



Synthesis of Pd–CNT nanocomposites and investigation of their catalytic behavior in the hydrodehalogenation of aryl halides

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ABSTRACT

A catalytic system based on Pd–CNT nanocomposites for the hydrodehalogenation of aryl halides is described. Thiol groups were utilized as linkers to secure the Pd nanoparticles without agglomeration. The Pd–CNT nanocomposites effectively promoted the hydrodehalogenation of aryl halides at a low Pd content (~2.3%) and in the absence of any ligand. The results suggest that the CNTs could significantly influence the catalytic activities of CNT-supported metal catalysts for hydrodehalogenation.

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Palladium is an attractive catalyst for the hydrodehalogenation reaction because it promotes the cleavage of carbon–halogen bonds and facilitates hydrogenation.¹ In Pd-catalyzed hydrodehalogenations, the reactivity is highly affected by both Pd content and the ligand. Many researchers have reported that a number of ligands such as N-heterocyclic carbene,² triphenyl phosphine,³ and phosphite⁴ could be utilized to accomplish Pd-catalyzed hydrodehalogenations. Although these catalysts demonstrated excellent catalytic performance, the high Pd loading (5–10 wt %) and use of ligands are detrimental due to high cost, ligand contamination, and difficulties with respect to reuse and recovery. Recently, Sanjiki group reported Pd/C-catalyzed hydrodehalogenation, however, they employed hydrogen gas as a hydrogen source.⁵ Therefore, the development of inexpensive, convenient, and ligand-free heterogeneous catalysts for hydrodehalogenation reactions requires further study.

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 catalysts (e.g., Pt, Pd, Au, Ru, and RuO₂) exhibiting good catalytic behaviors under various chemical reaction conditions, involving methanol electro-oxidation,⁷ selective hydrogenation,⁸ Suzuki coupling,⁹ CO oxidation,¹⁰ and Fischer–Tropsch synthesis.¹¹ However, few studies have centered upon CNTs as catalyst supports for hydrodehalogenation reactions, a key approach in preventing environmental pollution.¹²

In the present work, the high-yielding hydrodehalogenations accomplished at low Pd contents (~2.3%) and in the absence of any ligand are reported. Catalytic behaviors were also compared with the reference systems. The Pd–CNT nanocomposites used in this work were prepared by depositing Pd₂(dba)₃ on thiolated multiwall carbon nanotube (MWNT) surfaces.

MWNTs were obtained from Carbon Nano Tech. Co., Ltd. (South Korea). Sodium hydrosulfide (NaSH) and tris(dibenzylideneacetone)dipalladium(0) [Pd₂(dba)₃] were purchased from Aldrich. Nitric acid (HNO₃), sulfuric acid (H₂SO₄), and tetrahydrofuran (THF) were of analytical grade and were used as received.

MWNTs were stirred in an acid solution of HNO₃ and H₂SO₄ (1:3 by volume) at 90 °C for 3 h. The MWNTs were then filtered, washed with distilled water, and dried in an oven at 110 °C. The acid-treated MWNTs were dispersed in THF and then the NaSH aqueous solution was added to produce the thiol groups on the MWNT surfaces. The thiolation was confirmed using the XPS spectrum in the sulfur 2p region. Finally, the thiolated MWNTs were dispersed in THF and then the Pd₂(dba)₃/THF solution was added. The mixture was stirred for 20 h until all Pd₂(dba)₃ precursors were anchored onto the MWNTs. The Pd–CNT nanocomposites 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 support effect, the mixture of Pd₂(dba)₃/CNT was also prepared by the following method. A 2.3 mg of Pd₂(dba)₃ and 100 mg of pristine CNT were added in THF and the reaction mixture was stirred at room temperature for 3 h. The solvent was evaporated and the residue was dried in vacuum for 12 h.

The size and structure of Pd–CNT nanocomposite were examined by scanning electron microscopy (SEM, Jeol JSM-7500F) and transmission electron microscopy (TEM, Jeol JEM-2010, 200 kV). X-ray photoelectron spectroscopy (XPS) was measured with VG

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multilab 2000 equipment (ThermoVG scientific) using the Mg K α X-ray line of 1253.6 eV excitation energy.

The typical hydrodehalogenation reactions were performed in a round-bottomed flask fitted with a water-cooled condenser. 4-Bromotoluene (3.0 mmol), Pd–CNT (0.069 mmol), and Cs₂CO₃ (3.6 mmol) were added in 20 mL cyclohexanol solvent. The reaction mixture was stirred and heated at 100 °C for 10 h. The product was separated by distillation method and identified by GC measurements. The remained Pd–CNT was washed with Et₂O and dried in vacuum, and used again for the second run.

