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Palladium Nanoparticles Supported on Carbon Nanotubes from Solventless Preparations: Versatile Catalysts for Ligand-Free Suzuki Cross Coupling Reactions

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Palladium nanoparticles supported on single- or multi-walled carbon nanotubes (Pd/SWCNT and Pd/MWCNT) were prepared by a rapid, solventless method that does not require reducing agents or electric current. The method involves a straightforward process using dry mixing of a precursor Pd salt (e.g., palladium acetate) with carbon nanotubes at ambient temperature by ball-milling (mechanochemical route) or with subsequent annealing at 300 °C (thermal route) in an inert atmosphere. The Pd/MWCNT sample with Pd nanoparticle size of 1-3 nm and uniform dispersion prepared by mechanochemical ball-milling at room temperature [designated as $(Pd/MWCNT)_{M}$] displayed remarkable catalytic activity towards Suzuki cross coupling reactions with a high turn over number (TON) of 7250 and turn over frequency (TOF) of 217,500 h⁻¹. These nanoparticles were characterized by a variety of techniques including transmission electron microscopy (TEM), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). Additionally, the (Pd/MWCNT)_M sample was successfully employed in Suzuki cross coupling reactions with wide variety of functionalized substrates.

Introduction

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Carbon nanotubes including single-walled (SWCNT) and multi-walled (MWCNT) nanotubes have attracted considerable interests due to their remarkable thermal conductivity,¹⁻³ mechanical,⁴⁻⁶ and electrical properties.^{6,7} In addition, their excellent chemical and mechanical stability and large surface area make them an ideal and potentially useful choice for applications in optics,⁷⁻⁸ electronics,⁹ catalysis,¹⁰⁻¹¹ polymer composites,¹² and many others.¹³ In this context, the deposition of the metal nanoparticles on carbon nanotubes (also referred to as "decoration") has provided further promising utilities for these materials in a wide range of applications from hydrogen storage, solar cells, sensor devices, energy storage, as well as catalysis.^{14,15} As such, one of the potential areas in which carbon nanotubes may be utilized as an effective solid support is in cross coupling reactions.¹⁶⁻²⁰

Metal catalyzed carbon-carbon bond forming reactions such as Suzuki, Heck, and Sonogashira and many others have rapidly become one of the most effective tools in organic synthesis for the assembly of highly functionalized molecules.²¹⁻²⁵ These reactions are typically performed under homogeneous reaction conditions, which require ligands to stabilize the catalyst and broaden the range of their reactivity.²¹⁻²⁵ The use of homogeneous catalysis in cross coupling reactions, however, has some major limitations in large scale pharmaceutical and industrial synthesis mainly due to the lack of recyclability, difficulty in separation of the catalyst from the reaction mixture, and therefore the potential concern over residual contamination of the metals in the reaction products.^{26,27} One promising solution to address this issue is to employ solid-supported metal nanocatalysts capable of not only efficiently catalyzing the reactions, but also

providing a unique opportunity to leverage the reactivity and stability of these materials along with the ease of separation and reusability in subsequent reactions. Thus, numerous efforts have been undertaken in recent years to develop novel metal nanocatalysts for cross coupling reactions in which the metal is fixed on a variety of solid supports such as zeolites,^{28,29} polymers,^{30,31} mesoporous silica,^{32,33} inorganic oxides,^{34,35} and activated carbons.^{36,37} Among these support systems, graphene³⁸⁻⁴⁵ and carbon nanotubes¹⁶⁻²⁰ have attracted significant attention due to the high specific surface area, thermal stability, and remarkable structural and electronic features capable of stabilizing the metal nanoparticles.

The preparation of metal nanoparticles supported on graphene or carbon nanotubes has typically required the use of a reducing agent⁴⁶⁻⁴⁸ or electrochemical reduction ^{49,50} for the conversion of metal ions to zero valence metal. Alternatively, we have recently reported a series of solventless methods to prepare bulk quantities of metal nanoparticles supported on carbon nanotubes starting from solid mixtures of carbon nanotubes and precursor metal salts (typically acetates or acetylacetonates).⁵¹⁻⁵³ The mixture was subjected to either conventional heating in a nitrogen oven (the "thermal" route)⁵¹ or rapid heating using a microwave reactor (the "microwave" route).⁵³ Without the presence of any other additional reagent, the metal salts thermally decomposed into metals (mostly noble metals including Ag, Au, Pt, Pd) or metal oxides (most other transition metals). An interesting observation when using a mechanical mixer for the salt-nanotube blending was that the precursor salt would undergo partial decomposition just by the mechanical energy provided during the aggressive ball-milling process and form ultrafine (typically < 10 nm) nanoparticles without the need of additional heating (the "mechanochemical"

