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Abstract: Carbon nanotube–supported palladium nanoparticles prepared by a supercritical fluid deposition method show high activities for catalyzing Suzuki coupling reactions, and the catalysts can be recycled and reused at least six times without losing activity.

Keywords: Carbon nanotube, palladium nanoparticles, supercritical fluid, Suzuki coupling

INTRODUCTION

The palladium-catalyzed Suzuki coupling reactions between arylboronic acids and aryl halides are widely used in organic syntheses.^[1] Both homogeneous and heterogeneous catalysts have been used for the coupling reactions. In general, heterogeneous catalysis is less effective than homogeneous catalysis but has advantages, including easy separation of catalysts for recycling. The efficiency of heterogeneous catalysis can be improved by employing nanoparticle catalysts because of their extremely large surfaceto-volume ratios. An early study using palladium nanoclusters stabilized by tetraalkylammonium salts or by poly(vinylpyrrolidone) (PVP) as catalysts for Suzuki coupling reactions was reported by Reetz and coworkers.^[2]

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Recent reports showed that the shape of catalytic metal nanoparticles stabilized by PVP could affect catalysis, and near-spherical palladium nanoparticles were very effective for catalyzing the Suzuki coupling reactions.^[3] Because metal nanoparticles are generally unstable, exploration of appropriate supports for stabilizing catalytic nanoparticles is a key factor for their successful applications in heterogeneous catalysis. Carbon nanotubes provide a new type of support for stabilizing catalytic nanoparticles. Because of their small sizes, carbon nanotubes can be uniformly dispersed in a solution by mechanical stirring, thus increasing contacts between the reactants and the catalyst. Attaching metal nanoparticles to carbon nanotubes in aqueous solutions usually involves tedious processes with little control of particle size and distribution. A simple method of depositing metal nanoparticles on surfaces of multiwalled carbon nanotubes (MWCNT) using supercritical fluid carbon dioxide as a medium was reported recently.^[4] The method involves chemical reduction of a metal precursor dissolved in supercritical carbon dioxide in the presence of carbon nanotubes. Condensation and aggregation of the reduced metal lead to formation of metal nanoparticles on surfaces of curved carbon substrates. Near-spherical palladium nanoparticles with narrow size distributions can be formed on carbon nanotube surfaces. The curvature of the nanotubes is probably responsible for the formation of metal nanoparticles of a certain size range due to the contact angles allowed by the substrate surface during condensation.^[4] The catalytic activities of carbon nanotube-supported metal nanoparticles prepared by this method for organic reactions, including coupling reactions, have not been investigated. We have recently studied a number of Suzuki coupling reactions in methanol catalyzed by multiwalled carbon nanotube-supported palladium nanoparticles (Pd/MWCNT) prepared by a supercritical fluid deposition method. Very efficient Suzuki coupling reactions were observed under moderate temperatures without expensive ligands, and the Pd/MWCNT catalyst could be easily recycled for repeated use without losing activity. This new type of palladium catalyst appears to offer opportunities for a wide range of applications including organic syntheses and chemical manufacturing processes.

EXPERIMENTAL

The Pd/MWCNT catalyst was prepared according to a procedure described in a previous report.^[4] The method involved hydrogen reduction of palladium (II)–hexafluoroacetylacetone in supercritical fluid CO_2 in the presence of MWCNT at 80°C and 150 atm. After preparation, the samples were washed and sonicated in methanol and then dried for characterization. Transmission electron microscopy (TEM) images showed spherical particles attached to the surfaces of carbon nanotubes, and XPS (X-ray photon spectroscopy) showed that the Pd (3d_{5/3}) and Pd (3d_{3/2})

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peaks at 335.3 eV and 340.6 eV, respectively, were consistent with the literature data for zero-valent metallic palladium. Energy dispersive X-ray fluorescence (EDS) was used for quantitative analysis of the Pd metal loading in our carbon nanotube catalysts, which was about 3% by weight. A commercial palladium/carbon black (Pd/C) catalyst was obtained from Aldrich.

General Procedures for Suzuki Coupling Reactions

A 100 mL, three-necked, round-bottomed flask with a magnetic stirring bar was charged with Pd/MWCNT (10 mg, 3% Pd by weight), phenylboronic acid (1.1 mmol), aryl halide (1.0 mmol), sodium acetate (2.2 mmol), and methanol (25 mL). The mixture was vigorously stirred under reflux conditions in the open air. The extent of reaction was monitored by thin-layer chromatography (TLC) and 300 MHz nuclear magnetic resonance (NMR) spectroscopy (Bruker AMX 300).

After the reaction completion, the Pd/MWCNT settled down to the bottom of the flask. The organic layer was carefully removed. The solution was added with water and extracted with dichloromethane. The combined organic solution was dried with anhydrous MgSO₄ and concentrated in vacuo. The residue was purified by flash chromatography on silica gel with ethyl acetate-hexane = 1:10 as the eluent to give the desired products. The products were identified by comparison with ¹H NMR with those of authentic samples. The Pd/CNT was recovered almost quantitatively. After washing with methanol, the catalyst was reused for the next coupling experiment.

