

Ligand Effect in Recycled CNT-Pd Heterogeneous Catalyst for Decarboxylative Coupling Reactions

Ji Dang Kim, Ayoung Pyo, Kyungho Park, Gwui Cheol Kim,[†] Sunwoo Lee,^{*} and Hyun Chul Choi^{*}

Department of Chemistry and Institute of Basic Science, Chonnam National University, Gwangju 500-757, Korea

^{*}E-mail: sunwoo@chonnam.ac.kr (S. Lee); chc12@chonnam.ac.kr (H. C. Choi)

[†]Jeonnam Nano Bio Research Center, Jeollanam-do 515-806, Korea

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We present here an efficient and simple method for preparation of highly active Pd heterogeneous catalyst (CNT-Pd), specifically by reaction of dichlorobis(triphenylphosphine)palladium ($\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$) with thiolated carbon nanotubes (CNTs). The as-prepared CNT-Pd catalysts demonstrated an excellent catalytic activity for the carbon-carbon (C-C) cross-coupling reactions (*i.e.* Suzuki, Stille, and decarboxylative coupling reactions) under mild conditions. The CNT-Pd catalyst could easily be removed from the reaction mixture; additionally, in the decarboxylative coupling of iodobenzene and phenylpropionic acid, it showed a six-times recyclability, with no loss of activity. Moreover, once its activity had decreased by repeated recycling, it could easily be reactivated by the addition of phosphine ligands. The remarkable recyclability of the decarboxylative coupling reaction is attributable to the high degree of dispersion of Pd catalysts in CNTs. Aggregation of the Pd catalysts is inhibited by their strong adhesion to the thiolated CNTs during the chemical reactions, thereby permitting their recycling.

Key Words : CNT-Pd catalyst, Decarboxylative reaction, Recycling, Reactivation, Ligand effect

Introduction

One of the most important issues in current organic synthesis is the development of new, efficient carbon-carbon (C-C) and carbon-heteroatom bond-forming reactions. In this regard, transition metal-based catalysts generally have been used for these reactions. Among them, palladium (Pd) probably is the most versatile catalyst for C-C bond-forming reactions, and there is a great deal of literature on its properties in many reactions.¹ Although soluble Pd complexes traditionally have been used as homogeneous catalysts for these coupling reactions, there remain problems that need to be addressed concerning catalyst-product separation and the non-recyclability of homogeneous catalysts. Such problems are of great significance to industrial applications, due to economical and environmental concerns. As a potential solution, the development of heterogeneous catalysts wherein the catalyst is immobilized on solid supports including mesoporous materials,² dendrimers,³ ionic liquids,⁴ carbon nanotubes (CNTs),⁵ polymers,⁶ and magnetic particles,⁷ has attracted much attention in recent years. However, heterogeneous systems exhibit generally lower activity than is observed with homogeneous catalysts, and that activity decreases, gradually, further in recycled systems, due to Pd leaching from the support.⁸ Therefore, the development of Pd catalysts offering high activity, stability, and recyclability currently is a very popular research focus.

A variety of recyclable catalytic systems based on Pd nanoparticles have been developed and applied in cross-couplings such as Suzuki-Miyaura, Mizoroki-Heck and Sonogashira reactions.⁹ CNT-supported Pd nanoparticles and their

catalytic activity in cross-coupling reactions have been reported on by the present research group and others.¹⁰ Although various heterogeneous Pd catalysts have shown recyclability in cross-coupling reactions, decreases in their activity, and relatively low recycle numbers, frequently have been observed. Recently, we were the first to report decarboxylative coupling reactions of alkynylcarboxylic acids and aryl halides productive of aryl alkynes in the presence of a homogenous Pd catalyst.¹¹ This, notably, is a very useful tool for the employment of low-molecular-weight alkynes.¹² Positively too, this method does not result in the homocoupled by-products often formed in the Sonogashira coupling reaction, and shows high functional-group tolerance as well. In light of these advantages, a variety alkynyl carboxylic acid coupling reactions have been reported.¹³ However, there is no report on the recyclable catalytic system as it pertains to decarboxylative coupling reactions. Neither is there any report on catalytic reactivation when activity is decreased by recycling. Development of a more efficient recyclable catalytic system, certainly, is required. Herein we report an efficient CNT-supported Pd catalyst (denoted CNT-Pd) formed by deposition of dichlorobis(triphenylphosphine)palladium [$\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$] on thiolated multiwall CNT surfaces. The prepared catalyst was easily recovered, and exhibited high activity and recyclability in the decarboxylative coupling reactions. Moreover, this catalyst could be reactivated by phosphine ligands once its activity had decreased after repeated recycling.

