Synthesis of carbon nanotubes and carbon nanofilaments over palladium supported catalysts

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Abstract

The synthesis of carbon nanotubes (CNTs) and carbon nanofilaments (CNFs) was investigated using the catalytic decomposition of acetylene over alumina-supported palladium catalysts prepared with the impregnation of palladium acetylacetonate (Pd/Al₂O₃) and deposition of dodecanethiol-protected palladium nanoparticles (DT-Pd/Al₂O₃). The synthesized carbon products consisted of multi-walled carbon nanotubes together with a significant number of CNFs. At 700 °C over Pd/Al₂O₃, the carbon products were mainly made up of CNFs in the range of 9–26 nm in diameter, while CNTs with well-defined layer structures were synthesized at 800 °C. When Pd loading was 0.5 wt.%, carbon tubules showed better crystallinity than those of 2.5 wt.% at 700 °C. DT-Pd/Al₂O₃, showing better dispersion of DT-Pd nanoparticles, showed narrower size-distribution of CNTs than that of Pd/Al₂O₃. Over several supports (Al₂O₃, SiO₂–Al₂O₃, SiO₂, and Y) with DT-Pd nanoparticles, we obtained amorphous carbon-free CNTs showing a narrower diameter range of 6–21 nm at 700 °C.

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1. Introduction

Since their discovery by Iijima in 1991 [1], carbon nanotubes (CNTs) have stimulated researchers all over the world to investigate their unique properties. Since 1993, the catalytic growth of CNTs during the decomposition of hydrocarbons has been widely investigated [2,3]. The catalytically produced nanotubes have been assumed to be analogous to those synthesized by arc discharge and laser vaporization methods and show similar properties [4]. Basically the catalytic methods are very similar with chemical vapour deposition in the synthesis principle and nanotube growth; they consist of passing a gaseous flow of a certain proportion of carbonaceous feed gas, such as methane, acetylene, ethylene, or carbon monoxide, usually as a mixture with hydrogen gas, over transition metal particles (iron, cobalt, nickel, etc.). The formation of carbon filaments by the catalytic decomposition of carbon-containing gases over transition metal particles has been known for several decades and the mechanisms of filament formation have been actively debated over the years [4,5]. Many parameters, such as reaction temperature, gas composition and flow rate, duration of treatment, and catalyst natures and sizes, have been reported to affect the nature of the carbon species in the resulting material [6–9]. The advantage of the chemical decomposition method compared with the arc discharge one is the formation of nanotubes with various structures, such as straight, bent and also helical, and much longer lengths [6].

Rodriguez reviewed an investigation concerned with the materials preparation by impregnating a suitable substrate (graphite, Al₂O₃, SiO₂, etc.) with a desired metallic salt and proposed that the active species for filament and nanotube formation are metals, not carbides [4]. On the other hand, Wang reported the formation of wormlike carbon nanostructures by the arc discharge method with graphite rod and PdO [10]. A few studies related to the formation of carbon nanostructures using Pd as catalyst precursor have been reported. Vajtai et al. [11] have reported the growth of a carbon nanotube
network on palladium seeds. More recently, for field emission devices using CNTs, Wong et al. [12] have introduced Pd film over silicon substrates in the CNT growth using thermal CVD. These authors applied Pd catalysts, prepared with substrate seeding or general method of catalyst preparation, to CNT synthesis, in which the Pd particles showed a wide range of diameters. On the other hand, since nanometric Pd particles preformed through chemical reduction show a relatively narrow size distribution, we expect that Pd nanoparticles well-dispersed over suitable supports will form CNTs or CNFs having uniform diameters and structures.

In this study, we have introduced palladium acetylacetonate and palladium nanoparticles as catalyst precursors and carried out the synthesis of CNTs over Pd supported catalysts. We show that the two types of catalysts show a difference in the morphology of the carbon products, and that palladium nanoparticles play a critical role in the synthesis of CNTs using the catalytic decomposition of acetylene, showing good activity for CNT formation.

2. Experimental section

2.1. Materials

Palladium chloride (99.5%, Wako) was used as purchased. Tetraoctylammonium bromide (TOAB, Lancaster Synthesis) was used as a phase transfer catalyst in chemical reduction for the preparation of Pd nanoparticles. Dodecanethiol (DT, Wako) was used as a protective agent for the Pd nanoparticles. Pd(acac)₂ (palladium acetylacetonate; 99.5%, Wako) was introduced as a catalyst precursor. All the supports used in the preparation of the Pd catalysts were purchased from Aldrich. Methanol, ethanol, and toluene were guaranteed grade and used without further purification.