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route).⁵² We present herein the preparation of Pd nanoparticles supported on singlewalled and multi-walled carbon nanotubes using the thermal $[(Pd/MWCNT)_T, (Pd/SWCNT)_T]$ and mechanochemical routes $[(Pd/MWCNT)_M (Pd/SWCNT)_M]$, as well as the excellent catalytic activity of the latter in Suzuki cross coupling reactions. Importantly, these methods are facile, low-cost, and environmental friendly, allowing for a large scale preparation of Pd nanoparticles supported on carbon nanotubes which can be further employed in industrial and pharmaceutical applications.

Experimental

Materials and methods

MWCNTs of a broad diameter distribution (~20-150 nm) were purchased from the University of Kentucky. SWCNTs were obtained from Carbon Solutions, Inc. Palladium (II) acetate (99.9+%) were obtained from Aldrich Chemical Co. Aryl bromides and iodides, potassium carbonate, aryl substituted boronic acid were also purchased from Aldrich and used as-received. A mixture of ethanol/deionized water was used for the Suzuki cross coupling reactions.

Transmission electron microscopy (TEM) images were acquired using a JEOL JEM-1230 electron microscope operated at 120 kV equipped with a Gatan UltraScan 4000SP 4K x 4K CCD camera. Samples for TEM were prepared by placing a droplet of a colloid suspension in toluene onto a Formvar carbon- or holey carbon-coated copper grid (Ted Pella or Structure Probes, Inc.) and allowed to evaporate in air at room temperature. The X-ray diffraction (XRD) patterns were measured using PANalytical X-ray diffraction system.

The X-ray photoelectron spectroscopy (XPS) analysis was performed on a Thermo Fisher Scientific ESCALAB 250 using a monochromatic Al KR X-ray. The Pd content in each of the Pd nanoparticles supported on carbon nanotubes were determined using an Inductively Coupled Plasma equipped with Mass Spectrometry (ICP-MS, Varian 820-MS). Gas chromatography - mass spectroscopy (GC-MS) analyses were performed on an Agilent 6890 gas chromatograph equipped with an Agilent 5973 mass selective detector. A CEM Discover microwave instrument was used for cross coupling reactions. The reactions were performed at operator selectable power output of 250 W. ¹H and ¹³C NMR were acquired on a Mercury 300 MHz spectrometer. High resolution mass spectrometry analyses were obtained for the products of the Suzuki reactions in Table 2 from the Virginia Commonwealth University mass spectrometry facilities.

Syntheses of Pd-carbon nanotube catalysts

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Both Pd/SWCNT and Pd/MWCNT catalysts were prepared using the same procedures except for variations in the Pd-to-C ratio. Examples are given below for catalysts prepared using the mechanochemical route and the thermal route, respectively.

Mechanochemical Route. In a typical experiment to prepare Pd/MWCNT with a Pdto-C weight ratio of 1:10 (or ~9 wt% Pd), MWCNT powder (500 mg) and palladium acetate (105 mg) were added to a 20-mL volume ceramic vial (SPEX CertiPrep). After adding two ceramic balls (d = 1.3 cm), the vial was subjected to mechanical shaking in a ball-mill mixer (SPEX CertiPrep 8000D High-Energy Shaker Mill) for 30 min to yield the final product (Pd/MWCNT)_M. When in operation, the ball-mill mixer typically provides mechanical motions of ~1060 lateral cycles per minute with 5.7 cm back-andforth and 2.5 cm side-to-side movements.

Thermal Route. In a typical experiment, the product from the mechanochemical reaction, $(Pd/MWCNT)_M$, was transferred to a glass vial or an aluminum pan and heated in a nitrogen oven (Blue M Electric A-5245-Q Inert Gas Oven, nitrogen flow rate at ~80 cm³/min) to 300 °C over 1 h and held isothermally for 3 h. The product was then obtained as $(Pd/MWCNT)_T$.

Procedure for determining catalyst concentration effects (Fig. 4)

Bromobenzene (50 mg, 0.32 mmol, 1 eq.) was dissolved in a mixture of 4 mL H_2O :EtOH (1:1) and placed in a 10 mL microwave tube. To this was added phenyl boronic acid (47 mg, 0.382 mmol, 1.2 eq.), and potassium carbonate (133 mg, 0.96 mmol, 3 eq.). Palladium catalysts (*X* mmol, *Y* mol% as indicated in Fig. 4) were then added, and the tube was sealed and stirred at room temperature (r.t.). An aliquot of the reaction mixtures was taken after 5, 15, 30, 60, 120, 180, 240, 300 minutes, diluted with 10 mL of CH₃CN and injected into the GC/MS. The percent conversions of the products were then calculated based on the consumption of bromobenzene starting material as determined from GC-MS spectroscopy.

