



Synthesis of carbon nanotube supported Pd catalysts and evaluation of their catalytic properties for C–C bond forming reactions

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ABSTRACT

A simple method of depositing Pd nanoparticles onto carbon nanotubes (CNTs) as catalyst supports is devised for C–C bond forming reactions. Thiol groups were utilized as linkers to secure the Pd nanoparticles without agglomeration. The samples were characterized by TEM, XPS and Raman spectroscopy. The prepared CNT-Pd nanocomposites effectively promoted the formation of C–C bonds at a low Pd content (~2.0%) and in the absence of any ligand. This result indicates that surface thiolation is an effective way to obtain highly dispersed metal nanoparticles on the surface of CNTs and markedly improves their catalytic activity.

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1. Introduction

One of the most important issues in current organic synthesis is the development of new efficient carbon–carbon and carbon–heteroatom bond forming reactions. In this regard, transition metal-based catalysts have generally been used for these reactions. Among them, palladium has been recognized as an indispensable catalyst for C–C bond forming reactions and there is a great deal of literature on its properties in many reactions [1–3]. Although palladium catalysts demonstrate excellent catalytic performance in C–C bond forming reactions, there are still some problems that need to be addressed in terms of their efficiency and susceptibility. The high activity of these catalysts largely depends on the use of a high Pd loading (5–10 wt.%) and the use of ligands which increase their cost and risk of the contamination by the ligands. Also, their deactivation caused by absorbed intermediates limits their stability. Since the catalysis reaction occurs entirely on the surface of the Pd particles, a high dispersion is required to improve the catalytic activity and reduce the cost of the catalysts. For this reason, many attempts have been made to synthesize new types of Pd supports, such as zeolites or active carbons, due to their large surface areas and unique pore structures [4,5].

Recently, carbon nanotubes (CNTs) have received considerable attention as catalyst supports in both heterogeneous

catalysis and electrocatalysis, due to their high mechanical strength, large surface area, good electrical conductivity, and durability under harsh conditions [6]. Some researchers have reported CNT-supported metal catalysts (e.g., Pt, Pd, Au, Ru and PtRu) exhibiting good catalytic behaviors under various chemical reactions, involving methanol electro-oxidation [7], selective hydrogenation [8], Suzuki coupling [9], CO oxidation [10], and hydrodehalogenation [11]. The enhanced catalytic performances are generally attributed to the metal–CNT interaction [12]. This interaction induces a peculiar microstructure or modification of the electron density in the metal clusters and enhances the catalytic activity. The adsorption of organic species is also favored by van der Waals interactions between the CNTs and aromatic rings, leading to favorable reactant–product mass transportation [13].

However, there are difficulties in dispersing metal nanoparticles onto CNTs due to their hydrophobic nature and their tendency to agglomerate. To overcome these problems, non-covalent and covalent methods have been developed to activate the surface of the CNTs, including plasma treatment [14], polymer wrapping [15], electrochemical treatment, [16] and surface functionalization with functional groups such as carboxyl, amine, and sulfone groups [17–19]. In this work, we report a simple and effective process to prepare CNT-Pd nanocomposites by depositing Pd(dba)₂ on thiolated multiwall carbon nanotube (MWNT) surfaces. A high-yield C–C bond forming reaction accomplished at a low Pd content (~2.0%) and in the absence of any ligand is observed. This synthetic approach should be broadly applicable for preparing CNT-supported metal catalysts and markedly improves the catalytic activity.