![Fig. 1. TEM images of Pd particles formed over Pd/Al₂O₃ prepared by (a, b) impregnation method and (c) deposition of thiol-protected Pd nanoparticles: the Pd loadings are fixed to (a) 2.5 and (b, c) 0.5 wt.%. (d) TEM images of dodecanethiol-protected Pd nanoparticles prepared by a chemical reduction method containing their size distribution diagram.]
2.2. Preparation of Pd nanoparticles protected with dodecanethiol

The preparation of Pd nanoparticles (DT-Pd) was carried out with reference to the Brust two-phase reaction procedure [13–15]. An H2PdCl4 (0.6 mmol) aqueous solution (60 ml), prepared by mixing 0.107 g PdCl2, 6 ml of 0.2 M HCl, and 54 ml of water, was added to TOAB (1.2 mmol) in toluene (160 ml), and the mixture was vigorously stirred. After mixed with DT (0.6 mmol) in toluene (20 ml) and stirring the solution for 30 min at room temperature, an aqueous solution (60 ml) of sodium borohydride (6 mmol) was added and stirring continued for 30 min. The organic phase was then separated, evaporated in a rotary evaporator at 40 °C, and dried in vacuo at 30 °C for a day. The crude solid obtained was dissolved in 30 ml of toluene and mixed with 300 ml of methanol to remove excess DT and TOAB. The dark brown precipitate was filtered off, washed with methanol, and dried in vacuo at room temperature for a day. The specimens for TEM observation were prepared by placing a few drops of Pd nanoparticles redispersed in toluene solution onto carbon-coated copper grids.

2.3. Preparation of Pd catalysts

The Pd catalysts were prepared with an impregnation method using Pd(acac)2 and an deposition method using DT-Pd nanoparticles as catalyst precursors, which were abbreviated to Pd/Al2O3 and DT-Pd/Al2O3, respectively. The Pd loading supported onto Al2O3 was fixed to 0.5 and 2.5 wt.%. Besides Al2O3, SiO2-Al2O3, SiO2, and Y zeolite were tested as supports for DT-Pd nanoparticles. The fresh supports were dried for more than 12 h at 130 °C prior to use. To deposit the Pd nanoparticles onto a support from toluene solution, toluene was evaporated with a rotary evaporator and the recovered solids were dried at 130 °C for 3 h. All the Pd supported catalysts were calcined under 30 ml/min of air at a heating rate of 5 °C/min up to 400 °C and held for 30 min. SiO2-Al2O3, SiO2, and Y zeolite were used as supports.

2.4. Apparatus and procedures

Acetylene (99.5%) was used as the carbon source in the decomposition reaction and nitrogen (99.95%) as the dilute gas, both of which were obtained from Nihon Gas Co. The decomposition of acetylene was performed in a quartz fixed-bed reactor vertically set in an electronic furnace. The feed gas was regulated with a mass flow controller and flowed through a moisture trap before reaction. The flow rates of nitrogen and acetylene were 100 and 10 ml/min, respectively. The catalytic decomposition of acetylene was carried out for 30 min at each reaction temperature of 700 and 800 °C.

2.5. Characterization of catalysts and carbon products

The carbon deposit formed over Pd/Al2O3 was separated from the catalyst surface by melting the catalysts with a
mixed acid of nitric acid and hydrochloric acid. The carbon deposit thus obtained was analyzed with a Raman spectrometer (ISA, DILOR-JOBIN YVON-SPEX, He-Ne laser: 632.8 nm). The samples after the reaction were observed with transmission electron microscope (TEM, H-7100, Hitachi, 125 kV; high-resolution TEM, H-9000NAR, Hitachi, 300 kV) and scanning electron microscope (SEM, S-4100, Hitachi, 20 kV). The catalyst samples were cast with holey carbon-coated copper grids after dispersion in ethanol.

3. Results and discussion

3.1. Microscopic study of carbon tubules produced over Pd/Al₂O₃

The Pd supported catalysts (Pd loading: 0.5 and 2.5 wt.%) prepared by the impregnation method (Pd/Al₂O₃) were first used in the decomposition reactions for CNT synthesis at two different temperatures, 700 and 800 °C. The Pd/Al₂O₃, previously calcined at 400 °C, shows good dispersity over Al₂O₃ in TEM observations (Fig. 1(a) and (b)), wherein the Pd particles have average diameters of 8.4 ± 2.7 nm for 0.5 wt.% and 14.8 ± 5.1 nm for 2.5 wt.%. The DT-Pd nanoparticles in Fig. 1(d), used as another catalyst precursor, have narrow size-distribution and average diameter of 1.2 ± 0.2 nm. The alumina-supported Pd nanoparticles (DT-Pd/Al₂O₃) (Fig. 1(c)) show a much smaller average diameter of 4.3 ± 0.7 nm than those in Fig. 1(a) and (b) after calcination.