RESULTS AND DISCUSSION

The results of Suzuki coupling between phenylboronic acid and 1-iodo-4nitrobene catalyzed by the Pd/MWCNT are shown in Table 1. In entry 1, after 30 min of reaction at 65°C, the isolated yield showed at least 94% conversion to the product (nitro-biphenyl) with a turnover frequency (TOF) of 709 h⁻¹. In comparison with a commercially available Pd/C catalyst, the TOF of the commercial catalyst for the same reaction under the same conditions was only 30 h⁻¹, about 24 times slower. Similarly, in the case of coupling between phenylboronic acid and iodobenzene, it required about 2 h to reach 95% of conversion. The TOF of MWCNT-supported Pd catalyst was also higher than that found with the commercial Pd/C catalyst by about a factor of 7 (Table 1).

The Suzuki cross-coupling reactions between phenylboronic acid and iodobenzene catalyzed by PVP-Pd colloidal in 40% EtOH aqueous solution under reflux conditions (temperature of boiling 40% EtOH about 80°C) were reported by Li et al.^[5] The reaction required 12 h to reach 95%

Table 1. Comparison of Pd/MWCNT with conventional Pd/C for Suzuki coupling

	→B(OH) ₂ +		Pd/MWCNT CH ₃ OH /	R	
Entry	Aryl halide	Rxn time (h)	Product	Isolated yield %	TOF/h
1	1-Iodo-4- nitrobenzene	0.5 ^{<i>a</i>}	R=NO ₂	93 ^{<i>a</i>}	709
2	1-Iodo-4- nitrobenzene	3.5^{b}	R=NO ₂	94 ^b	30
3	Iodobenzene	2^a	R=H	95^a	177
4	Iodobenzene	4^b	R=H	95^{b}	27

^{*a*}10 mg Pd/CNT(3%) as described in the experimental section.

^b10 mg of conventional palladium catalyst on activated carbon (Pd content 10%, dry wt.) was used after dried in a oven for 2 h at 100°C.

conversion, and the Pd nanoparticles were agglomerated after one cycle, resulting in a loss of catalytic activity.

The speed of the coupling reaction depends on the nature of the substituted aryl halide. Table 2 shows the results of Suzuki coupling of phenylboronic acid and aryl halides with different substitution groups. With electron-withdrawing substitution groups (-NO2, -COCH3), the reaction rate is faster than nonsubstituted aryl halide. On the contrary, for the electron-donating groups $(-OCH_3)$, the reaction rate is slower than nonsubstituted aryl halide. Aryl bromide is slower than corresponding aryl iodide for the coupling reaction with phenylboronic acid, but the reaction still proceeds well

Rxn Isolated TOF/h Entry Aryl halide time (h) Product yield % ()—()—сосн 1 4-Iodoacetophenone 0.75 94 473 🔶 сосн 2 1.5 94 4-Bromoacetophenone 236 🔶 ссн, 3 4-Iodoanisole 3.5 92 118 $\bigcirc \prec^{\circ}$ 4 2.5 94 2-Iodothiophene 142 5 5 $\bigcirc \bigcirc \bigcirc \bigcirc \bigcirc$ 95 1,4Diiodobenzene 71 92 6 1-Bromo-4-nitrobenzene 1 355 7 $\bigcirc \bigcirc$ 95 Bromobenzene 3.5 101

Table 2. Pd/MWCNT catalyzed Suzuki coupling of phenylboronic acid with aryl halides

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Table 3. Suzuki coupling reaction of 4-iodobenzene and phenylboronic acid using recycled Pd/MWCNT as catalyst

Pd/CNT	Conversion %	Isolated yield %	
Fresh	>99	94	
1st reused	>99	96	
2nd reused	>99	95	
3rd reused	>99	94	
4th reused	>99	95	
5th reused	>99	96	
6th reused	>99	96	

with good conversion using the Pd/CNT catalyst. In a previous report, Kabalka et al. used a large amount of palladium black (50 mg) as catalyst for Suzuki coupling with aryl bromides, and the substrates were found ineffective.^[6] In entry 4, coupling between 2-iodothiophene and phenylboronic acid was also studied, and the reaction proceeded well, as shown in Table 2. However, coupling of 1,4-diiodobenzene with 2 molecules of phenylboronic acid to form triphenyl is the slowest reaction observed in this study, requiring 5 h to reach 95% conversion.

The activity of the recycled Pd/MWCNT was tested by the reaction of 4-iodobenzene with phenylboronic acid. As shown in Table 3, the activity of the MWCNT-supported Pd catalyst remained almost unchanged even after recycling six times. TEM micrographs of the recycled Pd/MWCNT catalysts showed little change of the particle density on the MWCNT surfaces, but some larger particles up to 40 nm were observed after six uses.

CONCLUSION

In summary, we have shown that Pd/MWCNT made by a supercritical fluid deposition method can efficiently catalyze the Suzuki coupling reactions without expensive ligands and can be reused many times without loss of catalytic activity. Biaryl structures are present in a variety of common natural products,^[7] conjugated polymers,^[8] and liquid crystalline materials^[8,9] that require Suzuki coupling reactions for synthesis. The Pd/CNT catalyst described in this report should have a wide range of applications in organic synthesis and design for durable nanoparticle catalysis.

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