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ARTICLE

## Palladium NPs Supported on Novel Imino-Pyridine-Functionalized MWCNTs: Efficient and Highly Reusable Catalyst for the Suzuki-Miyaura and Sonogashira Coupling Reactions

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Mehdi Adib,<sup>a\*</sup> Rahman Karimi-Nami,<sup>a</sup> Hojat Veisi<sup>b</sup>

In this article the new heterogeneous nanocatalyst based on palladium supported on functionalized multi-walled carbon nanotubes (MWCNTs) has been introduced. The synthetic process of preparation of mentioned nanocatalyst, MWCNT-imino-pyridine/Pd, has been described. The characterization of the MWCNTs-imino-pyridine/Pd was afforded by the SEM, EDX, TEM, FTIR, ICP, and XRD. The surface structure of the materials was confirmed using Fourier transform infrared (FTIR) spectroscopy. The catalytic activity of MWCNT-imino-pyridine/Pd was tested in Sonogashira and Suzuki-Miyaura cross-coupling reactions affording various derivatives of both aryl alkynes and biaryls. The catalyst can be readily recovered and recycled at least six times without significant loss of catalytic activity.

### Introduction

Heterogeneous catalysts have attracted significant attention in organic synthesis as a result of numerous advantages over related homogenous catalysts, such as avoidance of formation of inorganic salts, recyclability, non-toxicity, ease of handling, safety, shelf life, ease of removal via filtration or centrifugation, and ease and safety of disposal.<sup>1-7</sup> Among heterogeneous catalysts, nano transition metals supported on functionalized carbon nanotubes (CNTs) and fullerenes (C60) have been applied in a wide range of organic reactions for carbon-carbon bond formation. Here, the functionalization of the carbon nanotube surface with a ligand for immobilization of the transition metal is a very important step. Complexation of the ligand to the transition metal prevents leaching and agglomeration of nanoparticles and improves reusability of the heterogeneous catalyst.<sup>8-12</sup> Among the fundamental transition metal supported on functionalized CNTs and fullerene, palladium nanoparticles have occupied a very particular place. Specifically, these catalysts have been applied in Suzuki-Miyaura coupling reactions for the synthesis of biaryls and heteroaryls from aryl halides with organoboron compounds,<sup>13</sup> as well as the sonogashira coupling reaction between a terminal alkyne and an aryl or vinyl halide. We can mention synthesis of

biguanide-functionalized single-walled carbon nanotubes (SWCNTs) hybrid materials<sup>14</sup> and functionalization of fullerene (C60) with metformine to immobilized palladium<sup>15</sup> as two novel heterogeneous and reusable nanocatalysts in the Suzuki-Miyaura coupling reaction at room temperature. Biaryls are important skeletons in the structures of biologically active compounds,<sup>16</sup> agrochemicals, pharmaceuticals,<sup>17</sup> ligands,<sup>18</sup> and functional materials.<sup>19</sup> There have been reported many approaches using heterogeneous catalysts for the synthesis of biaryls. In addition to the two above described methods,<sup>14,15</sup> we can mention ligand free palladium supported on solid supports too, such as activated carbon,<sup>20</sup> zeolites and molecular sieves,<sup>21</sup> metal oxides,<sup>22</sup> and clays.<sup>23</sup> Also, various palladium catalysts are applied to form sp<sup>2</sup>-sp bonds between aryl or alkenyl halides or triflates and terminal alkynes. This coupling reaction has become the most important method for the preparation of arylalkynes and conjugated enynes, which are precursors for natural products, pharmaceuticals, and molecular organic materials.<sup>24</sup> However, the catalytic activity of Pd<sup>2+</sup> in most cases decreased gradually when the catalyst was used repeatedly. This could be ascribed to the weak interaction between palladium and the non-functionalized support material, as well as the agglomeration and accumulation of Pd nanoparticles on the surface of the material.<sup>25,26</sup> Accordingly, development of novel ligands in order to increase of stability, recyclability, and applicability of heterogeneous catalysts is one of the most important criteria in the field of heterogeneous catalysts. Unfortunately the ligands that have been used until now for the functionalization of solid beds suffer from high cost. Here, we imagined that Schiff bases could offer a solution as simple and inexpensive alternatives for functionalization of supports and preparation of Pd Schiff base complexes.<sup>27-29</sup> Herein, we attempted to use ethylenediamine and pyridine

<sup>a</sup> School of Chemistry, University College of Science, University of Tehran, P. O. Box 14155 – 6455, Tehran, Iran. E-mail: madib@khayam.ut.ac.ir

<sup>b</sup> Department of Chemistry, Payame Noor University, Tehran, Iran

<sup>c</sup> Address here.