Procedure for recycling the (Pd/MWCNT)_M and (Pd/SWCNT)_M nanocatalysts using bromo and iodobenzenes (Table 1)

Bromobenzene (50 mg, 0.32 mmol, 1 eq.) was dissolved in a mixture of 4 mL H_2O :EtOH (1:1) and placed in a 10 mL microwave tube. To this was added phenyl boronic acid (47 mg, 0.382 mmol, 1.2 eq.), potassium carbonate (133 mg, 0.96 mmol, 3 eq.). (Pd/MWCNT)_M (2 mg, 1.6 µmol, 0.5 mol%) or (Pd/SWCNT)_M (2.3 mg, 1.6 µmol, 0.5 mol%) were then added, the tube was sealed, and heated at 80 °C for 10 min under microwave irradiation (250 W, 2.45 MHz). The progress of the reaction was monitored by GC-MS analysis. After the completion of the reaction, the mixture was diluted with 10 mL of EtOH and shaken. The entire mixture was centrifuged and the solvent above the Pd nanoparticle catalyst was completely decanted. The EtOH washing followed by centrifugation was repeated two additional times to ensure the removal of all the products from the catalyst surface. The (Pd/MWCNT)_M catalyst was then directly transferred to

another microwave tube along with fresh reagents for the next run. This procedure was repeated for every run and the percent conversion of product was determined by the means of GC-MS spectroscopy. The same experimental details were applied for recycling the (Pd/MWCNT)_M and (Pd/SWCNT)_M nanoparticles using iodobenzene with the amount of reagents as follows: Iodobenzene (50 mg, 0.245 mmol), phenylboronic acid (36 mg, 0.294 mmol, 1.2 eq.), potassium carbonate (102 mg, 0.735 mmol, 3 eq.), and (Pd/MWCNT)_M (1.5 mg, 1.2 µmol, 0.5 mol%) or (Pd/SWCNT)_M (1.7 mg, 1.6 µmol, 0.5 mol%) in 4 mL (H₂O:EtOH) (1:1), heated at 80 °C under microwave irradiation for 10 min.

General procedure for diversity scope in Suzuki reactions (Table 2)

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Aryl bromide (0.32 mmol, 1 eq.) was dissolved in a mixture of 4 mL H₂O:EtOH 1:1 and placed in a 10 mL microwave tube. To this was added the arylboronic acid (0.384 mmol, 1.2 eq.) and potassium carbonate (0.96 mmol, 3 eq.). A (Pd/MWCNT)_M sample (2 mg, 1.6 µmol, 0.5 mol%) was then added, and the tube was sealed and heated under microwave irradiation (250 W, 2.45 MHz) at a specific temperature and time indicated in Table 2. After completion, the reaction mixture was diluted with H₂O (30 mL) and extracted with dichloromethane (CH₂Cl₂ 3×50 mL). The organic layers were combined, dried over MgSO₄, and filtered. The solvent in the filtrate was then removed *in vacuo* to give a solid which was further purified by flash chromatography using hexane:ethyl acetate as eluent.

Results and Discussion

Pd/MWCNT samples were prepared using the solventless procedures that were previously established in our lab with the most detailed investigations conducted mainly on Ag/MWCNT systems.^{51,52} In those systems, silver acetate was the precursor salt for metallic Ag nanoparticles. As previously discussed in those published reports,⁵¹⁻⁵³ the Pd/MWCNT system behaved very similarly. Mechanistically, the formation of Pd nanoparticles on MWCNT surface was due to the direct decomposition of the precursor salt, palladium acetate, into palladium metal along with volatile by-products such as CO, CO₂, acetic acid, and water. The salt decomposition was triggered by either the mechanical energy (mechanochemical route) or subsequent heat treatment (thermal route). The decomposition reaction can be viewed as a partial disproportionation process, thus no reducing agent was needed. The nanotubes used were pristine and therefore contained minimal surface functional groups. However, there were intrinsic surface defect sites on the nanotube surface, which provided strong Pd nanoparticle anchoring especially in the thermal route.⁵¹ Other factors that might have affected the nanoparticle anchoring include the nanotube diameter and impurity content.