Fig. 2 shows SEM and TEM images of carbon products formed over Pd/Al₂O₃ at 700 and 800 °C. At temperatures below 700 °C, the carbon products over Pd/Al₂O₃ with Pd loading of 2.5 wt.% chiefly contained amorphous carbon particles and spiral carbon fibers. On the other hand, the CNFs having average diameter of 16.9 ± 4.3 nm started to be vigorously formed over Pd/Al₂O₃ at 700 °C. The nanotubes formed at 800 °C have average diameters of 48.5 ± 8.0 nm and show significant changes in structure, compared to those at 700 °C (Table 1).

To inspect the graphene layers of the tubules formed, the solid samples after reaction were observed with high resolution transmission electron microscopy (Fig. 3). In these micrographs, the tubules produced over Pd/Al₂O₃ at 700 and 800 °C present different morphologies according to

![Fig. 1](image1)

![Fig. 2](image2)

![Fig. 3](image3)

Table 1

| Catalysts                  | Outer diameter (nm) | D_{ave} (nm) | σ (nm) | Interlayer spacing (nm) | Orientation angle\(^b\) (degree) |
|----------------------------|---------------------|--------------|--------|-------------------------|---------------------------------|
| Pd/Al₂O₃ (2.5, @700 °C)   | 9–26                | 16.9         | 4.3    | 0.357                   | 10–15                           |
| Pd/Al₂O₃ (2.5, @800 °C)   | 30–68               | 48.5         | 8.0    | 0.338                   | 0–10                            |
| Pd/Al₂O₃ (0.5, @700 °C)   | 7–19                | 12.0         | 3.0    | 0.342                   | <15                             |

\(^a\) The Pd loading wt.% supported over each catalysts.
\(^b\) The angle between the graphite basal planes and the tube axis.
reaction temperature and Pd loading. When the Pd content was 2.5 wt.%, the tubules formed at 700 °C consisted of CNFs having an orientation angle (the angle between the graphite basal planes and the growth axis of carbon tubules) of 10–15° (Fig. 3(b)). Under the above reaction conditions, the interlayer spacing was 0.357 nm (Table 1). Contrary to this aspect, the tubules synthesized at 800 °C over Pd/Al2O3 with the same Pd loading of 2.5 wt.% (Fig. 3(c)) showed different structure from those at 700 °C. The tubules had amorphous carbon layers with a thickness about 10–17 nm, which covered the nanotubes existing inside the tubules. The inside tubes showed orientation angle of <10° and their interlayers spacing was approximately 0.338 nm, similar to that of graphite. On the other hand, it is noted that when Pd content decreased to 0.5 wt.%, the calcined Pd/Al2O3 showed a much narrower size distribution of Pd particles than with the 2.5 wt.% (Fig. 1(b)) and the carbon tubules formed at 700 °C also showed a narrower size distribution (average diameter: 12 ± 3.0 nm, Table 1). High resolution TEM images of the carbon tubes (Fig. 3(a)) indicate similar aspects, consisting of the orientation angle of <15° and the interlayer spacing of 0.342 nm. The graphene layers are curled or bent, but have more stratic structure than those with 2.5 wt.% Pd shown in Fig. 3(b). To compare with these results, DT-Pd nanoparticles deposited onto several different types of supports were used for the catalytic decomposition of acetylene under the same conditions as Pd/Al2O3 prepared by impregnation method.

Fig. 4 shows SEM images of carbon products produced over DT-Pd nanoparticle supported onto SiO2–Al2O3, SiO2, Al2O3, and Y zeolite. These carbon tubes have outer diameters in the range of 6–21 nm and curled layers. The results for the carbon products formed over DT-Pd/Al2O3 (Fig. 4(a)) show the relatively smaller average diameter and narrower size-distribution of outer diameters of the CNTs. In Fig. 4(b) and (d), SiO2–Al2O3 and Y zeolite showed similar activity for nanotube growth and the tubes over these catalysts had average diameters of 13.4 ± 4.0 and 12.2 ± 2.7 nm, respectively. For SiO2 with a Pd loading of 0.5 wt.% (Fig. 4(c)), the outer diameters in size and range indicated almost same results as the others: 13.8 ± 4.1 nm and 7–26 nm.