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carbaldehyde to prepare imino-pyridine ligands for the synthesis of palladium nanocatalyst supported on imino-pyridine-functionalized multi-walled carbon nanotubes (MWCNTs) hybrid materials. This immobilized palladium represents a new recyclable heterogeneous nanocatalyst (Scheme 1) for Suzuki-Miyaura (Scheme 3) and Sonogashira cross-couplings (Scheme 2).

## Experimental

### 2.1 Materials

All the reagents were purchased from Aldrich and Merck and were used without any purification. The pure MWCNTs without functional groups were purchased from Petrol Co. (Tehran, Iran). HCl, H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>, deionized water, NaH (80%), ethylenediamine, 2-pyridine carbaldehyde, acetonitrile, PdCl<sub>2</sub>, and *N,N*-dicyclohexylcarbodiimide (DCC) were obtained from Sigma Aldrich and Merck.

### 2.2 Synthesis of carboxylic derivative of multi walled carbon nanotubes (MWCNTs-COOH)

First MWCNTs were added to 50 mL HCl (10 %) then, after sonication for 15 min, the solution was stirred for 24 h to purification of MWCNTs by remove the metal ions and other impurities adsorbed on it. Then the purified MWCNTs were precipitated and separated using 9000 rpm centrifuging. Then 1000 mg of purified MWCNTs was suspended in 400 mL of concentrated HNO<sub>3</sub> and refluxed for 12 h with vigorous stirring. The product (MWCNTs-COOH) was separated by 9000 rpm centrifuging and washed with deionized water to neutral and dried under vacuum at 80 °C for 12 h (Scheme 1).

### 2.3 Synthesis of MWCNTs-EDA

In the next step a 1000 mg amount of MWCNTs-COOH was added to 50 mL of ethylenediamine (EDA). After heating and stirring for 5 min, the DCC was added to the solution and refluxed for 48 h. Then the prepared MWCNTs-EDA was separated by centrifuge, washed with ethanol and dried in an oven at 80 °C for 8 h. The synthesis route of MWCNTs-EDA is illustrated in scheme 1.2.4. Synthesis of imino-pyridine functionalized MWCNTs

For the synthesis of MWCNTs-imino-pyridine, the prepared MWCNTs-EDA was suspended in 25 mL ethanol, and 4 mmol of pyridine 2-carbaldehyde was added to the solution. After 12 h stirring at room temperature the pure product was separated by centrifugation and washed with ethanol (3 × 10 mL).

### 2.4 Synthesis of MWCNT-imino-pyridine/Pd<sup>2+</sup> and MWCNT-imino-pyridine/Pd<sup>0</sup>

The imino-pyridine functionalized MWCNTs (1000 mg) and PdCl<sub>2</sub> (70 mg, 0.4 mmol) were dispersed separately in acetonitrile (30 ml) until soluble at 40 °C. The two solutions were mixed together and sonicated for 10 min. The mixture was stirred for 24 h at room temperature to complete attainment of coordination. Then yielded MWCNT-imino-pyridine/Pd<sup>2+</sup> nanocatalyst was subjected to centrifugation, washed with acetonitrile and DI water and dried in vacuum at 50 °C for 12 h

The overall synthesis of MWCNT-imino-pyridine/Pd<sup>2+</sup> nanocatalyst is schematically demonstrated in Scheme 1.

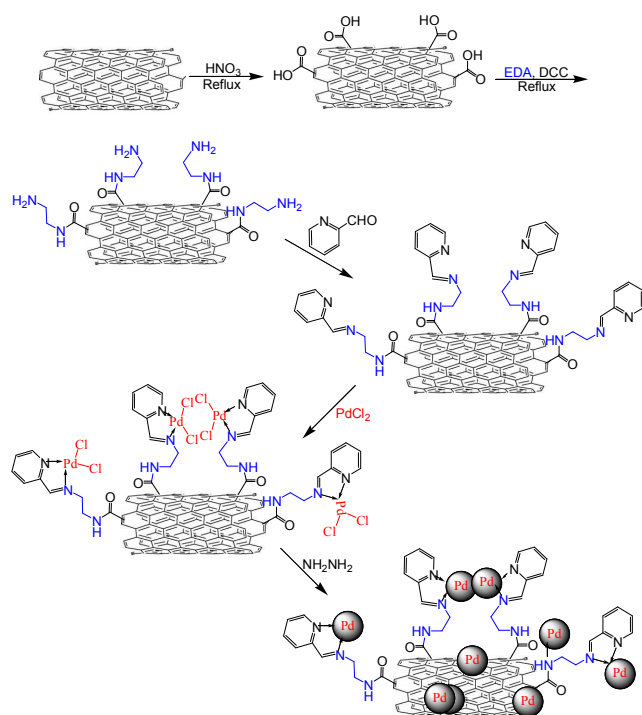
The reduction of MWCNT-imino-pyridine/Pd<sup>2+</sup> by hydrazine hydrate was performed as follows: 30 mg of MWCNT-imino-pyridine/Pd<sup>2+</sup> was dispersed in 60 mL of water, and then 100 μL of hydrazine hydrate (80%) was added. The pH of the mixture was adjusted to 10 with 25% ammonium hydroxide and the reaction was carried out at 95 °C for 2 h. The final product MWCNT-imino-pyridine/Pd<sup>0</sup> was washed with water and dried in vacuum at 50 °C. Scheme 2 depicted the synthetic procedure of MWCNT-imino-pyridine/Pd<sup>2+</sup> and MWCNT-imino-pyridine/Pd<sup>0</sup>. The concentration of palladium in MWCNT-imino-pyridine/Pd<sup>2+</sup> and MWCNT-imino-pyridine/Pd<sup>0</sup> were 19 and 17 wt%, respectively, which were determined by ICP-AES and TGA.

