Preparation of Si-carbon nanotube composite by decomposition of tetramethylsilane (TMS) and its hydrogen storage property

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Received 9 April 2006; received in revised form 28 June 2006; accepted 20 July 2006

Abstract

Hydrogen storage property of Si-carbon nanotube composite was studied. It was found that the carbon nanotube coated Si particle was prepared by the decomposition of tetramethylsilane by using Ni catalyst. The obtained composite was consisted of the spherical Si particle with 300 nm diameter and the surface of Si particle was coated with carbon nanotube with 10 nm diameter. The obtained Si-carbon nanotube composite shows a fairly large hydrogen storage capacity of 2.5 wt%. The amount of storage H2 increased with increasing the preparation temperature and the largest hydrogen storage amount could be achieved at 1273 K for 6 h. Fairly large hydrogen storage capacity could be sustained after 3 cycles of adsorption and desorption.

Keywords: Hydrogen storage; Carbon nanotube; Tetramethylsilane; Composite; Ni/Si

1. Introduction

Hydrogen is strongly anticipated as a new and clean energy carrier and is now produced industrially by the steam reforming reaction of CH4. However, hydrogen is a gas phase and so the most significant research subjects for the use of H2 as an energy carrier are to develop storage methods. At present, alloys such as LaNi5 [1] or Mg based alloys [2] are considered for the hydrogen storage. However, the amount of hydrogen storage in these alloys at room temperature is not large and furthermore, these alloys are heavy and easily degrade to powder during H2 storage and release. Therefore, at present, alternative materials of hydrogen storage are strongly sought. Recently, several numbers of materials such as hydrate, hydrocarbon, and alkaline metals are proposed and studied extensively. Among them, carbon nanotubes have attracted much interest as a new material for H2 storage, since it has been reported that large amounts of H2 (close to 50 wt%) can be adsorbed into carbon nanotubes [3,4]. In spite of many efforts, reproducibility of such large H2 storage capacity in carbon nanotubes has not been achieved and it is generally considered that the capacity of H2 storage in carbon nanotube is around the few wt% level [5]. Although there are many reports on H2 storage in carbon nanotubes with single wall or multi-walls [6–15], further systematic studies into H2 storage in carbon nanotubes is still required. In our previous study, the hydrogen adsorption property on the multi-wall carbon nanotube, which was obtained by decomposition of CH4, was investigated and it was found that about 1 wt% of H2 can adsorb on the multi-wall carbon nanotubes obtained by using Ni–Li/SiO2 catalyst [16]. In this study, we investigated the hydrogen storage capacity on the carbon nanotube upon silicon particles, which was prepared by decomposition of tetramethylsilane (TMS). During the work on Si materials for Li ion rechargeable battery, we found that the silicon particle covered with carbon nanotube exhibits the interesting performance for Li intercalation [17]. Therefore, it is considered that this metal composite is also attractive from the hydrogen storage materials because of its unique structure.

2. Experimental

Carbon nanotubes coating Si particle were obtained by the decomposition of tetramethylsilane (TMS, reagent
grade, Wako), using a conventional fixed bed reactor with a Si-supported Ni catalyst. The catalyst of Ni/Si was prepared by the incipient wetness techniques by using Ni(NO₃)₂ as the starting chemical reagents. Commercial Si powders (Wako, 99.99% in purity) were used as a support. Unless otherwise stated, the amount of loaded Ni was always kept to be 10 wt%. Before the reaction, the catalyst was oxidized under air gas flow (40 ml/min) at 673 K for 6 h and then reduced in H₂ atmosphere at 723 K for 2 h. The obtained catalyst was pressed into a disk, then crushed and sieved between 16 and 32 meshes.

The catalyst of 1 g was always fixed in the quartz tube reactor and the gaseous mixture of tetramethylsilane (TMS) and nitrogen (TMS:N₂ = 1:2) was fed to the catalyst bed at \( W/F = 34 \text{ g-cat.h/mol} \), where \( W \) and \( F \) are the catalyst weight and the feed gas rate, respectively. TMS was kept in the gas cylinder heated at 323 K and the flow rate of gaseous TMS was controlled by the valve also heated at 323 K. Catalytic decomposition of TMS was generally performed at 1273 K for 6 h. The conversion of TMS was estimated by the amount of hydrogen formed in the outlet of catalyst bed was analyzed by gas chromatographs with TCD detector. The conversion of TMS is defined as

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\text{TMS conversion} = \frac{[\text{H}_2]_{\text{out}}}{(6 \times [\text{TMS}]_{\text{in}})} \times 100,
\]

by assuming the following reaction:

\[(\text{CH}_3)_4\text{Si} = \text{Si} + 4\text{C} + 6\text{H}_2.\]

Hydrogen storage experiments were performed using the conventional volumetric adsorption equipment with ca. 70 ml dead volume. After evacuation of the carbon nanotubes at 473 K for 2 h, the sample was cooled to 283 K and a known amount of H₂ was introduced to the sample. The amount of H₂ storage was estimated by using equilibrium pressure based on the ideal gas. The hydrogen storage amount was compensated by subtracting the H₂ adsorption amount in a blank test from that of observed one.