The average size, distribution and the composition of Pd nanoparticles decorated on the MWCNT surfaces from the two routes investigated were distinctively different. As shown in the TEM images in Fig. 1, the nanotube-attached Pd nanoparticles from the mechanochemical route (Pd/MWCNT)_M were much smaller (and denser in decoration) than those from thermal route (Pd/MWCNT)_T (3.4 ± 1.3 nm vs. 9.4 ± 3.6 nm) and displayed a more uniform distribution of Pd nanoparticles on the surface of MWCNT. In contrast, significant increase in sizes of the Pd nanoparticles was apparent over the large

areas of several microns on the TEM image of Pd nanoparticles prepared by the thermal route $(Pd/MWCNT)_T$ (Fig. 1b). The size increase of Pd nanoparticles in this sample was apparently the result of the additional heating at 300 °C. Such heating in the thermal route induced the complete decomposition of palladium acetate (see below) and the simultaneous Ostwald ripening of the existing sub-5 nm nanoparticles from mechanochemical mixing. Compared to the kinetically formed smaller Pd nanoparticles during mixing, the formation of larger nanoparticles from the subsequent heating should be more thermodynamically driven. Similarly, the TEM images of two Pd/SWCNT samples prepared by mechanochemical and thermal methods exhibited average particle sizes of 6.6 \pm 2.1 nm and 10.7 \pm 3.6 nm for (Pd/SWCNT)_M and (Pd/SWCNT)_T, respectively. Significant size increase of the Pd nanoparticles was also observed on the broad areas of the TEM image of the thermally obtained sample (Pd/SWCNT)_T in comparison to the mechanochemically obtained sample (Pd/SWCNT)_M (Fig. 1c-d). It should be noted that it was challenging to identify individual or even bundles of SWCNTs after ball-milling because the nanotubes were partially amorphortized by the mechanical forces. In addition, the impurities (amorphous carbon, catalyst nanoparticles, etc) from the pristine SWCNT sample might have also masked the nanotubes. Nevertheless, the Pd content in all Pd-carbon nanotube samples were well controlled by the amount of Pd salt used. This was further confirmed by inductively coupled plasma equipped with mass spectroscopy (ICP-MS). For Pd/nanotube samples with a targeted Pd content of ~9 wt%, ICP-MS analysis indicated Pd content values of 8.5 wt%, 7.3 wt%, 7.3 wt%, 7.0 wt% for $(Pd/MWCNT)_M$, $(Pd/MWCNT)_T$, $(Pd/SWCNT)_M$, and (Pd/SWCNT)_{T.} respectively.

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Fig. 1 TEM images of Pd/MWCNT and Pd/SWCNT nanoparticles a) $(Pd/MWCNT)_{M}$ b) $(Pd/MWCNT)_{T}$ c) $(Pd/SWCNT)_{M}$ d) $(Pd/SWCNT)_{T}$





Fig. 2a displays the XRD patterns of Pd/MWCNT nanoparticles prepared by mechanochemical and thermal routes. The peaks at $2\theta \sim 26^{\circ}$ were assigned to the signature graphitic layered structure, the (002) peak, of MWCNTs in (Pd/MWCNT)_M and (Pd/MWCNT)_T, respectively (Fig. 2a, b). The typical XRD patterns of Pd(0) (ICPDS #05-0681) can be observed in the (Pd/MWCNT)_T spectrum in Fig. 2b. For example, the peak at 2θ value of 40.1° corresponds to the (111) d-spacing of 2.2 Å of metallic Pd. Other peaks were of lower intensity, consistent with the standard pattern. The broadening of the peaks was due to the nanoscale nature of the crystalline phase. For the (Pd/MWCNT)_M sample, most peaks from Pd(0) were discernible but of much lower intensity (Fig. 2a). This was likely due to the lower salt-to-metal conversion and the smaller particle size (broadening effect) in this sample. XRD results on the Pd/SWCNTs were similar (Fig. S1, Supporting Information), despite significant impurity peaks from the pristine nanotubes.