### 2.5 General procedure for synthesis of biphenyls

A mixture of MWCNTs-imino-pyridine/Pd<sup>0</sup> (2 mg), bromobenzene (1 mmol), phenylbromic acid (1.2 mmol, 145 mg), and K<sub>2</sub>CO<sub>3</sub> (2 mmol, 276 mg) in EtOH/ H<sub>2</sub>O (1:1, 2 mL) was stirred at room temperature for the appropriate time as indicate in Table 4. After completion of the reaction, as indicated by TLC, the catalyst was separated from the reaction mixture by centrifugation. Solvent was then evaporated and pure reaction product was obtained by column chromatography using hexane: ethyl acetate as the eluent and product was purified by recrystallization with the mixture of EtOH/ H<sub>2</sub>O (1:1). The catalyst was washed with ethanol, dried and preserved for next run.

### 2.6 General procedure for synthesis of 1,2-diphenylethylene

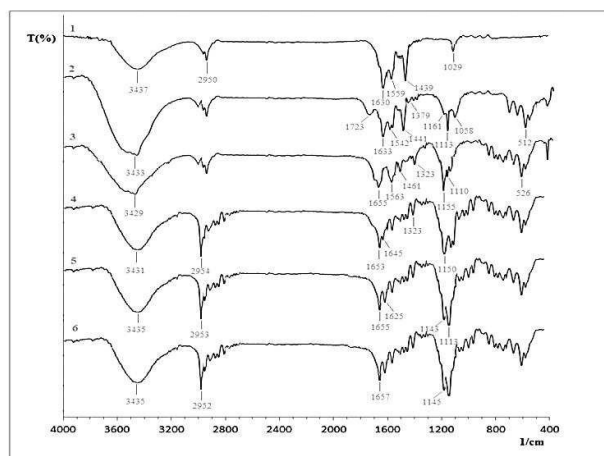
A mixture of ethynylbenzene (102 mg, 1 mmol), bromobenzene (157 mg, 1 mmol), K<sub>2</sub>CO<sub>3</sub> (138 mg, 1 mmol) and MWCNTs-imino-pyridine/ Pd<sup>0</sup> (2 mg) added to round bottom flask under aerobic atmosphere at DMF (2mL). The resulting mixture was placed in an oil bath preheated to 120 °C and stirred for 40 min (as indicated by TLC) After cooling down the reaction to the room temperature, the catalyst was separated from the reaction mixture by centrifugation and the reaction mixture was diluted with EtOAc (20 mL) and H<sub>2</sub>O (20 mL). The combined organic layers were washed with 3 mL brine and dried (MgSO<sub>4</sub>). The solvent was removed in vacuum, and the product was purified by column chromatography on silica gel using a mixture of EtOAc/hexanes as the eluent. Finally, the white solid (169 mg, 95%) was obtained. The catalyst was washed and preserved for the next run in the same manner as described in the general procedure for synthesis of Suzuki- Miyaura product.



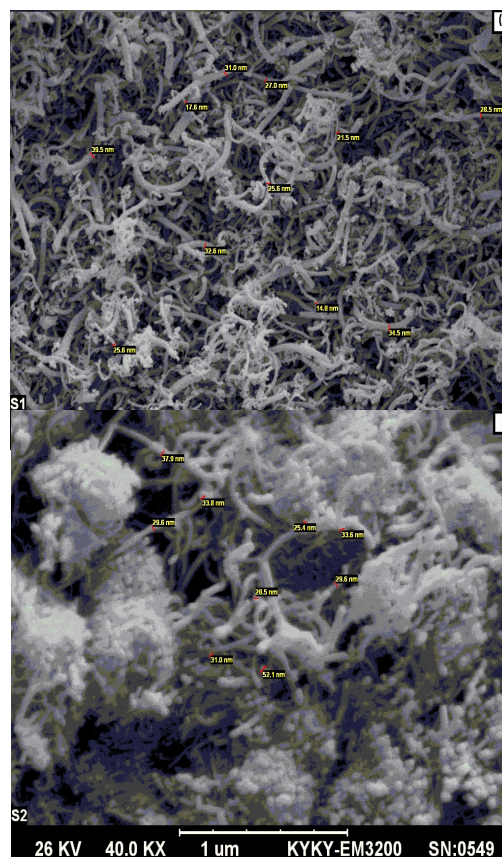
**Scheme. 1** Synthesis of MWCNT-imino-pyridine/Pd<sup>2+</sup> and MWCNT-imino-pyridine/Pd<sup>0</sup>.