Experimental

Chemicals. Both multiwall carbon nanotubes (MWNTs)

and $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ were used as supports and catalysts in this study. MWNTs were obtained from Carbon Nano Tech. Co., Ltd. (South Korea). Reagent grade $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ was purchased from Alfa Aesar. Sodium hydrosulfide hydrate ($\text{NaSH}\cdot x\text{H}_2\text{O}$, Aldrich) was used as a linker to secure the Pd catalysts. Tris(dibenzylideneacetone)dipalladium (0) [$\text{Pd}_2(\text{dba})_3$] was obtained from Aldrich. All other reagents and solvents were of analytical grade and were used as received.

Preparation of CNT-Pd. 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, washed with distilled water, and dried in an oven at 110°C . The acid-treated MWNTs were dispersed in THF, after which an NaSH aqueous solution was added to produce thiol groups on their surfaces, thereby affording the carbon nanotubes (denoted CNT-SH). The thiolation was confirmed by reference to the XPS spectrum in the sulfur 2p region (see Fig. S1). Finally, the thiolated MWNTs were dispersed in THF, to which a $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2/\text{THF}$ solution was then added. The mixture was stirred for 20 h until all of the $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ precursors were anchored onto the MWNTs, thus producing the CNT-supported Pd catalyst (denoted 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.

Characterization. Transmission electron microscopy (TEM) observations were carried out with 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 onto a Cu grid, and the solvent was allowed to evaporate in air. X-ray photoelectron spectroscopy (XPS) analysis was performed using a VG multilab 2000 spectrometer (ThermoVG Scientific) in an ultra-high vacuum. This system incorporates an unmonochromatized Mg K_α (1253.6 eV) source and a spherical section analyzer. Survey scan data were collected using a pass energy of 50 eV. The content of Pd in the CNT-Pd catalysts was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) with an OPTIMA 4300 DV (Perkin Elmer). Prior to the measurement, the sample was treated with a mixture of HNO_3 , HF and HBO_3 in order to dissolve it completely. Raman spectra were obtained at room temperature using an inVia Reflex (Renishaw 1000) micro-Raman spectrometer with a 532 nm laser line.

Catalytic Activity. The catalytic activity of the prepared CNT-Pd for the Suzuki-Miyaura, Stille, and decarboxylative coupling reactions was examined. These reactions were used as standard test reactions to probe the reactivity of Pd-catalyzed C-C bond formation.

Suzuki Coupling. A 20 mL flask (or vial) was charged with 4-iodotoluene (654.1 mg, 3.0 mmol), phenylboronic acid (402.4 mg, 3.3 mmol), CNT-Pd (0.06 mmol), K_2CO_3 (621.9 mg, 4.5 mmol), and DMF (10 mL). The reaction mixture was tightly sealed and heated at 100°C for 12 h. After cooling, the mixture was poured into ethyl acetate (EtOAc, 50.0 mL) and washed with water (3×25.0 mL),

brine (3×25.0 mL), and then dried over MgSO_4 and passed through a celite pad. The evaporation of the solvent under reduced pressure provided the crude product, which was purified by column chromatography (hexane:EtOAc = 10:1), affording 4-methylbiphenyl (463.2 mg, 2.76 mmol, 92%).

Stille Coupling. A 20 mL flask (or vial) was charged with 4-iodotoluene (654.1 mg, 3.0 mmol), tributylphenyl stannane (1,021 mg, 3.3 mmol), CNT-Pd (0.06 mmol), CsF (683.5 mg, 4.5 mmol), and 1,4-dioxane (10 mL). The reaction mixture was tightly sealed and heated at 80°C for 12 h. After cooling, the mixture was poured into EtOAc (50.0 mL) and washed with water (3×25.0 mL), brine (3×25.0 mL), and then dried over MgSO_4 and passed through a celite pad. The evaporation of the solvent under reduced pressure provided the crude product, which was purified by column chromatography (hexane:EtOAc = 10:1), affording 4-methylbiphenyl (443.5 mg, 2.64 mmol, 88%).

