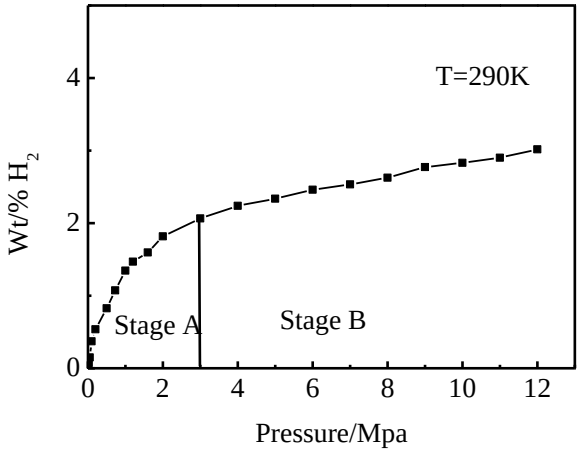

Fig. 4（b）H_2 adsorption on the carbon nanotubes with copper catalyst (at 290 K)

Fig. 4a shows the curve of H_2 adsorption on carbon nanotubes without copper catalyst. The physical character of H_2 adsorption on carbon nanotubes without copper catalyst, is confirmed by the fact that the P–C–T curve at room temperature of carbon nanotubes does not show a plateau in the whole range of pressure. On the other hand, the H_2 adsorption on carbon nanotubes with copper catalyst is quite different. The entire period can be divided into two stages: in stage A (0–3MPa), there is a remarkable increase in H_2 storage capacity, this period is mainly physics adsorption, and in stage B (more than 3MPa), the curve shows a slow growth with the about 1.8% of uptake capacity under 3MPa pressure and about 3.07% under 12MPa pressure, this period is mainly chemistry adsorption. Past studies have indicated that the mechanism of H_2 uptake in carbon nanotubes is via physics adsorption, and there are no obvious plateau[13,14]. We can infer that catalyst play an important role in the H_2 uptake experiment.

3.4 Influence of vacuum heat treatment on H_2 adsorption of MWNTs with catalyst

In order to increase the adsorption efficiency of carbon nanotubes with catalyst, we used vacuum heat treatment. An impurity layer containing organic groups is produced on the surface of carbon nanotubes when exposed to air for a long time, which prevents H_2 from reacting with the nanotubes[15]. In the treatment process, the samples were evacuated by a mechanical pump under of 0.1 Pa pressure and at a temperature of 200°C, 400°C, and 600°C for 5 h respectively, then cooled down to the room temperature in vacuum.

The effect of heat treatment was evaluated by infrared spectral analysis. In the FTIR curves (Fig. 5), it can be seen that before heat treatment there were many organic functional groups on the nanotubes: the bond at 3440 cm^{-1} is related to the stretching vibration mode of –OH, that at 1648 cm^{-1} is related to the stretching vibration mode of –C=O, and that at 1170 cm^{-1} is a characteristic of the bending vibration mode of –OH. After heat treatment, the organic groups absorb peaks became weak and there was almost no absorb peaks in the sample after 600°C.

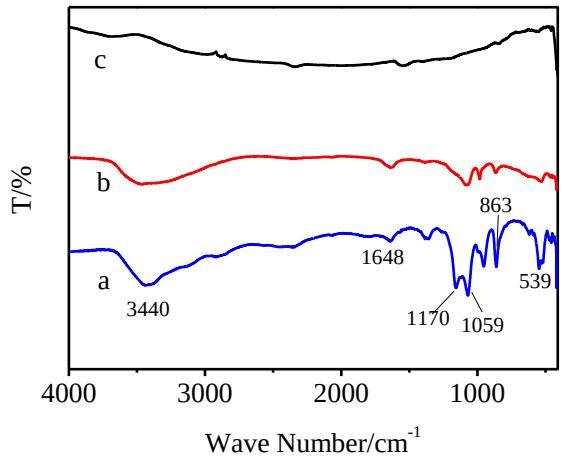

Fig. 5 The FTIR curves of carbon nanotubes before and after vacuum treatment (a, Untreated; b, Treated at 400°C; c, Treated at 600°C)