## Results and discussion

The characterization of the MWCNTs-imino-pyridine/Pd<sup>0</sup> was afforded by the SEM, EDX, TEM, FTIR, ICP, and XRD. The surface structure of the materials was confirmed using Fourier transform infrared (FTIR) spectroscopy. Figure 1 shows the FT-IR spectra obtained for (1) MWCNTs, (2) MWCNTs-COOH, (3) MWCNTs-CO-EDA, (4) MWCNTs-CO-imino-pyridine, (5) MWCNTs-CO-imino-pyridine/Pd(II), (6) MWCNTs-CO-imino-pyridine/Pd<sup>0</sup>. Comparison of the FT-IR spectra of MWCNTs-COOH with MWCNTs, a new band 1723 cm<sup>-1</sup>, the band at 1723 cm<sup>-1</sup> corresponds to the carbonyl stretch of the carboxylic acid group. Also the FT-IR spectrum of MWCNTs-CO-EDA exhibits several signals originating from amino ethyl groups, which are related to C-H stretching modes of the ethyl. These signals appear in the area of 1461–1563 cm<sup>-1</sup> and 2858–2931 cm<sup>-1</sup>. In curve 3 the peak at 1680 cm<sup>-1</sup> is attributed to the carbonyl stretching of the amide groups (-CONH-). The doublet peak at 3300 cm<sup>-1</sup> corresponds to the amine group. Also, in curve 4 the band in the spectral region of 1645 cm<sup>-1</sup> can be assigned to the imine (C=NH) bond of the attached pyridine-2-carbaldehyde. These results indicate that the pyridine-2-carbaldehyde is bound to the surface of MWCNTs through amidation reaction. The C=NH bands of complex 5 were shifted to a lower frequency in the IR spectrum (1625 cm<sup>-1</sup>) compared to that of 4. The lowering in frequency of the C=NH peak is indicative of the formation of a metal-ligand bond. Also, scanning electronic microscopy (SEM) analysis of MWCNTs before (a) and after (b) functionalization with pyridine-2-carbaldehyde (Figure 2) confirmed the successful functionalization of multi-walled carbon nanotubes.



**Fig. 1** FT-IR spectra of (1) MWCNTs, (2) MWCNTs-COOH, (3) MWCNTs-CO-EDA, (4) MWCNTs-CO-imino-pyridine, (5) MWCNTs-CO-imino-pyridine/Pd(II), (6) MWCNTs-CO-imino-pyridine/Pd<sup>0</sup>.



**Fig. 2** SEM images of MWCNT before (a) and after (b) functionalization by imino-pyridine.

Transmission electron microscopy (TEM) investigations were carried out to observe the morphology and distribution of palladium particles supported on MWCNTs-imino-pyridine/Pd. The existence of Pd nanoparticles deposited on f-MWCNTs is clearly distinguishable as dark spots in Fig. 3. From Fig. 3 the Pd can be observed to be well dispersed on the surface of imino-pyridine modified MWCNTs. The results indicate that imino-pyridine plays an important role in improving the dispersibility of Pd.

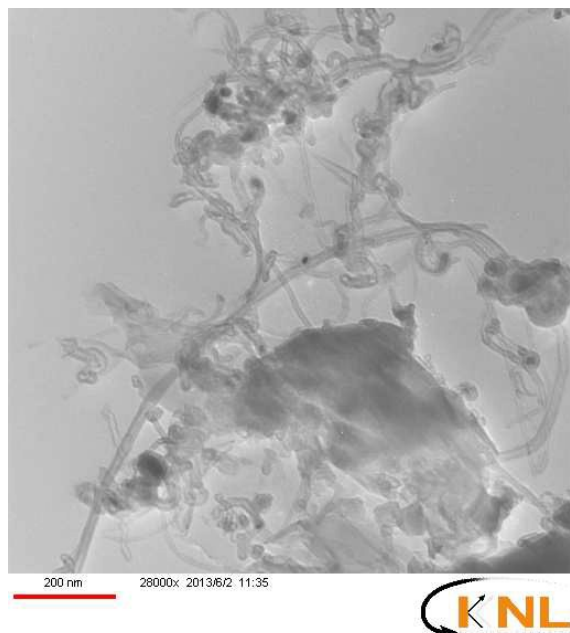


Fig. 3 TEM image of MWCNT-imino-pyridine/Pd.