Figure 1a shows a typical SEM image of pristine CNT with a diameter in the range of 10–20 nm. All of the tubes had a clean surface. For the Pd–CNT nanocomposite, the SEM image clearly shows that nano-sized particles were highly dispersed on the CNTs (Fig. 1b). Smaller and highly dispersed nanoparticles were much more abundant than larger aggregated ones. The average particle size was estimated to be ~8.0 nm. The TEM images further reveal the nanoparticles attached to the sidewall of the CNTs (Fig. 1c). According to EDXS analysis (Fig. 1d), the species supported on the CNT was Pd.

Figure 2 shows the XPS survey spectrum of the Pd–CNT nanocomposites as well as the spectrum of the reference material (pristine CNT). The XPS results indicated that C, O, and Pd elements exist on the Pd–CNT surface. The relative surface atomic ratio was estimated from the corresponding peak areas, corrected with tabulated sensitivity factors. The estimated value of the Pd content was about 2.3 atomic %.

In order to investigate the activity of Pd–CNT nanocomposites in the hydrodehalogenations, reactions of aryl halides with Pd–CNT nanocomposites in the presence of base and a solvent bearing a beta-hydrogen, isopropanol, and cyclohexanol, were initially carried out. Based on our previous work,⁴ arylchloride was reacted with NaO^tBu in the isopropanol (entries 1–3) and aryl bromide was reacted with Cs₂CO₃ in the cyclohexanol (entries 4–8). As expected, the reactions with both electron-withdrawing and electron-donating substituents gave the desired hydrodehalogenated products in good to excellent yields. The results are summarized in Table 1.

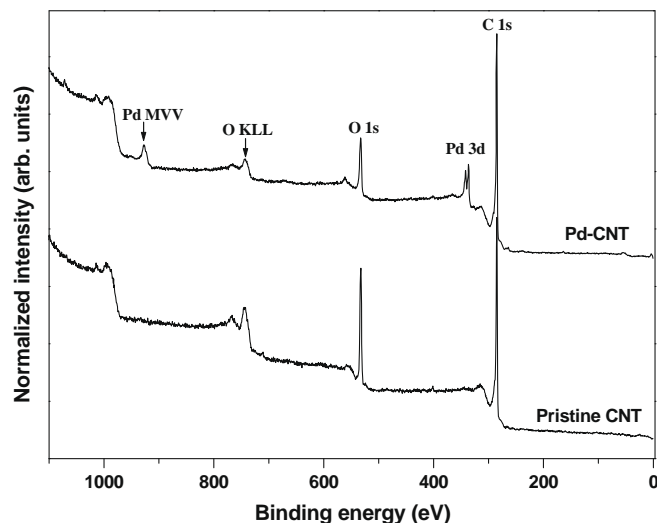


Figure 2. XPS survey spectra of pristine CNT and Pd–CNT nanocomposite.

When the catalyst was recovered and used again in the hydrodehalogenation of aryl halides, the yields were acceptable.

To verify the support effect upon hydrodehalogenation, a comparative experimental using Pd–CNT nanocomposite, Pd₂(dba)₃, and a Pd₂(dba)₃/CNT mixture under identical conditions was conducted. Figure 3 shows the relationship between the reaction time and product yield of the hydrodehalogenation of 4-bromotoluene. The curves clearly indicate that the activity of Pd–CNT nanocomposites was much higher than that of the others. This difference can be attributed to the metal–CNT interaction and mass transfer induced by the CNTs. Some researchers suggested that CNT-supported catalysts showed much better activity and/or selectivity than other supports due to the metal–CNT interaction.¹³ This interaction induces a peculiar microstructure or modification of the electron density in the metal cluster, and enhances

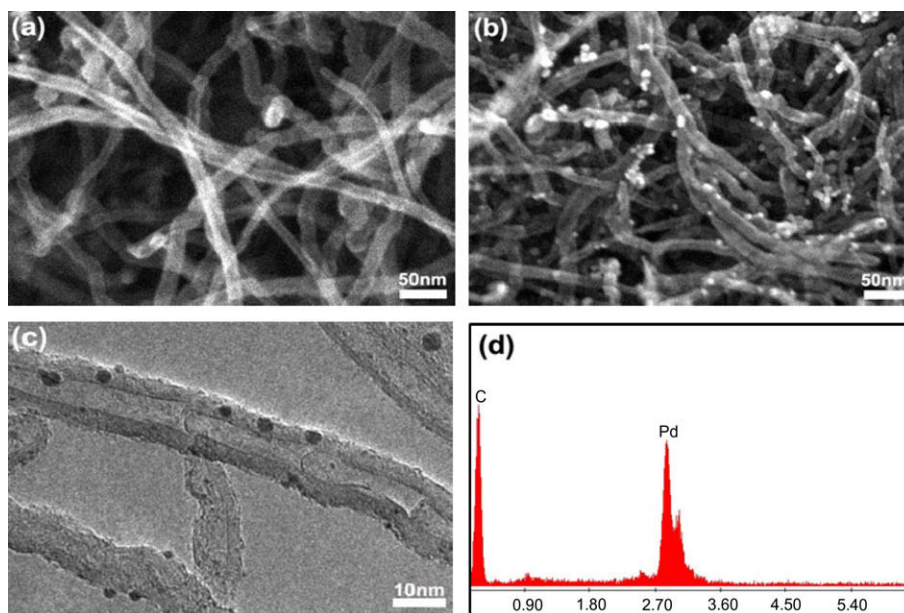
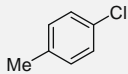
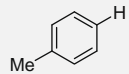