Decarboxylative Coupling. A 20 mL flask (or vial) was charged with 4-bromotoluene (342.0 mg, 2.0 mmol), phenylpropionic acid (481.8 mg, 2.2 mmol), recovered CNT-Pd (0.04 mmol), dppf (55.4 mg, 0.10 mmol), DBU (203.2 mg, 4.0 mmol), and DMSO (7.0 mL). The reaction mixture was tightly sealed and heated at 90°C for 12 h. After cooling, the mixture was poured into EtOAc (25.0 mL) and washed with water (3×15.0 mL), brine (3×15.0 mL), and then dried over MgSO_4 and passed through a celite pad. The evaporation of the solvent under reduced pressure provided the crude product, which was purified by column chromatography (hexane:EtOAc = 10:1), affording 1,2-diphenylethyne (220.7 mg, 1.24 mmol, 62%).

Results and Discussion

Figure 1(a) shows the TEM images of CNT-Pd, which indicate clearly that the nano-sized precipitates of $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ were highly deposited onto the surfaces of the CNTs. Smaller and highly dispersed precipitates were much more abundant than larger, aggregated ones. The corresponding energy-dispersive X-ray (EDS) analysis showed that the species supported on the CNTs was Pd [Fig. 1(b)]. The magnified image reveals that the precipitates were strongly adhered to the sidewalls of the CNTs [Fig. 1(c)]. Moreover, the adhered precipitates could not be separated from the CNTs even after thorough washing and prolonged sonication. This particularly strong adhesion might have resulted from the relatively high binding energy (BE) between the Pd precipitates and the thiol groups.

Figure 2(a) shows a series of XPS survey spectra from the pristine CNTs, thiolated CNTs and CNT-Pd. The data for the pristine CNTs show distinct C and O 1s peaks, with no other elements detected. However, post-thiolation, the S 2p and 1s photoelectron signals were detected. The relative surface atomic ratio was estimated from the corresponding peak areas, and corrected with the tabulated sensitivity factors.¹⁴ The estimated value of the S content was about 3.3 atomic %. Since the XPS signal is obtained by collection of photo-emitted electrons, this technique is very sensitive to the

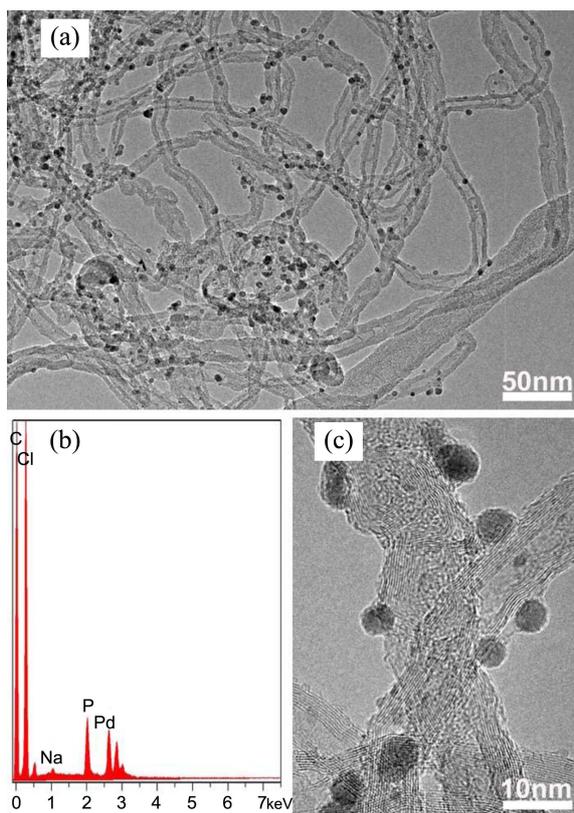


Figure 1. (a) Low-magnification TEM image of CNT-Pd catalyst. (b) EDS spectrum of CNT-Pd catalyst. (c) High-magnification TEM image of CNT-Pd catalyst.