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In our previous work,⁵¹ it was established that the mechanical energy during ballmilling might not be sufficient to fully decompose the metal salt used. Unlike the case of silver acetate, the XRD patterns of residual palladium acetate were not readily identifiable in the products from room temperature mechanochemical reactions (Fig. 2 a). Therefore, the XPS data was further employed to determine the composition of the Pd species in both samples (Fig. 3). The XPS spectrum of (Pd/MWCNT)_M indicates the presence of a mixture of Pd(0) and Pd(II) (52% to 48%) as evident from the measured binding energy of the Pd 3d^{5/2} and 3d^{3/2} electrons at 335.8 and 341 eV for Pd(0) and 338.1 and 343.2 eV for Pd(II), respectively (Fig. 3a). Consistently, the XPS data of (Pd/MWCNT)_T shows a dominating Pd(0) (~90%) due to two significant binding energies of the Pd 3d^{5/2} and 3d^{3/2} electrons at 336 and 341.4 eV, indicating the further decomposition of palladium acetate into Pd metal under the thermal conditions used. As previously discussed, the nearly complete decomposition of the Pd salt under the thermal conditions was likely a major contribution to the size increase of the Pd nanoparticles.



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Fig. 3 XPS Spectra of a) (Pd/MWCNT)_M b) (Pd/MWCNT)_T c) (Pd/SWCNT)_M d) (Pd/SWCNT)_T

Similarly, the XPS spectra of $(Pd/SWCNT)_M$ shows the measured binding energies of the Pd 3d^{5/2} and 3d^{3/2} electrons at 338.2 and 343.6 eV that correspond to the presence of Pd(II) as the major palladium species (74%) in these nanoparticles. Further decomposition of Pd salt under thermal conditions of 300 °C led to the formation of Pd(0)

as the dominant peaks (80%) in the XPS data of $(Pd/SWCNT)_T$ as evident from the measured binding energies at 335.4 and 340.7 eV (Fig. 3d).

Catalytic activity of Pd/MWCNT in Suzuki cross coupling reactions

The catalytic activity of Pd/MWCNT prepared by mechanochemical and thermal routes were investigated using the Suzuki cross coupling reaction of bromobenzene and phenylboronic acid in a mixture of H_2O :EtOH (1:1) at room temperature using various catalyst concentrations. Fig. 4 illustrates the % conversion of the reaction in Eq. 1 for different loadings of nanocatalysts. At 0.5 mol% loading, the $(Pd/MWCNT)_M$ nanoparticles showed complete conversion (100%) of any bromide to the biphenyl product within 5 min, at ambient temperature. Under the same concentration, the thermal route product $(Pd/MWCNT)_T$ with the same catalyst loading demonstrated lower reactivity and afforded only 78% conversion after 6 h at room temperature. Notably, commercially available Pd supported on activated carbon (10% Pd/C), the most often used catalyst in heterogeneous Pd-catalyzed coupling reactions, exhibits only 75% conversion after 5 hours at room temperature. When 0.5 mol% of (Pd/SWCNT)_M was employed in Suzuki cross coupling reaction, a 95 % conversion was obtained after 30 min at room temperature. Under the same reaction conditions, the (Pd/SWCNT)_T sample exhibited a very weak catalytic activity and provided only 70% biphenyl product within 6 h at room temperature. Thus, the (Pd/MWCNT)_M catalyst system appears to be the most reactive towards the Suzuki cross coupling reaction of bromobenzene and phenylboronic acid at room temperature.

Lowering the catalyst loading of $(Pd/MWCNT)_M$ to 0.05 mol%, afforded a 98% conversion in 30 minutes. At an even lower loading of 0.008 mol%, $(Pd/MWCNT)_M$ provided 100% conversion after 3 h at room temperature. Interestingly, at this low concentration, $(Pd/MWCNT)_M$ is capable of converting 58% of the bromobenzene to the biphenyl product at 80 °C under microwave heating for 2 min, and 100% formation of product was observed after 5 min. These results demonstrate the remarkable catalytic activity of $(Pd/MWCNT)_M$ with a turnover number (TON) of 7250 and turnover frequency (TOF) of 217,500 h⁻¹ in microwave assisted Suzuki cross coupling reaction at



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 80° C. The excellent catalytic activity of (Pd/MWCNT)_M can be attributed in part to the small particles size of Pd nanoparticles (1-3 nm), and uniform distribution on MWCNT with no observed agglomeration during the mild preparation method of ball-milling at ambient temperature for 30 min.⁵³ However, the MWCNT support system may also play a significant role in accelerating reaction rates by activating the Pd nanoparticles on the electron rich surface of the carbon nanotubes. It should also be noted that microwave irradiation can have a significant impact on the efficiency of the Suzuki reactions due to increasing the reaction rates by providing a direct, rapid and consistent energy for the cross coupling reactions. The remarkably high TON and TOF values observed with the (Pd/MWCNT)_M catalyst may also be ascribed to the ability of the Pd particles to more efficiently absorb microwave irradiation and thus function effectively even at very low catalyst concentrations (e.g. 0.008 mol%) and a short reaction times.