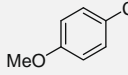
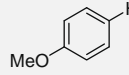
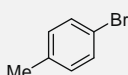
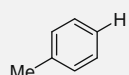
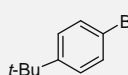
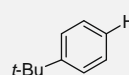
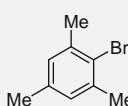
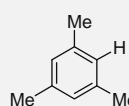
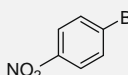
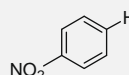




Figure 1. (a) SEM image of pristine CNT. (b) SEM image of the Pd–CNT nanocomposite. (c) TEM image of the Pd–CNT nanocomposite. (d) EDXS spectrum of the Pd–CNT nanocomposite.

Table 1
Hydrodehalogenation of aryl halides using Pd–CNT nanocomposites

Entry	Ar–X	Method ^a	Product	Yield ^b (%)
1		A		99(95) ^c
2		A		98(94) ^c
3		A		96(92) ^c
4		B		94(92) ^c
5		B		95(89) ^c
6		B		98(95) ^c
7		B		88(83) ^c
8		B		85(82) ^c

^a Reaction method A: 2.3 mol % of Pd, Aryl chloride 3.0 mmol, and NaO^tBu 3.6 mmol were reacted in the isopropanol at 80 °C for 10 h. Reaction method B: 2.3 mol % of Pd, aryl bromide 3.0 mmol, and Cs₂CO₃ 3.6 mmol were reacted in the cyclohexanol at 100 °C for 10 h.

^b All compounds are characterized by comparison of gas chromatography (GC) analysis, ¹H and ¹³C NMR spectra with authentic samples or literature data.

^c Yields were obtained from the second use of Pd–CNT. In this study, the product yield is determined by GC, ¹H and ¹³C NMR spectra.

the catalytic activity. Adsorption of aryl halides is also favored by van der Waals interactions between the CNTs and aromatic rings, which could show favorable reactant–product mass transportation.¹⁴

In summary, we examined the hydrodehalogenation of aryl halides with Pd–CNT nanocomposite under ligandless conditions. The Pd–CNT nanocomposites were prepared by depositing Pd₂(dba)₃ on thiolated nanotube surfaces. They effectively promoted the hydrodehalogenation of aryl halides at low Pd content (~2.3%) in the absence of any ligand, and exhibited higher activity than that of the reference systems. The results suggest that the CNTs could significantly influence the catalytic activities of the CNT-supported metal catalysts for hydrodehalogenation.

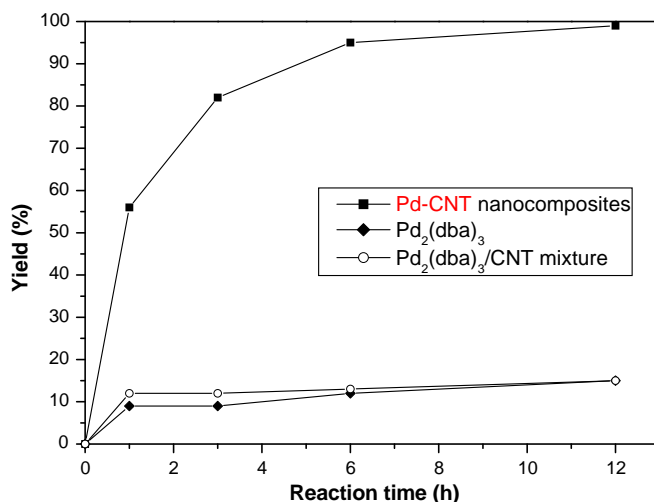


Figure 3. Catalytic activities of Pd–CNT, Pd₂(dba)₃, and a Pd₂(dba)₃/CNT mixture in the hydrodehalogenation of 4-bromotoluene.