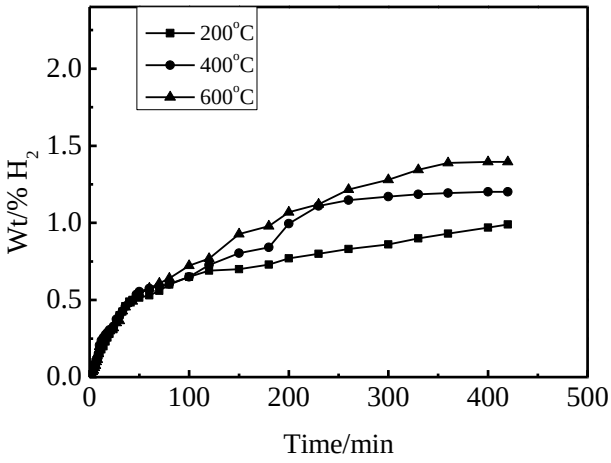

Fig. 6 H_2 uptake rate of carbons nanotubes with catalyst at 0.5MPa at different heat treatment temperature

Furthermore, we investigated the effect of vacuum heat treatment temperature on H_2 uptake of nanotubes with catalyst (Fig. 6). The amount of H_2 adsorption of the samples enhance with the increasing of heat treatment temperature (the total time of vacuum heat treatment was 5 h).

This is because the impurity functional groups on the surface of carbon nanotubes were moved gradually, and the crystalline degree of nanotubes and the catalyst enhanced with the increasing heat treatment temperature. The H_2 uptake obtained at a heat treatment temperature of 200°C was about 0.91 wt%, and it was increased to 1.42 wt% at a temperature of 600°C heat treatment at the same initial pressure.

3.5 The H_2 uptake at different starting pressure of MWNTs with copper catalyst

The relationship of H_2 uptake rate at different initial pressure was observed. The H_2 uptake rate of the carbon nanotubes with catalyst at different pressure of 0.2, 0.4, and 0.6MPa was compared (as shown in Fig. 7). It can be observed from the chart that H_2 uptake volume increased with the extension of time. Fig. 7 also shows that the H_2 uptake volume of the carbon nanotubes at higher pressure was more than that at lower pressure. For example, the H_2 uptake volume at 0.4MPa at 50 min was 0.27% and at 100 min it increased to 0.51% up to an equilibrium phase of 1.3% at 250 min; the H_2 uptake volume at 0.2MPa at 100 min was 0.23%— for comparison, the H_2 uptake volume at 0.6MPa was 0.94% at 400min. This is because the H_2 storage is a complex and complicated physical and chemical process, it takes time for completion. The reason for the increase in H_2 uptake volume with the increase in H_2 pressure is that at higher pressure more H_2 molecules can contact the surfaces of carbon nanotubes and get absorbed by the carbon nanotubes.

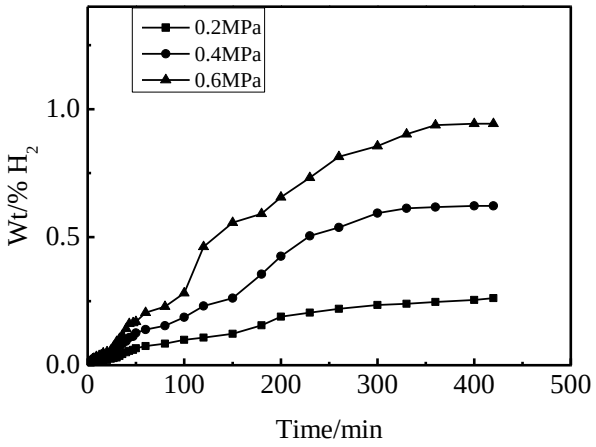

Fig. 7 H_2 uptake rate of carbons nanotubes at different initial pressure

4. Conclusions

In summary, we performed experiments on multi-walled carbon nanotubes synthesized by the pyrolysis method using copper nanoparticles as a catalyst. The diameter of the catalyst particles was larger by one magnitude order than that of growing carbon nanotubes. The H_2 uptake capacity of the carbon nanotubes with copper catalyst is higher than the ones without catalyst. The H_2 uptake capacity of the samples with catalyst is about 3.07 wt% at 12MPa. The amount of H_2 adsorption of carbon nanotubes with copper catalyst increased with the increase in H_2 pressure. The H_2 uptake rate of carbon nanotubes with copper catalyst increased with the increase of heat treatment temperature, thus and the rate of H_2 uptake of carbon nanotubes with copper catalyst may be improved with the increase of initial pressure.

Acknowledgement

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