To further investigate the mechanism of this catalytic reaction, the Suzuki cross coupling of bromobenzene and phenyl boronic acid was performed in the presence of 0.5 mol% of the (Pd/MWCNT)_M and potassium carbonate at 80°C for 10 min using a mixture of H₂O:EtOH (1:1) as solvents (Fig. 5). The reaction mixture was then hot filtered over celite and the filtrate solution was analyzed by ICP-MS in which the amount of Pd content was determined to be 120 ppb. Moreover, after the removal of the supported Pd nanoparticles from the reaction mixture by filtration over celite, the resulting filtrate solution was subjected to the microwave irradiation in the presence of fresh amount of bromobenzene, phenyl boronic acid, and potassium carbonate. No further catalytic activity was observed in this solution after heating the reaction mixture under microwave at 80°C for 10 min. While the small amount of leached Pd (120 ppb) may not be

consistent with the complete heterogeneity of the catalytic mechanism, the lack of reactivity after the removal of the supported catalyst indicates the vivid interaction of the carbon nanotube support system with Pd nanoparticles in inducing the catalytic activity. Thus, these results combined with our recycling experiments (Table 1) provide consistent evidence for the proposed interfacial release-redeposition mechanism, by which a small quantity of Pd nanoparticles leach off of the support surface, catalyzes the reaction, and re-deposit onto the surface of the carbon nanotube. We are currently investigating the surface interactions between the solvent system, the Pd particles and the support surface in order to obtain a more fundamental understanding of the extraordinary catalytic activity as well as the remarkable recyclability of this catalyst system.



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Effect of the ball-milling time on the catalytic performance

The duration of ball-milling time for the preparation of $(Pd/MWCNT)_M$ and its affect on Suzuki cross coupling catalytic activity was also investigated. Samples of

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(Pd/MWCNT)_M were prepared at different ball-mill time of 10 min, 30 min and 60 min and their catalytic activity were tested for Suzuki cross coupling reaction of bromobenzene with phenylboronic acid at room temperature (reaction in Eq. 1). Interestingly, using 0.5 mol% of each of these nanocatalysts in Suzuki reactions provided the biphenyl product in a quantitative yield (100%) after 5 minutes at room temperature, thus indicating no significant difference in catalytic activity between the three samples. The TEM images of all of these $(Pd/MWCNT)_M$ samples demonstrated an average particles size of 3-4 nm with uniform distributions of the Pd nanoparticles on the surface of MWCNT (Fig. S2, Supporting Information). Alternatively, to evaluate the effect of the ball-milling technique in providing the necessary mechanical energy for facile decomposition of the Pd salt in the presence of carbon nanotubes, samples of the catalysts were prepared by mixing the Pd salt using a mortar and pestle at both room temperature and thermal condition of 300 °C. Both samples demonstrated poor catalytic activity (10% conversion after 60 min at room temperature) in Suzuki coupling reaction described in Eq. 1. Unlike the $(Pd/MWCNT)_M$ samples prepared by ball-milling, the manually mixed Pd/MWCNT sample did not contain any significantly active Pd nanoparticles, which were required for the catalysis. Therefore, the ball-milling operations proved not only to be a facile and scalable methodology for catalyst preparation, but also to provide a consistent and necessary mechanical force to produce catalytically active materials.

Recyclability of $(Pd/MWCNT)_M$ and $(Pd/SWCNT)_M$ for Suzuki cross coupling reaction

The recyclability of $(Pd/MWCNT)_M$ was also examined using the microwave assisted Suzuki cross coupling reaction of bromobenzene with phenylboronic acid at 80 °C for 10 min (Eq. 1). In this case, full conversions were obtained in runs 1-4. The activity slightly dropped in the run 5 yielding 85% conversion and further dropped in runs 6, 7 to 60% and 42 % conversions, respectively. We examined the $(Pd/MWCNT)_M$ samples by TEM after the 6th run (Fig. 6) and found a significant amount of agglomeration of the Pd nanoparticles. Utilizing iodobenzene as the arylhalide, the $(Pd/MWCNT)_M$ (0.5 mol%)

Run	Conversion (%) ^a (Pd/MWCNT) _M	Conversion (%) ^b (Pd/MWCNT) _M	Conversion (%) ^a (Pd/SWCNT) _M	Conversion (%) ^b (Pd/SWCNT) _M
1	100	100	100	100
2	100	100	100	100
3	100	100	98	100
4	100	100	78	100
5	85	100	60	100
6	60	100	45	100
7	42	100	-	100
8	-	100	-	100
9	-	100	-	62
10	-	70	-	48
11	-	52	-	-