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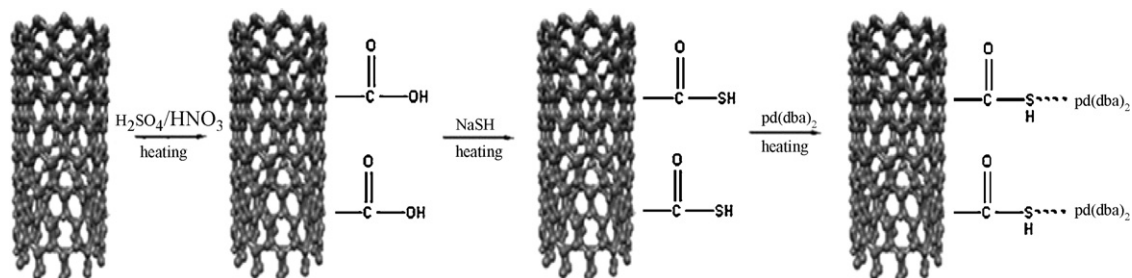


Fig. 1. Schematic illustrations of the synthetic route of the CNT-Pd nanocomposites.

2. Experimental

MWNTs were obtained from Carbon Nano Tech. Co., Ltd. (South Korea). Bis(dibenzylideneacetone)palladium (0), $\text{Pd}(\text{dba})_2$, was prepared according to a previously reported method [20]. Sodium

hydrosulfide (NaSH) was purchased from Aldrich. Nitric acid (HNO_3), sulfuric acid (H_2SO_4) and tetrahydrofuran (THF) were of analytical grade and were used as received.

The MWNTs were stirred in an acid solution of HNO_3 and H_2SO_4 (1:3 by volume) at 90°C for 3 h. The MWNTs were then filtered,