properties of the surface. For the CNT-Pd, the photoemitted electrons from S atoms are screened by deposited Pd precipitates, which resulted in the featureless S profiles. The XPS data also confirmed the presence of Pd in the sample. The Pd content was estimated to be 2.8 atomic %. According to ICP experiments, the amount of Pd contained in the sample was 3.1 wt %, which was consistent with that of the XPS result. Figure 2(b) provides the Pd 3d core-level XPS spectra for Pd(PPh₃)₂Cl₂, CNT-Pd, and the reference Pd metal. It can be seen that the BEs of the CNT-Pd's Pd 3d_{5/2} and 3d_{3/2} are similar to those of the Pd precursor, indicating that precipitates on the CNTs are Pd(II) complex. Since the Pd BE depends strongly on the nature of the ligands,¹⁵ the observed results suggested that the Pd precursors were successfully anchored onto the CNTs without structural modification. Moreover, no significant changes were observed in the BEs or in the intensities of the survey or Pd 3d core-level spectra after exposing the CNT-Pd to air for two months, which, significantly, demonstrated the stability of the CNT-Pd catalyst.

Raman spectroscopy was used to obtain information on the average crystallinity of the CNT-Pd compared with that of the thiolated CNTs. As shown in Figure 3, the spectrum consists of two bands at ~1330 cm⁻¹ (D band) and 1570 cm⁻¹ (G band). The D band is a disorder-induced feature originating from the vibrations of C atoms with dangling bonds. The G band arises from the C atoms' tangential shear mode that

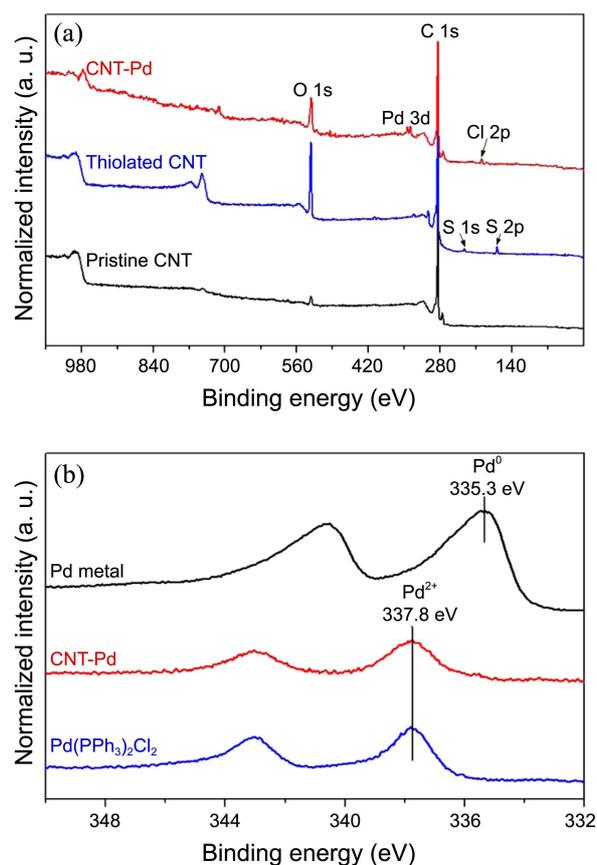


Figure 2. (a) XPS survey spectra of pristine CNTs, thiolated CNTs, and CNT-Pd catalyst. (b) Pd 3d core-level XPS spectra of Pd(PPh₃)₂Cl₂, CNT-Pd, and the reference Pd metal.

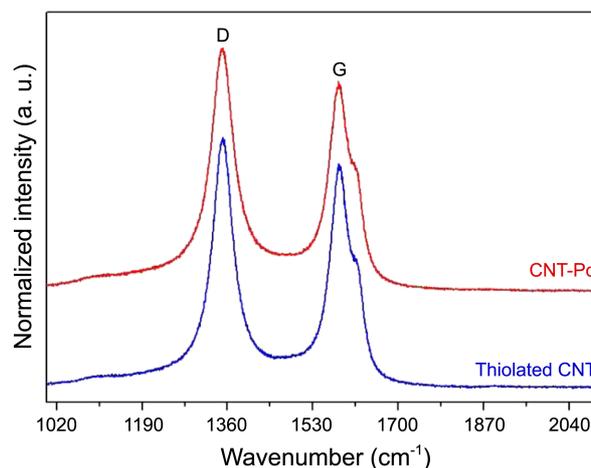
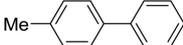
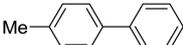
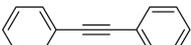