X-ray diffraction spectra (XRD) patterns of MWCNTs-imino-pyridine/Pd are displayed in Fig. 4. The wide diffraction peak at  $2\theta = 26^\circ$  can be assigned to disorderedly stacked hexagonal graphite structure [15]. The well-defined peaks around  $39^\circ$  and  $47^\circ$  can be assigned to (111) and (200) crystal planes of Pd<sup>0</sup>.<sup>14</sup> Thus the XRD results indicate efficient immobilization of fcc structured Pd nanoparticles on f-MWCNTs.

The existence of metallic Pd in imino-pyridine-functionalized multi-walled carbon nanotubes was also confirmed by the EDX detector coupled to the SEM which showed the presence of C, O and N in Figure 5. The peaks derived from Cu were from the copper grid used in SEM measurements.

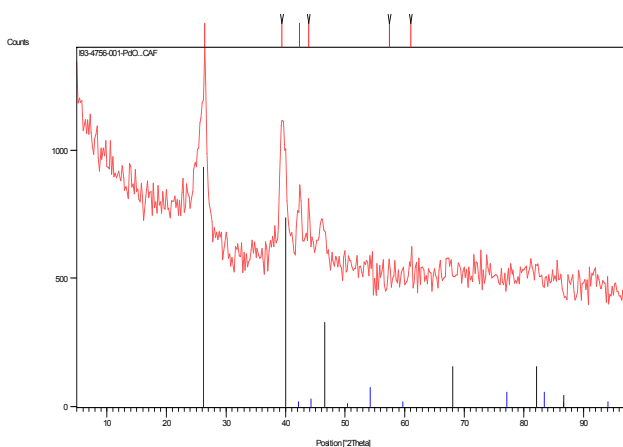


Fig. 4 The XRD patterns for MWCNTs-imino-pyridine/Pd

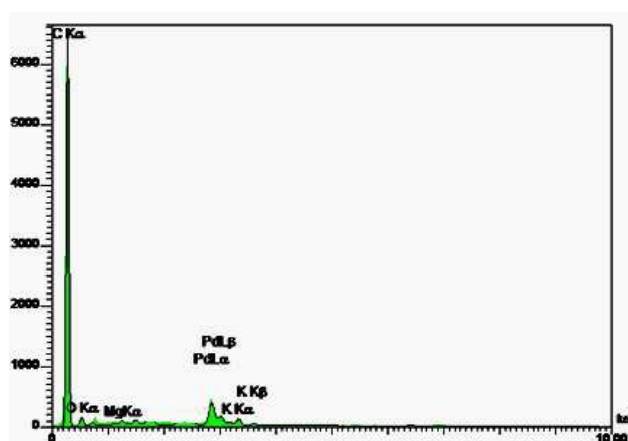


Fig. 5 EDS of MWCNTs-imino-pyridine/Pd.

To check the thermal stability of the catalyst (MWCNTs-imino-pyridine/Pd), a thermo-gravimetric analysis (TGA) was done which showed a slight weight loss up to  $130^\circ\text{C}$  followed by continuous weight loss up to  $500^\circ\text{C}$ . The analysis indicated the stability of catalyst up to a range of  $0\text{--}130^\circ\text{C}$  and hence is safe to be used in carrying out the reaction under chosen conditions (room temperature, and  $120^\circ\text{C}$ ) (Fig. 6). The actual weight loss corresponding to the combustion of supported ligand was determined by thermogravimetry as the weight loss between  $150$  and  $600^\circ\text{C}$ , i.e., excluding the weight loss due to desorption of water. The first mass loss occurs at temperature range of  $100^\circ\text{C}$  that is related to the loss of solvent or water trap in the composite. Another mass loss occurs at temperature range of  $130\text{--}600^\circ\text{C}$  that is related to the loss of ligand (imino-pyridine) the surface of carbon nano tubes. The TGA exhibited a weight loss of 24% in the temperature range from  $150\text{--}600^\circ\text{C}$  due to degradation of imino-pyridines grafted onto CNTs, which indicates that the amount of imino-pyridines grafted to CNTs was 24 wt% (Fig. 6).