3.2. Raman scattering of carbon products formed over Pd catalysts

The carbon products obtained through catalytic decomposition of acetylene at 700 °C were measured by Raman spectroscopy. Fig. 5 shows the Raman spectra of the tubes formed over several DT-Pd nanoparticle-supported catalysts (containing SiO2–Al2O3, SiO2, Al2O3, and Y zeolite), in which two main peaks located at 1326 and
1595 cm\(^{-1}\) are observed and designated as disorder-induced (D) mode and C–C stretching (G) mode, respectively [16–18]. There were no peaks observed at the band area of breathing mode (under 250 cm\(^{-1}\)) related to single-walled carbon nanotubes. The peak intensities of the D and G bands for DT-Pd/SiO\(_2\)–Al\(_2\)O\(_3\) appeared much larger than those for other catalysts (DT-Pd/SiO\(_2\), DT-Pd/Al\(_2\)O\(_3\), and DT-Pd/Y zeolite). The samples formed over DT-Pd/Al\(_2\)O\(_3\) have another peak observed around 1450 cm\(^{-1}\). Holden et al. [18] identified this peak with fullerenes in their work for carbon related materials, but from the TEM results of this sample, we could not verify the existence of fullerenes. Jawhari et al. [19] reported that a broad band around 1500–1550 cm\(^{-1}\) was noticed in several carbon-based materials and was associated with amorphous sp\(^2\)-based forms of carbon. The unassigned peak at 1450 cm\(^{-1}\) was assigned to be disordered carbons attributed to interstitial defects.

### 3.3. Growth mechanism of carbon nanofilaments and nanotubes over Pd catalysts

Many reports have published on the synthesis of CNTs through decomposition of hydrocarbons over metal catalysts and proposed the ‘tip-growth’ and ‘base-growth’ models [20–23]. The CNTs and CNFs formed through decomposition of acetylene over Pd catalysts in our study can be also explained by these models. On the other hand, we propose the modified mechanism related to the structure of Pd nanoparticles. Generally, metal particles significantly affect the diameters and structures of CNTs and CNFs, which sometimes have similar diameter with the metal particles. Fig. 6(a) shows Pd particles supported on Pd/Al\(_2\)O\(_3\) and the carbon tubules grown from the particles at 700 °C; the tubules show much smaller diameters than those of supported Pd particles. It is supposed that the partial outer surface of Pd particles produces graphene layers during the nucleation step of CNT/CNF growth and that the layers formed partially at a position of the Pd surface continuously grow to produce tubules by supplying carbon atoms from the rest surface of Pd particles. In our study, Pd particles used as catalysts for CNT synthesis plays an important role in the growth mechanism of carbon tubules. Fig. 3(b) and (c) show the images of carbon tubules with well-defined layers. At 700 °C the Pd particle had an acute angle for the upward growth axis (Fig. 6(b)). During the decomposition of acetylene, produced carbon atoms diffuse along the plane of Pd particles and carbon layers of CNFs are formed as shown in Fig. 3(b) [4]. At 800 °C the Pd particle had an almost rectangular form (Fig. 6(c)). Carbon layers produced at 800 °C are more turbostratic, when compared with those formed on the surface of Pd particles at 700 °C. Depending on a change of reaction temperature, Pd particles showed different shapes and carbon tubules also showed different morphologies.

The carbon tubules (Fig. 4), which were formed over several catalysts using DT-Pd nanoparticles, showed
similar shapes with the CNTs reported by Wong et al. [13]. When Pd loading was 0.5 wt.% (Fig. 3(a)) or Pd nanoparticles were used (Fig. 4), the carbon tubules had randomly been twisted or curled in shapes. We think that small Pd nanoparticles may have irregular shapes during the reaction. However, the origin of the straticity (Fig. 3(a)) is not clear. Instead, from the proposed CNT/CNF growth mechanism on the partial surface of Pd particles, we suppose that carbon atoms diffuse over Pd nanoparticles faster than large-sized Pd particles and that the CNTs formed over Pd catalysts by deposition of DT-Pd nanoparticles show much narrower size distribution in diameter than that by impregnation.

4. Conclusions

For the synthesis of CNTs through the decomposition of acetylene, we have examined the catalytic activity of Pd catalysts prepared by two methods, impregnation of palladium acetylacetonate (Pd/Al2O3) and deposition of DT-Pd nanoparticles (DT-Pd/Al2O3). From SEM and TEM studies of carbon products formed over the Pd catalysts, it was found that Pd/Al2O3 show selective activity for CNT and CNF growth at different reaction temperatures (700 and 800 °C) and Pd loading (0.5 and 2.5 wt.%). When compared with conventional transition metal-supported catalysts, the CNTs formed over Pd/Al2O3 were obtained with a significant number of CNFs. The Pd/Al2O3 with lower Pd loading produced CNTs with a well-defined layer structure. Over DT-Pd/Al2O3, the formed CNTs showed a much narrower size distribution and a smaller average diameter. When considering the growth mechanism of CNTs and CNFs, we suggested the modified mechanism related to the size and structure of Pd nanoparticles according to temperature and Pd loading. At present, we are developing the synthesis of CNTs over modified Pd nanoparticles, to advance the quality and yield of the tubes.

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