Figure 3. Raman spectra of thiolated CNTs and CNT-Pd catalyst.

corresponds to the stretching mode in the graphite plane. The integrated intensity ratio of the D band to the G band (I_D/I_G) has a linear relation to the inverse of the in-plane crystallite dimension. The I_D/I_G value was about 1.06 for the thiolated CNT, and about 1.13 for the CNT-Pd. These results suggest that the structural change during the deposition of the Pd precursor onto the CNTs is negligible.

The catalytic activity of the prepared CNT-Pd for the

Table 1. Palladium-catalyzed coupling reactions^a

Entry	Ar-X	Y-R	Condition	Product/Yield (%) ^c
1	4-Tol-I	PhB(OH) ₂	K ₂ CO ₃ (1.5 equiv), DMF, 100 °C, 12 h	 92 (8) ^d (90) ^e
2	4-Tol-I	PhSnBu ₃	CsF (1.5 equiv), dioxane, 80 °C, 12 h	 88 (4) ^d (84) ^e
3	PhI	PhCCCO ₂ H	DBU (2.0 equiv), DMSO, 90 °C, 10 h	 90 (46) ^d (87) ^e

^aReaction condition: ArX (3.0 mmol), R-Y (3.3 mmol) were used. ^b2.0 mol % Pd catalyst was employed based on 2.8 wt % Pd in CNT. ^cIsolated yield. ^dThe yield was obtained from the reaction in the presence of commercial Pd/C catalyst (Aldrich, 10 wt % Pd on activated charcoal). ^eThe yield was obtained from the reaction in the presence of commercial Pd(PPh₃)₂Cl₂.

Suzuki-Miyaura, Stille, and decarboxylative coupling reactions was examined. These reactions are generally catalyzed by Pd (0) or Pd (II) species.¹⁶ As shown in Table 1, the coupling reaction of 4-iodotoluene with phenylboronic acid produced the 4-methylbiphenyl in a 92% yield in the presence of CNT-Pd (entry 1). The reaction with tributylphenyl stannane showed a good yield as well (entry 2). The decarboxylative coupling reaction of iodobenzene with phenyl propionic acid afforded 1,2-diphenylethyne in a 90% yield (entry 3). In this study, the product yield was determined by the ¹H and ¹³C NMR spectra (see ESI). The obtained NMR spectra were in good agreement with the previous reports.¹⁷ In all of these coupling reactions, the yield of the prepared CNT-Pd was higher than that of the commercial Pd/C catalyst (Aldrich, 10 wt % Pd on activated charcoal), and similar with that of the Pd(PPh₃)₂Cl₂.

Next, the decarboxylative coupling of iodobenzene and phenylpropionic acid, as a model reaction, was used to evaluate the recyclability of CNT-Pd. The results of the reaction, monitored by gas chromatography with an internal standard, are summarized in Table 2. The first run showed the desired product in a 92% yield (entry 1). When diethyl ether (Et₂O) was added to the resulting reaction mixture, two layers were formed (see Fig. S2): the upper Et₂O layer containing the product, and the lower, catalyst layer. The lower layer was separated, washed with EtOAc, and dried in vacuum, after which the recovered catalyst was reused for the next run. The product yields were maintained high up to the sixth run (entries 2-6). With the seventh run, the catalytic activity began to decrease. The remarkable recyclability of the decarboxylative coupling reaction is attributable to the high degree of dispersion of Pd catalysts in CNTs.¹⁸ Aggregation of Pd catalysts (Pd black) is inhibited by the strong BE between them and thiolated CNTs during chemical reactions, thereby permitting their recycling.