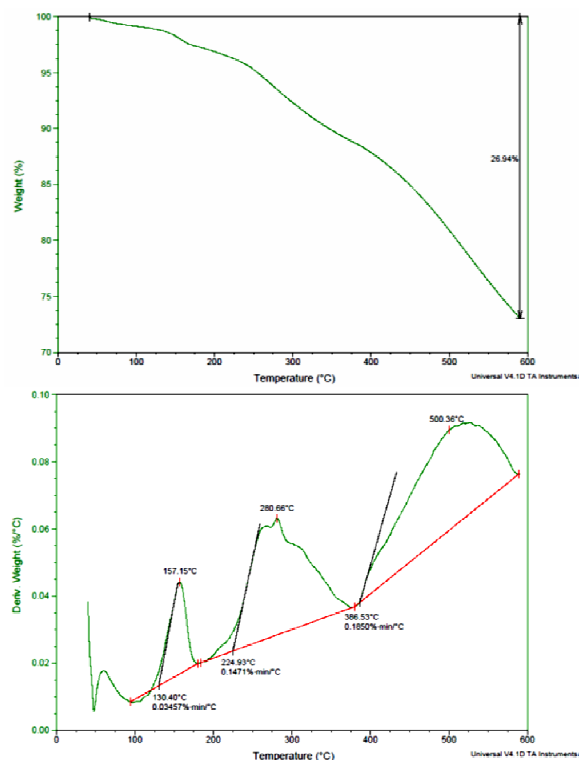


Fig. 6. TGA of MWCNT-imino-pyridine/Pd.

The XPS spectroscopic analysis of the heterogeneous catalyst is a quantitative technique to indicate the electron properties of the species immobilized on the surface, such as oxidation state, the electron environment and the binding of the core electron (E binding) of the metal. Fig. 4 displays the Pd binding energy of MWCNT-imino-pyridine/Pd. The study of the MWCNT-imino-pyridine/Pd at the Pd 3p level shows peaks at 531.8 and 553.9 eV for Pd 3p<sub>3/2</sub>, which clearly indicates that the Pd nanoparticles are stable as metallic state in the nanocomposite structure. In comparison to the standard binding energy of Pd<sup>0</sup>, with Pd 3p<sub>3/2</sub> of about 532.4 eV and Pd 3p<sub>1/2</sub> of about 560.2 eV, it can be concluded that the Pd peaks in the MWCNT-imino-pyridine/Pd shifted to lower binding energy than Pd<sup>0</sup> standard binding energy. The previous studies<sup>30,31</sup> indicated that the position of Pd 3p peak is usually influenced by the local chemical/physical environment around Pd species besides the formal oxidation state, and shifts to lower binding energy when the charge density around it increases. Therefore, the peaks at 553.9 and 531.8 could be due to Pd<sup>0</sup> species bound directly to imino-pyridine groups in the MWCNT-imino-pyridine/Pd.

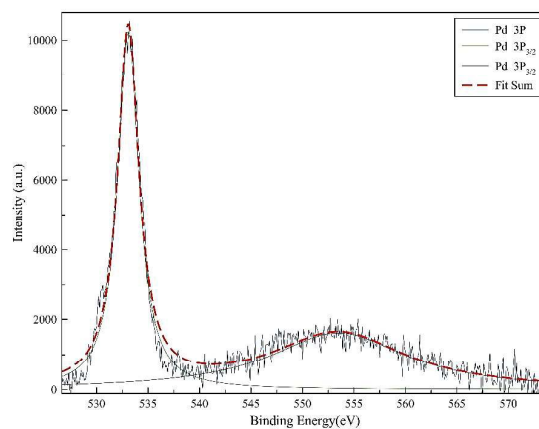
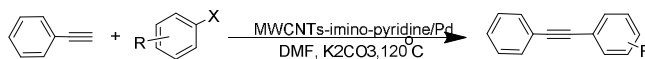


Fig. 7. XPS spectra of MWCNT-imino-pyridine/Pd for Pd 3p.

The reaction of ethynylbenzene and bromobenzene was selected as a model reaction for optimization of Sonogashira coupling conditions (Table 1).



Scheme. 2 Synthesis of 1,2-diphenylethylene derivatives through the Sonogashira reaction.

The effect of different solvents such as DMF, CH<sub>3</sub>CN, and H<sub>2</sub>O along with effect of various bases such as Et<sub>3</sub>N and K<sub>2</sub>CO<sub>3</sub> at different temperatures was studied. All experiments were performed with catalyst loadings of 2 mg of MWCNTs-imino-pyridine/Pd. Optimization studies identified DMF as the most effective solvent and K<sub>2</sub>CO<sub>3</sub> as the most effective base. After 40 min at 120 °C the desired product was formed in 95 % yield. When solvent was excluded from the reaction yields suffered (~40%)

Table 1 The effect of various solvents, bases, and temperatures on product yield.<sup>a</sup>