TEM and SEM observations were performed by using JEOL, JEM 2010 (200 kV accelerate voltage) and JEOL, JSM-6700 equipped with the field emission-type electronic gun (20 kV accelerate voltage), respectively.

3. Results and discussion

Effects of the reaction temperature on the products by decomposition of TMS were firstly studied. Fig. 1 shows the TMS conversion on Ni/Si as a function of reaction temperature. Due to the small surface area of Si support, Ni/Si catalyst is not active to TMS decomposition and at 973 K, TMS conversion is as low as 10%. However, TMS conversion monotonically increased with increasing the reaction temperature and at 1273 K, it attained a value of 88%. Therefore, the high TMS conversion can be obtained at 1273 K. The amount of deposited carbon was also estimated by TG-DTA analysis. The weight decreased with exothermic reaction was observed around 873 K and the content of carbon in the sample is estimated to be 2.47 wt% from this weight loss.

Fig. 2 shows the X-ray diffraction (XRD) patterns of the sample obtained at different temperature. It is seen that the XRD peaks from Si became significant with increasing the reaction temperature. In particular, it is clearly observed on the sample obtained at 1273 K. In addition, the formation of amorphous like carbon is observed since the broad diffraction peak was also observed around 2\( \theta = 26^\circ \). Therefore, by decomposition of TMS, it is seen that the composite of Si and the carbon forms and the yield of composite drastically increased with increasing temperature. It is reported that SiC phase starts to form at the temperature higher than 1273 K for CVD of TMS [18,19]. In addition, the highest temperature for the used reactor is 1273 K, therefore, we fixed the reaction temperature at 1273 K for the preparation of sample.

Fig. 3 shows the SEM observation results of the resultant sample by the decomposition of TMS at
1273 K. The sample was consisted of the large particles of catalyst, Ni/Si and the quite small and spherical particles, which may be assigned to Si from TMS. Therefore, it is seen that the shape of the product in the decomposition of TMS is the small spherical particles. Further detail observation of the microstructure of the obtained sample was performed by TEM.

TEM image of the spherical particle in the sample was shown in Fig. 4. It is seen that the surface of the spherical particles was covered with the fine fiber like compound and the diameter of the particle is around 300 nm. On the other hand, from the high-resolution observation (Fig. 4), it is seen that the fiber like compound is tubular shape, since the outer part of tube is low electron transmission. The estimation of the diameter of surface nanotube is not easy; however, it can be roughly estimated to be around 5–10 nm. In addition, thickness of the surface layer is around 30 nm, which might suggest that the length of the surface fiber is around 30 nm. Considering the EDX analysis and XRD patterns, it is seen that the spherical shape particle at the center can be assigned to Si and outer tubular fiber is the carbon nanotube. In any way, the shape of the sample obtained by decomposition of TMS over Ni/Si is quite unique and interesting from the absorbent of various gases. This is because the unique adsorption property is expected for the nano-size cavities.

Fig. 5 shows the hydrogen adsorption amount of the specimens prepared at different decomposition temperature. In case of carbon nanotubes prepared by CH₄ decomposition, the hydrogen storage capacity is ca. 0.7 wt% at largest. However, it is seen that the specimens obtained by decomposition of TMS exhibits a fairly large hydrogen adsorption capacity such as 1.5 wt%, although the irreversible adsorption is also observed. It increased with increasing reaction temperature and attained a maximum at 1273 K. On the sample prepared at 1273 K, the capacity of hydrogen adsorption is as high as 2.5 wt% at 10 MPa and 283 K. BET surface area of this sample is 13.1 m²/g and it is also noted that the amount of observed H₂ is larger than that of monolayer adsorption of hydrogen. On the other hand, H₂ storage capacity decreased with further increasing the reaction temperature and this might be explained by the formation of SiC, which shows small H₂ storage capacity as discussed later. It is also noted that Ni catalyst was remained in the sample, however, it was confirmed that no hydrogen absorption is observed on the Ni/Si catalyst before TMS decomposition. Therefore, it is considered that the Ni residue has no influence on the hydrogen adsorption. In any case, it is obvious that the high H₂ adsorption storage is exhibited on the sample prepared at 1273 K.