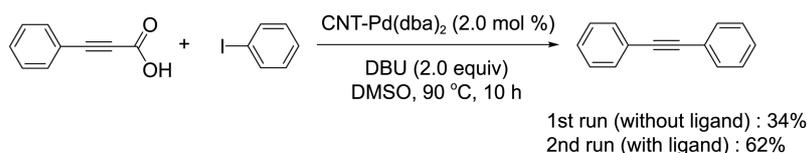
When the catalyst was run in the tenth run, a 31% product yield was obtained (entry 10). Surprisingly, in the eleventh run (entry 11), the yield was increased to 98% when the reaction was carried out with added 1,1'-bis(diphenylphosphino)ferrocene (dppf). However, in the twelfth run without ligands (entry 12), the catalytic activity could not sustain that high level. We found that the high catalytic activity was

Table 2. The recycle of catalyst in the decarboxylative coupling^a

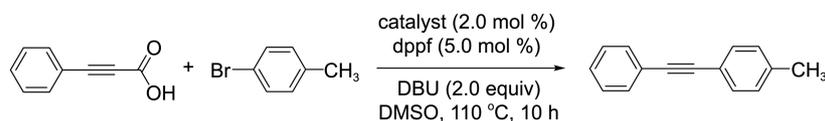
Entry	Number of recycle	Addition of ligand	Conversion (%) ^b	Yield (%) ^c
1	1	-	94	92
2	2	-	87	85
3	3	-	91	82
4	4	-	96	87
5	5	-	89	89
6	6	-	91	90
7	7	-	90	76
8	8	-	72	52
9	9	-	51	34
10	10	-	50	31
11	11	5 mol % dppf	100	98
12	12	-	54	42
13	13	5 mol % dppf	96	92
14	14	-	65	55

^aReaction condition: PhI (1.0 mmol), Phenylpropionic acid (1.1 mmol), DBU (2.0 mmol) and catalyst (2.0 mol % based on 2.8 wt % of CNT-Pd) were reacted in DMSO at 90 °C for 10 h. ^bDetermined by gas chromatography with internal standard. ^cIsolated yield

recovered every time the ligand was added (entry 13). However, it is not clear why the yield was decreased in the 12th and 14th in Table 2. Recently, Rossi *et al.* reported that a Pd nanoparticle catalyst prepared on a phosphine-functionalized support was more active and selective than a similar Pd nanoparticle catalyst prepared on an amino-functionalized support.¹⁹ Similar results were observed for a Pd catalyst based on polymer-supported dialkylphosphinobiphenyl ligands.²⁰ Such activity enhancement generally is attributed to the ligand effects, by which phosphine groups are softer donors and, thereby, better stabilizers for active catalytic Pd species. Correspondingly, in the present study, the reactivation of Pd catalysts after addition of the phosphine ligand also could be explained according to the ligand effects, by which, specifically, the oxidized Pd species was, during the reactions, reduced to the Pd (0) state which is catalytic active species in the decarboxylative coupling, thus restoring high



Scheme 1. The ligand effect in the decarboxylative coupling reaction.



Scheme 2. The decarboxylative coupling of 4-bromotoluene with the recovered catalyst after 14th run.

catalytic activity. In investigating the role of ligands, decarboxylative coupling reactions were carried out with CNT-Pd(dba)₂, showing low activities in the presence of a ligand. As Scheme 1 demonstrates, the product yield was increased in the presence of ligand even with a second-run catalyst. Surprisingly, according to Scheme 2, when, after the 14th run, the recovered catalyst was employed with dppf in the coupling reaction of phenyl propiolic acid and 4-bromotoluene (which is less reactive than 4-iodotoluene), the desired product was obtained in a 62% yield. These results suggest that the addition of ligand significantly influences activity in the heterogeneous catalytic reaction. The relationship between ligand type and catalytic activity will be reported in forthcoming studies.²¹

Conclusions

We developed novel, efficient and reusable CNT-supported Pd catalysts for C-C coupling reactions. A TEM analysis indicated that well-dispersed Pd catalysts were anchored onto the surface of the CNTs. XPS results suggest that the Pd content was about ~2.8 atomic %. The prepared CNT-Pd effectively promoted C-C bond-forming reactions (*i.e.* Suzuki, Stille, and decarboxylative coupling reactions) at a low Pd content. Most notably, this catalytic system provided good product yields for the decarboxylative coupling of iodobenzene with phenylpropionic acid, even after six-times recycling, and its reactivity was recovered when ligand was added. The remarkable reactivity and recyclability of the decarboxylative coupling reaction is attributable to the high degree of dispersion of Pd catalysts in CNTs. The aggregation of Pd catalysts is inhibited by their strong adhesion to the thiolated CNTs during chemical reactions, thereby permitting their recycling.