Entry	Solvent	Base	Temperature (°C)	Yield <sup>b</sup> (%)	Time (min)
1	DMF	Et <sub>3</sub> N	80	70	60
2	DMF	Et <sub>3</sub> N	Reflux	80	40
3	DMF	K <sub>2</sub> CO <sub>3</sub>	120	95	40
4	CH <sub>3</sub> CN	Et <sub>3</sub> N	Reflux	50	90
5	CH <sub>3</sub> CN	K <sub>2</sub> CO <sub>3</sub>	Reflux	65	90
6	EtOH/H <sub>2</sub> O <sup>c</sup>	Et <sub>3</sub> N	80	10	120
7	EtOH/H <sub>2</sub> O <sup>c</sup>	K <sub>2</sub> CO <sub>3</sub>	Reflux	20	120
8	Free	K <sub>2</sub> CO <sub>3</sub>	90	-	150
9	Free	K <sub>2</sub> CO <sub>3</sub>	110	10	150
10	Free	Et <sub>3</sub> N	90	40	150

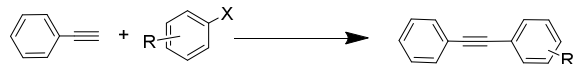
<sup>a</sup>Reaction conditions: Ethynyl benzene (1 mmol), bromobenzene (1 mmol), MWCNTs-imino-pyridine/Pd (2 mg, 1 mol%), solvent (4 ml).

<sup>b</sup>isolated yield

<sup>c</sup>EtOH/ H<sub>2</sub>O= 1:1

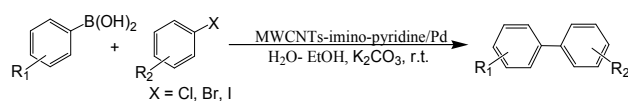
In an effort to establish the scope of this Sonogashira coupling we applied these conditions for the cross-coupling of a variety of aryl halides. These results are summarized in Table 2. Steric and electronic variation of the aryl halide did not significantly influence yields and a number of useful functional groups were tolerated. Aryl bromides and iodides were demonstrated to be equally effective coupling partners. In all cases, excellent yields (80-95%) were obtained. These results attest to the reliability of this catalyst for Sonogashira coupling reactions.

**Table 2.** Synthesis of 1,2-diphenylethylene derivatives by use of various aryl halides.



Entry	R	X	Time (min)	Yield (%)
1	H	Br	40	95
2	1-Naphthyl	Br	45	93
3	2-CH <sub>3</sub>	Br	45	89
4	4-CH <sub>3</sub> O	Br	40	95
5	4-CH <sub>3</sub>	Br	40	91
6	3-NO <sub>2</sub>	Br	60	89
7	4-Cl	Br	45	92
8	4-CN	Br	60	88
9	H	I	30	98
10	4-CH <sub>3</sub>	I	30	96
11	4-CH <sub>3</sub> O	I	30	95
12	5-Pyrimidinyl	Br	60	89
13	3-Pyridinyl	Br	60	88

The efficiency of MWCNTs-imino-pyridine/Pd<sup>0</sup> as a catalyst for the Suzuki-Miyaura cross-coupling was next examined. For this purpose the reaction between bromobenzene and phenylboronic acid was chosen as a model system. For optimization of the reaction various solvents, bases, and temperature were tested and the products yield were compare to each other. In all case 2 mg of MWCNTs-imino-pyridine/ Pd was used as catalyst. These experiments identified that the reaction in EtOH/H<sub>2</sub>O (1:1) as solvent and K<sub>2</sub>CO<sub>3</sub> as base afforded the highest yield. Results are shown in Table 3.



**Scheme 3.** Synthesis of biaryles through the Suzuki cross-coupling reaction.

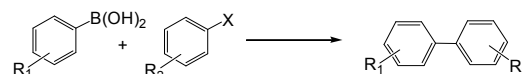
**Table 3.** The optimization of Suzuki-Miyaura coupling reaction.<sup>a</sup>

Entry	Solvent	Catalyst (mg)	Base	Time (min)	Yield (%) <sup>b</sup>
1	EtOH	2	K <sub>2</sub> CO <sub>3</sub>	120	60
2	H <sub>2</sub> O	2	K <sub>2</sub> CO <sub>3</sub>	120	30
3	EtOH/H <sub>2</sub> O <sup>c</sup>	2	K <sub>2</sub> CO <sub>3</sub>	25	98
4	EtOH/H <sub>2</sub> O <sup>c</sup>	2	NaOAc	120	65
5	EtOH/H <sub>2</sub> O <sup>c</sup>	2	Et <sub>3</sub> N	120	80
6	EtOH/H <sub>2</sub> O <sup>c</sup>	1	K <sub>2</sub> CO <sub>3</sub>	60	95
7	EtOH/H <sub>2</sub> O <sup>c</sup>	3	K <sub>2</sub> CO <sub>3</sub>	25	98