Fig. 6 shows the comparison of the H₂ adsorption isotherms on the compounds contained in the sample. The sample is not a single phase but the composite of Si, Ni, and graphitic carbon from XRD measurement and the coexisting of SiC is also anticipated, since the formation of SiC is also detected by XRD when the decomposition of TMS was performed at 1373 K. As shown in Fig. 5, almost no hydrogen storage is observed for Si, which is well agreed
with no hydride solid compound existing in case of Si. On the other hand, multi-walled carbon nanotube (MWCN), which was prepared by CH$_4$ decomposition at 873 K, and the commercial SiC powder exhibit the hydrogen storage and the capacity was achieved almost 1 wt% for the storage and 0.5 wt% for the released one. Hydrogen storage capacity of carbon nanotube is almost the same value with that of reported one\[7\]. On the other hand, it is also interesting that SiC powder exhibits the hydrogen storage at 283 K, which is comparable with that of carbon nanotube. In contrast to that of MWCN and SiC, the composite obtained by TMS decomposition exhibits fairly large capacity for hydrogen storage, 2.5 wt% at 10 MPa and 283 K, while fairly large irreversible capacity was observed. Considering the content of SiC is not large and negligible amount of hydrogen storage is exhibited on Si, it is considered that hydrogen might be mainly adsorbed on the surface carbon nanotube on Si particle. Great improvement in the hydrogen adsorption amount by the combination of carbon nanotube and Si is highly interesting. At present, the detail mechanism for this increase in hydrogen adsorption is not clear. One explanation for this seems to be the exposed large surface area of graphitic carbon sheet when the small size carbon nanotube was obtained. However, simple size effects cannot be explained by the increase in the hydrogen storage amount and some chemical interaction between carbon nanotube and Si seems to be reasonably expected. Imamura et al.\[20,21\] also studied on the hydrogen adsorption on Mg and carbon composite, which is prepared by the milling method and reported that the hydrogen storage amount could be much improved by modification of Mg with carbon. They claimed that the interaction between carbon and Mg positively works for increasing the hydrogen adsorption capacity. Furthermore, it is predicted by a first principle study that a single Ti atom on a single wall carbon nanotube adsorbed hydrogen strongly and lead to large amount of hydrogen storage capacity up to 8 wt%\[22\]. Therefore, similar effects are also expected for the present Si-carbon nanotube composites. This means that the unusual adsorption may occur in the nano-sized channel in the small carbon nanotube deposited on Si particle with small diameter. Detail adsorption mechanism is now under investigation and the results will be reported elsewhere.

**Fig. 5.** Hydrogen adsorption amount of the specimens prepared at different decomposition temperature.

**Fig. 6.** Adsorption isotherms of H$_2$ in Si, SiC, carbon nanotube obtained from CH$_4$ at 873 K, and the Si-carbon composite obtained by TMS decomposition. Open symbol means adsorption and closed one is desorption.

**Fig. 7.** Effects of cycle number on the hydrogen adsorption isotherms of the composite obtained by TMS decomposition. Cubic symbol means adsorption and circle desorption.
that stable hydrogen adsorption and desorption is exhibited on the present Si-carbon nanotube composites. Consequently, the composite of Si and carbon nanotube is highly interesting as the hydrogen storage materials. At present, the content of carbon, which was estimated by TG-DTA analysis, is just around 3 wt% and so, if the adsorption site for hydrogen is carbon nanotube, then the amount of hydrogen adsorption capacity could be improved by increasing the content of carbon. In any case, this study revealed that the metal composite of Si and carbon nanotube is new, but highly interesting materials from the hydrogen storage.

4. Conclusions

Hydrogen storage was studied on the Si and carbon nanotubes composite, which was obtained by the decomposition of tetramethylsilane on Ni/Si catalysts. The obtained sample consisted of the large particles of Si support and small spherical particles for Si and carbon nanotube composite. Conversion of TMS monotonically increased with increasing the reaction temperature and it attained ca. 88% at 1273 K. The product at this temperature is carbon nanotube coated Si particle with ca. 300 nm in diameter. Although the multi-walled carbon nanotube does not exhibit large capacity for the hydrogen storage, this Si-carbon nanotube composite exhibits fairly large capacity for the hydrogen adsorption in spite of large content of Si of which hydrogen storage capacity is negligibly small. At present, the detail adsorption mechanism of this composite is not clear, however, carbon nanotube close to the Si particle might positively work for increasing the hydrogen capacity. Effects of interaction between metal and carbon materials are not studied systemically; this study suggests that the metal–carbon nanotubes composite may open a new family of hydrogen storage materials.