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References

- Tsuji, J. *Palladium Reagents and Catalysts*, 2nd ed.; Wiley: Chichester, 2004.
- (a) Mehnert, C. P.; Weaver, D. W.; Ying, J. Y. *J. Am. Chem. Soc.* **1998**, *120*, 12289-12296. (b) Mehnert, C. P.; Ying, J. Y. *Chem. Commun.* **1997**, 2215-2216.
- (a) Gopidas, K. R.; Whitesell, J. K.; Fox, M. A. *Nano Lett.* **2003**, *3*, 1757-1760. (b) Yeung, L. K.; Crooks, R. M. *Nano Lett.* **2001**, *1*, 14-17.
- (a) Hamill, N. A.; Hardacre, C.; McMath, S. E. *J. Green Chem.* **2002**, *4*, 139-142. (b) Deshmukh, R. R.; Rajagopal, R.; Srinivasan, K. V. *Chem. Commun.* **2001**, 1544-1555.
- (a) Kim, J. Y.; Park, K.; Bae, S. Y.; Kim, G. C.; Lee, S.; Choi, H. C. *J. Mater. Chem.* **2011**, *21*, 5999-6005. (b) Kim, J. Y.; Jo, Y.; Kook, S. K.; Lee, S.; Choi, H. C. *J. Mol. Catal. A-Chem.* **2010**, *323*, 28-32. (c) Yoon, B.; Wai, C. M. *J. Am. Chem. Soc.* **2005**, *127*, 17174-17175.
- (a) Pathak, S.; Greci, M. T.; Kwong, R. C.; Mercado, K.; Prakash, G. K. S.; Olah, G. A.; Thompson, M. E. *Chem. Mater.* **2000**, *12*, 1985-1989. (b) Klingelhöfer, S.; Heitz, W. A.; Ostereich, S.; Förster, S.; Antonietti, M. *J. Am. Chem. Soc.* **1997**, *119*, 10116-10120.
- (a) Du, Q.; Zhang, W.; Ma, H.; Zheng, J.; Zhou, B.; Li, Y. *Tetrahedron* **2012**, *68*, 3577-3584. (b) Wittmann, S.; Schaetz, A.; Grass, R. N.; Stark, W. J.; Reiser, O. *Angew. Chem. Int. Ed.* **2010**, *49*, 1867-1870. (c) Amali, A. J.; Rana, R. K. *Green Chem.* **2009**, *11*, 1781-1786.
- (a) Soomro, S. S.; Ansari, F. L.; Chatziapostolou, K.; Köhler, K. *J. Catal.* **2010**, *273*, 138-146. (b) Richardson, J. M.; Jones, C. W. *J. Catal.* **2007**, *251*, 80-93. (c) Heidenreich, R. G.; Krauter, J. G. E.; Pietsch, J.; Köhler, K. *J. Mol. Catal. A-Chem.* **2002**, *182*, 499-509.
- (a) Yuan, B.; Pan, Y.; Li, Y.; Yin, B.; Jiang, H. *Angew. Chem. Int. Ed.* **2010**, *49*, 4054-4058. (b) Li, P.; Wang, L.; Zhang, L.; Wang, G.-W. *Adv. Synth. Catal.* **2012**, *354*, 1307-1318. (c) Dutta, P.; Sarkar, A. *Adv. Synth. Catal.* **2011**, *353*, 2814-2822. (d) Stevens, P. D.; Li, G.; Fan, J.; Yen, M.; Gao, Y. *Chem. Commun.* **2005**, 4435-4437.
- (a) Rumi, L.; Scheuermann, G. M.; Muelhaupt, R.; Bannwarth, W. *Helv. Chim. Act.* **2011**, *94*, 966-976. (b) Jo, Y.; Kim, J. Y.; Oh, I.-K.; Choi, H. C.; Lee, S. *Bull. Korean Chem. Soc.* **2010**, *31*, 1735-1738. (c) Sullivan, J. A.; Flanagan, K. A.; Hain, H. *Catal. Today* **2009**, *145*, 108-113. (d) Scheuermann, G. M.; Rumi, L.; Steurer, P.; Bannwarth, W.; Mülhaupt, R. *J. Am. Chem. Soc.* **2009**, *131*, 8262-8270.
- Moon, J.; Jeong, M.; Nam, H.; Ju, J.; Moon, J. H.; Jung, H. M.; Lee, S. *Org. Lett.* **2008**, *10*, 945-948.
- Kolarovič, A.; Schnürch, M.; Mihovilovic, M. D. *J. Org. Chem.* **2011**, *76*, 2613-2618.
- (a) Moon, J.; Jang, M.; Lee, S. *J. Org. Chem.* **2009**, *74*, 1403-