<sup>a</sup>Reaction conditions: Bromobenzene (1 mmol), PhB(OH)<sub>2</sub> (1.1 mmol), MWCNTs-imino-pyridine/Pd (2 mg, 1 mol%), room temperature, solvent (4 mL), <sup>b</sup>isolated yield, <sup>c</sup>EtOH/ H<sub>2</sub>O= 1:1

After optimization of the reaction conditions, the generality of the reaction was confirmed by testing the various aryl halides and phenylboronic acids (Table 2, entries 1-23). In all cases biaryl products were afforded in good to nearly quantitative yields. It is noteworthy that the MWCNTs-imino-pyridine/Pd is effective in the coupling of conventionally challenging aryl chlorides in addition to aryl bromides and iodides (Table 4, entries 3, 5, 6, 16, 17).

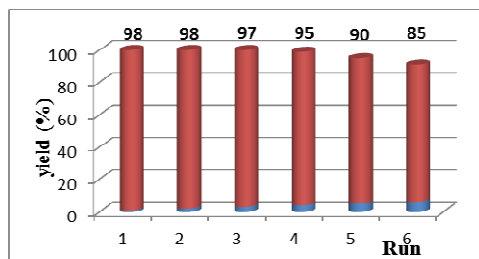
**Table 4.** Suzuki cross-coupling reaction of aryl halides with phenylboronic acids.



Entry	R <sub>1</sub>	R <sub>2</sub>	X	Time (min)	Yield (%)
1	H	H	I	10	98
2	H	H	Br	30	98
3	H	H	Cl	180	89
4	H	4-Cl	Br	30	98
5	H	4-CH <sub>3</sub> O	Cl	150	85
6	H	4-CH <sub>3</sub>	Cl	150	86
7	H	4-CN	Br	45	90
8	H	4-NO <sub>2</sub>	Br	30	92
9	H	4-CHO	Br	30	95
10	H	4-COCH <sub>3</sub>	Br	30	95
11	H	3-NO <sub>2</sub>	Br	30	90
12	H	2-CHO	Br	240	72
13	H	3-Pyridinyl	Br	60	87
14	H	2-Thienyl	Br	180	60
15	H	2-Thienyl	I	60	90
16	H	4-Pyridinyl	Cl	360	55
17	H	3-Pyridinyl	Cl	360	30
18	H	2-NO <sub>2</sub>	Br	120	65
19	H	4-CH <sub>3</sub> O	I	20	98
20	4-NO <sub>2</sub>	H	Br	120	95
21	4-NO <sub>2</sub>	4-COCH <sub>3</sub>	Br	120	90
22	4-CH <sub>3</sub>	H	Br	45	96
23	4-CH <sub>3</sub>	4-COCH <sub>3</sub>	Br	60	96

Also, in order to confirm reusability of MWCNTs-imino-pyridine/Pd in the Suzuki-Miyaura cross-coupling reaction between aryl halides and phenylboronic acid, the reaction between iodobenzene and phenylboronic acid was chosen as a model reaction. After each reaction, the catalyst was washed with a mixture of ethanol and ethyl acetate (1: 1) and dried at 60 °C for three hours. The results showed that the catalyst can

be reused six times without significant loss of its catalytic activity (Fig. 8).



**Fig. 8** The recycling of MWCNTs-imino-pyridine/Pd in the Suzuki-Miyaura reaction.

Several studies have successfully determined the amount of metal leaching using a hot-filtration technique. A reaction mixture of bromobenzene with phenylboronic acid in the above-described catalytic system was stirred at 40 °C for 10 min, resulting in a yield of 45%. The hot reaction mixture was then filtered through a dried Celite pad under nitrogen to remove the MWCNTs-imino-pyridine/Pd catalyst and any insoluble species, and the clear filtrate was introduced to another Schlenk tube at 40 °C. Further detection by GC demonstrated improvement of the yield to only 49% after 2 h. This result shows that no active species were dissolved in the solution to catalyze the coupling reaction. We further determined the Pd-content in the filtrate by ICP-AES, and only 0.6 ppm of palladium was found in the solution, which indicated that the catalytic activity may mainly result from the grafted palladium complex.

## Conclusions

Briefly, in the present research we demonstrated the catalytic activity of a new reusable Pd catalyst. The most significant properties of this catalyst are commercially inexpensive and available starting materials, convenient experimental procedure, high catalytic performance and reusability with minimal palladium leaching. The MWCNTs-imino-pyridine/Pd was demonstrated to promote Suzuki-Miyaura and Sonogashira coupling reactions under mild and environmental friendly conditions. Also, reaction set up and purification was demonstrated to be straightforward with these heterogeneous catalysts. We anticipate that this approach will be beneficial for the advancement of heterogeneous nanocatalysis.

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