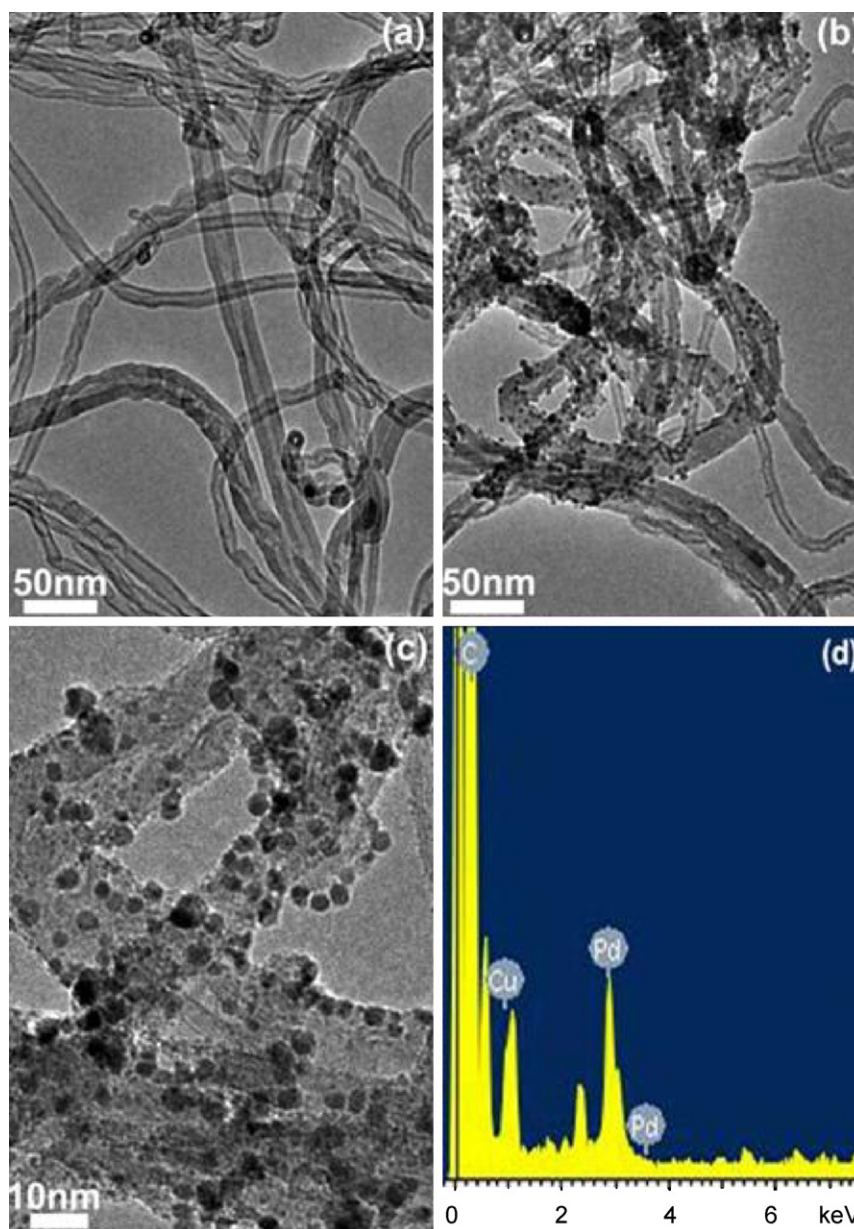


Fig. 2. (a) TEM image of pristine CNT at low magnification. (b) TEM image of the CNT-Pd nanocomposite at low magnification. (c) TEM image of the CNT-Pd nanocomposite at high magnification. (d) EDS spectrum of the CNT-Pd nanocomposite.

washed with distilled water, and dried in an oven at 110 °C. The acid-treated MWNTs were dispersed in THF and then a NaSH aqueous solution was added to produce thiol groups on their surfaces, and the resulting CNTs are denoted as CNT-SH. The thiolation was confirmed using the XPS spectrum in the sulfur 2p region. Finally, the thiolated MWNTs were dispersed in THF and then a Pd(dba)₂/THF solution was added. The mixture was stirred for 20 h until all of the Pd(dba)₂ precursors were anchored onto the MWNTs, and the resulting CNTs are denoted as CNT-Pd. These samples were separated from the mixture by filtration, washed several times with pure ethanol and DI water, and dried in a vacuum oven at 50 °C for 4 h. To verify the effect of the support, a mixture of Pd(dba)₂/CNTs was also prepared by the following method. 2.0 mg of Pd(dba)₂ and 100 mg of pristine CNTs were added to THF and the reaction mixture was stirred at room temperature for 3 h. The solvent was evaporated and the residue was dried in a vacuum for 12 h.

The transmission electron microscopy observations were carried out in a JEM-2200FS microscope at 200 kV. Samples for the TEM analysis were prepared by extensive sonication of the CNTs in ethanol. A drop of the solution was deposited on a gold grid and the solvent was allowed to evaporate in air. XPS analysis was performed using a VG multilab 2000 spectrometer (ThermoVG scientific) in an ultra high vacuum. This system uses an unmonochromatized Mg K α (1253.6 eV) source and a spherical section analyzer. Survey scan data was collected using a pass energy of 50 eV. The content of Pd in the Pd-CNT nanocomposite was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) with an OPTIMA 4300 DV (PerkinElmer). Prior to the measurement, the sample was treated with a mixture of HNO₃, HF and HBO₃ in order to dissolve it completely. Raman spectra were obtained at room temperature using an inVia Reflex (Renishaw 1000) micro-Raman spectrometer with 632.8 nm laser line.

The catalytic activity of the prepared CNT-Pd for the Stille and Hiyama coupling reaction was examined. These reactions were used as a standard test reaction to probe the reactivity of Pd-catalyzed carbon-carbon bond forming reactions. The coupling reaction was performed in a round-bottom flask fitted with a water-cooled condenser. 4-Iodotoluene was employed as a standard substrate for the coupling reactions. The reactions were carried out with 0.3 mol.% of palladium under the previously reported conditions [21,22].