Table 1 Recycling experiments with $(Pd/MWCNT)_M$ and $(Pd/SWCNT)_M^c$

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a) bromobenzene (50 mg, 0.32 mmol boronic acid, phenylboronic acid (47 mg, 0.382 mmol, 1.2 eq.), potassium carbonate (133 mg, 0.96 mmol, 3 eq.), and (Pd/MWCNT)_M (2 mg, 1.6 µmol, 0.5 mol%) or (Pd/SWCNT)_M (2.3 mg, 1.6 µmol, 0.5 mol%) in 4 mL (H₂O:EtOH) (1:1) was heated at 80 °C (MWI) for 10 min. b) lodobenzene (50 mg, 0.245 mmol), phenylboronic acid (36 mg, 0.294 mmol, 1.2 eq.), potassium carbonate (102 mg, 0.735 mmol, 3 eq.), and (Pd/MWCNT)_M (1.5 mg, 1.2 µmol, 0.5 mol%) or (Pd/SWCNT)_M (1.7 mg, 1.6 µmol, 0.5 mol%) in 4 mL (H₂O:EtOH) (1:1) was heated at 80 °C (MWI) for 10 min. c) Conversions were determined by GC-MS.

successfully afforded quantitative conversion in Suzuki cross coupling reaction with phenylboronic acid at 80 °C microwave irradiation in 10 min for 9 consecutive recycles

without any loss of reactivity. The activity of the catalyst dropped in runs 10 and 11 to 70 and 52% conversions, respectively. The $(Pd/SWCNT)_M$ demonstrated slightly lower recyclability in Suzuki cross coupling reactions with iodo- and bromobenzene. As indicated in Table 1 with bromobenzene, the $(Pd/SWCNT)_M$ can be re-used three times affording quantitative yields of the product in each run. The catalytic activity subsequently diminished to 78% in run 4. Using iodobenzene, the catalyst was recycled 7 times yielding a 100% conversion in each run. The catalytic activity diminished to 62 and 48 % in runs 9 and 10, respectively.

TEM images of $(Pd/MWCNT)_M$ after the 6th run and $(Pd/SWCNT)_M$ after the 5th run revealed significant agglomeration of Pd nanoparticles on the surface of carbon nanotubes indicating the possible mechanism for deactivation of the catalyst due to the decrease in the surface area and saturation of the coordination sites (Fig. 6). It should also be noted that the diameter of the MWCNTs (~20-150 nm) is significantly greater than the SWCNTs (~1.5 nm) which may provide the opportunity for stronger surface interactions and a more effective anchor for the Pd particles, thus providing less opportunity for agglomeration. The higher catalytic activity and improved recyclability of (Pd/MWCNT)_M compared to (Pd/SWCNT)_M may also be attributed to the higher concentration of Pd nanoparticles in this sample, greater degree of dispersion on the surface of the MWCNT, and smaller particle size (1-3 nm) as is evident by TEM images (Fig. 1a, c).

Notably, the Pd content measured by ICP-MS in the reaction solution of $(Pd/MWCNT)_M$ and $(Pd/SWCNT)_M$ after the 6th and 5th recycling experiments were determined to be 150 and 350 ppb, respectively. The smaller amount of Pd leaching in

 $(Pd/MWCNT)_M$ once again suggests a stronger surface interaction between Pd nanoparticles with MWCNT in this sample, which increases the catalyst-support interaction, and thus contributes to the enhancement of the catalytic activities of these nanoparticles.

Fig. 6 Significant agglomeration of a) $(Pd/MWCNT)_M$ after the 6th run b) $(Pd/SWCNT)_M$ after the 5th run



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As shown from the recycling experiments, the $(Pd/MWCNT)_M$ exhibited excellent catalytic activity and recyclability towards Suzuki cross coupling reactions. Since this catalyst contained a significant amount of Pd(II) species as determined by XPS, the in situ reduction of Pd(II) to Pd(0) is most likely facilitated during the cross coupling reaction by the protic solvents under basic conditions to increase the concentration of Pd(0) for further recycling reactions.^{38,40,41} Alternatively, since the carbon nanotubes are effective microwave energy absorbers, the microwave-induced situ in reduction/decomposition of Pd(II) to Pd(0) on the carbon nanotube surface could also occur during the catalytic reaction,⁵³ thus increasing the concentration of the Pd(0) in these nanocatalysts as an active species in the Suzuki coupling reaction. Fig. 7 displays

the XPS spectra of (Pd/MWCNT)_M and (Pd/SWCNT)_M prepared before and after the first

Suzuki reactions during the recycling experiments.