1406. (b) Kim, H.; Lee, P. H. *Adv. Synth. Catal.* **2009**, *351*, 2827-2832. (c) Kolarovič, A.; Fáberová, Z. *J. Org. Chem.* **2009**, *74*, 7199-7202. (d) Park, K.; Bae, G.; Moon, J.; Choe, J.; Song, K. H.; Lee, S. *J. Org. Chem.* **2010**, *75*, 6244-6251. (e) Ranjit, S.; Duan, Z.; Zhang, P.; Liu, X. *Org. Lett.* **2010**, *12*, 4134-4136. (f) Jia, W.; Jiao, N. *Org. Lett.* **2010**, *12*, 2000-2003. (g) Zhang, W.-W.; Zhang, X.-G.; Li, J.-H. *J. Org. Chem.* **2010**, *75*, 5259-5264. (h) Feng, C.; Loh, T.-P. *Chem. Commun.* **2010**, *46*, 4779-4781.
14. King, J. C. R. C. *Handbook of X-ray Photoelectron Spectroscopy*; Physical Electronics Inc.: 1995; pp 118-119.
15. (a) Wang, L.; Dehe, D.; Philippi, T.; Seifert, A.; Ernst, S.; Zhou, Z.; Hartmann, M.; Taylor, Singh, R. N. K. A. P.; Jia, M.; Thiel, W. *R. Catal. Sci. Technol.* **2012**, *2*, 1188-1195. (b) Cai, M.; Sha, J.; Xu, Q. *J. Mol. Catal. A-Chem.* **2007**, *268*, 82-86. (c) Cairns, G. R.; Cross, R. J.; Stirling, D. *J. Mol. Catal. A-Chem.* **2011**, *172*, 207-218.
16. (a) Rodríguez, N.; Goossen, L. *J. Chem. Soc. Rev.* **2011**, *40*, 5030-5048. (b) Seechurn, C. C. C. J.; Kitching, M. O.; Colacot, T. J.; Snieckus, V. *Angew. Chem. Int. Ed.* **2012**, *51*, 5062-5085.
17. (a) Park, K.; Bae, G.; Moon, J.; Choe, J.; Song, K. H.; Lee, S. *J. Org. Chem.* **2010**, *75*, 6244-6251. (b) Mino, T.; Shirae, Y.; Sakamoto, M.; Fujita, T. *J. Org. Chem.* **2005**, *70*, 2191-2194.
18. (a) Saleem, F.; Rao, G. K.; Singh, P.; Singh, A. K. *Organometallics* **2013**, *32*, 387-395. (b) Sullivan, J. A.; Flanagan, K. A.; Hain, H. *Catal. Today* **2009**, *145*, 108-113.
19. Costa, N. J. S.; Kiyohara, P. K.; Monteiro, A. L.; Coppel, Y.; Philippet, K.; Rossi, L. M. *J. Catal.* **2010**, *276*, 382-389.
20. Parrish, C. A.; Buchwald, S. L. *J. Org. Chem.* **2001**, *66*, 3820-3827.
21. We found that the activity of CNT-Pd was dependent on both the source of palladium and ligand type. To elucidate the reason for the enhanced activity, we prepared the CNT-Pd using the Na₂PdCl₄ precursor and examined the relationship between ligand type and catalytic activity in the decarboxylative coupling. The detailed results will be reported in forthcoming publications.
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