3. Results and discussion

The synthetic procedures of the CNT-Pd nanocomposites routes are shown in Fig. 1. Thiol (-SH) groups were utilized as linkers between the Pd nanoparticles and CNTs. The Pd nanoparticles are anchored to the surface of the CNTs due to their interaction with the free electron pairs of the S atoms. The detailed morphology of the CNT-Pd nanocomposites was examined by TEM. Fig. 2(a) shows a typical TEM image of a pristine CNT with a diameter in the range of 10–20 nm. All of the tubes had a clean surface. For the CNT-Pd nanocomposites, the TEM image shows that smaller and highly dispersed nanoparticles were much more abundant than larger aggregated ones [Fig. 2(b)]. The magnified image reveals that the nanoparticles are strongly adhered on the sidewalls of the CNTs [Fig. 2(c)]. The average particle size is estimated to be ~6.0 nm. The EDS analysis shows that the species supported on the CNT was Pd [Fig. 2(d)].

Raman spectroscopy was used to obtain information about the average crystallinity of the CNT-Pd compared with that of the pristine CNTs. As shown in Fig. 3, the spectrum consists of three bands at ~1330 cm⁻¹ (D band), 1570 cm⁻¹ (G band), and ~1610 cm⁻¹ (D' band) [23,24]. The D band is a disorder induced feature originating from the vibrations of C atoms with dangling bonds. The G

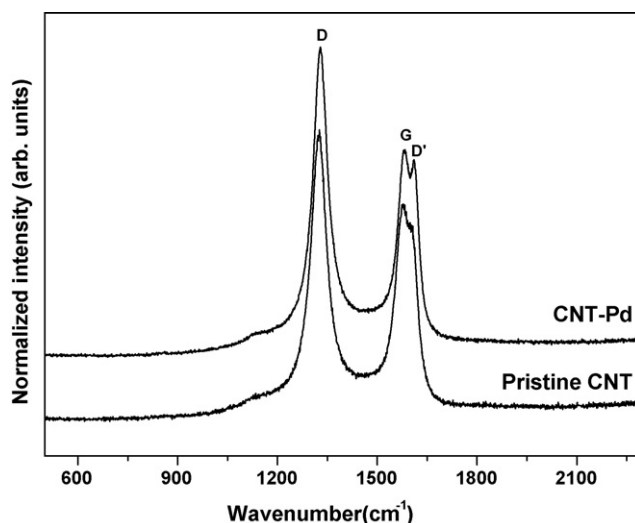


Fig. 3. Raman spectra of pristine CNTs and CNT-Pd nanocomposites.

band arises from a tangential shear mode of the C atoms that corresponds to the stretching mode in the graphite plane. The D' band, which is a shoulder of the G band at a higher frequency, corresponds to second-order Raman scattering from the variation of the D-band. The intensity ratio of the D band to G band (I_D/I_G) has a linear relation with the inverse of the in-plane crystallite dimension. The value of I_D/I_G is about 1.38 for the pristine CNTs and about 2.56 for the CNT-Pd. These results suggest that the functionalization of the CNTs results in a decrease of their crystallinity.

Fig. 4 shows a series of XPS survey spectra from the pristine CNTs, CNT-SH and CNT-Pd. For the pristine CNTs, the XPS data shows distinct C and O 1s peaks and no other elements are detected. However, after their thiolation, the presence of S element is detected from the CNT-SH. The relative surface atomic ratio was estimated from the corresponding peak areas, corrected with the tabulated sensitivity factors. The estimated value of the S content is about 2.7 at.%. Since the XPS signal is obtained by collection of photoemitted electrons, this technique is very sensitive to the properties of the surface. For the Pd-CNT, the photoemitted electrons from S atoms are screened by deposited Pd nanoparticles, which resulted in the featureless S 2p profile. The XPS data also confirmed the presence of Pd in the nanocomposites. The Pd content is estimated to be 2.0 at.%. According to ICP experiments, the