Acknowledgments

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References and notes

- (a) Zawisza, A. M.; Muzart, J. *Tetrahedron Lett.* **2007**, *48*, 6738–6742; (b) Arcadi, A.; Cerichelli, G.; Chiarini, M.; Vico, R.; Zorzan, D. *Eur. J. Org. Chem.* **2004**, *16*, 3404–3407.
- Navarro, O.; Marion, N.; Oonishi, Y.; Kelly, R. A., III; Nolan, S. P. *J. Org. Chem.* **2006**, *71*, 685–692.
- Chen, J.; Zhang, Y.; Yang, L.; Zhang, X.; Liu, J.; Li, L.; Zhang, H. *Tetrahedron* **2007**, *63*, 4266–4270.
- Moon, J.; Lee, S. *J. Organomet. Chem.* **2009**, *694*, 473–477.
- (a) Monguchi, Y.; Kume, A.; Hattori, K.; Maegawa, T.; Sajiki, H. *Tetrahedron* **2006**, *62*, 7926–7933; (b) Kume, A.; Monguchi, Y.; Hattori, K.; Nagase, H.; Sajiki, H. *Appl. Catal. B: Environ.* **2008**, *81*, 274–282.
- (a) Kim, Y.-T.; Mitani, T. *J. Catal.* **2006**, *238*, 394–401; (b) Itoh, T.; Danjo, H.; Sasaki, W.; Urita, K.; Bekyarova, E.; Arai, M.; Imamoto, T.; Yudasaka, M.; Iijima, S.; Kaneko, H.; Kaneko, K. *Carbon* **2008**, *46*, 172–175; (c) Chen, L.; Yang, L.; Liu, H.; Wang, X. *Carbon* **2008**, *46*, 2137–2143; (d) Li, J.; Liang, Y.; Liao, Q.; Zhu, X.; Tian, X. *Electrochim. Acta* **2009**, *54*, 1277–1285.
- (a) Wang, Z.-C.; Ma, Z.-M.; Li, H.-L. *Appl. Surf. Sci.* **2008**, *254*, 6521–6526; (b) Chetty, R.; Kundu, S.; Xia, W.; Bron, M.; Schuhmann, W.; Chirila, V.; Brandl, W.; Reinecke, T.; Muhler, M. *Electrochim. Acta* **2009**, *54*, 4208–4215.
- Corma, A.; Garcia, H.; Leyva, A. *J. Mol. Catal.* **2005**, *230*, 97–105.
- (a) Kitamura, Y.; Sakurai, A.; Uduz, T.; Maegawa, T.; Monguchi, Y.; Sajiki, H. *Tetrahedron* **2007**, *63*, 10596–10602; (b) Zhang, P.-P.; Zhang, X.-X.; Sun, H.-X.; Liu, R.-H.; Wang, B.; Lin, Y.-H. *Tetrahedron Lett.* **2009**, *50*, 4455–4458.
- Lu, C.-Y.; Wey, M.-Y. *Fuel* **2007**, *86*, 1153–1161.
- Abbaslou, R. M. M.; Tavasoli, A.; Dalai, A. K. *Appl. Catal. A* **2009**, *355*, 33–41.
- Castro, C. E. *Rev. Environ. Contam. Toxicol.* **1998**, *155*, 1–67.
- (a) Planeix, J. M.; Coustel, N.; Coq, B.; Brotons, V.; Kumbhar, P. S.; Dutartre, P.; Geneste, P.; Bernier, P.; Ajayan, P. M. *J. Am. Chem. Soc.* **1994**, *116*, 7935–7936; (b) Choi, H. C.; Shim, M.; Bangsaruntip, S.; Dai, H. *J. Am. Chem. Soc.* **2002**, *124*, 9058–9059; (c) Tzitzios, V.; Georgakilas, V.; Oikonomou, E.; Karakassides, M.; Petridis, D. *Carbon* **2006**, *44*, 848–853; (d) Vu, H.; Goncalves, F.; Philippe, R.; Lamouroux, E.; Corrias, M.; Kihn, Y.; Plee, D.; Kalck, P.; Serp, P. *J. Catal.* **2006**, *240*, 18–22.
- (a) Vermisoglou, E. C.; Georgakilas, V.; Kouvelos, E.; Pilatos, G.; Viras, K.; Romanos, G.; Kanellopoulos, N. K. *Micropor. Mesopor. Mater.* **2007**, *99*, 98–105; (b) Vermisoglou, E. C.; Romanos, G. E.; Tzitzios, V.; Karanikolos, G. N.; Akyllas, V.; Delimitis, A.; Pilatos, G.; Kanellopoulos, N. K. *Micropor. Mesopor. Mater.* **2009**, *120*, 122–131.