Fig. 7 XPS spectra of $(Pd/MWCNT)_M$ a) before the Suzuki reaction b) after the Suzuki reaction, and $(Pd/SWCNT)_M$ c) before the Suzuki reaction d) after the Suzuki reaction



These results indicate that the majority of Pd(II) concentration was reduced in situ to Pd(0) during the first reaction for both catalytic systems which is consistent with our previous observations.⁴⁰ The presence of Pd(0) in both Pd nanoparticles is confirmed by the major binding energies of $3d^{5/2}$ and Pd $3d^{3/2}$ electrons at 335.8 and 341.1eV correspond to Pd(0) species formed during the first Suzuki recycling reaction.

Diversity of substrates in Suzuki cross coupling reactions using (Pd/MWCNT)_M

The versatility of Suzuki cross coupling reactions was further investigated using a broader range of functionalized aryl bromides and phenyl boronic acids. $(Pd/MWCNT)_{M}$ nanoparticles were employed exclusively in these reactions due to the greater catalytic activity established in our previous studies (Table 2). Thus, the reactions of diversely substituted aryl bromide and phenyl boronic acids were performed in the presence of potassium carbonate (3 eq.) and 0.5 mol% of (Pd/MWCNT)_M catalyst using a mixture of $H_2O:EtOH$ (1:1), which is an environmentally benign solvent system. The reactions were either conducted at room temperature or heated at 80 °C for 10 min under microwave irradiation. As shown in Table 2, a series of aryl bromides containing various functional groups on the phenyl rings including cyano (1a, b), aldehyde (1c), ketone (1e), ester (1h), and nitro (1d) can effectively undergo Suzuki cross coupling reactions providing high yields of the corresponding biphenyl products. In addition, phenyl boronic acids bearing functional groups such as dimethylamino (1c, h), thiomethyl (1d), electron donors methoxy and ethoxy groups (1e, f), as well as 4-aminocarbonyl (1g) all worked well in this coupling reaction scheme and afforded high yields of the corresponding Suzuki products.

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a) Aryl halide (0.51 mmol), Boronic acid (0.61 mmol), potassium carbonate (0.96 mmol), and Pd/G (0.3 mol%) in 4 mL (H₂O:EtOH) (1:1) was heated at 80 °C (MWI) for 10 min. b) Reactions were completed at r.t. after 30 min. c) Isolated yields.

Conclusions

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In summary, a mild, rapid and solventless mechanochemical ball-milling method was developed to prepare Pd nanoparticles supported on single- and multi-walled carbon nanotubes (Pd/SWCNT and Pd/MWCNT) at ambient temperature as well as heating at 300 °C without the necessity for any reducing agent. The nanoparticles prepared by ball-milling at ambient temperature $[(Pd/MWCNT)_M, (Pd/SWCNT)_M]$ demonstrated greater catalytic activity towards the Suzuki cross coupling reactions than those prepared under thermal conditions $[(Pd/MWCNT)_T, (Pd/SWCNT)_T]$, mainly due to the smaller particle size, uniform dispersion of Pd nanoparticles on the surface of single- and multiwalled carbon nanotubes, and lack of agglomeration of these nanoparticles during the mechanochemical preparation at room temperature. While both $(Pd/MWCNT)_M$ and $(Pd/SWCNT)_M$ exhibited excellent catalytic activity in Suzuki cross coupling reaction under ligand free ambient conditions in an environmentally benign solvent system, $(Pd/MWCNT)_M$ showed a slightly better reactivity and recyclability with the TON of

7250 and TOF of 217,500 h^{-1} . The superior catalytic activity and increased recyclability of (Pd/MWCNT)_M may be attributed to the larger diameter of the MWCNTs (~20-150 nm) which provides stronger surface interactions and a more effective anchor for the Pd particles, thus facilitating the deposition of the greater number of Pd nanoparticles on the surface of MWCNTs. In addition, the higher Pd content of 8.5 wt% in this sample, smaller particles size (1-3 nm), and the more uniform distribution of the Pd nanoparticles on the surface are also considered to be contributing factors to the overall catalyst performance of the (Pd/MWCNT)_M. This catalyst was effective over a broad range of Suzuki cross coupling reactions with a wide variety of functionalized substrates. Studies towards applying the same mechanochemical ball-milling methods to prepare Pd nanopaticles deposited on other solid supports such as graphene and investigating their catalytic activities is currently underway in our laboratory.

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