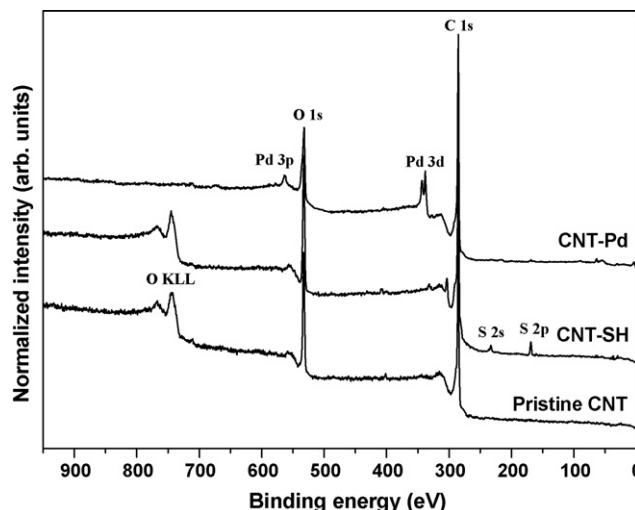


Fig. 4. XPS survey spectra of pristine CNTs, CNT-SH, and CNT-Pd nanocomposites.

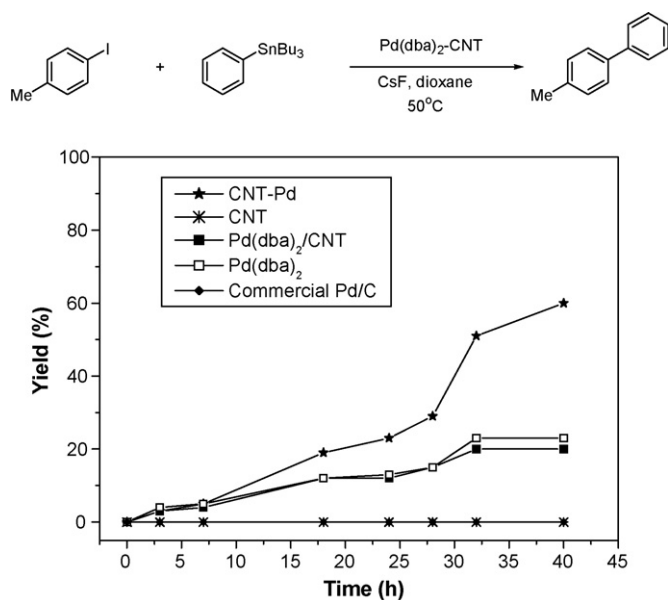


Fig. 5. Stille coupling reactions of 4-iodobenzene and tributylphenylstannane.

amount of Pd contained in the nanocomposite was 2.47 wt.%, which was consistent with that of the XPS result.

To verify their catalytic activity in the Stille and Hiyama coupling reaction, a comparative experiment using the CNT-Pd nanocomposite, Pd(dba)₂, CNTs, Pd(dba)₂/CNT mixture, and a commercial Pd/C catalyst (purchased from Aldrich) under identical conditions was conducted. 0.3 mol.% of the catalyst was employed in both reactions. For the Stille reaction, the coupling of 4-iodotoluene and tributylphenylstannane afforded the desired product with 60% yield in 40 h at 50 °C. As shown in Fig. 5, similar reactivity was observed at the initial reaction time, however the CNT-Pd afforded better reactivity than the other catalysts, including the pristine Pd(dba)₂, CNTs, Pd(dba)₂/CNT mixture and a commercial Pd/C catalyst. The Hiyama coupling reaction of 4-iodotoluene and trimethoxysilylbenzene (see Fig. 6) was also carried out in the presence of the CNT-Pd, with TBAF as an activator, in *p*-xylene at 50 °C. Only the CNT-Pd afforded the coupled product, 4-methylbiphenyl, with 98% yield in 20 h. The other catalysts, viz. the pristine Pd(dba)₂, CNTs, the mixture of CNTs and Pd(dba)₂, and the commercial Pd/C

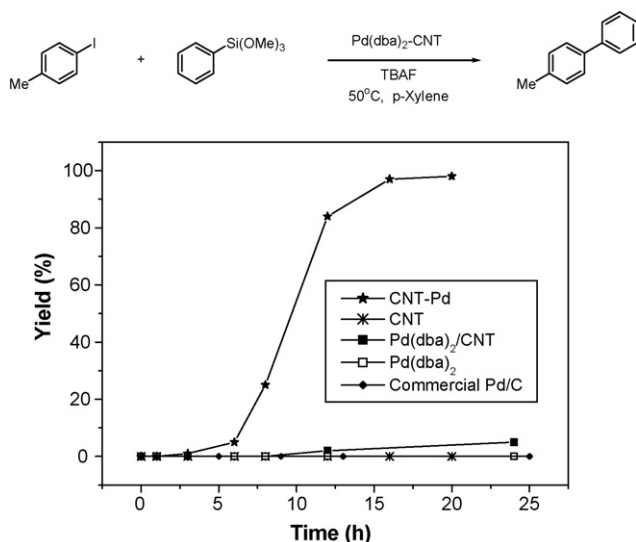


Fig. 6. Hiyama coupling reactions of 4-iodobenzene and trimethoxysilylbenzene.

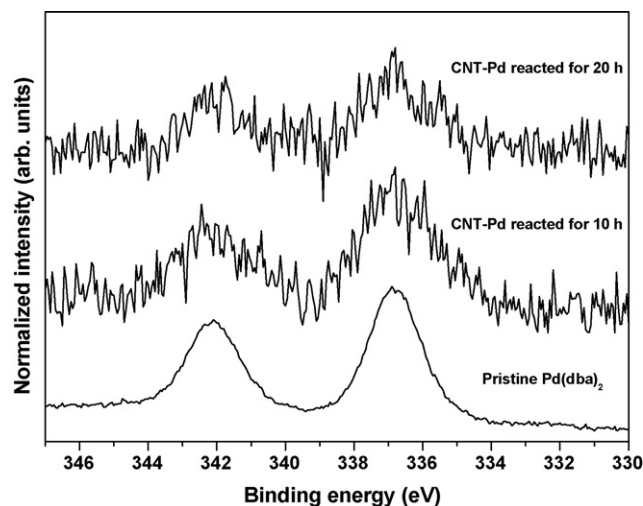


Fig. 7. Comparison of the Pd 3d XPS spectra from the pristine Pd(dba)₂ and CNT-Pd nanocomposites reacted for 10 and 20 h. The two samples were extracted from the Hiyama coupling reactions.

catalyst did not produce the desired coupled product. Both the Stille and Hiyama coupling reactions showed low yields at the beginning of the reactions, which means that they might require an induction period for the activation of the CNT-Pd: the Stille reaction needed 7 h and the Hiyama reaction needed 5 h for their activation. Both proceeded under ligand-free conditions. Generally, in the absence of a ligand, the active palladium species is converted to inactive palladium black. In the case of the CNT-Pd, the CNT supports inhibit the formation of inactive palladium black and maintain the active Pd(0) state during the reaction time (see Fig. 7), which may be responsible for the good catalytic activity of the nanoparticles in the chemical reactions.

4. Conclusions

We demonstrated that thiolated CNTs can be effectively used as a catalyst support for C–C bond forming reactions. The TEM studies indicate that well-dispersed Pd nanoparticles were anchored onto the surface of the CNTs and the size range of these nanoparticles was about 3–10 nm. The XPS results suggest that the Pd content was about ~2.0 at.%. The prepared CNT-Pd effectively promoted C–C bond forming reactions, such as the Stille and Hiyama reactions, at a low Pd content in the absence of any ligand and exhibited higher activity compared with that of the pristine CNTs. The results suggest that the CNTs significantly influenced the catalytic activities of the CNT-supported metal catalysts for the C–C bond forming reactions.

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